INFRARED SPECTROSCOPIC STUDY OF THE ASSOCIATION BEHAVIOUR OF SOME DIOL MONOALKYL ETHERS

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CONTENTS

Appendix 1 : A reprint of

Infrared Study and Thermodynamics of
Hydrogen Bonding in Ethylene Glycol
Monoalkyl Ethers. Evidence for a
Ten Membered Ring Dimer
By L.S. PRABHUMIRASHI and C.I. JOSE
Published in J.C.S. Faraday Transactions II,
1975, 71, pp. 1545-54.

Appendix 2 : A reprint of

Infrared Study and Thermodynamics of
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Monoalkyl Ethers.
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PREFACE

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Self association of alcohols is an interesting phenomenon resulting from hydrogen bonding. As the OH group can act as a proton donor as well as an acceptor, H-bonding of alcohols in nonpolar solvents gives rise to a variety of self associated species such as open and/or closed dimers, trimers, tetramers etc. Alcohols containing an additional proton acceptor such as halo-ethanols, diols, diol mono ethers etc. can also exhibit intramolecular H-bonding when the hydroxyl proton lies at a distance of 1.4 - 2.5 from the additional proton acceptor. Due to their small strength ($\sim$0.1 - 60 kJ mol^{-1}) and frequent intermolecular collisions, the H-bonds in liquids and vapours are constantly breaking and reforming resulting in rapid, dynamic equilibria between the free and various types of H-bonded molecules.

The literature on H-bonding in alcohols is quite extensive. The self-association of alcohols capable of intramolecular H-bonding is however little studied. This would be specially interesting because of the additional proton acceptor in them, which can lead to different types of self-associated species not possible in simple alcohols. With this view the association behaviour, i.e. the nature of self-associated species of a number of diol monoalkyl ethers in carbon tetrachloride solutions, has been investigated in the present work. Infrared spectroscopy is used as the analytical tool since this is the most versatile technique enabling the observation and study of individual types of species by their characteristic absorption bands. The method of integrated absorption intensities has been adopted for estimating the required concentrations. The equilibrium constants for the equilibria between different types of H-bonded species and free monomers have been determined to estimate the thermodynamic quantities which are further analysed to arrive at the most likely associated species in the concentration range studied. The subject matter in the thesis is presented in eight chapters as outlined below.

The present state of understanding of the self-association of alcohols is briefly reviewed in Chapter I. The relevent theory of infrared spectroscopy is outlined in Chapter II. Some of the important aspects of H-bonding such as its theory, effects, thermodynamics etc. are summarized in Chapter III. The experimental procedure for preparation/purification of the compounds studied, spectroscopic measurements and the method of calculations are explained in Chapter IV.

The results on the self association of ethylene glycol monoalkyl ethers $RO(CH_2)_2OH$ are discussed in Chapter V. The effect of an additional ether oxygen on the association behaviour was investigated by studying the H-bonding in diethylene glycol monoalkyl ethers $RO(CH_2)_2O(CH_2)_2OH$, the results of which are presented in Chapter VI. The alkyl group R was varied from CH_3 to C_2H_5 and C_4H_9 for finding the effect of its chain length on H-bonding behaviour of these systems. The H-bonding in tri- and tetramethylene glycol monomethyl ethers, $CH_3O(CH_2)_3OH$ and

$CH_3O(CH_2)_4OH$, was investigated for understanding the effect of the number of methylene groups between the ether and hydroxylic oxygen atoms and the results are discussed in Chapter VII. A general discussion of the spectroscopic and thermodynamic properties associated with H-bonding in the different types of systems studied together with the conclusions are presented in Chapter VIII. This is followed by a collective list of all the References in the order of their occurrence in the text. The results on the study of ethylene- and diethylene glycol monoalkyl ethers have been published as two papers, the reprints of which are presented in the form of two Appendices.

CHAPTER I

SELF-ASSOCIATION OF ALCOHOLS - A REVIEW

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I.1. Intermolecular Hydrogen Bonding :

Extremely dilute solutions of alcohols in non-polar solvents ($C \sim 10^{-3}$ mol dm^{-3}) exhibit a single band in the 3640-3610 cm^{-1} region due to the hydroxyl stretching vibrations of the monomer[1-3] units. The corresponding band in alcohol vapours at very low pressure occurs in the 3690-3640 cm^{-1} region[4]. The monomeric OH bands of a number of alcohols, other than methanol and tertiary butanol, are found to be asymmetric[2,5-1]. This has been attributed to conformational isomerism, i.e. existence of molecules in different configurations in which the OH groups vibrate in slightly different force fields. With increasing concentration, additional OH bands appear, first at $\sim$ 3500 cm^{-1} and then in the 3300 cm^{-1} region. While it is accepted that the 3300 cm^{-1} bands are due to polymeric species[3]; the type of species giving rise to the 3500 cm^{-1} bands is not well-established. Thus this band has been ascribed to open dimers[1,4,13-27] closed dimers[28-34] or to a mixture of both[35-40]. In some cases trimers[22,34,41-45] and/or tetramers[46-52] are also considered to contribute to this band.

Bellamy and Pace[21], using the cancellation technique, have shown that the dimers of methanol ($\bar{v}$ = 3534 cm^{-1}) and phenol ($\bar{\nu}$ = 3481 cm^{-1}) in CCl_4 are of an open type. Study of overtone bands by Fletcher and Heller[23] and the theoretical calculations by Murthy et al[26] and those by Hoyland and Kier[27] are in agreement with an open dimer structure for methanol. The $\Delta H°$ value of ~5 kcal mol^{-1} for the dimer of ethanol in CCl_4, obtained by Coburn and Grunwald[17], is attributed to a single hydrogen bond implying the dimer to be of open type. Ibbitson and Moore[22], from dielectric polarization study of ethanol in CCl_4 have shown that at low concentrations (weight fraction ~ 0.002 open dimers are the absorbing species at ~3500 cm^{-1}. Similarly Bordewijk et al[25], from static dielectric constant measurements, have concluded the dimers of n-heptanol in CCl_4 to be of open type. Barnes and coworkers[13,24] from i.r. study of methanol, ethanol and hexafluoro propan-2-ol in Argon matrix and later from a similar study[4] of methanol, ethanol, isopropanol, tertiary butanol and trifluoro ethanol in vapour phase have concluded that the dimers of these alcohols have an open chain structure.

Liddel and Becker[28], using the method of limiting slopes of apparent extinction coefficient vs concentration curves, have obtained $\Delta H°$ values of ~ 5-7 kcal mol^{-1} for the dimer-monomer equilibrium in methanol, ethanol and tertiary butanol. Considering this value of $\Delta H°$ to be quite high for a single hydrogen bond, they have proposed the dimers to be cyclic, containing two bent H-bonds. The cyclic structure for the dimer of ethanol has been supported[29] on the basis of the chemical shift and equilibrium constants calculated from the limiting slopes of p.m.r. frequency vs concentration curves. Van Thiel et al[30], using the matrix isolation technique, have shown that methanol dimers are cyclic in solid nitrogen at 20 K as well as in solutions at room temperature. Following Liddel and Becker[28], a number of other workers[31-33] also have proposed cyclic dimers for various alcohols from the observed $\Delta H°$ values. Gold and Perrine[34], from dielectric polarization study have concluded that cyclic dimers and/or cyclic trimers are favoured in dilute solutions.

Several other workers[35-40], from i.r. and n.m.r. study of a variety of alcohols such as methanol, ethanol, isopropanol, tertiary butanol, pentanol, cyclohexanol, ditertiary butyl carbinol etc. have proposed the dimers to be the associated species responsible for the 3500 cm^{-1} bands. However in the absence of a definite evidence for either the open or the cyclic structure, they have concluded that dimers of either type or a mixture of both might be present.

The infra red frequency shifts for polymers ($\sim$ 250-400 cm^{-1} are found to be considerably larger than those for dimers ($\sim$ 100-150 cm^{-1}). This has been explained by Liddel, Becker etc.[28,30] by assuming the O-H...O atoms in polymers - whether open or closed - to be nearly collinear giving rise to normal hydrogen bonds. The bent and hence weaker hydrogen bonds in cyclic dimers would then explain the smaller frequency shifts than those for polymers. The results for methanol are explained on this basis using the matrix isolation technique[30]. Bellamy and Pace[21] on the other hand proposed that the dimers are open chain systems with normal hydrogen bonds. They further argued that the oxygen atom of an OH group whose proton is engaged in hydrogen bonding would be more basic than that of the free OH group and similarly the hydrogen atom of an OH group whose oxygen is engaged in hydrogen bonding would be more acidic than that of the free OH group. The polymers would therefore tend to be cyclic due to the cooperative interactions giving rise to stronger hydrogen bonds and hence larger frequency shifts than those for the dimers. The small frequency shifts for trimers ($\sim$ 200 cm^{-1}) are attributed[63] to the cyclic structure with bent hydrogen bonds and the constant frequency shifts for tetramers and all higher polymers ($\sim$ 250-400 cm^{-1}) are supposed to indicate that the hydrogen bonds in tetramers have become nearly collinear so that an increase in polymeric size produces no further change in the hydrogen bond energy.

It has been proposed by Mecke[41] that there are practically no dimeric species in alcohol solutions and the association begins with trimers-presumably cyclic. The mean association energy for methanol and tertiary butanol in CCl_4 has consequently been reported to be $\sim$ 4.7 and $\sim$ 5.3 kcal mol^{-1} respectively. Cohen and Reid[42], from p.m.r. study of a series of alcohols in CCl_4, found almost zero limiting slopes for the curves of the proton chemical shift vs concentration, concluding trimers and tetramers to be more stable than dimers. Similarly Saunders and Hyne[43], using the n.m.r. and curve fitting methods have proposed cyclic trimers for alcohols. Tucker and coworkers[44,45] using i.r., n.m.r. and vapour pressure methods have also shown that the 3600 cm^{-1} band of methanol and tertiary butanol solutions is ascribable to open trimers. Ibbitson and Moore[22] from dielectric polarization study of alcohols in CCl_4 at high concentrations (weight fraction > 0.007) have concluded that the species absorbing at ~ 3600 cm^{-1} may be open trimers in addition to open dimers.

Weltner and Pitzer[46] from vapour pressure study have determined cyclic tetramer ($\Delta H° = 24.2$ kcal mol^{-1}) as the stable species in methanol vapour. Study of P-V-T relationships[47] and n.m.r. studies[49-51] of methanol in CCl_4 are in agreement with this. Ens and Murray[48], studying the overtone bands ($\lambda \sim 1.42\ \mu$) of methanol, ethanol, iso-butanol, tertiary amyl alcohol and octan-2-ol in CCl_4 over a wide concentration range (~ 0.1-7 mol dm^{-3}) have suggested the formation of cyclic tetramers. Inskeep and coworkers[18,19], from vapour phase i.r. study of methanol and deuterated methanol (CH_3OD) have concluded that the equilibria consist of the monomers, open dimers ($\Delta H° \sim 3.5$ kcal mol^{-1}) and cyclic tetramers ($\Delta H° \sim 14$-18 kcal mol^{-1}). Fletcher and Heller[50,52] have criticised the 'a priori' assignment of the 3600 cm^{-1} band to dimers. They have shown that the first overtone bands ($\lambda \sim 1.4$-$1.6\ \mu$) of n-butanol, n-octanol and deuterated ethanol (CH_3CH_2OD) in n-decane can be explained only in terms of monomers, open tetramers ($\Delta H° \sim 5.4$ kcal mol^{-1} $bond^{-1}$) and cyclic tetramers ($\Delta H° \sim 4.8$ kcal mol^{-1} $bond^{-1}$); the smaller value of $\Delta H°$ for the cyclic structures being ascribed to bent hydrogen bonds. Hammeker et al[38] agree with Fletcher and Heller in that the 3500 cm^{-1} band should be carefully considered for each system separately as it may not always be due to OH---OH dimers only. They have however confirmed that in the case of methanol, ethanol and ditertiary butyl carbinol this band is due to dimers only. Later study by Fletcher and Heller[23] on methanol in CCl_4, using the overtone bands is in agreement with this.

I. 2. Intramolecular Hydrogen Bonding :

The i.r. frequencies and p.m.r. chemical shifts for a variety of compounds containing intramolecular H-bonds are extensively reported (cf. e.g. the review by M. Tichy[54] and the references sited therein). However the thermodynamic properties ($\Delta H°$ and $\Delta S°$) which are more useful in understanding the extent of H-bonding and interaction energies are estimated in a few cases only. The thermodynamic and structural aspects of alcohols capable of intramolecular H-bonding such as β-substituted ethanols XCH_2CH_2OH (X = F, Cl, Br, I, CN, NO_2, NH_2 and C_6H_5), alkane diols and their monoalkyl/aryl ethers are summarized below because of their similarity with the compounds studied in the present work. Of the cis, trans and gauche rotamers possible for these compounds, the gauche/cis conformers are stabilized by intramolecular hydrogen bonding.

Mizushima et al[55], from i.r. and Raman study, have determined the skeletal frequencies and force constants of the stretching vibrations of 2-chloroethanol. The energy difference between the H-bonded and non-bonded conformations obtained by them (0.96 kcal mol^{-1}) is considerably smaller than that determined by Zumwalt and Badger[56] (2 kcal mol^{-1}) from the study of overtone bands. Krueger and Mettee[31,57,58], from i.r. study, have estimated the ΔH° values for gauche-trans conversion in various halo- as well as cyano-, nitro- and amino ethanols by assuming the absorption coefficients of the free and intramolecularly H-bonded OH's to be identical and independent of temperature. However, as these assumptions are not valid, their values are not reliable. In the case of O-and N-methyl derivatives of 2-amino ethanol, their results indicated[58] the intramolecularly H-bonded gauche conformers to be less stable than the non-bonded trans isomers which they have explained by considering the repulsive forces between the N and O atoms to be greater than the attractive forces responsible for H-bonding. Buckley, Giguere and Yamamoto[59], from i.r. and Raman study of 2-fluoroethanol in solid, liquid and vapour phases have shown that these molecules exist, almost entirely, in the gauche form ($\Delta H^\circ \sim$ 3-4 kcal mol^{-1}) and only in vapours at temperatures above 60°C, weak bands due to trans isomers are observed. Similarly, 2-chloro and 2-bromo ethanol are found[60] to exist mainly as intramolecularly H-bonded gauche isomers with ΔH° values of 1.45 and 1.20 kcal mol^{-1} respectively, obtained from the measurements on carbon-halogen stretching bands. The corresponding ΔH°'s derived from measurements on OH stretching bands were 1.90 and 1.66 kcal mol^{-1}; the apparent discrepancy between the two sets of values being ascribed to the presence of a second, non-bonded gauche isomer. The force constants obtained from normal coordinate analysis of 2-chloro, 2-bromo and 2-cyano ethanols are in agreement with the gauche forms[61]. The interaction of the OH group with the π-electrons in 2-phenyl ethanol is reported[62] to result in intramolecular hydrogen bonding with $\Delta H^\circ \sim$ 1-1.5 kcal mol^{-1} and $\Delta S^\circ \sim$ 3-4 e.u. mol^{-1}.

Krueger and Mettee[63] from i.r. study of 1,2 ethane diol $(CH_2OH)_2$ have proposed a 'box-type' structure for the intramolecularly H-bonded monomer involving two mutual hydrogen bonds between the two hydroxyl groups. However such a structure would be highly strained and hence seems unlikely. Buckley and Giguere[64] from i.r. study of $(CH_2OH)_2$, $(CD_2OH)_2$ and $(CH_2OD)_2$ in the solid, liquid and vapour phases, have shown that these molecules exist only as gauche isomers. From a study of torsional frequencies, they have further estimated the barriers to internal rotation about the C-C and C-O bonds as 10 and 3-4 kcal mol^{-1} respectively. Buc and coworkers[65] have determined the spectral characteristics of the free and intramolecularly H-bonded OH bands of 1,3 propane diol (free OH : $\bar{\nu}$ 3635 cm^{-1}, $\Delta\bar{\nu}_{1/2}$ = 40 cm^{-1} and B = 5.6 x 10^3 dm^3 mol^{-1} cm^{-2}; intra. OH : $\bar{\nu}$ = 3567 cm^{-1}, $\Delta\bar{\nu}_{1/2}$ = 59 cm^{-1} and B = 6.8 x 10^3 dm^3 mol^{-1} cm^{-2}) and reported the ΔH° for bonded-nonbonded conversion as 2-2.9 kcal mol^{-1}. The different conformations and effect of substituents on the C-C-C bond angle in 1,3 propane diol have been investigated by Schleyer[66]. Johansson and Kollman[67] have carried out 'ab initio' molecular orbital calculations for the bonded and non-bonded conformations of 1,3 propane diol. The energy difference between the H-bonded and non-bonded cis conformations is calculated to be 0.9 kcal mol^{-1} while that between the cis and trans conformations is 4.8 kcal mol^{-1}. Fishman and Chen[68] found that the ΔH° values for intramolecular hydrogen bonding in 1-2, 1-3 and 1-4 butane diols, were in the order : 1-4 diol > 1-3 diol > 1-2 diol; while the O....H distances followed the reverse order, viz. 1.2, 1.8 and 2.1 Å respectively.

A number of workers[69-73] have studied α-ω diols $HO(CH_2)_nOH$ with n = 2-6. Kuhn[69] has proposed a correlation between the frequency shift ($\Delta\bar{\nu}$ cm^{-1}) on intramolecular hydrogen bonding and the O....H distance (L cm) as $\Delta\bar{\nu} = 250 \times 10^{-8}/L - 74$. Kuhn and coworkers[70] have determined the intensity ratios for the free and H-bonded OH bands of various diols from which it is observed that intramolecular association persists to a large extent in 1,2-ethane-1,3 propane- and 1,4 butane diols but falls drastically in 1,6- and higher diols. Yonezawa et al[71], from measurements of proton chemical shifts and molecular orbital calculations, have estimated the diamagnetic shielding constants of the protons and shielding due to paramagnetic anisotropy of the oxygen atoms. Morantz and Waite[72], from a study of the first overtone bands (at ~ 7000-7100 cm^{-1}) of a number of diols in CCl_4 (C ~ 0.005-0.010 mol dm^{-3}), have found that the mechanical anharmonicity of the free and intramolecularly H-bonded OH stretching vibrations is nearly the same (~ 0.02) suggesting the observed spectral changes (i.e. those in $\Delta\bar{\nu}$, $\Delta\bar{\nu}_{1/2}$ and B) to depend mainly on the electrica anharmonicity. Busfield and coworkers[73] have determined the thermodynamic quantities for the equilibria between the free and intramolecularly H-bonded monomers for various diols and found th Badger-Bauer rule[74] (i.e. linerity of $\Delta H°$ and $\Delta\bar{\nu}$) to be obeyed.

The intramolecular hydrogen bonding in monoalkyl/aryl ethers of diols has been investigated by several workers[2,75-86]. The larger frequency shifts of the intramolecularly H-bonded OH groups of diol monoethers as compared to those of simple diols have been attributed[76-77] to greater basicity of the ether oxygen than that of the hydroxylic one. Infrared study of 2-aryloxy ethanols showed[78] that electron donor substituents in m- and p-positions favoured intramolecular H-bonding; the OH...π bonding and steric effects were however found to be negligible. Miyake[79] and Srinivasan et al[80,81], from a study of CH_2 deformation modes of monoalkyl ethers of mono-, di- and triethylene glycols have shown that the OCH_2CH_2O skeletons exist predominantly in the gauche form. Buckley and Brochu[82], from microwave study of 2-methoxy ethanol have determined its dipole moment (2.36 D), rotational constants and the dipole moment components along the three principal axes. Kuhn and Wires[83], from i.r. study of intramolecular H-bonding in 2-methoxy ethanol, 3-methoxy propanol and 4-methoxy butanol have reported that, though the $\Delta\bar{\nu}$ for these compounds varied as 30, 86 and 180 cm^{-1} respectively, the $\Delta H°$ was practically constant ($\sim$ 2.2-2.7 kcal mol^{-1}). The non-applicabilit of the Badger-Bauer rule has been attributed to conformational interactions. It may however be noted that the results on intramolecular hydrogen bonding in various diols[68,73] are consistent with the Badger-Bauer rule.

The 3635 and 3600 cm^{-1} bands of alkoxy ethanols are generally attributed to the free and intramolecularly H-bonded OH groups respectively. Flett[2] however has ascribed both these bands to 'free' OH groups resulting from two different molecular configurations with slightly different force fields. Shapetko et al[84] on the other hand have showed the presence of intramolecular H-bonding in methoxy ethanol from the chemical shift of the OH protons at infinite dilution. Saito et al[77] did not observe the 3635 cm^{-1} band of alkoxy ethanols and have therefore concluded intramolecularly H-bonded monomers (absorbing at ~ 3610 cm^{-1}) as the only species in dilute CCl_4 solutions. Lodygina et al[85], who also did not observe the 3635 cm^{-1} band of ethoxy ethanol, on the other hand, have considered intramolecular H-bonding to be absent and only 'free' monomers ($\bar{\nu}$ ~ 3610 cm^{-1} band) to be present in dilute CCl_4 solutions. Markevich et al[86] have reported three OH bands, viz. at ~ 3617, ~ 3586 and ~ 3486 cm^{-1} in dilute CCl_4 solutions of diethylene glycol monoethyl ether and attributed them to the free and the intramolecularly H-bonded five- and eight membered ring monomers respectively. Lodygina et al[85], in this case also, did not observe the 3617 cm^{-1} band and have ascribed the latter two bands to the free and intramolecularly H-bonded eight membered ring monomers respectively.

3. Summary :

From the literature on intermolecular association of alcohols, it is thus observed that the results obtained for different systems are hardly comparable with one another as the alcohol studied together with the solvent and concentrations used, method of investigation and the nature of approxiations have varied widely. Since no direct method is available for the identification of different types of hydrogen bonded species, the interpretation of experimental data rests heavily on the association model proposed and the curve fitting procedure. Most of the earlier i.r. work is restricted to low concentrations where the first associated species absorbing at $\sim 3500\ cm^{-1}$ could, almost certainly, be the dimers only. In the work based on p.m.r., i.r. overtone region, dielectric polarization and vapour pressure methods, relatively high concentrations have been employed. In such systems containing various types of polymers, it is obvious that the dimers may not be the major associated species and the species absorbing at $3500\ cm^{-1}$ are likely to be trimers in addition to the dimers. There is however no evidence for tetramers or still higher associated species absorbing at $\sim 3500\ cm^{-1}$. The structure of the dimer (open or closed) is also not well established. In the case of intramolecular hydrogen bonding, there is relatively little controversy as the nature of species is well defined. There is however little work on intermolecular association of alcohols capable of intramolecular H-bonding.

CHAPTER II

INFRARED SPECTROSCOPY

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INFRA RED SPECTROSCOPY

II.1. Vibrations and Infra Red Spectra of Polyatomic Molecules :

An n-atomic molecule possesses 3n degrees of freedom, out of which 3 each in general correspond to the translational and rotational motions of the molecule as a whole, leaving 3n-6 as the vibrational degrees of freedom. (Linear molecules form a special case as they have only 2 rotational and hence 3n-5 vibrational degrees of freedom). These independent vibrations a molecule can undergo are termed the 'normal' or 'fundamental modes' of vibration. The apparently complicated vibrational motion of a molecule can be understood in terms of its normal modes.

The energy levels of the molecule corresponding to each of the $i(= 1,2,...3n-6)$ normal modes are given by

$$\epsilon_{v_i} = (v_i + 1/2)\left[1 - (v_i + 1/2)\, x_i\right]\bar{\omega}_i \quad \mathrm{cm}^{-1}$$

where v_i $(= 0,1,2,...)$, $\bar{\omega}_i$ and x_i are respectively the vibrational quantum number, natural frequency (in cm^{-1}) and the anharmonicity $(\sim 10^{-2})$ corresponding to the i^{th} normal mode. The force constant (k_i), which is a measure of the stiffness of a chemical bond, is related to the natural frequency by the relation

$$k_i = 4\pi^2 c^2 \bar{\omega}_i^2 \mu,$$

c being the speed of light (3×10^{10} cm sec^{-1}) and μ the reduced mass of the system. The normal modes associated with a change of dipole moment are infrared active and can give rise to vibrational bands in the infrared region. For a particular normal mode, the absorption frequency for a transition $v'' \longrightarrow v'$ (where the single and double primes refer to the upper and lower states respectively) is given by

$$\bar{\nu}_{v',v''} = (v' - v'')\ 1 - (v' + v'' + 1)x_1\ \bar{\omega}_1 \quad \mathrm{cm}^{-1}$$

with the selection rule $\Delta v = 1,2,3,\ldots$ etc. At ordinary temperatures, almost all the molecules are in the vibrational ground level ($v'' = 0$) so that the transitions from all the higher (i.e. $v'' = 1,2\ldots$) levels are of negligible intensity. The transition from the ground level ($v'' = 0$) to the first excited level ($v' = 1$), known as the fundamental transition, gives rise to the band at frequency $\bar{\nu}_{1,0} = (1-2\ x_1)\bar{\omega}_1 \approx \bar{\omega}_1$ cm^{-1} (as $x_1 \ll 1$) Similarly the transitions from $v'' = 0$ to $v' = 2,3,\ldots$ levels, termed as the first overtone, second overtone, ... etc. give rise to bands at frequencies $\sim 2\bar{\omega}_1, \sim 3\bar{\omega}_1, \ldots$ etc. The intensities of the overtone bands are 1-2 orders of magnitude lower than those of the fundamentals and therefore of little use in quantitative analysis.

The interactions among different normal modes give rise to a number of combination bands at frequencies $a\bar{\omega}_1 \pm b\bar{\omega}_j \pm c\bar{\omega}_k \pm$ etc. (where a,b,c,... are integers 0,1,2,3 etc.) which make the i.r. spectra very complex and characteristic of the molecules. Further, various chemical groups are found to display absorption bands at essentially constant frequencies . e.g. All the molecules containing an OH-group consistently have an absorption band in the 3600 cm^{-1} region. Such empirical correlations between various functional groups and their absorption bands have led to the concept of characteristic group frequencies, which also includes the bands arising from vibrations of multiple bonds. The unique nature of the i.r. spectra of different molecules together with the approximate constancy of absorption frequencies of various functional groups are of great help in the identification of different compounds. However it must be realized that the concept of characteristic group frequencies is only a simplification. The group frequencies are dependent on several factors such as the relative positions of different groups in the molecule, their polarities, steric factors, physical state of the system, (i.e. solid, liquid or gaseous), the solvent etc. These factors give rise to various intra- and intermolecular interactions which influence the positions of absorption bands as well as their intensities. All such factors have therefore to be taken into account while using i.r. spectroscopy for identification and analytical purposes.

II.2. Integrated Absorption Intensity[87-89] :

Normally an i.r. absorption band is characterized by its frequency at the absorption maximum ($\bar{\nu}_{max}$ or $\bar{\nu}_o$ cm^{-1}), half-band width i.e. the width of the band at half the maximum intensity ($\Delta\bar{\nu}_{1/2}$ cm^{-1}). Similarly when a certain group is present in different molecules, the integrated absorption intensity (see below) can help in characterizing the immediate surrounding of the group. For example, the integrated intensities of carbonyl groups in certain steroid acetates, ketones and δ-lactones, all of which absorb in the 1735-1745 cm^{-1} region were found to be appreciably different to enable their characterization[90].

The fundamental absorption law (Beer-Lambert law) is expressed as

$$I_\nu = I_{o\nu} e^{-\alpha_\nu CL}$$

where $I_{o\nu}$ and I_ν are the incident and transmitted intensities of monochromatic radiation of frequency ν; α_ν is the absorption coefficient (or absorptivity) at frequency ν; C is the concentration of the absorbing species and L is the path length in cm. The absorption coefficient is therefore given by

$$\alpha_\nu = (1/CL)\ln(I_o/I)_\nu$$

and is a measure of absorption of radiation of frequency ν by the absorbing group. The true integrated absorption intensity (A) of a band is defined as

$$A = \int \alpha_\nu d\nu = (1/CL)\int \ln(I_o/I)_\nu d\nu$$

and is a measure of total energy absorbed by the group over the entire absorption region. The integrated intensity is thus a better criterion of band intensity than the maximum absorption coefficient ($\alpha_{\nu max}$) as the former takes cognizance of variations in band heights as well as in band widths. Further the integrated intensity is related to other fundamentally important quantities as noted below.

(i) The dipole moment derivative near the equilibrium position $(d\mu/dr)_0$, i.e. the variation of dipole moment associated with a particular vibration is related to A as

$$A = (\pi n_0/3c)(d\mu/dr)_0^2$$

where n_0 is the number of molecules per cm^3.

(ii) The matrix elements of spectral transition probability given by expressions of the form $M_x = (\partial\mu/\partial x)_0 \int \Psi_i^* x \Psi_j d\tau$ are related to A through the expression

$$A = (8\pi^3 n_0 \nu/3ch)(M_x^2 + M_y^2 + M_z^2)$$

where the Ψ's are the wave functions of the states participating in the transition and ν is the absorption frequency.

(iii) The molecular polarizability (α_m) and the molar atomic polarization ($P_a = 4\pi N\alpha_m$, N = Avogadro number) are related to A through the expressions

$$\alpha_m = (c/4\pi^3 n_0 \nu^2)A \quad \text{and} \quad P_a = (cv_m/3\pi^2\nu^2)A$$

where $v_m = N/n_0$ is the molar volume.

The integrated intensity of a band is thus a fundamental and hence characteristic property of the absorbing group which can therefore be used to distinguish between similar groups absorbing in the same spectral region.

The definitions of the absorption coefficient and integrated intensity given above are true for monochromatic radiations only. In practice however, due to the use of finite slit width, the radiation cannot be strictly monochromatic. Further, the quantity recorded is not the intensity (I) of the radiation but the transmittance (T) which is the ratio of transmitted and incident radiant powers ($T = P/P_0$). The quantitie actually measured are therefore the apparent absorption coefficient (α_ν^a) and the apparent integrated intensity (B) which are given by

$$\alpha_\nu^a = (1/CL)\ln(T_0/T)_\nu$$

and

$$B = (1/CL)\int \ln(T_0/T)_\nu \, d\nu$$

where T_0 and T are the transmittances (i.e. apparent intensities) of the incident and transmitted radiation when the spectrometer is set at frequency ν.

The values of apparent absorptivities depend on the spectra slit width. Increase in spectral slit width results in a decrease in peak height ($\ln(T_0/T)_{\nu_{max}}$) and an increase in band width. The apparent absorptivities therefore can differ considerably from the true values (by $\sim$ 10-20%). The true and apparent integrated intensities are however found to differ only by $\sim$ 3-5%, the decrease in peak height being roughly compensated by the increase in band width. The integrated intensities therefore are more reliable measures for quantitative analysis than the absorption coefficients.

The infrared absorption bands of liquids are in general much broader ($\Delta\bar{\nu}_{1/2} \sim 10^1 - 10^2$ cm^{-1}) than those of gases and vapours

($\Delta\bar{\nu}_{1/2} \sim 10^{-2}$- 10^{-1} cm^{-1}). The determination of integrated intensity therefore requires a knowledge of the band shape for evaluating the quantity $\int \ln(T_0/T)_\nu d\nu$, which can be treated as the band area. There are mainly four factors which determine the shape of an i.r. absorption band; viz. (i) vibration-rotation structure, (ii) radiation damping (or natural line width), (iii) Doppler broadening and (iv) collision broadening. However it has been observed that the vibrational bands of liquids do not show rotational fine structure[91] except those of liquid hydrogen, liquid methane, ammonia in aqueous solution and water in CCl_4 or CS_2. The band broadening due to radiation damping and Doppler effect are shown to be of the order of 10^{-6} and 10^{-3} cm^{-1} respectively, which are entirely negligible in comparison with the large half-band widths of liquids. The principal cause of band broadening in liquids is the collision broadening[88,89] resulting from perturbation of energy levels of the absorbing molecules by close approach of others. This aspect of line broadening was first dealt with by Lorentz and later by Van Vleck and Weisskopf who were primarily interested with electronic processes in atoms. The line shape derived by them can be expressed as

$$\ln(I_0/I)_{\bar{\nu}} = a\Big/\left[(\bar{\nu} - \bar{\nu})^2 + b^2\right]$$

which is known as the 'Lorentz shape'. The constants 'a' and 'b' are related to the peak intensity and half intensity width by the expressions

$$\ln(I_0/I)_{\bar{\nu}_0} = a/b^2 \quad \text{and} \quad \Delta\bar{\nu}_{1/2} = 2b .$$

The Lorentz shape has been widely assumed to apply also to the profiles of infrared absorption bands of liquids. Sheshadri and Jones[89] have shown that for the i.r. absorption bands of liquids, the absorption coefficient at frequency $\bar{\nu}$ is given by

$$\alpha_{\bar{\nu}} = (K/\pi)\left\{1/2\Delta\bar{\nu}_{1/2}\Big/\left[(\bar{\nu} - \bar{\nu}_o)^2 + (1/2\Delta\bar{\nu}_{1/2})^2\right]\right\}$$

where K is a constant for the absorption band under consideration. The shape functions given above are of the form

$$y = a/(x^2 + b^2)$$

and are more generally known as the Cauchy functions. Band widening also results from the presence of different species of absorbing molecules, different conformational forms of polyatomic molecules and complex solute-solvent interactions[89]. These factors induce a Gaussian component in the band shape which is of the form

$$y_g = (a/b^2)\exp(-x^2 \ln 2/b^2) \qquad \text{where} \quad x = (\bar{\nu} - \bar{\nu}_o)$$

The i.r. absorption bands of liquids would thus be a superposition of the Cauchy and Gaussian forms giving rise to the so-called 'true band shape'. This is further modified by a number of instrumental factors which cause optical, electronic and mechanical distortions while recording the band resulting in the 'apparent band shape'. These factors viz., the spectral slit width (s), signal-to-noise ratio (R), filter time constant (τ) and the scanning speed ($d\bar{\nu}/dt$), are not entirely independent of one another. In practice the determining factor is the maximum obtainable resolution with optimum signal to noise ratio and scanning speed, the instrumental operating conditions being regulated by the expressions[89]

$$R \propto s^2/(d\bar{\nu}/dt)^{1/2} \quad \text{and} \quad (d\bar{\nu}/dt) \propto 1/\tau$$

Having known the shape of an absorption band, its integrated intensity can be determined by a number of methods[88], such as (i) the method of direct integration, (ii) the method of Wilson and Wells and (iii) the method of absorption areas. There are no universally accepted units for the integrated intensity and hence a variety of units having different physical significance are observed in the literature. To curb the introduction of still more units, the Commission on Molecular Structure and Spectroscopy of I.U.P.A.C. has provisionally recommended the following units[89].

(i) An absolute unit $1/n_oL\int \ln(I_o/I)_\nu d\nu$ where n_o is the number of molecules per cm^3, L the path length in cm and ν the frequency in Hz. The dimensions of this intensity unit are therefore cm^2 $molecule^{-1}$ sec^{-1}.

(ii) A secondary unit $1/n_oL\int \ln(I_o/I)_\nu d\ln\nu$ with dimensions of cm^2 $molecule^{-1}$.

(iii) A practical unit $1/CL\int \log(I_o/I)_{\bar{\nu}} d\bar{\nu}$ with C in mole dm^{-3}, L in cm and $\bar{\nu}$ in cm^{-1}. The dimensions of this unit are dm^3 mol^{-1} cm^{-2}.

The chemical spectroscopists concerned mainly with empirical or semiempirical applications of intensity measurements commonly use the unit proposed by Ramsay and Jones[88] viz.

$$1/CL\int \ln(I_0/I)_\nu d\nu = \frac{2.303}{CL}\int \log(I_0/I)_{\bar{\nu}} d\bar{\nu}$$

with C in mole dm^{-3}, L in cm and $\bar{\nu}$ in cm^{-1}. This unit differs from the IUPAC practical unit by a factor of 2.303.

II.3. Quantitative Analysis :

I.R. spectroscopy can be conveniently used for quantitative analysis when the substance to be analysed is soluble in some organic solvent such as CCl_4 with its components exhibiting characteristic and reasonably strong absorption bands that are relatively free from others. The concentration of the desired component can then be estimated by either of the following two methods.

