12-7-95

THERMODYNAMICS OF BINARY NON - ELECTROLYTE MIXTURES

A THESIS
SUBMITTED TO
THE UNIVERSITY OF POONA
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
(CHEMISTRY)

BY

ANIL KUMAR
M. Sc.

PHYSICAL CHEMISTRY DIVISION
NATIONAL CHEMICAL LABORATORY
POONA - 411 008 (INDIA)
1980

THERMODYNAMICS OF BINARY NON - ELECTROLYTE MIXTURES

A THESIS
SUBMITTED TO
THE UNIVERSITY OF POONA
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
(IN CHEMISTRY)

BY

ANIL KUMAR
M. Sc.

PHYSICAL CHEMISTRY DIVISION
NATIONAL CHEMICAL LABORATORY
POONA - 411 008 (INDIA)

1980

To

Shri Mahā Shakti

ACKNOWLEDGEMENT

It gives me immense pleasure to record my deep sense of gratitude to Dr. S.S. Katti, Physical Chemistry Division, National Chemical Laboratory, Poona for his valuable and inspiring guidance and to Dr. A.P.B. Sinha, Deputy Director, National Chemical Laboratory, Poona for his constant encouragement throughout the course of this investigation.

I am highly indebted to Dr. Gopal Pathak and Dr. S.D. Pradhan for their kind help and wholehearted generous cooperation throughout the work. I will be failing in my duty, if I do not place on record my gratitude to my colleagues particularly Mr. Chunnilal Morwal, Dr. A.G. Gaonkar, Dr. H.G. Damle and Mr. V.S. Kulkarni for their help towards the accomplishment of this work.

I am grateful to the Director, National Chemical Laboratory, Poona for allowing me to submit the present work in the form of a thesis.

July 1980

(ANIL KUMAR)

CONTENTS

CHAPTER I

INTRODUCTION

CHAPTER II

EXPERIMENTAL

CHAPTER III

RESULTS AND DISCUSSION

I. INTRODUCTION

INTRODUCTION

Considerable amount of work[1-11] has been carried out on the excess thermodynamic properties of non-electrolyte binary mixtures. The data collected on these properties seems to have been explained on the basis of simple liquid mixture theories which may lead to qualitative and quantitative explanation of the nature and behaviour of the binary liquid mixtures.

Literature survey reveals that it is rather difficult to explain the thermodynamic excess properties based on the simple theories especially mixtures such as alcohols, amines and acids which exhibit high self association properties. In order to simplify the application of these existing theories to the less complicated systems it was thought worthwhile to undertake comparatively simpler systems like alcohols and hydrocarbons.

It is well established fact that the aliphatic alcohols are strongly associated with hydrogen bonding and these hydrogen bonds are broken on dilution with nonpolar solvent. It would be interesting to choose such systems which have one aliphatic alcohol viz. isomeric butanols and other nonpolar component viz. n-heptane in order to consider the changes in thermodynamic properties such as excess volume (V^E), excess free energy (G^E) excess enthalpy (H^E) and excess entropy (S^E) which occur on diluting butanols with n-heptane.

In the following the results on excess thermodynamic properties of isomeric butanols with n-heptane have been reported. Such results are useful in understanding the nature of interactions between different isomeric butanols on breaking of hydrogen bonds.

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)

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

Therefore all excess functions for an ideal solution are zero. In the case of a real solution the excess functions may be positive or negative. 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

$$V^E = V^M_{(real)} - V^M_{(ideal)}$$

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

$$\begin{aligned} G^E &= G^M_{(real)} - G^M_{(ideal)} \\ &= RT\left[x \ln \gamma_1 x + (1-x) \ln \gamma_2 (1-x)\right] \\ &- RT\left[x \ln x + (1-x) \ln (1-x)\right] \\ &= RT\left[x \ln \gamma_1 + (1-x) \ln \gamma_2\right] \qquad (2) \end{aligned}$$

where γ_1 and γ_2 are the activity coefficients of the two components. The molar enthalpy of mixing ΔH^M for a binary liquid mixture is given by the relation

$$H_{(P,T,x)} = H_{(P,T,x)} - (1-x)\,H_{(P,T,0)} - x\,H_{(P,T,1)} \tag{3}$$

where $H_{(P,T,x)}$ is the enthalpy of mixing at pressure P, temperature T of one mole of the mixture containing mole fraction x of one of the components.

The difference between the enthalpy of mixing of a real system ($\triangle H^M$) and the enthalpy of mixing of an ideal mixture of the same composition is denoted by excess enthalpy (H^E)

$$H^E = \triangle H^M_{(real)} - \triangle H^M_{(ideal)} \tag{4}$$

For an ideal mixture the enthalpy of mixing is zero hence

$$H^E = \triangle H^M \tag{5}$$

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

$$G^E = H^E - TS^E \tag{6}$$

$$A^E = U^E - TS^E \tag{7}$$

$$H^E = U^E + PV^E \tag{8}$$

The partial derivatives of these functions are analogous to those of the total functions

$$\left[\frac{\partial G^E}{\partial P}\right]_{T,x} = V^E \tag{9}$$

$$\left[\frac{\partial G^E}{\partial T}\right]_{P,x} = -S^E \tag{10}$$

$$\left[\frac{\partial(G^E/T)}{\partial(1/T)}\right]_{P,x} = H^E \qquad (11)$$

The thermodynamic excess properties of alcohols with benzene and other aromatic hydrocarbons[12-24], with normal alkanes[25-32] and with carbon tetrachloride[32-35] have been studied by many authors. There seems to be a general agreement that the alcohols undergo self association due to hydrogen bond formation in their pure state as well as in their solutions in non-polar solvents and that the degree of self association decreases with the increase in dilution of the alcohols. However there is no specific explanation about the type and the energy of self association of alcohols. The mixing of alcohols with a non-polar solvent is accompanied by an absorption of heat. This has been attributed to the breaking of alcohol-alcohol hydrogen bonds of self association alcohol species as a result of dilution of the alcohol.

The volume change on mixing for alkanol-n-alkane have widely been studied [26,29,36-47]. Pardo and VanNess[21] have reported the excess volumes for ethanol-hydrocarbon mixtures. Brown and Smith[48] have measured the excess volumes of various alcohols such as methanol, ethanol, propanol and various butanols with benzene at 25°, 35° and 45°C. They observed the positive excess volumes increase with the increase in temperature. Direct measurements of excess volumes of tert-butanol with hydrocarbons have been reported by Rocko[42] and Otin[49] at 30-50°C.

Varma and Kumaran[50] have studied the excess volumes of carbon tetrachloride with ethanol, n-propanol, iso-propanol, n, iso- and tert-butanols at 25°C by dilatometer. The curves of excess volumes vs x_1 are sigmoid for all normal alcohols. The positive excess volumes were reported in high concentration region of CCl_4 while the negative V^E in lower concentration range. It was also observed when alkyl group in alcohol becomes more branched and bulky, the negative part of the curves diminishes. Marsh and Burfitt[38] have reported the excess volumes of ethanol in many non-polar solvents. They found that the excess volumes increase rapidly in dilute regions. The partial molar excess volume have the same behaviour as partial molar excess enthalpies would exhibit.

Benson and Tressesanowics[41] have studied the excess volumes for n-alcohols with n-heptane at 25°C by successive dilution dilatometer and concluded that excess volumes decrease rapidly in magnitude with increasing chain length of the n-alkanol. They have also reported the partial molar excess volumes.

The isobaric vapour liquid equilibrium of n-butanol with n-heptane have been studied by Vijayaraghavan et al[51,52]. Ramalho and Delmas[53] have obtained the interesting isothermal and isobaric vapour liquid equilibrium for cyclohexane-butanol and ethanol heptane systems at various temperatures. Subramanium et al[54] reported the absence of azeotropes in the case of isobaric vapour liquid equilibrium of ethylene dichloride-n-butanol. The vapour liquid equilibrium of various butanols with benzene were measured by Brown et al[26] and

Echevarria[55] at different temperatures. Brown et al have mentioned that excess free energy calculated from vapour liquid equilibrium data decreases with increase in temperature. Furthermore they have interpreted the data on the basis of idealised model whereas Echevarria has correlated his data with different equations such as Van Laar and Margules. Fajans[56] has discussed the excess free energy of benzene-tert-butanol system in terms of ideal association at 50° and 70°C.

Vilou and Cencise[57] reported the isothermal vapour liquid equilibrium of benzene and isobutanol system at 45° and 55°C. It has been observed that the azeotropes are independent of temperature. Lower values of free energy at 55° than at 45°C were considered due to decrease in temperature. Vapour pressures of n-butanol with n-heptane have been measured long back at 50°C by Smith et al[58].

Brown and coworkers[26] have correlated the excess enthalpy with the ratio of hydroxyl group to the number of carbon atoms in the mixture. According to them the process of hydrogen and bond breaking depends upon the hydroxyl group contribution and the change in the energy of interaction on the separation of alkyl chains. They have compared the thermodynamic properties of normal alcohols in benzene and n-hexane solution with the corresponding properties of branched alcohol solutions. An idealised model was proposed to explain qualitatively the changes which took place on varying the composition, temperature, solvent and alcohol structure in these solutions.

Although a good amount of work has been carried out on the study of thermodynamic properties of the mixtures of aliphatic alcohols and non-polar solvents[17,18,19,21,59], most of the results are used for qualitative explanation of the particular thermodynamic behaviour. Only a small number of papers are devoted to the determination of enthalpy of hydrogen bonding of the alcohol. Stokes[60] has attempted to calculate the enthalpy of formation of hydrogen bonds in alcohol with non-polar solvents on the basis of some assumptions using Flory theory[61] and IR data of ethanol-n-heptane system reported by Van Ness et al[62].

Van Ness et al[22,27,28] determined the hydrogen bond energies of a number of primary alcohols by plotting H^E/x_1x_2 vs x_1 curve to zero concentration of alcohol. They showed that the energy associated with the breaking of alcohol- alcohol bonds decreases slightly with increase in the chain length of the alcohol.

Elbe[63] measured the H^E of methanol, ethanol, propanol and n-butanol in n-hexane at 30°C at very low concentrations i.e. 10^{-2} to 10^{-6} mole/cc of solution. Otin et al[64] determined the enthalpies of hydrogen bonding of tert-butanol in a number of solvents. Moelwyn Hughes and Missen[65] measured the excess properties such as G^E and H^E of a number of n-alcohols + CCl_4 systems which exhibited positive deviations. However some cases e.g. methanol-CCl_4 at low temperature and in certain concentration range showed negative deviations indicating a significant alcohol-CCl_4 interaction.

Woycicka et al[66] have reported the excess enthalpies for four isomeric butanols in n-heptane at 30° as well as excess heat capacities of n- and tert-butanols in n-heptane at 30° and 40°C at high dilutions. The association of butanol isomers was found to be largely affected by steric factors. The excess heat capacities of n- and tert-butanols were found to have similar negative values which decreased in a similar manner with the increase in temperature. They have also calculated the association constants assuming the values of enthalpy of dimerisation and trimerization as suggested by Bellamans[82].

Murakami and Benson[67] have studied the excess thermodynamic properties of all isomeric butanol mixtures. Veseley and Pick[68] measured H^E for n-alcohols with cyclohexane at 25°C and applied Brown's theory to interprete their data. Smirnova et al[69] have studied the thermodynamics of series of binary alcohol hydrocarbon solutions at a range of temperatures. Savini et al[27] have measured the heats of mixing of ethanol + n-hexane, n-propanol + n-heptane and n-butanol + n-heptane etc. at 30° and 45°C using an isothermal dilution calorimeter. The calculated H^E/x_1x_2 data are adequate to indicate a general trend with number of carbon atoms of the alcohol and with temperature. Huong et al[70] have measured heats of mixing of n-alcohol-n-alkane systems at 15° and 55° using isothermal dilution calorimeter. It may be mentioned here that these authors have also carried out the experiments for n-butanol + n-heptane system at 55° which we have also carried out.

The excess thermodynamic properties in the case of alcohol - hydrocarbon systems have been well correlated in terms of models. Kretschmer and Wiebe[71] have investigated the probability of a simpler treatment based on continued association to predict excess properties. In this treatment some of the departures from random, spatial and orientational distribution caused by the intermolecular forces have been mentioned. Redlich and Kister[72] have presented a model based on few assumptions. They have made an attempt to find out the relationship between free energy and the stoichiometric mole fractions of alcohols and non-polar solvents.

