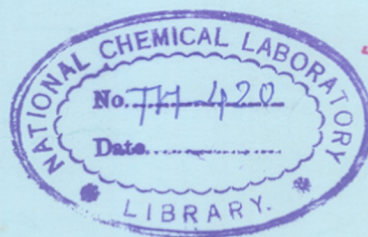


EXCESS THERMODYNAMIC PROPERTIES OF
NON-ELECTROLYTE BINARY LIQUID MIXTURES

COMPUTERISED

A THESIS
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To my mother

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NOTATIONS AND ABBREVIATIONS

A	angstrom, work function
$A_0, A_1 \dots A_n$	least square constants
B	second virial coefficient, burette
BuOH	butyl alcohol
C	capillary
c	critical
c.c.	cubic centimetre
corr.	corrected
const.	constant
conc.	concentrated
calc.	calculated
dil.	dilute
dev.	deviation
d	density
EDA	ethylenediamine
Expt.	Experimental
Fig.	Figure
g	gravity
H	hydrogen
Hg	mercury
h	height
i.d.	internal diameter
J	Joule
K	temperature in Kelvin
Lit.	literature
max.	maximum

Na	Sodium
n	No. of parameters, moles, normal
obs.	observed
P	total pressure
p or p ^s	pressure of pure component
R	gas constant
Ref.	Reference
Std.	standard
sec.	secondary
tert.	tertiary
T	Temperature
U	Internal energy
V	Volume (vol.)
VLE	Vapour Liquid Equilibrium
vs	versus
x	liquid mole fraction,
y	vapour mole fraction
V _m ^E	molar excess volume
G _m ^E	molar excess free energy
H _m ^E	molar excess enthalpy
S _m ^E	molar excess entropy
C _{p,m} ^E	molar excess heat capacity
K _s	isentropic compressibility
V _i ^{E,∞}	partial molar excess volume
α	volatility ratio
σ	standard deviation
Σ	summation
γ	activity coefficient
1, 2, 1	components

CHAPTER - I
INTRODUCTION

INTRODUCTION

As a part of the research programme of the measurement of the excess thermodynamic properties of non-electrolyte binary mixtures of our laboratory, the present work on the excess properties of isomeric butanols with n-octane, with ethylene-diamine (EDA) and toluene-EDA systems was undertaken with a view to understand the nature and behaviour of these binary systems which involves various intermolecular interactions.

The measurement of excess thermodynamic properties includes, (i) the excess molar free energy, G_m^E , (ii) the excess molar volumes V_m^E , (iii) the excess molar enthalpy, H_m^E , (iv) the excess molar heat capacity, $C_{P,m}^E$ and (v) isentropic compressibility, K_s^C . The results of the measurements of the first two excess properties (G_m^E and V_m^E) as a function of composition have been reported in this dissertation, for the nine binary systems mentioned above. Before the results obtained for these binary mixtures are described, it is essential to understand the meaning of excess properties and their significance.

It is known that the real solutions always show some deviation from ideality. If the deviations are

negligible, then the behaviour of the mixture can be easily determined. If, however, as in the most practical situations, deviations are significant and their magnitude is not even predictable, one must resort to experimental measurements to determine the real behaviour of the solution. In thermodynamics, the deviation from ideality is described as excess property or so-called property of mixing. The significance of excess thermodynamic properties can be summarised as follows:

- i) Excess properties provide key values for calculation of multi-component mixture properties from pure component data.
- ii) Excess properties are often used to define the various kinds of solutions.
- iii) They are useful in the development and testing of solution theories.
- iv) They can provide data for evaluation of parameters characterising interactions between unlike molecules, in the mixture.
- v) The excess free energy of mixing, G_m^E , is one of the most useful thermodynamic concept for expressing the non-ideality of liquid mixtures.
- vi) The excess enthalpy of mixing, H_m^E , is a very useful property in predicting isothermal vapour-

liquid equilibrium data (VLE) and testing the thermodynamic consistency of non-isothermal vapour-liquid measurements (VLE).

- vii) G_m^E is the most useful quantity for determining phase stability, phase separation and in the design of separation equipment in chemical engineering.

The availability of reliable excess thermodynamic data is required in the process design and development. The most useful feature of solution theories is that it would permit reliable prediction of thermodynamic properties of mixtures of any composition by knowing solely the corresponding properties of pure components or those of some other related mixtures. The fact that it is impossible to measure experimentally the properties of every mixture of interest has led to numerous theoretical attempts. Because the interaction force between two unlike molecules cannot be precisely predicted, in most cases, by the combination of those between like molecules, the success of such attempts has been limited. The averaging techniques are unsatisfactory for many mixtures. Since exact analytical formulae have not been established, current theories of solution with suitable modifications still provide significant results.

The increasing use of alcohols and amines in many industrial processes and the theoretical interest for the understanding of the behaviour of associated liquids in the binary as well as multi-component mixtures have greatly stimulated the need of extensive studies in excess thermodynamic properties of alcohols, amines and alkanes and their mixtures. It was therefore thought worthwhile to undertake studies on excess properties of simple systems like alcohol - alkane and amine - alkane and more complex systems like alcohol - amine, with an objective to investigate the contribution of a methyl group in different chemical environments, i.e. the effect of branching of alkyl chain of the alcohol on the excess properties.

The difference between any thermodynamic function X on mixing (denoted by superscript M) for a real system and the corresponding value for an ideal solution at the same temperature, pressure and composition is called the thermodynamic excess function (denoted by superscript E).

$$X^E = X^M \text{ (real solution) } - X^M \text{ (ideal solution) } \\ \text{at } T, P, X \qquad \qquad \qquad \text{at } T, P, X \\ \dots (1)$$

Therefore all excess functions for an ideal solution are zero.

Most of the solutions do not behave ideally. In the case of a real solution the excess functions may be positive or negative, depending on the non-ideality of the mixture. When the excess thermodynamic property X^E of a solution is greater than zero the solution is said to exhibit a positive deviation from ideality, whereas if it is less than zero the deviation from ideality is said to be negative.

The excess volume, V^E is then given by the relation

$$V^E = V_{(\text{real})}^M - V_{(\text{ideal})}^M \quad (2)$$

The excess free energy of mixing for a binary mixture containing x and $(1-x)$ mole fractions of two components is given by the relation

$$\begin{aligned} G^E &= G_{(\text{real})}^M - G_{(\text{ideal})}^M \\ &= RT [x \ln \gamma_1 + (1-x) \ln \gamma_2] - RT [x \ln x + (1-x) \ln (1-x)] \\ &= RT [x \ln \gamma_1 + (1-x) \ln \gamma_2] \quad (3) \end{aligned}$$

where γ_1 and γ_2 are the activity coefficients of the two components. Similarly the difference between the enthalpy of mixing of real system (ΔH_{real}^M) and the enthalpy of mixing

of an ideal mixture of the same composition ($\Delta H_{\text{ideal}}^M$) can be denoted by excess enthalpy H^E .

$$H^E = \Delta H_{(\text{real})}^M - \Delta H_{(\text{ideal})}^M \quad (4)$$

The relations between the thermodynamic excess functions are exactly the same as those between the total functions, e.g.

$$G^E = H^E - TS^E \quad (5)$$

$$A^E = U^E - TS^E \quad (6)$$

$$H^E = U^E - PV^E \quad (7)$$

where A = free energy function, U = internal energy, S = entropy. Similarly the partial derivatives of these functions are analogous to those of the total functions.

$$\left[\frac{\partial G^E}{\partial P} \right]_{T, X} = V^E \quad (8)$$

$$\left[\frac{\partial G^E}{\partial T} \right]_{P, X} = -S^E \quad (9)$$

and

$$\left[\frac{\partial (G^E/T)}{\partial (1/T)} \right]_{P, X} = H^E \quad (10)$$

Of the various thermodynamic functions of mixing process, the excess volume of mixing at constant pressure is one of the most interesting, yet certainly still one of the least understood. The reason for this is that it is easily influenced by the specific shapes of constituent molecules and therefore cannot be predicted accurately by a simple theory. It is important to know the volume change, especially of the partial molar volume, not only for its intrinsic interest but for the information that gives about the state of solution of solute. In addition, this information is needed in order to calculate the entropy of solution at constant volume from those at constant pressure.

The low pressure VLE is always preferred to get the composition dependence of excess free energy, G_m^E , because for low pressure VLE the problem of equipment design and operation is less formidable than for high pressure. At low pressures the pressure dependence of G_m^E is weak, and it depends strongly on temperature T. Low pressure isothermal VLE data are more easily reduced to useful form than are isobaric data. Therefore, low pressure isothermal VLE data were preferably obtained. Isobaric VLE data are more useful for the process design because separation process are nearly isobaric than

isothermal. After having understood the importance and significance of the excess thermodynamic properties, it is now necessary to know the present status of the various binary systems studied in the literature. In the following, a brief literature survey has been given of the relevant systems.

a) Alcohol-alkane

The excess thermodynamic properties of alcohols with normal alkanes and aromatic hydrocarbons have been studied by a number of workers¹⁻¹². It is agreed that the alcohols undergo self-association due to hydrogen bond formation in their pure liquid state, as well as their solutions in non-polar solvents. The degree of self-association of the pure alcohols decreases with increase in the temperature and in non-polar solvent it decreases with the increase in dilution. However, there is no agreement about the type and energy of self-association of alcohols. The hydrogen bonds between alcohol molecules are broken on mixing the alcohol with a non-polar solvent and self-association decreases with dilution.

Although a considerable amount of work has been done on the study of the excess thermodynamic properties of mixtures of aliphatic alcohols and non-polar solvents, most of the results are used for qualitative explanation

of the particular thermodynamic behaviour. Van Ness et al², Brown and others³, and Wierzchocki⁵⁻⁷ have studied various excess thermodynamic properties (G_m^E , H_m^E , TS_m^E) for normal alcohols with alkanes and the temperature dependence of excess functions was discussed. Suehnel and Mueller⁴ have determined V_m^E , G_m^E and H_m^E for n-butanol and n-octanol with aromatic solvents. Barro et al⁹ have obtained isothermal vapour-liquid equilibrium data and excess volumes for 1-butanol and 2-methyl-1-propanol in n-hexane. The vapour liquid equilibrium data were reduced according to the maximum likelihood principle and the parameters of Wilson, NRTL and UNIQUAC equations were calculated. The excess free energy values are positive for both the systems and decreases with the branching of alcohol chain. V_m^E are S-shaped for n-butanol and highly positive for 2-methyl-1-propanol.

The excess volumes of mixing for alcohol-alkane systems have widely been studied¹³⁻¹⁷. Treszczanowicz et al¹⁸⁻²⁰ have studied various alcohol-alkane binary systems. The excess volume behaviour and the corresponding partial molar volumes of both components have been interpreted in terms of a balance of three basic contributions: Chemical - due to breaking of hydrogen bonds, physical - due to disruption of molecular order

and structural - due to interstitial accommodation free volumes etc.

Awad and Pethrick²¹ have reported the volume change of mixing and excess compressibilities for mixtures of isomeric octanols and n-octane at 298.15 K. The data were interpreted in terms of the competing effects of the alkane chain taking up the free volume in the system, and the disturbance of the distribution between cyclic and linear structures and monomer forms in the mixtures. Kimura and Benson²² have determined the excess volumes for 1-hexanol with hexane isomers at 298.15 K using successive dilution dilatometer. The excess volumes curves are sigmoid and are negative over most of the mole fraction range; the positive values are limited to $x < 0.1$. Results on these binary mixtures could not be explained on any suitable theoretical model. Brown and Smith²³ have measured excess volumes by batch dilatometer for $C_1 - C_4$, C_6 and C_8 alcohols, 2-propanol and isomeric butanols with benzene at 25, 35 and 45°C. The excess volumes are positive, and values of V_m^E increases with molecular weight and with an increase in temperature. For isomeric butanols - benzene, the values of V_m^E , increases in the order primary, iso, sec and tert.

Anilkumar et al¹¹ have determined the volume changes on mixing of isomeric butanols with n-heptane at 25°C. The volume changes are positive. The excess volumes have been found to vary in the order of tert > sec > iso > n-butanol. The results are interpreted in terms of H-bond breaking and random distribution of n-heptane molecules. Otin and others²⁴ have obtained excess volumes for tert-butanol with iso-octane, benzene and CCl₄ at 30, 40 and 50°C.

Gupta, Naidu and Rao²⁵ have measured excess volumes of 1-propanol, 1-butanol, 1-pentanol and 1-hexanol with n-octane at 303.15 K. The values of excess volumes were positive and decreased with the increase in chain length of alcohol. The analysis of results showed that the mixtures of alkan-1-ol + n-octane do not obey the principle of congruence even approximately. Kumaran and Benson²⁶ have reported excess molar volumes of ethanol, propan-1-ol, butan-1-ol, pentan-1-ol and hexan-1-ol with n-heptane for mole fractions of alcohols less than about 0.04. Values of the limiting excess partial molar volumes $V_1^{E\infty}$ and thence of limiting partial molar volumes V_1^∞ of the alcohols in n-heptane have been derived.

The excess free energy of mixing G_m^E and isothermal vapour-liquid equilibrium (VLE) studies for alkanol-alkane

systems have been carried out by several authors²⁷⁻³¹. The isobaric vapour-liquid equilibrium of isomeric butanols with n-hexane have been studied by Govindswamy et al³²⁻³⁶. Vijayaraghavan and others^{37,38} have obtained isobaric vapour-liquid equilibrium data for n-butanol with n-heptane. Ramalho and Delmas³⁹ have obtained isothermal VLE data for butanol-cyclohexane and ethanol-heptane systems at various temperatures, and the isobaric VLE data were determined by cross-plotting the isothermal data. Soublikova and Lu⁴⁰ have studied VLE and excess free energy of mixing for n-octane-ethanol by dynamic method at 45°, 55°, 65° and 75°C. The values of activity coefficients (γ) were calculated and $\log \gamma$ values correlated by Redlick-Kister equation. The azeotrope formation was observed at all temperatures. Seetharamaswamy and others⁴¹ reported isothermal and isobaric VLE data for butanol-toluene system at 90°C and at 760 mm using modified Colburn still. γ values were calculated. Azeotrope formation was observed for both the methods.

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Rytting, Anderson and Higuchi have done vapour pressure studies of isomeric butanols with iso-octane by gas chromatography, at 25°C. The vapour pressure data were treated in terms of various association models. The results suggest that chain branching decreases the extent

of association and leads towards the formation of smaller polymer species. Anilkumar and Katti¹⁰ have studied isothermal VLE of isomeric butanols with n-heptane. The excess free energy is positive. The decreasing values of G_m^E from n to tert-butanol gives an indication of the effect of branching of alkyl chain on G_m^E .

Kogan, Fridman and Romanova⁴³ have made a study of the isobaric liquid-vapour equilibrium in mixtures of butyl alcohol with n-heptane, n-octane and n-nonane. Kehlen⁴⁴ has determined G_m^E values for butanols with butyl ether and butyl acetate and the H-bonding is discussed. Janaszewski et al⁴⁵ have obtained isothermal static VLE data for ethanol, 1-butanol with n-hexane, n-heptane and n-octane at 313.15 K and compared with literature data. Brown and Smith^{46,47} have studied n-alcohol + n-alkane mixtures by IR and NMR spectroscopy. The excess energies other than H-bonding are discussed. Verral and his colleagues⁴⁸ have done association studies of 1-butanol n-heptane as a function of temperature by near-IR spectroscopy. The dimer and tetramer species are predominant.

b) Alcohol-amine

Thermodynamic excess properties of amines are not studied as extensively as alcohols. The excess properties for some amine-alcohol binary systems have been reported

in the literature⁴⁹⁻⁵⁴. The experimental results implies that the H-bonds formed between unlike molecules after mixing are more stronger than those in two pure components. Hence specific interactions are involved and complex formation takes place between unlike molecules, resulting in negative excess properties. The complex formation decreases with the increase in temperature for most of the systems. Gladden and Ghaffari⁵⁵ have reported G_m^E , V_m^E , H_m^E and S_m^E for mixtures of ethylenediamine (EDA) + ethylene glycol at 25°C. G_m^E is small and negative at low concentration of EDA and positive at high concentration of EDA. H_m^E is highly negative and V_m^E is also negative throughout the concentration. H_m^E and S_m^E are nearly equal. Singh et al⁵⁶ have determined V_m^E and H_m^E of MeOH with pyridine, β -picoline and 1,4-dioxane at 303.15 K and 308.15 K. The results have been analysed using Barker's theory.

Pradhan⁵⁷ has determined volumes of mixing for methanol with each isomeric butylamine at 25°C. All the systems show negative volume change on mixing. This behaviour was attributed to the possibility of 1:1 type complex formation. The trend in V_m^E is tert > sec > iso > n-butylamine. Nakanishi and Shirai⁵⁸ have obtained excess volumes for ethanol, methanol with amines and other

associated liquids which show negative deviations. The excess volumes of binary solutions of aliphatic alcohols were critically reviewed.

Excess volumes for n-alcohols with pyridine bases are reported⁵⁹⁻⁶¹ at various temperatures. The results are discussed on the basis of pure component structure and intermolecular interactions. Excess volumes for three binary liquid mixtures viz. cyclohexane + toluene, toluene + amyl alcohol and ethylene glycol + pyridine, have been measured by Islam and Ibrahim⁶². The values of V_m^E are positive for first two systems except at higher amyl alcohol concentration and negative for last system. A positive value of $\frac{dV_m^E}{dT}$ for the second system indicates complex formation. The excess volumes of mixing for ethanol and methanol with secondary amines have been determined for the entire composition range at 293.15 K and 323.15 K⁶³. The excess volumes are negative and the temperature dependence of mixtures were explained by means of association theory. Huffman and others⁶⁴ have reported V_m^E for EDA and methanol.

Rao et al⁶⁵⁻⁶⁷ have measured excess volumes of ethylenediamine with n-, iso- and sec-alcohols ($C_3 - C_6$) at 303.15 K, using batch dilatometer. The excess volumes are negative for all the systems except for EDA - hexanols,

where the excess volumes are positive at higher mole fractions of EDA. The experimental results were interpreted in terms of 'bond breaking' and 'bond making' effects.

The isothermal vapour-liquid equilibrium of ethanol and n-propanol with n-butylamine has been studied at three temperatures by Datta Choudhury⁶⁸ and Pradhan⁶⁹. The calculated values of G_m^E and H_m^E are negative for all the systems indicating a specific interaction between n-butylamine and n-alcohols. Komarov and Krichevstov^{70,71} have obtained VLE data for n-butanol with n-butylamine, ethyl butylamine and diethylamine and a method of correlating the data based on properties of pure components was proposed. Nakanishi et al⁷² have studied isobaric VLE of methanol with n-butylamine di- and tri-ethylamine. For binary systems⁷³ of ethanol, 1-propanol, 1-butanol with triethylamine, the G_m^E values are found to be positive and V_m^E values are negative.

Chun and others⁷⁴ have studied VLE of triethylamine with n, sec and tert-butanol at 10-40°C. For tert-butanol, G_m^E values were positive while for n-butanol the values were negative. Warycha⁷⁵⁻⁷⁷ measured the vapour pressure isotherms of binary mixtures of methanol, ethanol, 1-propanol and isomeric butanols with pyridine bases at 313.15 K. The excess free energy values increased with the increase

in chain length of aliphatic alcohol and decreased with the branching of alkyl chain. Kristof et al⁷⁸ have reported isothermal VLE data for n-propylamine-n-propanol at 318.15 and 312.3K. The results are correlated using UNIQUAC equation.

Abraham and Nasehzadeh⁷⁹ have calculated excess properties for triethylamine with 28 solvents at 25°C from literature data. Specific Et₃N-solvent interactions were observed. The vapour-liquid equilibrium studies of ethylenediamine⁸⁰⁻⁸² with water shows specific interactions between unlike molecules.

IR absorption spectra of some alcohols with pyridine derivatives have been studied⁸³ and thermodynamic consistency was calculated. H-bonded ion-pair (1:1 proton transfer complex) formation between p-nitrophenol + EDA in mixed solvents like methanol, ethanol, dioxane and in their aqueous mixtures was studied by Moulick et al⁸⁴.

c) Amine-alkane

Letcher and Bayles⁸⁵ have studied V_m^E , G_m^E and H_m^E of butylamine, diethylamine and triethylamine with benzene and heptane. The results are interpreted in terms of interactions between H-bonded amines and non-bonding electrons of other molecules. Badoo and Philippe⁸⁶

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have reported the values of G_m^E and H_m^E of triethylamine with hexane, octane and tributylamine with hexane at 298.15 K. G_m^E and H_m^E are positive for first two systems while for tributylamine-hexane they are negative. Geometric factor may be responsible for negative values.

Kehiaian et al⁸⁷ have obtained G_m^E and H_m^E data for sec and normal amines with n-alkane. The data is interpreted by quasi-chemical group contribution theory which is applicable to H-bonds of type N-H...N. The work of Letcher^{88,89} reports the excess volumes for number of binary systems containing primary, secondary and tertiary amines with hexane, heptane, benzene, substituted benzene compounds and cycloalkanes at 25°C, using density method. The values are positive for the amine-alkanes but negative for chloro and nitro alkane + amines and alkane + cycloalkane systems. The results were fitted to Redlich-Kister type polynomial equation.

Garrett and Pollock⁹⁰ have obtained V_m^E data for benzene and toluene with pyridines and methyl pyridines at 298.15 K and 313.15 K. All excess volumes are negative for toluene systems in contrast to benzene. Rao et al⁹¹ have studied excess volumes for (EDA) with toluene, benzene and xylenes at 303.15 K. The excess volumes for all the systems are positive due to structure breaking effect.

Markuzin and Flekhotkin⁹² have done vapour liquid equilibrium (VLE) studies of EDA-benzene system at 20°C. Counsell et al⁹³ obtained vapour-liquid equilibrium data for various binary systems containing aliphatic amines.

Schhelzer and Quitzsch⁹⁴ have reported excess free energy values for EDA-benzene at various temperatures and pressures. G_E^E values were positive. Carta and Marrelli⁹⁵ have studied vapour-liquid equilibrium of EDA-toluene system.

Kollman and Allen⁹⁶ have discussed the theory of hydrogen bonding. H-bonding occurs between a proton donar group A-H and a proton acceptor group B, where A is electronegative atom, O, N, S, X (Cl, Br, I, F) or C and the acceptor group is a loan pair of electrons of an electronegative atom. Alcohols and amines form hydrogen bonds in their pure form and in their mixtures.

The construction of theoretical and empirical expressions for excess properties of mixtures has been and is the subject of much research. As yet none of the expressions postulated are generally superior to others so that it can be cited as being the best. There are different approaches used to explain and predict the properties of liquid mixtures⁹⁷. The equation-of-state treatments are used for explaining the properties of

mixtures of aliphatic hydrocarbons. The perturbation theory is used to explain the results for mixtures containing simple polar molecules. In both of these methods pure component data is used to predict mixture properties. The properties of more complex organic mixtures are considered in terms of interaction parameters and chemical equilibria resulting from interactions between both like and unlike molecules. The regular solution theory given by Scatchard and Hildebrand, Barker-Guggenheim Lattice theory, Flory-Huggins quasi-lattice theory and the Wohl, Van Laar, Margules equations are the some of most important theories developed. Redlich and Kister⁹⁸ introduced a simple, highly successful empirical representation for excess property.

The interaction parameter approach forms the basis of various predictive methods including the Barker, Wilson, NRTL, UNIQUAC, ASOG and UNIFAC methods, which have been used with some success in the correlation of VLE for complex organic mixtures. The concept of local mole fraction was first introduced by Wilson⁹⁹ to propose a two parameter equation that represents with great accuracy the behaviour of binary miscible systems. Renon and Prausnitz¹⁰⁰ have modified Wilson's equation by introducing a constant for accounting the non-randomness of liquid solutions.

Hanks, Gupta and Christensen¹⁰¹ have proposed a method for predicting VLE data from H_m^E data.

Thus the above literature survey reveals that very few and scattered work on various thermodynamic properties of isomeric butanols with n-octane, with EDA and toluene-EDA systems has been reported. Therefore, in the present study a systematic work on the measurements of excess thermodynamic properties viz. (V_m^E and G_m^E) for the above mentioned systems has been undertaken.

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CHAPTER-II
EXPERIMENTAL

EXPERIMENTAL

In this chapter, purification of various organic compounds and methods of measurements used for different thermodynamic properties viz. volume change of mixing and free energy of mixing have been described. The details of design of the apparatus used and experimental procedures followed have been given along with calibrations and errors involved.

PURIFICATION OF COMPOUNDS

1. Benzene

BDH, analytical reagent grade benzene was repeatedly treated with concentrated H_2SO_4 until free of thiophene. It was then thoroughly washed with distilled water and filtered through silica gel. The acid free benzene was dried over anhydrous K_2CO_3 . Fractionally crystallised and then twice fractionally distilled over P_2O_5 , which was stored over molecular sieves 4A.

2. Cyclohexane

Analytical reagent grade cyclohexane (Reanal Hungary) was fractionally crystallised. Then passed through silica gel column. Fractionally distilled over metallic sodium and stored over Na wire.

3. Toluene

BDH, analar grade toluene was treated with concentrated H_2SO_4 to remove thiophene. Washed with distilled water repeatedly and dried over K_2CO_3 . It was then fractionally distilled over Na and stored over Na wire.

4. Ethanol

Analar grade ethanol obtained from BDH was refluxed with alkaline silver nitrate and fractionally distilled. The middle fraction boiling at constant temperature was separated and stored over 4A molecular sieves.

5. Butanols

n-Butanol and iso-butanol purchased from S.D. Fine Chemicals, Bombay and sec-butanol and tert-butanol from SISCO Research Laboratory, Bombay (all analytical reagent grade) were used. The butanols were refluxed over NaOH pellets for 6 hours and then fractionally distilled using 1 meter long column packed with glass helices with a reflux ratio 30:1. The constant boiling middle fraction was again fractionally distilled in the same manner. All the butanols were stored over 4A molecular sieves.

6. n-Octane

A product of S.D. Fine Chemicals, Bombay (LR grade) was dried with Na and twice fractionally distilled over Na and stored over 4A molecular sieves.

7. Ethylenediamine

Reagent grade ethylenediamine was refluxed over NaOH for several hours and twice fractionally distilled over Na. Stored over molecular sieves 4A. Since it is highly hygroscopic in nature, it was freshly distilled before use and minimum exposed to air.

8. Water

Freshly distilled water was redistilled using alkaline KMnO_4 in an all glass apparatus and used without further purification.

9. Mercury

Commercially available distilled mercury was used. The mercury was allowed to fall in a fine spray into a column of dil. HNO_3 . Procedure was repeated twice and then it was passed through distilled water. Thereafter it was treated with sodium carbonate solution and again washed thoroughly with water and then with acetone. It was dried by manifold filtration through a pricked filter paper.