(i) The Use of Absorbance Measurements : The absorbance at the band maximum is given by

$$\log(I_0/I)_{\bar{\nu}_0} = \alpha_{\bar{\nu}_0} CL$$

The concentration of a particular species can therefore be easily evaluated by comparing the absorbance at the band maximum of one of its characteristic bands with that of a standard solution of the same substance. This method is quite convenient if the bands to be used for analysis are free from overlap. In the case of overlapping bands however the estimated concentration can be in error due to improper choice of the base line (I_0 level) for the band concerned. Further in the case of systems involving intermolecular association, particularly H-bonding; this method becomes inapplicable since, due to the presence of various associated species, the linearity of the absorbances, of different bands and the stoiciometric concentration as demanded by the above equation is not obeyed. A serious limitation arising from the dependance of peak height on the spectral slit width is that the data obtained by this method are not transferable from one instrument to another.

(ii) The Use of Integrated Intensities : The absorbance has little theoretical significance when inherent oscillator strength of a particular vibration is to be considered, for it does not differentiate between narrow and broad absorption bands. Obviously a broad band results from greater absorption of i.r. energy than a narrow band of equal peak height. The integrated intensity B on the other hand is a measure of the total energy absorbed by a vibrational mode and as mentioned previously, is of much deeper theoretical significance.

Since $B = 1/CL\int \ln(T_0/T)_{\nu}\, d\nu = A/CL$ where A is the area of the absorption band, the concentration C can be evaluated from $C = A/BL$. Since the B value is effectively the area of the absorption band per unit concentration and unit path length, only a single measurement (at the desired temperature) of a standard solution is needed for the calibration. As the area beneath the absorption curve is independent of the spectral slit function, the data obtained using the integrated intensity is transferable to other spectrometers of comparable resolving power. This method suffers from two main limitations viz. for obtaining accurate band areas, the base line chosen must be precise over the entire frequency range of integration which is sometimes difficult in practice; and a great deal of labour is involved in resolving the absorption bands and measuring their areas. This method is however very useful in the study of systems involving intermolecular association if the overlapping bands can be resolved satisfactorily and as such is employed in the present work.

CHAPTER III

HYDROGEN BONDING

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III.1. Nature of Hydrogen Bonding :

H-bonding is a type of inter- or intramolecular interaction that occurs because of an involvement of the H-atom of a proton donor group A-H with a proton acceptor group B, where A is an electronegative atom such as O, N, F, S, etc. and B is a localized site of high electron density such as a lone electron pair of an electronegative atom, a π-electron orbital of an unsaturated or aromatic system etc. H-bonding is a distinctly directional and specific interaction whereby it is more localized than any other type of weak intermolecular interaction such as repulsion-, polarization-, dispersion- or charge transfer interactions. The strength of H-bonds is small (0.5 - 60 kJ mol^{-1}) in comparison with ordinary chemical bonds (200-800 kJ mol^{-1}). Due to the weakness of the H-bonding interaction and frequent collisions of molecules in gases and liquids, the H-bonds in them are continually breaking and reforming resulting in a rapid dynamic equilibrium between the nonbonded and various types of H-bonded species so that at ordinary temperatures, only a fraction of molecules is in the associated form.

Early attempts to explain the phenomenon of H-bonding were based on simple electrostatic models[92] which considered the H-bonding interaction in a complex A-H...B to be the sum of the interactions between the charge distributions associated with the unperturbed groups A-H and B. These electrostatic interactions include the mutual Coulombic interactions of the charges, dipoles and multipoles with one another. However the simple electrostatic models were inadequate in explaining several experimental results regarding the energy of H-bond, its length, band intensities of H-bonded groups etc. It is also known that the formation of a H-bond perturbs the charge distributions of the donor and acceptor groups as against the assumption of unperturbed charge distributions underlying the electrostatic model. It is therefore an over-simplification to consider the H-bond to be a purely electrostatic interaction.

There are several reviews dealing with the modern (i.e. quantum mechanical) theory of H-bonding notable of them being those by Bratoz[93], Lin[94], Kollman et al[95]. The quantum mechanical treatments can be classified into the Molecular Orbital-, Valency Bond- and Charge Transfer Theories. Since rigorous calculations of energy of H-bonded systems are not possible and the errors resulting from various approximations are very large (of the same magnitude as the H-bond energy itself!); the quantum mechanical treatments have generally been semiquantitative.

Coulson[96] has considered four distinct interactions in H-bonding, viz.
(i) Electrostatic interaction resulting from Coulombic attractions between the positive charge on the H-atom and negative charge on the acceptor atom; (ii) Delocalization interaction due to the approach of the proton donor A-H to the proton acceptor B

resulting in mutual distortion and redistribution of their charge clouds; (iii) Dispersion interaction due to the coordinated motion of electrons in the donor and acceptor groups giving rise to a fluctuating dipole in the former and an induced fluctuating dipole in the latter; and (iv) Repulsive interaction resulting from the overlapping of the charge clouds of A, H and B whereby too many electrons are crowded in a certain small volume. All these effects have a simple physical model associated with each of them and within certain limitations, the details of each of these effects and their contributions to the bond energy, vibration frequency, dipole moment etc. can be calculated.

Semiquantitative models of H-bonds in A-H...B systems consider the potential function of the H-atom to be a combination of individually analytical potential functions for the A-H and H...B bonds. The combined potential is substituted in the Schrodinger equation for obtaining the vibrational energies of the proton in the A-H..B system. Lippincott et al[97], in their one dimensional potential function model for the H-bond, have expressed the complete potential (V) for the A-H..B system as made up of four terms, viz., $V = V_1 + V_2 + V_3 + V_4$ where the functions V_1 to V_4 correspond respectively to the covalent potential for the A-H bond, covalent potential for the H-bond (H..B), Van der Waals' repulsive potential between atoms A and B and the electrostatic attractive potential for the atoms A and B. By choosing appropriate forms for these functions, these authors have shown that the proposed model agrees reasonably well with the observed data for a number of H-bonded systems such as O-H..O, N-H..O, N-H..N, O-H..N, N-H..Cl, O-H..Cl etc. One important feature of this model is that only one empirically evaluated parameter is necessary to describe the H-bonding properties of various systems. Further, the model can also be used for bent bonds by introducing an additional parameter viz. an angle between the normal A-H direction and the A..B axis.

III.2. Self-Association :

The molecules capable of H-bonding can be conveniently classified into three groups such as those having (i) only donor groups, e.g. acetylenes, halogenated compounds, haloforms etc.; (ii) only acceptor groups, e.g. ketones, ethers, esters, olefins etc.; and (iii) both donor as well as acceptor groups, e.g. water, alcohols, phenols, amines, carboxylic acids etc.

Molecules in group (i) can form H-bonded complexes, generally in 1:1 ratio, with those in group (ii), the strength of H-bonding being dependent on the acidity and basicity of the groups concerned. Molecules in group (i) or (ii) can also form H-bonded complexes with those in group (iii) giving rise to several H-bonding equilibria depending on competing nature of the donor groups of (i) or the acceptor groups of (ii) and those of (iii). Molecules in group (iii) can self-associate giving rise to inter- or intra-molecularly H-bonded species. Because of the donor and acceptor sites within the same molecule, the nature and strength of H-bonding depends on the relative acidity and basicity of the donor and acceptor sites and in the case of intramolecular H-bonding, on their spatial arrangement.

Intramolecular hydrogen bonding can occur when the proton-donor and -acceptor sites on the same molecule are in a favourable spatial configuration, i.e. the distance between the acceptor and the hydrogen atom of the proton donor is between 1.4 - 2.7 A and the angular orientation of the acceptor site does not deviate greatly from the A-H bond axis. Typical molecules exhibiting intramolecular H-bonding are : 1,2 dicarboxylic acids and their mono-anions, orthohalophenols, o-hydroxy ketones, some diols and their mono-alkyl- or aryl ethers etc. A cis- or gauche configuration is necessary for intra-molecular H-bonding. Self-association through intermolecular H-bonding can lead to a variety of species such as open and/or closed (i.e. cyclic) dimers, trimers, tetramers etc. The H-bonds that form part of a ring as in the intramolecularly or cyclic intermolecularly associated species are generally stronger than those in the simple 1:1 type complexes between similar proton-donor and acceptor groups.

III.3. Effects of H-Bonding :

Intramolecular H-bonding affects only the shape and electronic structure of the molecule while intermolecular H-bonding changes the number, mass, shape as well as electronic structure of the participants. The physical properties such as molecular weight, melting and boiling points, heat of vaporization and Trouton's constant, viscosity, polarity, dielectric constant and dipole moment etc. for the intermolecularly H-bonded species are generally larger than those of the participants whereas they are generally unaffected on intramolecular H-bonding. Similarly intramolecular H-bonding generally does not affect the molar volume whereas intermolecular H-bonding in inorganic crystals shows an increase and that in organic compounds a decrease of molar volume, the changes being of the order of 2-10 cm^3. Such changes in physical properties however do not provide an unambiguous proof or a quantitative measure of H-bonding as other intermolecular interactions such as orientation and charge transfer forces also result in similar effects.

Spectroscopic methods are powerful tools for investigating the nature of H-bonding as they are capable of providing definite evidence regarding the formation of these bonds, the involvement of a specific covalently bound hydrogen atom and the participation of a specific acceptor group. The spectroscopic methods useful in H-bonding study are (i) Proton Magnetic Resonance spectroscopy for investigating the effects on the chemical shift of the A-H proton; (ii) Electronic Absorption and Fluorescence spectroscopy for studying the changes in electronic levels of the participants and (iii) Infra-Red and Raman spectroscopy for studying the changes in the stretching and bending vibration frequencies of the A-H bonds and the acceptor group. Since the present work is based on the use of infrared spectroscopy; the effects of H-bonding on the vibrational spectra are summarized below.

(a) Since H-bonding as in A-H...B weakens the force constant of the A-H stretching mode, the absorption band due to the A-H stretching vibration is shifted to a lower frequency, the shift being of the order of 10^1- 10^3 cm^{-1}. The anharmonicity and rate of change of dipole moment ($d\mu/dr$) associated with the A-H stretching vibration increase on H-bonding resulting in an increase in the half band width (from a few to a few hundred cm^{-1}) and the integrated absorption intensity (by a factor of 2 to 100). The extent of these changes depends more or less directly on the strength of H-bonding interaction.

(b) Formation of H-bond increases the A-H deformation force constants by constraining the deformation modes thereby shifting the latter to higher frequencies. These shifts however are appreciably smaller than that for the A-H stretching mode. The half band widths and integrated absorption intensities of the deformation modes, though not well investigated, show very little changes.

(c) The vibrational modes of the proton acceptor B are also shifted by H-bonding. These shifts, which may be positive or negative, are however much smaller than those for the donor A-H vibrations.

(d) New vibrational modes corresponding to the H..B bond stretching and bending are found in the far infrared region (at 100-200 cm^{-1}).

III.4. Thermodynamics of H-Bonding :

The extent of interaction between a proton donor and an acceptor can be understood from the thermodynamic quantities $\Delta H°$, $\Delta S°$ etc. associated with the formation of the H-bond. There have been many efforts to correlate such thermodynamic quantities with the spectroscopic properties such as i.r. frequency shift, change of intensity, p.m.r. chemical shift etc. A large variety of such correlations have been reviewed by Joesten and Schaad[98]. Again, because of the use of i.r. spectroscopy in the present work, the correlations of i.r. frequency shifts and changes of integrated intensities with ΔH° values are briefly considered here.

A linear relationship between the shift in i.r. stretching frequency caused by H-bonding($\Delta\bar{\nu}$)and ΔH° was first suggested by Badger and Bauer[74] from a study of H-bonding of phenols with various bases. Since $\Delta\bar{\nu}$ depends on the extent of interaction between the proton donor and acceptor, it is reasonable to expect larger frequency shifts for stronger H-bonds, i.e. those with larger ΔH°. This idea seems to be widely accepted because of its simplicity. There have been attempts to provide some theoretical basis for the linear $\Delta\bar{\nu}$-ΔH° relationships[99]. However there are also several systems where such linear $\Delta\bar{\nu}$-ΔH° relationships are found to be inapplicable. Rao and co-workers[100] have observed that the linear $\Delta\bar{\nu}$-ΔH° relationship is approximately applicable for ΔH°'s in the range 12-24 kJ mol^{-1} only, with serious deviations outside this range. Kuhn and Wires[83] from their study of intramolecular H-bonding in 2-methoxy ethanol, 3-methoxy propanol and 4-methoxy butanol have reported that while $\Delta\bar{\nu}$ increased from 30 to 180 cm^{-1}, ΔH° was practically the same. In the case of phenol-cyclohexyl halide systems[101] as well as in orthohalophenols[10 a reversal of $\Delta\bar{\nu}$-ΔH° relationship has been reported; i.e. $\Delta\bar{\nu}$ changes in the order $I > Br > Cl$ whereas ΔH° varies in the opposite order. The nonapplicability of the Badger-Bauer rule is attributed to special factors such as conformational interactions[83], differences in atomic size and polarizability[101,102] relative basicity and acidity of the proton acceptor and donor[103] etc.

Such frequency shift correlations have been restricted to the fundamental bond stretching vibrations only. Far less data are available for the overtone vibrations as the band intensities are much less than those of the fundamentals[104] and the bands cannot always be located with certainty. In the case of bending vibrations, the frequency shifts are found to occur in opposite directions[105].

Iogansen[106] has proposed a relationship $\Delta H^\circ = 5.3(\Gamma_1^{1/2} - \Gamma_2^{1/2})$ where $\Gamma = 1/CL\int \ln(I_0/I)_{\bar{\nu}} d\ln\bar{\nu} \approx B/\bar{\nu}_0$, Γ_1 and Γ_2 being the intensities of the H-bonded and the free OH groups respectively. This relationship is apparently found to be obeyed by a variety of H-bonded systems such as phenol-ether, phenol-alcohol, self association of carboxylic acids etc. Accurate measurements of Γ are however difficult because of a large width of the H-bonded OH..O band and its overlap with the neighbouring bands.

Because of the empiricism involved in such correlations, they are of little use in quantitative analysis. A proper understanding of the interaction energy and the types of associated species present in an H-bonding system is based on experimental determation of the thermodynamic quantities ΔH°, ΔS° and ΔG°, which is explained in the next chapter.

CHAPTER IV

EXPERIMENTAL

CHAPTER IV

EXPERIMENTAL

IV.1. Preparation/Purification of Compounds and Preparation of Solutions :

Ethanol (spectrosol), ethylene glycol monomethyl, -ethyl and -butyl ethers (Merck, AnalaR grade, purity > 98%) and diethylene glycol monomethyl and -ethyl ethers (BDH, purity > 98.5%) used in the present work were freed from the traces of moisture by treating them successively with anhydrous Na_2SO_4, sodium metal and $LiAlH_4$. The middle fractions of the final distillations were collected over activated Al_2O_3 and stored in a desiccator over P_2O_5. The final purity of the compounds, as checked by v.p.c., was found to be > 99%.

Tri- and tetramethylene glycol monomethyl ethers were prepared by the method of Smith and Sprung[107]. For this a large quantity (~160-180 g) of the respective diol was heated to ~ 120°C in a flask fitted with a stirrer and reflux condenser and 5 g of sodium dissolved piecewise with vigorous stirring. The solution was cooled to 20°C and 30 g methyl iodide added dropwise. The reaction mixture was then heated slowly and refluxed at 70°C for about three hours. During the addition of methyl iodide and the process of refluxing, ice water was constantly circulated through the reflux condenser. The desired monoether in each case was separated by fractional distillation (yield ~ 10-11 g ; boiling points - $H_3CO(CH_2)_3OH$, 147°C and $H_3CO(CH_2)_4OH$, 164°C). These were further refractionated twice to obtain the final products of 99% purity as checked by v.p.c.

AnalaR grade carbon tetrachloride (Merck, Pro-Analyst), stored over P_2O_5, was used as the solvent. Before use, it was filtered through a fine sintered glass. Generally a stock solution of concentration 0.5 mol dm^{-3} was first prepared, the solutions of desired concentration being then obtained by successive dilutions. Preparation of solutions and filling the cells were carried out in a dry box maintained at positive pressure with a stream of dry air.

IV.2. Spectroscopic Measurements :

The spectra in the hydroxyl stretching vibration region (3700-3200 cm^{-1}) were recorded on a Perkin-Elmer 221 spectrophotomete calibrated with the atmospheric moisture-and CO_2 bands. The spectral slit width at 3500 cm^{-1} was determined to be 1.2 cm^{-1}. Standard settings of the Slit Programme (927), Attenuator Speed (1100), Amplifier Gain (2) and Suppression (4) were used. To facilitate the resolution of overlapping bands, the frequency scale was expanded four times (12.5 cm^{-1}/cm) and the recording speed reduced to 25 cm^{-1}/min.

Variable path length cells (Perkin-Elmer) fitted with NaCl windows were used throughout the work. The cell-zero was periodically checked by obtaining interference fringes and using the relationship $h = n/2(\bar{\nu}_1-\bar{\nu}_2)$ where h is the path length in cm and n the number of fringes between the frequencies $\bar{\nu}_1$ and $\bar{\nu}_2$. The path length of the cells could be varied from 0.01 to 1.0 cm.

The solution cell was fitted with a nichrome heating element the current passing through which was controlled by a variac. A copper-constantan thermocouple inserted in one of the cell-windows was used to determine the temperature. Measurements were made over the temperature range of 298 to 338 K at intervals of 5 K. No detectable change in the base line was observed by heating the sample cell upto 338 K against the reference cell at room temperature (298 K), both the cells being filled with CCl_4 at equal path lengths. The spectra of solutions at various temperatures were therefore recorded against the reference cell at room temperature.

IV.3. Computation of Band Area :

The overlapping bands of the free and H-bonded OH groups were first resolved, the procedure for which is described at appropriate places in the following chapters. The area of an individual band $\int \ln(T_o/T)_\nu d\bar{\nu}$ can be obtained by the method of direct integration if its exact shape (Loretzian, Gaussian etc.) is known. As the experimental bands were neither purely Lorentzian nor Gaussian due to several factors mentioned earlier (Section II-2) their areas A' were evaluated by graphical integration, i.e. by summing the respective $\ln(T_o/T)_{\bar{\nu}}$ values over the entire band and multiplying by the common frequency interval $\delta\bar{\nu}$ (generally 2.5 cm^{-1} used. Thus

$$A' = \sum \ln(T_o/T)_\nu \delta\bar{\nu} = 2.303 \times 2.5 \times \sum \log(T_o/T)_{\bar{\nu}}$$

Wing Correction[88] - As the absorption falls to $\sim 1\%$, the experimental error becomes of the same order of magnitude as the absorbance reading. The area of an experimental band can therefore be measured over only a finite frequency range $|\bar{\nu}-\bar{\nu}_0| \approx$ 50-100 cm^{-1} on both sides of the band center. Since the band is considered to extend indefinitely, the residual area under the 'wings' becomes an appreciable fraction of the total band area; for though the absorption is small, the frequency interval by which it is multiplied is very large. The correction for this residual area called the 'wing correction' can be conveniently expressed as a percentage of the measured band area and depends on the value of $(\bar{\nu}-\bar{\nu}_0)/b$ where $b = 1/2\ \Delta\bar{\nu}_{1/2}$. Ramsay[88] has determined the wing corrections for various values of $(\bar{\nu}-\bar{\nu}_0)/b$. The experimental band areas (A') were corrected by using appropriate wing corrections (Table IV.1)[*] derived from Ramsay's tables[88].

Density Correction - The expansion of CCl_4 at higher temperatures results in lowering of the effective concentrations of different species in solution and thereby diminishing the band areas. A correction to the measured band areas due to a change in the density of CCl_4 is therefore necessary. The density corrections (Table IV.2)[*] were determined using the relation[108]

$$d_t = 1.63255 - 1.911 \times 10^{-3}\ t - 0.69 \times 10^{-6}\ t^2$$

where d_t is the density of CCl_4 at the temperature t°C. The band areas so obtained i.e. after applying the wing- and density corrections are denoted by A.

The uncertainty in the measured band areas (A') was estimated to be ~3-4%. This together with various instrumental and experimental factors involved[89,90] results in an overall error of ~5% in the final band areas (A). In the case of the weak bands of the free OH groups of ethylene- and diethylene glycol monoalkyl ethers, this error might be somewhat larger (~10%).

IV.4. Determination of Concentrations and Integrated Intensities of Different Species in Solutions :

Since the free as well as H-bonded molecules are present in solutions of the present compounds at all concentrations, their individual concentrations cannot be determined by any direct method. The concentrations of the free and intramolecularly H-bonded OH groups were first determined from the respective band areas and integrated intensities as explained below.

The concentration of the free OH group was determined by assuming its integrated intensity to be identical with that of the free OH band of ethanol. This assumption is reasonable in view of the observed constancy of the position, half-band width and intensity of the free OH band of a number of primary, unbranched alcohols ($\bar{\nu}_0$ = 3630 - 3640 cm^{-1}, $\Delta\bar{\nu}_{1/2}$ = 25 - 30 cm^{-1} and $\varepsilon^a_{max} \sim 60$ at 300 K)[2,3,109]. To determine the integrated intensity, the free OH band of ethanol in CCl_4 ($C = 0.075$ mol dm^{-3}, $L = 1.0$ cm) was recorded at various temperatures in the range 298-338 K and its area determined as explained above. The values of the measured and corrected band areas together with the integrated intensities (B_F)

calculated from the relation $B = A/CL$ are given in Table IV.3.[*] The spectroscopic properties of this band measured in the present study ($\bar{\nu}_o = 3635 \pm 2.5$ cm^{-1}, $\Delta\bar{\nu}_{1/2} = 27.5 \pm 2.5$ cm^{-1}, $B_F = 4.7 \times 10^3$ dm^3 mol^{-1} cm^{-2} and $dB/dT = -19$ dm^3 mol^{-1} cm^{-2} K^{-1}) are in good agreement with those reported in literature[2,28].

The concentrations of the free OH groups $C_{OH(F)}$ in all the systems at various temperatures were estimated from the respective band areas and the corresponding values of B_F using the relation $C = A/BL$. The concentrations of the intramolecularly H-bonded OH groups $C_{OH(I)}$ in very dilute solutions of ethylene-, trimethylene- and tetramethylene glycol monoalkyl ethers were obtained by subtracting $C_{OH(F)}$ from the solution concentration (C_3), i.e. $C_{OH(I)} = C_3 - C_{OH(F)}$. The integrated intensities of the intramolecularly H-bonded OH groups (B_I) were then calculated from the respective band areas. The method of calculations is illustrated in Table IV.4.[**] Similar procedure has been used by Buc and Neel[65] and by Kuhn and Wires[83].

Because of the presence of two ether oxygens in diethylene glycol monoalkyl ethers, there are two types of intramolecularly H-bonded OH groups, viz. those in the five- and eight membered ring monomers (M_5 and M_8 respectively). The spectral characteristics of the intramolecularly H-bonded OH band of M_5 are identical with those of the intramolecularly H-bonded (five membered ring) monomer of ethylene glycol monoalkyl ethers, viz. $\bar{\nu}_o = 3600 \pm 2.5$ cm^{-1} and $\Delta\bar{\nu}_{1/2} = 32.5 \pm 2.5$ cm^{-1}. The integrated intensity of the former (B_5)

was therefore assumed to be identical with that of the latter. The concentration of the five membered ring OH group (C_5) could then be determined from the respective band areas (A_5) as usual viz. $C_5 = A_5/B_5L$ where $B_5 = B_I$ of ethylene glycol monoalkyl ethers. The concentration of the eight membered ring OH group (C_8) in dilute solutions was then estimated by subtracting the C_F and C_5 from the solution concentration C_S, i.e. $C_8 = C_S - (C_F + C_5)$. The integrated intensities of the eight membered ring OH band (B_8) at various temperatures were then calculated using the corresponding band areas and concentrations.

In very dilute solutions where only the monomers (free and intramolecularly H-bonded) are present, their concentrations (C_F and C_I respectively) are the same as the corresponding free and intramolecularly H-bonded OH group concentrations, viz. $C_F = C_{OH(F)}$ and $C_I = C_{OH(I)}$. At higher concentrations containing intermolecularly associated species (n-mers), the group concentrations $C_{OH(F)}$ and $C_{OH(I)}$ may not be the same as the monomer concentrations C_F and C_I because the n-mers are also likely to contribute to $C_{OH(F)}$ or $C_{OH(I)}$ depending on their exact structure such as open, closed etc. The procedure for determining the concentrations of the n-mer and monomers is based on the assumption of only one type of n-mer (such as dimer, trimer etc.) making a significant contribution to the self association over the concentration range studied . This assumption is justifiable since the solutions used were relatively dilute. Similar method has been adopted by Saunders and Hyne[43]. The concentration of the n-mer would then be given by

$$C_n = \frac{1}{n} (C_S - (C_F + C_I))$$

where C_S is the concentration of the solution used. The values of C_F, C_I and C_n are then determined in terms of C_S, $C_{OH(F)}$ and $C_{OH(I)}$ based on the particular self-association model such as open or closed dimer, trimer etc. Since the exact nature of the n-mer would depend on the type of compound and the concentration range studied, the method for determining the concentrations of the n-mer (C_n) and the two types of monomers (C_F and C_I) is separately explained at appropriate places.

IV.5. Determination of Thermodynamic Quantities :

Thus the systems under investigation exhibit multiple equilibria involving free monomer (M_F), intramolecularly H-bonded monomer/s (M_I) and intermolecularly H-bonded species (n-mer). As the temperature is increased, the concentrations of the H-bonded species decrease resulting in an overall increase in the concentration of the free monomer. The significant equilibria are therefore represented as

$$\text{n-mer} \rightleftharpoons n\,M_F \qquad \text{and} \qquad M_I \rightleftharpoons M_F,$$

with the equilibrium constants defined as

$$K_{nF} = C_F^n / C_n \qquad \text{and} \qquad K_{IF} = C_F/C_I \, .$$

The thermodynamic quantities $\Delta G°$, $\Delta H°$ and $\Delta S°$ for each of the equilibrium are then determined using the relations

$$\Delta G^\circ = -RT\ln K = \Delta H^\circ - T\Delta S^\circ$$

or alternatively

$$\ln K = -(\Delta H^\circ/R)(1/T) + (\Delta S^\circ/R)$$

The values of ΔH° and ΔS° are calculated respectively from the slope and intercept of the graph of log K vs 1/T, the best values together with their error limits being estimated by the method of least squares.

TABLE IV.1 : Wing corrections (%) for various OH bands

Compound	Free	Type of OH Band Intra. H-bonded	Associated
Ethanol	20	-	-
Ethylene glycol monoalkyl ethers	28	20	26
Diethylene glycol monoalkyl ethers	28	17^a, 24^b	*
Trimethylene glycol monomethyl ether	14	20	*
Tetramethylene glycol monomethyl ether	16	21	*

a and b : for the five- and eight membered ring monomers resp.

* : Association band not resolvable.

TABLE IV.2 : Density corrections for CCl_4

Temperature T/K	Density correction %	Temperature T/K	Density correction %
298	0.0	323	3.2
303	0.6	328	3.9
308	1.3	333	4.6
313	1.9	338	5.3
318	2.6	343	6.0

TABLE IV.3 : Areas and integrated intensities of the free OH band of ethanol
($C = 7.5 \times 10^{-3}$ mol dm^{-3}, $L = 1.0$ cm)

Temp. T/K	Band area Measured A'	Band area Corrected A	Integrated intensity $B = A/CL$ /dm^3 mol^{-1} cm^{-2} x 10^{-3}
298	29.6	35.4	4.7
303	-	-	4.6*
308	27.9	33.8	4.5
313	27.3	33.2	4.4
318	26.4	32.5	4.3
323	25.4	31.4	4.2
328	-	-	4.1*
333	24.2	30.3	4.0
338	23.6	29.7	3.9

*Obtained from the graph of B_F vs T (cf Fig. VIII.2).

TABLE IV.4 : The method of calculations - an illustration:
Ethylene Glycol Monomethyl Ether
$C_S = 10 \times 10^{-3}$ mol dm^{-3}, L = 1.0 cm, T = 298 K.

	Free OH	Intramolecularly H-bonded OH
Measured band area A'	3.17	48.9
Wing correction	28%	20%
Area corrected for wings	4.1	58.7
Density correction	-	-
Final band area A	$A_F = 4.1$	$A_I = 58.7$
Concentration C/mol dm^{-3}	$C_{OH(F)} = A_F/B_F^{*}L$ $= 0.87 \times 10^{-3}$	$C_{OH(I)} = C_S - C_{OH(F)}$ $= 9.13 \times 10^{-3}$
Integrated intensity B/dm^3 mol^{-1} cm^{-2}	$B_F^{*} = 4.7 \times 10^3$	$B_I = A_I/C_I L$ $= 6.4 \times 10^3$
Equilibrium constant	$K_{IF} = C_F/C_I = 9.5 \times 10^{-2}$	
Free energy change	$\Delta G^\circ_{IF} = -2.303 RT \log K = 5.9$ kJ mol^{-1}	

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*From Table IV.3 .

CHAPTER V

ASSOCIATION BEHAVIOUR OF ETHYLENE GLYCOL MONOALKYL ETHERS

CHAPTER V

ASSOCIATION BEHAVIOUR OF ETHYLENE GLYCOL MONOALKYL ETHERS

V.1. Introduction :

Ethylene glycol monoalkyl ethers $RO(CH_2)_2OH$ in very dilute CCl_4 solutions ($C_S \leqslant 0.01$ mol dm^{-3}) exhibit two OH bands at ∼ 3635 and 3600 cm^{-1}, the relative intensities of which are constant and independent of concentration. With increasing concentration, an additional OH band appears at ∼ 3475 cm^{-1}, the relative intensity and asymmetry of which increase rapidly with concentration (Fig. V.1). The 3635 and 3600 cm^{-1} bands are attributed to the OH groups of free (trans or non H-bonded gauche) and intramolecularly H-bonded (cis or gauche) monomers respectively[63,76,80,83]. (cf Fig. V.3(a) and (b)). The 3475 cm^{-1} band is symmetric in the concentration range 0.01 - 0.1 mol dm^{-3} and comparable with the first association band of simple alcohols at 3500 cm^{-1}. The asymmetry of the 3475 cm^{-1} band above 0.1 mol dm^{-3} and the absence of any additional OH bands unlike simple alcohols (in the 3300 cm^{-1} region) then suggest the formation of closely similar associated species.

The symmetric 3475 cm^{-1} band in the case of solutions having concentrations $C_S \leqslant 0.1$ mol dm^{-3} must be due to a single type of intermolecularly associated species (n-mer). The free monomer (M_F), intramolecularly H-bonded monomer (M_I) and the

ETHYLENE GLYCOL MONOALKYL ETHERS

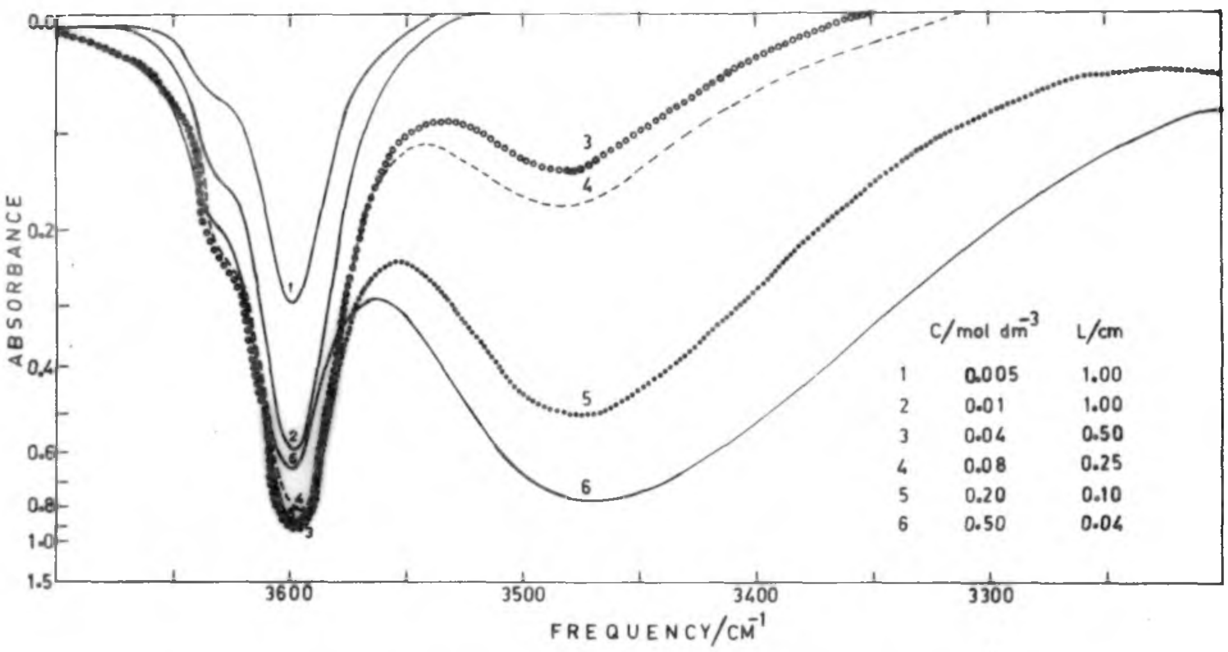

FIG-V-1: OH BANDS AT VARIOUS CONCENTRATIONS (T = 298 K)

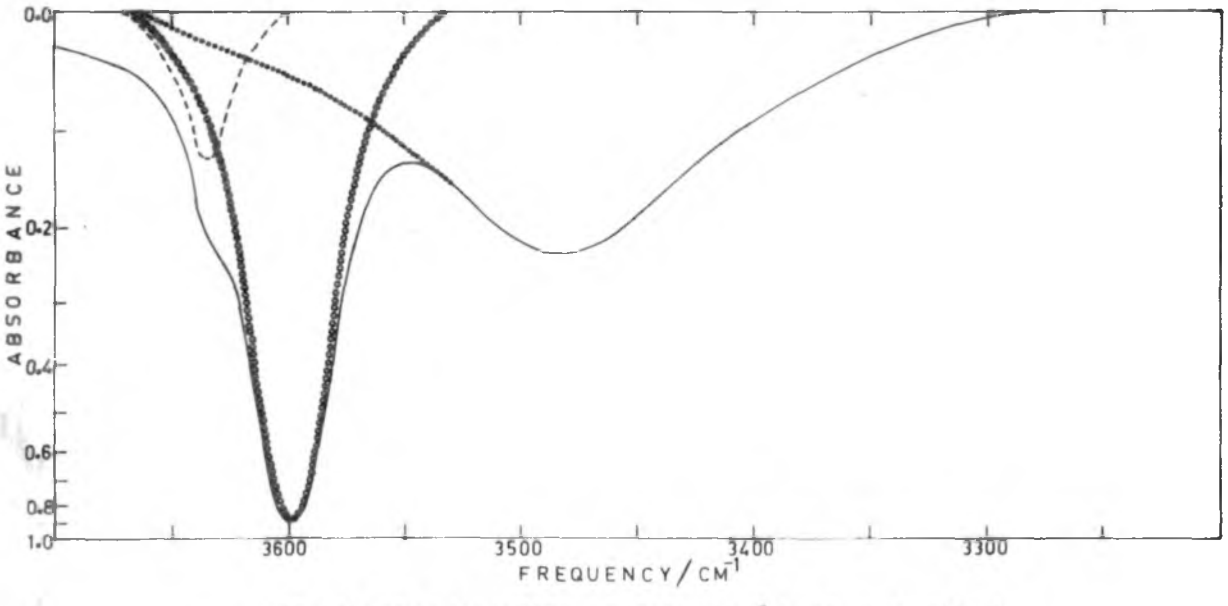

FIG-V-2: BAND RESOLUTION (C = 0.01 mol dm^{-3}, L = 1.0 cm, T = 298 K) n-mer in the concentration range $C_S = 0.01 - 0.1$ mol dm^{-3} would then be in a three way equilibrium viz.

$$\text{n-mer} \rightleftharpoons nM_F, \quad \text{n-mer} \rightleftharpoons nM_I \quad \text{and} \quad M_I \rightleftharpoons M_F \qquad ..\ (1)$$

the equilibrium constants for which can be defined as

$$K_{nF} = C_F^n/C_n, \quad K_{nI} = C_I^n/C_n \quad \text{and} \quad K_{IF} = C_F/C_I \qquad ..\ (2)$$

where C_F and C_I are the concentrations of the respective monomers and C_n that of the n-mer calculated as

$$C_n = \frac{1}{n}(C_S - (C_F + C_I)) \qquad ..\ (3)$$

To determine C_F, C_I and C_n, it is necessary to know the concentrations of the free and intramolecularly H-bonded OH groups which were calculated from the respective band areas. The overlapping bands were therefore first resolved as follows (Fig. V.2)

The low frequency side of the 3475 cm^{-1} band is free from any overlap which was reflected across the band maximum to generate the high frequency side. The low frequency side of the 3600 cm^{-1} band was then obtained by subtracting the high frequency side of the 3475 cm^{-1} band from the experimental spectrum in the region 3600-3500 cm^{-1} which in turn was reflected across the band maximum at 3600 cm^{-1} to obtain the high frequency side. The same procedure was repeated to resolve the 3635 cm^{-1} band. At concentrations $\leqslant$ 0.01 mol dm^{-3}, there are only two OH bands (at ~3635 and ~ 3600 cm^{-1}) which were resolved in the same manner by starting with the low frequency side of the 3600 cm^{-1} band.