Barker[73] has given a general method for evaluating the effect on thermodynamic properties of cooperative orientation in solutions. This theory has been applied to the systems via methanol-benzene, methanol-carbon tetrachloride and chloroform-ethanol. Theoretical curves for excess free energy of mixing, heats of mixing and entropy of mixing as functions of composition were presented. Renon and Prausnitz[74] have proposed a model for high concentration of alcohols based on the assumptions of Kretschemer and Wiebe[71] and Redlich and Kister[72] theories. The model has been used to deduce experimental data for mixtures of alcohols and saturated hydrocarbons.

Goates et al[59] and Dacre and Benson[35] have tested the generalised quasilattice theory in the case of alcohols - benzene systems. The theory was based on the fact that each molecule was assigned a definite number of sites in the lattice and three different types of contact points were assigned to the alcohol molecules. Nitta and Katayama[75,76] have correlated the excess thermodynamic properties by a continuous linear association model. The model dealt with the self associated system by making distinctions between the association constant and association energy of dimer formation and those of polymer formation. Wiehe and Bagley[77] put forward the theory to calculate isothermal vapour liquid equilibrium composition curves and heats of mixing of binary aliphatic hydrocarbons and alcohol mixtures based on a single experimental point. A great deal of the work[78-82] has been carried out to explain the interactions in terms of statistical thermodynamics.

Hydrogen bonding in butanols has also been studied by NMR as well as IR spectroscopy. Ching et al[83] have discussed the NMR chemical shifts for isomeric butanols in carbon tetrachloride. The effect of solvent on the bonding of butanols has been reported by Huyskens et al[84] by IR and NMR techniques. Geisler et al[85] have studied the association behaviour of isomeric butanols and their mixtures in n-heptane by IR spectroscopy. They found that the enthalpies of self association of the four isomeric butanols decrease from n to tert-butanol.

Thus the above literature survey reveals that scattered work on various excess thermodynamic properties of isomeric butanols with n-heptane has been reported for a certain concentration range. In the present study a systematic work on excess thermodynamic properties of isomeric butanols with n-heptane has been undertaken.

REFERENCES

1. Garrett, P.R. Pollock, J.M. and Morcom, K.W., J.Chem.Thermodyn. 3, 135 (1971)
2. Andrews, A. Morcom, K.W. Duncan, W.A. Swinton, F.L. and Pollock, J.M., J. Chem. Thermodyn. 2, 93, (1970)
3. Garrett, P.R. Pollock, J.M. and Morcom, K.W., J. Chem. Thermodyn. 5, 569 (1973)
4. Garrett, P.R. and Pollock, J.M., J. Chem. Thermodyn. 9, 561 (1977)
5. Garrett, P.R. and Pollock, J.M., J. Chem. Thermodyn. 9, 1045 (1977)
6. Pradhan, S.D. and Mathur, H.B., Proc. Indian Acad. Sci. 87A, 23 (1978)
7. Pradhan, S.D. and Mathur, H.B., Proc. Indian Acad. Sci. 88A, 337 (1979)
8. Pradhan, S.D., Proc. Indian Acad. Sci. 88A, 47 (1979)
9. Dutta Choudhury, M.K. and Mathur, H.B., J. Chem. Eng. Data, 19, 145 (1974)
10. Pathak, G. Katti, S.S. and Kulkarni, S.B., Indian J. Chem. 8, 357 (1970)
11. Murakami, S. and Fujishiro, R., Bull Chem. Soc. Japan 39, 720 (1966)
12. Brown, I. and Smith, F., Aust. J. Chem. 7, 264 (1954)
13. Brown, I. and Fock, W., Aust. J. Chem. 12, 407 (1959)
14. Brown, I. and Fock, W., Aust. J. Chem. 8, 361 (1955)
15. Brown, I. Fock, W. and Smith, F., Aust. J. Chem. 9, 364 (1956)
16. Brown, I. and Fock, W., Aust. J. Chem. 10, 417 (1957)
17. Brown, I. and Fock, W., Aust. J. Chem. 14, 387 (1961)

18. Schnaible, H.W. Van Neww, H.C. and Smith, J.M., Amer. Inst. Chem. Eng. J. 3, 1 (1957)

19. Mrazek, V.R. and Van Ness, H.C., Amer. Inst. Chem. Eng. J. 7, 190 (1961)

20. Savini, C.G. Winterhalter, D.R. Kovach, L.H. and Van Ness, H.C., J. Chem. Eng. Data, 11, 40 (1966)

21. Pardo, F. and Van Ness, H.C., J. Chem. Eng. Data, 10, 163 (1965)

22. Van Ness, H.C. Soczek, C.A. Peloquin, G.L. and Machado, R.L., J. Chem. Eng. Data, 12, 217 (1967)

23. Williamson, A.G. and Scott, R.L., J. Phys. Chem. 64, 440 (1960)

24. Gonsalez, F.C. Nanez, L. and Villar, E., J. Chem. Thermodyn. 4, 275 (1972)

25. Brown, I. Fock, W. and Smith, F., Aust. J. Chem. 17, 1106 (1964)

26. Brown, I. Fock, W. and Smith, F., J. Chem. Thermodyn. 1, 273 (1969)

27. Savini, C.G. Winterhalter, D.R. and Van Ness, H.C., J. Chem. Eng. Data, 10, 168 (1965)

28. Savini, C.G. Winterhalter, D.R. and Van Ness, H.C., J. Chem. Eng. Data, 10, 171 (1965)

29. Van Ness, H.C. Soczek, C.A. and Kochar, N.K., J. Chem. Eng. Data, 12, 346 (1967)

30. Pahlke, H. Wolf, J. and Wahage, K., Z. Physik Chem. (Frankfurt), B28, 1 (1935)

31. Elbe, G. Von., J. Chem. Phys. 2, 73 (1934)

32. Paraskevopoulos, G.C. and Missen, R.W., Trans. Fara. Soc. 58, 869 (1962)

33. Otterstedt, J.E.A. and Missen, R.W., Trans. Farad. Soc. 58, 879 (1962)

34. Moelwyn-Hughes, E.A. and Missen, R.W., J. Phys. Chem. 61, 361 (1955)

35. Dacre, B. and Benson, G.C.,
Can. J. Chem. 41, 278 (1963)

36. Dias Pena, M. and Rodrigues Cheda, D.,
Ann. Quim. 66, 637 (1970)

37. Gupta, B.M.C.V., Naidu, P.R. and Rao, M.V.P.,
J. Chem. Thermodyn. 8, 191 (1976)

38. Marsh, K.N. and Burfitt, C.,
J. Chem. Thermodyn. 7, 955 (1975)

39. Ruel, M., Ann. Quim 69, 821 (1973)

40. Staveley, L.A.K. and Spice, B.,
J. Chem. Soc. 406 (1952)

41. Treszczanowicz, A.J. and Benson, G.C.,
J. Chem. Thermodyn. 9, 1189 (1977)

42. Recko, W., Bull. Acad. Polon. Sci. Ser.
Sci. Chim. 13, 655 (1965)

43. Huyskens, P. and Cracio, F.,
Bull. Soc. Chim. Belges 69, 422 (1960)

44. Jones, W.J. Bowden,S. T. Yarnold, W.W. and Jones, W.H.,
J. Phys. Chem. 52, 753 (1948)

45. Summer, K.M. and Thompson, A.R.,
J. Chem. Eng. Data, 12, 489 (1967)

46. Sosnkowska-Kehiaian, K. Recko, W. and Woycicki, W.,
Bull. Acad. Polon. Sci. Ser. Sci. Chim.
14, 475 (1966)

47. Brzostowski, W. and Hardman, T.M.
Bull. Acad. Polon. Sci. Ser. Sci. Chim.
11, 447 (1963)

48. Brown, I. and Smith, F. Aust. J. Chem. 15, 1 (1962)

49. Otin, S. Gracia, M. and Gutierrez, Losa. C.,
Rev. Acad. Cienc. Exactas, Fis Quim Natur. Zaragoza
27, 259 (1972)

50. Varma, K.T.R., Kumaran, M.K. & Seetharaman, T.S.,
J.Chem.Thermodyn. 8, 651 (1976)

51. Vijayaraghavan, S.V. Deshpande, P.K. and Kuloor.
N.R., J. Chem.Eng. Data, 11, 147 (1966)

52. Vijayaraghavan, S.V. Deshpande, P.K. and Kuloor, N.R., J. Chem. Eng. Data, 12, 13 (1967)

53. Ramalho, R.S. and Delmas, J., J. Chem. Eng. Data, 13, 161 (1968)

54. Subramanium, D. Nageshwar, G.D. and Meno, P.S., J. Chem. Eng. Data, 14, 421 (1969)

55. Echevarria, H.R., Collection Czechoslov. Chem. Commun. 38, 1295 (1973)

56. Fajans, A., Bull. De. L' Academie Polonaise, Des. Sciences, 12, 877 (1964)

57. Vilcu, R. and Cencise, Z., Rev. Roum. Chim. 18(3), 377 (1973)

58. Smith, C. P. and Engel, E.W., J. Amer. Chem. Soc. 51, 2660 (1929)

59. Goates, J.R. Snow, R.H. and James, M.R., J. Phys. Chem. 65, 335 (1961)

60. Stokes, R.H., Aust. J. Chem. 21, 1334 (1968)

61. Flory, P.J., J. Chem. Phys. 12, 425 (1944)

62. Haskell, R.W. Hollinger, H.B. and Van Ness, H.C., J. Phys. Chem. 72, 4534 (1968)

63. Elbe, G. Von., J. Chem. Phys. 2, 73 (1934)

64. Otin, S. Gracia, M. and Gutirres, L., J. Chim. Phys. Chim. Bull. 71(5), 637 (1974)

65. Moelwyn Hughes, E.A. and Missen, R.W., J. Phys. Chem. 61, 365 (1955)

66. Waycicka, M.K. and Kalinowska, B., Bull. De. L' Acad. Polon. Des. Sci. Ser. Sci. Chim. 25, 639 (1977)

67. Murakami, S. and Benson, G.C., Bull. Chem. Soc. Japan. 46(1), 74 (1973)

68. Veseley, F. and Pick, J., Collect. Czech. Chem. Commun. 34, 1854 (1969)

69. Smirnova, N. and Kurtynina, L.M.,
Zh. Fiz. Khim. 43(7), 1883 (1969)

70. Huong, T.N. and Ratcliff, G.A.,
J. Chem. Eng. Data, 20, 252 (1975)

71. Kretschmer, C.B. and Wilbe, R.,
J. Chem. Phys. 22, 1697 (1954)

72. Redlich, O. and Kister, A.T.,
J. Chem. Phys. 15, 849 (1947)

73. Barker, J.A., J. Chem. Phys. 20, 1526 (1952)

74. Renon, H. and Prausnitz, J.M.,
Chem. Eng. Sci. 22, 299 (1967)

75. Nitta, T. and Katayama, T.,
J. Chem. Eng. Japan 6, 1 (1973)

76. Nitta, T. and Katayama, T.,
J. Chem. Eng. Japan 6, 224 (1973)

77. Wiehe, I.A. and Bagley, E.B.,
Ind. Eng. Chem. Fundam. 6(2), 209 (1967)

78. Lee, T.W. Greenkorn, R. A. and Chao, K. L.,
Chem. Eng. Sci. 28(4), 1005 (1923)

79. Treszczanowicz, A. and Kehiaian, H.,
Bull. Acad. Polon. Sci. Ser. Sci. Chim.
18, 723 (1970)

80. Chao, K.C. Chia, M. and Robinson, R.L.,
Ind. Eng. Chem. Fundam. 9, 564 (1970)

81. Kehiaian, H. and Kehiaian, H.S.,
Bull. Acad. Polon. Sci. Ser. Sci. Chim.
11, 583 (1963)

82. Bellamans, A., Roczniki Chemii 50, 1749 (1976)

83. Ching, C.C., and Wei, Chuwan, Lin.
J. Chin. Chem. Soc. 13(2), 49 (1966)

84. Huyskens, P. Huyskens, T.Z. and Dierckx, A.M.,
Ann. Soc. Sci Bruxelles. Ser I, 78(3), 175 (1964)

85. Geisler, G. Fruwert, J. and Seidel, H.,
Spectrochim. Acta 27(9)A, 1893 (1971)

....

II. EXPERIMENTAL

EXPERIMENTAL

The various apparatus used for measuring different thermodynamic properties viz. volume change on mixing, free energy of mixing and enthalpy of mixing have been described along with their experimental procedures, calibrations and errors involved.