Before every experiment, the mercury was cleaned by washing with dil. HNO_3 , water and with acetone. Then it was dried and evacuated.

The purity of all the above compounds (except water and mercury) was checked by gas chromatographic analysis

Table 1: Densities of pure liquids (gm/cm³)

Sr.No.	Substance	T °K	d(obs)	d(lit)	Ref.No.
1.	n-Butanol	298.15	0.80572	0.80572	2
2.	iso-Butanol	298.15	0.79803	0.79820	2
3.	sec-Butanol	298.15	0.80260	0.80260	1
4.	tert-Butanol	299.15	0.77984	-	-
5.	n-Octane	298.15	0.69878	0.69882	2
		299.15	0.69780	-	-
6.	Benzene	298.15	0.87370	0.87366	2
7.	Cyclohexane	298.15	0.77389	0.77383	2
8.	Ethanol	298.15	0.78504	0.78508	2
9.	Water	298.15	0.99707	0.99705*	4
10.	Toluene	303.15	0.85771	0.85770	2
11.	EDA	298.15	0.89120	0.8910	3
		299.15	0.89020	-	-
		303.15	0.88600	0.88600	1
12.	Mercury	298.15	13.534	13.534	4

* Density of water taken as standard.

and was found to be greater than 99.5%. The purities of all the samples were also confirmed by determining the densities and comparing them with the literature¹⁻⁴ (Table 1).

APPARATUS, DESIGN, EXPERIMENTAL PROCEDURES AND CALIBRATIONS

a) Excess volumes of mixing

The excess volumes of mixing (V_m^E) are normally determined by two methods, (i) direct (by dilatometer) and (ii) indirect (by density measurements). The majority of excess volumes for liquid mixtures reported in the literature have been calculated indirectly from the measurement of density at known composition. To achieve a reasonable accuracy in V_m^E density measurements have to be made highly accurate upto 1×10^{-5} gm/cc. To achieve this accuracy on mixtures containing a volatile component is very difficult, as the assumption made when applying correction for evaporation during the preparation and transfer of the mixture are often inadequate. Even then the excess volumes have been determined by density measurements using pycnometers by many authors⁵⁻⁸.

Recently Kiyohara and Benson⁹, Goates, Ott and Grigg¹⁰ and Cibulka et al¹¹ have determined excess volumes using precision vibrating tube densitometers. Weeks and Benson¹² have used magnetic float technique for density measurements.

A simple and most accurate method of measurements of V_m^E , is to determine it directly using dilatometer. Dilatometers are of three types, (i) batch dilatometer, (ii) semi-continuous dilatometer and (iii) continuous dilution dilatometer.

Swinton et al¹³ used a simple batch dilatometer. Rastogi and Nath¹⁴, Radojkovic et al¹⁵ and Palta and Lark¹⁶ also used single shot dilatometer for excess volume measurements. Other modifications on batch dilatometer have been described^{17,18}. Different types of dilatometers have been described in the review article of Battino¹⁹. Stookey et al²⁰ have discussed in detail the potential sources of errors in the single shot dilatometer. Janssens and Ruel²¹ and Caceres et al²² have described a semi-continuous dilatometer.

Dilution dilatometers for measuring excess volumes offer the advantage that the composition range can be covered in two runs and partial molar excess volumes are readily obtained. If the bath temperature is controlled to better than $5 \times 10^{-3} \text{K}$, we can get the precision of $\pm 0.001 \text{ cm}^3 \cdot \text{mol}^{-1}$ in the excess volumes. Based on the principle of Greffcken and coworkers²³, a number of dilution dilatometers for measuring excess volumes, have been described in the literature²⁴⁻²⁶. Those dilatometers, however, have a greased stopcocks which is one of often

discussed sources of errors. Bottomley and Scott²⁷ have described a tilting dilution dilatometer without any stopcock. The major drawbacks of their improved design are (a) calibration is tedious, (b) loading must be done under vacuum and (c) only small volume changes can be measured. Kumaran and McGlashan²⁸ have redesigned Bottomley and Scott's tilting dilatometer which does not have the above mentioned disadvantages and the two liquids in the dilatometer are separated by mercury at all stages of a run. There are no possible errors due to diffusion. Cibulka and Holub²⁹ slightly modified the Kumaran and McGlashan's dilatometer. At present Kumaran and McGlashan's dilatometer is supposed to be a better dilatometer as regards accuracy and ease of operation. Tanaka et al³⁰ have described micrometer syringe dilatometer.

In the present work we have constructed a dilatometer based on the combined version of the design of Kumaran - McGlashan and that of Cibulka and Holub.

The Dilatometer design and calibration

The dilution dilatometer is shown in Fig. 1. It consists of a burette B, with a bulb BB blown at one end, capillaries C₁, C₂ and C, a mixing bulb A (all corning glass) and teflon stopcocks T₁, T₂.

DILUTION DILATOMETER

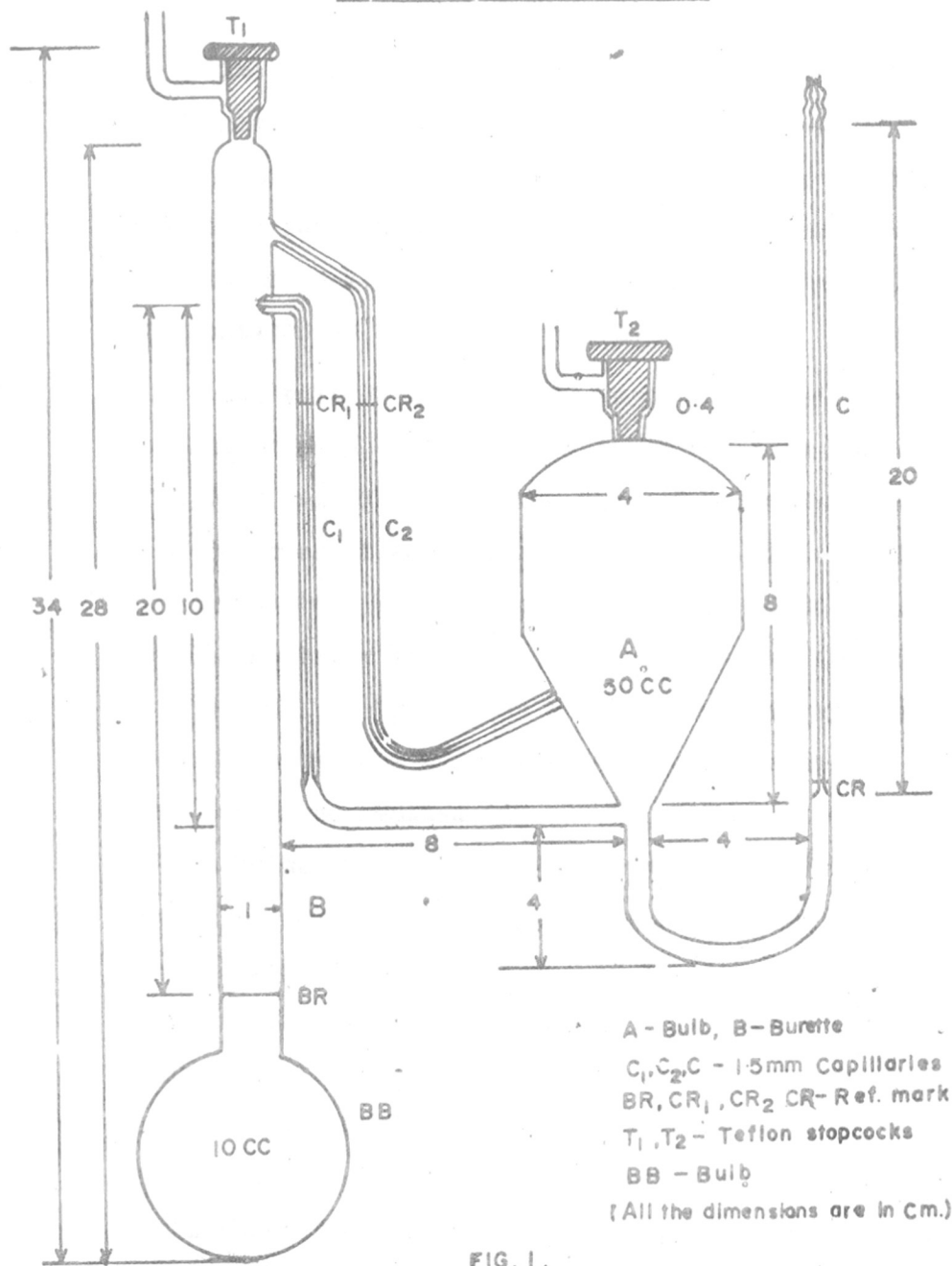


FIG. 1.

The necessary calibrations were done before the dilatometer was assembled, care being taken to avoid the calibrated parts during subsequent glass-blowing and flame-annealing of the seals. The calibrations of burette and bulb were carried out in a water-bath thermostated at 298.15 K to within ± 0.01 K.

The bulb BB of capacity about 10 cm^3 was blown at one end of a 25 cm long precision bore glass tube (burette B) of i.d. 1 cm. The reference mark BR was made. When the tube had been thoroughly cleaned it was filled with cyclohexane and clamped in its upright position inside the thermostat with the open end well above the water level in the bath. A known mass of purified mercury was transferred into the tube from a small beaker, displacing the cyclohexane; This technique avoided air bubbles being trapped by mercury in the bulb. The volume of mercury so added was just enough to reach close to the mark BR. After thermal equilibration, the difference of heights of mercury meniscus and the mark BR was measured with a cathetometer readable to 0.01 mm. The mercury level was then raised in steps by addition of known masses of mercury, the difference of height being measured after each addition, until the mercury level was about 20 cm above BR. The entire set of measurements was done three times. From the density and mass of mercury added, the volume of the

bulb BB upto mark BR and the cross-sectional area of burette B were calculated. The average values with a root-mean square deviation and largest deviation are given in Table 2.

The calibrations of capillaries C_1 , C_2 and C were done by measuring a length of mercury thread inside the capillary at several places, and weighing the mercury. From the density, mass and length of mercury thread the cross-section of capillaries was found. The average cross-sectional areas with standard deviation and largest deviation for all the three capillaries are given in Table 2.

The mixing bulb A had a tapered bottom so as to reduce the mass of mercury needed. It had a cylindrical middle part with i.d. about 4 cm. The top part was hemispherical and its volume was so chosen that at the beginning of a dilution run the mercury meniscus in A was in the cylindrical middle part. The total volume of the bulb A was about 50 cm³. Throughout a complete dilution run, the mercury level was lowered by only 1.2 to 1.3 cm, so as to ensure that the mercury level never reached near the outlet from the capillary tube C_2 , and to make Δh_A (see eqn.3) as small as possible; in most cases negligible. The burette B and mixing bulb A were closed by the PTFE needle valves T_1 and T_2 (4 mm bore) respectively.

Table 2: Calibration of dilatometer parts at 298.15 K

1.	Cross-sectional area of Burette (B) = a_B	= 1.2270 cm ²
	std.dev.	= 0.001
	max. dev.	= 0.002
2.	Cross-sectional area of Capillary (C) = a_C	= 0.01666 cm ²
	std.dev.	= 0.00002
	max.dev.	= 0.00003
3.	Cross-sectional area of Capillary (C ₁) = a_{C_1}	= 0.01676 cm ²
	std.dev.	= 0.00007
	max.dev.	= 0.0001
4.	Cross-sectional area at Capillary (C ₂) = a_{C_2}	= 0.01495 cm ²
	std.dev.	= 0.0001
	max.dev.	= 0.0002
5.	Volume of the bulb (BB)	= 11.767 cm ³
	std.dev.	= 0.002
	max.dev.	= 0.015
6.	Working length of Burette (B)	= 19 cm
7.	Working length of Capillary (C)	= 15 cm

At the beginning of each run the apparatus was thoroughly cleaned (pure HNO_3 , distilled water, pure ethanol, pure acetone). The open end of capillary C was then connected to vacuum, and when the needle valves T_1 and T_2 were free of acetone the PTFE male pieces were replaced and screwed home. Evacuation was continued until the apparatus was completely dry. The male pieces of T_1 and T_2 were removed.

Loading and Measurement Procedure

The dilatometer was mounted on a frame which could be rotated about a fixed horizontal axis in a thermostat bath and which was arranged at this stage so that the open parts of dilatometer were kept well above the water surface. Mercury was introduced into A, the bottom of A being reached with a stainless steel needle attached to a hypodermic syringe. The end of the needle was held always slightly above the rising mercury level so as to avoid trapping any air bubble. The bulb A was completely filled with mercury. After thermal equilibration the mercury level was carefully adjusted so that it just touched at the bottom of needle valve T_2 , when it was closed. The heights of mercury menisci in C_1 and C_2 and C were determined with respect to marks CR_1 , CR_2 and CR respectively.

The burette B was filled with a degassed diluent liquid (component 2) through T_1 by hypodermic syringe, until its level was just above the top of C_1 . The dilatometer was slowly tilted by anti-clockwise rotation of its frame so as to transfer mercury from A to BB. Mercury always dropped through a liquid and so no air bubble was trapped. The level of liquid in B rose up and excess liquid was removed, time to time. The transfer of mercury was continued until the mercury level was near BR. The vacant space in A was filled with a second liquid and both T_1 and T_2 were closed. The volume of second liquid (component 1) added is equivalent to the volume of mercury displaced in bulb BB. This is one method²⁸ of knowing the quantity of second component added. Another method²⁹ is to withdraw about 10 ml of mercury from completely filled in A (upto the bottom of T_2) and then to add equivalent amount of the second liquid. Knowing the mass of mercury withdrawn and from the changes of mercury minisci in capillaries C_1 , C_2 and C, the number of moles of second component added can be calculated. Both the methods are equally accurate, but the second method was more convenient and was adopted in the present work.

After closing both the valves T_1 and T_2 the contents of the dilatometer were in contact with the atmosphere

only through the mercury piston in the capillary C. The frame carrying the dilatometer was then lowered so that only the top of C was above the water level, in the thermostat. After thermal equilibration the heights of mercury miniscii in C_1 , C_2 , C and B were read with respect to the corresponding marks. The apparatus was then ready for a series of measurements of volume changes caused by mixing on dilution of liquid in A with a diluent liquid in B.

The dilatometer was tilted by anti-clockwise rotation of the frame so that mercury flowed from C_1 into B displacing an equal volume of the diluent liquid through C_2 into A. When the required amount of diluent had been introduced into A the dilatometer was brought back to its vertical position. This procedure completely separated the liquid mixture in A from diluent liquid in B at all stages. The liquid mixture in A was stirred repeatedly by rocking the dilatometer manually, until the change in height of mercury miniscus in C (due to volume change) was constant (no magnetic stirrer was used). The heights of mercury minisci in B, C_1 , C_2 and C were determined with respect to the corresponding reference marks. The entire procedure was repeated again and again until we get at least about 10 readings, and mercury level in B was about 16 to 17 cm above BR. During the series of measurements, the mercury

level in C was adjusted whenever necessary by drawing mercury out of it or introducing more mercury into C through a stainless steel needle attached to a syringe. The same procedure was repeated for second run, just by taking the component 1 in burette B and component 2 in A. In the two dilution runs, excess volumes for the whole range of mole fractions are obtained. The values of excess volumes, $V_m^E(x_1)$ overlap through some range of x_1 which is a sensitive check on the quality of measurements. For two runs only 50 cm^3 of each component was needed.

Control and measurement of temperature

The temperature of the water in the thermostat (50 dm^3 capacity) was controlled to $\pm 0.01 \text{ K}$ by a toluene regulator, and measured by a Beckmann thermometer.

Measurements for compression correction

Compression corrections have been taken into account since the changes in pressure arising from changes in mercury levels during measurements were greater than the experimental uncertainty.

The apparatus used for determining the compression corrections is shown in Fig.2. The U-tube (80 cm height) was half filled with mercury. T_3 is the vacuum stopcock to which a rubber aspirator bulb is connected at E. The

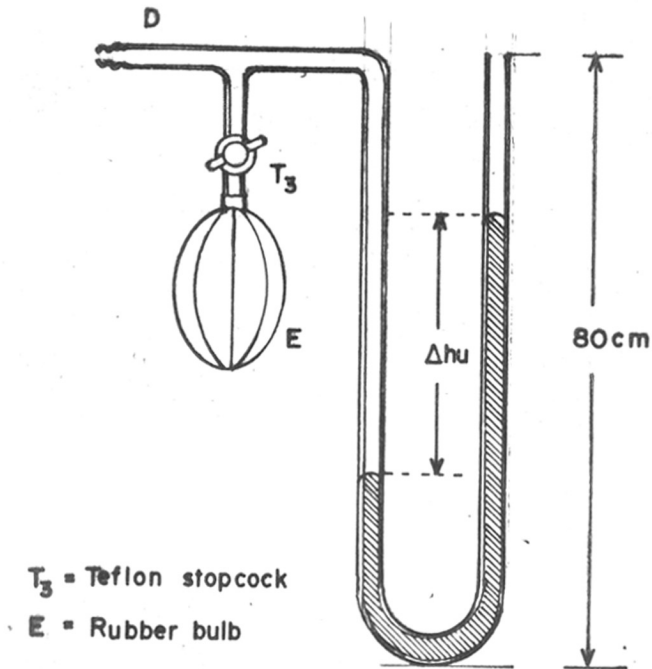


FIG.2. APPARATUS FOR COMPRESSION MEASUREMENT

apparatus is connected at D by a rubber pressure tubing to the top of C of a dilatometer. Keeping T_3 open and squeezing the aspirator bulb, an overpressure was applied (about 25 kPa). The tap T_3 was closed and after thermal equilibration of the apparatus, the difference in heights of mercury levels in U-tube and reduction in the height of mercury level in C was measured. Such measurements were carried out four or five times during the run.

Calculations

The volume V_1 of the pure liquid in A at the beginning of run and the corresponding amount of substance n_1 (moles) are given by

method 1:

$$V_1 = n_1 \cdot V_{m,1} = V_{BB} + (h_B - h_{BR})a_B + \Delta h_{C_1}^1 \cdot a_{C_1} + \Delta h_{C_2}^1 \cdot a_{C_2} + \Delta h_C^1 \cdot a_C \quad (1a)$$

where $V_{m,1}$ = molar vol. of pure liquid 1 in cc.

V_{BB} = calibrated volume of bulb BB upto BR.

a_B = cross-section of the burette B

a_{C_1} = cross-section of capillary C_1

a_{C_2} = cross-section of capillary C_2

a_C = cross-section of capillary C

$(h_B - h_{BR})$ = change in height of mercury level in B.

$\Delta h_{C_1}^1$, $\Delta h_{C_2}^1$ and Δh_C^1 are changes (negative) in the heights of mercury columns in C_1 , C_2 and C respectively after the initial transfer of mercury from A to BB.

Method 2 :

$$V_1 = V + \Delta h_{C_1}^1 + \Delta h_{C_2}^1 + \Delta h_C^1 \quad (1b)$$

where V = volume of mercury withdrawn = mass x density

and $\Delta h_{C_1}^1$, $\Delta h_{C_2}^1$ and Δh_C^1 have the same meaning as above.

Method 2 was adopted in this work. The volume ΔV_2 of diluent pure liquid and its corresponding amount n_2 added after each dilution is given by

$$\Delta V_2 = n_2 \cdot V_{m,2} = \Delta h_B \cdot a_B + \Delta h_{C_1} \cdot a_{C_1} + \Delta h_{C_2} \cdot a_{C_2}$$

where $V_{m,2}$ = molar volume of pure diluent liquid

Δh_B , Δh_{C_1} , Δh_{C_2} = changes in the heights of mercury levels in B, C_1 and C_2 respectively.

The true volume change (V^E) following any one dilution can be calculated from the measured increase in height Δh_C of the mercury column in the capillary C as given in the following equation (Δh_C decreases for negative volume changes).

$$V^E = \Delta h_C \cdot a_C \left[1 - \frac{\Delta h_C^{\pi}}{\Delta h_U} \right] \left[1 - \frac{\Delta h_A}{\Delta h_C} \right] \quad (3)$$

where Δh_C^{π} = increase (actually negative) in the height of mercury column in C due to applied over-pressure during the measurements for compression correction.

Δh_U = difference in heights of mercury in U-tube (Fig.2) due to applied over-pressure.

Δh_A = the small increase (actually negative) of height in the level of mercury in A following the dilution

$$[= 0.104 \times \text{change in } \Delta h_B].$$

Molar excess volumes

$$V_m^E = \frac{V^E}{n_1 + n_2} \quad \text{cm}^3 \cdot \text{mol}^{-1} \quad (4)$$

The proper working of the apparatus was checked by measuring the excess molar volumes at 298.15 K of benzene + cyclohexane, a recommended system by Powel and Swinton³¹. The results are presented in Table 3 and plotted in Fig.3. The agreement between the present values and those reported by Kumaran and McClashan²⁸ as shown in Fig.3 is quite good. The results were fitted to the polynomial equation.

Table 3: The excess volumes of mixing for cyclohexane (1)
+ benzene (2) at 298.15K.

Mole fraction x_1	V_m^E ($\text{cm}^3 \cdot \text{mol}^{-1}$)	Mole fraction x_1	V_m^E ($\text{cm}^3 \cdot \text{mol}^{-1}$)
0.0354	0.0872	0.4438	0.6342
0.0849	0.2021	0.4893	0.6457
0.1012	0.2371	0.4760	0.6472
0.1633	0.3509	0.4944	0.6495
0.1656	0.3532	0.5144	0.6486
0.2088	0.4238	0.5270	0.6496
0.2341	0.4598	0.5644	0.6454
0.2498	0.4800	0.5765	0.6378
0.3011	0.5405	0.6424	0.6043
0.3450	0.5800	0.7165	0.5351
0.3766	0.6046	0.7231	0.5271
0.3945	0.6142	0.8028	0.4226
0.4113	0.6242	0.8034	0.4195
0.4163	0.6239	0.8933	0.2620
0.4273	0.6305	0.9256	0.1923

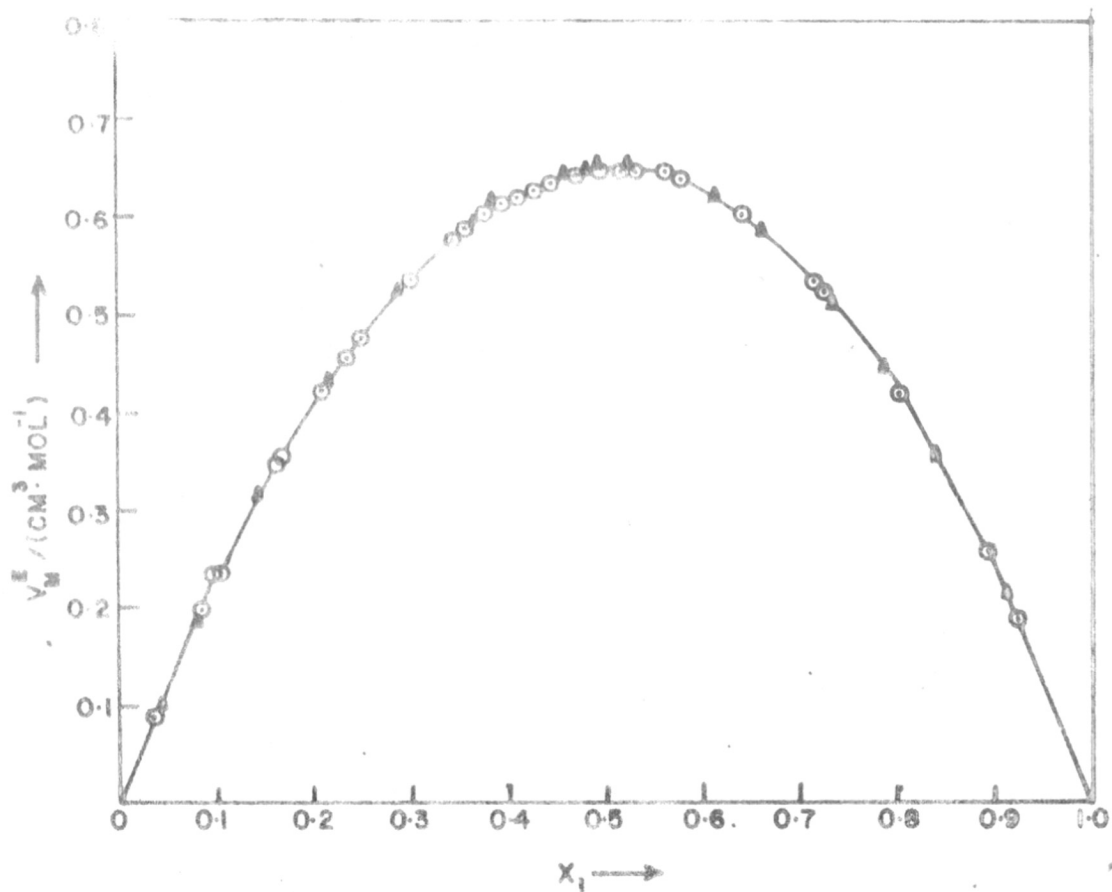


FIG. 3. EXCESS VOLUMES FOR CYCLOHEXANE (1) + BENZENE (2) AT 298.15 K

○ PRESENT WORK ▲ REF. 28

$$V_m^E = x_1 (1-x_1) \sum_{n=0}^3 A_n (2x_1-1)^n \quad (5)$$

The least square constants are $A_0 = 2.58764$, $A_1 = 0.07272$, $A_2 = 0.11320$, $A_3 = 0.06055$ and standard deviation = 0.0025. The accuracy of the results is better than $\pm 0.002 \text{ cm}^3 \cdot \text{mol}^{-1}$.

b) Excess free energy of mixing

The molar excess Gibbs free energy, G_m^E , cannot be measured directly. The majority of G_m^E values are derived from isothermal vapour-liquid equilibrium data obtained either by using recirculating stills (dynamic) or with the static vapour-pressure technique. The advantages and disadvantages can be claimed for both the methods. The static method is more precise and can also be used for very low pressures. The major difficulty is the need to remove completely all the traces of air from the system and the liquids. This method also involves lot of computer calculations to determine the vapour phase composition (y). In the dynamic method getting true equilibrium and accurate analysis of vapour composition is somewhat difficult. We have made use of the dynamic recirculation method due to the existing facilities in the laboratory.

In the dynamic method both liquid and vapour phases are circulated at whatever rate they are generated till a

steady state is reached. Then the total vapour pressure P , mole fraction y in vapour phase and mole fraction x in liquid phase are determined. Hala et al³² have reviewed a large number of recirculating stills. In the present work a modified Jones-Colburn still³³ has been used, because it was possible for us to conduct experiments with small quantities of liquid mixtures (i.e. about 25 ml/experiment) and also to obtain a thermal equilibrium in a comparatively short period of time.