The areas of the resolved bands were measured and corrected by applying appropriate wing- and density corrections. Using very dilute solutions ($C \leqslant 0.01$ mol dm^{-3}), the integrated intensities of the intramolecularly H-bonded OH bands (B_I) were determined (Table V.12). In more concentrated solutions (containing associated species), the concentrations of the free and intramolecularly H-bonded OH groups ($C_{OH(F)}$ and $C_{OH(I)}$) were estimated from the corresponding band areas and integrated intensities using the relations

$$C_{OH(F)} = A_F/B_F L \quad \text{and} \quad C_{OH(I)} = A_I/B_I L \qquad .. (4)$$

The measured areas of various OH bands of ethylene glycol monomethyl-, -ethyl- and -butyl ethers in CCl_4 solutions of different concentrations are given in Tables[*] V.1-3. A comparison of the respective band areas of the three compounds at comparable concentrations shows that they are directly proportional to one another indicating the association behaviour of these compounds (i.e. type of associated species present, the thermodynamic quantities involved etc.) to be identical. The detailed treatment of the experimental data for ethylene glycol monomethyl ether only is therefore presented in Tables[*] V.4-9, while the final results for all the three monoethers are summarized in Tables[*] V.10-13.

V.2. Intramolecular H-Bonding :

The spectroscopic properties of the intramolecularly H-bonded OH's (Tables V. 13) as well as the thermodynamic quantities associated with the M_I-M_F equilibrium (Table V. 11) are found to be the same for the three monoethers studied showing little effect of chain length of the alkyl group on intramolecular H-bonding. The present values of $\bar{\nu}_o$, $\Delta\bar{\nu}_{1/2}$ and B for the free and intramolecularly H-bonded OH's are in close agreement with literature values[2,69,80,83]. The values of $\Delta H^{\circ}_{IF} \sim 14$ kJ mol^{-1} and $\Delta G^{\circ}_{IF} = 5.8$ kJ mol^{-1} are comparable with those of Kuhn and Wires[83], viz. 10 ± 2 and 5.4 kJ mol^{-1} respectively, the differences between the two sets of values being due to different procedures used. The frequency shift on intramolecular H-bonding in ethylene glycol monoalkyl ethers ($\Delta\bar{\nu} = 35$ cm^{-1}) is found to be larger than that for ethylene glycol ($\Delta\bar{\nu} = 25$ cm^{-1})[75,76] suggesting higher basicity of the ether oxygen as a proton acceptor than that of the hydroxylic oxygen. It is notable that this small difference in the basicity of the proton acceptors in simple diols and diol monoalkyl ethers results in an appreciable difference in relative populations of their free and intramolecularly H-bonded monomers. Thus while the intramolecularly H-bonded monomer predominates over the free monomer in the case of ethylene glycol monoalkyl ethers (Table V.8), the reverse is true for ethylene glycol[73].

The gauche isomers are stabilized by intramolecular H-bonding of the hydroxylic proton oriented towards one of the lone electron pairs on the ether oxygen resulting in a nonplaner five membered ring. The OH...O bond angle would be much less than 180° resulting in a bent H-bond. The O...H distance of 2.3 A calculated using the relation proposed by Kuhn[69] (viz. $\Delta\bar{\nu} = 250 \times 10^{-8}/$ -74, L in cm) is comparable with that of 2.1 A in butane 1,2 diol reported by Fishman and Chen[68]. Thus the proton cannot get very close to the acceptor resulting in small H-bonding interaction.

The bent and weak H-bond so formed gives rise to an enthalpy change of ~14 kJ mol^{-1} only. It is however noteworthy that this small $\Delta H°$ stabilizes the gauche isomers to such an extent that only a small fraction of molecules (~8-10% at 298 K) is in the free form (Table V.8). Miyake[79] and Srinivasan et al[80], from study of CH_2 rocking modes (at ~800 cm^{-1}) have found that the OCH_2CH_2O skeletons of various ethylene glycol monoalkyl ethers in the liquid state as well as in solutions exist, almost exclusively, in the gauche form.

V.3. Intermolecular H-Bonding :

As mentioned earlier (Section IV. 4), it is reasonable to assume a single type of associated species predominating over others because the solutions used were relatively dilute. The possibility of different types of dimers (Fig. V.3(c)-(g)) as well as similar trimers and tetramers was therefore examined as explained below.

Feeney and Walker[49] have suggested an open dimer for ethylene glycol monomethyl ether from n.m.r. study (concentration range 0.1-1.3 mol dm^{-3}). At such high concentrations, more than one type of associated species are indeed formed as shown by asymmetric nature of the 3475 cm^{-1} band above 0.1 mol dm^{-3}. To test the possibility of any open n-mer, it can be seen that its free OH group would absorb in the same spectral region as that of the free monomer thus contributing to the 3635 cm^{-1} band. Therefore

$$C_{OH(F)} = C_F + C_n \qquad .. (5)$$

and consequently

$$C_n = \frac{1}{n}\left(C_S -(C_{OH(F)} + C_{OH(I)}) \right) \quad \text{and} \quad C_I = C_{OH(I)} \qquad .. (6)$$

These equations imply $C_{OH(F)} > C_n$. The concentrations of open dimer, trimer and tetramer along with the $C_{OH(F)}$ values for ethylene glycol monomethyl ether solutions at 298 K, as an illustration, are shown in Table V. 6, from which it is evident that the requirement of $C'_{OH(F)} > C_n$ is in general not satisfied by the present systems. Equilibria involving open n-mers were therefore ruled out.

Saito et al[77] have suggested a dimer involving association of a free monomer with an intramolecularly H-bonded monomer (Fig. V. 3(e)). The intramolecularly H-bonded OH group of such a dimer would absorb in the same spectral region as that of the intramolecularly H-bonded monomer, contributing to the 3600 cm^{-1} band. Thus

$$C_{OH(I)} = C_I + C_D \qquad .. (7)$$

and therefore

$$C_D = \frac{1}{2}\left(C_S -(C_{OH(F)} + C_{OH(I)}) \right) \quad \text{and} \quad C_F = C_{OH(F)} \qquad .. (8)$$

(In the case of dimer, here and hereafter, the letter 'n' has been replaced by 2 and/or D for convenience).

Finally in the case of cyclic n-mers, their OH groups (e.g. Fig. V. 3(f)/(g)) would contribute neither to the 3635 - nor to the 3600 cm^{-1} band and hence

$$C_{OH(F)} = C_F, \quad C_{OH(I)} = C_I \quad \text{and} \quad C_n = \frac{1}{n}\left(C_s -(C_{OH(F)} + C_{OH(I)})\right) .. (9)$$

ETHYLENE GLYCOL MONOALKYL ETHERS

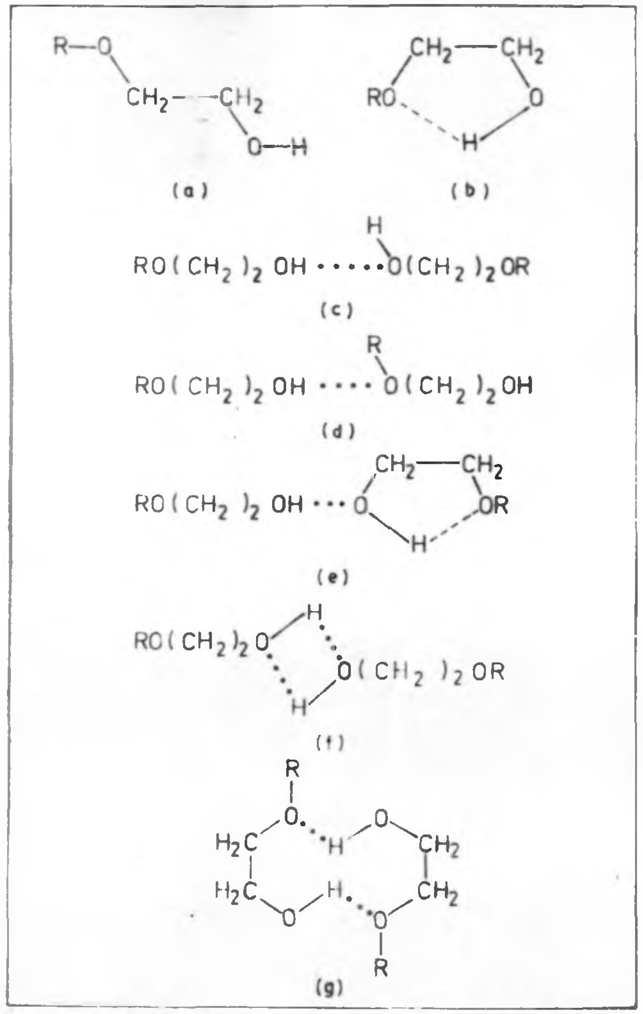

FIG-V-3: TYPICAL STRUCTURES FOR MONOMERS (a & b) AND

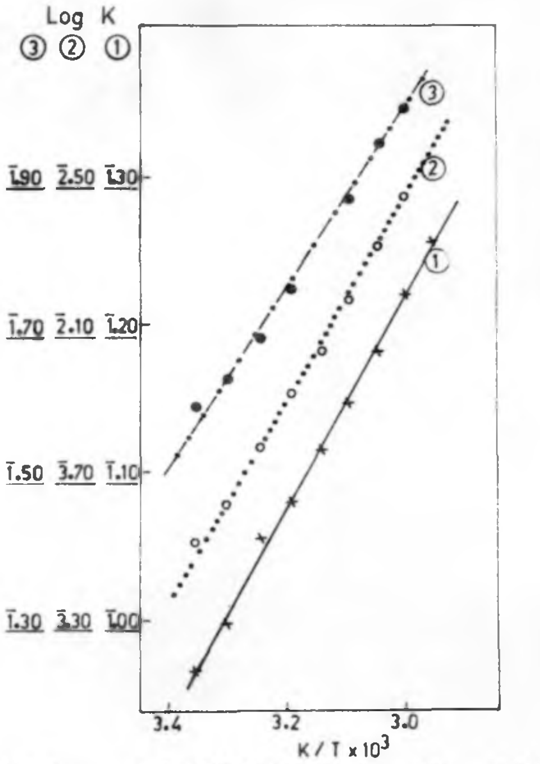

FIG-V-4: GRAPHS OF (1) Log K_{IF}, (2) Log K_{DF} and (3) Log K_{DI} vs 1/T.

The concentrations of various species calculated on the basis of equations (7)-(9) are included in Table V. 6 . The corresponding equilibrium constants calculated using equations (2) are given in Table V. 7 . As can be seen, the equilibrium constants for cyclic trimers, cyclic tetramers and those for the dimer suggested by Saito et al[77] exhibit wide variations eliminating these as the possible predominant species. The equilibrium constants for cyclic dimers (Fig. V. 3(f)/(g)) on the other hand show good constancy and the corresponding plots of log K vs 1/T exhibit good linearity (Fig. V.4) suggesting these as the possible predominant species in the present systems.

The concentrations of the two monomers and the dimer calculated on the basis of cyclic dimers as the associated species in different solutions of ethylene glycol monomethyl ether at various temperatures are therefore given in Table V. 8. The corresponding equilibrium constants are presented in Table V. 9 and the mean values of various K's over the concentration range studied in Table V. 10. The graphs of log $\bar{K}$ vs 1/T for the three equilibria are shown in Fig. V.4 , the good linearity of which supports the association model considered. The thermodynamic quantities obtained from these graphs are presented in Table V. 11. The integrated intensities of the dimer band at various temperatures were determined from its areas in the spectra of 0.10 mol dm^{-3} concentrated solution and are given in Table V. 12. As mentioned before, since the association behaviour of the other two monoethers (-ethyl, and -butyl) was found to be almost identical with that of the monomethyl ether, only the final results for them viz. the integrated intensities, mean values of the equilibrium constants and the thermodynamic and spectroscopic properties are presented along with those for the monomethyl ether in respective tables.

V.4. Structure of The Dimer :

The constancy of the equilibrium constants and the linearity of the log K vs 1/T plots have shown cyclic dimers as the main associated species. The cyclic dimer however can be either a four- or a ten membered ring species depending upon the involvement of the hydroxylic or the ether oxygens in H-bonding (Fig. V.3(f) and (g)). As the thermodynamic quantities ΔH°_{DF} and ΔS°_{DF} would be considerably different for these two types, the observed thermodynamic quantities were analysed to arrive at the final structure.

The four membered ring (Fig. V. 3(f)) with the hydroxyl oxygens involved in H-bonding will be considerably strained because of the unfavourable O-H..O angle. The weak H-bonds of such species would result in small ΔH° value. The ΔS° value would also be small as the free rotations of only the OH groups are restricted leaving rest of the groups free to rotate as in the free monomers. Such dimers have been proposed[28-31] for some alcohols with ΔH° and ΔS° values ranging over 12-24 kJ mol^{-1} and 30-80 JK^{-1} mol^{-1} respectively. The observed values of $\Delta H^\circ_{DF} = 55$ kJ mol^{-1} and $\Delta S^\circ_{DF} = 136$ JK^{-1} mol^{-1}, which are considerably higher, therefore do not favour the four membered ring structure for the dimer.

The ten membered ring (Fig. V. 3(g)) is strain free and involves the more basic ether oxygens in H-bonding. The H-bonds in such a structure would therefore be stronger resulting in larger ΔH°_{DF} value. The ΔS°_{DF} value will also be much higher due to the larger ring size restricting rotations about various C-C and C-O bonds. The observed values of ΔH°_{DF} and ΔS°_{DF} thus clearly favour the ten membered ring structure for the dimer. The ten membered ring structure had earlier been suggested for ethoxy ethanol by Srinivasan et al[80b] from a qualitative study and by Lodygina et al[85] from the shift of the ether absorption frequency from 1132 cm^{-1} in pure liquid to 1125 cm^{-1} in very dilute CCl_4 solutions. Lodygina et al[85] have reported the thermodynamic quantities for the equilibrium between the species represented by the 3470 and 3610 cm^{-1} bands, assuming them to be due to the dimer and 'free' monomer respectively, but not taking into account the 3635 cm^{-1} band due to the free monomer. (They probably did not observe this band). The present thermodynamic values therefore cannot be compared with theirs.

Formation of the ten membered ring dimer naturally requires the $O-CH_2CH_2-O$ skeletons of the constituent monomers in gauche conformation. The intramolecularly H-bonded monomers with the OCH_2CH_2O group in gauche conformation are already present in large numbers. The formation of the ten membered ring dimer can therefore be understood in terms of an association of two gauche monomers, preserving their configurations. The stronger intermolecular H-bonding would stabilize the system by lowering the free energy. The probability of formation of such a dimer would of course be small because of the requirement of a greater number of bonds in suitable orientations resulting in larger decrease of entropy than that for the intramolecularly H-bonded monomer. The observation that $C_I >> C_D$ (Table V. 8) in spite of $\Delta H^\circ_{IF} << \Delta H^\circ_{DF}$ (Table V.11) is thus explained. The larger values of $\Delta\bar{\nu}_{1/2}$ and B for the dimer than those for the intramolecularly H-bonded monomer (Table V.13) are consistent with the larger H-bonding interaction in the former. Similarly the larger magnitudes of $\Delta\bar{\nu}_{1/2}$ and B for the dimer are explainable on the flexibility of the ten membered ring structure causing larger anharmonicity and change of dipole moment associated with the vibrations of the H-bonded OH's of the dimer than that in the relatively rigid five membered ring of the intramolecularly H-bonded monomer.

TABLE V.1 : Measured areas (A') of various OH bands of ethylene glycol monomethyl ether.

C_S*	10		40		60		80		100		
L/cm	1.0		0.48		0.32		0.24		0.18		
T/K	a	b	a	b	a	b	a	b	a	b	c
298	3.17	48.9	5.21	83.2	4.81	78.6	4.66	73.1	4.06	65.6	111
303	-	-	-	-	-	-	-	-	4.21	66.7	96.8
308	-	-	5.98	80.1	5.67	77.0	5.48	73.0	-	-	-
313	3.50	45.7	6.64	79.0	6.04	76.5	5.73	73.0	5.29	67.2	74.8
318	3.61	44.6	6.52	78.2	6.06	76.2	6.10	72.5	-	-	-
323	3.82	43.8	7.16	77.1	-	-	6.25	72.9	5.79	66.8	54.8
328	4.05	42.3	7.63	75.9	7.38	73.9	7.17	71.8	6.56	66.2	47.3
333	4.27	41.2	7.68	74.8	-	-	7.91	70.4	-	-	-
338	4.48	39.8	7.86	73.9	8.30	72.4	7.60	71.5	7.27	65.4	35.5

*C_S (solution concentration) in mol $dm^{-3} \times 10^3$

a - 3635 cm^{-1} band; b - 3600 cm^{-1} band and c - 3475 cm^{-1} band.

TABLE V.2 : Measured areas (A') of various OH bands of ethylene glycol monoethyl ether

C_s*	9		40		60		75		100		
L/cm	1.0		0.40		0.267		0.213		0.16		
T/K	a	b	a	b	a	b	a	b	a	b	c
298	2.34	43.5	4.48	63.8	4.19	59.7	4.09	59.1	3.83	55.9	94.8
303	-	-	-	-	-	-	-	-	-	-	-
308	-	-	5.00	63.7	-	-	4.82	59.4	-	-	-
313	3.24	39.9	5.10	63.7	5.06	60.2	4.95	59.1	4.46	57.0	71.9
318	3.38	38.9	5.46	63.1	5.36	59.9	-	-	5.07	57.0	61.5
323	3.50	37.9	5.91	62.2	6.02	59.7	5.53	59.7	-	-	-
328	3.71	36.6	7.63	61.0	7.38	59.0	7.17	58.4	6.56	56.5	51.6
333	3.97	35.7	7.68	59.6	-	-	7.91	55.6	-	-	-
338	4.10	34.4	7.86	59.0	8.30	57.6	7.60	57.5	7.27	56.1	38.6

*C_s (solution concentration) in mol $dm^{-3} \times 10^3$.

a - 3635 cm^{-1} band; b - 3600 cm^{-1} band; c - 3475 cm^{-1} band .

TABLE V.3 : Measured areas (A') of various OH bands of ethylene glycol monobutyl ether

C_S*	8		40		50		75		100		
L/cm	1.0		0.40		0.32		0.213		0.12		
T/K	a	b	a	b	a	b	a	b	a	b	c
298	-	-	4.57	66.5	4.13	64.4	3.71	59.4	-	-	-
303	2.55	38.1	-	-	-	-	-	-	2.68	43.5	60.2
308	2.56	37.2	5.23	65.1	5.03	63.9	4.46	60.7	3.15	43.9	52.5
313	2.77	36.1	5.75	64.7	5.58	63.1	5.01	60.3	3.64	44.0	47.0
318	2.87	35.2	5.92	63.7	5.77	62.2	5.22	59.8	3.77	43.6	40.8
323	2.94	32.2	6.13	59.1	6.09	58.0	5.35	56.4	3.84	41.0	35.4
328	3.14	31.3	6.42	58.0	6.22	57.1	5.74	55.5	4.22	40.5	30.2
333	3.21	30.5	6.60	56.9	6.46	56.0	6.12	54.6	4.60	39.8	25.1
338	3.28	29.5	6.95	56.0	6.91	55.4	6.46	54.7	4.85	40.1	22.8

*C_S (solution concentration) in mol $dm^{-3} \times 10^3$.

a - 3635 cm^{-1} band; b - 3600 cm^{-1} band; c - 3475 cm^{-1} band.

TABLE V.4 : Corrected areas (A) of various OH bands of ethylene glycol monomethyl ether

C_S*	10		40		60		80		100		
L/cm	1.0		0.48		0.32		0.24		0.18		
T/K	a	b	a	b	a	b	a	b	a	b	c
298	4.07	58.7	6.69	99.8	6.17	94.3	5.99	87.7	5.21	78.7	111
303	-	-	-	-	-	-	-	-	5.44	80.5	96.8
308	-	-	7.79	97.3	7.37	93.6	7.13	88.7	-	-	-
313	4.58	55.9	8.69	96.6	7.91	93.5	7.50	89.2	6.93	82.2	74.8
318	4.75	54.8	8.59	96.3	7.98	93.8	8.03	89.2	-	-	-
323	5.07	54.2	9.49	95.5	-	-	8.29	90.3	7.67	82.8	54.8
328	5.40	52.7	10.2	94.6	7.85	92.1	9.58	89.2	8.75	82.5	47.3
333	5.73	51.7	10.3	93.9	-	-	10.6	88.3	-	-	-
338	6.05	50.2	10.6	93.4	11.2	91.5	10.3	90.3	9.83	82.6	35.5

*C_S (solution concentration) in mol $dm^{-3} \times 10^3$

a - 3635 cm^{-1} band; b - 3600 cm^{-1} band and c - 3475 cm^{-1} band.

TABLE V.5 : Concentrations of the free- and intramolecularly H-bonded OH groups in ethylene glycol monomethyl ether solutions of different concentrations (All concentrations in mol $dm^{-3} \times 10^3$)

C_S T/K	10		40		60		80		100	
	$C_{OH(F)}$	$C_{OH(I)}$	$C_{OH(F)}$	$C_{OH(I)}$	$C_{OH(F)}$	$C_{OH(I)}$	$C_{OH(F)}$	$C_{OH(I)}$	$C_{OH(F)}$	$C_{OH(I)}$
298	0.87	9.13	2.97	32.3	4.11	45.8	5.31	56.7	6.16	67.9
303	-	-	-	-	-	-	-	-	6.56	70.2
308	-	-	3.60	32.1	5.11	46.4	6.59	58.5	-	-
313	1.04	8.96	4.10	32.2	5.60	46.8	7.08	59.5	8.72	73.1
318	1.10	8.90	4.14	32.4	5.78	47.4	7.75	60.1	-	-
323	1.20	8.80	4.68	32.5	-	-	8.12	61.4	10.1	75.1
328	1.31	8.69	5.14	32.5	7.45	47.5	9.66	61.5	11.8	75.6
333	1.42	8.58	5.33	32.6	-	-	10.9	61.2	-	-
338	1.54	8.46	5.62	32.7	8.91	48.1	10.9	63.4	13.9	77.2

TABLE V.6 : Concentrations of various species (in mol $dm^{-3} \times 10^3$) in ethylene glycol monomethyl ether solutions at 298 K.

Structure type (cf Fig.V.3)	Species	$C_S \times 10^3$/mol dm^{-3}			
		40	60	80	100
		Concentrations $\times 10^3$/mol dm^{-3}			
	free OH	2.97	4.11	5.31	6.16
	intramolecularly bonded OH	32.3	45.8	56.8	67.9
(c)/(d)	open dimer	4.72	10.1	17.9	25.9
	open trimer	2.36	5.04	8.96	12.9
	open tetramer	1.57	3.36	5.98	8.63
(e)	'Saito' dimer	4.72	10.1	17.9	25.9
	intramolecularly H-bonded monomer	27.6	35.7	38.83	42.0
(f)/(g)	cyclic dimer	2.36	5.04	8.96	12.9
	cyclic trimer	1.57	3.36	5.97	8.63
	cyclic tetramer	1.18	2.52	4.48	6.47

TABLE V.7 : Equilibrium constants in ethylene glycol monomethyl ether solutions at 298 K (cf Table V.6 for concentrations)

associated species	equilibrium constant K	Solution concentration $C_S \times 10^3$ mol dm^{-3} 10	40	60	80	100	$\bar{K}$	maximum deviation (%) from $\bar{K}$
Fig.V.3(e)	$K_{IF} \times 10^2$	9.49	10.4	11.5	13.7	14.7	11.9	22
	$K_{DF} \times 10^3$	-	1.87	1.67	1.57	1.47	1.65	12
	$K_{DI} \times 10$	-	1.73	1.27	0.84	0.68	1.13	47
cyclic dimer (Fig.V.3(f)/(g)	$K_{IF} \times 10^2$	9.49	9.18	8.95	9.35	9.07	9.21	3
	$K_{DF} \times 10^3$	-	3.67	3.31	3.14	2.93	3.26	12
	$K_{DI} \times 10$	-	4.35	4.12	3.60	3.56	3.97	10
cyclic trimer	$K_{IF} \times 10^2$	9.49	9.18	8.95	9.35	9.07	9.21	3
	$K_{3F} \times 10^5$	-	1.66	2.06	2.50	2.71	2.23	24
	$K_{3I} \times 10^2$	-	2.14	2.86	3.06	3.63	2.92	26
cyclic tetramer	$K_{IF} \times 10^2$	9.49	9.18	8.95	9.35	9.07	9.21	3
	$K_{4F} \times 10^7$	-	0.66	1.13	1.77	2.23	1.45	54
	$K_{4I} \times 10^3$	-	0.92	1.75	2.32	3.31	2.07	58

K_{nF} and K_{nI} in (mol dm^{-3})$^{(n-1)}$

TABLE V.8 : Concentrations of M_F, M_I and cyclic dimer (D) in ethylene glycol monomethyl ether solutions of different concentrations (All concentrations in mol dm^{-3} x 10^3)

C_S	10		40			60			80			100		
T/K	C_F	C_I	C_F	C_I	C_D	C_F	C_I	C_D	C_F	C_I	C_D	C_F	C_I	C_D
298	0.87	9.13	2.97	32.3	2.36	4.11	45.8	5.04	5.31	56.7	8.97	6.16	67.9	12.9
303	-	-	-	-	-	-	-	-	-	-	-	6.56	70.2	11.6
308	-	-	3.60	32.1	2.14	5.11	46.4	4.26	6.59	58.5	7.43	-	-	-
313	1.04	8.96	4.10	32.2	1.85	5.60	46.8	3.82	7.08	59.5	6.71	8.72	73.1	9.12
318	1.10	8.90	4.14	32.4	1.73	5.78	47.4	3.43	7.75	60.1	6.10	-	-	-
323	1.20	8.80	4.68	32.5	1.42	-	-	-	8.12	61.4	5.20	10.1	75.1	7.41
328	1.31	8.69	5.14	32.5	1.18	7.45	47.5	2.54	9.66	61.5	4.44	11.8	75.6	6.31
333	1.42	8.58	5.33	32.6	1.05	-	-	-	10.9	61.2	3.89	-	-	-
338	1.54	8.46	5.62	32.7	0.82	8.91	48.1	1.48	10.9	63.4	2.88	13.9	77.2	4.45

TABLE V.9 : Equilibrium constants in different solutions of ethylene glycol monomethyl ether (cf Table V.8 for the respective concentrations)

C_S*	10	40			60			80			100		
T/K	$K_{IF}\times10^2$	$K_{IF}\times10^2$	$K_{DF}\times10^3$	$K_{DI}\times10$	$K_{IF}\times10^2$	$K_{DF}\times10^3$	$K_{DI}\times10$	$K_{IF}\times10^2$	$K_{DF}\times10^3$	$K_{DI}\times10$	$K_{IF}\times10^2$	$K_{DF}\times10^3$	$K_{DI}\times10$
298	9.49	9.18	3.67	4.35	8.95	3.31	4.12	9.35	3.14	3.59	9.07	2.93	3.56
303	-	-	-	-	-	-	-	-	-	-	9.35	3.70	4.24
308	-	11.2	6.04	4.82	11.5	6.11	5.04	11.3	5.85	4.61	-	-	-
313	11.6	12.7	8.88	5.60	12.0	8.21	5.72	11.9	7.47	5.28	11.9	8.30	5.82
318	12.4	12.8	9.94	6.07	12.2	9.73	6.54	12.9	9.86	5.91	-	-	-
323	13.6	14.4	15.4	7.43	-	-	-	13.3	12.9	7.26	13.4	13.7	7.61
328	15.1	15.8	22.4	8.95	15.7	21.9	8.88	15.7	21.0	8.51	15.6	22.0	9.16
333	16.6	16.4	27.1	10.1	-	-	-	17.9	31.0	9.65	-	-	-
338	18.2	17.2	38.7	13.2	18.5	53.8	15.7	19.0	45.1	12.5	18.0	43.2	13.4

*C_S in mol dm^{-3} x 10^3. K_{DF} and K_{DI} in mol dm^{-3}.

TABLE V.10 : Mean values of the equilibrium constants ($\bar{K}$) in the three-way equilibrium

	Ethylene glycol monomethyl ether			Ethylene glycol monoethyl ether			Ethylene glycol monobutyl ether		
T/K	$K_{IF} \times 10^2$	$K_{DF} \times 10^3$	$K_{DI} \times 10$	$K_{IF} \times 10^2$	$K_{DF} \times 10^3$	$K_{DI} \times 10$	$K_{IF} \times 10^2$	$K_{DF} \times 10^3$	$K_{DI} \times 10$
298	9.2	3.2	3.9	9.7	3.1	3.1	9.4	3.0	3.3
303	9.3	3.7	4.2	-	-	-	9.5	3.2	4.0
308	11	6.0	4.8	11	5.8	4.3	11	5.9	4.7
313	12	8.2	5.6	12	7.1	5.0	12	8.9	5.4
318	13	9.8	6.2	13	10	5.8	13	11	6.1
323	14	14	7.4	14	15	7.2	14	15	7.7
328	16	22	8.9	16	22	8.5	15	21	8.7
333	17	29	9.9	18	31	9.7	17	27	9.7
338	18	45	14	19	48	14	18	45	14

K_{DF} and K_{DI} in mol dm^{-3}.

TABLE V.11 : Thermodynamic quantities associated with the three-way equilibrium in ethylene glycol monoalkyl ethers

Type of equilibrium	Thermodynamic property	$CH_3O(CH_2)_2OH$	$C_2H_5O(CH_2)_2OH$	$C_4H_9O(CH_2)_2OH$
$M_I \rightleftharpoons M_F$	$K_{IF} \times 10^2$	9.2	9.7	9.5
	ΔG°_{IF}/kJ mol^{-1}	5.9	5.8	5.8
	ΔH°_{IF}/kJ mol^{-1}	15 ± 0.8	14 ± 0.6	14 ± 0.6
	ΔS°_{IF}/JK^{-1} mol^{-1}	29 ± 2	27 ± 2	26 ± 2
$D \rightleftharpoons 2M_F$	$K_{DF} \times 10^3$/mol dm^{-3}	3.3	3.1	3.0
	ΔG°_{DF}/kJ mol^{-1}	14.2	14.3	14.5
	ΔH°_{DF}/kJ mol^{-1}	55 ± 2.4	57 ± 2.8	57 ± 2.3
	ΔS°_{DF}/JK^{-1} mol^{-1}	136 ± 8	142 ± 9	142 ± 7
$D \rightleftharpoons 2M_I$	$K_{DI} \times 10$/mol dm^{-3}	3.9	3.1	3.3
	ΔG°_{DI}/kJ mol^{-1}	2.3	2.9	2.7
	ΔH°_{DI}/kJ mol^{-1}	25 ± 1.8	30 ± 1.7	28 ± 1.4
	ΔS°_{DI}/JK^{-1} mol^{-1}	76 ± 6	89 ± 5	83 ± 5

K's and ΔG°'s at 298 K.

TABLE V.12 : Calculated integrated intensities (B) of different OH bands of ethylene glycol monoalkyl ethers at various temperatures

T/K	Ethylene glycol monomethyl ether		Ethylene glycol monoethyl ether		Ethylene glycol monobutyl ether	
	B_I	B_D	B_I	B_D	B_I	B_D
298	6.42	59.5	6.25	-	-	-
303	-	58.2	-	60.8	6.32	57.1
308	-	-	-	-	6.23	55.8
313	6.24	58.1	6.08	59.1	6.14	56.3
318	6.16	-	6.02	58.5	6.08	55.8
323	6.12	56.8	5.94	-	6.04	55.8
328	6.07	57.4	5.87	58.9	5.98	55.9
333	6.03	-	5.84	57.4	5.90	54.6
338	5.94	55.4	5.73	58.1	5.81	54.1

*All B's in $dm^3\ mol^{-1}\ cm^{-2} \times 10^{-3}$

(I - intramolecularly H-bonded OH band, D - dimeric OH band).

TABLE V.13 : Spectroscopic properties of OH groups of ethylene glycol monoalkyl ethers (T = 298 K)

Type of OH group	Spectral property	$CH_3O(CH_2)_2OH$	$C_2H_5O(CH_2)_2OH$	$C_4H_9O(CH_2)_2OH$
Free	$\bar{\nu} \pm 2.5$ / cm^{-1}	3635	3635	3635
	$\Delta\bar{\nu}_{1/2} \pm 2.5$ / cm^{-1}	26	28	27
	$B_F \times 10^{-3}/dm^3\ mol^{-1}\ cm^{-2}$	-	-	-
Intra-molecularly H-bonded	$\bar{\nu} \pm 2.5$ / cm^{-1}	3600	3600	3600
	$\Delta\bar{\nu} \pm 2.5$ / cm^{-1}	35	35	35
	$\Delta\bar{\nu}_{1/2} \pm 2.5$ / cm^{-1}	32.5	32.5	32.5
	$B_I \times 10^{-3}/dm^3\ mol^{-1}\ cm^{-2}$	6.4	6.3	6.4
Dimeric	$\bar{\nu} \pm 5$ / cm^{-1}	3475	3475	3475
	$\Delta\bar{\nu} \pm 5$ / cm^{-1}	160	160	160
	$\Delta\bar{\nu}_{1/2} \pm 5$ / cm^{-1}	150	150	145
	$B_D \times 10^{-3}/dm^3\ mol^{-1}\ cm^{-2}$	59	61	57

CHAPTER VI

ASSOCIATION BEHAVIOUR OF DIETHYLENE GLYCOL MONOALKYL ETHERS

CHAPTER VI

ASSOCIATION BEHAVIOUR OF DIETHYLENE GLYCOL MONOALKYL ETHERS

VI.1. Introduction :

Diethylene glycol monoalkyl ethers $RO(CH_2)_2O(CH_2)_2OH$ in dilute carbon tetrachloride solutions ($C \leqslant 0.03$ mol dm^{-3}) exhibit three bands in hydroxyl stretching region, at ~ 3635, 3600 and 3470 cm^{-1}. The relative intensities of these bands remain constant and independent of further dilution (Fig. VI.1A). indicating them to be due to three types of monomeric species (Fig. VI.2) in equilibrium. The bands at 3635 and 3600 cm^{-1} can be ascribed to free monomer (M_F), and intramolecularly H-bonded five membered ring monomer (M_5) respectively from their similarity with the corresponding bands of ethylene glycol monoalkyl ethers. (cf Tables V.13 and VI.7)*. The 3470 cm^{-1} band is then attributable only to the eight membered ring monomer (M_8) formed by intramolecular H-bonding of the hydroxylic proton with the second ether oxygen. The three monomeric bands were resolved like those of ethylene glycol monoalkyl ethers (cf Fig. V.2). The concentrations of M_F, M_5 and M_8 (C_F, C_5 and C_8 respectively) were determined from the respective band areas as explained in Section IV.4.

$$C_F = A_F/B_F L, \quad C_5 = A_5/B_5 L \quad \text{and} \quad C_8 = C_S - (C_F + C_5) \qquad .. (1)$$

The equilibrium constants for the three equilibria (Fig. VI

DIETHYLENE GLYCOL MONOALKYL ETHERS

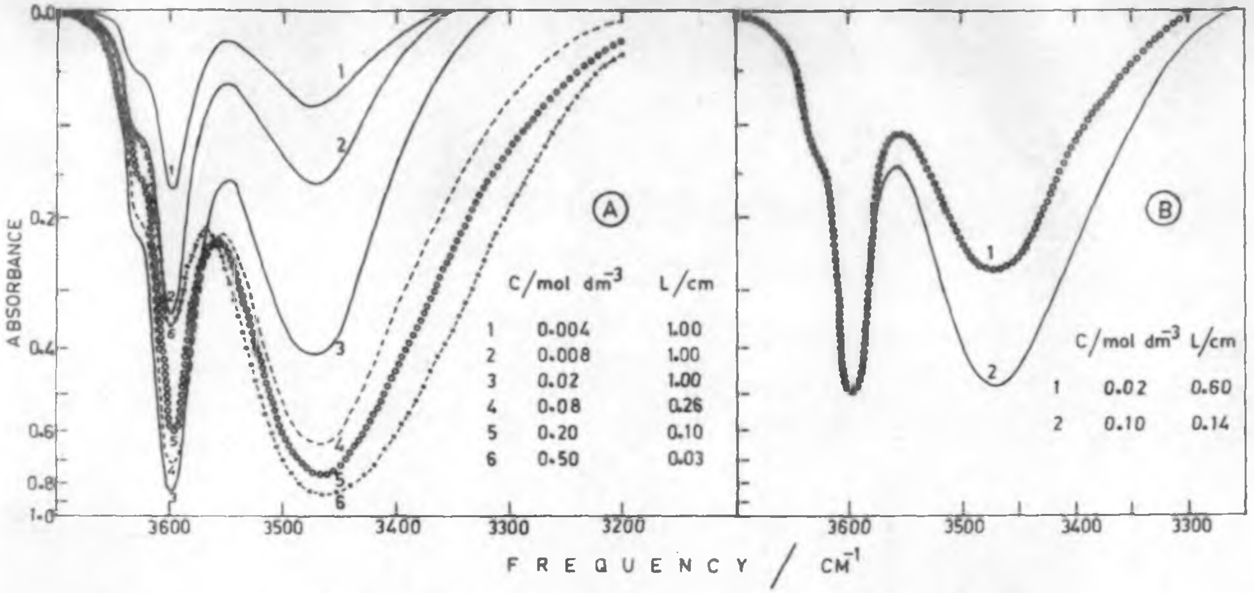

FIG-VI-1: OH BANDS AT VARIOUS CONCENTRATIONS (T = 298 K).