(a) VOLUME CHANGE ON MIXING :

The volume change on mixing is normally determined by two methods. The first involves the direct measurement of change in volumes on mixing of the two liquids. Various types of apparatii for such a method have been described in the literature(1-7). Such equipments are constructed in two basic ways a) one composition per loading of the apparatus at a particular temperature and b) a number of compositions per loading at a constant temperature. The second method is related to the deduction of volume change on mixing from density measurements of mixtures. For this purpose the density of the mixture at different compositions is determined with a high accuracy.

Due to development of some new techniques it has now been easier to determine the density with a very high precision. In the literature one can find a large number of references on the same. The magnetic float method has been used recently upto 5th & 6th place of decimal in the density measurements. The apparatus discussed by Benzamin[8] is sensitive down to ± 0.001%.

The sensitivity of ± 0.0001% for a cell with a 600 cm^3 capacity has been observed by Franks and Smith[9] in their recent magnetic float technique. Millero[10], Dorst-Henson[11] et al and Wirth[12] have described the apparatus with a precision of ± 0.0002%. Different types of dilatometers have been described in the review article of Battino[13]. Washington and Battino[14] described a dilatometer with an accuracy of ± 0.003 cm^3 $mole^{-1}$ in excess volume measurements. A number of pyknometers are described by Bauer and Lewin[15], few of which gave an accuracy of 10^{-5} gm/ml.

In the present investigation the volume change on mixing has been determined by determination of density with a Lipkin type pyknometer.

Pyknometer and its calibration :

A two arm pyknometer (shown in Fig. 1) was made of corning glass, having a volume of 34.06 ml. The two arms were made of two fine capillary tubes having an inner diameter 0.5 mm. The two marks were made at the lower side of the two arms above the bulb of pyknometer by etching the glass.

The evenness of the bore of several capillary tubes was checked by measuring the length of mercury thread at several places by a travelling microscope before using it for the construction of the pyknometer. The pyknometer thus made was annealed several times at 110°C before using it for the measurement of density. The pyknometer was calibrated for its volume at 25°C by double distilled water. The temperature of the thermostatted water bath was maintained constant to

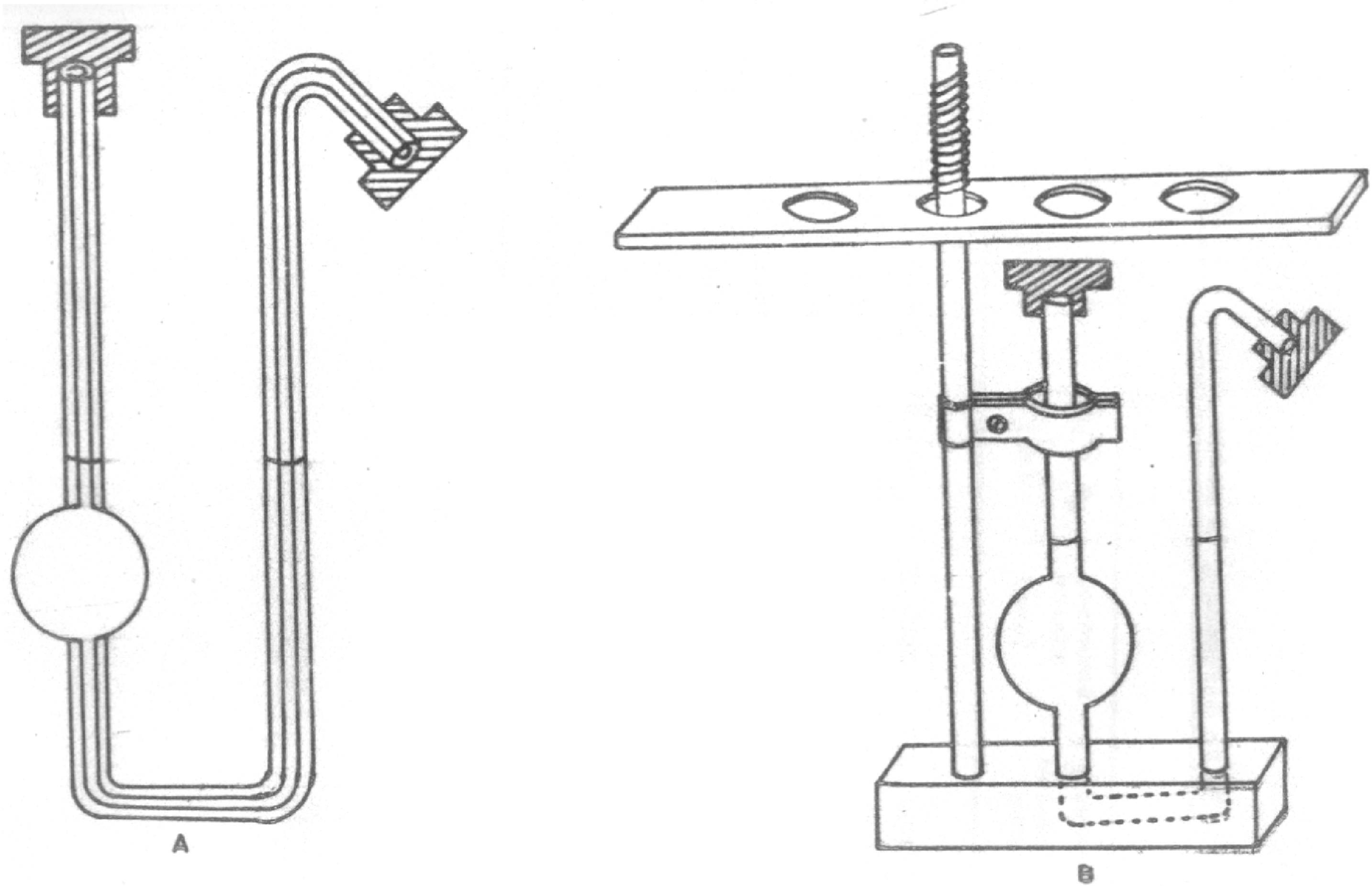


FIG.1. PYKNOMETER AND IT'S ASSEMBLY

Table 1 : Calibration of pyknometer at 25°C

Sr. No.	h_1 (cm)	h_2 (cm)	$h_1 + h_2$ (cm)	Measured weight (gms)	Corrected weight (gms)	Volume (ml)
1	6.099	4.585	10.684	33.9275	33.9651	34.0673
2	5.710	3.848	9.558	33.9251	33.9627	34.0648
3	3.830	4.343	8.173	33.9330	33.9606	34.0627
4	3.021	3.642	6.663	33.9198	33.9574	34.0595
5	2.801	2.761	5.562	33.9179	33.9555	34.0576
6	1.331	2.661	3.992	33.9148	33.9524	34.0545
7	1.146	1.840	2.986	33.9132	33.9508	34.0529
8	0.216	1.072	1.288	33.9099	33.9474	34.0496

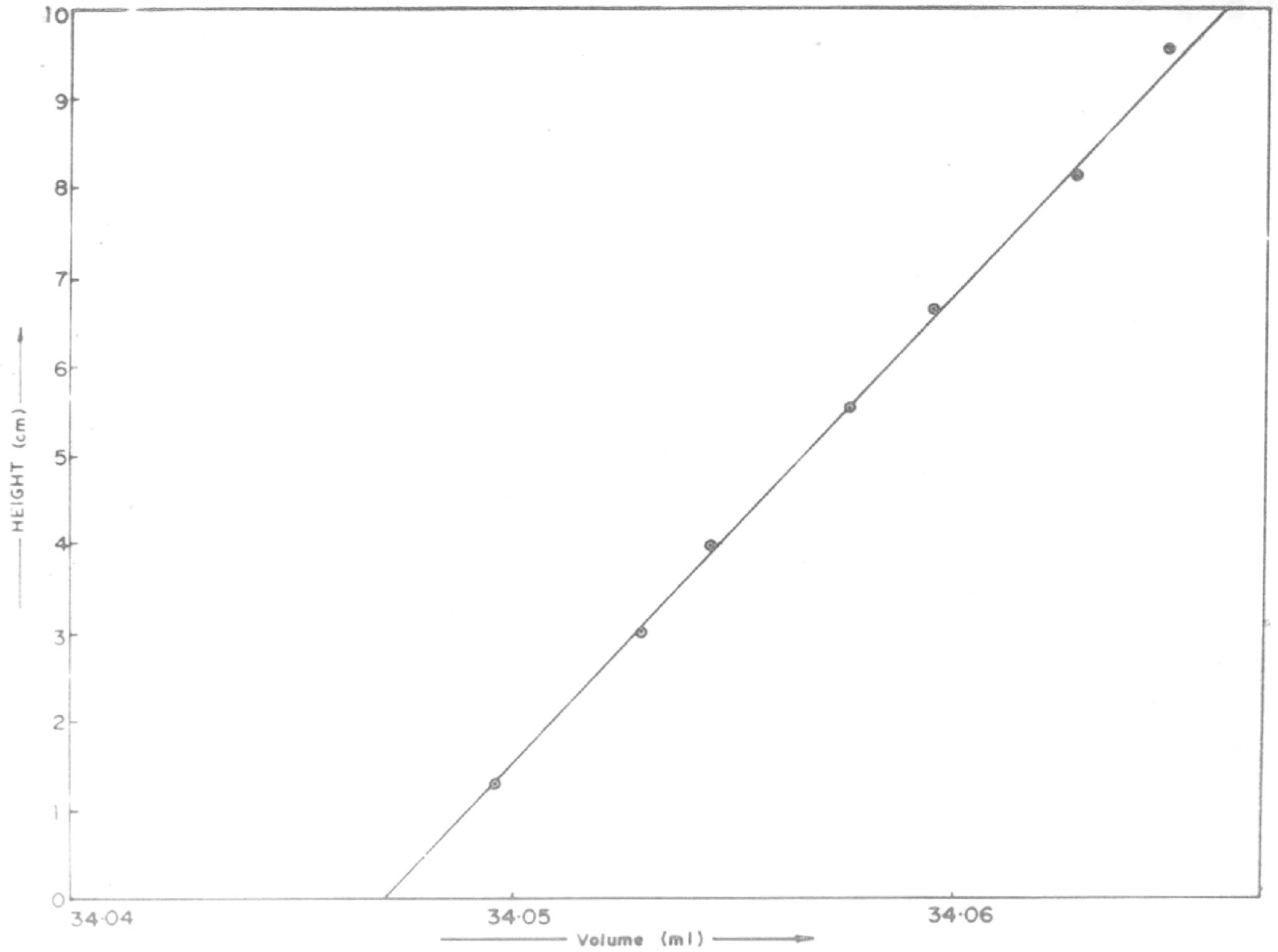


FIG. 2. PYKNOMETER CALIBRATION CURVE

± 0.01°C. The pyknometer was filled with distilled water and mounted on a brass stand as shown in Fig. 1B. It was immersed in the thermostat and allowed to attain the temperature of the bath. The attainment of thermal equilibrium was indicated by a steady state of the liquid i.e. water meniscus in the pyknometer remained constant to ± 0.02 mm. The heights of the water level above the glass marks were measured by a travelling microscope. The pyknometer was taken out from water bath and then dried by absorbent tissue papers and weighed in a single pan semi microbalance. The weights are accurate to ± 0.1 mg. From the weight of water, the volume of pyknometer for the corresponding heights was calculated after appropriate corrections. The sum of the heights in two arms was plotted against the volume of the water. A good straight line was obtained indicating that the volume increased linearly with the height and the deviation from linearity is less than 10^{-4} ml. Calibration results and the curve are shown in Table 1 and Fig. 2 respectively.

The pyknometer was again heated and cooled for several times and the volume was again checked. It was found that heating and cooling did not change the volume of pyknometer and hence the calibration.

Errors involved in the measurement of the volume of pyknometer and the mass of the liquid contained therein were estimated as 10^{-4} ml and 10^{-4}g respectively. Each error produced an uncertainty of 4×10^{-6} units in the density measurement, and hence the maximum error by a combination of these two errors is

8×10^{-6} g/ml. The density measurements were reproducible to 10^{-5} g/ml.

Determination of volume change on mixing :

Liquid mixture of the required composition was prepared by taking weighed quantities of the liquids in a tightly stoppered conical flask and mixing them thoroughly. The pyknometer was filled by capillary action while filling the pyknometer care was taken so that minimum liquid is exposed to air. Since the systems undertaken in the present study are highly hygroscopic, both openings of capillary were closed by polythene caps (Fig. 1B). The total heights were measured in the same way as in calibration and were plotted against the corresponding volumes (Fig. 2). The pyknometer was weighed after the determination of volume and the density was calculated in the usual way. Density for each composition was measured three times and the maximum standard deviation was found to be 6×10^{-6} g/ml.