Recirculating Still

The modified Jones-Colburn still has been shown in Fig.4. The still was made up of corning glass. It had a reserve vessel A containing liquid mixture. The reserve vessel was electrically heated by a heater H_1 , and all the portion was thermally insulated with an asbestos rope. A calibrated thermometer (with 0.1°C accuracy) was dipped in silicone oil in a thermometer pocket T, to measure the equilibrium temperature. Its lower end was always above the liquid level in the vessel A. The teflon stopcock K_2 at the bottom of reserve vessel A served as an outlet for liquid sampling. The vapours formed from the liquid mixture passed through a tube heated with another heater H_2 and then condensed in a condenser C_1 . It was then collected in receiver B. After the level of

To vacuum system
via micrometer
regulating middle
metal valve

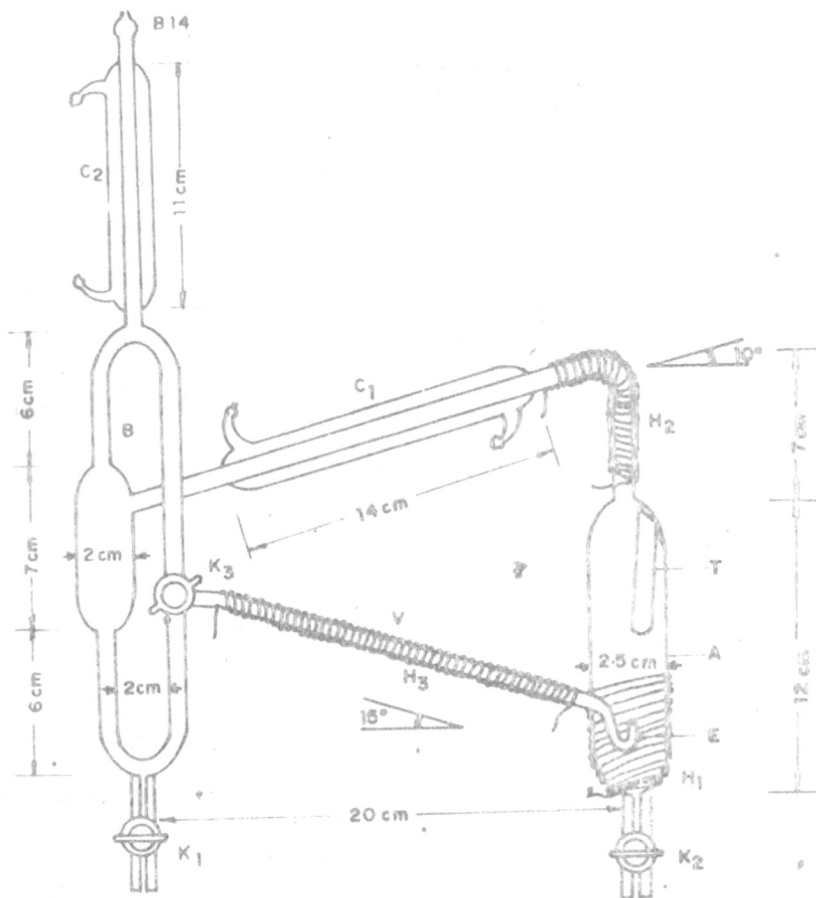


FIG. 4. MODIFIED JONES-COLBURN STILL

condensed vapours reached the three way teflon stopcock K_3 , it slowly fell through the inclined glass tube E whose another end is immersed in the vessel A. This tube is also heated with heater H_3 . The receiver B contained a condenser C_2 which on the other side was connected to vacuum system via standard B-14 ground joint, and a stopcock K_1 for vapour sampling. The system pressure was adjusted to a desired value with the help of a micrometer needle regulating metal valve, and a vacuum pump.

Determination of total vapour pressure (P)

A binary liquid mixture (about 25 ml) of the desired concentration was transferred to the still through B-14 joint of the condenser C_2 . The liquid enters in both the receivers A and B. All the three heaters H_1 , H_2 and H_3 were put on. As soon as the mixture started boiling the desired pressure was maintained by connecting the still to vacuum system and adjusting the micrometer needle valve, to get a constant temperature. The still was kept in the same condition for one hour to reach the thermal equilibrium. It was indicated by a constant temperature and system pressure. The difference in the manometer levels was read by a cathetometer accurately down to 0.01 mm. The room temperature and barometric pressure were noted. The heaters were put off, the vacuum in the still was released and stopcock K_3 was simultaneously rotated

to cut off the circulation of the liquid. The samples of the liquid from vessel A and condensed vapour from vessel B were collected through stopcocks K_2 and K_1 respectively for analysis. The equilibrium pressure was determined from the difference of the barometer reading and the manometer reading after appropriate barometric and gravitational corrections. A value of 'g' equal to 978.59 cm/sec^2 ; valid for Poona was used for gravity corrections. For isobaric VLE, only temperature T and composition x and y were noted.

Analysis of liquid and vapour samples (x,y)

Liquid and vapour samples were analysed by density measurements. Densities were determined at 298.15K for all the systems except that tert-butanol systems at 299.15K and toluene-EDA system at 303.15K. Two Lipkin type pycnometers of about 3.5 ml capacity were used.

Pycnometer and its calibration

A two arm pycnometers (shown in Figs. 5 and 6) were made of corning glass, having a volume of about 3.5 ml. The two arms of each pycnometer were made up of two fine capillaries of i.d. 0.5 mm. Two reference marks were etched on the lower side of two arms above the bulb of the pycnometer. The evenness of the bore of capillaries was checked before using them for the construction of a pycnometer.

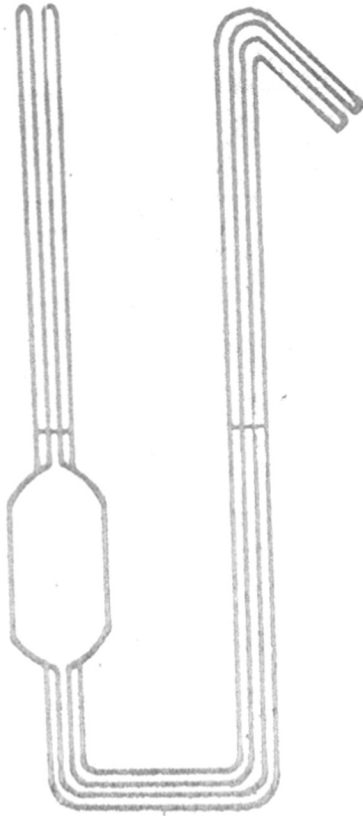


FIG. 5. PYKNOMETER - A

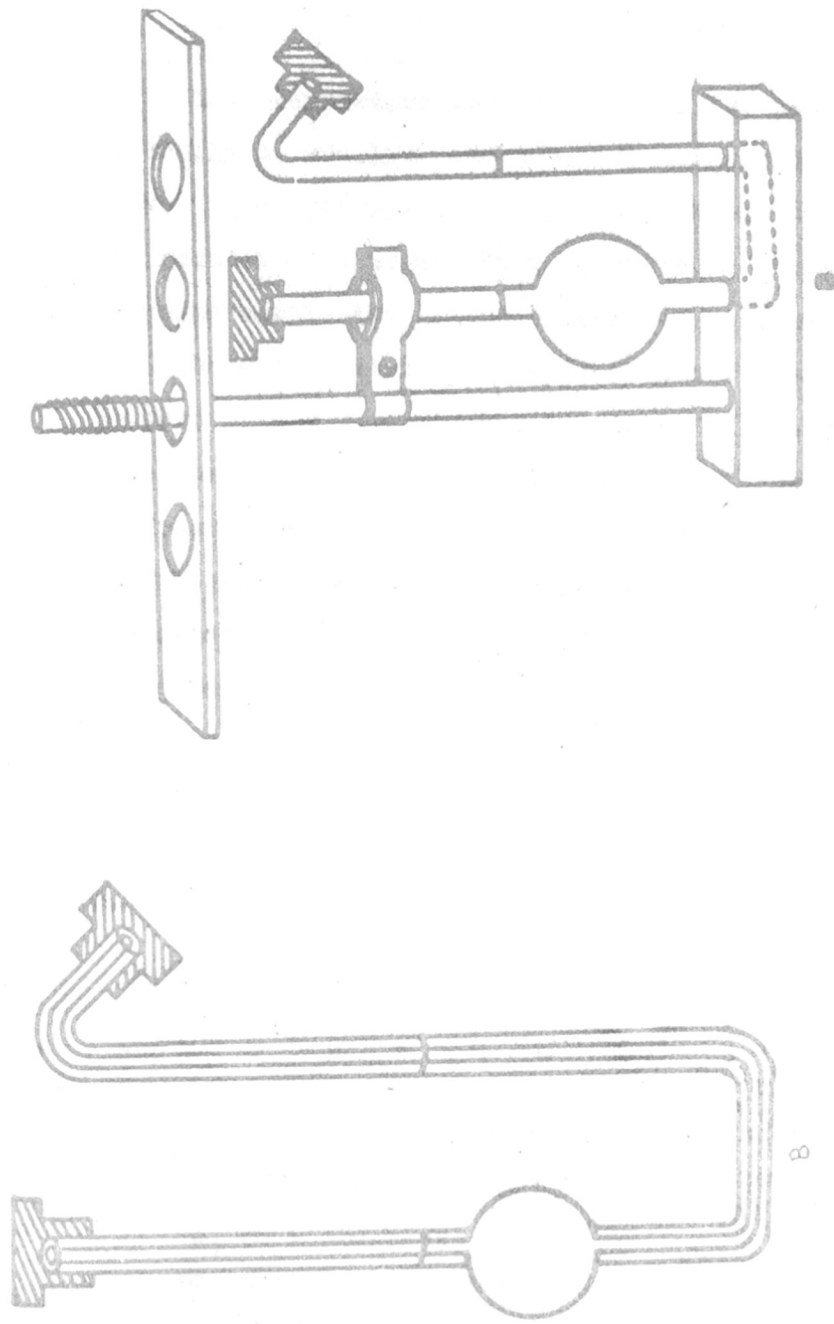


FIG. 6. PYCNOMETER AND IT'S ASSEMBLY

The pycnometers were calibrated for their volumes at 298.15 K, 299.15 K and 303.15 K, using double distilled water. The pycnometer was filled with distilled water and mounted on a brass stand as shown in Fig. 5B. It was immersed vertically in the thermostat keeping the open ends well above the water surface to attain a thermal equilibrium. Heights of the water levels in the capillaries were measured with respect to marks by a travelling microscope. The pycnometer was taken out, dried by absorbent tissue papers and weighed in a single pan microbalance. The weights are accurate down to ± 0.1 mg. From the weight of water and known density, the volume for the corresponding height ($h_1 + h_2$) was calculated after appropriate correction. Readings were taken for different heights. These calibration results for both pycnometers are given in Table 4. The results were least square fitted to two simultaneous equations:

$$m \sum x^2 + C \sum x = \sum xy \quad (1)$$

$$\text{and } m \sum x + n \cdot C = \sum y \quad (2)$$

where x = total height ($h_1 + h_2$) in both arms

y = volume corresponding to $h_1 + h_2$

m, C = constants

and n = No. of readings.

Thus knowing the height, volume can be calculated (see Table 4) and hence the density of unknown samples. The density measurements are reproducible upto $\pm 5 \times 10^{-5}$ gm.cm⁻³.

Table 4: Calibration of Pycnometers at 298.15 K

Sr. No.	h_1 (cm)	h_2 (cm)	h_1+h_2 (cm)	W (gm)	W corr. (gm)	V (cc)	$\delta V \times 10^5$
<u>Pycnometer A</u>							
1.	8.057	7.882	15.939	3.52740	3.53159	3.54200	9
2.	7.302	7.225	14.527	3.52270	3.52689	3.53729	-8
3.	6.481	6.388	12.869	3.51688	3.52107	3.53145	2
4.	5.430	5.190	10.620	3.50928	3.51347	3.52383	15
5.	4.074	3.981	8.055	3.50015	3.50434	3.51467	13
6.	3.011	3.091	6.102	3.49355	3.49744	3.50805	-1
7.	2.080	2.010	4.090	3.48662	3.49081	3.50110	-2
<u>Pycnometer B</u>							
1.	7.130	7.150	14.280	3.41710	3.42115	3.43127	-3
2.	6.110	6.230	12.340	3.41382	3.41787	3.42798	-3
3.	5.145	5.460	10.605	3.41087	3.41492	3.42502	0
4.	4.185	4.305	8.490	3.40725	3.41130	3.42139	4
5.	3.230	3.345	6.575	3.40404	3.40809	3.41817	2
6.	2.220	2.310	4.530	3.40058	3.40463	3.41470	2
7.	0.735	0.785	1.520	3.39557	3.39962	3.40968	-6

* For Pycnometer A : Volume = $0.0034617 (h_1+h_2) + 3.48692$

" B : Volume = $0.0016941 (h_1+h_2) + 3.40705$

* Valid for 298.15 K, 299.15 K and 303.15 K

The vapour and liquid composition were determined by density method using the equation:

$$\frac{1}{d_m} = \frac{w_1}{d_1} + \frac{(1-w_1)}{d_2} + \delta \quad (3)$$

where d = density, w = wt. fraction. The δ values for corresponding d_m were obtained from excess volume measurements. The uncertainty in mole fractions was less than 5×10^{-4} .

Calculation of excess free energy of mixing G_m^E

The excess free energies of mixing were calculated from isothermal P - x - y data at 333.15 K, throughout the concentration range, for all the systems. The liquid phase activity coefficients γ_1 and γ_2 of the two components were calculated by the equations:

$$\ln \gamma_1 = \ln \frac{y_1 P}{x_1 P_1^S} + \frac{(B_{11} - V_1^L)(P - P_1^S)}{RT} + \frac{P \delta_{12} y_2^2}{RT} \quad (4)$$

$$\ln \gamma_2 = \ln \frac{y_2 P}{x_2 P_2^S} + \frac{(B_{22} - V_2^L)(P - P_2^S)}{RT} + \frac{P \delta_{12} y_1^2}{RT} \quad (5)$$

where P is the total pressure P_1^S and P_2^S are the vapour pressures; x_1 and x_2 are the mole fractions in liquid phase; y_1 and y_2 are mole fractions in the vapour phase; V_1^L and V_2^L are the molar volumes of the liquids and B_{11} and B_{22} are second virial coefficients of pure components 1 and 2 respectively, and

$$\delta_{12} = 2 B_{12} - B_{11} - B_{22}$$

where B_{12} is the second virial cross coefficient of the mixture.

The term of cross virial coefficients was not taken into the calculations of activity coefficients because of large uncertainty involved in the calculated and actual values of B_{12} . The second virial coefficients, B for isomeric butanols, n-octane and toluene were calculated using Tsonopoulos equation³⁴ and for ethylenediamine by Pitzer-Curt equation³⁵.

Tsonopoulos equation

$$\frac{B.P_c}{R.T_c} = f^{(0)}(Tr) + w f^{(1)}(Tr) + f^{(2)}(Tr) \quad (6)$$

$$\text{where, } f^{(0)}(Tr) = 0.1445 - 0.330 Tr^{-1} - 0.1385 Tr^{-2} - \\ 0.0121 Tr^{-3} - 0.000607 Tr^{-8}.$$

$$f^{(1)}(Tr) = 0.0637 + 0.331 Tr^{-2} - 0.423 Tr^{-3} - 0.008 Tr^{-8}$$

$$f^{(2)}(Tr) = a Tr^{-6} - b Tr^{-8}.$$

Pitzer-Curt equation

$$\frac{B.P_c}{R.T_c} = (0.1445 + 0.073 w) - (0.330 - 0.46w) Tr^{-1} - \\ (0.1385 + 0.5 w) Tr^{-2} \\ -(0.0121 + 0.097w) Tr^{-3} - (0.0073w) Tr^{-8} \quad (7)$$

$$\text{where, } w > 0, \quad w = -(1 + \log Pr) Tr = 0.7 \quad (8)$$

Table 5: Molar volumes of pure liquids at different temperatures (K).

Sr. No.	Compound	Molar volume (ml/mole)			
		298.15 K	299.15 K	303.15 K	333.15 K
1.	n-Butanol	91.97	-	-	95.2
2.	iso-Butanol	92.91	-	-	96.38
3.	sec-Butanol	92.35	-	-	96.01
4.	tert-Butanol	-	95.03	-	99.75
5.	n-Octane	163.47	163.70	-	170.64
6.	EDA	67.45	67.50	67.84	70.0
7.	Toluene	-	-	107.43	111.0
8.	Benzene	89.41	-	-	-
9.	Cyclohexane	108.76	-	-	-

Table 6: Second virial coefficients (B) of pure liquids
at 333.15 K

Sr.No.	Compound	T_c ($^{\circ}$ K)	P_c (atm.)	B_{11} ($\text{cm}^3/\text{mol}^{-1}$)
1.	n-Butanol	563.05	43.55	-2360
2.	iso-Butanol	547.78	42.39	-2634
3.	sec-Butanol	536.01	41.39	-2288
4.	tert-Butanol	506.20	39.20	-1740
5.	n-Octane	568.60	24.60	-3003
6.	EDA	319.80	62.10	-1485
7.	Toluene	318.57	40.55	-1850

R is gas constant, T_c , P_c are critical temperature and pressure, w is the accentric factor, $P_r =$ reduced pressure $= P/P_c$ and $T_r =$ reduced temperature $= T/T_c$, a and b are constants for polar compound. For non-polar compound $a = b = 0$. In the literature there are many expressions for calculating the second virial coefficient^{36,37}, but they could not be used for want of constants. The changes in the values of second virial coefficient may not affect much the calculations of the excess free energy.

The molar volumes V_1^L , for all the compounds at various temperatures are given in Table 5 and the calculated second virial coefficients along with the values of T_c and P_c used for all the compounds at 333.15 K are given in Table 6.

If the vapour phase is an ideal gas which is mostly true at low pressures, the last two terms in equations (4) and (5) become insignificant and then we have

$$\gamma_1 = \frac{y_1 P}{x_1 P_1^s} \quad \text{and} \quad \gamma_2 = \frac{y_2 P}{x_2 P_2^s} \quad (9)$$

The molar excess free energy of mixing was calculated using the equation

$$G_m^E = RT (x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \quad (10)$$

The uncertainty in G_m^E values was less than $\pm 15 \text{ J.mol}^{-1}$.

Table 7: The vapour-liquid equilibrium data
for ethanol (1) + water (2) system at 323.15 K.

Sr.No.	Liquid x_1	Vapour y_1	P (mm)	$\log \gamma_1/\gamma_2$
1.	0.0176	0.1708	101.54	0.6831
2.	0.0382	0.2861	128.74	0.6264
3.	0.0968	0.4557	157.20	0.5153
4.	0.1126	0.4900	163.40	0.5017
5.	0.2510	0.5800	189.10	0.2375
6.	0.3441	0.6190	195.87	0.1135
7.	0.4200	0.6350	201.20	-0.0032
8.	0.6186	0.7251	213.90	-0.1670
9.	0.7594	0.7937	217.80	-0.2915
10.	0.8203	0.8371	219.82	-0.3260
11.	0.9911	0.9903	221.80	-0.4151

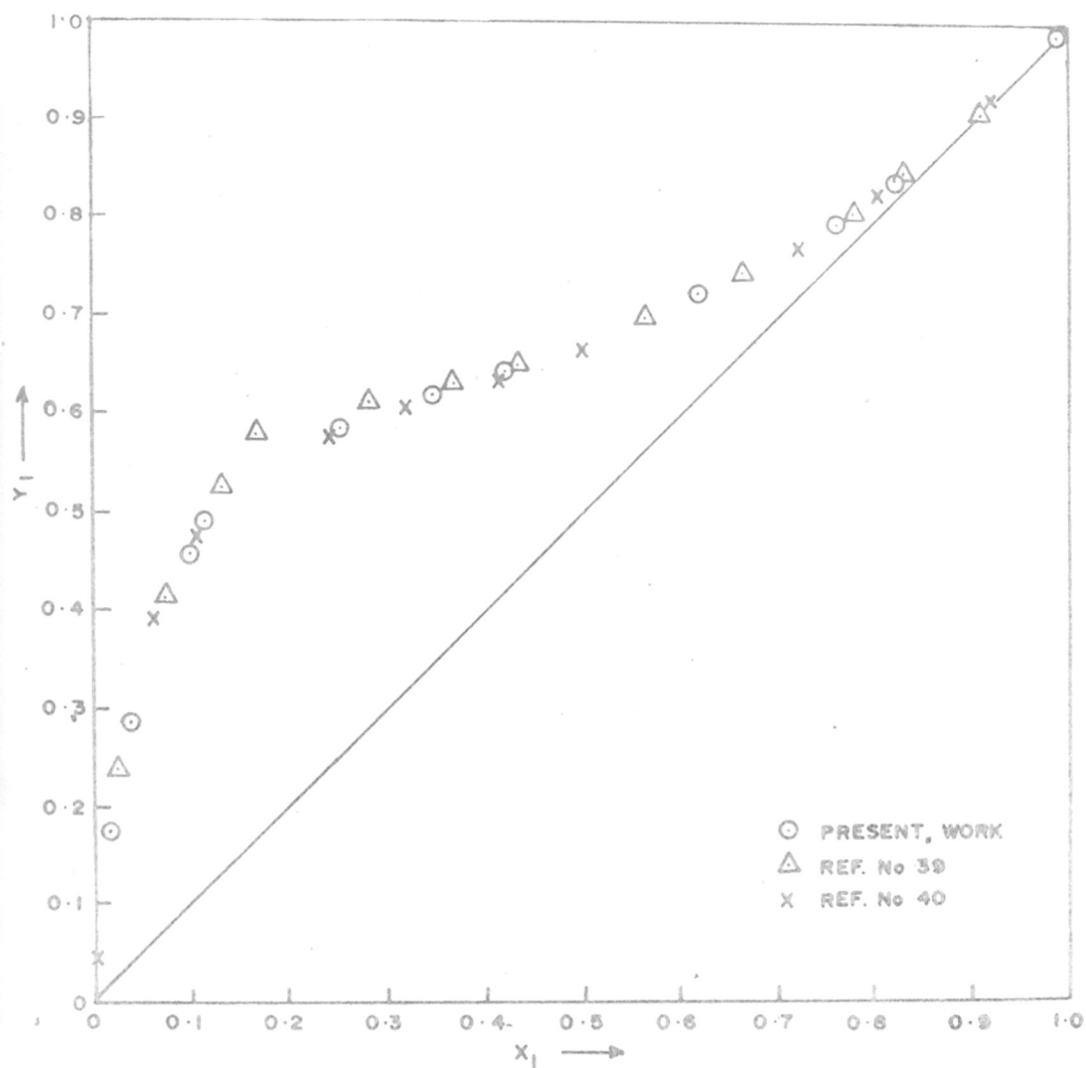


FIG. 7. X-Y DIAGRAM FOR ETHANOL(1) + WATER(2) SYSTEM AT 323.15 K

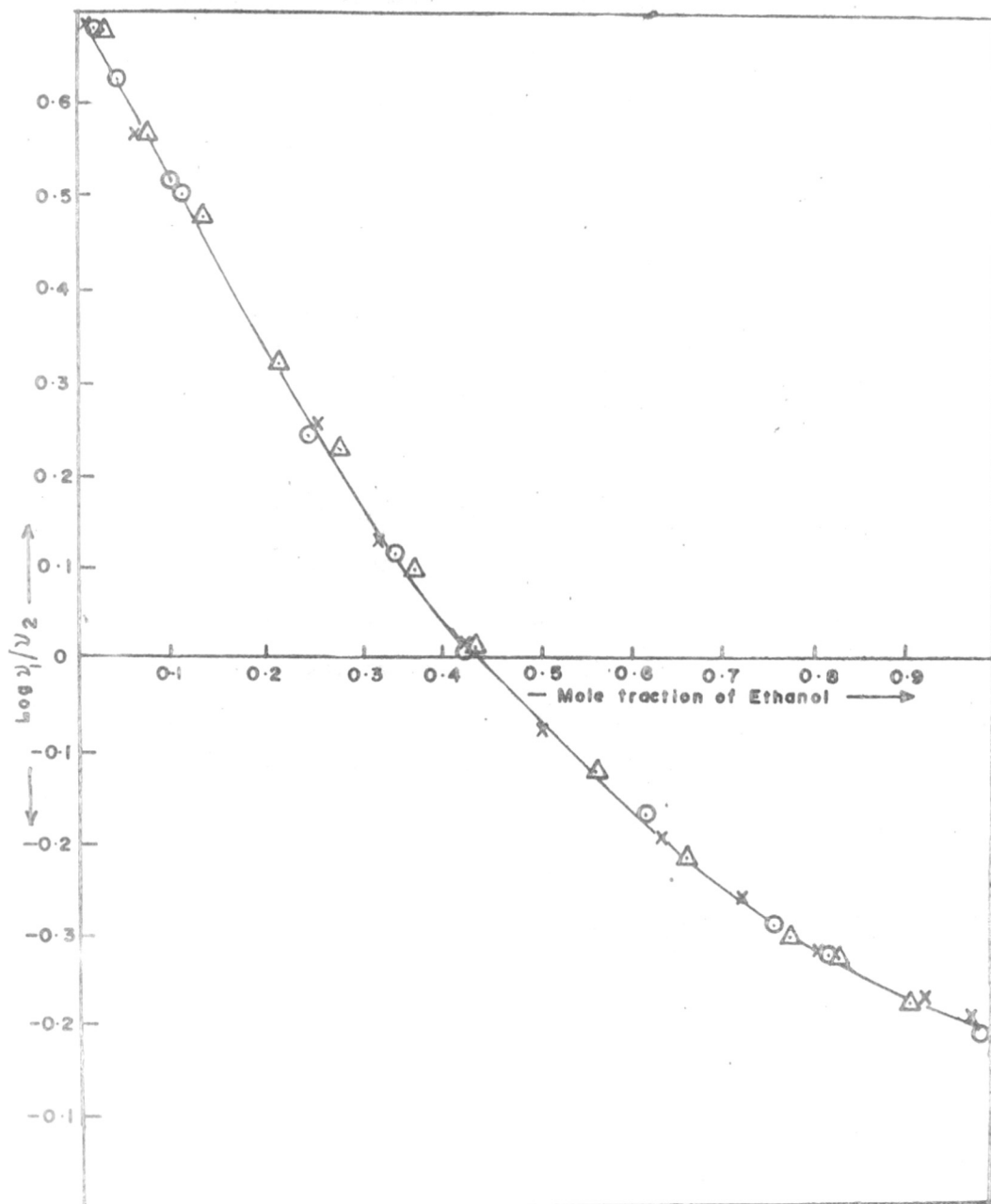


FIG 8: THERMODYNAMIC CONSISTENCY TEST FOR ETHANOL + WATER SYSTEM AT 323.15 K

Testing of equilibrium data for thermodynamic consistency

All the experimental data were checked by Harington's method³⁸ of internal thermodynamic consistency test, using equation:

$$\int_0^1 \log \frac{p_1}{p_2} dx_1 = 0 \quad (11)$$

Equation (11) indicates that the algebraic area bounded by $x = 0$ and $x = 1$ in the plot of $\log \frac{p_1}{p_2}$ vs x_1 should be zero.