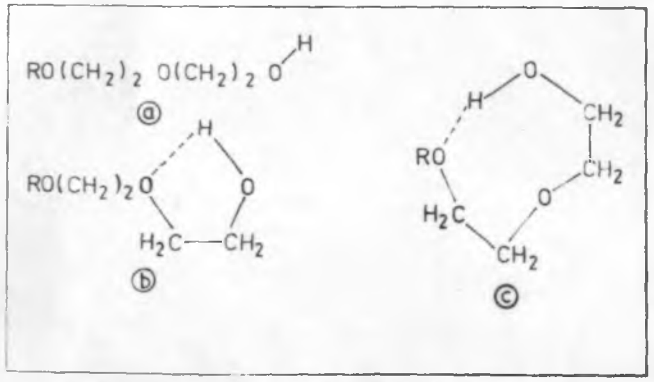

FIG-VI-2: FREE AND INTRAMOLECULARLY H-BONDED MONOMERS.

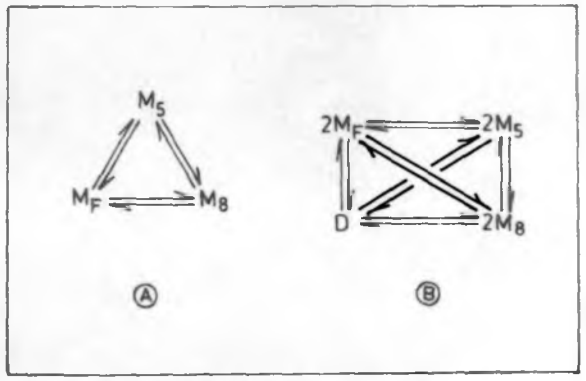

FIG-VI-3: EQUILIBRIA IN Ⓐ DILUTE AND Ⓑ CONCENTRATED SOLUTIONS.

$$M_5 \rightleftharpoons M_F \;,\; M_8 \rightleftharpoons M_F \text{ and } M_8 \rightleftharpoons M_5 \;,$$

were then calculated as

$$K_{5F} = C_F/C_5 \;,\; K_{8F} = C_F/C_8 \text{ and } K_{85} = C_5/C_8 \qquad .. (2)$$

At higher concentrations ($C > 0.03$ mol dm^{-3}) till ~ 0.5 mol dm^{-3}, there are no new OH bands but the band near 3475 cm^{-1} becomes increasingly asymmetric on the lower frequency side. Its relative intensity also increases rapidly indicating the presence of intermolecularly associated species. Since these absorb nearly in the same spectral region as the dimers of ethylene glycol monoalkyl ethers, the major associated species in the concentration range 0.03 - 0.15 mol dm^{-3} were assumed to be dimeric and the equilibrium constants for the equilibrium $D \rightleftharpoons 2M_F$ in the multiple equilibria (Fig. VI.3B) were calculated as

$$K_{DF} = C_F^2/C_D \qquad .. (3)$$

The constancy of the calculated K_{DF} values (Table VI.5)* supports the assumption of dimer as the main associated species upto concentration 0.15 mol dm^{-3}.

The individual bands of M_8 and D are not resolvable due to extensive overlap. The composite 3470 cm^{-1} band was isolated by extending its high frequency side from ~ 3525 cm^{-1} downwards to zero absorbance at ~ 3625 cm^{-1}. The high frequency side of the 3470 cm^{-1} band so obtained was subtracted from the experimental spectrum in the region 3525-3625 cm^{-1} to obtain the low frequency side of the 3600 cm^{-1} band. Similar procedure has been used by Fox and Martin[1], Baker and Teaman[110] etc. The 3600 cm^{-1} band was then resolved in the usual manner and used for the estimation of M_5. Concentrations of M_8 and M_F were then calculated from M_5 using the equilibrium constants determined for dilute solutions as in equations (2). Thus

$$C_5 = A_5/B_5 l \ , \ C_F = K_{5F} C_5 \text{ and } C_8 = C_5/K_{85} \qquad .. (4)$$

The dimer concentration C_D was then calculated by subtracting the total monomer concentration (= $C_5 + C_8 + C_F$) from the solution concentration C_S and dividing by 2 viz.

$$C_D = (C_S - (C_5 + C_8 + C_F))/2 \qquad .. (5)$$

The measured areas of various bands of diethylene glycol monomethyl- and -ethyl ethers (abbrivated as DEGM and DEGE, respectively, for convenience) are given in Tables* VI.1 and 2 which were corrected and used to estimate the concentrations of the corresponding species as usual. The calculated concentrations of different species in a number of solutions of DEGM and DEGE at 298 K and the corresponding equilibrium constants are shown in Table* VI.3 from which it is evident that the association behaviour of these compounds is identical. The equilibrium constants for various equilibria over the temperature range 298-338 K are given in Tables* VI.4 and 5. The thermodynamic and spectroscopic properties are summarized in Tables* VI.6 and VI.7 respectively.

VI.2. Intramolecular H-Bonding :

For DEGM and DEGE, the equilibrium constants in the triangular equilibrium (Fig. VI.3A, eq.(2)) over the temperature range 298-338 K and the respective thermodynamic and spectroscopic

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* pp 85-91.

properties are found to be nearly the same (Tables VI.4, 6 and 7) confirming their intramolecular H-bonding behaviour to be identical. The spectral characteristics $(\bar{\nu}, \Delta\bar{\nu}, \Delta\bar{\nu}_{1/2})$, of the free and intramolecularly H-bonded five membered ring monomer OH bands as well as the thermodynamic quantities for the equilibrium $M_5 \rightleftharpoons M_F$ for the present compounds are observed to be nearly the same as those for ethylene glycol monoalkyl ethers (of Tables V.11, V.13, VI.6 and VI.7). This is expected since the participants in H-bonding as well as their relative positions are identical in both the cases. The values of $\bar{\nu}$ and $\Delta\bar{\nu}_{1/2}$ for the OH bands of these compounds are in good agreement with those reported for similar compounds[2,80,81]. Markevich et al[86] however reported somewhat different frequencies and relative intensities for the three OH bands of DEGE, viz. a broad and strong 3617 cm^{-1} band well separated from a weak 3586 cm^{-1} band. Similarly Lodygina et al[85] did not report the 3635 cm^{-1} band in DEGE and ascribe, erronously, the 3610 cm^{-1} band to free OH. (Probably they, as in the case of ethylene glycol monoalkyl ethers, did not observe the 3635 cm^{-1} band). It may be noted that as the free and intramolecularly H-bonded OH bands of the present compounds arise from groups identical with those in ethylene glycol monoalkyl ethers their relative intensities should also be similar. All other reported data[2,76,80,81,83] are in agreement with a strong 3600 cm^{-1} band (due to intramolecularly H-bonded OH) with 3635 cm^{-1} band (due to free OH) appearing as a shoulder in various ethylene- and diethylene glycol monoalkyl ethers as observed in the present work.

A comparison of the $\Delta\bar{\nu}$, $\Delta\bar{\nu}_{1/2}$ and B values for the intramolecularly H-bonded hydroxyl of the eight and five membered ring monomers shows that they are 3-4 times larger for the former (Table VI.7). Similarly the $\Delta H°$ for the M_8- M_F equilibrium is nearly 1.6 times larger than that for the M_5- M_F equilibrium (Table VI.6). This is understandable since the OH group can get closer to the second ether oxygen resulting in a shorter hydrogen bond and hence larger H-bonding interaction. The $\Delta\bar{\nu}_{1/2}$ and B values, in addition to being measures of H-bonding interaction also depend on the anharmonicity and the rate of change of dipole moment ($\partial\mu/\partial r$) associated with the vibration. The higher values of these quantities for the eight membered ring monomer are attributable to its larger flexibility as compared to that of the five membered ring monomer.

Finally the larger value of $\Delta S°$ for the eight membered ring structure is explainable from the larger ring size and increased restriction on rotation about various bonds. This last factor results in smaller population of the eight membered ring monomer compared to the five membered one (Table VI.3) because the number of favourable conformations and hence the probability of formation is smaller for the former. Lodygina et al[85] also have reported the thermodynamic quantities for the equilibrium between the species absorbing at 3450 and 3610 cm^{-1} assuming them, as mentioned before, due to M_8 and 'M_F' respectively. However as the assignment of the latter band is incorrect and the participation of the actual free monomer (absorbing at ~ 3635 cm^{-1})

in the equilibria unaccounted, their values cannot be compared with the present ones.

In both the five- and eight-membered ring monomers, the gauche configurations of the OCH_2CH_2O groupings are stabilized by intramolecular H-bonding. This is in agreement with the earlier observation[81] of predominantly gauche conformations of the two OCH_2CH_2O groups of diethylene glycol monoalkyl ethers in solution.

VI.3. Structure of the Dimer :

The assumption of a dimer as the most likely associated species in the concentration range 0.03 - 0.15 mol dm^{-3} is valid from the constancy of the K_{DF} values (Table VI.5) and linearity of the log K_{DF} vs 1/T plot (VI.4). Amongst the three equilibria between the dimer and the three monomers (Fig. VI.3B), the thermodynamic quantities for the $D \rightleftharpoons 2M_F$ equilibrium only are significant because of their direct implications on the structure of the dimer. Because of the presence of three proton acceptors (oxygen atoms) in these molecules, there are several ways in which dimerization can occur (Fig. VI.5(a)-(f)). Though it is rather difficult to decide on a unique structure from the thermodynamic quantities alone; a consideration of various factors enables one to arrive at the most probable structure as discussed below.

An open dimer (a) having a single hydrogen bond and very little restriction to internal rotation would yield relatively small values of ΔH°_{DF} and ΔS°_{DF}. The high values of ΔH°_{DF} and ΔS°_{DF} of $\sim$58 kJ mol^{-1} and $\sim$153 JK^{-1} mol^{-1} respectively (Table VI.6)

DIETHYLENE GLYCOL MONOALKYL ETHERS

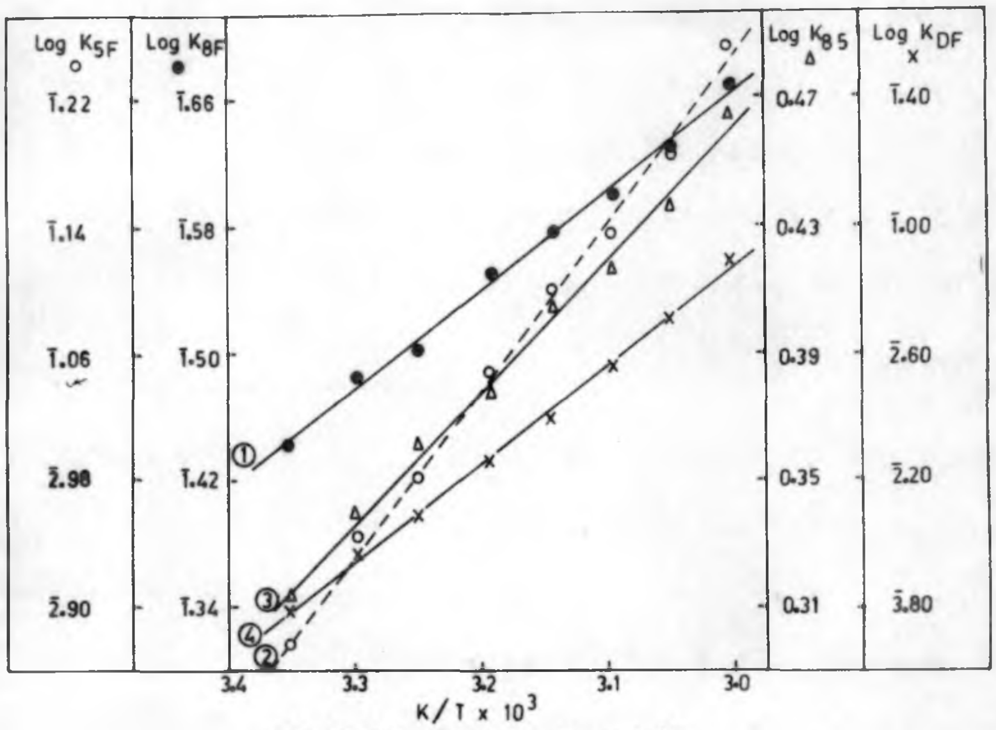

FIG-VI-4: PLOTS OF Log K vs 1/T.

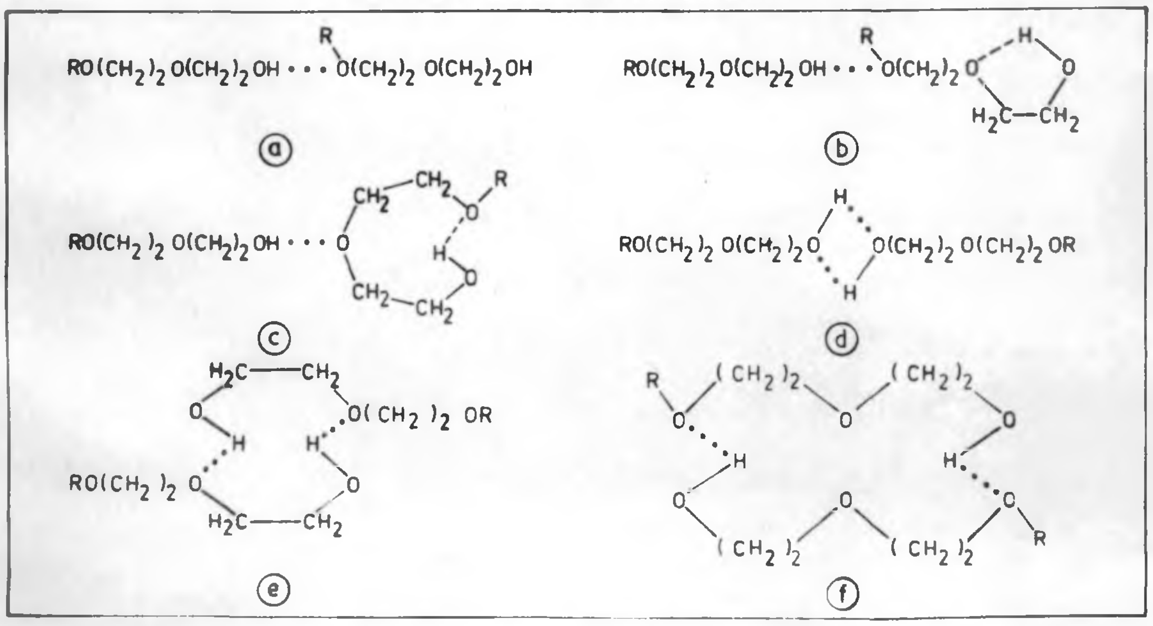

FIG-VI-5: TYPICAL STRUCTURES FOR DIMER.

therefore exclude open dimers. The dimer involving intermolecular association of a free monomer with a five membered ring monomer (b) also seems to be unlikely for the same reason. Further, if dimers of this type were present, the relative intensities of the 3635 and 3600 cm^{-1} bands in the spectra of concentrated solutions (containing dimers) would be different from those of dilute solutions (with no dimers). This possibility was tested by recording the spectra of solutions of two different concentrations with the path lengths adjusted so as to have the 3600 cm^{-1} band intensities same in both. Then the 3635 cm^{-1} band intensities also were observed to be the same (Fig. VI.1b) showing the absence of such dimers. For the dimer resulting from H-bonding of a free monomer with an eight membered ring monomer (c), the $\Delta S°$ value would be nearly the same as that for M_8 since the latter is mainly responsible for the entropy change. Actually $\Delta S°_{DF} >> \Delta S°_{8F}$ (153 vs 55 JK^{-1} mol^{-1}) which makes such a structure improbable. The four membered ring structure (d) can be ruled out on the same basis as for ethylene glycol monoalkyl ethers. The present values of $\Delta H°_{DF}$ and $\Delta S°_{DF}$ are comparable with those for ethylene glycol monoalkyl ethers for which the ten membered ring dimer resulting from mutual H-bonding of two molecules via their ether oxygens (in β-position) was found to be the most likely associated species (Section V.4). Such dimer (e) would therefore be the most probabl associated species in DEGM and DEGE. The somewhat larger magnitudes of the present $\Delta H°_{DF}$ and $\Delta S°_{DF}$ as compared to those for ethylene glycol monoalkyl ethers might be due to the sixteen membered ring dimer (f) present in small amount. The population of this will, of course, be very small as compared to that of (e) because of the larger ring size leading to considerably larger decrease of entropy. These last two structures are also in agreement with the earlier results showing the existence of the OCH_2CH_2O groups predominantly in gauche conformations[81].

The concentration of the dimer as compared to the two intramolecularly H-bonded monomers is very small (Table VI.3), which can be understood as the former requires a larger number of bonds in suitable conformations (larger decrease of entropy). This, together with the formation of the eight membered ring monomer having hydrogen bond strength comparable to that of the dimer (cf $\Delta\bar{\nu}$, $\Delta\bar{\nu}_{1/2}$ and $\Delta H°$ values) but requiring relatively smaller entropy decrease, results in a smaller extent of dimerization. This explains larger values of K_{DF} for the present compounds than those for ethylene glycol monoalkyl ethers (cf Tables V.10 and VI.5).

Since the dimer band overlaps with the M_8 band very extensively, its spectral characteristics ($\bar{\nu}$, $\Delta\bar{\nu}_{1/2}$, B, etc.) could not be determined with certainty. In order to have an approximate idea, a number of spectra at higher concentrations (upto 0.5 mol dm^{-3}) were studied from which the dimer band appears to have its maximum at $\sim$ 3440 cm^{-1} ($\Delta\bar{\nu} \sim 195$ cm^{-1}, $\Delta\bar{\nu}_{1/2} \sim 160$ cm^{-1}). As the concentration of M_8 was already determined, its equivalent area was calculated using the relation $A_8 = B_8CL$. An approximate area for the dimer band was then obtained by subtracting the M_8 band area from total area of the 3470 cm^{-1} band. The integrated intensity calculated from the estimated values of band area and concentration was thus found to be ~ 12 x 10^4 dm^3 mol^{-1} cm^{-2} at 298 K. (Table VI.8).* The larger value of $\Delta\bar{\nu}$ for the dimer is consistent with large ΔH°_{DF} value. Similarly the large magnitudes of $\Delta\bar{\nu}_{1/2}$ and B suggest greater anharmonicity and dipole moment derivative associated with hydroxyl group vibration. This is understandable in view of greater flexibility of the ten membered ring structure.

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* page 92.

TABLE VI.1 : Measured areas (A') of various OH bands of diethylene glycol monomethyl ether

C_S*		10		80	100	125
L/cm		1.0		0.26	0.25	0.20
T/K	A'_F	A'_5	A'_8	A'_5	A'_5	A'_5
298	2.34	34.3	56.4	64.7	75.8	75.4
303	2.50	34.0	50.7	65.3	76.4	76.4
308	2.56	33.8	47.2	65.6	77.3	77.5
313	2.76	33.3	42.7	65.4	77.5	77.4
318	2.91	32.9	38.3	65.4	77.5	77.4
323	3.06	32.4	35.7	64.9	77.7	77.2
328	3.20	32.0	31.9	64.7	77.5	76.7
333	3.40	31.7	26.6	64.5	77.1	76.3

*C_S (solution concentration) in mol dm^{-3} x 10^3.

TABLE VI.2 : Measured areas (A') of various OH bands of diethylene glycol monoethyl ether

C_S*		12.5		75	95	120
L/cm		1.0		0.28	0.25	0.20
T/K	A'_F	A'_5	A'_8	A'_5	A'_5	A'_5
298	2.86	43.1	87.5	65.6	73.9	72.5
303	3.09	42.5	81.8	66.0	74.4	72.8
308	3.19	42.1	74.6	66.4	74.6	73.7
313	3.42	42.0	66.4	66.8	74.6	74.0
318	3.63	41.5	60.1	66.3	74.6	74.1
323	3.81	41.1	54.2	66.1	74.3	74.4
328	3.99	40.5	49.6	66.1	74.0	74.0
333	4.23	40.1	44.4	65.9	73.9	73.9

*C_S (solution concentration) in mol $dm^{-3} \times 10^3$.

TABLE VI.3 : Concentrations of different species and equilibrium constants in solutions of DEGM and DEGE at 298 K.

Compound	solution concentration x 10^3/mol dm^{-3}	Concentrations of various species x 10^3/mol dm^{-3}				Equilibrium constants			
	C_S	C_F	C_5	C_8	C_D	K_{5F} x 10^2	K_{8F} x 10^2	K_{85}	K_{DF}^* x 10^3
DEGM	10	0.64	6.33	3.03	-	10	21	2.1	-
	20	1.26	12.5	6.19	-	10	24	2.0	-
	80	4.63	46.0	22.3	3.51	-	-	-	6.1
	100	5.63	56.0	27.2	5.56	-	-	-	5.7
	125	7.01	69.7	33.9	7.21	-	-	-	6.8
DEGE	12.5	0.78	7.96	3.76	-	9.8	21	2.1	-
	75	4.25	43.3	20.4	3.48	-	-	-	5.2
	95	5.36	54.7	25.8	4.59	-	-	-	6.3
	120	6.58	67.1	31.6	7.36	-	-	-	5.9

* K_{DF} in mol dm^{-3}.

TABLE VI.4 : Intramolecular H-bonding in diethylene glycol monoalkyl ethers

	Diethylene glycol monomethyl ether Equilibrium constants (C_s = 0.01 mol dm^{-3})			(DEGM)	Diethylene glycol monoethyl ether Equilibrium constants (C_s = 0.0125 mol/dm^{-3})			(DEGE)
T/K	$K_{5F} \times 10^2$	$K_{8F} \times 10^2$	K_{85}	$B_8 \times 10^{-3}$ dm^3 mol^{-1} cm^{-2}	$K_{5F} \times 10^2$	$K_{8F} \times 10^2$	K_{85}	$B_8 \times 10^{-3}$ dm^3 mol^{-1} cm^{-2}
298	10	21	2.1	23	9.8	21	2.1	29
303	11	24	2.2	22	11	24	2.2	28
308	11	26	2.3	21	11	26	2.3	27
313	13	30	2.4	20	12	31	2.5	26
318	14	34	2.5	19	13	35	2.6	24
323	15	38	2.6	18	14	39	2.7	23
328	16	43	2.7	17	16	44	2.8	22
333	17	50	2.9	15	17	52	3.1	21

TABLE VI.5 : Equilibrium constants K_{DF}($\times 10^3$/mol dm^{-3}) for the D - $2M_F$ equilibrium

T/K	Diethylene glycol monomethyl ether $C_S \times 10^3$/mol dm^{-3}				Diethylene glycol monoethyl ether $C_S \times 10^3$/mol dm^{-3}			
	80	100	125		75	95	120	
	K_{DF}	K_{DF}	K_{DF}	$\bar{K}_{DF}$	K_{DF}	K_{DF}	K_{DF}	$\bar{K}_{DF}$
298	6.1	5.7	6.8	6.2	5.2	6.3	5.9	5.8
303	9.2	8.3	10	9.3	8.1	9.9	8.5	8.8
308	12	11	14	12	12	13	12	12
313	18	18	19	18	17	17	16	17
318	24	23	28	25	22	25	23	23
323	33	37	39	36	30	33	35	33
328	48	53	51	51	51	48	48	49
333	78	82	74	78	79	75	69	74

TABLE VI.6 : Thermodynamic quantities associated with the multiple equilibria in diethylene glycol monoalkyl ethers

Type of equilibrium	Thermodynamic property	DEGM	DEGE
$M_5 \rightleftharpoons M_F$	$K_{5F} \times 10^2$	10.1	9.8
	ΔG°_{5F}/kJ mol^{-1}	5.70	5.8
	ΔH°_{5F}/kJ mol^{-1}	11.9 ± 0.4	12.6 ± 0.3
	ΔS°_{5F}/JK^{-1} mol^{-1}	21 ± 1.3	23 ± 0.8
$M_8 \rightleftharpoons M_F$	$K_{8F} \times 10^2$	20.3	20.8
	ΔG°_{8F}/kJ mol^{-1}	3.9	3.9
	ΔH°_{8F}/kJ mol^{-1}	19.7 ± 0.6	21.2 ± 0.5
	ΔS°_{8F}/JK^{-1} mol^{-1}	53 ± 1.8	58 ± 1.7
$M_8 \rightleftharpoons M_5$	K_{85}	2.0	2.1
	ΔG°_{85}/ kJ mol^{-1}	-1.8	-1.9
	ΔH°_{85}/ kJ mol^{-1}	7.8 ± 0.3	8.6 ± 0.4
	ΔS°_{85}/ JK^{-1} mol^{-1}	32 ± 0.8	35 ± 1.2
$D \rightleftharpoons 2M_F$	$K_{DF} \times 10^3$/mol dm^{-3}	6.2	5.8
	ΔG°_{DF}/kJ mol^{-1}	12.6	12.8
	ΔH°_{DF}/kJ mol^{-1}	58.4 ± 1.4	58.3 ± 1.7
	ΔS°_{DF}/JK^{-1} mol^{-1}	153 ± 4.4	152 ± 5.3

K's and ΔG°'s at 298 K.

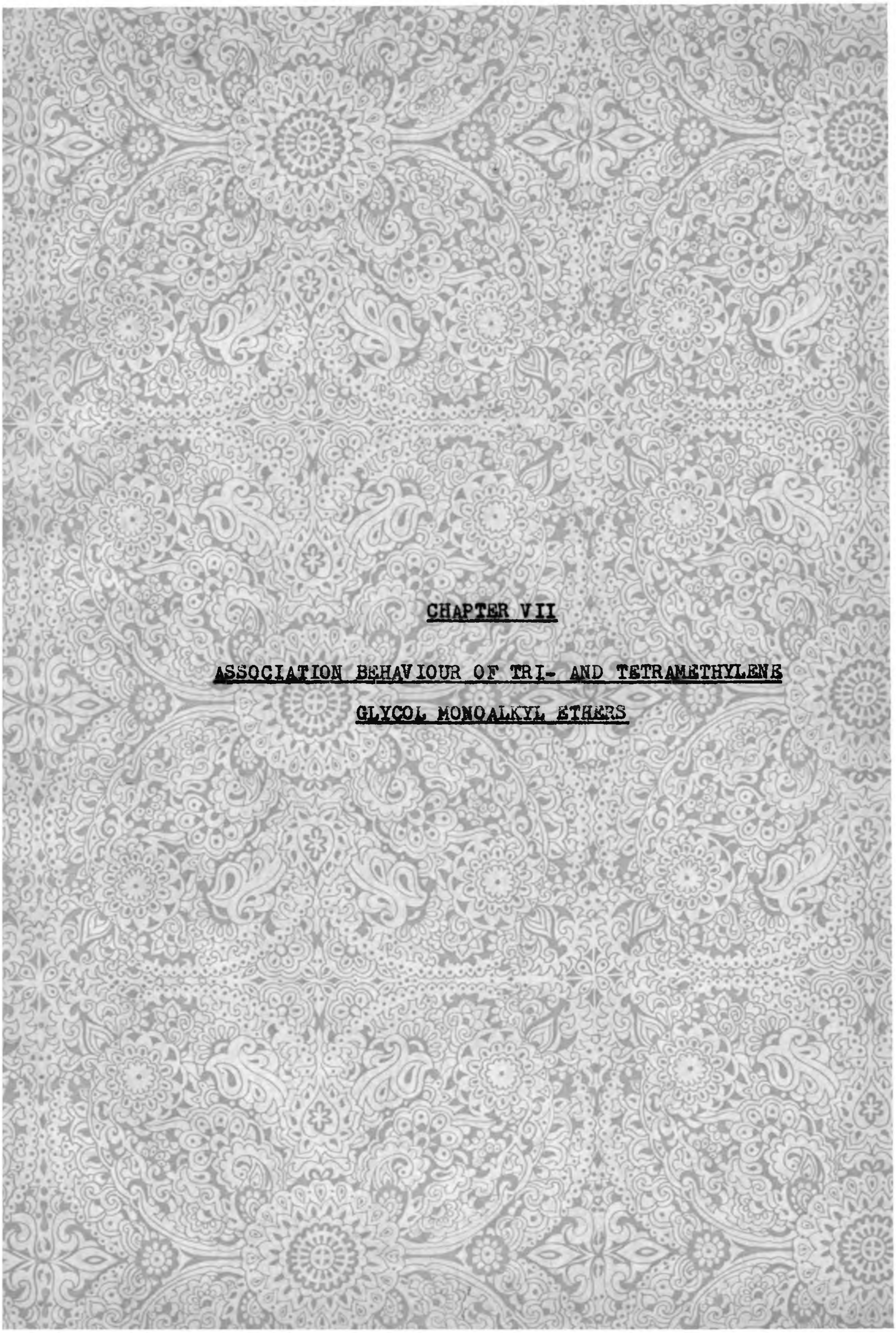
TABLE VI.7 : Spectroscopic properties of different types of OH groups of diethylene glycol monoalkyl ethers ($T = 298$ K)

Type of the OH group	Spectral property	DEGM	DEGE
Free	$\bar{\nu} \pm 2.5 / \mathrm{cm}^{-1}$	3635	3635
	$\Delta\bar{\nu}_{1/2} \pm 2.5 / \mathrm{cm}^{-1}$	25	25
	$B_F \times 10^{-3} / \mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{cm}^{-2}$	-	-
Intra-molecularly H-bonded five-membered ring	$\bar{\nu} \pm 2.5 / \mathrm{cm}^{-1}$	3600	3600
	$\Delta\bar{\nu} \pm 2.5 / \mathrm{cm}^{-1}$	35	35
	$\Delta\bar{\nu}_{1/2} \pm 2.5 / \mathrm{cm}^{-1}$	32.5	32.5
	$B_5 \times 10^{-3} / \mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{cm}^{-2}$	-	-
Intra-molecularly H-bonded eight-membered ring	$\bar{\nu} \pm 5 / \mathrm{cm}^{-1}$	3475	3470
	$\Delta\bar{\nu} \pm 5 / \mathrm{cm}^{-1}$	160	165
	$\Delta\bar{\nu}_{1/2} \pm 5 / \mathrm{cm}^{-1}$	100	105
	$B_8 \times 10^{-3} / \mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{cm}^{-2}$	23	29
Dimeric	$\bar{\nu} \pm 5 / \mathrm{cm}^{-1}$	3440	3440
	$\Delta\bar{\nu} \pm 5 / \mathrm{cm}^{-1}$	195	195
	$\Delta\bar{\nu}_{1/2} \pm 5 / \mathrm{cm}^{-1}$	160	160
	$B_D \times 10^{-4} / \mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{cm}^{-2}$	12.6	11.3

TABLE VI.8 : Calculation of integrated intensity of the dimer (B_D) of diethylene glycol monoalkyl ethers at 298 K

		I	II
Solution concentration	$C_S \times 10^3/\mathrm{mol\ dm^{-3}}$	100	95
Path length	L/cm	0.25	0.25
Measured area of the 3470 $\mathrm{cm^{-1}}$ band	A'	265	254
Wing correction = 25%, density correction 0%			
Corrected area of the 3470 $\mathrm{cm^{-1}}$ band	A	331	317
Concentration of M_8, (cf Table VI.3)	$C_8 \times 10^3/\ \mathrm{mol\ dm^{-3}}$	27.2	25.8
Integrated intensity of M_8, (cf Table VI.4)	$B_8 \times 10^{-3}/\ \mathrm{dm^3\ mol^{-1}\ cm^{-2}}$	23	29
Equivalent area for M_8	$A_8 = B_8 C_8 L$	156	187
Area for the dimer	$A_D = A - A_8$	175	130
Concentration of the dimer, (cf Table VI.3)	$C_D \times 10^3/\mathrm{mol\ dm^{-3}}$	5.56	4.59
Integrated intensity of the dimer	$B_D\ (= A_D/C_D L) \times 10^{-4}\ /\mathrm{dm^3\ mol^{-1}\ cm^{-2}}$	12.6	11.3

I : $CH_3O(CH_2)_2O(CH_2)_2OH$, II : $C_2H_5O(CH_2)_2O(CH_2)_2OH$.



CHAPTER VII

ASSOCIATION BEHAVIOUR OF TRI- AND TETRAMETHYLENE GLYCOL MONOALKYL ETHERS

CHAPTER VII

ASSOCIATION BEHAVIOUR OF TRI- AND TETRA-METHYLENE GLYCOL MONOMETHYL ETHERS

VII.1. Introduction :

Tri- and tetra-methylene glycol monomethyl ethers ($CH_3O(CH_2)_3OH$ and $CH_3O(CH_2)_4OH$) in carbon tetrachloride show two OH bands, one of them is common at $\sim$3630 cm^{-1} and the second at $\sim$3540 and 3450 cm^{-1} respectively. In very dilute solutions ($C_S \leqslant 0.03$ mol dm^{-3}), the relative intensities of these bands are constant (Fig. VII.1 and VII.2) indicating them to be due to monomeric species in equilibrium. The 3630 cm^{-1} band is due to the free OH group whereas the 3540 and 3450 cm^{-1} bands are attributable to intramolecularly H-bonded monomeric OH's of $CH_3O(CH_2)_3OH$ and $CH_3O(CH_2)_4OH$ forming six- and seven membered rings respectively. The free and intramolecularly H-bonded OH bands of these compounds are well separated from one another. Because of the asymmetry of the intramolecularly H-bonded OH bands (cf Section VII.2), the free OH band was first resolved by reflecting its high frequency side across the band maximum. The concentrations of the two monomers and the equilibrium constants in the $M_I \rightleftharpoons M_F$ equilibria were determined as before viz.,

$$C_F = A_F/B_F L, \qquad C_I = C_S - C_F \quad \text{and} \quad K_{IF} = C_F/C_I \qquad .. (1)$$

At higher concentrations upto $\sim$0 2 mol dm^{-3}, there are no new OH bands but the relative intensity and asymmetry of the lower frequenc

TRI-AND TETRAMETHYLENE GLYCOL MONOALKYL ETHERS

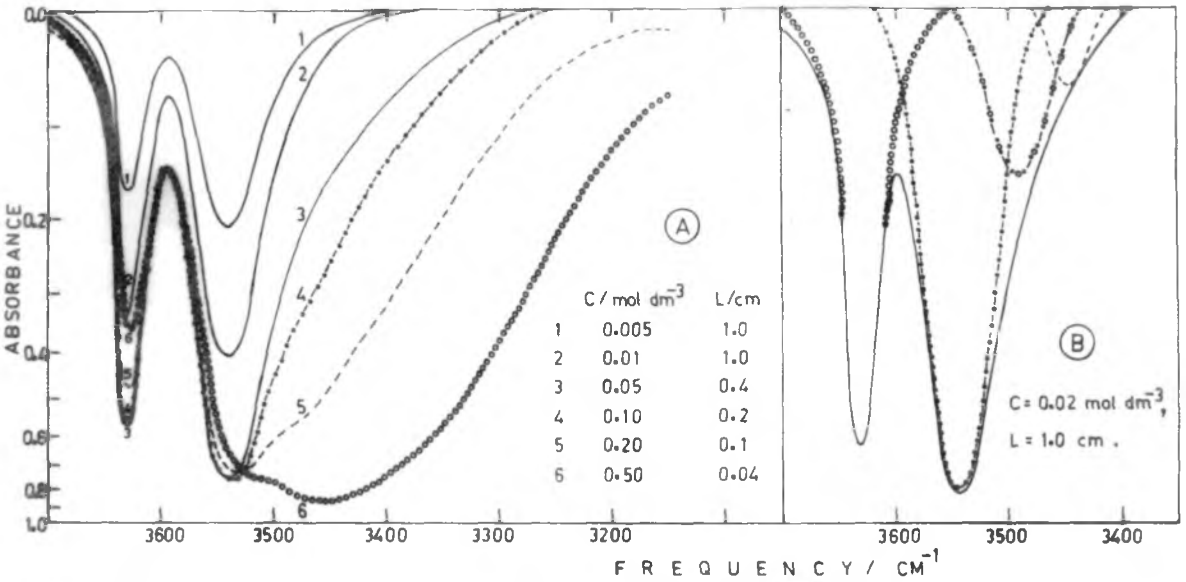


FIG-VII·1: OH BANDS OF $CH_3O(CH_2)_3OH$ AT VARIOUS CONCENTRATIONS (T=298 K). Ⓑ BAND RESOLUTION.