The excess volume (V^E) was calculated as

$$V^E = V_{obs.} - V_{ideal}$$

$$V_{obs} = M^* / d_{obs}$$

where V_{obs} and d_{obs} were the observed molar volume and density of the mixture respectively. The mass M^* of 1 mole of a mixture was calculated from their individual molecular weights M_1 and M_2 and mole fractions x_1 and x_2 respectively.

Table 2 : Volume change on mixing of Benzene (1) - n-heptane (2) system at 25°C

Sr. No.	x_1 mole fraction of Benzene	d_M density of mixture	V^E volume change on mixing	100 V^E/V^o
1	0.0000	0.67950	-	-
2	0.1004	0.69116	0.1852	0.1308
3	0.1662	0.69872	0.3395	0.2463
4	0.2856	0.71491	0.4493	0.3433
5.	0.3827	0.72889	0.6197	0.4948
6	0.4008	0.73252	0.5403	0.4352
7	0.5020	0.74933	0.5999	0.5070
8	0.5673	0.76131	0.6205	0.5417
9	0.5780	0.76342	0.6426	0.5642
10	0.5894	0.76563	0.6188	0.5464
11	0.6982	0.78880	0.5570	0.5209
12	0.7846	0.80951	0.4600	0.4514
13	0.8909	0.83833	0.3047	0.3182
14	1.0000	0.87350	-	-

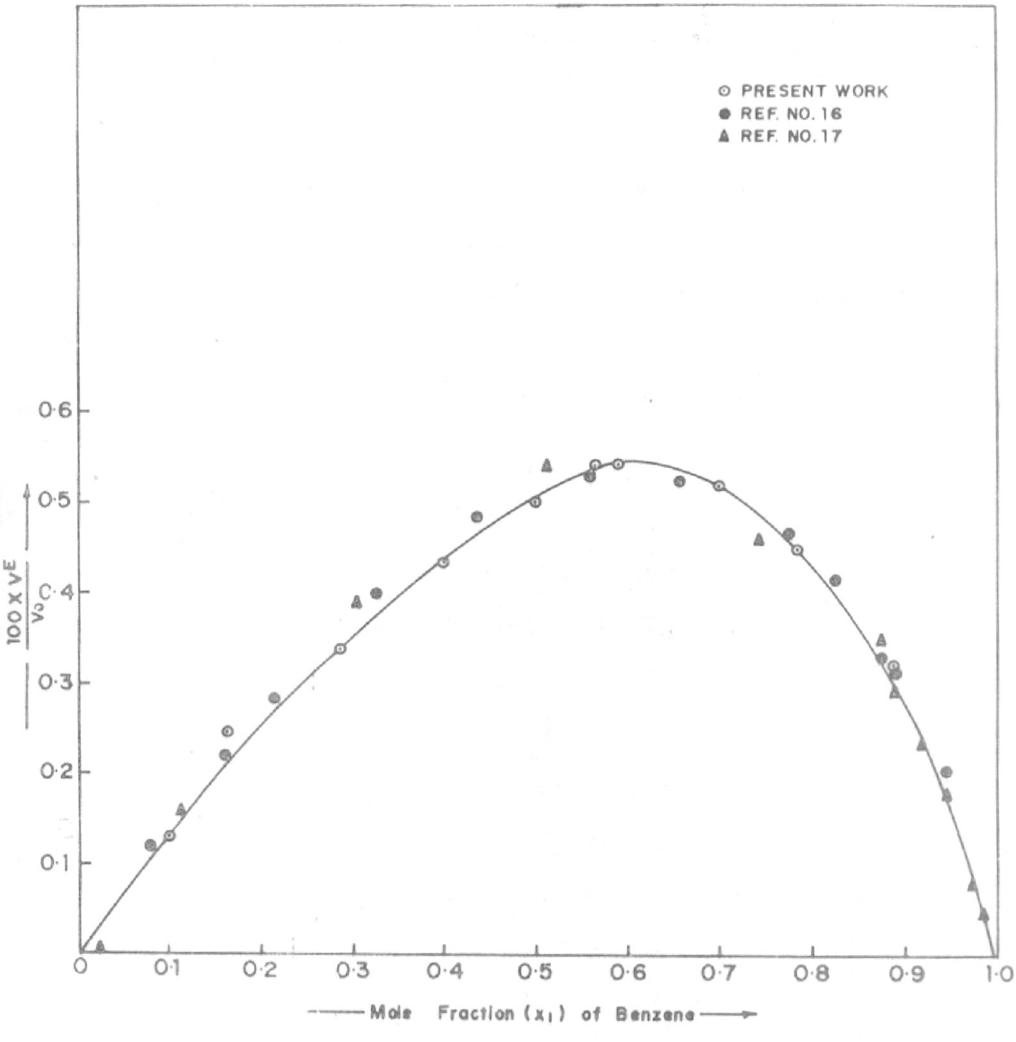


FIG.3. VOLUME CHANGE ON MIXING OF BENZENE(1)—n-HEPTANE(2) SYSTEM AT 25°C

V_{ideal} is the ideal volume of the mixture calculated as

$$V_{ideal} = \frac{M_1 x_1}{d_1} + \frac{M_2 x_2}{d_2}$$

where d_1 and d_2 are the densities of the two pure liquids.

The proper working of the apparatus was checked by studying volume change on mixing of benzene and n-heptane system at 25°C. The results obtained for the above system presented in Table 2 and plotted in Fig.3 agree fairly well with those reported by Brown & Ewald[16] and Jain et al[17].

(b) EXCESS FREE ENERGY OF MIXING :

The determination of excess free energy involves the measurement of isothermal vapour liquid equilibrium. It can be studied by two methods i.e. static and dynamic. The static method is very precise and can be used for very low pressure also. However, we have made use of the dynamic recirculating method due to the existing facilities in the laboratory.

In dynamic recirculating method both liquid and vapour phases are circulated at whatever rate they are generated till a steady state is reached. Liquid and vapour compositions are then determined experimentally. Hala et al[18] have reviewed a large number of recirculating stills. In the present work a modified Jones Colburn still[19] has been used because it was possible for us to conduct experiments with small quantities of the mixtures i.e. 20 ml and also to obtain a thermal equilibrium at a comparatively short period of time. This prevents the shift of the equilibrium condition due to change of barometric pressure as well as the possible small change in composition due to continuous running of vacuum pump.

Recirculating still :

The modified Jones Colburn recirculating still has been shown in Fig. 4. The entire still was made up of pyrex glass. It had a reserve vessel A containing liquid mixture. The reserve vessel was electrically heated by a heater H_1. The remaining portion used as disengaging chamber for the liquid and vapour phases was thermally insulated with an asbestos rope. A thermometer to measure the equilibrium temperature wad dipped in silicone oil in a thermometer pocket T, whose lower end was always above the liquid level in the reserve vessel A. The reserve vessel was fitted to a teflon stopcock K_2 which acts as an out let. The vapour formed from heated liquid mixture in vessel A passed through a tube heated with another heater H_2 and then condensed to liquid in condenser C_1. It was then collected in the receiver B. After the level of the condensed vapour reached the three way teflon stopcock K_3, it slowly fell through the inclined glass tube E, immersed in the liquid mixture in the reserve vessel A. The receiver B was attached with a condenser C_2 which on the other side was connected to vacuum system via standard B-14 ground joint. The desired values of pressure were obtained by connecting a micrometer needle regulating metal valve which regulates the pressure.

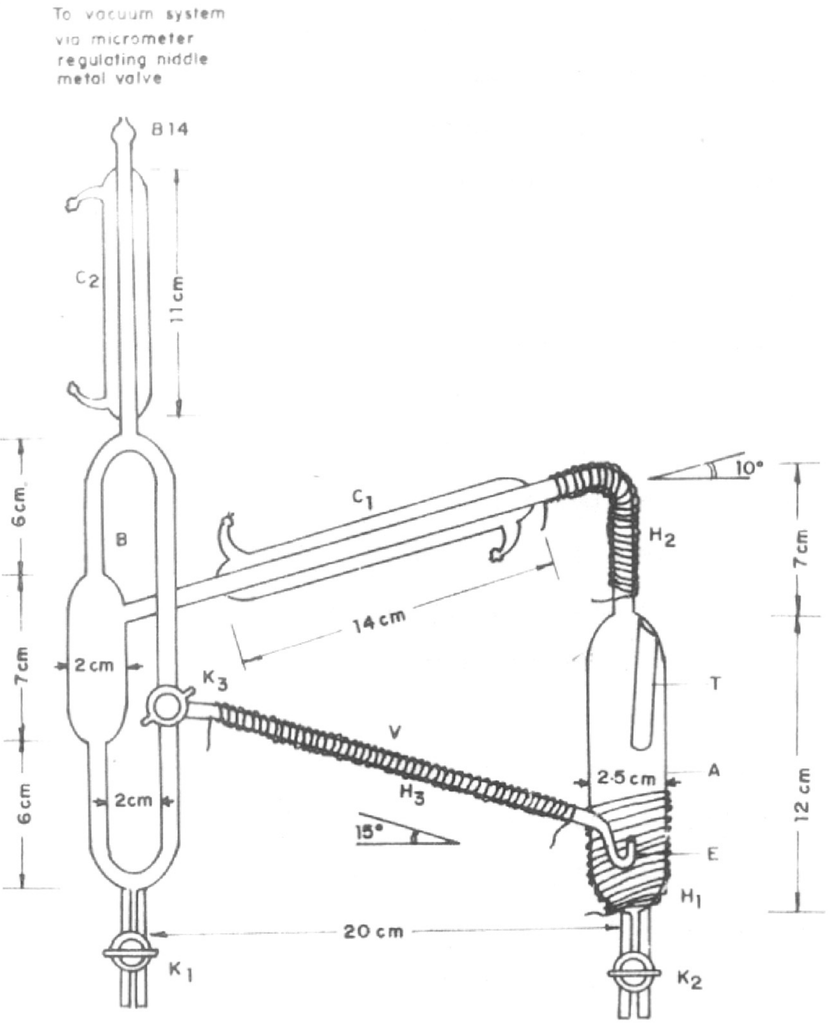


FIG. 4. MODIFIED JONES-COLBURN STILL

Determination of vapour pressure :

A binary mixture 20 ml of the desired concentration was transferred to the still through B-14 joint ofthe condenser C_2, so that its level reached upto the stopcock K_3 in the receiver vessel B and its level was slightly above the opening of the bent tube E in the reserve vessel A. 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 adjusting micrometer needle valve connected to vacuum system. The still was kept in the same condition for one hour so that thermal equilibrium should reach. It was indicated by a constant temperature and system pressure. The pressure difference by on the manometer was read by a cathetometer. Room temperature and atomospheric pressure were noted. The heater switches were put off. The vacuum in the still was released slowly. The stopcock K_3 was simultaneously rotated to cut off the circulation of the liquid. The samples of the liquid from the vessel A and condensed vapour from vessel B were collected through teflon stopcock 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 corrections for expansion of mercury and for the difference in the room temperature of calibration of cathetometer. A value of g equal to 978.59 cm/sec^2 valid for Poona was used in the calibration of pressure.

Analysis of samples :

Liquid and vapour samples were analysed by density measurements. Density of the liquids were determined at 25°C with the help of Lipkin type pyknometer of about 3.6 ml capacity. Such a pyknometer has been shown in Fig. 5. Its construction and calibration have already been given in Section (a) "volume change on mixing" of this chapter. The calibration curve i.e. height vs volume obtained from the results reported in Table 3 has been plotted in Fig. 6. The straight line curve obtained for calibration confirms the uniformity of the diameter of the capillary tube of the pyknometer. The thermostat was obtained at 25 ± 0.01°C. The readings of the heights h_1 and h_2 were taken in the same way as mentioned in II (a) and the density of each liquid was calculated at 25°C.