The general working of Jones-Colburn still was checked by studying ethanol-water system at 323.15 K. The data is given in Table -7 and plotted in Fig.7, which agree fairly well with those reported by Datta Choudhary³⁹ and by Pemberton et al.⁴⁰. These experimental data were subjected to the above thermodynamic consistency test and agree well with the data reported earlier^{39,40} (see Fig. 8).

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CHAPTER - III
RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

The results of the excess thermodynamic properties, V_m^E and G_m^E obtained and the vapour-liquid equilibrium data for n-octane-isomeric butanols, ethylenediamine-isomeric butanols and toluene-ethylenediamine binary systems have been presented and discussed here.

a) Excess volumes of mixing, V_m^E

1) n-Octane (1) + isomeric butanol (2) systems

The excess volumes of mixing of n-, iso- and sec-butanols with n-octane were determined at 298.15 K and of tert-butanol at 299.15 K, over the entire concentration range. The results obtained are given in Tables 8, 9, 10 and 11 for all the four systems.

Gupta et al¹ have also measured the excess volumes of n-octane with n-butanol at 303.15 K, using batch dilatometer. Our results for this system at 303.15 K are given in Table 12 and plotted along with their data in Fig.10. Their values are somewhat higher than ours, for mole fraction of n-octane < 0.8. This discrepancy could not be explained. Zheng et al²⁹ have compared the results for binary mixtures of n-hexane isomers determined with single shot dilatometer with those obtained by dilution dilatometer. The values obtained by batch dilatometer are higher (about 10 times the experimental error). They also could not explain this difference.

Table 8: V_m^E of n-octane (1) + n-butanol (2)
at 298.15 K.

x_1	V_m^E ($\text{cm}^3 \cdot \text{mol}^{-1}$)	x_1	V_m^E ($\text{cm}^3 \cdot \text{mol}^{-1}$)
0.0548	0.059	0.4730	0.3088
0.1320	0.1297	0.5091	0.3059
0.1694	0.1637	0.5449	0.3166
0.2246	0.2148	0.5705	0.3166
0.2555	0.2376	0.6348	0.3172
0.3079	0.2583	0.7318	0.3182
0.3410	0.2786	0.7506	0.3135
0.3810	0.2880	0.8418	0.2883
0.4139	0.2958	0.9502	0.1492
0.4521	0.3088	0.9694	0.1059

Table 9: V_m^E of n-octane (1) + iso-butanol (2) at
298.15 K.

x_1	V_m^E (cm ³ .mol ⁻¹)	x_1	V_m^E (cm ³ .mol ⁻¹)
0.0499	0.759	0.4902	0.4183
0.1078	0.1430	0.5067	0.4233
0.2025	0.2465	0.5238	0.4284
0.2700	0.2973	0.5556	0.4345
0.3337	0.3416	0.5680	0.4338
0.3715	0.3600	0.6196	0.4362
0.3945	0.3802	0.6794	0.4263
0.4142	0.3890	0.7324	0.4124
0.4533	0.4069	0.8341	0.3326
0.4534	0.4092	0.9251	0.2150

Table 10: V_m^E of n-octane (1) + sec-butanol (2)
at 298.15 K.

x_1	V_m^E ($\text{cm}^3 \cdot \text{mol}^{-1}$)	x_1	V_m^E ($\text{cm}^3 \cdot \text{mol}^{-1}$)
0.0663	0.1253	0.4836	0.6155
0.1400	0.2654	0.5169	0.6195
0.2047	0.3766	0.5458	0.6236
0.2765	0.4742	0.6284	0.6118
0.3453	0.5413	0.7049	0.5854
0.3740	0.5644	0.7317	0.5680
0.4107	0.5862	0.8748	0.3948
0.4386	0.5991	0.9429	0.2260
0.4403	0.5999	0.9529	0.1905

Table 11: V_m^E of n-octane (1) + tert-butanol (2)
at 299.15 K.

x_1	V_m^E ($\text{cm}^3 \cdot \text{mol}^{-1}$)	x_1	V_m^E ($\text{cm}^3 \cdot \text{mol}^{-1}$)
0.0241	0.1203	0.4244	1.0160
0.0685	0.3197	0.4337	1.0200
0.1086	0.4857	0.4517	1.0120
0.1637	0.6730	0.5107	0.9640
0.2230	0.8388	0.5870	0.9257
0.2844	0.9424	0.6803	0.8102
0.3490	1.0010	0.7697	0.7042
0.3696	1.0116	0.8686	0.5368
0.3789	1.0150	0.9581	0.2339

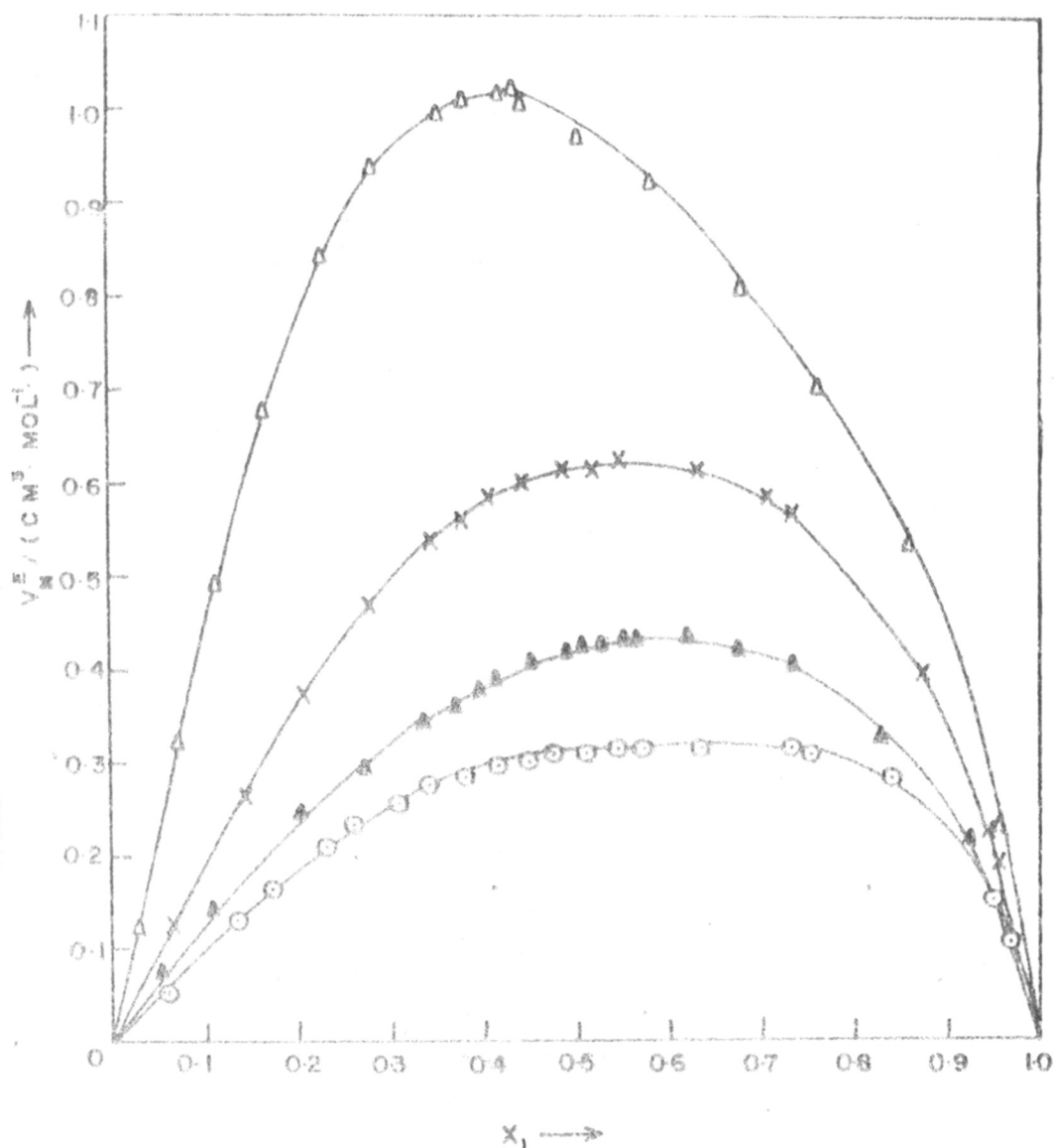


FIG. 9. EXCESS VOLUMES FOR *n*-OCTANE (1) + isomeric -BUTANOL (2) SYSTEMS AT 298.15 K

O - *n*-BUTANOL, ▲ - iso-BUTANOL, X - sec-BUTANOL, △ - tert-BUTANOL

Table 12: The excess volumes of mixing for n-octane (1) +
n-butanol (2) at 303.15 K.

Sr.No.	Mole fraction x_1	V_m^E ($\text{cm}^3 \cdot \text{mol}^{-1}$)
1.	0.0631	0.0561
2.	0.1146	0.0993
3.	0.1597	0.1360
4.	0.2085	0.1748
5.	0.2555	0.2095
6.	0.2897	0.2308
7.	0.3034	0.2490
8.	0.3264	0.2525
9.	0.3274	0.2658
10.	0.3590	0.2893
11.	0.3764	0.2951
12.	0.4070	0.3118
13.	0.4128	0.3186
14.	0.4612	0.3323
15.	0.5208	0.3539
16.	0.6020	0.3670
17.	0.7064	0.3565
18.	0.8090	0.2998
19.	0.9238	0.1903

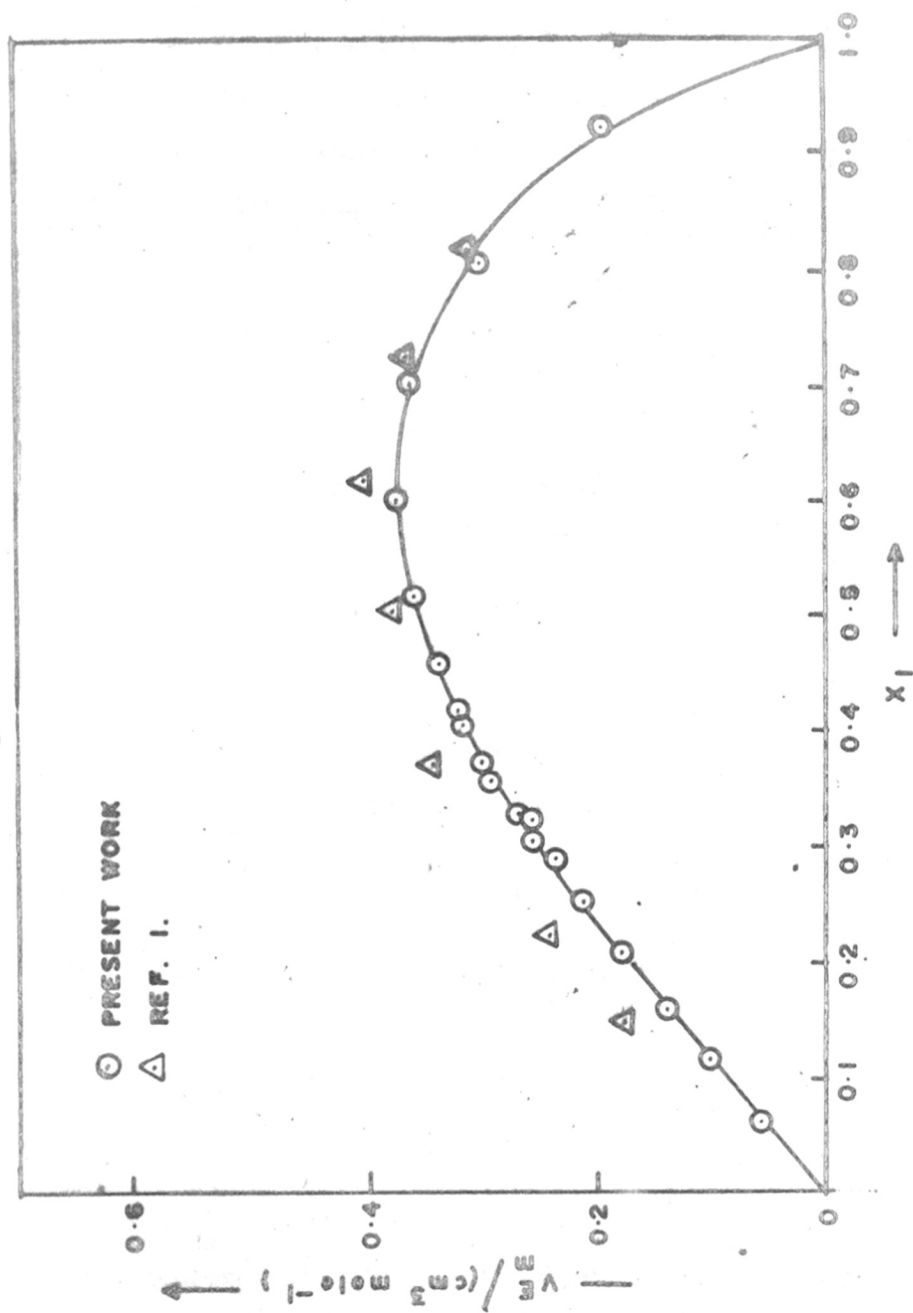


FIG. 10. EXCESS VOLUMES FOR n-OCTANE (1)+n-BUTANOL (2) AT 303.15

In general, all the experimental values of the excess thermodynamic functions, X_m^E (V_m^E and G_m^E) for binary liquid mixtures were fitted to Redlich-Kister² type polynomial equation.

$$X_m^E = x_1 (1-x_1) \sum_{k=0}^n A_k (2x_1-1)^k \quad (1)$$

where X_m^E represents any excess thermodynamic function, x_1 is the mole fraction of component 1, A_{ks} are the fitting parameters and n is the number of parameters preferably used. The A_k values can be obtained by a least square method, using suitable computer programme. With a proper choice of n , equation (1) can fit the experimental and derived results as accurately as desired, provided that the number of data points is not less than n . In most cases equation (1) with three parameters fits the data satisfactorily. We have employed the four-parameter equation for fitting the experimental V_m^E data, and is given by

$$V_m^E = x_1 (1-x_1) [A_0 + A_1 (2x_1-1) + A_2 (2x_1-1)^2 + A_3 (2x_1-1)^3] \dots \quad (2)$$

Equation (2) is a special case of equation (1).

The standard deviation σ for each system was calculated by the equation

$$\sigma = \sqrt{\frac{\sum_{k=1}^N (\Delta V)^2}{N-n}} \quad (3)$$

where $\Delta V = V_M^E$ (calc) - V_M^E (expt.)

N = number of experimental points

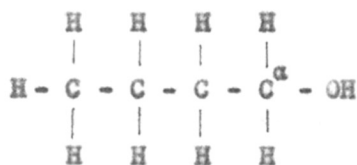
n = number of parameters used in the fitting ($n=4$).

The values of constants along with standard deviation, σ , are summarised in Table 19 for all the systems.

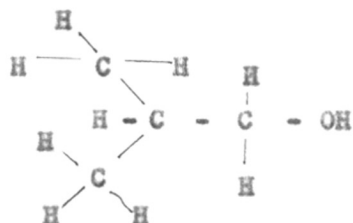
In Fig.9, the experimental values of V_M^E as a function of mole fraction of component 1 (x_1) are plotted together with the smooth curves calculated by means of equation (2), based on the appropriate values of parameters found in Table 19, for all the n-octane-isomeric butanol systems. It is clear from Fig.9 that V_M^E values are positive throughout the concentration range for all the four systems. This excess volume behaviour and the corresponding partial molar excess volumes of both the components can be interpreted³ in terms of a balance of three basic contributions: Chemical - due to breaking of H-bonds, physical - due to disruption of alkanol and alkane molecular order and so-called structural - due to interstitial accommodation steric effect, free volumes and/or the hole structure of liquids. It is known that the aliphatic alcohols contain both electron acceptor and electron donor groups and therefore strongly

associated due to hydrogen bonding⁴. These associated species are broken on dilution with a non-polar solvent, giving positive contribution to excess volumes.

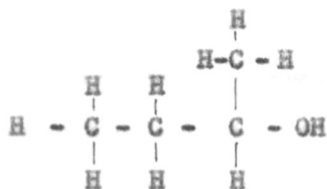
The physical contribution is due to non-specific interactions between n-octane molecules and the alcohol monomers and multimers which form a highly polar mixture. The mixing process disrupts the order of both alcohol and alkane. Thus in addition to the chemical effect of H-bond breaking, the disruption of the orientational order of molecules make a significant contribution to excess volumes. The general structure of isomeric butanols is shown below:



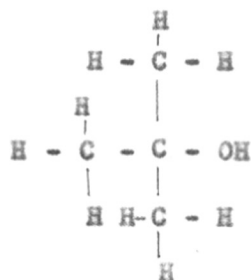
n-butanol



iso-butanol



sec-butanol



tert-butanol

The n-butanol molecules are linear and planar similar to those of n-octane. The molecular alignment of these molecules on mixing is therefore likely to be ordered due to Vander Waal's forces. The tert-butanol molecules, on the contrary are bulky and spherical and on mixing with n-octane these molecules are likely to be more randomly distributed indicating higher V_m^E . The values of V_m^E for iso- and sec-butanols are expected to be in between n- and tert-butanols.

The branching of the alkyl chain of alcohols has a considerable effect on the volume change of mixing. Due to the steric effect, the change in magnitude and symmetry is observed among the curves with the branching of alcohol. The maximum shifts towards the higher mole fraction of alcohol as the substitution of methyl group shifts towards the α -carbon atom. Thus the maximum excess volumes for n, iso, sec and tert-butanols are obtained nearly at 0.3, 0.35, 0.40 and 0.60 mole fractions of the respective alcohols. Anilkumar et al⁵ have studied the excess volumes of isomeric butanols with n-heptane and with benzene by Brown et al⁶ at 25°C. They also obtained the maxima at nearly the same mole fractions of alcohols.

The V_m^E vs x_1 curves (Fig. 9) suggest the probable stoichiometry of interactions. The higher polymeric species

decrease as the substitution of the methyl group approaches the α -carbon atom, while the steric hindrance increases as we go from iso to sec to tert-butanol. Thus the magnitude of the excess volumes for n-octane-isomeric butanols changes in the following order:



Anilkumar et al⁵ and Brown and Smith⁶ have also noted the same trend for these alcohols.

When the values of V_m^E/x_1x_2 vs x_1 are plotted and the extrapolated values of $x_1 \rightarrow 0$ and $x_2 \rightarrow 0$ give the partial excess molar volumes $V_m^{E,\infty}$ of both the components at infinite dilution. It is evident from equation (2) that the values of $(A_0 + A_1 + A_2 + A_3)$ and $(A_0 - A_1 + A_2 - A_3)$ represent the terminal values of V_m^E/x_1x_2 at $x_1 = 0$ and $x = 1$. Thus they are equivalent to the partial molar excess volumes of components 2 and 1 respectively⁷. The values of partial molar excess volumes of both the components (extrapolated from graph and calculated from least square constants) and the values of $(V_m^E)_{x_1 = x_2}$ ($= 0.25 A_0$) are given in Table 20.

Actually the results of V_m^E in the range $x < 0.1$ are needed to estimate the limiting behaviour of the alcohol in the mixture. The results of Kumaran and Benson⁸ and

Treszcsanowicz - Benson⁹ for n-butanol - n-heptane show that the partial excess molar volumes $V_1^{E,\infty}$, in both extrapolated from experimental values in the low x region and calculated from least square parameters are in agreement with each other. (Ref. 8 $V_1^{E,\infty} = 6.08 \pm 0.32$; Ref. 9 $V_1^{E,\infty} = 6.3$). $V_1^{E,\infty}$ values obtained from our systems seems to be reasonable even though the extrapolation has been done from the higher x region. Our values of partial molar excess volumes are precise enough to give a general idea about the trend in $V_1^{E,\infty}$. As seen from Table 20, the trend in $V_1^{E,\infty}$ is the same as obtained in the case of excess molar volumes. This means that both V_m^E and $V_1^{E,\infty}$ are affected by the structure and the extent of H-bonding of pure molecules.

2) Ethylenediamine (1) + isomeric butanol (2) systems

The excess volumes for each of the four isomeric butanols with ethylenediamine (EDA) were obtained at 298.15 K except that of tert-butanol at 299.15 K. The results are tabulated in Tables 13 to 16 and plotted as function of x_1 , the mole fraction of EDA in Fig.11 along with the smooth curve obtained from appropriate parameters in Table 19. The least square constants were calculated by fitting the experimental data to equation (2), and are tabulated in Table 19 along with σ .

Rao et al^{10,15,16} have studied the excess volumes

Table 13: V_m^E of EDA (1) + n-butanol (2) at 298.15 K

x_1	V_m^E (cm ³ .mol ⁻¹)	x_1	V_m^E (cm ³ .mol ⁻¹)
0.0344	-0.1870	0.5125	-0.8060
0.1494	-0.6412	0.5384	-0.7704
0.2535	-0.8748	0.5629	-0.7363
0.3110	-0.9333	0.5854	-0.6952
0.3695	-0.9392	0.5998	-0.6740
0.4093	-0.9198	0.6421	-0.5992
0.4394	-0.8935	0.7111	-0.4791
0.4578	-0.8762	0.7667	-0.3760
0.4785	-0.8558	0.8282	-0.2611
0.4906	-0.8403	0.9470	-0.0765

Table 14: V_m^E of EDA (1) + iso-butanol (2) at 298.15 K.

x_1	V_m^E (cm ³ .mol ⁻¹)	x_1	V_m^E (cm ³ .mol ⁻¹)
0.0394	-0.2319	0.5142	-0.8877
0.1404	-0.6633	0.5305	-0.8741
0.2049	-0.8772	0.5633	-0.8171
0.2671	-0.9871	0.6008	-0.7478
0.3217	-1.0329	0.6492	-0.6374
0.3474	-1.0993	0.7240	-0.5762
0.4046	-1.0240	0.7663	-0.4287
0.4585	-1.9637	0.8247	-0.3181
0.4670	-0.9621	0.8626	-0.2420
0.4970	-0.9240	0.9563	-0.0726

Table 15: V_m^E of EDA (1) + sec-butanol (2) at 298.15K.

x_1	V_m^E ($\text{cm}^3 \cdot \text{mol}^{-1}$)	x_1	V_m^E ($\text{cm}^3 \cdot \text{mol}^{-1}$)
0.0302	-0.0928	0.5143	-0.5404
0.1420	-0.3745	0.5241	-0.5348
0.2516	-0.5476	0.5526	-0.5070
0.3167	-0.6035	0.5907	-0.4707
0.3628	-0.6147	0.6387	-0.4136
0.4175	-0.6028	0.7018	-0.3418
0.4463	-0.5922	0.7711	-0.2587
0.4566	-0.5795	0.8229	-0.1975
0.4839	-0.5639	0.8778	-0.1295
0.4905	-0.5608	0.9484	-0.0501

Table 16: V_m^E of EDA (1) + tert-butanol (2) at 299.15K

x_1	V_m^E (cm ³ .mol ⁻¹)	x_1	V_m^E (cm ³ .mol ⁻¹)
0.0570	-0.2152	0.5446	-0.5946
0.1752	-0.5072	0.5691	-0.5850
0.2633	-0.6223	0.5921	-0.5564
0.3103	-0.6645	0.6095	-0.5679
0.3900	-0.6737	0.6527	-0.4954
0.4523	-0.6632	0.7140	-0.4229
0.4715	-0.6552	0.7987	-0.3099
0.5010	-0.6438	0.8872	-0.1825
0.5329	-0.6118	0.9516	-0.0758

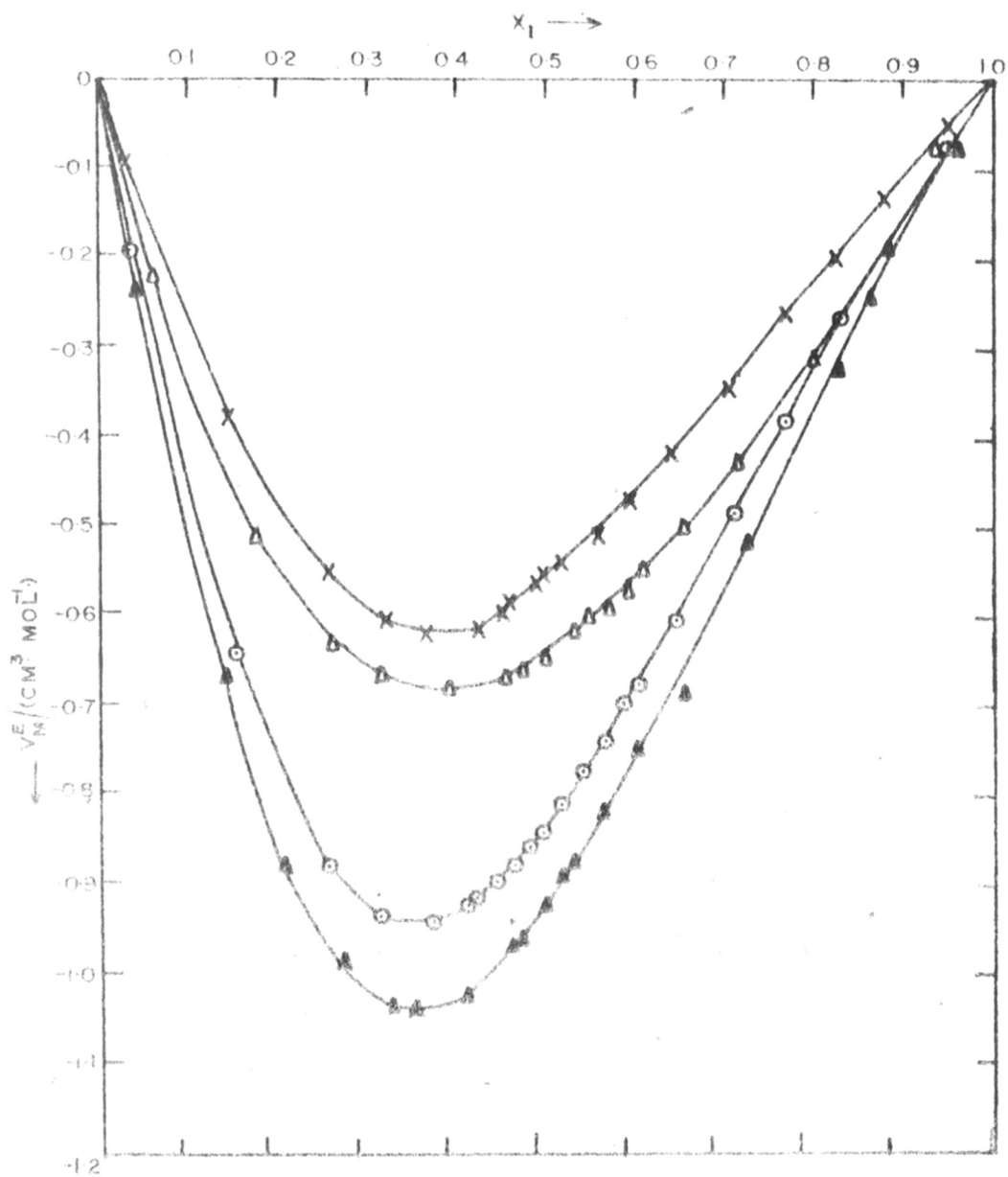


FIG. II EXCESS VOLUMES FOR EDA (1) + isomeric-BUTANOL (2) SYSTEM AT 298.15 K

\circ -n-BUTANOL, \blacktriangle -iso-BUTANOL, \times -sec-BUTANOL, \triangle -tert-BUTANOL.