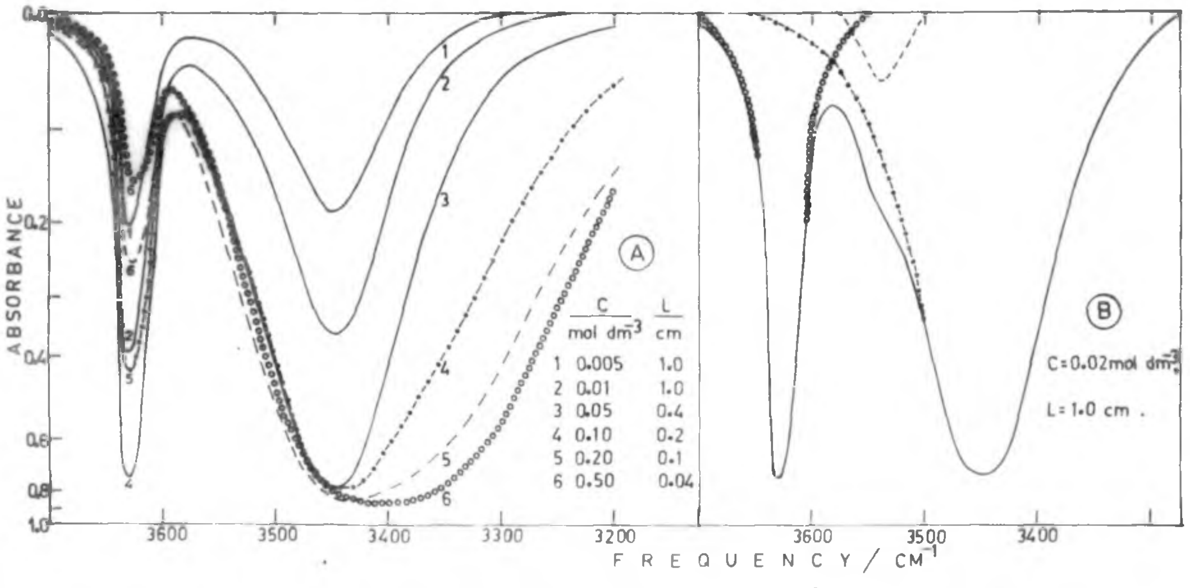


FIG-VII·2: OH BANDS OF $CH_3O(CH_2)_4OH$ AT VARIOUS CONCENCENTRATIONS (T=298K). Ⓑ BAND RESOLUTION.

bands increase rapidly suggesting the presence of intermolecularly H-bonded species. At still higher concentrations additional OH bands appear in the 3350-3400 cm^{-1} region as in the case of simple alcohols, indicating the formation of still higher associated species. The solution concentrations were therefore restricted upto 0.2 mol dm^{-3}. Due to their extensive overlap, the bands of intra- and intermolecularly associated OH groups are not resolvable. Concentrations of only the free OH groups $C_{OH(F)}$ were therefore estimated from the respective band areas, those of the free monomers and associated species (n-mers) being determined from $C_{OH(F)}$ and C_S as follows.

Since the concentrations of the free and intramolecularly H-bonded monomers are related by $K_{IF} = C_F/C_I$ (equation (1)), the total concentration of these two monomers will be

$$C_F + C_I = C_F + C_F/K_{IF} = K'C_F \quad \text{where} \quad K' = 1 + 1/K_{IF} \qquad .. (2)$$

The concentration of the n-mer (C_n) and the equilibrium constant (K_{nF}) in the equilibrium n-mer $\rightleftharpoons$ nM_F will be

$$C_n = (C_S - K'C_F)/n \quad \text{and} \quad K_{nF} = C_F^n/C_n \qquad .. (3)$$

To estimate C_n and K_{nF}, it is first necessary to determine the type of the associated species (open/closed dimer, trimer etc.) present. Since the solutions used were relatively dilute (C_S = 0.02 - 0.2 mol dm^{-3}), the major associated species were assumed to be dimer or trimers only. The possible structures for the dimers and trimers along with those for the free and intramolecularly H-bonded monomers are shown in Fig. VII.3. The concentrations of open/cyclic dimers and trimers were determined as follows.

In the case of any open n-mer, its end OH group would absorb in the same region as that of the free monomer (∼3630 cm^{-1}) thus contributing to $C_{OH(F)}$. The concentrations of the free monomer and open n-mer would then be related by the equations

$$C_F = C_{OH(F)} - C_n \quad \text{and} \quad C_n = (C_S - K'C_{OH(F)})/(n - K') \qquad ..\ (4)$$

In the case of closed n-mers, the 3630 cm^{-1} band results from OH groups of the free monomers only so that

$$C_F = C_{OH(F)} \quad \text{and hence} \quad C_n = (C_S - K'C_{OH(F)})/n \qquad ..\ (5)$$

The measured and corrected areas of the free and intramolecularly H-bonded OH bands in solutions of different concentrations are given in Tables* VII.1 and 2. The calculated concentrations and equilibrium constants in the systems $M_I \rightleftharpoons M_F$ at various temperatures along with the integrated intensities of the intramolecularly H-bonded OH bands are given in Table* VII.3. The calculated concentrations of the free OH group ($C_{OH(F)}$), free monomer (C_F) and open and cyclic dimers and trimers in different solutions of the two compounds at 298 K, as an illustration, are shown in Table* VII.4. The calculated equilibrium constants for the equilibria $D \rightleftharpoons 2M_F$ and $T \rightleftharpoons 3M_F$ (D = Dimer, T = Trimer) over the concentration and temperature range studied are presented in Tables* VII.5 and 6 and the thermodynamic quantities summarized in Table* VII.7. These are further analysed to understand the association behaviour of these compounds.

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* pp. 104-112.

VII.2. Intramolecular H-Bonding :

The assignment of the 3540 and 3450 cm^{-1} bands of $CH_3O(CH_2)_3OH$ and $CH_3O(CH_2)_4OH$ to OH groups of the respective intramolecularly H-bonded monomers is in agreement with the reported literature on these compounds[76,83] and the related diols[68-70,73]. These bands are found to be asymmetric (Fig. VII.1B and VII.2B) which however has not been reported by previous workers. Similar asymmetry has been observed[2,5-13] in the free OH bands of a number of simple alcohols and ascribed to the OH groups of different rotational conformers oscillating in slightly different force fields. The asymmetry in the present case is therefore attributable to two or more conformational isomers of the intramolecularly H-bonded monomers with their hydroxyl protons lying at somewhat different distances from the respective ether oxygens.

The frequency shifts and half-bands widths of the intramolecularly H-bonded OH bands, ($CH_3O(CH_2)_3OH$: $\Delta\bar{\nu} = 90\ cm^{-1}$, $\Delta\bar{\nu}_{1/2} = 60\ cm^{-1}$; $CH_3O(CH_2)_4OH$: $\Delta\bar{\nu} = 180\ cm^{-1}$, $\Delta\bar{\nu}_{1/2} = 95\ cm^{-1}$) are in good agreement with the literature[68-70,73,76,83] values for similar bands. The apparent integrated intensities (19 and 39 $\times 10^3\ dm^3\ mol^{-1}\ cm^{-2}$ for tri- and tetramethylene glycol monomethyl ethers respectively) are comparable with those reported by Kuhn and Wires[83] (14 and 34 $\times 10^3\ dm^3\ mol^{-1}\ cm^{-2}$ respectively). The differences in the numerical values might be due to the difference in procedures adopted for determining the integrated intensities. e.g. The B's in the present work are determined by computing the actual band areas whereas those of Kuhn and Wires are based on the formula $B = 2.3 \log (I_0/I)_{\bar{\nu}_{max}} \times \Delta\bar{\nu}_{1/2}/2CL$ which is applicable only to single symmetric bands having Lorentz shape.

The present thermodynamic quantities for the M_I - M_F equilibria [$CH_3O(CH_2)_3OH$: $K_{IF} = 1.4$ at 298 K, $\Delta H° = 15$ kJ mol^{-1} and $\Delta S° = 52$ JK^{-1} mol^{-1}; $CH_3O(CH_2)_4OH$: $K_{IF} = 2.2$ at 298 K, $\Delta H° = 18$ kJ mol^{-1} and $\Delta S° = 68$ JK^{-1} mol^{-1}] are higher than those reported by Kuhn and Wires[83] [$CH_3O(CH_2)_3OH$: $K_{IF} = 0.7$ at 293 K, $\Delta H° = 8.4$ kJ mol^{-1} and $\Delta S° = 28$ JK^{-1} mol^{-1}; $CH_3O(CH_2)_4OH$: $K_{IF} = 1.6$ at 293 K, $\Delta H° = 11.3$ kJ mol^{-1} and $\Delta S° = 44$ JK^{-1} mol^{-1}]. These differences, like those in the case of $RO(CH_2)_2OH$ (Chapter V) are due to the different estimates of integrated intensities of the free OH groups and therefore of their concentrations. The present thermodynamic values are all higher than those for $RO(CH_2)_2OH$ viz. $K_{IF} = 0.1$ at 298 K, $\Delta H° = 14$ kJ mol^{-1} and $\Delta S° = 30$ JK^{-1} mol^{-1}. The $\Delta\bar{\nu}$, $\Delta\bar{\nu}_{1/2}$ and B values for intramolecular H-bonding in the present compounds are also higher than those for $RO(CH_2)_2OH$, (cf Chapter V). The observed increasing trends in the thermodynamic and spectroscopic properties in the series $RO(CH_2)_nOH$ are consistent with each other indicating higher H-bonding interaction and smaller extent of intramolecular H-bonding with increasing n. (cf Chapter VIII, Section 2).

VII.3. Intermolecular Association :

The presence of two proton acceptors (i.e. the ether and hydroxylic oxygen atoms) in the present compounds can give rise to, as in the case of ethylene glycol monoalkyl ethers, several types of associated species. Thus the dimers, for example, can be 'open' with a free OH group, 'closed' resulting from H-bonding of a free monomer with an intramolecularly H-bonded monomer or 'cyclic' involving either the hydroxylic or the ether oxygens in mutual H-bonding of two monomer units. Such possibilities are shown in Fig. VII.3. In the relatively dilute solutions used in the present work (C_S = 0.02 - 0.20 mol dm^{-3}) the assumption of only dimers or at the most trimers as the major associated species present is reasonable. The thermodynamic quantities (K, $\Delta H°$ and $\Delta S°$) calculated on the assumption of different types of dimers and trimers (Table VII.7) were therefore analysed to decide the most probable associated species (Refer to Fig. VII.3).

The values of $\Delta H°$ and $\Delta S°$ for open dimers (c) would be small because of a single hydrogen bond and very little restriction to internal rotation. For the closed dimer resulting from H-bonding of a free monomer with an intramolecularly H-bonded monomer (d) there would be two hydrogen bonds resulting in $\Delta H°$ value nearly double of that for the intramolecularly H-bonded monomer alone. The $\Delta S°$ for such a dimer would however be nearly the same as that for the intramolecularly H-bonded monomer (b) since the latter is mainly responsible for the entropy change. The cyclic four membered ring dimer resulting from mutual H-bonding of two monomers via their hydroxylic oxygen atoms (e) would be associated with $\Delta H°$ and $\Delta S°$ values comparable with those for similar dimers of simple alcohols, viz. 12-24 kJ mol^{-1} and 30-80 JK^{-1} mol^{-1} respectively[28-31]. The ring size of the cyclic dimers resulting from mutual H-bonding of two monomers via their ether oxygens (f) would be very large

TRI-AND TETRAMETHYLENE GLYCOL MONOALKYL ETHERS

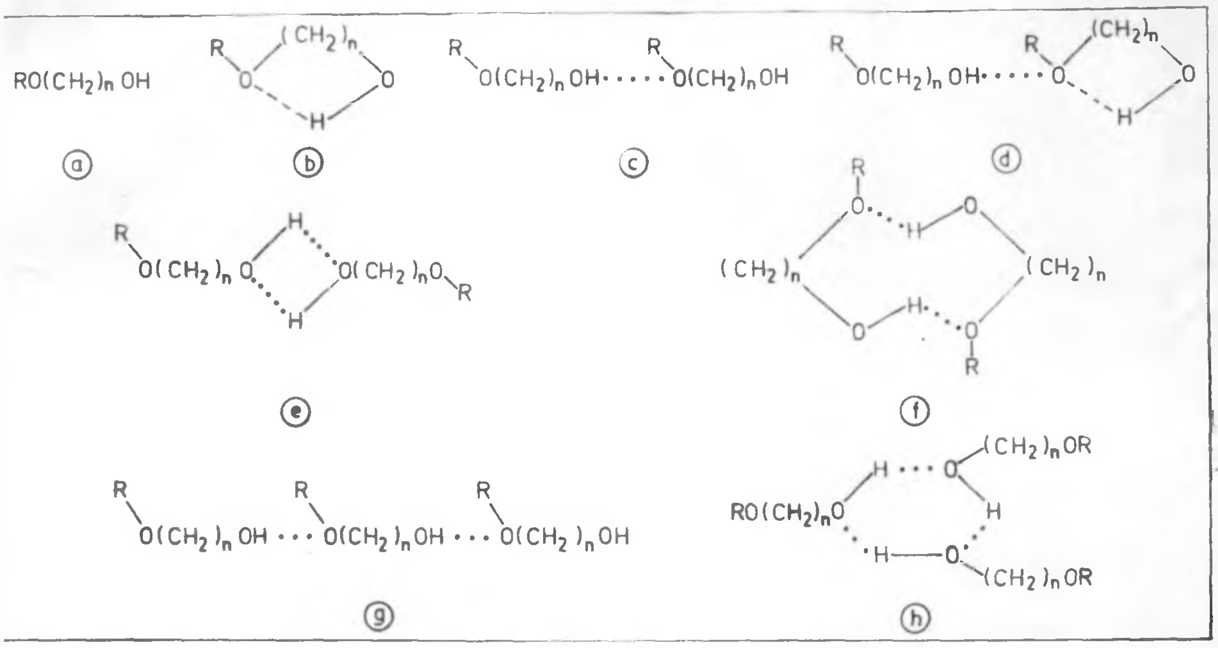

FIG-VII-3: TYPICAL STRUCTURES OF MONOMERS (a & b), DIMERS (c to f) AND TRIMERS (g & h).

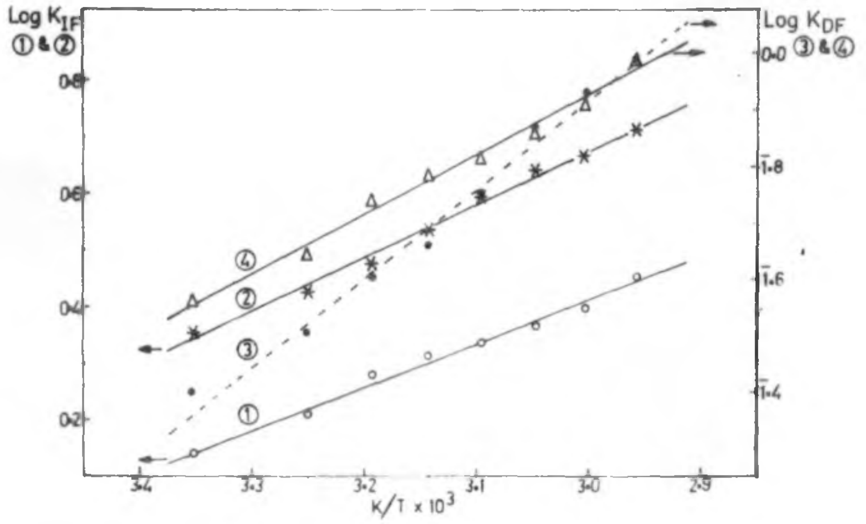

FIG-VII-4: PLOTS OF Log K_{IF} (1 & 2) AND Log K_{DF} (3 & 4) AGAINST 1/T.
① & ③ $CH_3O(CH_2)_3OH$; ② & ④ $CH_3O(CH_2)_4OH$.

(twelve-membered for $CH_3O(CH_2)_3OH$ and fourteen-membered for $CH_3O(CH_2)_4OH$). The $\Delta H°$ and $\Delta S°$ values for such associated species would be comparable with (in fact larger than) those for similar ten-membered ring dimers of ethylene- and diethylene glycol monoalkyl ethers ($\sim$56 kJ mol^{-1} and 140 JK^{-1} mol^{-1}). Open trimers (g with two hydrogen bonds and relatively small restriction to internal rotation would result in small $\Delta H°$ and $\Delta S°$ values. The cyclic trimers resulting from H-bonding via the ether oxygens would give rise to large entropy changes because of very big rings (eighteen-membered for $CH_3O(CH_2)_3OH$ and twentyone-membered for $CH_3O(CH_2)_4OH$) and as such the formation of such species would be less probable. The six-membered ring cyclic trimers (h) involving the hydroxylic oxygens in H-bonding would result in $\Delta H°$ comparable with that for similar structures in alcohols for which a value of $\sim$22 kJ mol^{-1} has been reported[41].

Trimethylene Glycol Monomethyl Ether : (cf Tables VII.5, VII.7 and Fig. VII.4) : The equilibrium constants calculated on the assumption of dimers and trimers of open type showed large variations The calculated $\Delta H°$ and $\Delta S°$ values of 94 kJ mol^{-1} and 266 JK^{-1} mol^{-1} for open dimers and 61 kJ mol^{-1} and 154 JK^{-1} mol^{-1} for open trimers are too high to be compatible with such structures. Open dimers and trimers were therefore ruled out as major associated species. The equilibrium constants calculated on the basis of closed/cyclic dimers and trimers showed good constancy. In the case of closed dimers, the calculated $\Delta H° = 30$ kJ mol^{-1} and $\Delta S° = 89$ JK^{-1} mol^{-1} cannot be ascribed to any single type of closed or cyclic structure. For the closed dimer (d), though the $\Delta H^\circ = 30$ kJ mol^{-1} might be consistent with two hydrogen bonds, the $\Delta S^\circ = 89$ JK^{-1} mol^{-1} is much higher than that for the intramolecularly H-bonded monomer ($\Delta S^\circ = 52$ JK^{-1} mol^{-1}) which is mainly responsible for the entropy change. The present ΔH° and ΔS° values are somewhat high for the four membered ring dimer (e) but considerably low for the twelve-membered ring dimer (f). The $\Delta H^\circ = 37$ kJ mol^{-1} and $\Delta S^\circ = 92$ JK^{-1} mol^{-1}, obtained on the assumption of cyclic trimer are in favour of the six membered ring structure (h) only since the other i.e. the eighteen membered ring structure would result in a much larger ΔS° value. Thus the calculated thermodynamic quantities cannot be ascribed to a single association model. The calculated ΔH° and ΔS° values indicate the presence of a mixture of the four- and twelve membered ring dimers with possibly a larger proportion of the former. Alternatively, the six membered ring trimer seems to be equally possible. It is therefore quite likely that all these three species might be coexisting as an equilibrium mixture.

Tetramethylene Glycol Monomethyl Ether : (cf Tables VII.6, VII.7 and Fig. VII.4) : The results for $CH_3O(CH_2)_4OH$ were analysed in the same way as for $CH_3O(CH_2)_3OH$. Thus large variation of equilibrium constants together with relatively very high values of $\Delta H^\circ = 57$ kJ mol^{-1} and $\Delta S^\circ = 157$ JK^{-1} mol^{-1} for a single hydrogen bond exclude the possibility of open dimers. Good constancy of the K's over the concentration range (0.02 - 0.2 mol dm^{-3}) together with $\Delta H^\circ = 20$ kJ mol^{-1} and $\Delta S^\circ = 58$ JK^{-1} mol^{-1} for cyclic dimers are compatible with the four membered ring structure rather than the fourteen-membered one. For open trimers the K's are reasonably constant over the concentration range studied; the $\Delta H^\circ = 40$ kJ mol^{-1} and $\Delta S^\circ = 96$ JK^{-1} mol^{-1} are however considerably higher. In the case of cyclic trimers on the other hand, though the $\Delta H^\circ = 26$ kJ mol^{-1} and $\Delta S^\circ = 60$ JK^{-1} mol^{-1} are compatible with the six-membered ring structure, the corresponding K's show wide variation. Thus no unique type of associated species can satisfactorily explain the calculated ΔH° and ΔS° values. The thermodynamic quantities suggest either the four membered ring dimer or a mixture of open and six-membered ring trimers as the major associated species. A mixture of these three species is therefore equally likely.

The association behaviour of the present compounds is thus seen to be similar to that of simple alcohols which exhibit a mixture of self-associated species in relatively dilute solutions. This is also evident from the additional OH bands which appear at $\sim$3450 and 3350 cm^{-1} in more concentrated solutions of tri- and tetra-methylene glycol monomethyl ethers respectively, like those of simple alcohols in the 3500-3300 cm^{-1} range.

TABLE VII.1 : Measured areas (A') of the free and intramolecularly H-bonded OH bands of tri- and tetramethylene glycol monomethyl ethers

	Trimethylene glycol monomethyl ether						Tetramethylene glycol monomethyl ether					
C_S*	20		80	100	125	150	20		80	100	150	200
L/cm	1.0		0.25	0.20	0.16	0.133	1.0		0.25	0.15	0.08	0.05
T/K	A'_F	A'_I	A'_F	A'_F	A'_F	A'_F	A'_F	A'_I	A'_F	A'_F	A'_F	A'_F
298	47.8	132	41.4	39.2	38.0	35.7	57.0	198	48.4	34.5	26.5	20.7
308	48.4	118	42.6	40.3	39.2	36.8	56.4	176	49.5	35.7	26.5	20.7
313	49.9	110	43.8	41.5	40.3	38.0	56.4	165	49.5	36.8	26.5	21.9
318	49.9	108	43.8	42.6	40.3	39.2	57.0	151	49.5	36.8	27.6	21.9
323	48.9	107	43.8	43.8	41.5	40.3	57.0	135	49.5	36.8	27.6	21.9
328	48.9	102	44.9	43.8	42.6	41.5	56.4	128	49.5	36.8	27.6	21.9
333	48.4	98	44.9	43.8	42.6	41.5	55.3	123	49.5	36.8	27.6	21.9
338	48.4	93	44.9	43.8	42.6	41.5	54.6	114	49.5	36.8	27.6	21.9

*C_S in mol $dm^{-3} \times 10^3$.

TABLE VII.2 : Corrected areas (A) of the free and intramolecularly H-bonded OH bands of tri- and tetramethylene glycol monomethyl ethers

	Trimethylene glycol monomethyl ether						Tetramethylene glycol monomethyl ether					
C_S*	20		80	100	125	150	20		80	100	150	200
L/cm	1.0		0.25	0.20	0.16	0.133	1.0		0.25	0.15	0.08	0.05
T/K	A_F	A_I	A_F	A_F	A_F	A_F	A_F	A_I	A_F	A_F	A_F	A_F
298	54.5	158	47.2	44.6	43.3	40.7	65.3	234	55.6	39.7	30.5	23.8
308	55.8	143	49.2	46.5	45.2	42.5	65.8	216	57.6	41.6	30.8	24.1
313	57.9	134	50.8	48.2	46.8	44.2	66.3	203	58.0	43.2	31.0	25.6
318	58.3	133	51.2	49.8	47.1	45.8	67.1	187	58.4	43.4	32.6	25.8
323	57.7	132	51.5	51.2	48.7	47.4	67.6	179	58.8	43.7	32.8	26.0
328	57.8	127	53.2	51.8	50.4	49.1	67.3	161	59.2	44.0	33.0	26.1
333	57.6	123	53.5	52.2	50.8	49.4	66.5	156	59.5	44.3	33.2	26.3
338	58.3	118	53.9	52.2	51.1	49.7	66.1	146	59.9	44.6	33.4	26.5

*C_S in mol dm^{-3} x 10^3.

TABLE VII.3 : Intramolecular H-bonding in tri- and tetramethylene glycol monomethyl ethers.

	Trimethylene glycol monomethyl ether $C_S = 20 \times 10^{-3}$ mol dm^{-3}				Tetramethylene glycol monomethyl ether $C_S = 20 \times 10^{-3}$ mol dm^{-3}			
T/K	C_F	C_I	$K_{IF} = C_F/C_I$	B_I	C_F	C_I	$K_{IF} = C_F/C_I$	B_I
298	11.6	8.4	1.38	19	13.9	6.1	2.28	39
308	12.4	7.6	1.63	19	14.6	5.4	2.70	40
313	13.1	6.9	1.90	20	15.0	5.0	3.0	41
318	13.5	6.5	2.07	20	15.5	4.5	3.44	42
323	13.7	6.3	2.17	21	16.0	4.0	4.0	42
328	14.0	6.0	2.33	21	16.3	3.7	4.41	43
333	14.3	5.7	2.61	22	16.5	3.5	4.71	45
338	14.8	5.2	2.85	22	16.8	3.2	5.25	46

C_F and C_I in mol dm^{-3} x 10^3, B_I in dm^3 mol^{-1} cm^{-2} x 10^{-3}.

TABLE VII.4 : Calculated concentrations of various species according to different association models for tri- and tetramethylene glycol monomethyl ethers (cf equations 3-5) (All concentrations in mol dm^{-3} x 10^3)

Compound	Soln. conc. C_S	$C_{OH(F)}$	Association model Open dimer C_F	 Open dimer C_D	 Cyclic dimer C_F	 Cyclic dimer C_D	 Open trimer C_F	 Open trimer C_T	 Cyclic trimer C_F	 Cyclic trimer C_T
$CH_3O(CH_2)_3OH$	80	40	1	39	40	6	31	9	40	4
	100	47	*	64	47	9	33	14	47	6
	125	58	*	89	58	13	38	20	58	8
	150	65	*	136	65	19	35	30	65	13
$CH_3O(CH_2)_4OH$	80	47	25	22	47	6	39	8	47	4
	100	56	21	34	56	10	47	12	56	6
	150	81	21	60	81	17	60	21	81	11
	200	101	28	98	101	27	66	35	101	18

F = Free monomer, D = Dimer, T = Trimer .

*C_F cannot be determined as $C_{OH(F)} < C_D$, cf equations (4).

TABLE VII.5 : Calculated equilibrium constants for various postulated equilibria in different solutions of trimethylene glycol monomethyl ether (Solution concentration C_S in mol dm^{-3} x 10^3).

Equilibrium	Open Dimer $\rightleftharpoons$ Free Monomer					Cyclic Dimer $\rightleftharpoons$ Free Monomer				
C_S	80	100	125	150		80	100	125	150	
T/K	K_{DF}	K_{DF}	K_{DF}	K_{DF}	$\bar{K}_{DF}$	K_{DF}	K_{DF}	K_{DF}	K_{DF}	$\bar{K}_{DF}$
298	0	*	*	*	*	29	24	26	22	25
308	1	0	0	*	0	35	32	33	28	32
313	3	2	0	0	1	47	40	38	33	40
318	5	4	1	1	3	49	52	40	43	46
323	8	8	3	2	5	60	63	52	52	57
328	13	11	8	6	10	74	79	72	69	74
333	18	15	12	9	13	94	85	83	77	85
338	28	20	15	12	18	121	100	88	86	99

* K_{DF} could not be obtained since $C_{OH(F)} < C_D$, cf equations (4).

K_{DF}'s in mol dm^{-3} x 10^2.

TABLE VII.5 (continued)

Equilibrium	Open Trimer $\rightleftharpoons$ Free Monomer					Cyclic Trimer $\rightleftharpoons$ Free Monomer				
C_S	80	100	125	150		80	100	125	150	
T/K	K_{TF}	K_{TF}	K_{TF}	K_{TF}	$\bar{K}_{TF}$	K_{TF}	K_{TF}	K_{TF}	K_{TF}	$\bar{K}_{TF}$
298	3	3	3	1	3	17	17	24	22	20
308	6	5	6	4	5	26	25	31	30	28
313	11	9	8	6	8	32	33	37	37	35
318	12	13	10	11	11	35	45	41	51	43
323	17	20	16	16	17	44	56	56	66	56
328	26	31	29	27	22	58	76	83	92	77
333	29	34	38	34	34	74	83	99	107	91
338	47	48	34	42	44	98	100	106	122	107

K_{TF} in $mol^2\ dm^{-6} \times 10^3$.

TABLE VII.6 : Calculated equilibrium constants for various postulated equilibria in different solutions of tetramethylene glycol monomethyl ether (Solution concentration C_S in mol $dm^{-3} \times 10^3$).

Equilibrium	Open Dimer $\rightleftharpoons$ Free Monomer					Cyclic Dimer $\rightleftharpoons$ Free Monomer				
C_S	80	100	150	200		80	100	150	200	
T/K	K_{DF}	K_{DF}	K_{DF}	K_{DF}	$\bar{K}_{DF}$	K_{DF}	K_{DF}	K_{DF}	K_{DF}	$\bar{K}_{DF}$
298	3	1	1	0	1	37	33	40	38	37
308	7	4	2	1	3	47	44	42	42	44
313	10	10	3	3	6	56	60	46	57	55
318	11	14	7	5	9	58	64	61	62	61
323	14	13	9	6	11	63	68	65	66	65
328	15	17	12	9	13	65	78	74	73	72
333	20	22	16	11	14	77	89	85	79	82
338	32	28	20	14	23	106	102	94	87	97

K_{DF} in mol $dm^{-3} \times 10^2$.

TABLE VII.6 (continued)

Equilibrium	Open Trimer $\rightleftharpoons$ Free Monomer					Cyclic Trimer $\rightleftharpoons$ Free Monomer				
C_S	80	100	150	200		80	100	150	200	
T/K	K_{TF}	K_{TF}	K_{TF}	K_{TF}	$\bar{K}_{TF}$	K_{TF}	K_{TF}	K_{TF}	K_{TF}	$\bar{K}_{TF}$
298	8	7	10	8	8	26	28	48	57	40
308	13	12	13	12	12	36	40	54	68	50
313	17	22	15	24	19	45	58	60	99	65
318	19	25	27	29	25	48	64	86	110	77
323	22	28	31	34	29	53	70	94	122	85
328	24	35	40	43	35	56	83	111	139	97
333	31	43	50	50	43	68	97	132	154	113
338	48	54	60	61	56	99	114	149	176	135

K_{TF} in $mol^2\ dm^{-6} \times 10^3$.

TABLE VII.7 : Calculated thermodynamic quantities involved in various equilibria in tri- and tetramethylene glycol monomethyl ethers.

Type of Equilibrium	Thermodynamic Property	$CH_3O(CH_2)_3OH$	$CH_3O(CH_2)_4OH$
$M_I \rightleftharpoons M_F$	K_{IF}	1.4	2.2
	$\Delta G^\circ/kJ\ mol^{-1}$	-0.8	-2.0
	$\Delta H^\circ/kJ\ mol^{-1}$	15 ± 0.6	18 ± 0.7
	$\Delta S^\circ/JK^{-1}\ mol^{-1}$	52 ± 2	68 ± 2.3
$D^*_{open} \rightleftharpoons 2\ M_F$	$K_{DF}/mol\ dm^{-3}$	-	0.01
	$\Delta G^\circ/kJ\ mol^{-1}$	-	11
	$\Delta H^\circ/kJ\ mol^{-1}$	94 ± 6.6	57 ± 5.1
	$\Delta S^\circ/JK^{-1}\ mol^{-1}$	266 ± 20	157 ± 16
$D^*_{cyclic} \rightleftharpoons 2\ M_F$	$K_{DF}/mol\ dm^{-3}$	0.25	0.37
	$\Delta G^\circ_{DF}/kJ\ mol^{-1}$	3.4	2.5
	$\Delta H^\circ_{DF}/kJ\ mol^{-1}$	30 ± 1.4	20 ± 1.2
	$\Delta S^\circ_{DF}/JK^{-1}\ mol^{-1}$	89 ± 4.4	58 ± 3.9
$T^{**}_{open} \rightleftharpoons 3\ M_F$	$K_{TF}/mol^2\ dm^{-6}$	0.002	0.008
	$\Delta G^\circ_{TF}/kJ\ mol^{-1}$	15	12
	$\Delta H^\circ_{TF}/kJ\ mol^{-1}$	61 ± 1.6	41 ± 1.2
	$\Delta S^\circ\ /JK^{-1}\ mol^{-1}$	154 ± 5	96 ± 3.7
$T^{**}_{cyclic} \rightleftharpoons 3\ M_F$	$K_{TF}/mol^2\ dm^{-6}$	0.02	0.04
	$\Delta G^\circ/kJ\ mol^{-1}$	9.7	8
	$\Delta H^\circ/kJ\ mol^{-1}$	37 ± 1.1	26 ± 0.5
	$\Delta S^\circ/JK^{-1}\ mol^{-1}$	92 ± 3.5	60 ± 1.5

K's and ΔG°'s at 298 K.

*D = Dimer.

**T = Trimer.

CHAPTER VIII

GENERAL DISCUSSION AND CONCLUSIONS

CHAPTER VIII

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VIII.1. Introduction :

The spectroscopic properties of the free and various types of H-bonded OH stretching bands of ethylene-, trimethylene- and tetramethylene glycol monoalkyl ethers $RO(CH_2)_nOH$ (n = 2,3 and 4 respectively) are summarised in Table VIII.1.* Similarly the thermodynamic quantities associated with the conversion of different types of H-bonded species into the free monomers are represented in Table VIII.2.** It can be seen that all the spectroscopic as well as thermodynamic quantities associated with intramolecular H-bonding in the series $RO(CH_2)_nOH$ show an increase with the number of methylene groups in the chain. The plots of ΔH° and B against $\Delta\bar{\nu}$ are found to be linear (Fig. VIII.1). No such regularities are however found in the case of intermolecular association in these systems. The spectroscopic and thermodynamic quantities associated with intramolecular H-bonding in diethylene glycol monoalkyl ethers, $RO(CH_2)_2O(CH_2)_2OH$, which are also include in the same tables and figures, show somewhat different trends.

VIII.2. Intramolecular H-Bonding :

As mentioned earlier (Chapter III) the frequency shift is a measure of the H-bonding interaction. Similarly the half band width $\Delta\bar{\nu}_{1/2}$ and integrated intensity B of the H-bonded OH groups,

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* page 126. ** page 127.

which are related respectively to the anharmonicity and the dipole moment derivative associated with the vibrations of the groups concerned, both depend on the extent of H-bonding interaction. The increasing magnitudes of these properties involved in intramolecular H-bonding in $RO(CH_2)_nOH$ then imply increase in H-bond strength with n. This is expected since with an increase in the number of methylene groups in the chain, the hydroxyl proton can get closer to the acceptor i.e. the ether oxygen atom resulting in a shorter and hence stronger H-bond. The O...H distances calculated using Kuhn's relation ($\Delta\bar{\nu} = 250 \times 10^{-8}/L - 74$, L in cm)[69], viz. 2.3, 1.6 and 1A for intramolecularly H-bonded monomers of $RO(CH_2)_nOH$ with n = 2,3 and 4 respectively, are comparable with those obtained by Fishman and Chen[68] viz. 2.1, 1.8 and 1.2A for 1-2, 1-3 and 1-4 butane diols respectively.