Excess free energies of mixing from vapour liquid equilibrium :

The excess free energies of mixing of the systems were calculated by isothermal P-x,y data at 55°, 65° and 75°C throughout the concentration range. P denotes the total solution pressure while x and y the liquid and vapour compositions. The liquid phase activity coefficients γ_1 and γ_2 were calculated as

$$\ln \gamma_1 = \ln \frac{y_1 P}{x_1 p_1^s} + \frac{(B_{11} - V_1^L)(P - p_1)}{RT} + \frac{P\,\delta_{12}\,y_2^2}{RT} \tag{1}$$

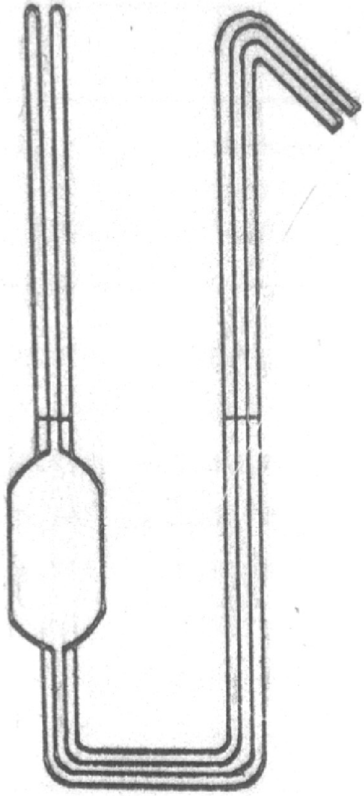


FIG.5. PYKNOMETER

Table 3 : Calibration of pyknometer at 25°C

Sr. No.	h_1 (cm)	h_2 (cm)	$h_1 + h_2$ (cm)	Measured weight (gms)	Corrected weight (gms)	Volume (ml)
1	4.065	4.600	8.665	3.6070	3.6108	3.6215
2	3.685	4.247	7.932	3.6058	3.6096	3.6203
3	2.820	3.650	6.470	3.6033	3.6071	3.6178
4	2.634	2.915	5.549	3.6017	3.6055	3.6162
5	1.650	2.461	4.111	3.5992	3.6030	3.6137
6	1.502	1.508	3.010	3.5975	3.6013	3.6120
7	0.905	0.908	1.813	3.5955	3.5993	3.6100
8	0.502	0.552	1.054	3.5942	3.5980	3.6087

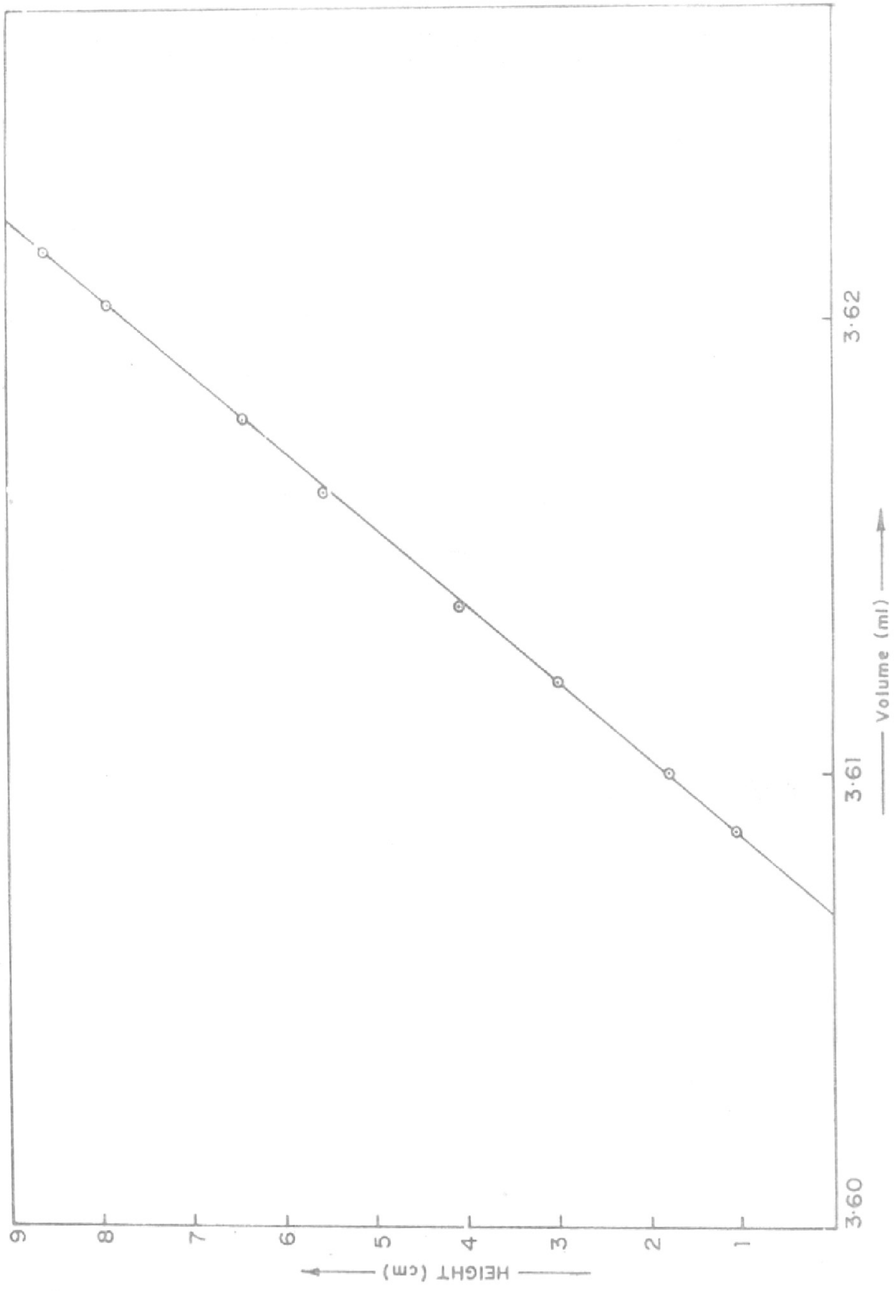


FIG.6. PYKNOMETER CALIBRATION CURVE

$$\ln \gamma_2 = \ln \frac{y_2 P}{x_2 p_2} + \frac{(B_{11} - V_2^L)\ (P - p_2)}{RT} + \frac{P\,\delta_{12}\,y_2^2}{RT} \qquad (2)$$

where p_1 and p_2 are the vapour pressure and x_1 and x_2 are the mole fractions in liquid phase, y_1 and y_2 are the mole fractions in the vapour phase, V_1^L and V_2^L are the molar liquid volumes of the component (1) and (2) respectively. B_{11} and B_{22} are the second virial coefficients of the pure components (1) and (2) respectively and

$$\delta_{12} = 2\,B_{12} - B_{11} - B_{22} \qquad (3)$$

where B_{12} is the second virial cross coefficient of the mixture and given by the expression

$$B_{12} = (B - y_1^2 \times B_{11} - y_2^2 \times B_{22})/\ 2\,y_1 y_2 \qquad (4)$$

where B is the virial coefficient of the mixture. The excess free energy of mixing is calculated from the equation

$$G^E = RT\,(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \qquad (5)$$

If the vapour phase is an ideal gas which is mostly true at low pressures, the last two terms of the equation (1) and (2) become insignificant and we then have

$$\gamma_1 = \frac{y_1 P}{x_1 p_1} \qquad (6)$$

$$\gamma_2 = \frac{y_2 P}{x_2 P_2} \qquad (7)$$

Since the values of second virial coefficients of isomeric butanols and n-heptane at 55°, 65° and 75°C were not available in the literature, they were calculated by Pitser-Curl equation[20]

$$B = \frac{R\,T_c}{P_c}\ (0.1445 + 0.073w) - (0.0330 - 0.46w)\ Tr^{-1}$$

$$- (0.1385 + 0.50w)\ Tr^{-2} - (0.0121 + 0.097w)\ Tr^{-3}$$

$$- 0.0073w\ Tr^{-8} \qquad (8)$$

where R is the molar gas constant, T_c and P_c are critical temperature and pressure, w, the accentric factor which is a macroscopic measure of the extent to which the force field around the molecule deviates from spherical symmetry and is found by equation

$$w = - \log (P_r)_{T_r = 0.7}\ ^{-1} \qquad (9)$$

where P_r is the reduced pressure and is equal to P/P_c and T_r is the reduced temperature which is equal to T/T_c.

In the literature there are many expressions for calculating the second virial coefficient as those of Black[21,22] and O'connell and Prausnits[23] but they could not be used for want of constants.

The change in the values of second virial coefficient may not effect much the calculation of the excess free energy. The calculated values of second virial coefficients for all the compounds at 55°, 65° and 75° are given in Table 4.

The values of δ_{12} used in equation (1) and (2) and defined by (3) can be calculated only if the value of B_{12} is known. It can be calculated by using O'connell and Prausnitz[23] method but due to lack of some constants, it could not be obtained. If the vapour phase is considered as ideal, the equation (3) becomes

$$B_{12} = \frac{1}{2} (B_{11} + B_{22}) \quad \text{where} \quad \delta_{12} = 0$$

and so the third term in equation (1) and (2) becomes zero. It is assumed B_{12} to be a geometric mean of B_{11} and B_{22} as

$$B_{12} = (B_{11} \times B_{22})^{1/2}$$

which has been followed by Boublikove and Lu etc[24].

The molar volumes V^L for all compounds at 55°, 65° and 75° C are given in Table 5.

<u>Testing of equilibrium data for thermodynamic consistency</u> :

All the experimental data were checked by Herington's method[25] of internal thermodynamic consistency test, by using the equation

$$\int_0^1 \log \frac{\gamma_1}{\gamma_2} \, dx_1 = 0 \qquad (10)$$

Equation (10) indicates the algebraic area bounded by $x_1 = 0$ and $x_1 = 1$ in the plot of log γ_1/γ_2 <u>vs</u> x_1 should be zero. Coulson and Herington [26], Redlich and Kister[27,28] have given

Table 4 : Values of second virial coefficient at different temperatures

Compound	Second virial coefficient (-cm^3 mole^{-1})		
	55°	65°	75°
n-butanol	1368	1208	1068
iso-butanol	1277	1013	815
sec-butanol	1149	1014	899
tert-butanol	946	836	742
n-heptane	1366	1222	1094

Table 5 : Values of molar volumes at different temperatures

Compound	Molar volume ($ml\ mole^{-1}$)		
	55°	65°	75°
n-butanol	94.78	95.74	96.72
iso-butanol	95.56	96.49	97.45
sec-butanol	94.94	95.84	96.75
tert-butanol	98.87	100.28	98.87
n-heptane	153.28	155.32	157.42

Table 6 : Vapour liquid equilibrium of Ethanol (1) and water (2) system at 50°C

(Present work)

Sr. No.	x_1	y_1	P (mm of Hg)	$\log \gamma_1/\gamma_2$
1	0.0000	0.0000	92.5	-
2	0.0169	0.1616	110.3	0.6716
3	0.0239	0.2070	112.3	0.6496
4	0.0426	0.3226	129.2	0.6514
5	0.1034	0.4842	157.8	0.5325
6	0.1368	0.5292	175.8	0.4726
7	0.1609	0.5394	184.2	0.4077
8	0.2256	0.5783	185.2	0.2945
9	0.3050	0.6071	195.9	0.1685
10	0.3748	0.6340	200.0	0.0823
11	0.4835	0.6655	205.7	-0.0507
12	0.6277	0.7262	212.3	-0.1813
13	0.7275	0.7732	218.1	-0.2719
14	0.9385	0.9364	213.3	-0.3927
15	1.0000	1.0000	220.9	-