Table 17: The excess volumes of mixing for EDA (1) +
sec-butanol (2) at 303.15 K.

Sr.No.	Mole fraction x_1	V_m^E ($\text{cm}^3 \cdot \text{mol}^{-1}$)
1.	0.0592	-0.1803
2.	0.1364	-0.3711
3.	0.2294	-0.5313
4.	0.2862	-0.5860
5.	0.3561	-0.6115
6.	0.3948	-0.6191
7.	0.4364	-0.6035
8.	0.4646	-0.5772
9.	0.4929	-0.5640
10.	0.5133	-0.5463
11.	0.5577	-0.5063
12.	0.6031	-0.4574
13.	0.6797	-0.0715
14.	0.7472	-0.2896
15.	0.8383	-0.1778
16.	0.9262	-0.0750

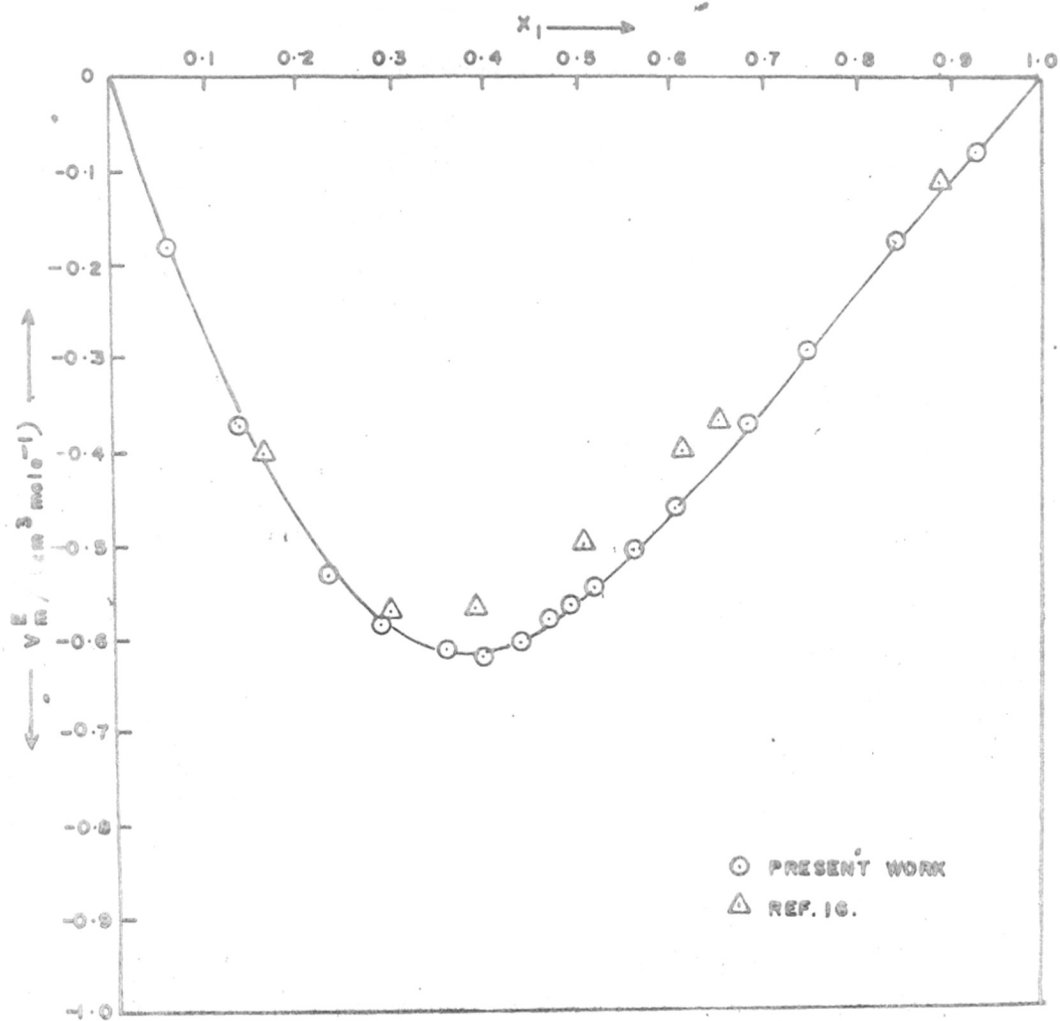


FIG. 12. EXCESS VOLUMES FOR EDA (1) + SEC - BUTANOL (2) SYSTEM AT 303.15 K

of n-, iso and sec-butanol with EDA at 303.15 K, using batch dilatometer. Our results for EDA-sec-butanol system at 303.15 K are presented in Table 17 and plotted in Fig. 12 together with their data¹⁶. Our results are more negative than theirs which may be due to that they have not applied compression corrections and also their apparatus is batch dilatometer whereas ours is a continuous dilution dilatometer. No data is reported for tert-butanol-EDA system in the literature.

It can be seen from the Fig.11 that the V_m^E for EDA-isomeric butanols are negative throughout the mole fraction range. The explanation for these results can be given in terms of two opposing effects: (a) mutual breaking of O - H ...O and N-H ...N bonds present in the self-associated alcohol and diamine, (b) formation of O-H... N bonds between unlike molecules. The former effect will contribute to expansion and the latter effect will lead to contraction. Actual V_m^E will depend upon the balance between these two contributions. The negative experimental values suggest that the latter effect is dominant in the mixture. Hence O-H...N bond is stronger than O-H ...O and N-H... N bonds, in the binary mixtures. This analogy of complex formation receives the support from the work of many authors¹⁰⁻¹⁴.

Pure butanols contain mainly multimers with cyclic and linear associated species. Diamine also contains both

electron donor as well as acceptor groups. On addition of amine to alcohol it forms a mixed associated species due to H-bonding between unlike molecules, giving negative excess volumes.

The curves in Fig.11 show that for n and iso-butanols the minima in V_M^E occur for x_1 between 0.3 and 0.4. This suggests that EDA forms 1:2 complex with alcohols i.e. two amino groups of EDA molecule simultaneously bind two molecules of alcohol. This view is supported by the work of Rao and Naidu¹⁰. The minima are slightly shifted to the side of higher concentration of EDA, for sec and tert-butanols, due to bulkier groups.

The absolute values of V_M^E for the four systems fall in the sequence of



Rao and others^{10,15,16} results are in the order of



Our sequence is in agreement with theirs. This order suggests that the branching of alcohol molecules decreases both self-association of alcohols and the association of unlike molecules. Here, actual trend should be



which is exactly opposite of the alcohol-alkane systems. But the experimental results show that the excess volumes of iso-butanol are more negative than n-butanol and tert-butanol values are also higher than the sec-butanol. This effect may be due to the interstitial accommodation (geometric fitting) of EDA molecules between the symmetrically branched iso- and tert-butanol molecules.

The partial molar excess volumes obtained (from the extrapolation and calculations) are given in Table 20 for all the systems along with $(V_m^E)_{x_1 = 0.5}$. The values of $V_1^{E, \infty}$ for all the isomeric butanols follow the sequence:

$$\text{iso} > \text{n-} > \text{tert} > \text{sec}$$

This trend is similar to that of excess volumes.

Thus V_m^E results for EDA-isomeric butanols show that complex formation takes place between unlike molecules and specific interactions are involved. The steric effect is also predominant in these systems.

3) Toluene(1) + EDA (2) system

The excess volumes for this system were measured at 303.15 K over the entire composition range. The results are tabulated in Table 18. Rao et al¹⁷ have also studied the excess volumes of toluene-EDA system at 303.15 K, using batch dilatometer. Our results are plotted in Fig.13,

Table 18: The excess volumes of mixing for
Toluene (1) + EDA (2) system at 303.15K

Sr.No.	Mole fraction x_1	V_m^E ($\text{cm}^3 \cdot \text{mol}^{-1}$)
1.	0.1235	0.1367
2.	0.2035	0.2103
3.	0.2883	0.2841
4.	0.3440	0.3391
5.	0.4248	0.3926
6.	0.4609	0.3974
7.	0.4740	0.4126
8.	0.5191	0.4316
9.	0.5403	0.4382
10.	0.5596	0.4436
11.	0.6193	0.4456
12.	0.7260	0.4332
13.	0.8690	0.3125

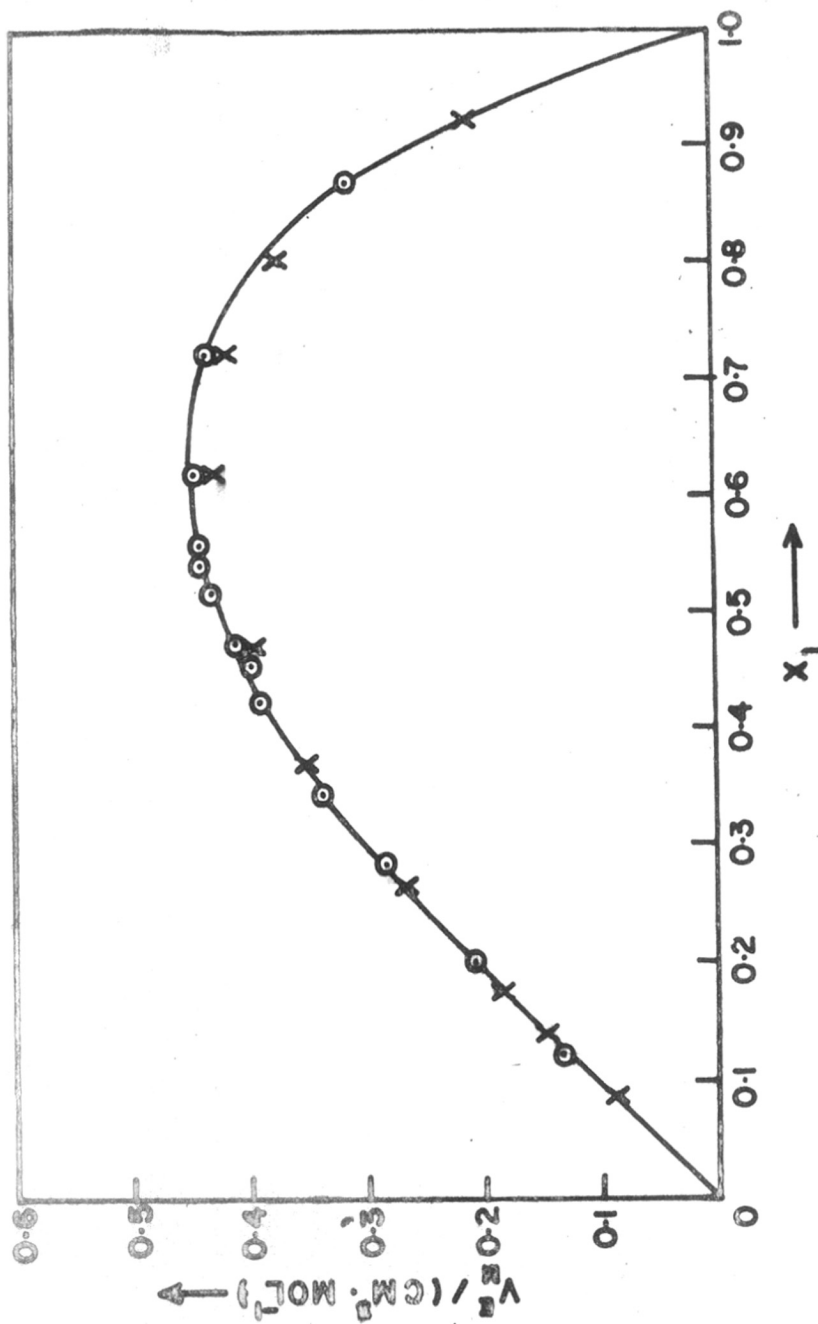


FIG 13 EXCESS VOLUMES FOR TOLUENE(1) + EDA(2) AT 303.15 K

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Table 19: The Least Square Constants in the V_M^E equation for all the systems.

$$V_M^E (\text{cm}^3/\text{mole}) = x_1 x_2 [A_0 + A_1 (x_2 - x_1) + A_2 (x_2 - x_1)^2 + A_3 (x_2 - x_1)^3]$$

System	A_0	A_1	A_2	A_3	(Std. dev.)
n-Octane (1) + n-butanol (2)	1.20431	0.12923	1.13988	1.34271	0.0068
n-Octane (1) + iso-butanol (2)	1.66108	0.52662	0.84890	0.47106	0.006
n-Octane (1) + sec-butanol (2)	2.46515	0.32589	0.78203	1.14912	0.0015
n-Octane (1) + tert-butanol (2)	3.90869	-1.31543	1.78956	2.04590	0.007
EDA (1) + n-butanol (2)	-3.31614	2.59117	-0.26533	-0.43933	0.0045
EDA (1) + iso-butanol (2)	-3.68218	2.79149	-0.29808	-0.53253	0.008
EDA (1) + sec-butanol (2)	-2.22997	1.51243	0.13914	-0.42355	0.0045
EDA (1) + tert-butanol (2)	-2.54138	1.24712	-0.38470	0.06804	0.0044
Toluene (1) + EDA (2)	1.68499	0.80037	0.56259	0.38054	0.0047

Table 20: The partial molar excess volumes of both the components and $(V_M^E/x_1=x_2)$ for all the systems.

System	$V_1^E, \infty (x_1 \rightarrow 0)$	$V_2^E, \infty (x_2 \rightarrow 0)$	$(V_M^E)_{x_1=x_2}$
	($\text{cm}^3 \cdot \text{mol}^{-1}$)	($\text{cm}^3 \cdot \text{mol}^{-1}$)	($\text{cm}^3 \cdot \text{mol}^{-1}$)
	Extrapolated	Calculated	Extrapolated
	Calculated	Calculated	Calculated
n-Octane (1) + n-butanol (2)	0.92	0.87	3.81
n-Octane (1) + iso-butanol (2)	1.52	1.52	3.50
n-Octane (1) + sec-butanol (2)	1.86	1.77	4.72
n-Octane (1) + tert-butanol (2)	4.98	4.77	6.43
EDA (1) + n-butanol (2)	-5.82	-5.73	-1.43
EDA (1) + iso-butanol (2)	-6.66	-6.70	-1.72
EDA (1) + sec-butanol (2)	-3.90	-4.01	-1.0
EDA (1) + tert-butanol (2)	-4.44	-4.09	-1.6
Toluene (1) + EDA (2)	1.13	1.06	3.43
Toluene (1) + Butylamine (2)	-	-	-
			0.3011
			0.4152
			0.6162
			0.9771
			-0.8290
			-0.9205
			-0.5575
			-0.6353
			0.4212
			0.156

along with their data. Their results are slightly lower than ours. This may be due to the fact that the compression correction have not been taken into account by them.

The excess volumes data were least square fitted to equation (2). The fitting parameters along with σ are included in Table 19. The values of V_M^E show that the excess volumes are positive over the entire range of composition for this system.

Ethylenediamine exhibits self-association due to hydrogen bonding in pure state¹⁸. The two amino groups in the amine presumably tend to participate in specific interactions with toluene. The V_M^E values suggest that expansion in volume due to break up of EDA aggregates by toluene might exceed the contraction in volume due to N-H ... π interactions between unlike molecules. Reduction in dipolar interactions between amine monomers and size difference might also augment expansion in volume.

The partial molar excess volumes obtained are given in Table 20 for both the components. The positive value of V_M^E ($x=0.5$) as shown in Table 20 is larger than that for n-butylamine + toluene¹⁹. This suggests that EDA might be associated to a greater extent in the pure state than n-butylamine.

b) Excess free energy of mixing, G_m^E

Isothermal vapour-liquid equilibrium (VLE) data were obtained at 333.15 K for all the nine binary systems studied. In addition, for toluene-EDA system isobaric VLE data were also collected at 712.00 mm (atmospheric pressure). The excess free energy of mixing for all the systems were calculated from the isothermal VLE data obtained at 333.15 K. No G_m^E data are reported in literature for the systems mentioned above.

1) n-Octane (1) + isomeric butanol (2) systems

The experimental VLE data for binary systems of n, iso, sec and tert-butanol with n-octane at 333.15 K are given in Tables 21, 22, 23 and 24 respectively. x_1 is the mole fraction of n-octane in liquid and y_1 is the corresponding mole fraction in vapour phase. P_1 and P_2 are the pure component vapour pressures at 333.15 K. P denotes the total pressure of the system in mm Hg. The activity coefficients γ_1 and γ_2 of both the components were calculated using equations 4 and 5 given in Chapter II(b). These values indicate the measure of non-ideality of the liquid mixture as they depart from unity. The values of G_m^E in column 7 were calculated by the equation 10 given in Chapter II(b) for all the systems. The last column denotes the so-called volatility ratio

Table 21: The vapour-liquid equilibrium data for
n-octane (1) + n-butanol (2) system at 333.15K.

Sr. No.	$P_1 = 78.6 \text{ mm}$			$P_2 = 59.2 \text{ mm}$			
	Liquid x_1	Vapour y_1	P mm.Hg	Activity coeff.		G_m^E $J.mol^{-1}$	Volatalit: ratio
				γ_1	γ_2		
1.	0.0359	0.2075	72.22	5.3159	1.0013	170	7.031
2.	0.0525	0.2601	76.80	4.8542	1.0105	258	6.344
3.	0.1234	0.4159	91.71	3.9357	1.0283	536	5.059
4.	0.1725	0.4800	99.61	3.5151	1.0523	717	4.428
5.	0.2599	0.5226	105.87	2.6971	1.1472	996	3.117
6.	0.3580	0.5534	110.13	2.1555	1.2863	1209	2.222
7.	0.4742	0.5784	112.30	1.7337	1.5115	1324	1.54
8.	0.5877	0.6002	112.72	1.4570	1.8347	1306	1.053
9.	0.6557	0.6117	112.35	1.3266	2.1268	1233	0.827
10.	0.7255	0.6293	110.93	1.2181	2.5124	1097	0.643
11.	0.7883	0.6448	109.64	1.1356	3.0889	939	0.487
12.	0.8297	0.6569	107.40	1.0771	3.6343	779	0.393
13.	0.8802	0.6892	105.50	1.0473	4.5943	619	0.302
14.	0.9266	0.7264	102.10	1.0147	6.3962	415	0.2103
15.	0.9450	0.7599	98.83	1.0080	7.2536	323	0.184
16.	0.9670	0.8390	90.48	0.9970	7.4290	175	0.178

Table 22: The vapour-liquid equilibrium data for
n-octane (1) + iso-butanol (2) system at 333.15K.

$$P_1 = 78.6 \text{ mm}$$

$$P_2 = 92.4 \text{ mm}$$

Sr.No.	Liquid x_1	Vapour y_1	P mm.Hg	Activity Coeff.		G_m^E J.mol ⁻¹	Volatility ratio
				γ_1	γ_2		
1.	0.0093	0.0372	96.61	4.9158	1.015	83	4.116
2.	0.0305	0.1107	102.07	4.7126	1.012	173	3.950
3.	0.1394	0.3171	123.0	3.5592	1.0521	611	2.867
4.	0.2250	0.3859	130.64	2.8279	1.1147	881	2.164
5.	0.3000	0.4168	133.74	2.3440	1.1993	1060	1.667
6.	0.4791	0.4695	135.8	1.6807	1.4904	1231	0.962
7.	0.5383	0.4808	135.00	1.5553	1.6047	1245	0.827
8.	0.6405	0.5073	132.68	1.3259	1.9575	1170	0.578
9.	0.6565	0.5127	131.23	1.2940	2.0028	1130	0.551
10.	0.6710	0.5161	130.20	1.2640	2.0622	1095	0.522
11.	0.7096	0.5389	129.60	1.2236	2.1825	1024	0.478
12.	0.8095	0.5835	119.06	1.0852	2.8072	728	0.330
13.	0.8341	0.5983	117.00	1.0656	3.0561	660	0.296
14.	0.8920	0.6602	109.62	1.0274	3.7242	460	0.235
15.	0.9450	0.7574	98.92	1.006	4.7176	251	0.181
16.	0.9600	0.7879	96.25	1.0014	5.5210	196	0.155

Table 23: Vapour Liquid Equilibrium data for n-octane (1) +
sec-butanol (2) at 333.15 K.

S.No.	Liquid x_1	Vapour y_1	P mm	Activity Coefficient		G^E J.mole ⁻¹	α
				γ_1	γ_2		
			$P_1 = 78.6$ mm	$P_2 = 135.8$ mm			
1.	0.0392	0.0953	149.40	4.5407	1.0275	236	2.581
2.	0.0640	0.1370	151.56	4.0819	1.0272	319	2.321
3.	0.1155	0.2033	155.33	3.4379	1.0280	463	1.954
4.	0.1837	0.2555	159.58	2.7891	1.0688	672	1.525
5.	0.2445	0.2879	162.14	2.3982	1.1220	833	1.249
6.	0.3097	0.3177	162.30	2.0913	1.1777	946	1.038
7.	0.3922	0.3426	162.30	1.7808	1.2887	1054	0.807
8.	0.4808	0.3643	160.82	1.5309	1.4458	1105	0.619
9.	0.5847	0.3864	159.60	1.3254	1.7317	1088	0.447
10.	0.6400	0.4073	158.82	1.2703	1.9204	1075	0.386
11.	0.7421	0.4519	151.30	1.1592	2.3636	918	0.286
12.	0.7936	0.4737	144.83	1.0888	2.7166	758	0.238
13.	0.8630	0.5228	137.13	1.0475	3.5168	588	0.174
14.	0.9196	0.6187	118.34	1.0070	4.1410	334	0.142
15.	0.9490	0.6931	108.53	1.0040	4.8243	233	0.121
16.	0.9830	0.8441	92.06	1.0038	6.2440	97	0.094

Table 24: Vapour Liquid Equilibrium data for n-octane (1) + tert-butanol (2) at 333.15 K

$P_1 = 78.6 \text{ mm}$ $P_2 = 289.6 \text{ mm}$

Sr.No.	Liquid x_1	Vapour y_1	P_{mm}	Activity Coefficient γ_1	Activity Coefficient γ_2	$G_m^E \text{ J.mol}^{-1}$	α
1.	0.0159	0.0187	290.51	4.2085	1.0002	64	1.179
2.	0.0554	0.0506	289.33	3.2556	1.0042	192	0.9087
3.	0.1372	0.1080	284.51	2.7607	1.0161	424	0.7614
4.	0.2130	0.1452	280.20	2.3565	1.0518	616	0.6276
5.	0.3263	0.1846	273.87	1.9133	1.1462	841	0.4674
6.	0.4097	0.2053	266.70	1.6521	1.2424	925	0.3722
7.	0.4616	0.2200	261.43	1.5416	1.3111	957	0.3290
8.	0.5450	0.2424	249.56	1.3737	1.4387	938	0.2671
9.	0.6260	0.2632	236.92	1.2370	1.6192	868	0.2164
10.	0.7152	0.2857	224.57	1.1162	1.9561	747	0.1593
11.	0.8360	0.3400	200.03	1.0160	2.7990	504	0.1010
12.	0.8778	0.3866	182.41	1.006	3.1918	407	0.0877
13.	0.9031	0.4168	172.93	1.0009	3.6312	348	0.0767
14.	0.9410	0.5231	142.81	1.0002	4.0381	229	0.0688
15.	0.9800	0.7652	101.80	1.007	4.1960	100	0.0665

(or relative volatility), which is defined as

$$\alpha = \frac{(y_1/y_2)}{(x_1/x_2)} \quad (4)$$

The α or K-ratio is of practical importance as a measure of separability of components of a mixture of distillation or fractionation processes.

The x-y diagrams for n-octane-isomeric butanols are plotted in Fig. 14. The pressure composition curves (P-x,y) for all the systems are shown in Figs. 15 and 16.

The x-y diagrams are 'S' shaped. Both x-y and P-x,y curves show the presence of azeotropes (x=y at azeotropic point). The mole fraction of n-octane, x_1 at which the azeotropes are formed are listed in Table 31 for all the systems.

The accuracy of the VLE data of all the systems was checked by Harington's internal thermodynamic consistency test²⁰. The plots of $\log \gamma_1/\gamma_2$ vs x_1 for these four systems are shown in Figs. 17 and 18. The data were found to be thermodynamically consistent (better than 1.5, 3, 1.8 and 2% for n, iso, sec and tert-butanol systems respectively).

The G_m^E vs x_1 plots for all the four systems are given in Fig.19, for ready comparison.