The enthalpy change $\Delta H°$ for the $M_I \rightleftharpoons M_F$ equilibrium is a measure of the energy difference between the free and the intramolecularly H-bonded monomers which is therefore directly related to the H-bond strength. The shorter and stronger H-bonds in bigger rings are therefore consistent with increasing magnitude of $\Delta H°$ in the $RO(CH_2)_nOH$ series. The increasing ring size (5-, 6- and 7-membered for n = 2,3 and 4 respectively) which is associated with increasing restriction to internal rotation, explains the larger values of $\Delta S°$. As the chain length increases in the series $RO(CH_2)_nOH$, the relative number of rotational conformations favourable for intramolecular H-bonding decreases. Further, the

(contd. on page 117.)

CAPTIONS

Fig.VIII.1 : Plots of (I) ΔH° and (II) B vs $\Delta\bar{\nu}$ for intramolecular H-bonding

1. $CH_3O(CH_2)_2OH$
2. $C_2H_5O(CH_2)_2OH$
3. $C_4H_9O(CH_2)_2OH$
4. $CH_3O(CH_2)_3OH$
5. $CH_3O(CH_2)_4OH$
6. $CH_3O(CH_2)_2O(CH_2)_2OH$
7. $C_2H_5O(CH_2)_2O(CH_2)_2OH$

(a) and (b) : five- and eight membered ring monomers (of (6) and (7)) respectively.

Fig. VIII.2 : Variation of integrated intensity with temperature

1: Free OH band of CH_3CH_2OH.

2, 3 and 4 : Intramolecularly H-bonded OH bands of ethylene glycol monomethyl,-ethyl and -butyl ethers respectively.

5 and 6 : Intramolecularly H-bonded OH bands of tri- and tetramethylene glycol monomethyl ethers respectively.

7 and 8 : Intramolecularly H-bonded eight membered ring monomeric OH bands of diethylene glycol monomethyl- and -ethyl ethers respectively.

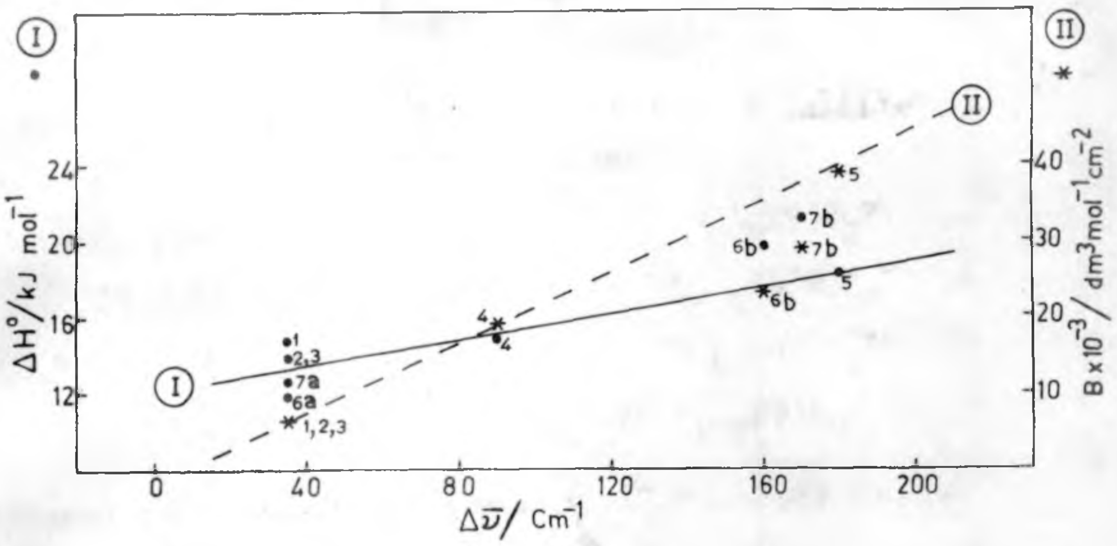

FIG-VIII-1: PLOTS OF (I) ΔH° AND (II) B vs Δν̄ FOR INTRAMOLECULAR H-BONDING

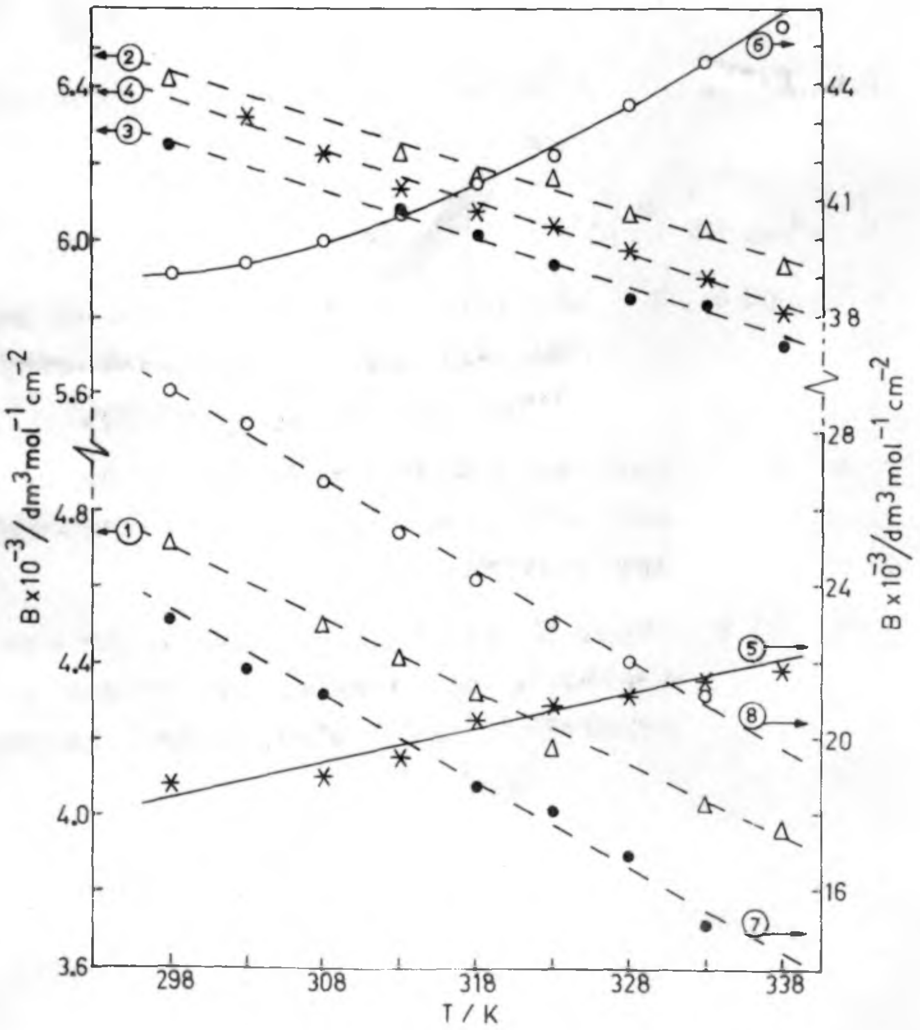

FIG-VIII-2: VARIATION OF INTEGRATED INTENSITY WITH TEMPERATURE.

larger entropy decrease required for forming the bigger rings lowers the probability of intramolecular H-bonding. The increase in the equilibrium constant K_{IF} ($= C_F/C_I$), which is a measure of the relative populations of the free and the intramolecularly H-bonded monomers, is therefore easily understandable.

The linearity of the ΔH°- $\Delta\bar{\nu}$ plot (Fig. VIII.1(I)) for intramolecular H-bonding in the $RO(CH_2)_nOH$ series is consistent with the well-known Badger-Bauer rule[74]. Khun and Wires[83] did not observe the ΔH°- $\Delta\bar{\nu}$ linearity for these compounds and concluded that the Badger-Bauer rule is inapplicable to intramolecular H-bonding because of conformational interactions. Busfield et al,[73] who have studied the intramolecular H-bonding in the corresponding diols $HO(CH_2)_nOH$ on the other hand have shown the applicability of the Badger-Bauer rule. Fishman and Chen[68] also have found that the Badger-Bauer rule is obeyed in intramolecular H-bonding in the series of 1-2, 1-3 and 1-4 butane diols. It is apparent that as the ring size increases, the attractive interaction due to H-bonding should increase because of closer approach of the donor and acceptor groups whereas the repulsive interactions should decrease because of flexibility of the bigger rings. The ΔH°, which is the sum of all the interactions associated with the H-bonding should therefore increase as found in the present case.

Huggins and Pimental[111] also have found linear variation of $\Delta\bar{\nu}_{1/2}$ with $\Delta\bar{\nu}$. Similarly Becker[112b] has reported a linear relationship between the integrated intensity of the H-bonded complex and the associated ΔH° and indicated a possibility of correlation between $\Delta H°$ and $\Delta\bar{\nu}_{1/2}$. The increasing magnitudes of $\Delta H°$, $\Delta\bar{\nu}_{1/2}$ and B are therefore consistent with an increase in $\Delta\bar{\nu}$ since all these properties are measures of H-bonding interaction and should therefore vary in a parallel manner. The high intensities of H-bonded stretching modes are attributed to increased ionic character of the A-H bond[113].

In the case of diethylene glycol monoalkyl ethers $RO(CH_2)_2O(CH_2)_2OH$, the spectroscopic and thermodynamic quantities associated with the intramolecularly H-bonded five membered ring monomers are comparable with those for ethylene glycol monoalkyl ethers $RO(CH_2)_2OH$. This is expected since in both the cases, the respective H-bonded monomers are quite similar. The numerical magnitudes of various quantities associated with the intramolecularly H-bonded eight membered ring monomer however do not follow the trends exhibited by the 5-, 6- and 7-membered ring monomers of $RO(CH_2)_nOH$ and the respective points do not lie along the otherwise linear plots. This is evidently due to the fact that the behaviour of the ether oxygen atom is markedly different from that of the methylene group. The gauche configurations of two OCH_2CH_2O units could constrain the eight membered ring in such a way that the hydroxyl proton cannot approach the ether oxygen as close as that in the 7-membered ring of $RO(CH_2)_4OH$ resulting in a smaller $\Delta\bar{\nu}$ value for the former. The presence of the middle oxygen atom (ether oxygen) however must be reducing the repulsive interactions which might explain the higher $\Delta H°$ value in spite of the lower $\Delta\bar{\nu}$ value.

VIII.3. Intermolecular Association :

In the case of $RO(CH_2)_2OH$, the $\Delta\bar{\nu}$, $\Delta\bar{\nu}_{1/2}$, as well as B for the dimer band are appreciably larger than those for the intramolecularly H-bonded monomer which in turn are larger than those for the free monomer (Table VIII.1). This implies higher values of the H-bonding interaction, anharmonicity and dipole moment derivative respectively for the dimer than those for the intramolecularly H-bonded monomer. These observations are consistent with higher value of $\Delta H°$ for the dimer. In the case of $RO(CH_2)_2O(CH_2)_2OH$, because of extensive overlap of the dimer and the eight membered ring monomer bands, the $\Delta\bar{\nu}$, $\Delta\bar{\nu}_{1/2}$ and B for the former could not be determined exactly. The approximate values determined as explained in Chapter VI (cf Table VI.8) are found to be quite large in comparison with those for the intramolecularly H-bonded monomers and can be explained in the same way as for $RO(CH_2)_2OH$ dimer. In the case of tri- and tetramethylene glycol monomethyl ethers the bands of the inter- and intramolecularly associated species overlap so extensively that they could not be resolved. It is also found that there are more than one type of associated species present. Their spectral characteristics therefore could not be determined exactly.

Simple alcohols at concentration of ~ 0.1 mol dm^{-3} in non-polar solvents are found to exhibit a number of infrared absorption bands in the 3500-3300 cm^{-1} region which are ascribable to a mixture of polymeric species. The monoalkyl ethers of ethylene- and diethylene glycols on the other hand do not exhibit any additional OH bands in the 3300 cm^{-1} region even upto a concentration of ~ 0.5 mol dm^{-3}. The thermodynamic quantities involved in their self-association have shown that the associated species at concentration of ~ 0.1 mol dm^{-3} are mainly the ten-membered ring dimers (Chapter V and VI). This peculiarity of the latter type of compounds is attributable to the ability of their OCH_2CH_2O groups to exist predominantly in the gauche configuration in dilute as well as concentrated solutions. The CH_2 rocking mode studies of a number of mono-, di- and tri-ethylene glycol monoalkyl ethers also have shown that the OCH_2CH_2O groups of these compounds exist almost exclusively in the gauche conformation in solutions as well as in pure liquids[79-81]. The tri- and tetra-methylene glycol monoalkyl ethers are found to exhibit a mixture of self-associated species at concentrations of ~ 0.1 mol dm^{-3} (Chapter VII). This shows that as the number of CH_2 groups between the two oxygen atoms is increased beyond two, the association behaviour of diol monoalkyl ethers tends to be similar to that of simple alcohols.

VIII.4. Spectroscopic Properties :

In the case of the free and the intramolecularly H-bonded hydroxyl bands, the positions of the absorption maxima ($\bar{\nu}_0$) as well as the half band widths ($\Delta\bar{\nu}_{1/2}$) were found to be practically constant over the temperature range studied (298-338 K). The dimer band of ethylene glycol monoalkyl ethers showed a small increase (of $\sim$ 5-10 cm^{-1}) in $\bar{\nu}$ and a small decrease (of $\sim$ 5 cm^{-1}) in $\Delta\bar{\nu}_{1/2}$. The intramolecularly H-bonded eight membered ring monomer band of $RO(CH_2)_2O(CH_2)_2OH$ also showed similar variations. In the case of the monoalkyl ethers of diethylene glycol as well as those of tri- and tetra-methylene glycols, the individual bands due to the inter- and intramolecularly associated species are not resolvable because of extensive overlap. The combined bands however showed similar variations as in the case of dimer band of $RO(CH_2)_2OH$.

The integrated intensity B of various bands on the other hand shows relatively larger variations. In the case of ethanol and ethylene- and diethylene glycol monoalkyl ethers (cf Tables IV.3, V.12 and VI.4), it is observed that the integrated intensity B decreases with increasing temperature (Fig. VIII.2). This trend is in agreement with that reported by others[28-30,109,114,112]. The decrease of integrated intensity of the OH band with increasing temperature is suggested to be due to a change in the polarisability of the OH group and a decrease of the force field on the absorbing molecules due to their neighbours with an increase in temperature[114]. As reported in literature[112], the B's in the present case are found to vary in a manner parallel to $\Delta H°$; e.g. in the case of $RO(CH_2)_2OH$, it is observed that $\Delta H°_{DF} > \Delta H°_{IF}$ as well as $B_D > B_I > B_F$. (cf Tables V.12, IV.3 and V.13). It is however interesting to note that over the temperature range 298-338 K, the fractional decrease of the B's with reference to their values at 298 K (i.e. $\Delta B/B_{298\ K}$ where $\Delta B = B_{298\ K} - B_{338\ K}$) follows exactly the opposite order.

Thus $\Delta B/B_{298\ K}$ for the dimer, intramolecularly H-bonded monomer and free monomer are found to be 5%, 8% and 16% respectively. Similar trends have been observed in the case of the intramolecularly H-bonded eight- and the five-membered ring monomers of $RO(CH_2)_2O(CH_2)_2OH$. Becker[112b] also has noted that the magnitude of the temperature effect on integrated intensities decreases systematically with increase in ΔH° of H-bond formation. In the case of tri- and tetra-methylene glycol monomethyl ethers, the integrated intensities of the intramolecularly H-bonded monomers showed rather irregular variations, with a tendency to increase with increasing temperature. This discrepancy is attributable to the presence of more than one type of intramolecularly H-bonded species, the intensities of which would not vary in the same manner. The observed effect which is the resultant of all the constituents therefore shows somewhat different trends from than those observed in the other cases. The temperature variation of integrated intensities of the intermolecularly associated species of diethylene- and tri- and tetramethylene glycol monoalkyl ethers could not be studied because of extensive overlap of their bands with those of the respective intramolecularly H-bonded monomers.

VIII.5. Conclusions :

The results of present investigation can now be summarized as follows :

The ethylene-, trimethylene- and tetramethylene glycol monoalkyl ethers in very dilute carbon tetrachloride solutions

($C \sim 0.01$ mol dm^{-3}) give rise to equilibria between free and intramolecularly H-bonded monomers. As the number of methylene groups between the two oxygen atoms is increased, the extent of intramolecular H-bonding (i.e. the relative population of intramolecularly H-bonded monomers with respect to the free species) is found to decrease whereas the strength of H-bonding interaction (e.g. $\Delta H^\circ = 14$, 15 and 18 kJ mol^{-1} respectively) is found to increase because of close proximity of the H-bonding groups. The $\Delta H^\circ - \Delta\bar{\nu}$ plot is linear, consistent with the Badger-Bauer rule.

The diethylene glycol monoalkyl ethers give rise to intramolecularly H-bonded five- and eight- membered ring monomers in equilibrium with the free species. The relative populations of the free and five membered ring monomers in these together with the corresponding frequencies and ΔH° value are comparable with those for the ethylene glycol monoalkyl ethers. The five- and eight membered ring monomers are present in the ratio of about 2:1 at 298 K, the $\Delta\bar{\nu}$ and ΔH° values for the latter being ~ 3.5 and 1.6 times larger respectively. The eight membered ring monomer shows deviation in the $\Delta H^\circ - \Delta\bar{\nu}$ plot which is attributable to structural difference of this species brought about by the presence of an additional ether oxygen atom.

At higher concentrations, these compounds associate giving rise to intermolecularly H-bonded species in equilibrium with the free and intramolecularly H-bonded monomers. The main associated species of ethylene- and diethylene glycol monoalkyl ethers in the concentration range of 0.01 - 0.15 are found to be ten membered ring dimers resulting from mutual H-bonding of two molecules via their ether oxygen atoms in the β-positions. The association behaviour of these compounds is thus markedly different from that of simple alcohols, which give rise to a mixture of different types of self-associated species. This peculiar behaviour of the ethylene- and diethylene glycol monoalkyl ethers is attributable to the ability of their OCH_2CH_2O skeletons to maintain gauche conformations in dilute as well as concentrated solutions. The extent of dimerization in diethylene glycol monoalkyl ethers is smaller than that in ethylene glycol monoalkyl ethers. This is ascribable to the formation of the eight membered ring monomer in the former having H-bond strength comparable with those in the dimer but smaller entropy decrease. The tri- and tetramethylene glycol monoalkyl ethers are found to give rise to a mixture of dimers and trimers of open and/or closed type. The association behaviour these compounds is thus similar to that of simple alcohols.

The frequency shifts $(\Delta\bar{\nu})$ and half-band widths $(\Delta\bar{\nu}_{1/2})$ of the hydroxyl bands of the free- and intramolecularly H-bonded five membered ring monomers are practically independent of temperature whereas in the case of the other intramolecularly H-bonded monomers (i.e. the six-, seven- and eight membered ring species) as well as the intermolecularly associated species, a slight decrease is observed with increasing temperature. The integrated intensities (B) also in general showed a decrease with a rise in temperature. The B's and ΔH°'s for different types of H-bonded species are found to vary in a parallel manner; i.e. those with higher value of ΔH°

have also a higher value of B. The fractional decrease of the B's with respect to their room temperature values however followed an opposite order. All these effects arise due to the changes in force fields of the solute and solvent molecules with temperature.

TABLE VIII.1 : Summary of spectroscopic properties of the free- and H-bonded OH bands of the diol monoalkyl ethers studied (T = 298 K)

	Compound	Free Monomer			Intramolecularly H-bonded Monomer						Associated Species*			
		$\bar{\nu}$	$\Delta\bar{\omega}_{1/2}$	$Bx10^{-3}$	$\bar{\nu}$	$\Delta\bar{\omega}$	$\Delta\bar{\omega}_{1/2}$	$Bx10^{-3}$	Ring size	R	$\bar{\nu}$	$\Delta\bar{\omega}$	$\Delta\bar{\omega}_{1/2}$	$Bx10^{-4}$
1	CH_3CH_2OH	3635	27	4.7	-	-	-	-	-	-	-	-	-	-
2	$CH_3O(CH_2)_2OH$	3635	26	-	3600	35	32	6.4	5	2.3	3475	160	150	5.9
3	$C_2H_5O(CH_2)_2OH$	3635	28	-	3600	35	32	6.3	5	2.3	3475	160	150	6.1
4	$C_4H_9O(CH_2)_2OH$	3635	27	-	3600	35	32	6.4	5	2.3	3475	160	145	5.7
5	$CH_3O(CH_2)_3OH$	3630	25	-	3540	90	60	19	6	1.5	3500	130	-	-
6	$CH_3O(CH_2)_4OH$	3630	26	-	3450	180	95	39	7	1.0	3430	200	-	-
7	$CH_3O(CH_2)_2O(CH_2)_2OH$	3635	25	-	3600	35	32	-	5	2.3	3440	195	160	12.6
					3475	160	100	23	8	1.1				
8	$C_2H_5O(CH_2)_2O(CH_2)_2OH$	3635	25	-	3600	35	32	-	5	2.3	3440	195	160	11.3
					3470	165	105	29	8	1.1				

$\bar{\nu}$, $\Delta\bar{\omega}$ and $\Delta\bar{\omega}_{1/2}$ in cm^{-1}; B in $dm^3\ mol^{-1}\ cm^{-2}$; R = O...H distance in A.

*Associated species in the concentration range studied :

Compound Nos. (2), (3), (4), (7) and (8) : Ten membered ring dimer.

Compound Nos. (5) and (6) : A mixture of dimers and/or trimers.

TABLE VIII.2 : Summary of thermodynamic properties associated with intra- and intermolecular H-bonding in the diol monoalkyl ethers studied.

	Compound	Intramolecular H-Bonding				Intermolecular H-Bonding				
		K_{IF}	ΔG°	ΔH°	ΔS°	Associated Species	$K^{*}x10^{3}$	ΔG°	ΔH°	ΔS°
1	$CH_3O(CH_2)_2OH$	0.09	5.9	15	29	Dimer[c]	3.3	14	55	136
2	$C_2H_5O(CH_2)_2OH$	0.10	5.8	14	27	Dimer[c]	3.1	15	57	142
3	$C_4H_9O(CH_2)_3OH$	0.09	5.8	14	26	Dimer[c]	3.0	14	57	142
4	$CH_3O(CH_2)_3OH$	1.4	-0.8	15	52	Dimer[d]	253	3.4	30	89
						Trimer[e]	20	9.7	37	92
5	$CH_3O(CH_2)_4OH$	2.3	-2.0	18	68	Dimer[d]	368	2.5	20	58
						Trimer[e]	40	8	26	60
6	$CH_3O(CH_2)_2O(CH_2)_2OH$	0.1[a] 2.0[b]	5.7[a] 3.9[b]	12[a] 20[b]	21[a] 53[b]	Dimer[c]	6.2	13	58	153
7	$C_2H_5O(CH_2)_2O(CH_2)_2OH$	0.1[a] 2.1[b]	5.8[a] 3.9[b]	13[a] 21[b]	23[a] 58[b]	Dimer[c]	5.8	13	58	152

K and ΔG° at 298 K; ΔG° and ΔH° in $kJ\ mol^{-1}$, ΔS° in $JK^{-1}\ mol^{-1}$

a : five membered ring monomer, b : eight membered ring monomer,

c : ten membered ring dimer, d : mixture of cyclic dimers,

e : six membered ring trimer

*K in $mol\ dm^{-3}$ for dimers and $mol^{2}\ dm^{-6}$ for trimers.

REFERENCES

REFERENCES

1. J.J. Fox and A.E. Martin, Proc.Roy.Soc. (London), 1937, A162, 419.
2. M.St.C. Flett, Spectrochim.Acta, 1957, 10, 21.
3. L.J. Bellamy, (a) 'Infra Red Spectra of Complex Molecules', (Methuen, London, Second Edition, 1959), p. 95; (b) 'Advances in I.R. Group Frequencies', (Methuen, London, 1968), p. 256.
4. A.J. Barnes, H.E. Hallam and D. Jones, Proc.Roy.Soc.(London), 1973, 335A, 97.
5. O.R. Wulf and U. Liddel, J.Amer.Chem.Soc., 1935, 57, 1464.
6. R.M. Badger and S.H. Bauer, J.Chem.Phys., 1936, 4, 711.
7. P. Barchewitz and R. Freymann, Compt.Rend., 1937, 204, 1729.
8. J.J. Fox and A.E. Martin, Trans.Faraday Soc., 1940, 56, 897.
9. A.M. Buswell, W.H. Rodebush and R.M. Whitney, J.Amer.Chem.Soc., 1947, 69, 770.
10. M. Oki and H. Iwamura, Bull.Chem.Soc.Japan, 1959, 32, 567 and 590.
11. F. Dalton, G. Meakins, J. Robinson and W. Zaharia, J.Chem.Soc., 1962, 1566.
12. P.J. Krueger and H.D. Mettee, Canad.J.Chem. 1963, 42, 347.
13. A.J. Barnes and H.E. Hallam, Trans.Faraday Soc., 1970, 66, 1920 and 1932.
14. J. Errera, R. Gaspart and H. Sack, J.Chem.Phys., 1940, 8, 63.
15. N.D. Coggeshall and E.L. Sair, J.Amer.Chem.Soc., 1951, 73, 5414.

16. F.A. Smith and E.C. Creitz, *J.Res.Natl.Bur.Std.*, 1951, **46**, 145.

17. W.C. Coburn, Jr. and E. Grunwald, *J.Amer.Chem.Soc.*, 1958, **80**, 1318.

18. R.G. Inskeep, J.M. Kelliher, P.E. McMahon and B.G. Somers, *J.Chem.Phys.*, 1958, **28**, 1033.

19. R.G. Inskeep, F.E. Dickson and H.M. Olson, *J.Mol.Spectroscopy*, 1960, **5**, 284.

20. L.P. Kuhn and R.E. Bowman, *Spectrochim.Acta*, 1961, **17**, 650.

21. L.J. Bellamy and R.J. Pace, *Spectrochim.Acta*, 1966, **22**, 525.

22. D.A. Ibbitson and L.F. Moore, *J.Chem.Soc.(B)*, 1967, 76 and 80.

23. A.N. Fletcher and C.A. Heller, *J.Phys.Chem.*, 1968, **72**, 1839.

24. A.J. Barnes and J. Murto, *J.Chem.Soc., Faraday Trans.II*, 1972, **68**, 1642.

25. P. Bordewijk, M. Kunst and A. Rip, *J.Phys.Chem.*, 1973, **77**, 548.

26. A.S.N. Murthy, R.E. Davis and C.N.R. Rao, *Theor.Chim.Acta*, 1969, **13**, 81.

27. J.R. Hoyland and L.B. Kier, *Theor.Chim.Acta*, 1969, **15**, 1.

28. U. Liddel and E.D. Becker, *Spectrochim.Acta*, 1957, **10**, 70.

29. E.D. Becker, U. Liddel and J.N. Shoolery, *J.Mol.Spectroscopy*, 1958, **2**, 1.

30. M. Van Thiel, E.D. Becker and G.C. Pimentel, *J.Chem.Phys.*, 1957, **27**, 95.

31. P.J. Krueger and H.D. Mettee, *Canad.J.Chem.*, 1965, **43**, 2888.

32. S. Singh and C.N.R. Rao, *J.Phys.Chem.*, 1967, **71**, 1074.

33. H.C. Van Ness, J. Van Winkle, H.H. Richtol and H.B. Hollinger, *J.Phys.Chem.*, 1967, **71**, 1483.

34. P.I. Gold and R.L. Perrin, *J.Phys.Chem.*, 1967, **71**, 4218.

35. J.C. Davies, Jr., K.S. Pitzer and C.N.R. Rao, *J.Phys.Chem.*, 1960, **64**, 1744.

36. W. Masschelein, *Spectrochim.Acta*, 1962, **18**, 1557.

37. H. Dunken and H. Fritzsche, *Spectrochim.Acta*, 1964, **20**, 785.

38. R.M. Hammeker, R.M. Clegg, L.K. Patterson, P.E. Rider and S.L. Rock, *J.Phys.Chem.*, 1968, **72**, 1837.

39. W.L. Chandler and R.H. Dinius, *J.Phys.Chem.*, 1969, **73**, 1596.

40. T.S.S.R. Murthy, *Canad.J.Chem.*, 1970, **48**, 184.

41. R. Mecke, *Discussions Faraday Soc.*, 1950, **9**, 161.

42. A.D. Cohen and C. Reid, *J.Chem.Phys.*, 1956, **25**, 790.

43. M. Saunders and J.B. Hyne, *J.Chem.Phys.*, 1958, **29**, 253.

44. E.E. Tucker, S.B. Farnham and S.D. Christian, *J.Phys.Chem.*, 1969, **73**, 3820.

45. E.E. Tucker and E.D. Becker, *J.Phys.Chem.*, 1973, **77**, 1783.

46. W. Weltner, Jr., and K.S. Pitzer, *J.Amer.Chem.Soc.*, 1951, **73**, 2606.

47. C.B. Kretschmer and R. Wiebe, *J.Amer.Chem.Soc.*, 1954, **76**, 2579.

48. A. Ens and F.E. Murray, *Canad.J.Chem.*, 1957, **35**, 170.

49. J. Feeney and S.M. Walker, *J.Chem.Soc.(A)*, 1966, 1148.

50. A.N. Fletcher and C.A. Heller, *J.Phys.Chem.*, 1967, **71**, 3742.

51. W.B. Dixon, *J.Phys.Chem.*, 1970, **74**, 1396.

52. A.N. Fletcher, *J.Phys.Chem.*, 1972, **76**, 2662.

53. G.C. Pimentel and A.L. McClellan, '*The Hydrogen Bond*', (W.H. Freeman, London, 1960), p. 110.

54. M. Tichy, *Adv.Org.Chem.*, 1965, **5**, 115.

55. S. Mizushima, T. Shimanouchi, T. Miyazawa, K. Abe and M. Yasumi, *J.Chem.Phys.*, 1951, **19**, 1477;
S. Mizushima, T. Shimanouchi, K. Kuratani and T. Miyazawa, *J.Amer.Chem.Soc.*, 1952, **74**, 1378.

56. L.R. Zumwalt and R.M. Badger, *J.Amer.Chem.Soc.*, 1940, **62**, 305.

57. P.J. Kruegner and H.D. Mettee, *Canad.J.Chem.*, 1964, **42**, 326, 340 and 347.

58. P.J. Krueger and H.D. Mettee, *Canad.J.Chem.*, 1965, **43**, 2970.

59. P. Buckley, P.A. Giguere and D. Yamamoto, *Canad.J.Chem.*, 1968, **46**, 2917.

60. P. Buckley, P.A. Giguere and M. Schneider, *Canad.J.Chem.*, 1969, **47**, 901.

61. P.A. Giguere and M. Schneider, *Canad.J.Chem.*, 1972, **50**, 152.

62. I.M. Goldman and R.O. Crisler, *J.Org.Chem.*, 1958, **23**, 751;
P.v.R. Schleyer, C. Wintner, D.S. Trifan and R. Bacskai, *Tetrahedron Lett.*, 1959, **14**, 1;
M. Oki and H. Iwamura, *Bull.Chem.Soc.Japan*, 1959, **32**, 950 and 955;
P.J. Krueger and H.D. Mettee, *Tetrahedron Lett.*, 1966, **15**, 1587;
H. Iwamura, *Tetrahedron Lett.*, 1970, **26**, 2227.

63. P.J. Krueger and H.D. Mettee, *J.Mol.Spectroscopy*, 1965, **18**, 131.

64. P. Buckley and P.A. Giguere, *Canad.J.Chem*., 1967, **45**, 397.

65. H. Buc and J. Neel, *Compt.Rend*., 1961, **252**, 1786; 1962, **255**, 2947;
H. Buc, *Ann.Chim.(Paris)*, 1963, **8**, 409.

66. P.v.R. Schlyer, *J.Amer.Chem.Soc*., 1961, **83**, 1368.

67. A. Johansson and P. Kollmann, *Chem.Phys.Lett*., 1973, **18**, 276.

68. E. Fishman and T.L. Chen, *Spectrochim.Acta*, 1969, **25A**, 1231.

69. L.P. Kuhn, *J.Amer.Chem.Soc*., 1952, **74**, 2492; 1954, **76**, 4323.

70. L.P. Kuhn, P.v.R. Schleyer, W.F. Baitinger, Jr. and L. Eberson, *J.Amer.Chem.Soc*., 1964, **86**, 650.

71. T. Yonezawa, H. Saito, S. Matsuoka and K. Fukui, *Bull.Chem.Soc.Japan*, 1965, **38**, 1431.

72. D.J. Morantz and M.S. Waite, *Spectrochim.Acta*, 1971, **27A**, 1133.

73. W.K. Busfield, M.P. Ennis and I.J. McEwen, *Spectrochim.Acta*, 1973, **29A**, 1259.

74. R.M. Badger and S.H. Bauer, *J.Chem.Phys*., 1937, **5**, 839.

75. F.T. Wall and W.F. Clausen, *J.Amer.Chem.Soc*., 1939, **61**, 2679.

76. A. Foster, A. Hains and M. Stacey, *Tetrahedron*, 1961, **16**, 177.

77. H. Saito, T. Yonezawa, S. Matsuoka and K. Fukui, *Bull.Chem.Soc.Japan*, 1966, **39**, 989.

78. C.P.N. Son, H.C. Beachell and N.H. Ngoc, Compt.Rend., 1971, C273, 210.

79. A. Miyake, J.Amer.Chem.Soc., 1960, 82, 3040.

80. T.K.K. Srinivasan, C.I. Jose and A.B. Biswas,
(a) Bull.Chem.Soc.Japan, 1964, 37, 1770;
(b) Int.Conf.Spectroscopy, 1967, 2, 293.

81. T.K.K. Srinivasan, C.I. Jose and A.B. Biswas, Canad.J.Chem., 1969, 47, 3877.

82. P. Buckley and M. Brochu, Canad.J.Chem., 1972, 50, 1149.

83. L.P. Kuhn and R.A. Wires, J.Amer.Chem.Soc., 1964, 86, 2161.

84. N.N. Shapetko, D.N. Shigorin, A.P. Skoblinov, T.S. Ryabchikova and L.N. Reshetova, Optics and Spectroscopy, 1964, 17, 247.

85. V.P. Lodygina, A.I. Ivanov, S.M. Baturin and S.G. Entelis, Russ.J.Phys.Chem., 1970, 44, 1068.

86. V.S. Markevich, V.A. Terent'ev and N.E. Shtivel', Russ.J.Phys.Chem., 1969, 43, 7.

87. (a) G.Herzberg, 'Infrared and Raman Spectra of Polyatomic Molecules', (D.Van Nostrand, Princeton, 1945), p.261;
(b) J.C.D. Brand and J.C. Speakman, 'Molecular Structure', (Edward Arnold Publishers, London, 1960), p.155.

88. D.A. Ramsay, J.Amer.Chem.Soc., 1952, 74, 72.

89. K.S. Sheshadri and R.N. Jones, Spectrochim.Acta, 1963, 19, 1013.

90. R.N. Jones, D.A. Ramsay, D.S. Keir and K. Dobriner, J.Amer.Chem.Soc., 1952, 74, 80.

91. Ref. 87(a), p. 531.

92. C.G. Cannon, Spectrochim.Acta, 1958, 10, 341.

93. S. Bratoz, *Adv.Quantum.Chemistry*, 1967, **3**, 209.

94. S.H. Lin, '*Physical Chemistry - An Advanced Treatise, Vol. V, Valency*', edited by H. Eyring (Academic Press, N.Y., 1970), p. 439.

95. P.A. Kollman and L.C. Allen, *Chem.Rev.*, 1972, **72**, 283.

96. C.A. Coulson, '*Hydrogen Bonding*', edited by D. Hadži and H.W. Thompson (Pergamon Press, 1959), p. 339.

97. E.R. Lippincott, J.N. Finch and R. Schroeder, '*Hydrogen Bonding*' ed. by D. Hadži and H.W. Thompson (Pergamon Press, 1959), p. 361.

98. M.D. Joesten and L.J. Schaad, '*Hydrogen Bonding*', (Marcel Dekker, New York, 1974), p. 195.

99. M.D. Joesten and R.S. Drago, *J.Amer.Chem.Soc.*, 1962, **84**, 3817;
K.F. Purcell and R.S. Drago, *J.Amer.Chem.Soc.*, 1967, **89**, 2874.