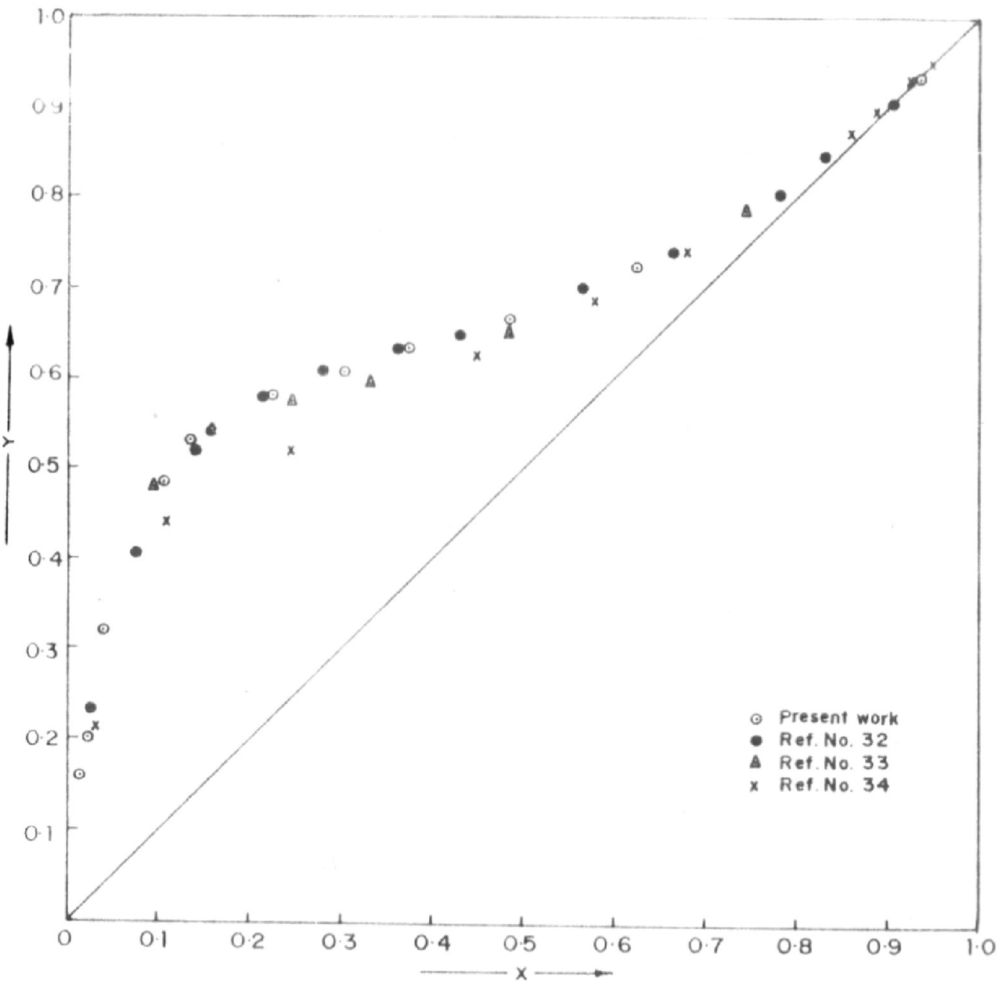


FIG. 7. X-Y DIAGRAM FOR ETHANOL - WATER SYSTEM AT 50°C

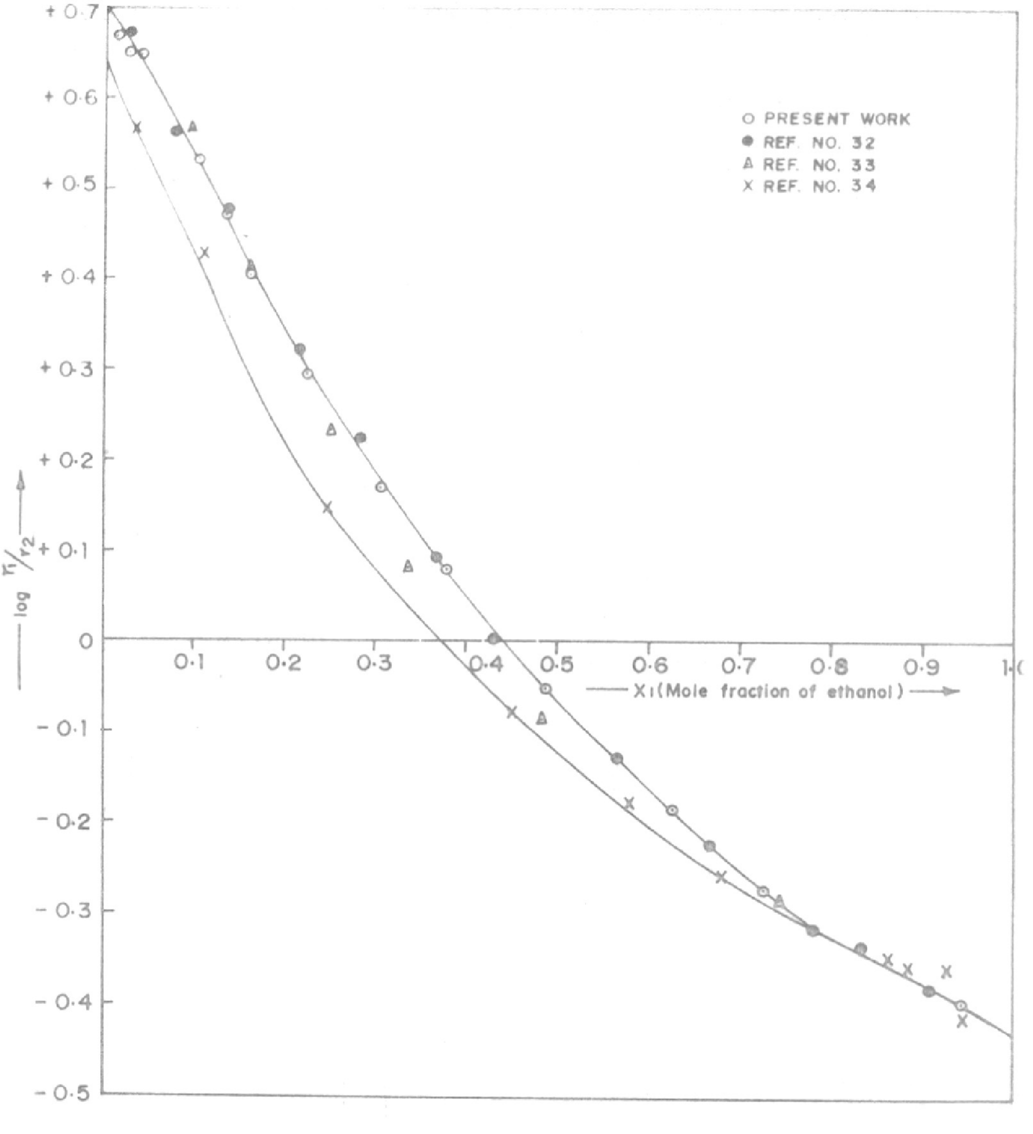


FIG. 8. THERMODYNAMIC CONSISTANCY TEST : ETHANOL-WATER SYSTEM AT 50°C

further details of this method. Inspite of several criticisms[29,30] Harington's method still seems to be useful for the consistency test as has been elaborated by him[31].

The general working of Jones Colburn still was checked by studying ethanol-water system at 50°C. The data given in Table 6 and Fig. 7 agree fairly well with those reported earlier[32,33,34]. The experimental data are subjected to the above thermodynamic consistency test which show a percentage deviation of 1-2% compared to 1.4% for the data of Dutta Choudhury[32], 4.8% for the data of Dulitskaya[33] and 23% for the data of Udovenko[34] as shown in Fig. 8.

(c) HEATS OF MIXING :

In last 25 years an appreciable amount of work has been carried out on the measurement of heats of mixing and in the development of various types of calorimeters[35-39]. McGlashan[40] has discussed various calorimeters and has mentioned about different factors and conditions which should be taken in account while constructing the apparatus and measuring the various parameters involved. It is worthmentioning that sufficient precautions should be taken to eliminate the vapour space in contact with liquid and to provide a space for the contraction or expansion of liquids on mixing. A number of such calorimeters[41-44] are described in the literature.

Van Ness[45] has described a new isothermal dilution calorimeter in which one liquid is successively diluted by the addition of the other component. The advantage lies in the fact that by taking a single experimental set up, one can measure the enthalpy of mixing at a series of decreasing concentrations. Such a calorimeter was meant initially for the endothermic heats of mixing but later on modified for exothermic[46-47] system. It gives data with an accuracy of 0.2% and can measure the heats of mixing from 0.01 to 0.99 mole fractions. The entire set up requires sophisticated instruments and an electronic shop. Recently flow calorimeters[48-51] have been introduced with an accuracy of one percent. The main problem in this method is to obtain a constant rate of flow.

The heats of mixing can also be calculated by temperature dependence of free energy but it gives the results of uncertain accuracy[40].

In the present investigation we have made use of a twin type calorimeter, similar to that of Adcock and McGlashan[43] with some minor modifications[52,53]. The further modifications for measuring the heats of mixing at high temperatures incorporated in the present investigation are discussed later on.

Calorimeter:

The calorimeter assembled in this investigation is shown in Fig. 9(a) with the left hand compartment of the calorimeter as assembled and the right hand compartment of the calorimeter dismantled.

The calorimeter was made up of two identical double jacketed corning glass mixing and reference vessels A_1 and A_2 with B 55

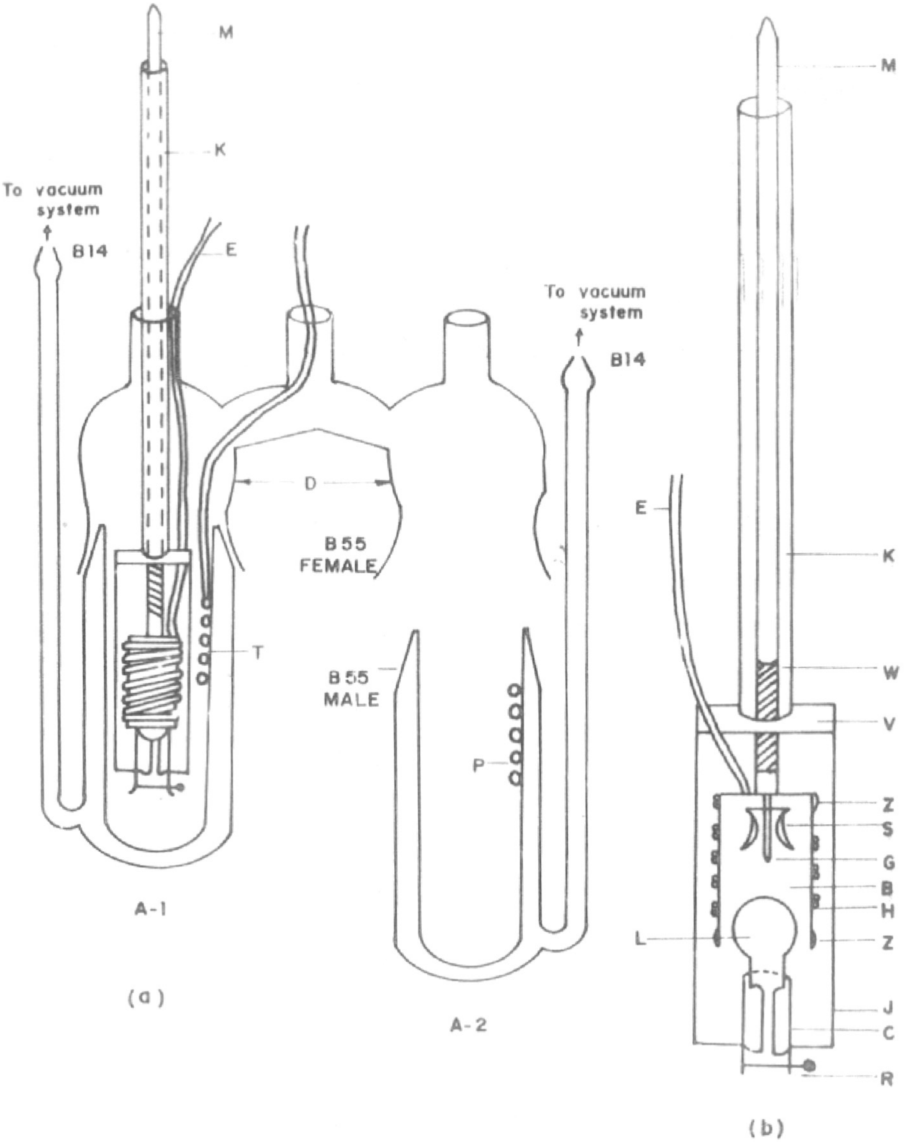


FIG.9. THE CALORIMETER

male ground joints. The outer jackets were connected to the side tubes with a B 14 male ground glass joints at the end for connecting them with vacuum system. Thermistors used as heat sensing elements were fixed in thick polythene tube with a suitable base inside the inner vessel of each calorimeter P. A double cap D with two B 55 female ground glass joints was used to close both the vessels A_1 and A_2 through male joints fixed to the mixing and reference vessels.

Mixing vessels :

Two liquids were mixed inside a stainless steel bell B. The bell and mixing arrangement are shown schematically in Fig. 9b. The bell was made of stainless steel cylindrical tubes of the size of 2 cm diameter and 5 cm length. One side of the cylinder was closed by stirrer blades S and a sharp pointer G. The bell was connected to a stainless steel rod M through a perspex (Lucite) piece W used for thermal insulation of the steel bell B from the steel rods. Both bells were made as identical as possible in respect of their weight and shape.