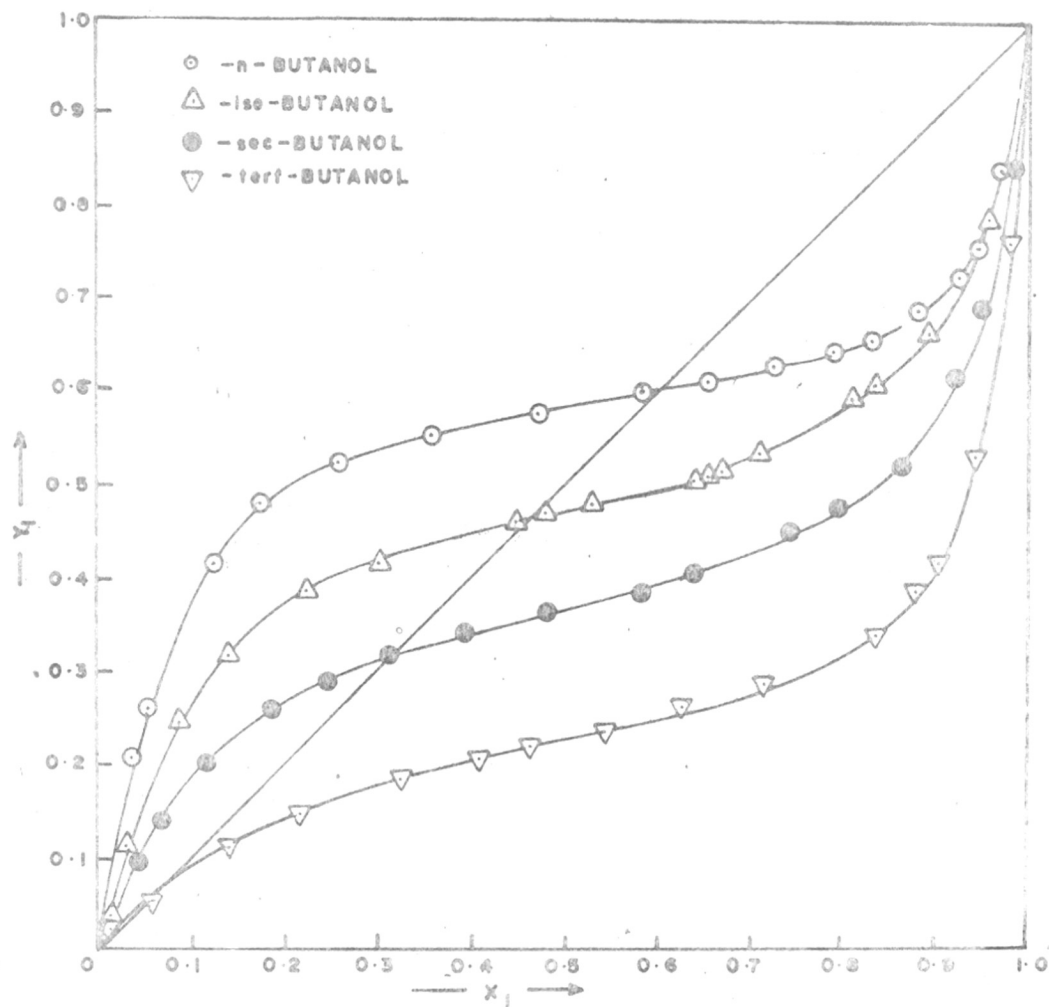


FIG. 14. X-Y DIAGRAM FOR n-OCTANE (1) + ISOMERIC BUTANOL (2) AT 333.15 K

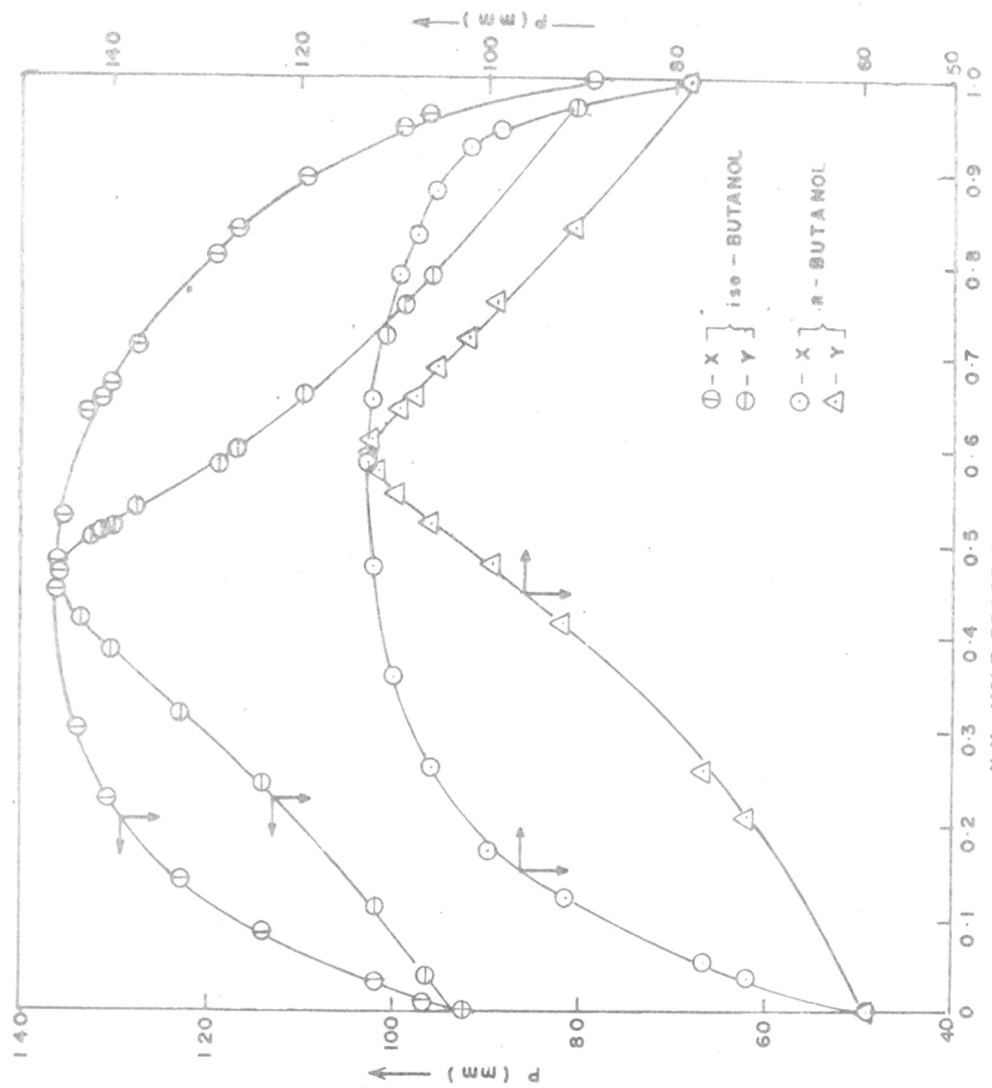


FIG. 15. P-x,y DIAGRAM FOR n-OCTANE (1)-n-BUTANOL (2), AND n-OCTANE (1)-iso-BUTANOL (2) AT 333.15 K

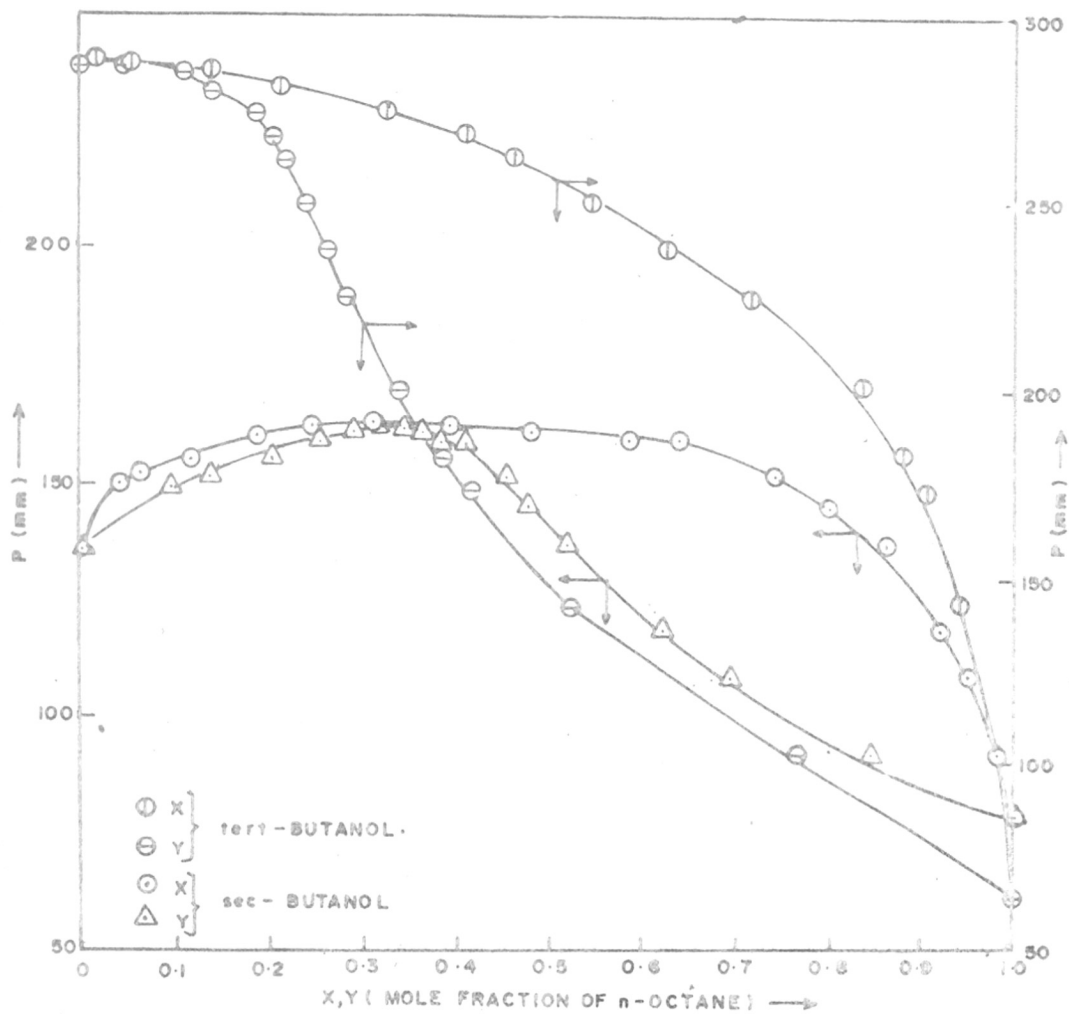


FIG 16 P-X,Y DIAGRAM FOR n-OCTANE(1) + sec-BUTANOL(2) AND n-OCTANE(1) + tert-BUTANOL(2) AT 333.15 K

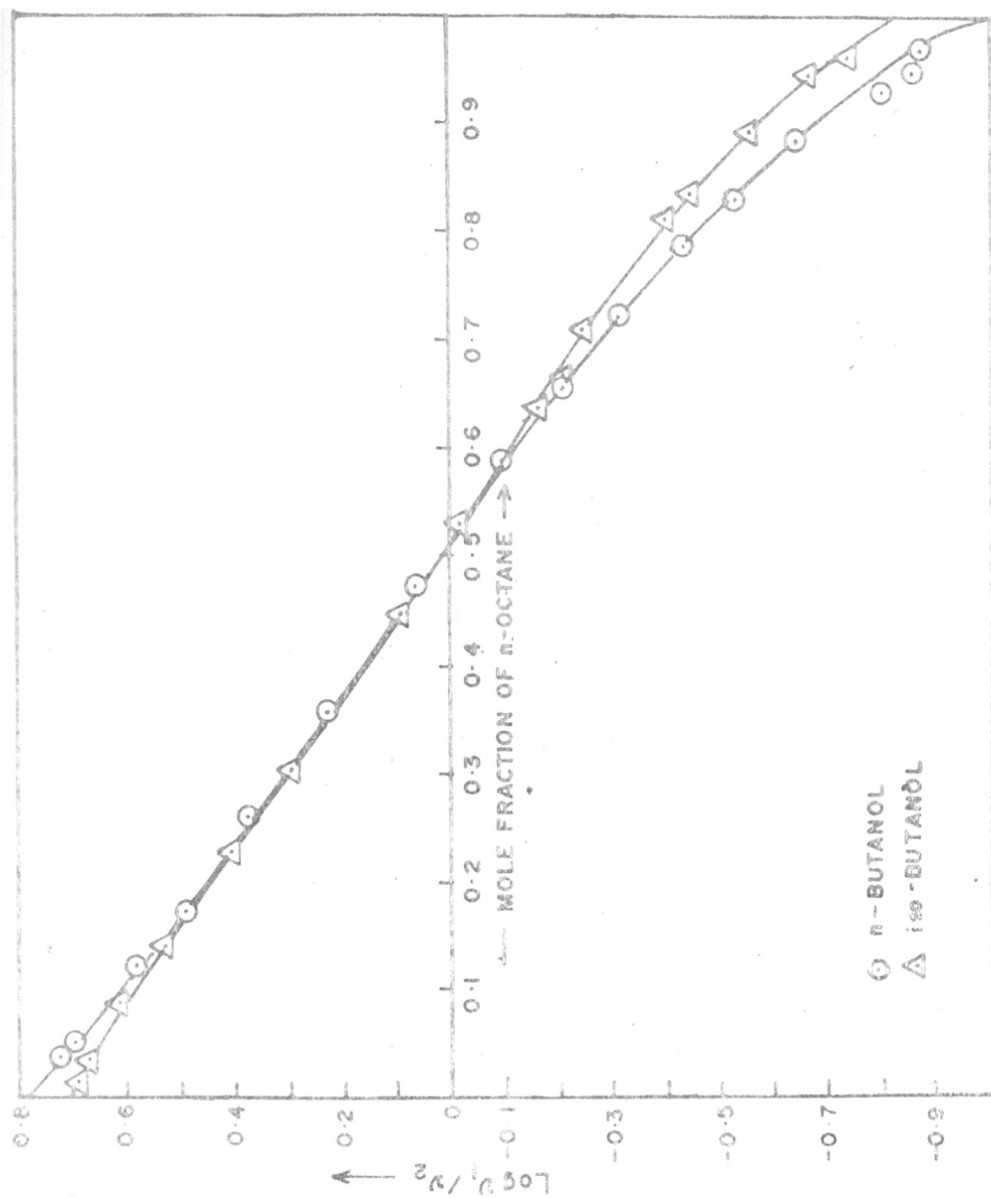


FIG.17. THERMODYNAMIC CONSISTENCY TEST FOR n-OCTANE(1)+n-BUTANOL(2) AND n-OCTANE(1)+iso-BUTANOL(2) SYSTEMS AT 333.15 K

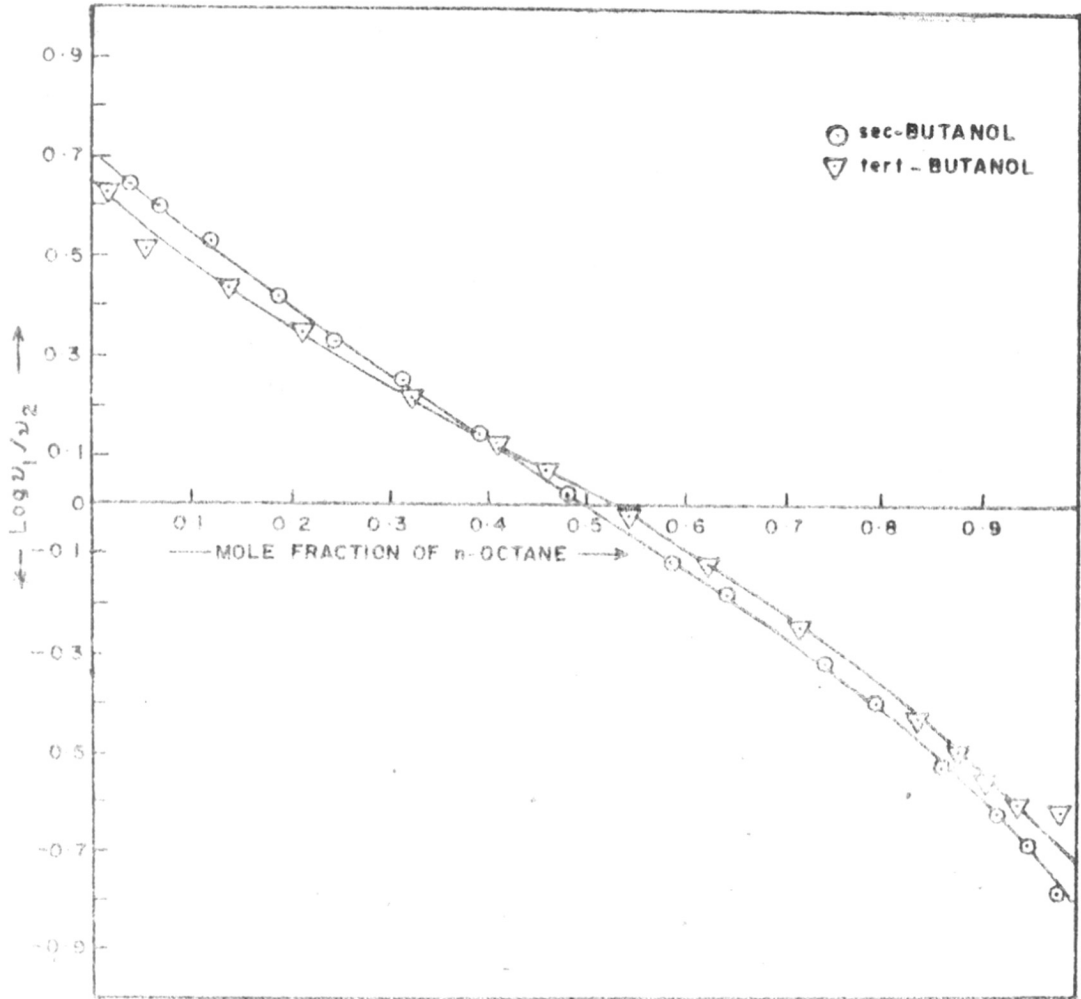


FIG 18 THERMODYNAMIC CONSISTENCY TEST FOR n-OCTANE (1) + sec BUTANOL (2) AND n-OCTANE (1) + tert-BUTANOL (2) SYSTEMS AT 333.15 K

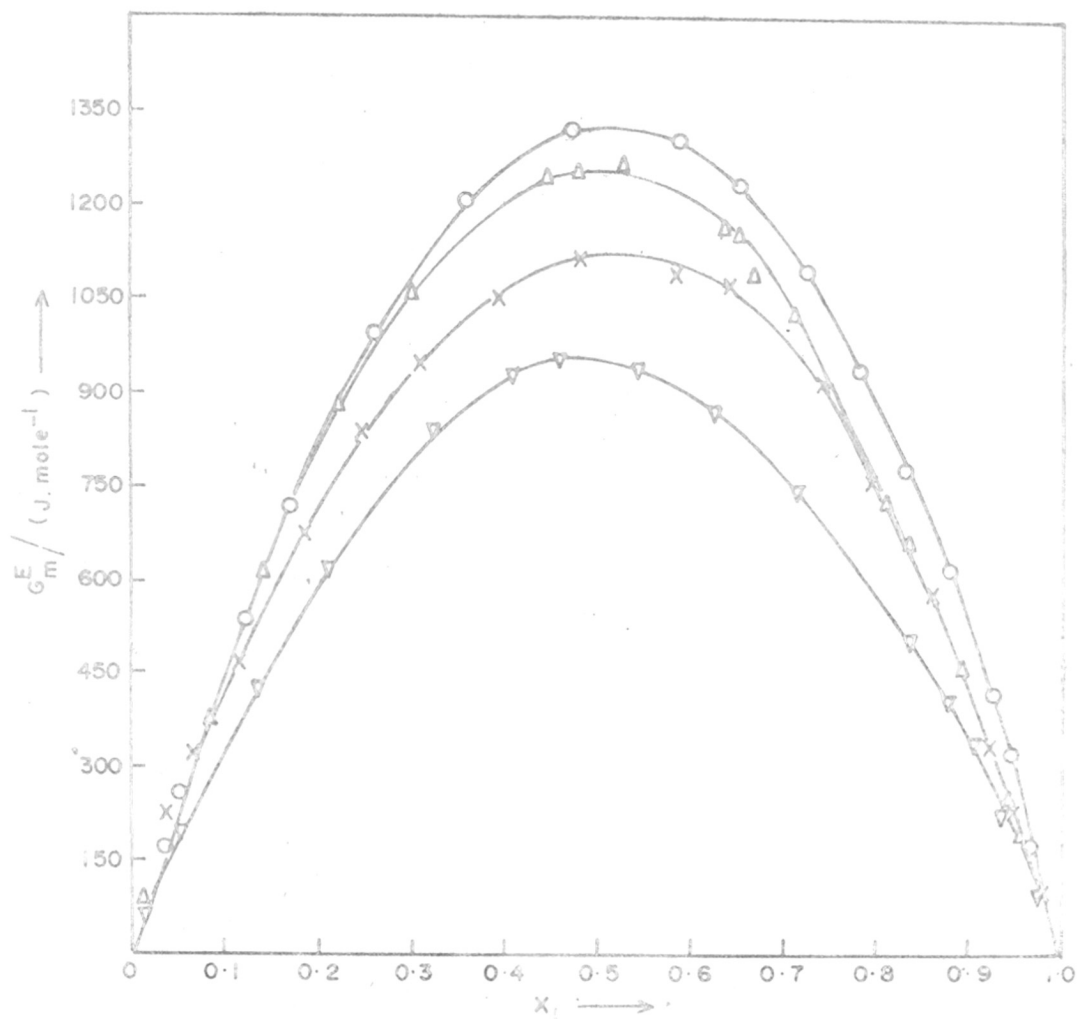


FIG 19 EXCESS FREE ENERGY OF MIXING FOR n-OCTANE (1) + isomeric BUTANOL (2) AT 333.15 K

○-n-BUTANOL, Δ-iso-BUTANOL, X-sec-BUTANOL, ▽-tert-BUTANOL

If vapour pressures can be regarded as a close approximation for fugacities, the relation of Raoult's law is derived as

$$p_1 = p_1^{\circ} x_1 \quad \text{and} \quad p_2 = p_2^{\circ} x_2 \quad (5)$$

where p_1 and p_2 are partial pressures of the components 1 and 2 at a composition x_1 and x_2 , while p_1° and p_2° are the vapour pressures of the pure components 1 and 2 (Total pressure $P = p_1 + p_2$). Thus an ideal system is one which obeys the Raoult's law.

The pressure-composition and G_m^E vs x_1 curves for n-octane-isomeric butanols indicate that these binary systems show highly non-ideal behaviour. The deviation is positive throughout the concentration range for all alcohols. The high positive values of G_m^E may be attributed to the breaking of hydrogen bonds in the self-associated molecules of butanols. The values of G_m^E decrease from n to tert butanol. G_m^E curves are symmetrical and maxima are observed at about mole fraction, $x_1 \approx 0.5$. There is no shifting of maxima towards high or low mole fraction range by the substitution of methyl groups.

Alcohols are strongly associated by hydrogen bonding and the changes occurred in the thermodynamic functions on diluting an alcohol with a non-polar solvent consist

of partly due to H-bond breaking and partly due to the mixing of alcohol homomorph with the solvent. Using the simple idealised model, Brown et al⁶ showed that excess free energy increases in the order tertiary > secondary > iso > normal butanol for isomeric butanols with n-alkane. Anilkumar et al²¹ also observed the same trend in G_M^E for isomeric butanols-n-heptane systems.

The experimental results suggest that chain branching decreases the extent of association and leads toward the formation of smaller polymers. The increase in vapour pressures and hence decrease in G_M^E from n to tert-butanol is largely due to the increased volatility of monomer with branching, while self-association differences are a less important but significant factor. This view is supported by Rytting et al²².

The $\log \gamma_1/\gamma_2$ vs x_1 plots (Figs. 17 and 18) are nearly linear indicating that butyl alcohols form regular solutions with n-octane. Kogan et al²³ observed similar behaviour for binary mixtures of n-butanol with heptane, octane and nonane, in their isobaric VLE studies.

2) Ethylenediamine (1) + isomeric butanol (2) systems

The VLE data for EDA with n, iso, sec and tert-butanol binary systems are given in Tables 25, 26, 27 and 28 respectively. The x-y diagrams are shown in Fig. 20 and

Table 25: Vapour Liquid Equilibrium data for M.A (1) + n-butanol (2)
at 333.15 K

$P_1 = 82.3$ mm $P_2 = 59.2$ mm

Sr.No.	Liquid x_1	Vapour y_1	P mm	Activity Coefficient γ_1	γ_2	G_m^E (J.mol ⁻¹)	α
1.	0.0802	0.0117	55.10	0.0979	1.0006	- 515	0.136
2.	0.1280	0.0349	51.77	0.1707	0.9678	- 710	0.244
3.	0.2093	0.1161	47.11	0.3184	0.8911	- 916	0.496
4.	0.2661	0.1895	45.80	0.3974	0.8575	- 993	0.645
5.	0.2760	0.2264	45.13	0.4511	0.8162	- 1016	0.768
6.	0.2966	0.2634	44.83	0.4851	0.7946	- 1043	0.848
7.	0.3427	0.3565	45.22	0.5732	0.7493	- 1054	1.062
8.	0.4162	0.5014	57.00	0.6898	0.6792	- 1054	1.410
9.	0.4680	0.5904	48.59	0.7467	0.6329	- 1053	1.638
10.	0.5461	0.6876	51.22	0.7854	0.5962	- 1016	1.829
11.	0.5885	0.7245	53.35	0.7998	0.6039	- 939	1.839
12.	0.6719	0.8158	58.52	0.8649	0.5553	- 805	2.162
13.	0.7820	0.9003	66.35	0.9293	0.5120	- 563	2.517
14.	0.8250	0.9283	68.65	0.9395	0.4745	- 504	2.746
15.	0.8654	0.9505	72.02	0.9617	0.4465	- 394	2.986
16.	0.9180	0.9725	75.20	0.9695	0.4250	- 276	3.159

Table 26: Vapour Liquid Equilibrium data for EDA (1) + iso-butanol (2) at 333.15 K.