100. S. Singh, A.S.N. Murthy and C.N.R. Rao, *Trans.Faraday Soc.*, 1966, **62**, 1056;
A.S.N. Murthy and C.N.R. Rao, *Appl.Spectroscopy Rev.*, 1968, **2**, 69.

101. R. West, D.L. Powell, L.S. Whatley, M.K.T. Lee and P.v.R. Schleyer, *J.Amer.Chem.Soc.*, 1962, **84**, 3222.

102. T. Lin and E. Fishman, *Spectrochim.Acta.* 1967, **23A**, 491.

103. E.M. Arnett, L. Joris, E. Mitchell, T.S.S.R. Murty, T.M. Gorrie and P.v.R. Schleyer, *J.Amer.Chem.Soc.*, 1970, **92**, 2365.

104. W.A.P. Luck and W. Ditter, *J.Mol.Struct.*, 1968, **1**, 261.

105. R.A. Nyquist, *Spectrochim.Acta*, 1963, **19**, 1655;
P.V. Huong, M. Couzi and J. Lascombe, *J.Chim.Phys.*, 1967, **64**, 1056.

106. A.V. Iogansen, *Dokl.Akad.Nauk.SSSR*, 1965, **164**, 610;

107. L.I. Smith and J.A. Sprung, *J.Amer.Chem.Soc.*, 1943, **65**, 1278.

108. '*International Critical Tables*', 1928, **3**, 28.

109. I. Motoyama and C.H. Jarboe, *J.Phys.Chem.*, 1966, **70**, 3226.

110. A.W. Baker and M.D. Teaman, *Spectrochim.Acta*, 1966, **22**, 1773.

111. C.M. Huggins and G.C. Pimentel, *J.Phys.Chem.*, 1956, **60**, 1615.

112.(a) H. Tsubomura, *J.Chem.Phys.*, 1956, **24**, 927;
(b) E.D. Becker, *Spectrochim.Acta*, 1961, **17**, 436.

113. G.M. Barrow, *J.Phys.Chem.*, 1955, **59**, 1129.

114. E.J. Slowinski, Jr. and G.C. Claver, *J.Opt.Soc.Amer.*, 1955, **45**, 396;
R.H. Hughes, R.J. Martin and N.D. Coggeshall, *J.Chem.Phys.*, 1956, **24**, 489;
U. Liddle and E.D. Becker, *J.Chem.Phys.*, 1956, **25**, 173;
J.N. Finch and E.R. Lippincott, *J.Chem.Phys.*, 1956, **24**, 908; *J.Phys.Chem.*, 1957, **61**, 894.

APPENDIX 1

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Infra-red Studies and Thermodynamics of Hydrogen Bonding in Ethylene Glycol Monoalkyl Ethers. Evidence for a Ten Membered Ring Dimer

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An i.r. study in the hydroxyl stretching region of three monoalkyl (methyl, ethyl and butyl) ethers
ethylene glycol in CCl_4 solutions (concentrations up to 0.1 mol dm^{-3}) has been carried out over
: temperature range 298-338 K. Apparent integrated intensities of the bands at ~3635, ~3600
1 ~3475 cm^{-1} of the free, intramolecularly and intermolecularly bonded OH groups have been
asured and used to evaluate the equilibria between the monomeric and associated species. Various
ssible structures including open and cyclic dimers, trimers and tetramers for the associated species
sorbing at ~3475 cm^{-1} have been considered. A cyclic ten-membered ring dimer involving the
ıer oxygens in hydrogen bonding satisfactorily explains the observed results. Various thermo-
namic quantities such as K, ΔH°, ΔG° and ΔS° in the three way equilibrium involving free
nomer, intramolecularly bonded monomer and the cyclic ten membered ring dimer have been
ıluated. The values of intra- and inter-molecular hydrogen bond strengths as calculated from the
pective ΔH° values are ~14.1 kJ mol^{-1} and ~28.2 kJ mol^{-1} respectively.

Intramolecular hydrogen bonding in β-substituted ethanols XCH_2CH_2OH, where
is a proton accepting group such as Cl, NH_2, OCH_3 etc., is well known [1-17] and
very dilute solutions, such compounds [2, 9-12] exist as equilibrium mixtures of non-
'drogen bonded free forms and intramolecularly hydrogen bonded gauche con-
rmers. The intermolecular association of such compounds is particularly interest-
g in view of the presence of the additional proton acceptor X, which can lead to
fferent types of self-associated species not possible in simple alcohols. For simple
cohols, the first associated species absorbing at ~3500 cm^{-1} are usually considered
be linear and/or cyclic dimers.[18-26] While this assumption is supported by most
cent work,[27-36] there is some evidence that this band may be due to linear and/or
clic trimers [37-39] and/or tetramers.[37, 40, 41] The results of self-association studies
ı 2-cyanoethanol [11] and 2-methoxyethanol [12, 42] have been interpreted on the basis
cyclic and open dimers respectively. The possible participation of the additional
oton acceptor X in the β-position in self-association has generally been ignored
cept for 2-ethoxyethanol.[43, 44] However, our previous work [43] was of a prelimi-
ry nature and in that of Lodygina *et al.*,[44] the presence of the band at ~3635 cm^{-1}
ıe to the non-hydrogen bonded free monomer, and consequently its participation
the equilibrium, was not considered. We have therefore carried out a detailed
vestigation of methoxy-, ethoxy- and butoxy-ethanol in CCl_4 solutions using inte-
ated intensities in place of the usually employed absorbance maxima to determine
e concentrations of the absorbing species. The data have been examined to deter-
ine which species, open and cyclic dimers, trimers and tetramers, absorb at ~3475

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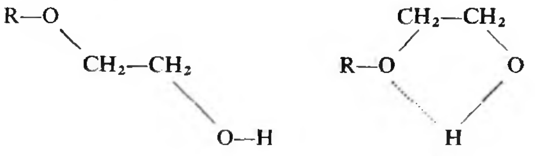
The alkoxyethanols in very dilute solutions ($C \leqslant 0.01$ mol dm^{-3}) in CCl_4 exhibit two bands at ~3635 cm^{-1} and ~3600 cm^{-1} which are attributed[5, 9, 12] to free and intra-molecularly hydrogen bonded OH groups respectively. In our preliminary work, the relative intensities of these bands are observed to be independent of concentration indicating the presence of an equilibrium between the non-hydrogen bonded free monomer (M_F) and the intramolecularly hydrogen bonded five membered ring monomer (M_I) (fig. 1). At concentrations above 0.01 mol dm^{-3}, an additional OH band appears at ~3475 cm^{-1}, the relative intensity of which increases with concentration indicating it to be due to intermolecular association. This band is symmetric in the concentration range 0.01-0.10 mol dm^{-3} and may therefore be attributed to a single associated species (n-mer). At higher concentrations no new OH bands are found as in the case of simple alcohols (at ~3300 cm^{-1})[2] but the band at ~3475 cm^{-1} becomes increasingly asymmetric on the lower frequency side due to more highly associated species.



I II

FIG. 1.—Free (I) and intramolecularly bonded (II) monomers.

The three species in solution (concentration up to 0.10 mol dm^{-3}), M_F, M_I and n, would be expected to be in equilibrium (fig. 2), with the equilibrium constants given by

$$K_{IF} = c_F/c_I, \; K_{nF} = c_F^n/c_n \quad \text{and} \quad K_{nI} = c_I^n/c_n \qquad (1)$$

where the subscripts F, I and n denote the free monomer, the intramolecularly bonded

TABLE 1.—SPECTROSCOPIC PROPERTIES OF THE VARIOUS OH GROUPS AT 298 K

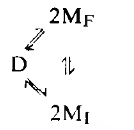
type of OH group	spectral property	ethanol	methoxy ethanol	ethoxy ethanol	butoxy ethanol
free	$\bar{\nu}$/cm^{-1} ± 2.5	3635	3635	3635	3635
	$\Delta\bar{\nu}_{\frac{1}{2}}$/cm^{-1} ± 2.5	27.5	—	—	—
	$B_F \times 10^{-3}$/dm^3 mol^{-1} cm^{-2}	4.70	—	—	—
	$(dB/dT)_F$/ dm^3 mol^{-1} cm^{-2} K^{-1}	−19	—	—	—
	$(\Delta B/B_{298})_F$*	−16.2%	—	—	—
intra-molecularly bonded	$\bar{\nu}$/cm^{-1} ± 2.5	—	3600	3600	3600
	$\Delta\bar{\nu}_{\frac{1}{2}}$/cm^{-1} ± 2.5	—	32.5	32.5	32.5
	$B_I \times 10^{-3}$/dm^3 mol^{-1} cm^{-2}	—	6.44	6.26	6.37
	$(dB/dT)_I$/ dm^3 mol^{-1} cm^{-2} K^{-1}	—	−12.4	−12.8	−13.5
	$(\Delta B/B_{298})_I$*	—	−7.7%	−8.2%	−8.4%
inter-molecularly bonded	$\bar{\nu}$/cm^{-1}	—	3475	3475	3475
	$\Delta\bar{\nu}_{\frac{1}{2}}$/cm^{-1} ± 5	—	150	150	145
	$B_D \times 10^{-4}$/dm^3 mol^{-1} cm^{-2}	—	5.9	6.1	5.7
	$(dB/dT)_D$/ dm^3 mol^{-1} cm^{-2} K^{-1}	—	−50	−80	−50
	$(\Delta B/B_{298})_D$*	—	−5.1%	−5.4%—	−3.5%

* $\Delta B = B_{338K} - B_{298K}$.

monomer and the intermolecularly bonded n-mer respectively. [For the dimer (fig. 2, eqn (6) and tables 1-4), the subscript $n = 2$ has been replaced by D for convenience.] The thermodynamic quantities, ΔH°, ΔG° and ΔS° involved in the respective equilibria were then calculated from the measured equilibrium constants (K) using the standard expressions

$$\Delta H^\circ = -R\left[\frac{\mathrm{d}\ln \bar{K}}{\mathrm{d}(1/T)}\right]; \qquad \Delta G^\circ = -RT\ln \bar{K} \quad \text{and} \quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad (2)$$

where $\bar{K}$ is the mean of the K values over the concentration range studied.



triangular equilibrium

FIG. 2.—The three way equilibrium considered.

TABLE 2.—CONCENTRATIONS ($\times 10^3$) OF VARIOUS SPECIES IN METHOXYETHANOL SOLUTIONS AT 298 K

OH species		solution concentration (10^3c_T/mol dm^{-3}) 40.0	60.0	80.0	1000.
free (OH)	$10^3c_{OH(F)}$/mol dm^{-3}	2.97	4.11	5.31	6.16
open dimer	10^3c_D/mol dm^{-3}	4.72	10.08	17.93	25.90
open trimer	10^3c_3/mol dm^{-3}	2.36	5.04	8.96	12.95
open tetramer	10^3c_4/mol dm^{-3}	1.57	3.36	5.98	8.63
	10^3c_F/mol dm^{-3}	2.97	4.11	5.31	6.16
cyclic dimer	10^3c_I/mol dm^{-3}	32.31	45.81	56.76	67.94
	10^3c_D/mol dm^{-3}	2.36	5.04	8.96	12.95

TABLE 3.—EQUILIBRIUM CONSTANTS IN THE THREE WAY EQUILIBRIA IN METHOXYETHANOL SOLUTIONS (AT 298 K)

associated species	equilibrium constant	solution concentration c_T/mol dm^{-3} 0.01	0.04	0.06	0.08	0.10	$\bar{K}$	maximum % deviation from $\bar{K}$
cyclic dimers	$K_{IF}\times 10^2$	9.49	9.18	8.95	9.35	9.07	9.21	3
	$K_{DF}\times 10^3$	—	3.67	3.31	3.14	2.93	3.26	12
	$K_{DI}\times 10$	—	4.35	4.12	3.60	3.56	3.91	10
cyclic trimers	$K_{IF}\times 10^2$	9.49	9.18	8.95	9.35	9.07	9.21	3
	$K_{3F}\times 10^5$	—	1.66	2.06	2.50	2.71	2.23	24
	$K_{3I}\times 10^2$	—	2.14	2.86	3.06	3.63	2.92	26
cyclic tetramers	$K_{IF}\times 10^2$	9.49	9.18	8.95	9.35	9.07	9.21	3
	$K_{4F}\times 10^7$	—	0.66	1.13	1.77	2.23	1.45	54
	$K_{4I}\times 10^3$	—	0.92	1.75	2.32	3.31	2.07	58
dimer type II	$K_{IF}\times 10^2$	9.49	10.38	11.49	13.68	14.66	11.94	22
	$K_{DF}\times 10^3$	—	1.87	1.67	1.57	1.47	1.65	12
	$K_{DI}\times 10$	—	1.73	1.27	0.84	0.68	1.13	47

K_{nF} and K_{nI} in (mol dm^{-3})$^{(n-1)}$.

TABLE 4.—THERMODYNAMIC QUANTITIES ASSOCIATED WITH THE THREE WAY EQUILIBRIUM I
ALKOXYETHANOLS

type of equilibrium	thermodynamic property	methoxyethanol	ethoxyethanol	butoxyethanol
$M_I \rightleftharpoons M_F$	$\bar{K}_{IF} \times 10^2/\text{mol dm}^{-3}$	9.21	9.72	9.45
	$\Delta H^\circ_{IF}/\text{kJ mol}^{-1}$	14.70±0.76	13.87±0.63	13.78±0.62
	$\Delta G^\circ_{IF}/\text{kJ mol}^{-1}$	5.91	5.78	5.85
	$\Delta S^\circ_{IF}/\text{J K}^{-1}\text{ mol}^{-1}$	29.22±2.38	26.95±1.98	26.40±1.94
$D \rightleftharpoons 2M_F$	$\bar{K}_{DF} \times 10^3/\text{mol dm}^{-3}$	3.26	3.13	2.95
	$\Delta H^\circ_{DF}/\text{kJ mol}^{-1}$	55.25±2.42	57.03±2.81	56.93±2.30
	$\Delta G^\circ_{DF}/\text{kJ mol}^{-1}$	14.20	14.30	14.45
	$\Delta S^\circ_{DF}/\text{J K}^{-1}\text{ mol}^{-1}$	136.44±7.64	142.10±8.80	141.65±7.25
$D \rightleftharpoons 2M_I$	$\bar{K}_{DI} \times 10/\text{mol dm}^{-3}$	3.91	3.12	3.34
	$\Delta H^\circ_{DI}/\text{kJ mol}^{-1}$	25.36±1.79	29.66±1.67	27.65±1.41
	$\Delta G^\circ_{DI}/\text{kJ mol}^{-1}$	2.33	2.89	2.72
	$\Delta S^\circ_{DI}/\text{J K}^{-1}\text{ mol}^{-1}$	76.41±5.65	89.22±5.22	83.34±4.45

$\bar{K}$ and ΔG° at 298 K. ΔH° and ΔS° are obtained from the method of least squares.

EXPERIMENTAL

AnalaR grade (Merck, purity >98%) alkoxyethanols $ROCH_2CH_2OH$ (R = CH C_2H_5 and C_4H_9) and ethanol were dried by treating them successively with anhydrou Na_2SO_4, sodium metal and $LiAlH_4$. The middle fractions of the final distillations wer collected over activated alumina and dried over P_2O_5. AnalaR grade CCl_4 (Merck, *Pr Analyst*) dried and distilled over P_2O_5 was used as the solvent. Operations including pre paration of solutions and filling the cells were performed in a dry box. Variable path lengt cells (l = 0.01-1.0 cm) with NaCl windows (calibrated by interference fringes) were use The spectral measurements were carried out on a Perkin-Elmer 221 spectrophotometer wit an abscissa expansion of 4×. The spectra were recorded over a temperature range 29 338 K at intervals of 5 K.

BAND RESOLUTION (FIG. 3)

Because of overlap between the three OH bands, the apparent integrated absorptio intensities (B) of the bands [instead of $\log(I_0/I)_{\max}$ values] were used to obtain the concentrations of the absorbing species. B is defined as

$$B = \frac{1}{cl}\int \ln(T_0/T)_\nu \, d\nu = A/Cl \qquad (3$$

where $A = \int \ln(T_0/T)_\nu \, d\nu$ and c are the band area and molar concentration of the grou concerned and l is the path length (in cm).

For determination of the band areas, the bands have first to be resolved. Reliabl resolution was possible in view of the following: (*a*) in solution, the absorption band of single absorbing species is symmetrical about its maximum; (*b*) the absorbances of two o more species at a common frequency are additive; and in the present case, (*c*) the lo frequency side of the band at ~3475 cm^{-1} was free from any overlap and the low frequenc side of the intramolecularly hydrogen bonded OH band was free from overlap with the fre OH band. The high frequency side of the 3475 cm^{-1} band therefore was first generated b reflection of the low frequency side across its maximum (~3475 cm^{-1}). The low frequenc side of the intramolecularly bonded OH band was then obtained by subtracting the reflecte side of the 3475 cm^{-1} band from the experimental spectrum in the region 3500-3600 cm^{-1} The same procedure was repeated to resolve the intramolecularly hydrogen bonded O band at ~3600 cm^{-1} and so also the free OH band at ~3635 cm^{-1}.[45]

The area of each band A was evaluated by graphical integration applying appropriat corrections for the area under the wings[46] and the change in the density of CCl_4 at highe ɜmperatures.[47] Because of various instrumental and experimental factors [48, 49] involved, ıe accuracy of the measured band areas and intensities is estimated to be ~5 %.

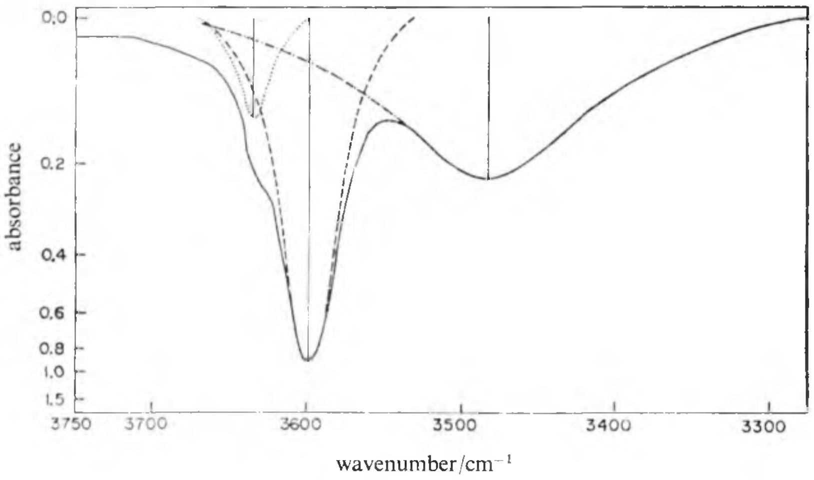


FIG. 3.—Resolution of spectral bands.

VALUATION OF CONCENTRATIONS OF FREE AND INTRAMOLECULARLY BONDED OH GROUPS: ($c_{\mathrm{OH(F)}}$ AND $c_{\mathrm{OH(I)}}$)

Because of the presence of both free and the intramolecularly bonded species even in the ıost dilute solutions of alkoxyethanols, it is not possible to evaluate the concentration of the ee OH group by any direct method. It is therefore necessary to assume that the intensity f the free OH group in alkoxyethanols is identical with that of a simple alcohol (e.g., ethanol). his assumption is reasonable in view of: (*a*) the positions and intensities of the free OH ·oups of various primary unbranched saturated alkanols are found to be almost the same $_{\mathrm{OH}} \approx 3630\text{-}3640\ \mathrm{cm}^{-1}$, $\varepsilon^{\mathrm{a}}_{\mathrm{OH}} \approx 60$ at 300 K) [3, 50]; (*b*) our observation, that the free OH equency in alkoxyethanols is the same as that of ethanol (~3635 cm⁻¹), is in good agreeıent with earlier work [3, 9]; and (*c*) the possible inductive effects of the alkoxy group in the ·position on the intensity of free OH group are negligible. The intensity of the free OH bsorption (B_{F}) of ethanol in CCl_4 solution ($c = 7.5 \times 10^{-3}$ mol dm^{-3}) was therefore meaıred at various temperatures and the plot of B_{F} against T was used as the calibration curve) estimate the concentration of the free OH group ($c_{\mathrm{OH(F)}}$) in alkoxyethanol solutions. A milar procedure was used by Buc and Neel [6] and also by Kuhn and Wires.[9] The concenation of the intramolecularly bonded OH group ($c_{\mathrm{OH(I)}}$) in solutions at concentrations ≨0.01 mol dm^{-3}, where the associated species are absent, was obtained by subtracting [9] $_{\mathrm{OH(F)}}$ from the solution concentration c_{T} ($\leqslant 0.01$ mol dm^{-3}). The band intensity of the ıtramolecularly bonded OH group (B_{I}) was then calculated at various temperatures and ıe corresponding plot of B_{I} against T was used as the second calibration curve to determine $_{\mathrm{OH(I)}}$ in solutions at concentrations $0.01 < c_{\mathrm{T}} \leqslant 0.1$ mol dm^{-3} where the associated species bsorbing at ~3475 cm⁻¹ are also present. The concentrations of the individual molecular ɔecies viz. c_{F}, c_{I} and c_n were then evaluated in terms of $c_{\mathrm{OH(F)}}$, $c_{\mathrm{OH(I)}}$ and c_{F}.

EVALUATION OF CONCENTRATIONS OF INDIVIDUAL MOLECULAR SPECIES: (c_{F}, c_{I} AND c_n)

As the OH groups of the associated species (n) will absorb in different regions depending n the nature of their association, the values of c_{F}, c_{I} and c_n will depend on the contributions f the OH groups of the associated species to $c_{\mathrm{OH(F)}}$ and/or $c_{\mathrm{OH(I)}}$ in addition to that of $_{\mathrm{OH}(n)}$. These possibilities were tested by considering various possible structures for dimer ; shown in fig. 4 as well as similar open and cyclic structures for trimers and tetramers.

In general, for an open n-mer of type I (a or b) (fig. 4), where the end OH group is free and will absorb in the same region as that of the free [2, 25, 40, 51, 52] monomeric OH (~3635 cm^{-1}), it can be shown that

$$c_n = \frac{1}{(n-1)}[c_T-(c_{OH(F)}+c_{OH(I)})], \qquad c_F = c_{OH(F)}-c_n \quad \text{and} \quad c_I = c_{OH(I)}. \tag{4}$$

For cyclic n-mers of type III or IV, the OH groups of the associated species would not contribute [52] to $c_{OH(F)}$ or $c_{OH(I)}$ and hence

$$c_n = \frac{1}{n}[c_T-(c_{OH(F)}+c_{OH(I)})] \quad \text{since} \quad c_F = c_{OH(F)} \quad \text{and} \quad c_I = c_{OH(I)}. \tag{5}$$

For the dimer, there are five possible structures including the two open and two cyclic species mentioned above. In the fifth type (structure II, fig. 4, suggested by Saito *et al.*[13]) the end OH of the open dimer is intramolecularly hydrogen bonded to the ether oxygen and therefore would absorb in the same position as the intramolecularly hydrogen bonded monomer (i.e., at ~3600 cm^{-1}). In this case it can be shown that

$$c_D = c_T-[c_{OH(F)}+c_{OH(I)}], \quad c_F = c_{OH(F)} \quad \text{and} \quad c_I = c_{OH(I)}-c_D. \tag{6}$$

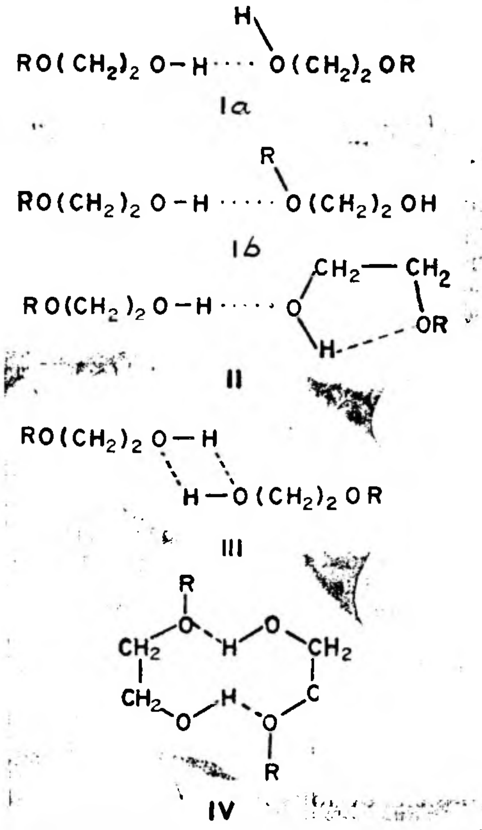


FIG. 4.—Possible structures for dimer in alkoxyethanols

RESULTS AND DISCUSSION

Since the spectroscopic and thermodynamic properties of the three alkoxyethanols were alike, the discussion will be confined to methoxyethanol.

SPECTROSCOPIC PROPERTIES

The band positions ($\bar{\nu}$), half band widths ($\Delta\bar{\nu}_{\frac{1}{2}}$), integrated intensities (B) and the fect of temperature on the intensities (dB/dT etc.) of the free OH absorptions of hanol and those of the intra- and inter-molecularly bonded OH absorptions of the ree alkoxyethanols are given in table 1. The various $\bar{\nu}$ and $\Delta\bar{\nu}_{\frac{1}{2}}$ values are in good reement with those reported in literature.[2, 3, 9] Our values of $B_F = 4.7\times10^3$ dm^3 ol^{-1} cm^{-2} at 298 K and $dB_F/dT = -19$ for the free OH group in ethanol, used to timate the concentration of the free OH group in alkoxyethanol solutions, are in od agreement with those of Liddel and Becker,[19] 4.6×10^3 dm^3 mol^{-1} cm^{-2} and 20 respectively. For the intramolecularly bonded OH group, our values of $B_I =$ 43×10^3 dm^3 mol^{-1} cm^{-2} at 298 K and $dB_I/dT = -12.4$ for methoxyethanol can ly be compared, in the absence of other data, with those of Kuhn and Wires.[9] heir values, $B_I = 7.25\times10^3$ dm^3 mol^{-1} cm^{-2} at 298 K (calculated from their value B_I at 293 K) and $dB_I/dT = -50$ are considerably higher than ours. Note hower that their value of the intensity of the free OH absorption of butanol $B_F =$ 4×10^3 dm^3 mol^{-1} cm^{-2} is also considerably higher than that reported for ethanol[19] d other aliphatic alcohols.[6] This might be due to the use of $\Delta\nu_{\frac{1}{2}}$ for the free OH butanol for calculating the intensity, which is however unsymmetrical[53, 54] due to erlapping of bands of two rotational isomers. The various OH band intensities und in the present work decrease with increasing temperature as reported in the erature.[9, 19-21, 50, 55] Note that the three band intensities vary in the order $> B_I > B_F$ while in the temperature range covered, the relative decrease of the values with respect to their values at 298 K, i.e., $\Delta B/B_{298}$ follows exactly the opposite der, $(\Delta B/B_{298})_D < (\Delta B/B_{298})_I < (\Delta B/B_{298})_F$. Becker[55] also found that the magtude of the temperature effect on the intensities decreases systematically with the crease in ΔH of hydrogen bond formation.

INTRAMOLECULAR HYDROGEN BONDING

The experimental values of the various thermodynamic quantities for the various uilibria in alkoxyethanol solutions are shown in table 4. Our values of 14.70 kJ ol^{-1} and 5.91 kJ mol^{-1} for ΔH_{IF} and ΔG°_{IF} at 298 K for intramolecular hydrogen nding in methoxyethanol are comparable with those of Kuhn and Wires,[9] 10 ± 2 mol^{-1} and 5.44 kJ mol^{-1} respectively. The differences between theirs and our lues might be due to their use of $\log(I_0/I)_{\max}$ values and ours of band resolving and values.

NATURE OF THE ASSOCIATED SPECIES

The possible structures for the associated species, open and cyclic dimers, trimers d tetramers, were considered separately to determine the most likely species absorbg at ~3475 cm^{-1}.

Feeney and Walker[42] suggested an open dimer (without specifying the type) for ethoxyethanol from their n.m.r. studies in the concentration range 0.1-1.3 mol dm^{-3}, t covered in the present studies. However, for any open n-mer (type Ia or Ib, fig. 4), obtain c_F, eqn (4) requires $c_{OH(F)}$ to be greater than c_n. In the majority of cases the present study this requirement is not fulfilled. As an illustration, the calculated lues of $c_{OH(F)}$ and those of c_n for various open n-mers in various solutions of methoxyhanol at 298 K are given in table 2(A). Equilibria involving open n-mers can there- re be ruled out. For cyclic trimers, cyclic tetramers and dimer type II (fig. 4), the lculated equilibrium constants show wide variations over the concentration range udied. Again, as a typical case the various K values in the three way equilibria together with the maximum variations from their respective mean values ($\bar{K}$) are shown in table 3. The log K against $1/T$ plots for these cases also showed large deviation from linearity thus eliminating these as possible predominant species. After ruling out the possibility of open n-mers, cyclic trimers, cyclic tetramers and dimer type II only cyclic dimers with structure III or IV (fig. 4) remain to be considered. Here, the better constancy of the respective K values in the equilibrium over the entire concentration range studied (e.g., table 3) together with excellent linearity of the log $\bar{K}$ agains $1/T$ plots (fig. 5) and that of ΔG° against T plots suggests these as the most probable species absorbing at ~ 3475 cm^{-1}.

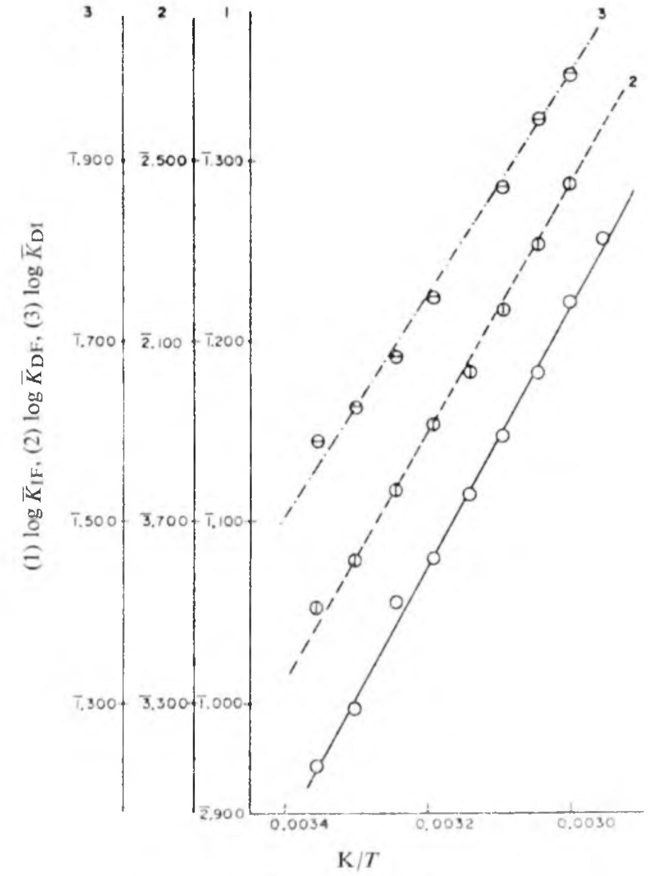


FIG. 5.—Plots of (1) log $\bar{K}_{\rm IF}$, (2) log $\bar{K}_{\rm DF}$ and (3) log $\bar{K}_{\rm DI}$ against $1/T$ for methoxyethanol [cf. dimer structures III and IV and eqn (5)].

The four membered ring structure III in which the hydroxyl oxygen atoms are involved in hydrogen bonding will be considerably strained because of the unfavourable O—H—O angles ($\sim\pi/2$ rad). The bent hydrogen bonds in such rings will be weak giving rise to small ΔH° values.[19] The ΔS° value will also be small due to the small ring size. Such dimers have been proposed for simple alcohols [19-21] and cyanoethanol [11] with ΔH° and ΔS° values ranging over 12-24 kJ mol^{-1} and 30-80 J K^{-1} mol^{-1} respectively. The present values of $\Delta H^\circ_{\rm DF} = 55.25$ kJ mol^{-1} and $\Delta S^\circ_{\rm DF} \sim$ 136.44 J K^{-1} mol^{-1} (table 4) are considerably higher suggesting the strain-free ten mem bered ring structure IV, with two hydrogen bonds involving the ether oxygens, as the most probable structure for the dimer. The larger ring restricting the rotation around various C—C bonds would explain the larger $\Delta S^{\circ}_{\mathrm{DF}}$ value compared to that in structure III. That the hydrogen bonding interaction with an ether oxygen will be larger than that with a hydroxylic oxygen is evident from the observed [1, 2, 5] larger frequency shifts ($\Delta\nu$) and smaller O—O distances in intramolecular hydrogen bonding in diol monomethyl ethers as compared to those in simple diols. Thus the absence of strain in the ring and the larger hydrogen-bonding interaction in structure IV explain the larger value of $\Delta H^{\circ}_{\mathrm{DF}}$ as compared to that in structure III. An ether oxygen atom is a better proton-acceptor than the hydroxylic oxygen so that, in a system containing both, hydrogen bonding will occur preferentially with the former. Structure IV naturally requires the O—CH_2—CH_2—O skeleton to be predominantly in the gauche conformation. Earlier studies [5, 6] on CH_2 rocking modes at ~800 cm^{-1} have shown that O—CH_2—CH_2—O in various ethylene glycol monoalkyl ethers in solution exist, almost exclusively, in the gauche conformation, in good agreement with the present structure IV for the dimer. The same ten-membered ring structure has been suggested for the ethoxyethanol dimer by Lodygina *et al.*[44] from an observation of the shift of the ether absorption from 1132 cm^{-1} in pure liquid to 1125 cm^{-1} in very dilute solutions. However, the values of various thermodynamic quantities as determined by them for an equilibrium between the 3610 cm^{-1} band (assumed due to free OH) and dimer are smaller than ours. This difference may occur since they ignore the 3635 cm^{-1} band (which is actually due to the free OH) and the three way equilibrium which exists. The present data for alkoxyethanols thus establish the ten membered ring dimer with the ether oxygen atoms participating in the intermolecular hydrogen bondng as the most likely associated species in solutions up to concentrations 0.1 mol dm^{-3}.

The close agreement among the various thermodynamic quantities (table 4) supports the postulated three way equilibrium. The approximate constancy of the espective spectroscopic properties (table 1) and that of the thermodynamic quantities table 4) for the three alkoxyethanols indicates that the size of the alkyl group does not affect their association behaviour. Note that the intramolecularly bonded monomer always predominates over the dimer, i.e., $c_{\mathrm{I}} > c_{\mathrm{D}}$ (table 2B), in spite of $\Delta H^{\circ}_{\mathrm{IF}}$ being much smaller than $\Delta H^{\circ}_{\mathrm{DF}}$. This is due to the fact that the formation of the dimer requires a greater number of bonds in a suitable conformation (larger decrease n entropy) than that for the intramolecularly bonded monomer consequently reducing he probability of its formation. Finally, ignoring factors such as conformational nteractions and solvent effects, the strengths of the intra- and inter-molecular hydrogen bonds in alkoxyethanols as calculated from the $\Delta H^{\circ}_{\mathrm{IF}}$ and ΔH_{DF} values, are ~14.1 kJ mol^{-1} and ~28.2 kJ mol^{-1} respectively.

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[1] F. T. Wall and W. F. Clausen, *J. Amer. Chem. Soc.*, 1939, **61**, 2679.

[2] L. P. Kuhn, *J. Amer. Chem. Soc.*, 1952, **74**, 2492; 1954, **76**, 4323.

[3] M. St. C. Flett, *Spectrochim. Acta*, 1957, **10**, 21.

[4] M. Kuhn, W. Lüttke and R. Mecke, *Z. Anal. Chem.*, 1959, **170**, 106.

[5] A. Foster, A. Hains and M. Stacey, *Tetrahedron*, 1961, **16**, 177.

[6] H. Buc and J. Neel, *Compt. rend.*, 1962, **255**, 2947.

[7] H. Buc, *Ann. Chim.*, 1963, **8**, 409.

[8] N. N. Shapetko, D. N. Shigorin, A. P. Skoblinov, T. S. Ryabchikova and L. N. Reshetova, *Optics and Spectr.*, 1964, **17**, 247.

[9] L. P. Kuhn and R. A. Wires, *J. Amer. Chem. Soc.*, 1964, **86**, 2161.

[10] P. J. Krueger and H. D. Mettee, *Canad. J. Chem.*, 1964, **42**, 326; 1965, **43**, 2970.