Stainless steel frame :

A rectangular stainless steel frame J of 12 cm x 3.2 cm hold a stainless steel bell. The frame consists of two stainless steel rods of 2 mm diameter. One end of the rods is joined to an ebonite plate V connected to a brass tube K at its centre. The other ends of the rods were connected to a clamp C with a lightening screw R. The brass tube K of 8 mm O.D. and 25 cm length was threaded at one end so as to be fitted to the threaded hole in the elbonite plate V.

Sampling bulb:

A small glass bulb L of 2 ml capacity with a soft glass tube of 9 mm in diameter was used for filling one of the components. The bulb was made very thin walled so that it should break when struck with the pointer G of the bell.

Thermal sensing element :

Thermistors as heat sensing elements were obtained from M/s Tempo Semiconductors Bombay. The resistance of the thermistors was 33 k ohms. The resistance as matched by the manufacturer was ± 1%. Since the equal temperature coefficient of the resistance of the matched thermistors is necessary, the pair was calibrated at different temperatures and the pair with ± 1% resistance was used as heat sensing element. Both leads of thermistors were soldered to two thin shielded wires. The soldered portions were coated with a thick layer of an epoxy resin.

Calorimeter heaters :

A 38 s.w.g. constantan wire was used to make the calorimeter heaters H shown in Fig. 9. The ends of constantan wires were finally soldered to a two 28 s.w.g. enamelled copper wires of about 1 meter length. The leads of constantan wire along with copper wire were inserted in a 24 s.w.g. teflon sleeve. The heater as such was wound non-inductively around the stainless steel bell B. The heater wires along with teflon sleeve were fixed to the bell with two teflon rings s on its both ends. The resistance was measured by a digital volt ohm meter (M/s Yamuna Electronics, Hyderabad). The correction for resistance of copper wire was applied. The resistance of heater was measured every time before the experiment.

Electrical circuit :

The electrical circuit used in the experimental set up is shown in Fig. 10. The current was provided by power supply B of 2 volts. H_1 and H_2 were the heaters for the reaction and reference vessels respectively. H_3, a dummy heater was used for passing current for an hour in order to stablise B. The potential across a standard 10 ohm resistance R_1 in series with the heater was measured by means of a potentiometer (accuracy 0.01 mV) to find out the value of current passing through the heaters H_1 or H_2. The time for which the current was passed through the heater was measured by an electronic timer. On stopping the timer, the current through the heater was simultaneously cut off, so as to measure the time accurately.

Wheatstone bridge circuit :

Fig. 11 shows the circuit of wheatstone bridge. Its four arms were formed by two matched thermistors and two 56 K ohm resistance in series with 10 K ohm wire wound potentiometer. Either of the two 56 K ohm arms was connected to a 500 ohm wire wound potentiometer. The output of the bridge was fed to a potentiometer recorder (25 mv Honeywell) whose pen can be adjusted by manipulation of 10 K ohms and 500 ohms course and

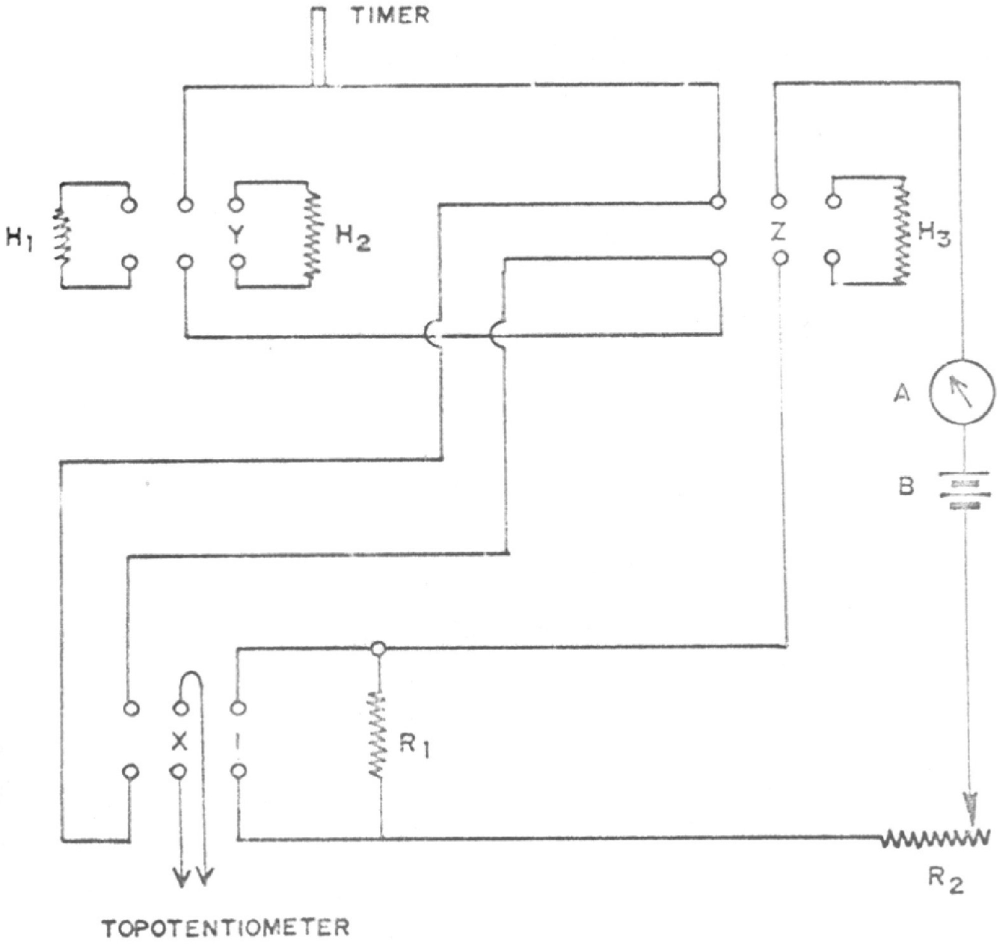


FIG.10. ELECTRICAL CIRCUIT

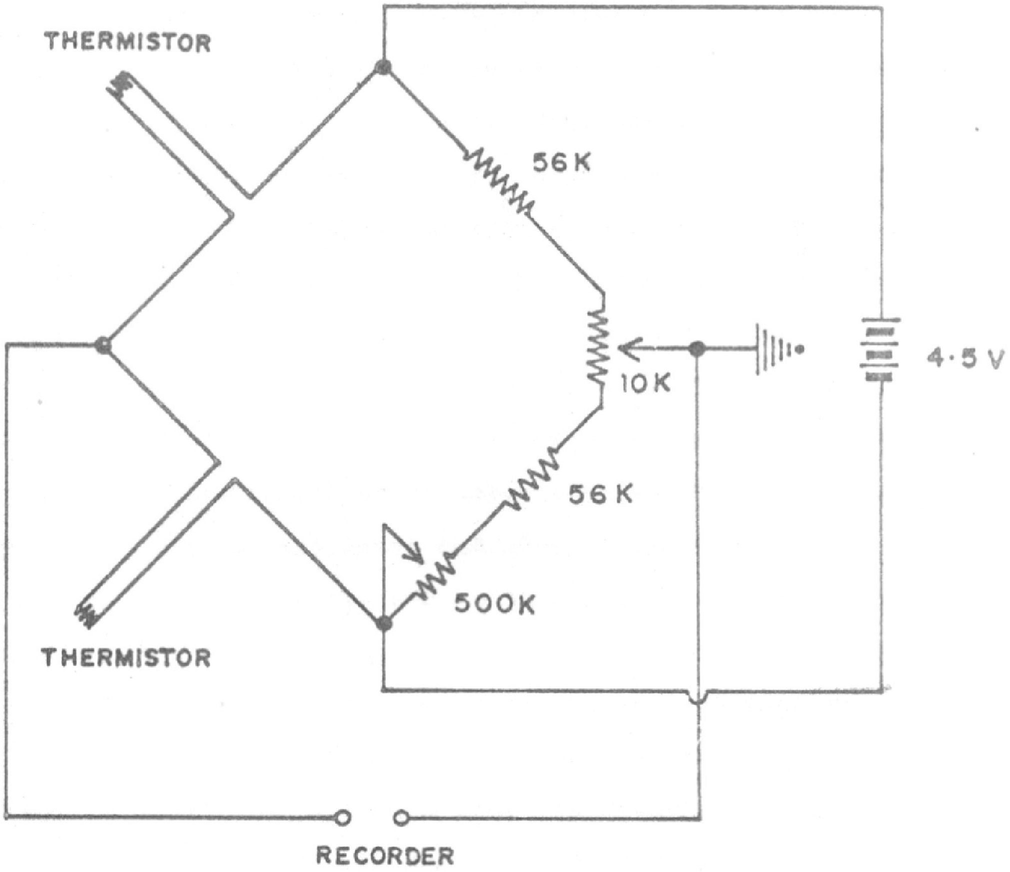


FIG.11. THERMISTOR BRIDGE CIRCUIT

fine variable resistances respectively.

Constant temperature bath :

The constant temperature bath was made up of two concentric water baths. The outer bath of 250 litres capacity contains the inner copper bath of 15 litres. Both water baths efficiently stirred by electric motors, In the outer bath the temperature was maintained by two heaters of 1500 w. The temperature was controlled by a coiled toluene mercury thermoregulator coupled with 200 w electric bulb and an electronic relay. In order to check the heat losses at high temperatures the inner bath was covered by an insulated lid. The calorimeter was immersed in the constant temperature inner water bath so that only the tubes for taking out the leads and steel rods were out of water. A small heater of 100 watts was continuously used for maintaining a temperature of 55°C in the inner bath. The consistency of the temperature was checked by Beckman thermometer with an accuracy of ± 0.01°C. The temperature inside the calorimeter was constant to within ± 0.01°C for 2 hrs as read by Beckman thermometer. The temperature of outer and inner baths were maintained at 55° ± 0.01°C.

Experimental set up :

The calorimeter was fixed on a heavy brass stand. Equal amount (78 ml) of mercury was filled in both vessels. The glass bulbs were fixed into two small frames L which in turn were placed inside the steel frame B, fixed to the tubes K. The bell was fixed by a ring of rubber bands in such a manner that the glass bulb was covered by the bell but the pointer G remained above the bulb. Such an arrangement is shown in Fig. 9b. The bells along with the bulbs were immersed completely in mercury in the two vessels. One of the liquids was taken in the bulb and other in the bell, both of which were immersed in mercury filled in vessels A_1 and A_2. The bulb was first evacuted by means of a syringe with a U shape stainless steel needle. One of the liquids was taken in an another air tight syringe and all air was carefully removed from the syringe. The syringe was weighed on a single pan balance and the liquid was immediately transferred into the bulb. The syringe was reweighed. The amount of the compound taken was noted. In the case of back sucking of mercury by syringe, the mercury was transferred into a beaker which was dried and weighed and correction was applied for the weight of the compound. The second liquid was also transferred in a similar way in the bell. The bell and the bulb of the reference vessel were also evacuted in a similar way for removing trapped air. The reference vessel was also charged with both the liquids for compensating for their heat capacities.

Then the thermistors were inserted in their pockets. The stainless steel rods of the bell, the lead wires of the thermistors and the heaters were taken out from the three opening of the lid (see Fig. 9B). The lid was fixed to the calorimeter vessel with the help of ground joints properly greased by high vacuum silicone grease. The calorimeter was kept in the inner constant temperature water bath and the heater and thermistor wires were connected to the electric circuit and wheatstone bridge respectively as shown in Fig. 11.

Determination of heats of mixing :

The charged calorimeter was kept in the inner constant temperature water bath maintained at 55°C for three to four hours in order to attain thermal equilibrium. The attainment of thermal equilibrium was indicated by a steady undrifted line traced by the recorder pen. On attaining the equilibrium the calorimeters was evacuted through vacuum system for about an hour. After passing the current through dummy heater which was done in order to stablise the current, the bulb was broken with the help of pointer G. The bell was stirred gently to ensure proper mixing. This temperature of the mixing vessel decreased because of endothermic reaction between alcohol and nonpolar hydrocarbon. This decrease in temperature caused the increase in resistance of the corresponding thermistor. Due to increase in resistance there was a imbalance in voltage distribution through the wheatstone bridge which was traced by pen on recorder. Simultaneously the heater of the reaction vessel was put on. In the mean time the current passing through the heater was measured by potentiometer. Due to heating in the reaction vessel the recorder pen moved to opposite direction for compensation of heat absorbed during the reaction. The heater was put off before reaching to an exact compensation to make the allowance for residual heat. Gently stirring was continued in both the vessels till the tracing of steady straight line parallel to chart paper was obtained. The time (t) for which the heater was heated was noted by electronic timer.