$P_1 = 82.3$ mm $P_2 = 92.4$ mm

Sr. No.	Liquid x_1	Vapour y_1	P mm	Activity Coefficient γ_1	γ_2	G_M^E (J.mol ⁻¹)	α
1.	0.1040	0.0152	81.16	0.1441	0.9668	- 641	0.133
2.	0.1228	0.0203	78.67	0.1581	0.9526	- 745	0.145
3.	0.2118	0.0605	68.85	0.2392	0.8909	- 1091	0.240
4.	0.2739	0.1296	62.82	0.3619	0.8181	- 1175	0.395
5.	0.3182	0.1942	59.76	0.4439	0.7677	- 1215	0.516
6.	0.3651	0.2673	58.27	0.5193	0.7310	- 1214	0.634
7.	0.4131	0.3860	56.94	0.6477	0.6477	- 1203	0.893
8.	0.4680	0.5009	56.94	0.7419	0.5808	- 1188	1.140
9.	0.5238	0.5931	58.76	0.8099	0.5458	- 1105	1.325
10.	0.5576	0.6306	59.70	0.8217	0.5418	- 1054	1.355
11.	0.5883	0.6736	60.30	0.8403	0.5196	- 1031	1.444
12.	0.6507	0.7548	63.28	0.8932	0.4826	- 909	1.652
13.	0.6899	0.8033	65.67	0.9302	0.4526	- 819	1.837
14.	0.7418	0.8494	68.84	0.9592	0.4347	- 681	1.969
15.	0.8188	0.8987	73.46	0.9803	0.4456	- 451	1.971
16.	0.8987	0.9453	77.38	0.9893	0.4531	- 249	1.948
17.	0.9184	0.9507	78.08	0.9887	0.5728	- 180	1.713

Table 27: Vapour Liquid Equilibrium data for KDA (1) + s-butanol (2)
at 333.15 K

$P_1 = 82.3$ mm

$P_2 = 135.8$ mm

Sr. No.	Liquid x_1	Vapour y_1	P mm	Activity Coefficient γ_1	γ_2	G_m^E (J.mol ⁻¹)	α
1.	0.0512	0.0060	130.08	0.1836	1.0041	-229	0.1120
2.	0.0984	0.0239	122.08	0.3592	0.9748	-343	0.224
3.	0.1854	0.0503	109.34	0.3597	0.9416	-661	0.233
4.	0.2803	0.1105	98.13	0.4695	0.8970	-804	0.319
5.	0.3490	0.1744	91.08	0.5534	0.8550	-855	0.394
6.	0.4188	0.2803	84.53	0.6873	0.7753	-845	0.540
7.	0.4705	0.3664	80.75	0.7643	0.7160	-840	0.651
8.	0.5268	0.4502	79.56	0.8262	0.6851	-774	0.735
9.	0.5739	0.5162	79.26	0.8664	0.6670	-706	0.793
10.	0.6153	0.5666	79.03	0.8845	0.6599	-652	0.817
11.	0.6366	0.5969	79.16	0.9021	0.6508	-614	0.845
12.	0.6564	0.6190	78.76	0.9027	0.6473	-600	0.850
13.	0.6808	0.6566	78.58	0.9211	0.6266	-568	0.895
14.	0.7619	0.7458	78.68	0.9383	0.6226	-447	0.917
15.	0.8408	0.8296	79.52	0.9540	0.6308	-313	0.922
16.	0.9400	0.9370	81.05	0.9817	0.6300	-124	0.949

Table 28: Vapour Liquid Equilibrium data for EDA (1) + tert-butanol (2)
at 333.15 K

$P_1 = 82.3$ mm $P_2 = 289.6$ mm

Sr.No.	Liquid x_1	Vapour y_1	P mm	Activity Coefficient γ_1	Activity Coefficient γ_2	G_m^E (J.Mol ⁻¹)	α
1.	0.0621	0.0025	263.01	0.1269	0.9681	-271	0.038
2.	0.1405	0.0158	244.60	0.33019	0.9710	-501	0.0981
3.	0.1921	0.0300	220.52	0.41415	0.9333	-624	0.130
4.	0.2888	0.0621	192.44	0.4820	0.8965	-816	0.155
5.	0.3608	0.0975	174.07	0.5676	0.8573	-838	0.191
6.	0.4213	0.1456	156.51	0.6535	0.8074	-839	0.234
7.	0.4605	0.1872	147.20	0.7097	0.7886	-795	0.260
8.	0.5218	0.2407	137.34	0.7666	0.7632	-742	0.290
9.	0.5809	0.2999	129.05	0.8067	0.7505	-672	0.309
10.	0.6336	0.3618	121.65	0.8416	0.7426	-605	0.328
11.	0.6680	0.4079	117.98	0.8730	0.7377	-531	0.342
12.	0.6969	0.4628	113.50	0.9137	0.7055	-467	0.375
13.	0.7610	0.5606	105.77	0.9450	0.6825	-372	0.400
14.	0.8205	0.6607	100.27	0.9797	0.6655	-251	0.426
15.	0.8837	0.7674	94.05	0.9894	0.6609	-160	0.435
16.	0.9002	0.7950	92.16	0.9884	0.6652	-142	0.430

P-x,y curves are plotted in Figs. 21 and 22. The thermodynamic consistency of the data was checked by Harringtons equal area method. The plots of $\log \gamma_1/\gamma_2$ vs x_1 are given in Figs. 23 and 24 for all the systems and the values of G_m^E as a function of x_1 , the mole fraction of EDA are plotted in Fig. 25. x-y diagrams are nearly S-shaped. x-y and P-x,y curves indicate the formation of azeotropes for n, iso and secondary butanols. For EDA-tert-butanol system no azeotrope formation was observed. The values of mole fractions x_1 , at which the azeotropes were formed are listed in Table 31, for all the systems. All the EDA-isomeric butanol systems show poor thermodynamic consistency. It may be due to the imperfect behaviour of vapour phase, as both the components are highly associated.

It is clear from P-x,y and G_m^E vs x_1 curves that all the systems show negative deviation from Raoult's law. G_m^L values decrease with the branching of alcohol. The symmetry is observed for all the G_m^E curves and minima in G_m^E were found near about the mole fraction x_1 between 0.35 to 0.4. The sequence of G_m^E values is



Similar trend is observed in our V_m^E values. The G_m^E studies of iso, sec and tert-butanol with pyridines by Warycha²⁴ showed the same trend.

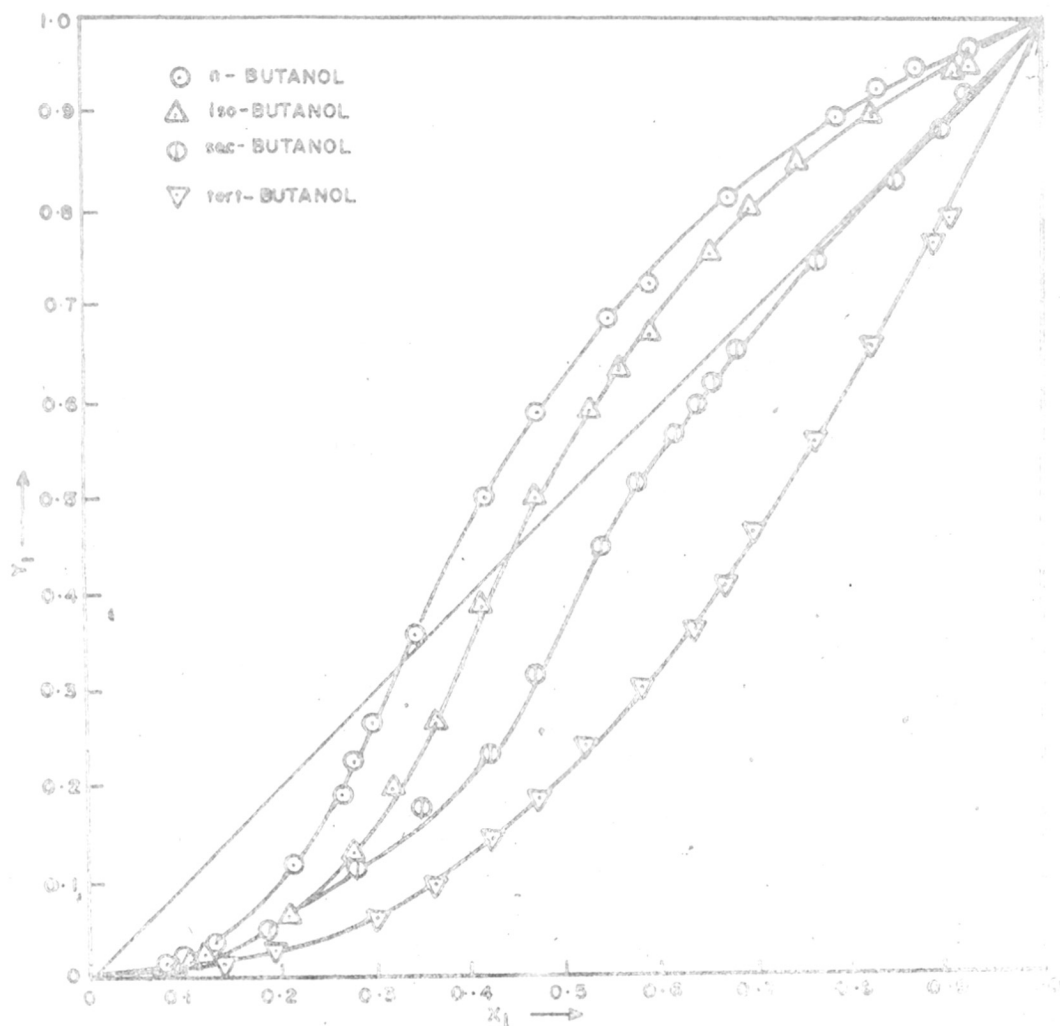


FIG. 20. X-Y DIAGRAM FOR EDA (1)-ISOMERIC BUTANOLS (2) SYSTEM AT 333.15 K

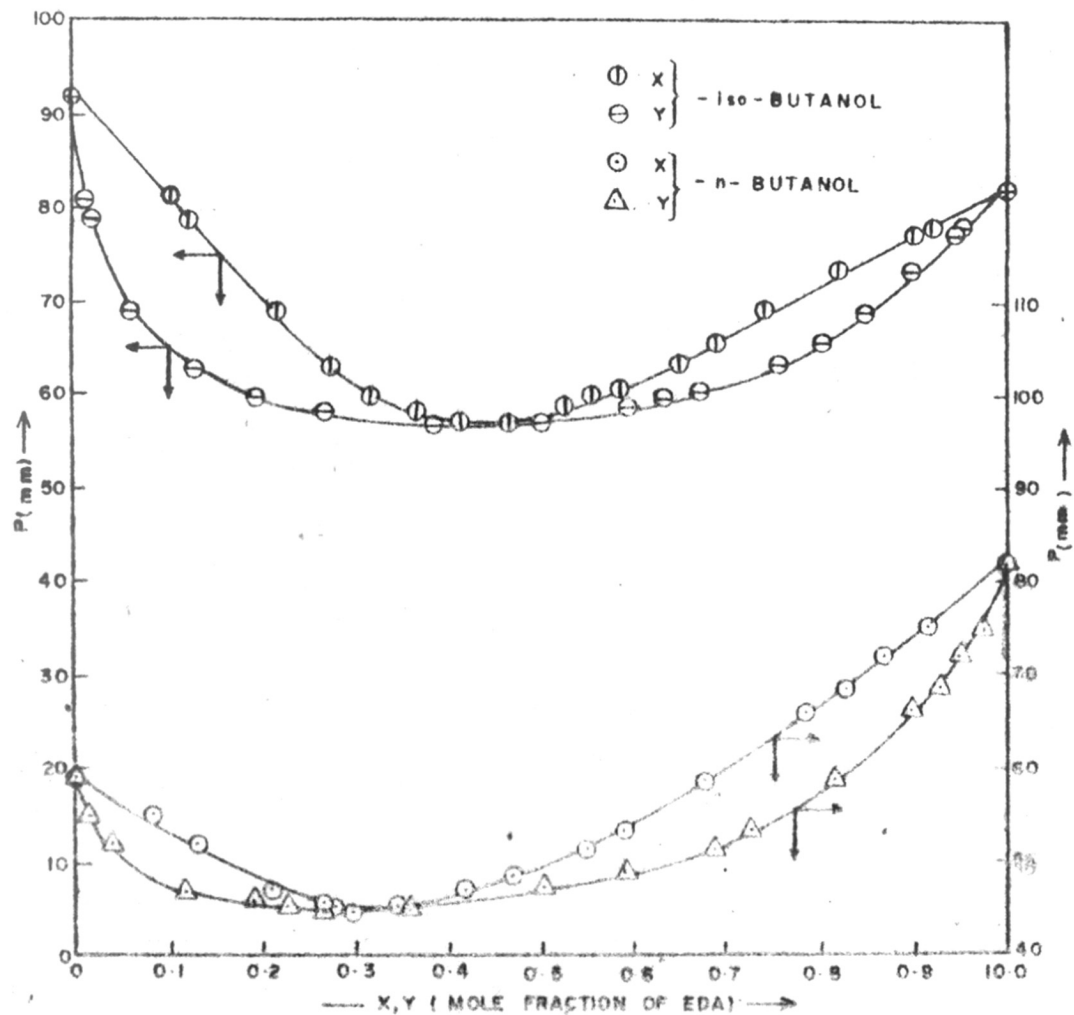


FIG. 21. P-X,Y DIAGRAM FOR EDA (1) + n-BUTANOL (2) AND EDA (1) + iso-BUTANOL (2) SYSTEMS AT 333.15 K

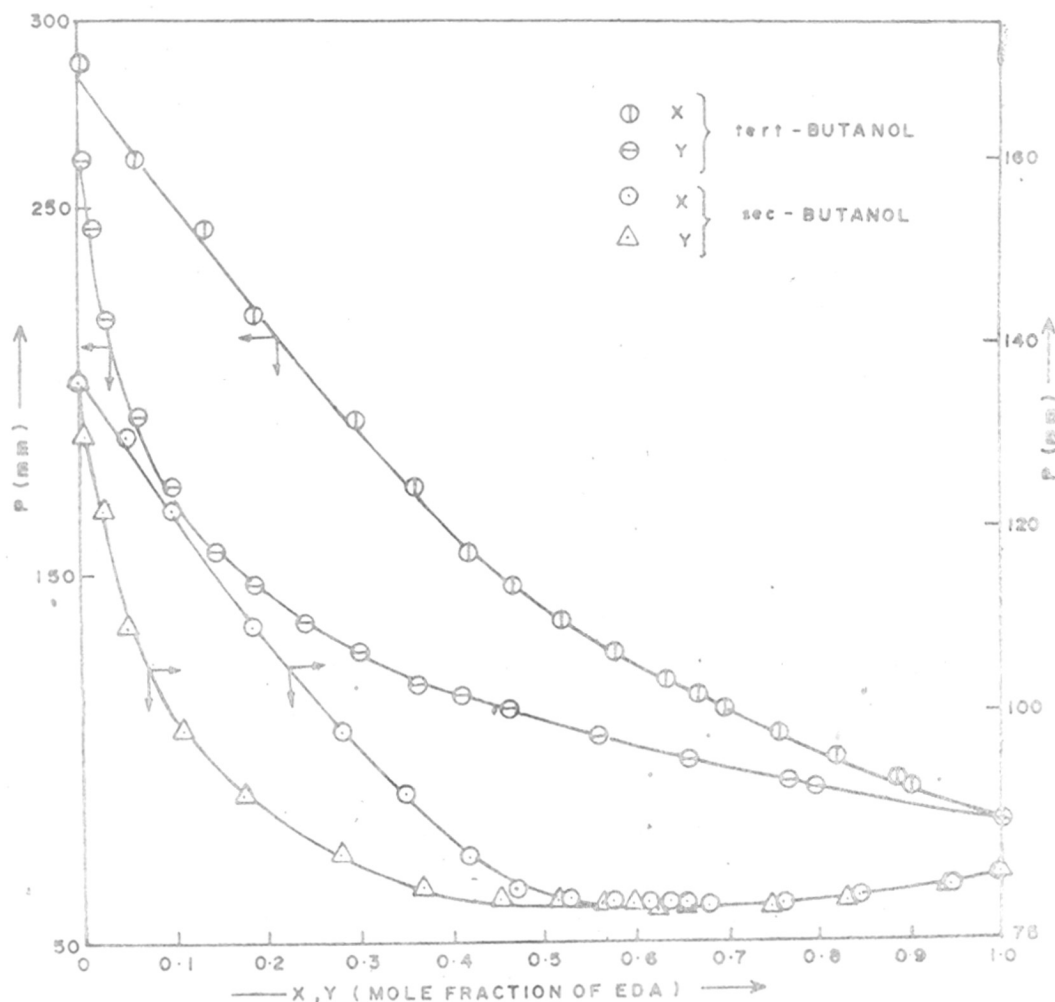


FIG. 22. P-X,Y. DIAGRAM FOR EDA (1) + sec-BUTANOL (2) AND EDA (1) + tert-BUTANOL (2) AT 333.15 K

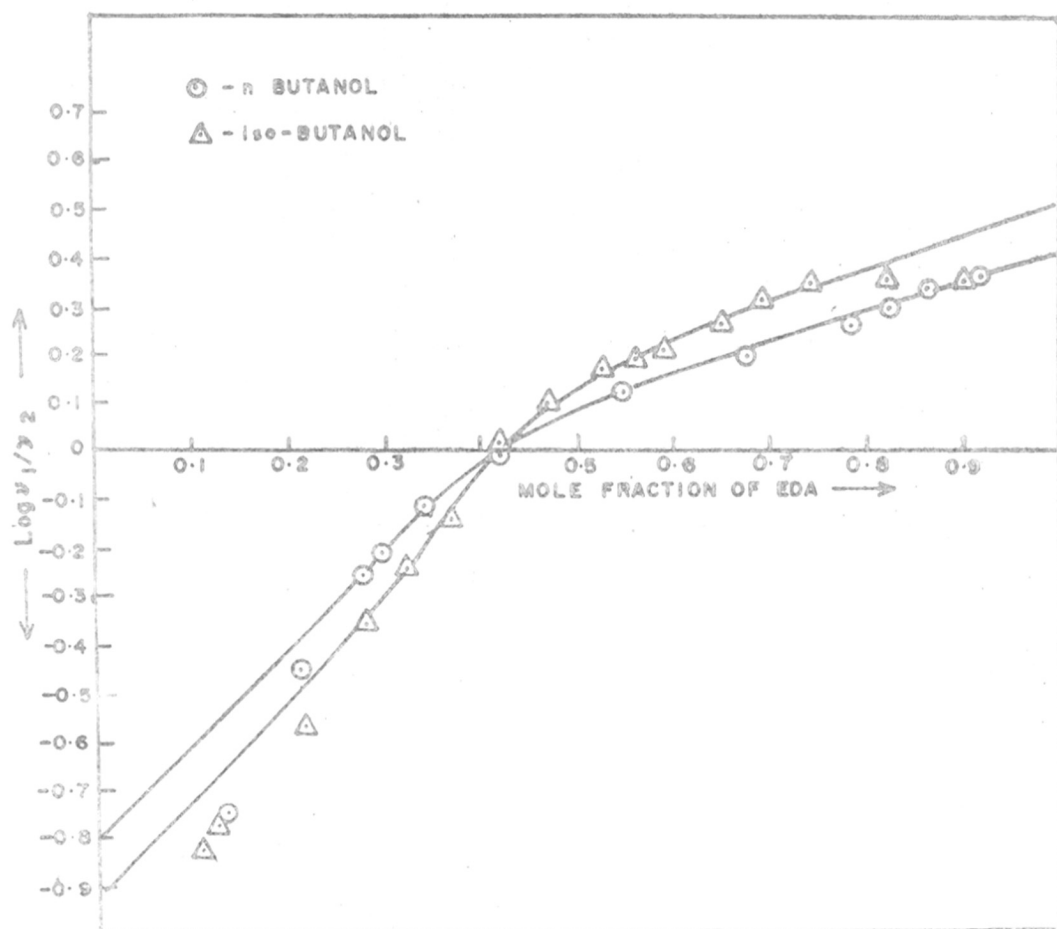


FIG. 23. THERMODYNAMIC CONSISTENCY TEST FOR EDA(1) + n-BUTANOL(2) AND EDA(1) + iso-BUTANOL(2) SYSTEMS AT 333.15 K

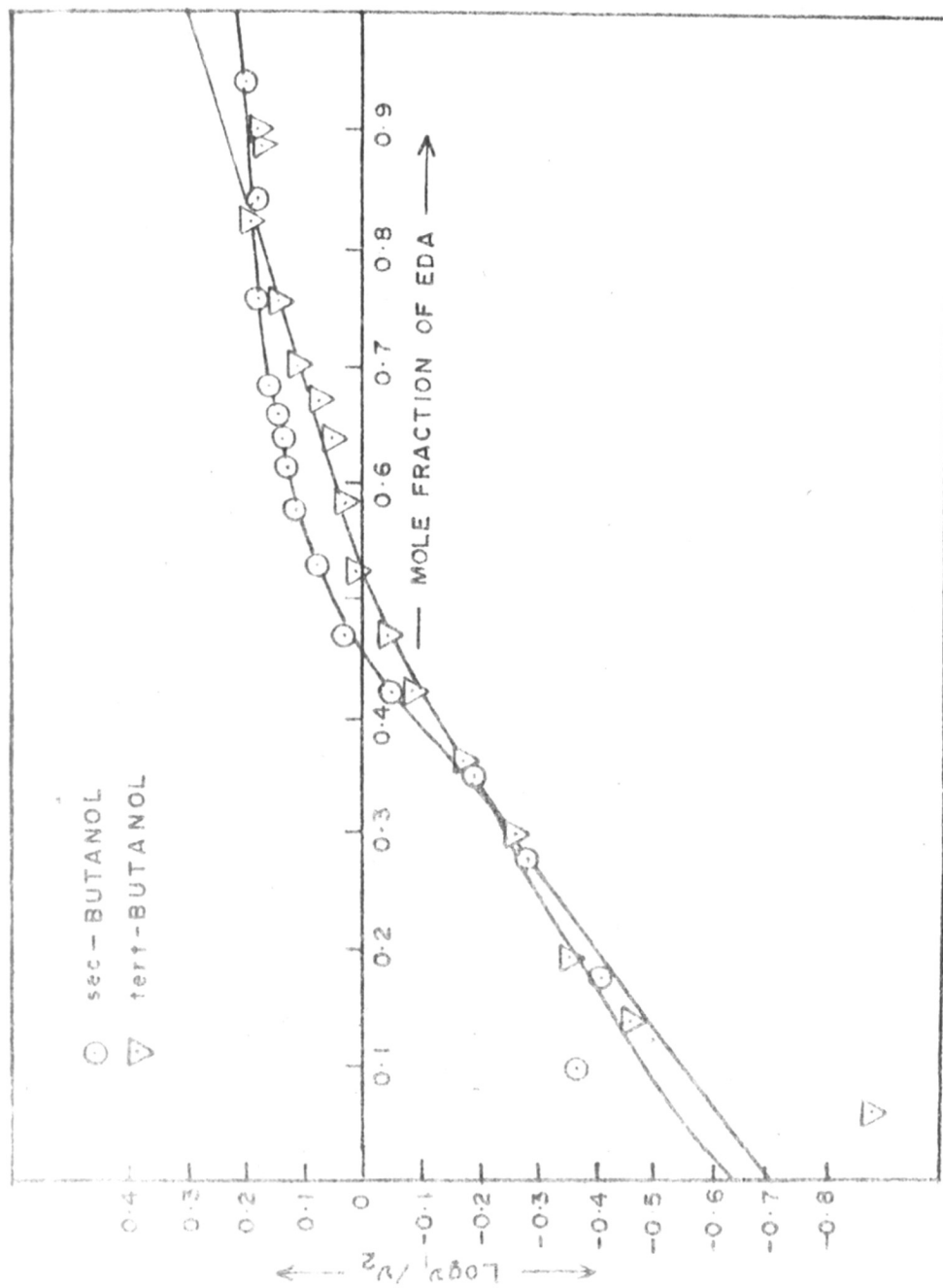


FIG.24. THERMODYNAMIC CONSISTENCY TEST FOR EDA (1) + sec. BUTANOL (2) AND EDA (1) + tert - BUTANOL (2) AT 333.15 K

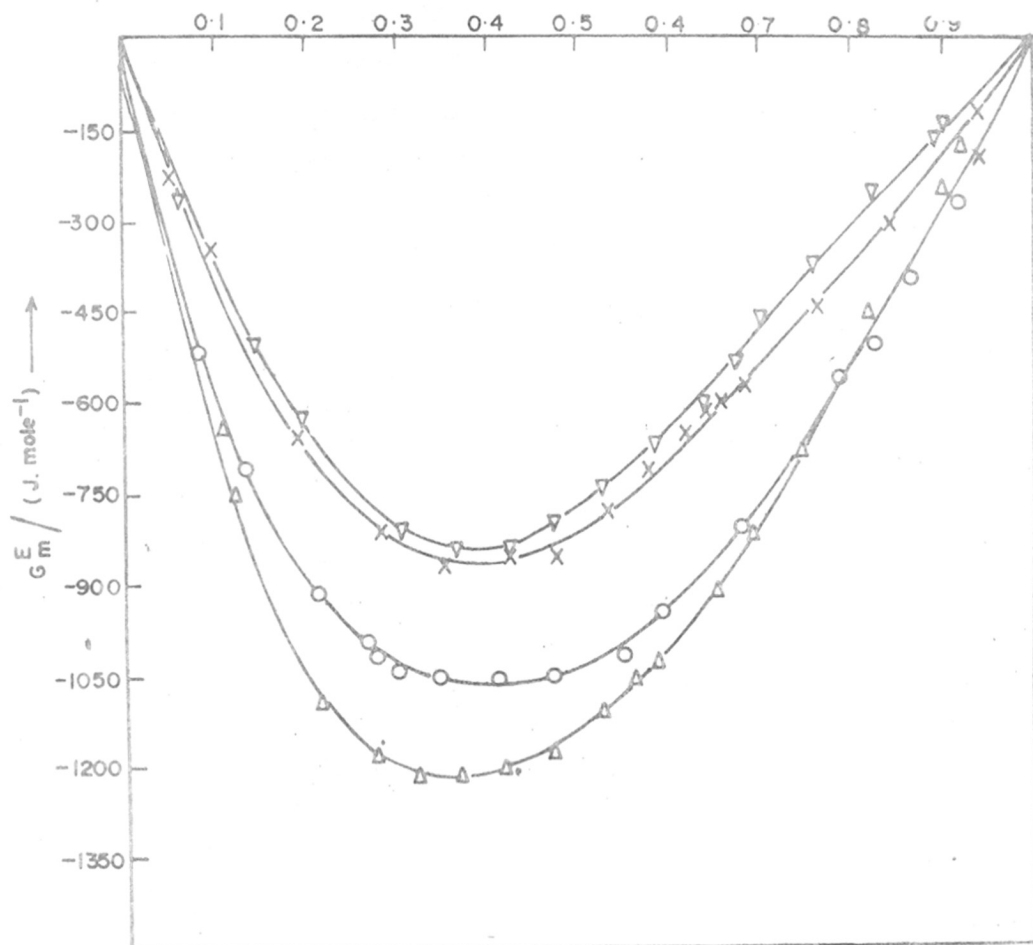


FIG.25. EXCESS FREE ENERGY OF MIXING FOR EDA (1) + ISOMERIC-BUTANOL (2) AT 333.15 K. O n-BUTANOL, Δ ISO-BUTANOL, X sec-BUTANOL, ∇ tert-BUTANOL.

The negative G_{∞}^E values for all the systems indicate a strong specific interaction between alcohol amine molecules, forming hydrogen bonded complexes. The results also suggest that the O-H...N bond is stronger than O-H...O and N-H...N bonds in the mixtures. This contention receives support from the work of many authors^{10,14,25-28}.