[11] P. J. Krueger and H. D. Mettee, *Canad. J. Chem.*, 1965, **43**, 2888.

[12] P. J. Krueger and H. D. Mettee, *J. Mol. Spectr.*, 1965, **18**, 131.

[13] H. Saito, T. Yonezawa, S. Matsuoka and K. Fukui, *Bull. Chem. Soc. Japan*, 1966, **39**, 989.

[14] P. Buckley and P. Giguere, *Canad. J. Chem.*, 1967, **45**, 397.

[15] H. Matsuura and T. Miyazawa, *Bull. Chem. Soc. Japan*, 1967, **40,** 85.
[16] P. A. Giguere, *Canad. J. Chem.*, 1972, **50,** 152.
[17] W. K. Busfield, M. P. Ennis and I. J. McEwen, *Spectrochim. Acta*, 1973, **29A**, 1259.
[18] F. A. Smith and E. C. Creitz, *J. Res. Nat. Bur. Stand.*, 1951, **46,** 145.
[19] U. Liddel and E. D. Becker, *Spectrochim. Acta*, 1957, **10,** 70.
[20] M. Van Thiel, E. D. Becker and G. C. Pimentel, *J. Chem. Phys.*, 1957, **27,** 95.
[21] E. D. Becker, U. Liddel and J. N. Shoolery, *J. Mol. Spectr.*, 1958, **2,** 1.
[22] W. C. Coburn, Jr. and E. Grunwald, *J. Amer. Chem. Soc.*, 1958, **80,** 1318.
[23] J. C. Davies, Jr., K. S. Pitzer and C. N. R. Rao, *J. Phys. Chem.*, 1960, **64,** 1744.
[24] L. P. Kuhn and R. E. Bowman, *Spectrochim. Acta*, 1961, **17,** 650.
[25] W. Masschelein, *Spectrochim. Acta*, 1962, **18,** 1557.
[26] H. Dunken and H. Fritzsche, *Spectrochim. Acta*, 1964, **20,** 785.
[27] H. C. Van Ness, J. Van Winkle, H. H. Richtol and H. B. Hollinger, *J. Phys. Chem.*, 19 **71,** 1483.
[28] P. I. Gold and R. L. Perrin, *J. Phys. Chem.*, 1967, **71,** 4218.
[29] D. A. Ibbitson and L. F. Moore, *J. Chem. Soc. B*, 1967, **76,** 80.
[30] A. N. Fletcher and C. A. Heller, *J. Phys. Chem.*, 1968, **72,** 1839.
[31] R. M. Hammeker, R. M. Clegg, L. K. Patterson, P. E. Rider and S. L. Rock, *J. Phys. Ch* 1968, **72,** 1837.
[32] W. L. Chandler and R. H. Dinius, *J. Phys. Chem.*, 1969, **73,** 1596.
[33] A. S. N. Murthy, R. E. Davies and C. N. R. Rao, *Theor. Chim. Acta*, 1969, **13,** 81.
[34] J. R. Hoyland and L. B. Kier, *Theor. Chim. Acta*, 1969, **15,** 1.
[35] T. S. S. R. Murthy, *Canad. J. Chem.*, 1970, **48,** 184.
[36] P. Bordewijk, M. Kunst and A. Rip, *J. Phys. Chem.*, 1973, **77,** 548.
[37] A. D. Cohen and C. Reid, *J. Chem. Phys.*, 1956, **25,** 790.
[38] E. E. Tucker, S. B. Farnham and S. D. Christian, *J. Phys. Chem.*, 1969, **73,** 3820.
[39] E. E. Tucker and E. D. Becker, *J. Phys. Chem.*, 1973, **77,** 1783.
[40] A. N. Fletcher and C. A. Heller, *J. Phys. Chem.*, 1967, **71,** 3742.
[41] A. N. Fletcher, *J. Phys. Chem.*, 1972, **76,** 2562.
[42] J. Feeney and S. M. Walker, *J. Chem. Soc. A*, 1966, 1148.
[43] T. K. K. Srinivasan, C. I. Jose and A. B. Biswas, *Proc. Int. Conf. Spectroscopy*, 1967, 293
[44] V. P. Lodygina, A. I. Ivanov, S. M. Baturin and S. G. Entelis, *Russ. J. Phys. Chem.*, 1 **44,** 1068.
[45] J. J. Fox and A. E. Martin, *Proc. Roy. Soc. A*, 1937, **162,** 419.
[46] D. A. Ramsay, *J. Amer. Chem. Soc.*, 1952, **74,** 72.
[47] *International Critical Tables*, 1928, **3,** 28.
[48] R. N. Jones, D. A. Ramsay, D. S. Keir and K. Dobriner, *J. Amer. Chem. Soc.*, 1952, **74**
[49] K. S. Sheshadri and R. N. Jones, *Spectrochim. Acta*, 1963, **19,** 1013.
[50] I. Motoyama and C. H. Jarboe, *J. Phys. Chem.*, 1966, **70,** 3226.
[51] L. J. Bellamy and R. J. Pace, *Spectrochim. Acta*, 1966, **22,** 525.
[52] L. J. Bellamy, *Advances in I.R. Group Frequencies* (Methuen, London, 1968), p. 256.
[53] M. Oki and H. Iwamura, *Bull. Chem. Soc. Japan*, 1959, **32,** 567.
[54] F. Dalton, G. Meakins, J. Robinson and W. Zaharia, *J. Chem. Soc.*, 1962, 1566.
[55] E. D. Becker, *Spectrochim. Acta*, 1961, **17,** ~~1013~~. 436.
[56] A. Miyake, *J. Amer. Chem. Soc.*, 1960, **82,** 3040; T. K. K. Srinivasan, C. I. Jose and A Biswas, *Bull. Chem. Soc. Japan*, 1964, **37,** 1770; *Canad. J. Chem.*, 1969, **47,** 3877.

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APPENDIX 2

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Infrared Study and Thermodynamics of Hydrogen Bonding in Diethylene Glycol Monoalkyl Ethers

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Diethylene glycol monoalkyl ethers in dilute CCl_4 solutions exhibit three OH bands, *viz.* at ~ 3635, 600 and ~ 3475 cm^{-1} attributable to a free monomer (M_F), an intramolecularly hydrogen bonded -membered ring monomer (M_5) and an intramolecularly hydrogen bonded eight-membered ring nomer (M_8) respectively. In concentrated solutions, the dimer (D) band appears at ~ 3440 $^{-1}$. The relative concentrations of these species involved in the multiple equilibria are observed e in the order $C_D \approx C_F \ll C_8 \approx \frac{1}{2}C_5$ at 298 K. The thermodynamic quantities for the equilibria $\rightleftharpoons M_F$, $M_8 \rightleftharpoons M_F$ and $D \rightleftharpoons 2M_F$ are $\Delta H^\circ_{5F} \sim 12$ kJ mol^{-1}, $\Delta S^\circ_{5F} \sim 22$ J K^{-1} mol^{-1}; $\Delta H^\circ_{8F} \sim$ kJ mol^{-1}, $\Delta S^\circ_{8F} \sim 56$ J K^{-1} mol^{-1} and $\Delta H^\circ_{DF} \sim 58$ kJ mol^{-1}, $\Delta S^\circ_{DF} \sim 153$ J K^{-1} mol^{-1} respec- ly. Finally a ten membered ring, involving the OH group of one molecule bonded to the β- gen of the other molecule, similar to that in alkoxy ethanols is found to be the most likely structure the dimer.

Studies on the self-association of alkoxy ethanols [1] in carbon tetrachloride (~ 0.1 l dm^{-3}) showed the associated species to be dimers, unlike simple alcohols which st as a mixture of polymeric species. The formation of the ten membered ring ner proved the participation of the ether oxygen as the proton acceptor. With a w to studying the role of an additional ether oxygen, intra- and intermolecular drogen bonding in diethylene glycol monomethyl and ethyl ethers (DEGM and EGE respectively) have been investigated in the present work. Earlier studies [2] on rotational isomerism of this type of compound had shown that the two OCH_2CH_2O ups preferentially adopt *gauche* conformations in solution.

Diethylene glycol monoalkyl ethers $R(OCH_2CH_2)_2OH$ in carbon tetrachloride ution exhibit three bands in the hydroxyl stretching region at ~ 3635, ~ 3600 and 3475 cm^{-1}. In concentrated solutions, the 3475 cm^{-1} band is very strong and mmetric but, on dilution, the intensity and asymmetry decrease very rapidly until 3 mol dm^{-3} [*cf.* fig. 1(*a*)]. Below this concentration, the relative intensities of all three bands remain constant and are independent of concentration, indicating them be due to three types of monomeric species in equilibrium [fig. 2 and 3(*a*)]. As orted earlier,[2] the three bands at ~ 3635, ~ 3600 and ~ 3475 cm^{-1} in dilute solu- ns can be ascribed to a free monomer (M_F), an intramolecularly hydrogen bonded -membered ring monomer (M_5) and an intramolecularly hydrogen bonded eight- mbered ring monomer (M_8) respectively (*cf.* fig. 2). The assignment of the 3635 d 3600 cm^{-1} bands to M_F and M_5 follows from their similarity to the corresponding ds in alkoxy ethanols (*cf.* table 1). The assignment of the 3475 cm^{-1} band to M_8 is tified in view of the stronger hydrogen bond possible in the eight-membered ring

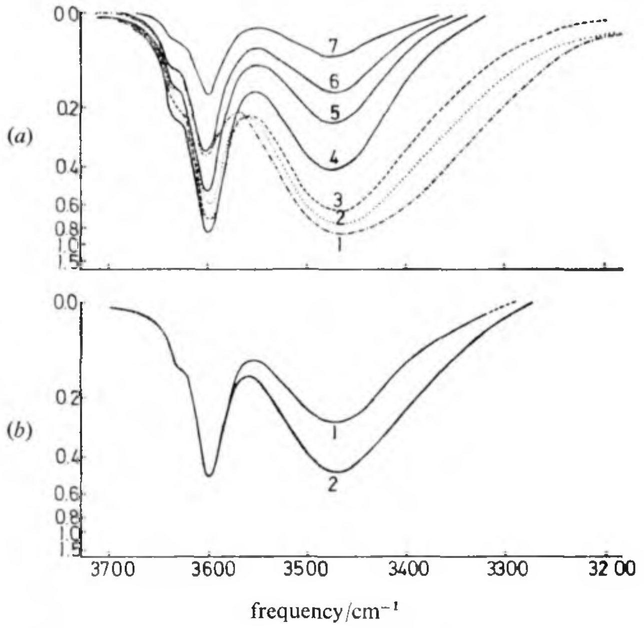

FIG. 1.—(*a*) Spectra 1-7: $c = 0.5, 0.2, 0.08, 0.02, 0.012, 0.008$ and 0.004 mol dm^{-3}; $l = 0.03$, and 0.26 cm for spectra 1 to 3 respectively and 1.0 cm for spectra 4 to 7; (*b*) (1) $c = 0.02$ mol dm $l = 0.6$ cm and (2) $c = 0.1$ mol dm^{-3}, $l = 0.14$ cm.

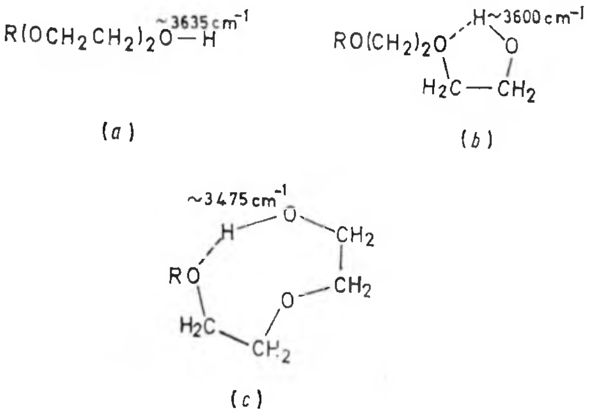

FIG. 2.—Typical structures for monomers.

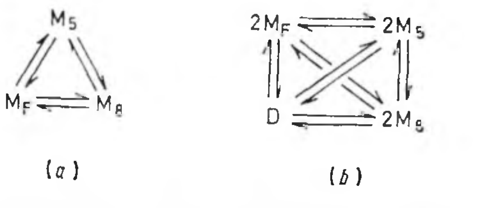

FIG. 3.—Equilibria in (*a*) dilute and (*b*) concentrated solutions.

here the OH can get closer to the second ether oxygen, thus giving rise to larger /drogen bonding interaction. Markevich *et al.*[3] and Lodygina *et al.*[4] also have cribed the bands at ~3486 and ~3450 cm^{-1} respectively to the M_8 species in DEGE. he asymmetry and increase in relative intensity of the 3475 cm^{-1} band at higher conntrations then must be due to the presence of intermolecularly hydrogen bonded

TABLE 1.—SPECTROSCOPIC PROPERTIES OF THE OH GROUPS AT 298 K

type of the OH group	spectral property	ethanol[1]	EGM[1]	DEGM	DEGE
ree	$\bar{\nu}$/cm^{-1}($\pm$2.5)	3635	3635	3635	3635
	$\Delta\bar{\nu}_{1/2}$/cm^{-1}($\pm$2.5)	27.5	25	25	25
	$B_F \times 10^{-3}$/dm^3 mol^{-1} cm^{-2}($\pm$0.5)	4.7	—	—	—
tramolecularly onded five-embered ring	$\bar{\nu}$/cm^{-1}($\pm$2.5)	—	3600	3600	3600
	$\Delta\bar{\nu}$/cm^{-1}($\pm$2.5)	—	35	35	35
	$\Delta\bar{\nu}_{1/2}$/cm^{-1}($\pm$2.5)	—	32.5	32.5	32.5
	$B_5 \times 10^{-3}$/dm^3 mol^{-1} cm^{-2}($\pm$0.4)	—	6.4	—	—
tramolecularly onded eight-embered ring	$\bar{\nu}$/cm^{-1}($\pm$5)	—	—	3475	3470
	$\Delta\bar{\nu}$/cm^{-1}($\pm$5)	—	—	160	165
	$\Delta\bar{\nu}_{1/2}$/cm^{-1}($\pm$5)	—	—	100	105
	$B_8 \times 10^{-3}$/dm^3 mol^{-1} $\bar{\nu}$ cm^{-2}	—	—	23$\pm$1.2	29$\pm$1.5
meric	$\bar{\nu}$/cm^{-1}($\pm$5)	—	3475	3440	3440
	$\Delta\bar{\nu}$/cm^{-1}($\pm$5)	—	160	195	195
	$\Delta\bar{\nu}_{1/2}$/cm^{-1}($\pm$5)	—	150	160	160
	$B_D \times 10^{-3}$/dm^3 mol^{-1} cm^{-2}	—	59$\pm$5	126$\pm$13	113$\pm$11

ABLE 2.—CONCENTRATIONS OF DIFFERENT SPECIES AND EQUILIBRIUM CONSTANTS IN SOLUTIONS OF DEGM AND DEGE AT 298 K

ompound	solution concentration $\times 10^3$/mol dm^{-3}	concentrations of various species $\times 10^3$/mol dm^{-3}				equilibrium constants			
	C_S	C_F	C_5	C_8	C_D	$K_{F5} \times 10^2$	$K_{8F} \times 10^2$	K_{85}	$K_{DF} \times 10^3$/ mol dm^{-3}
DEGM	10	0.64	6.33	3.03	—	10.1	21.1	2.09	—
	20	1.26	12.6	6.19	—	10.0	24.1	2.03	—
	80	4.63	46.0	22.3	3.51	—	—	—	6.10
	100	5.63	56.0	27.2	5.56	—	—	—	5.70
	125	7.01	69.7	33.9	7.21	—	—	—	6.81
DEGE	12.5	0.78	7.96	3.76	—	9.81	20.8	2.12	—
	75	4.25	43.3	20.4	3.48	—	—	—	5.19
	95	5.36	54.7	25.8	4.59	—	—	—	6.27
	120	6.58	67.1	31.6	7.36	—	—	—	5.88

ecies which absorb in the same spectral region. The similarity of the association and with that of alkoxy ethanols and the absence of any additional OH bands until concentration of ~0.5 mol dm^{-3} is reached suggest the associated species to be imers. The constancy of the equilibrium constants calculated on this basis (table 2) istifies this assumption.

EXPERIMENTAL AND CALCULATIONS

The experimental procedure is the same as described earlier.[1] Spectra in the 3700-3200 n^{-1} region were recorded over the temperature range 298-333 K at intervals of 5 K. The accuracies of computed areas and the intensities of the 3600 and 3475 cm^{-1} bands are est mated to be ~ 5-6 % while area under the 3635 cm^{-1} band is subject to an error of ~ 10-12 as the latter is very weak and appears only as a shoulder. At each temperature, the conce tration of the free monomer (C_F) was evaluated using the computed area of the 3635 cm band and the apparent integrated absorption intensity (B) of the free OH of ethanol. T concentration of the intramolecularly hydrogen bonded five-membered ring monomer (C was likewise evaluated using its computed band area and the intensity of the correspondi band in alkoxy ethanols. This is justified because the spectral characteristics of these ban are identical with those in alkoxy ethanols. In solutions below concentration 0. mol dm^{-3} containing the three monomers only; the concentration of the intramolecular hydrogen bonded eight-membered ring monomer (C_8) was obtained by subtracting C_F+ from the solution concentration C_s. Thus

$$C_F = A_F/B_F l,\ C_5 = A_5/B_5 l \text{ and } C_8 = C_s-(C_F+C_5) \qquad ($$

where A, B and l denote the band area, integrated absorption intensity and path leng respectively. The equilibrium constants in the triangular equilibrium [fig. 3(a)] were calc lated as

$$K_{5F} = C_F/C_5,\ K_{8F} = C_F/C_8 \text{ and } K_{85} = C_5/C_8. \qquad ($$

At higher concentrations, the dimer (D) absorbing nearly in the same region as that of produced an asymmetry in the 3475 cm^{-1} band. But since the profiles and characterist of the 3475 and 3600 cm^{-1} bands were already available from the dilute solution spectra, th could be resolved satisfactorily. The concentration of the five-membered ring monom (C_5) was first obtained from the 3600 cm^{-1} band as before. The concentrations of the oth two monomers (C_F and C_8) were then calculated from C_5 using the equilibrium constan K_{5F} and K_{85} obtained from dilute solutions. The dimer concentration (C_D) was th evaluated as

$$C_D = \tfrac{1}{2}[C_s-(C_F+C_5+C_8)]. \qquad ($$

The equilibrium constants for the system $D \rightleftharpoons 2M_F$ [fig. 3(b)] were calculated as

$$K_{DF} = C_F^2/C_D. \qquad ($$

Finally the thermodynamic quantities for the various equilibria as defined by eqn (2) and (were determined using the standard expressions

$$\Delta G^\circ = -RT \ln K = \Delta H^\circ - T\Delta S^\circ \qquad ($$

and the method of least squares.

RESULTS AND DISCUSSION

SPECTROSCOPIC PROPERTIES

The spectral characteristics ($\bar{\nu}$, $\Delta\bar{\nu}$, $\Delta\bar{\nu}_{\frac{1}{2}}$ and B) of the various OH bands of DEG and DEGE observed in the present work, together with those of ethanol and ethyle glycol monomethyl ether (EGM) from the previous work,[1] are given in table 1. T relative intensities of the 3635 and 3600 cm^{-1} bands in DEGM, DEGE and EGM a found to be the same [*cf.* fig. 1 and fig. 3, ref. (1)], showing little effect of the length the alkoxy group on the hydrogen bonding between the OH group and the β-oxyge Our values of $\bar{\nu}$ and $\Delta\bar{\nu}_{\frac{1}{2}}$ for the OH bands are in good agreement with those report in the literature [2, 5] for similar compounds. The positions and relative intensities the three OH bands of DEGE as reported by Markevich *et al.*[3] are, however, differe from ours; for example, their spectrum shows a broad and strong 3617 cm^{-1} ba well separated from the 3586 cm^{-1} band with relative intensity of the latter mu smaller than the former. We, on the other hand, find the 3635 cm^{-1} band to be mu weaker, appearing only as a shoulder to the 3600 cm^{-1} band. Since these two ban in the present compounds arise from groups similar to those in alkoxy ethanols, th relative intensities should also be similar. All other reported [1, 2, 5-8] data show a strong 3600 cm^{-1} band with 3635 cm^{-1} band as a shoulder in alkoxy ethanols and similar compounds.

A comparison of the $\Delta\bar{\nu}$, $\Delta\bar{\nu}_{\frac{1}{2}}$ and B values for the intramolecularly hydrogen bonded hydroxyls in the eight and five-membered ring monomers reveals that they are 3-4 times larger in the former. This is clearly due to the shorter hydrogen bond and the larger hydrogen bonding interaction possible in the eight membered ring monomer as compared with that in the five membered ring monomer (see later).

INTRAMOLECULAR HYDROGEN BONDING

The concentrations of the different molecular species and the equilibrium constants for the postulated equilibria [*cf.* fig. 3, eqn (1)-(4)] in some typical solutions of DEGM and DEGE at 298 K are represented in table 2. The observed constancy of the equilibrium constants and the linearity of the (log K, $1/T$) plots (fig. 4) support the postulated equilibria. The values of various thermodynamic quantities derived are given in table 3. Lodygina *et al.*[4], assuming the 3610 cm^{-1} band in DEGE to be due to free OH, have reported the thermodynamic quantities for the equilibrium between this species and M_8 absorbing at $\sim$3450 cm^{-1}. Since these authors have not reported the 3635 cm^{-1} band in DEGE (as well as in ethoxy ethanol) and not considered its participation in the equilibria, our values of the thermodynamic quantities cannot be compared with theirs.

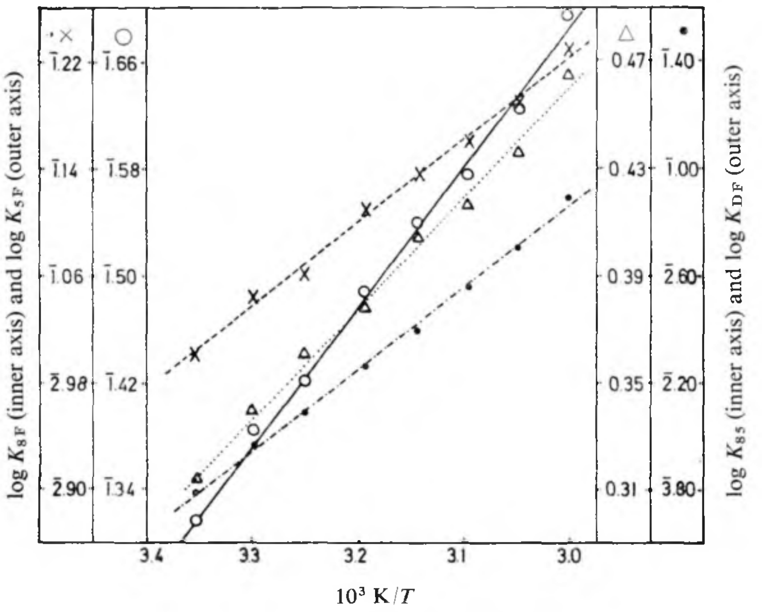

FIG. 4.—Plots of log K against $1/T$ for DEGM.

For the equilibrium $M_5 \rightleftharpoons M_F$, the values of K_{5F} and ΔG°_{5F} at 298 K for the present compounds are in close agreement with those for EGM.[1] The values of ΔH°_{5F} and ΔS°_{5F} are, however, somewhat smaller than those for EGM. The reason for this discrepancy might be the small relative intensity of the 3635 cm^{-1} band (<10 % of the 3600 cm^{-1} band), which causes some uncertainty in the estimation of the free monomer at various temperatures. The larger value of ΔH°_{8F} over ΔH°_{5F} can be understood since, in the eight-membered ring structure, the OH group can get closer to the et oxygen (larger hydrogen bonding interaction) than that in the five-membered r structure. Similarly, the increased restriction for rotation about various bonds in eight-membered ring structure explains the greater magnitude of ΔS°_{8F} as compa with ΔS°_{5F}. The dominance of the five-membered ring monomer over the eig membered ring monomer (*cf.* table 2) is explicable by the fact that, though the lat is favoured energetically, the probability of its formation (the number of favoura conformations) is small. The relatively small population of the free monomer, compared with that of the other two intramolecularly hydrogen bonded monom can be understood in view of the favourable positions of the ether oxygens leading the intramolecularly hydrogen bonded species.

TABLE 3.—THERMODYNAMIC QUANTITIES ASSOCIATED WITH THE MULTIPLE EQUILIBRIA DIETHYLENE GLYCOL MONOALKYL ETHERS

type of equilibrium	thermodynamic property*	EGM[1]	DEGM	DEGE
$M_5 \rightleftharpoons M_F$	$K_{5F} \times 10^2$	9.21	10.1	9.8
	ΔG°_{5F}/kJ mol^{-1}	5.9	5.7	5.8
	ΔH°_{5F}/kJ mol^{-1}	14.7±0.8	11.9±0.4	12.6±0.
	ΔS°_{5F}/J K^{-1} mol^{-1}	29±2.4	21±1.3	23±0.
$M_8 \rightleftharpoons M_F$	$K_{8F} \times 10^2$	—	20.3	20.8
	ΔG°_{8F}/kJ mol^{-1}	—	3.9	3.9
	ΔH°_{8F}/kJ mol^{-1}	—	19.7±0.6	21.2±0.
	ΔS°_{8F}/J K^{-1} mol^{-1}	—	53±1.8	58±1.
$M_8 \rightleftharpoons M_5$	K_{85}	—	2.03	2.12
	ΔG°_{85}/kJ mol^{-1}	—	−1.8	−1.9
	ΔH°_{85}/kJ mol^{-1}	—	7.8±0.3	8.6±0.
	ΔS°_{85}/J K^{-1} mol^{-1}	—	32±0.8	35±1.
$D \rightleftharpoons 2M_F$	K_{DF}/mol dm^{-3} $\times 10^3$	3.26	6.21	5.78
	ΔG°_{DF}/kJ mol^{-1}	14.2	12.6	12.8
	ΔH°_{DF}/kJ mol^{-1}	55±2.4	58±1.4	58±1.
	ΔS°_{DF}/J K^{-1} mol^{-1}	136±8	153±4	152±5

* K values and ΔG° values at 298 K

As mentioned earlier, the values of $\Delta\bar{\nu}$, $\Delta\bar{\nu}_{\frac{1}{2}}$ and B for the intramolecularly hydro bonded hydroxyl in the eight-membered ring monomer are 3-4 times larger than th in the five-membered ring monomer. The corresponding ΔH° values, however, only about 1.6 times larger. These results demonstrate the clear difference betw the spectroscopic properties ($\Delta\bar{\nu}$, $\Delta\bar{\nu}_{\frac{1}{2}}$ and B) which measure the hydrogen bond interaction of the hydroxyl group with the specific proton acceptor, and the entha change which is the result of all the attractive and repulsive interactions associa with the hydrogen bond formation. The lack of ($\Delta\bar{\nu}$, ΔH°) correlation (Badger–Ba rule) is attributable to the conformational interactions in intramolecular hydro bonding. Kuhn and Wires [6] also find that the $\Delta\bar{\nu}$ of the intramolecularly hydro bonded hydroxyls vary from 30 cm^{-1} in 2-methoxyethanol to 180 cm^{-1} in 4-metho butanol, while the ΔH° values change hardly at all (9.2±2.1 to 11.3±2.1 kJ mol^{-} The Badger–Bauer rule is obeyed if the interaction between the donor and accepto very large as compared with all other interactions, which is usually the case in int molecular association involving very little change in configuration.

NATURE OF THE DIMER

From an analysis of the spectra at various concentrations, the dimer band appears to have its maximum at ~3440 cm^{-1} ($\Delta\bar{\nu}$ ~ 195 cm^{-1}) with half band width $\Delta\bar{\nu}_{\frac{1}{2}}$ ~ 160 cm^{-1} and B ~ 120×10^3 dm^3 mol^{-1} cm^{-2}, indicating a large hydrogen bonding interaction. Of the three equilibria between the dimer and the three monomers [fig. 3(*b*)], only the equilibrium between the dimer and the free monomer is important because of its direct implications for the structure of the dimer. The large values of ΔH°_{DF} and ΔS°_{DF} (table 3) suggest that there are two hydrogen bonds, with considerable restriction to rotation of the constituent monomers as compared to the free monomers. The larger value of K_{DF} ($=C_F^2/C_D$) in the present compounds as compared with that in EGM indicates a smaller extent of dimerization in the former. This must be clearly due to the formation of the eight-membered ring monomer with hydrogen bond strength comparable with that of the dimer (*cf.* $\Delta\bar{\nu}$, $\Delta\bar{\nu}_{\frac{1}{2}}$ and ΔH° values) but relatively very small entropy decrease which favours the formation of M_8 over D.

Because of the presence of three oxygen atoms (*i.e.*, proton acceptors) in these molecules, there are several ways in which dimerization can occur. Some of the typical dimer structures are represented in fig. 5. Though it is difficult to decide on a unique structure for the dimer from the thermodynamic quantities alone; a consideration of various factors enables one to arrive at the most probable structure.

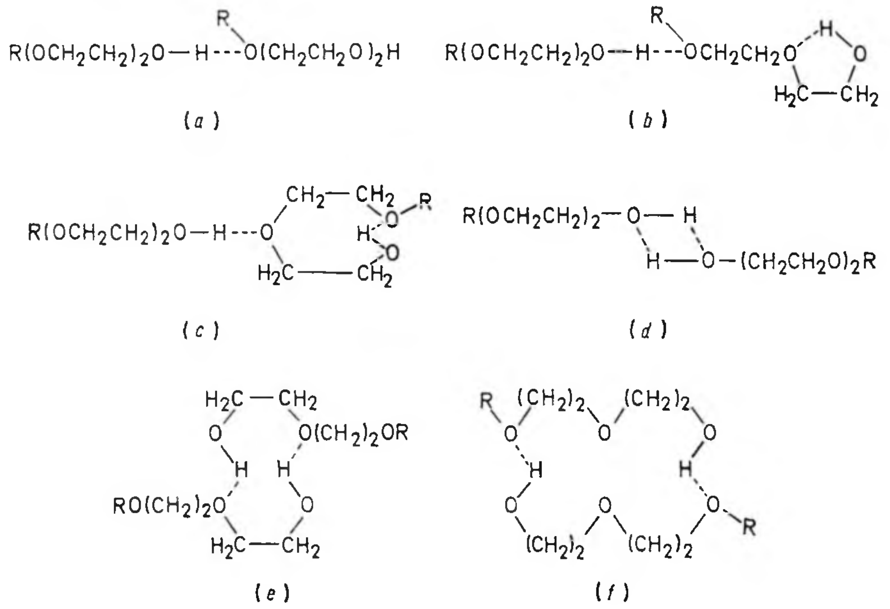

FIG. 5.—Typical structures for dimer.

The open dimer structure [fig. 5(*a*)] with a single hydrogen bond and having the constituent monomer conformations not much different from the free monomer species is very unlikely in view of the high values of ΔH°_{DF} ~ 58 kJ mol^{-1} and ΔS°_{DF} ~ 153 J K^{-1} mol^{-1}. The dimer involving an intermolecular association of a free monomer with a five-membered ring monomer [fig. 5(*b*)] also seems to be unlikely for the same reason. Further if such dimers were present, the relative intensities of the 3635 and 3600 cm^{-1} bands in the spectra of concentrated solutions (containing dimers) would be different from those in dilute solutions (with no dimers). Fig. 1*b* represents t spectra of solutions of two different concentrations with the path lengths adjusted such a way that the 3600 cm^{-1} band intensities are same in both. It is then observ that the 3635 cm^{-1} band intensities are also the same, showing the absence of su dimers. For the dimer resulting from hydrogen bonding of a free monomer with intramolecularly bonded eight-membered ring monomer [fig. 5(*c*)], though the Δ might be comparable with the observed $\Delta H^{\circ}_{\mathrm{DF}}$ value, the ΔS° would not be much high than that for M_8. Actually $\Delta S^{\circ}_{\mathrm{DF}} \gg \Delta S^{\circ}_{\mathrm{8F}}$, which makes such a structure improbab The four-membered ring structure [fig. 5(*d*)] would be considerably strained due unfavourable O—H---O angles. Dimers of this type have been suggested [9] for sim alcohols with ΔH° and ΔS° values ranging over 12-24 kJ mol^{-1} and 30-80 J K^{-1} mol respectively, which are considerably lower than the present values. Further, in system containing ether and hydroxylic oxygens, hydrogen bonding would occur p ferentially with the more basic ether oxygen. This structure, fig. 5(*d*), therefore, not acceptable for the dimer. The present values of $\Delta H^{\circ}_{\mathrm{DF}}$ and $\Delta S^{\circ}_{\mathrm{DF}}$ are in close agre ment with those of alkoxy ethanols [1] in which a ten-membered ring dimer involvi intermolecular hydrogen bonding of the hydroxyl with the oxygen in the β-positi of the other molecule was found to be present. Such dimers [fig. 5(*e*)] would thus the most probable species in DEGM and DEGE. However, in view of the somewh larger magnitude of the present values of $\Delta H^{\circ}_{\mathrm{DF}}$ and $\Delta S^{\circ}_{\mathrm{DF}}$ as compared with those alkoxy ethanols, it is possible that some small amount of dimers having the structu of fig. 5(*f*) (sixteen membered ring) may also be present. The population of t structure will of course be very small as compared with that of 5(*e*) because of t larger ring size, which leads to a larger decrease of entropy. These last two structu are in agreement with the results on CH_2 rocking modes which show [2, 8, 10] t OCH_2CH_2O groups to be present in predominantly *gauche* conformations in ethyle and diethylene glycol monoalkyl ethers.

CONCLUSIONS

The present work confirms the presence of three types of monomeric species : the free monomer ($\bar{\nu} \sim 3635$ cm^{-1}) and the intramolecularly hydrogen bonded fi and eight-membered ring monomers ($\bar{\nu} \sim 3600$ and 3475 cm^{-1} respectively) in dil carbon tetrachloride solutions ($c < 0.03$ mol dm^{-3}) of diethylene glycol monoal ethers. The predominance of the five-membered ring monomer over the eig membered ring monomer in spite of the stronger hydrogen bonding in the lat demonstrates how the entropy factor can influence the equilibrium. The associati power of these compounds in concentrated solutions ($c > 0.03$ mol dm^{-3}) is sm and they form mainly ten-membered ring dimers in such a way that the OCH_2CH groups maintain a *gauche* configuration. The identity of dimers in ethylene- a diethylene glycol monoalkyl ethers shows that the second ether oxygen in the latte too far removed for participation in association.

[1] L. S. Prabhumirashi and C. I. Jose, *J.C.S. Faraday II*, 1975, **71**, 1545.
[2] T. K. K. Srinivasan, C. I. Jose and A. B. Biswas, *Int. Conf. Spectroscopy*, 1967, **2**, 293 ; *Can J. Chem.*, 1969, **47**, 3877.
[3] V. S. Markevich, V. A. Terent'ev and N. E. Shtivel', *Russ. J. Phys. Chem.*, 1969, **43**, 7.
[4] V. P. Lodygina, A. I. Ivanov, S. M. Baturin and S. G. Entelis, *Russ. J. Phys. Chem.*, 1970, 1068.
[5] M. St. C. Flett, *Spectrochim. Acta*, 1957, **10**, 21.
[6] L. P. Kuhn and R. A. Wires, *J. Amer. Chem. Soc.*, 1964, **86**, 2161.
[7] A. B. Foster, A. H. Haines and M. Stacey, *Tetrahedron*, 1961, **16**, 177 ; P. J. Krueger and H. Mettee, *J. Mol. Spectr.*, 1965, **18**, 131 ; H. Saito, *Bull. Chem. Soc. Japan*, 1966, **39**, 989.

[8] T. K. K. Srinivasan, C. I. Jose and A. B. Biswas, *Bull. Chem. Soc. Japan*, 1964, **37**, 1770.

[9] U. Liddel and E. D. Becker, *Spectrochim. Acta*, 1957, **10**, 70; M. Van Thiel, E. D. Becker and G. C. Pimentel, *J. Chem. Phys.*, 1957, **27**, 95; E. D. Becker, U. Liddel and J. M. Shoolery, *J. Mol. Spectr.*, 1958, **2**, 1; P. J. Krueger and H. D. Mettee, *Canad. J. Chem.*, 1965, **43**, 2888.

[10] A. Miyake, *J. Amer. Chem. Soc.*, 1960, **82**, 3040.

(PAPER 5/2297)

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