3) Toluene (1) + EDA (2) system

The isothermal VLE data at 333.15 K for this system have been given in Table 29, and the isobaric VLE data at 712-00 mm Hg in Table 30. x-y diagrams are shown in Fig. 26 for both P-x,y and T-x,y curves are plotted in Figs. 27 and 28 respectively.

x-y diagrams are S-shaped. x-y, P-x,y and T-x,y curves show the formation of azeotrope (see Table 31). From both isobaric and isothermal VLE data, azeotrope formation was observed nearly at the same mole fraction.

The thermodynamic consistency of the data were checked by equal area method²⁰ $\log \frac{y_1}{y_2}$ vs x_1 plots are given in Fig. 29. The data show 2% deviation for isothermal and 3.5% for isobaric method. G_{∞}^E values calculated from isothermal VLE data are plotted against x_1 , the mole fraction of toluene in Fig. 30.

The excess free energies are positive throughout the concentration range. This behaviour may be due to the

Table 29: Vapour Liquid Equilibrium data for Toluene (1) + EDA (2)
at 333.15 K.

$P_1 = 139.0$ mm $P_2 = 82.3$ mm

Sr.No.	Liquid x_1	Vapour y_1	P mm	Activity Coefficient γ_1	Activity Coefficient γ_2	G_m^E (J.mol ⁻¹)	α
1.	0.0313	0.2802	108.05	6.979	0.974	97	12.05
2.	0.0470	0.3700	121.35	6.870	0.972	176	11.90
3.	0.1395	0.4812	145.27	3.6029	1.0592	632	5.72
4.	0.2164	0.5390	154.60	2.7662	1.0992	815	4.23
5.	0.3239	0.5686	162.14	2.0432	1.2486	1058	2.75
6.	0.4502	0.5954	164.0	1.5641	1.4575	1131	1.80
7.	0.5568	0.6095	165.21	1.2978	1.7577	1094	1.242
8.	0.6148	0.6177	167.00	1.2039	2.0011	1056	1.011
9.	0.7076	0.6517	165.13	1.0914	2.3752	872	0.772
10.	0.8057	0.6987	164.08	1.0212	3.0728	651	0.559
11.	0.9146	0.8184	159.0	1.0116	4.0849	387	0.420

Table 30: Isobaric Vapour Liquid Equilibrium data for Toluene (1) +
EDA (2) at 712 mm Hg. (Atm.p.)

Sr.No.	Liquid x_1	Vapour y_1	T °C	Activity Coefficient γ_1	γ_2	$\log \gamma_1 / \gamma_2$
1.	0.0322	0.2484	108.0	7.790	0.984	0.898
2.	0.0821	0.3843	104.5	5.230	0.958	0.737
3.	0.0907	0.4024	104.2	4.470	0.950	0.720
4.	0.2604	0.5094	102.5	2.320	1.016	0.359
5.	0.2948	0.5184	102.5	2.050	1.067	0.284
6.	0.3973	0.5628	102.2	1.70	1.123	0.180
7.	0.4868	0.5783	102.4	1.41	1.264	0.047
8.	0.6190	0.6190	102.0	1.20	1.558	-0.113
9.	0.7470	0.6889	103.0	1.08	1.851	-0.234
10.	0.8098	0.7235	103.5	1.03	2.147	-0.319
11.	0.8662	0.7819	105.0	0.995	2.287	-0.362
12.	0.9197	0.8144	105.8	0.954	3.158	-0.520
13.	1.000	1.000	108.0	1.0	-	-
14.	0.000	0.000	115.0	-	1.0	-

* Calculated from eqn.(9) in Chapter II(b).

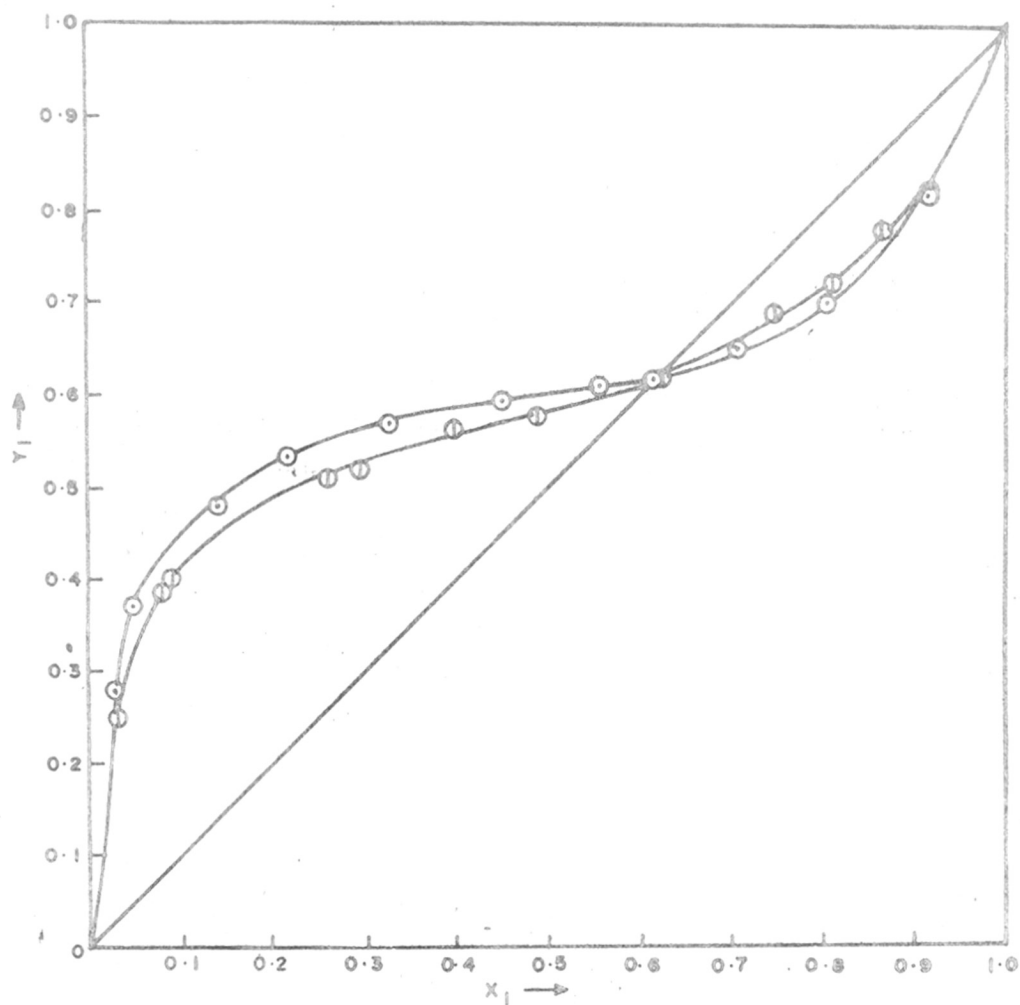


FIG. 26. X-Y DIAGRAM FOR TOLUENE (1) + ETHYLENE DIAMINE (2).

○ - AT 333.15 K (ISOTHERMAL) ; ⊖ - AT 712.0 mm (ISOBARIC)

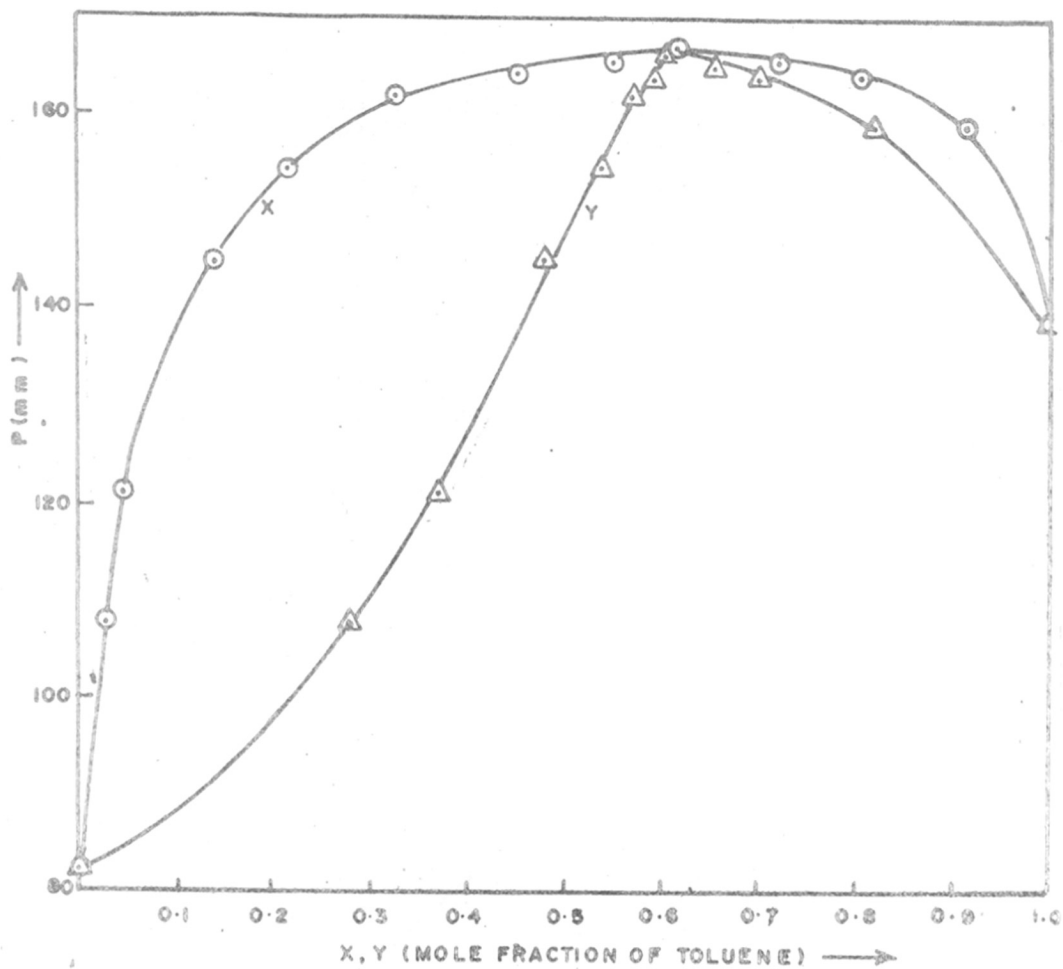


FIG. 27. P-X, Y DIAGRAM FOR TOLUENE (1) + EDA (2) SYSTEM AT 333.15K

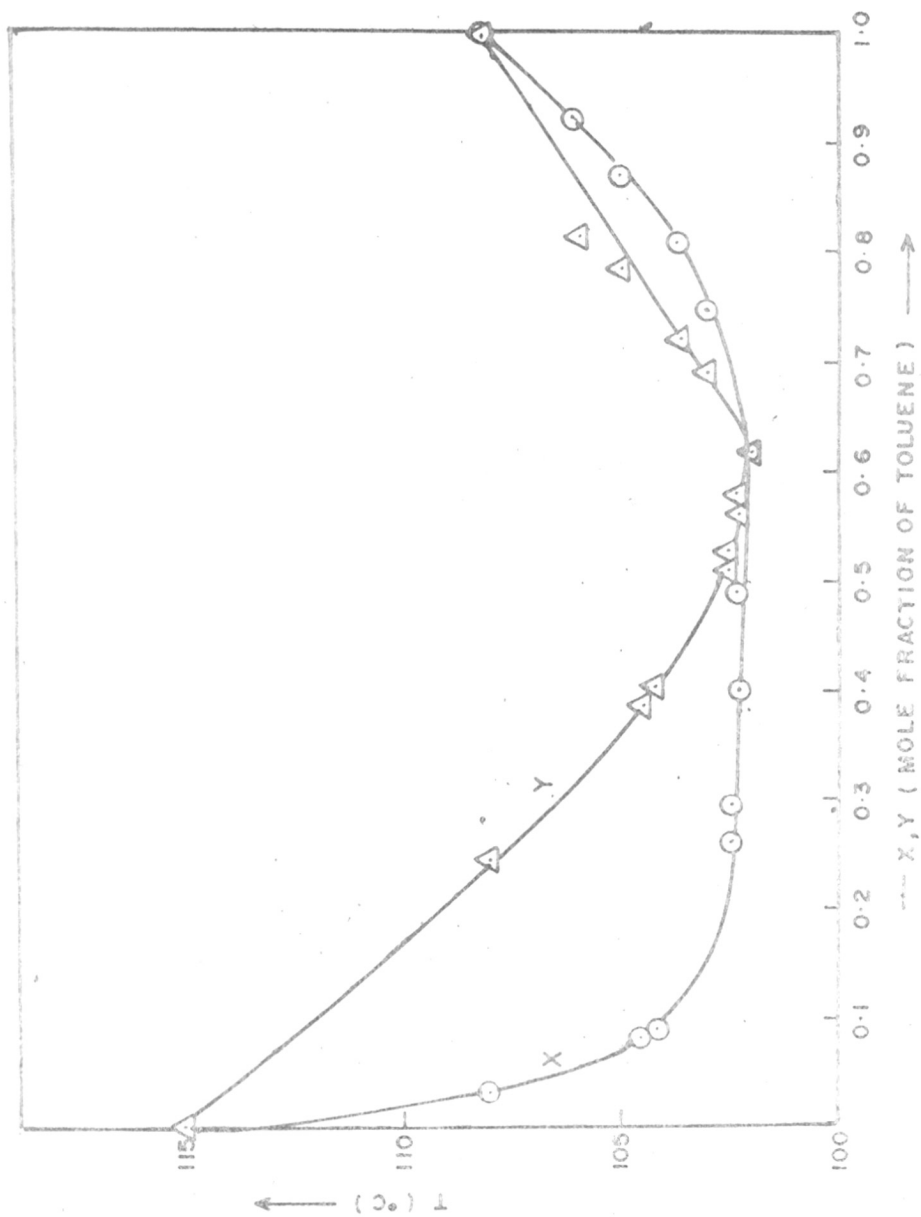


FIG 28. T-X,Y DIAGRAM FOR TOLUENE (1) + EDA (2) SYSTEM AT 712.0 mm

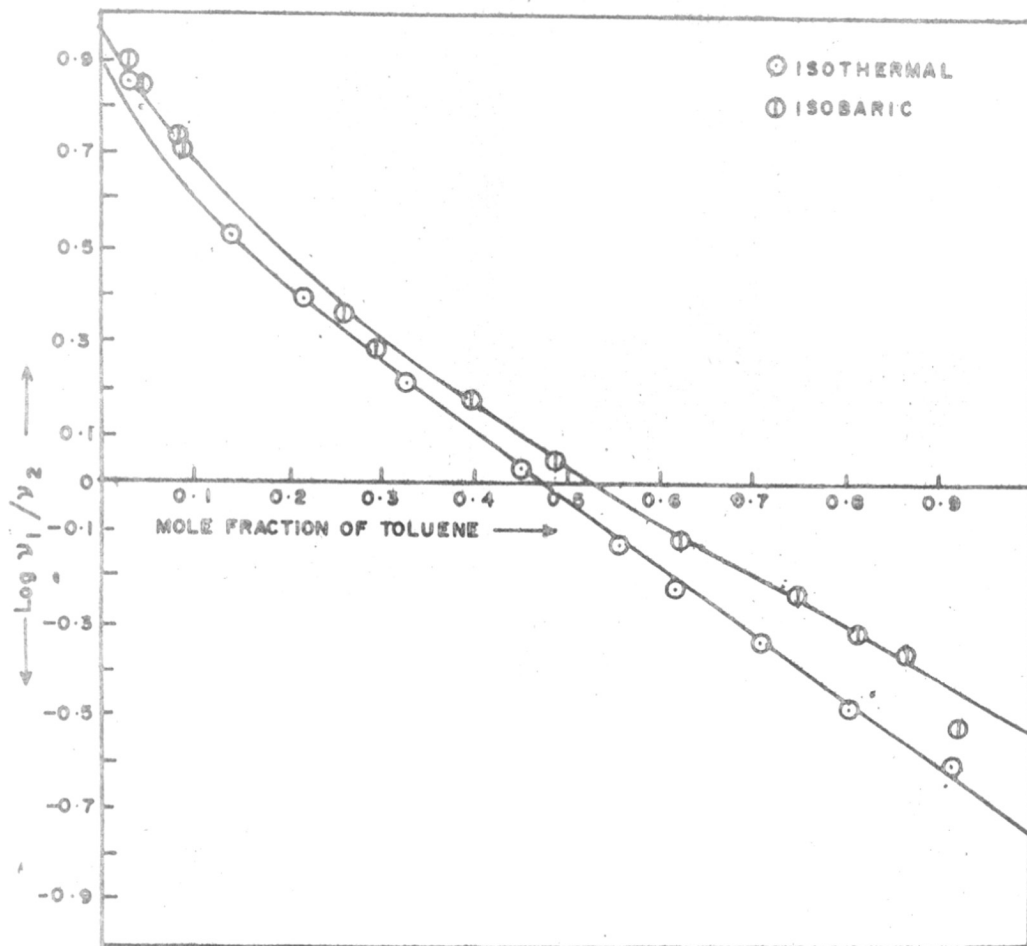


FIG 29 THERMODYNAMIC CONSISTENCY TEST FOR TOLUENE (1)+EDA(2) AT 333.15 K (ISOTHERMAL) AND AT 712.0 MM (ISOBARIC)

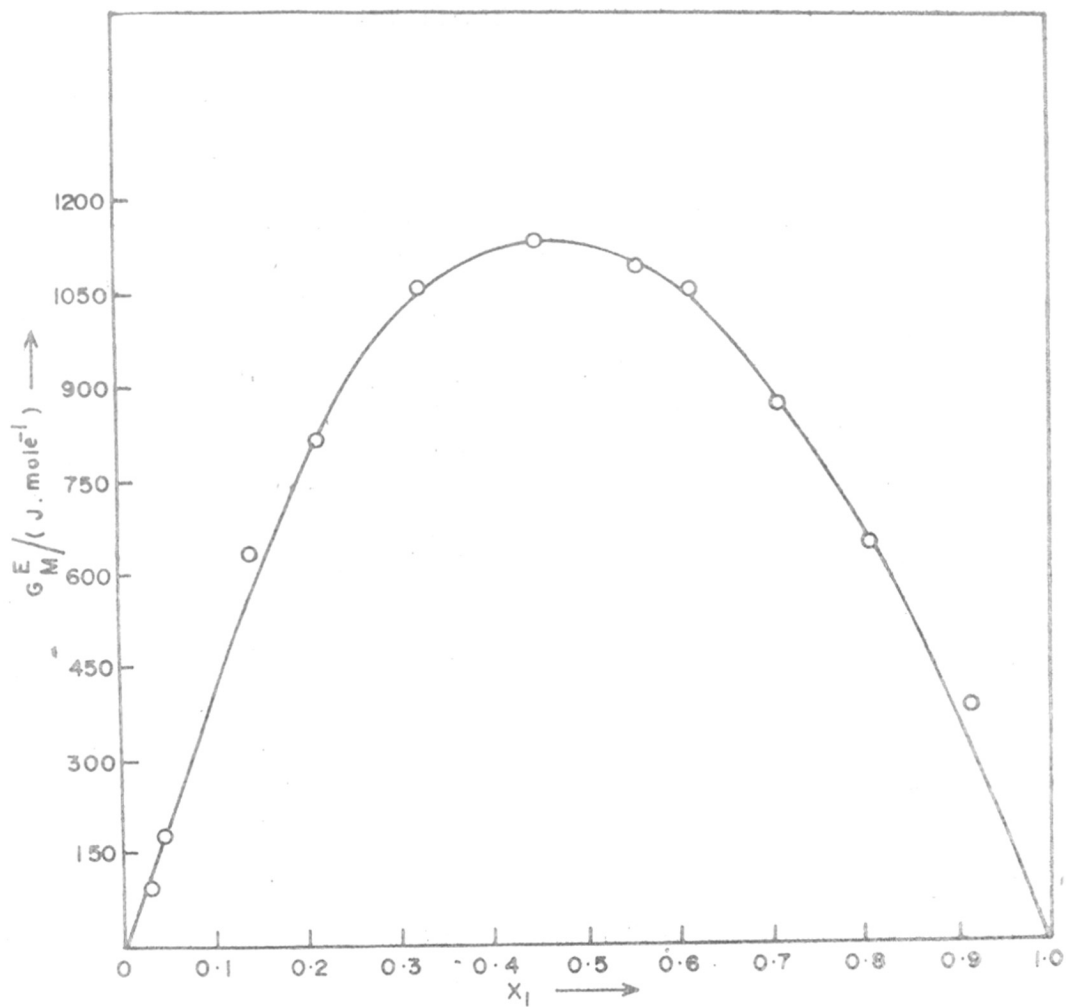


FIG 30 EXCESS FREE ENERGY OF MIXING FOR TOLUENE (1) + EDA (2)
AT 333.15 K

Table 31: Concentrations of component 1 forming azeotropes in the binary liquid mixtures at 333.15 K. °

Sr.No.	System	x_1 -mole fraction of component 1 forming azeotrope	System pressure (mm.Hg)
1.	n-Octane (1) + n-Butanol (2)	0.605	115.0
2.	n-Octane (1) + iso-Butanol (2)	0.465	137.0
3.	n-Octane (1) + sec-Butanol (2)	0.320	163.0
4.	n-Octane (1) + tert-Butanol (2)	0.045	290.0
5.	EDA (1) + n-Butanol (2)	0.325	44.0
6.	EDA (1) + iso-Butanol (2)	0.440	57.0
7.	EDA (1) + sec-Butanol (2)	0.950	81.0
8.	EDA (1) + tert-Butanol (2)	-	-
9.	Toluene (1) + EDA (2)	0.620	167.0
10.	Toluene (1) + EDA (2) (Isobaric)	0.619 (at 102°C)	712.0

structure breaking effect of toluene molecules on dilution with toluene. H-bonds between EDA molecules are broken giving positive contribution. Dipole-dipole interactions between amine monomers and multimers are also responsible for positive G_m^E .

The excess free energy data of all the nine systems were fitted to Redlich-Kister² polynomial equation.

$$G_m^E = x_1 x_2 \sum_{n=0}^3 A_n (x_2 - x_1)^n \quad (6)$$

The values of constants calculated by computer are given in Table 32 along with σ . The smooth curve in all G_m^E vs x_1 plots indicate that the experimental G_m^E data can be well represented by Redlich-Kister equation.

The G_m^E data were also fitted to Wilson equation³⁰ of the type

$$\frac{G_m^E}{RT} = -x_1 \ln(x_1 + \Lambda_{12} x_2) - x_2 \ln(x_2 + \Lambda_{21} x_1) \quad (7)$$

where Λ_{12} and Λ_{21} are two adjustable parameters, and

$$\Lambda_{12} = \frac{v_2}{v_1} \exp - \left(\frac{\lambda_{12} - \lambda_{11}}{RT} \right) \quad (8)$$

$$\Lambda_{21} = \frac{v_1}{v_2} \exp - \left(\frac{\lambda_{21} - \lambda_{22}}{RT} \right) \quad (9)$$

Table 32: The least square parameters in the G_m^E equation for all the systems at 333.15 K.

$$G_m^E \text{ (J/mole)} = x_1 x_2 \left[A_0 + A_1 (x_2 - x_1) + A_2 (x_2 - x_1)^2 + A_3 (x_2 - x_1)^3 \right]$$

System	A_0	A_1	A_2	A_3	(Std.dev.)
n-Octane (1) + n-butanol (2)	5313.8	429.9	165.7	70.5	11.0
n-Octane (1) + iso-butanol (2)	4760.7	872.4	995.8	-2249.1	28.0
n-Octane (1) + iso-butanol (2)	4327.5	391.6	1242.1	-810.9	29.0
n-Octane (1) + tert-butanol (2)	3641.3	-410.2	554.5	909.4	25.0
EDA (1) + n-butanol (2)	-4038.9	1557.3	-1591.7	684.7	18.0
EDA (1) + iso-butanol (2)	-4644.1	2391.0	-329.4	610.3	19.0
EDA (1) + sec-butanol (2)	-3196.3	1778.0	-161.1	-697.3	15.0
EDA (1) + tert-butanol (2)	-3071.9	1933.5	180.4	-171.8	12.0
Toluene (1) + EDA (2)	4600.4	-1699.5	-26.4	3136.8	36.0

Table 33: The parameters of Wilson Equation

System	Λ_{12}	Λ_{21}	J, mol^{-1}
n-Octane (1) + n-butanol (2)	0.3129	0.1883	20.6
n-Octane (1) + iso-butanol (2)	0.2565	0.3067	26.1
n-Octane (1) + sec-butanol (2)	0.3530	0.3093	26.5
n-Octane (1) + tert-butanol (2)	0.4284	0.4262	17.8
Toluene (1) + BDA (2)	0.2408	0.4360	36.40

where v = molar liquid volume of pure component

λ = constants proportional to energies of interaction.

The Wilson fitting parameters for all the systems are given in Table 33. This equation also fits the experimental G_M^E data well for isomeric butanol-n-octane and toluene-EDA systems. The data for EDA-isomeric butanols could not be fitted to Wilson equation, since these systems are complex in nature and gave large standard deviations.

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SUMMARY

SUMMARY

The present work consists of the measurement of excess thermodynamic properties viz. V_m^E and G_m^E as a function of composition. Nine binary systems namely isomeric butanols with n-octane, with EDA and toluene-EDA were undertaken for above study.

The excess volumes were measured directly by dilution dilatometer constructed in the laboratory. The data were obtained at 298.15 K for all the systems except for tert-butanol at 299.15 K and for toluene-EDA at 303.15 K. Isothermal VLE data were obtained at 333.15 K using a modified Jones-Colburn still. In addition, for toluene-EDA system, isobaric VLE data were also collected at 712.0 mm (atmospheric pressure).

The values of V_m^E for isomeric butanols-n-octane and toluene-EDA are positive, whereas for EDA-isomeric butanols negative V_m^E were observed. For n-octane-isomeric butanols, V_m^E increases from n to tert-butanol and for EDA-isomeric butanols the trend in V_m^E is

$$\text{iso} > \text{n} > \text{tert} > \text{sec-butanol}.$$

The excess volume behaviour is interpreted in terms of bond breaking and bond making effects, physical interactions and

structural effects. The change in magnitude and symmetry was observed among the curves with the branching of alcohol.

The G_m^E values were calculated from the isothermal VLE data at 333.15 K, for all the systems. In the case of isomeric butanols - n-octane and toluene-EDA system G_m^E values show positive deviation from Raoult's law, whereas negative deviations were observed for EDA-isomeric butanols. x-y diagrams are S-shaped and P-x-y curves show the formation of azeotropes, for all the systems except EDA-tert butanol. The thermodynamic consistency was checked by Harington's method. The V_m^E data were least square fitted to the polynomial equation. The G_m^E data were correlated using Redlich-Kister and Wilson equations.

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