Correction for inexact compensation :

In general it is not possible to obtain the final line coinciding with base line by heating the heater of the reaction vessel Fig. 12. In such cases a correction factor denoted by ($\triangle T$) for inexact compensation $\triangle_1$ was calculated by time calibration experiment. The heater of the reaction vessel was again heated for about 100 seconds. The separation between initial base line and final base line ($\triangle_2$, Fig. 12) was measured. The current and the time for which it was passed were also measured. The correction factor $\triangle T$ in the time of compensation corresponding to deflection $\triangle_1$ in an actual experiment could be calculated by an expression

$$\triangle T = \frac{\triangle_1 \; i_2^2 \; t_2}{\triangle_2 \; i_1^2} \qquad (13)$$

where t_2 = calibration time

i_2 = current passed through the heater at the time of calibration

i_1 = current passed through the heater at the time of actual experiment

The H^E was then calculated by

$$H^E = \frac{i^2 \; r \; (t \pm \triangle T)}{(n_1 + n_2)} \qquad (14)$$

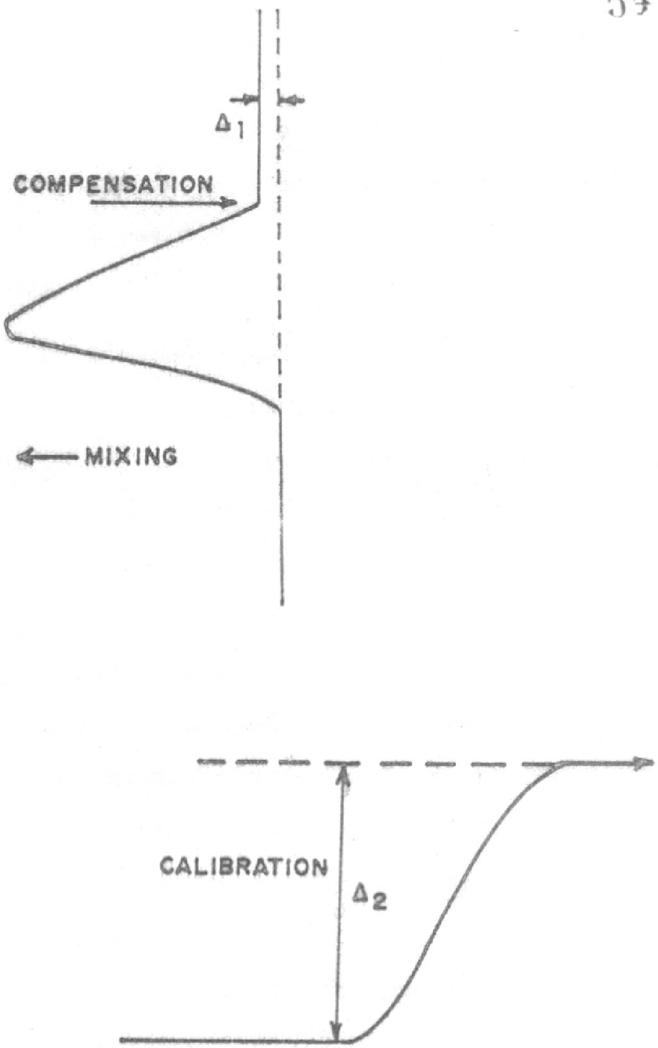


FIG.12. RECORDER TRACE FOR HEAT COMPENSATION

where γ is the resistance of the heater and n_1 and n_2 are the number of moles of the two liquids. i is the current passed through the heater during reaction.

Standarisation of calorimeter :

In order to establish the identical nature of two halves of calorimeter a dummy experiment was carried out. Two heaters of the same resistance were wound on each bell and equal amount of mercury was filled in the vessels. On attaining the thermal equilibrium in the constant temperature water bath the same amount of current was passed through both heaters for about five minutes. Both the bells were gently and continuously stirred. It was found that the base line was shifted by two small divisions. On heating a calorimeter by one heater the deflection by 200 small divisions was noted on passing the same current for the same time. It showed that heat capacity of the two calorimeters was matched to within one percent.

Since it was expected that some heat may be evolved during the breaking of the bulb, a dummy experiment was conducted to break the bulb. It was found that no deflection was recorded while breaking the bulb, the probable heat evolution was considered as negligible.

The overall working of the calorimeter was checked by studying the heats of mixing of sec-butanol-benzene system at 45°C. The result on H^E for this system obtained by us are given in Table 7 along with those obtained by Brown et al[54] in Table 8. Our data are plotted in Fig. 13 as H^E vs x_1 the mole

Table 7 : Heats of mixing of sec-butanol (1) and Benzene (2) system at 45°C

(Present work)

Sr. No.	x_1 mole fraction of sec-butanol	H^E J mole^{-1}
1	0.1301	1282
2	0.1355	1282
3	0.1358	1286
4	0.2157	1586
5	0.2638	1730
6	0.3248	1861
7	0.3998	1893
8	0.4098	1899
9	0.4276	1920
10	0.5600	1767
11	0.6524	1629
12	0.7005	1429
13	0.7444	1295
14	0.8382	921
15	0.8388	919

Table 8 : Heats of mixing of sec-butanol (1) and benzene (2) system at 45°C

(Literature value Ref. No. 54)

Sr. No.	x_1 mole fraction of sec-butanol	H^E J mole^{-1}
1	0.1	1100
2	0.2	1560
3	0.3	1790
4	0.4	1880
5	0.5	1840
6	0.6	1690
7	0.7	1430
8	0.8	1060
9	0.9	580

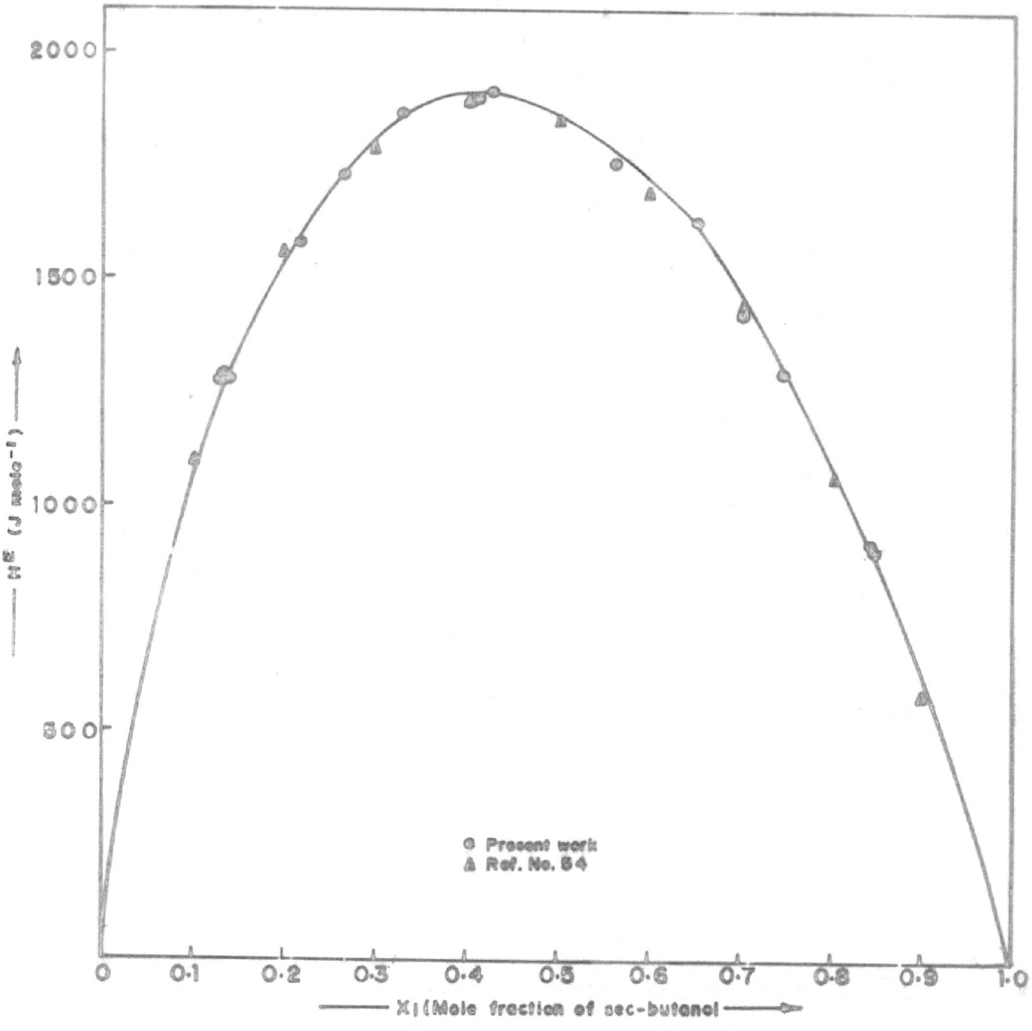


FIG. 13. HEATS OF MIXING OF sec-BUTANOL — BENZENE SYSTEM AT 45°C

fraction of butanol along with Brown et al results which agree fairly well.

Discussion on sources of errors:

Attention was paid on the following sources of errors involved in the heats of mixing experiments.

a) Change in the number of moles during weighing :

There are probabilities of evaporation of the liquid while weighing. It was avoided by taking air tight syringes with long piston and quick transfer of liquid inside the bulb and bell. The error estimated was ± 0.2%.

b) The change in resistance of heater during use :

It was noted that after every experiment the resistance of the heater did not change appreciably so as to cause error more than ± .005% as indicated by the digital ohmometer.

c) Heat effects due to improper stirring and breaking of bulb :

It was ensured by repeated breaking of bulb and stirring that their contribution was negligible as no indication was shown on the recorder.

d) Errors in the measurement of current :

To avoid the error due to small fluctuation in current, it was measured once at the start of heating and then at the end of heating. The mean value of the two readings was then used for further calculations. The error due to fluctuation was estimated to be of the order of ± 0.1%.

e) The contribution due to inexact matching of the two thermistors was estimated to be ± 1%.

f) The error due to inaccurate reading of inexact compensation was estimated to be of the order of ± 0.5 to 1%.

g) Some liquid was likely to be trapped inside the mercury. It was released by halting the stirring intermittently.

Taking into consideration all the above sources of errors the results may have the uncertainties of ± 2%.

(d) PURIFICATION OF CHEMICALS :

Benzene :

BDH analar grade benzene was repeatedly treated with concentric H_2SO_4 until free of thiophene. It was then washed thoroughly with distilled water. The acid free benzene was dried over anhydrous K_2CO_3. It was fractionally distilled over P_2O_5.

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 before use.

Isomeric butanols :

n-butanol (BDH pure grade), iso-butanol (BDH, LR grade) sec-butanol. (Renal Budapest) and tert-butanol, (Baeyer German Product) were used. The butanols were refluxed over NaOH pellets and thereafter fractionally distilled using 1m long

Table 9 : Densities of the pure materials at 25°C

Substances	Present work	Literature value	Reference no.
Benzene	0.87350	0.87363	55
n-heptane	0.67950	0.67951	55
n-butanol	0.80570	0.80570	56
iso-butanol	0.79790	0.79780	55
sec-butanol	0.80223	0.80260	55
tert-butanol*	0.77987	-	-
Ethanol	0.78503	0.78508	57

* at 26°C

column packed with glass helices with a reflux ratio 1 : 30. The constant boiling middle fraction was again fractionally distilled in the same manner. All butanols were refluxed over anhydrous CaO before use.

n-heptane :

A product of Reachim standard U.S.S.R. was purified in the same manner over P_2O_5 as mentioned above.

All the compounds were stored over molecular sieves type 4A before use. The purity of the compounds was checked by g.l.c. and was found to be 99.5%. The purity of these materials was also confirmed by determining the densities and comparing them with the literature[55,56,57] values summarised in Table 9.

REFERENCES

1. Bellamans, A., Bull. Soc. Chim. Belges. 66, 636 (1957)

2. Brown, I. and Smith, F., Aust. J. Chem. 15, 1, (1962)

3. Rastogi, R.P. and Nath, J., Indian J. Chem. 5, 249 (1967)

4. Wirth, H.E. and Mills, W.L., J. Chem. Eng. Data, 13, 102 (1968)

5. Staveley, L.A.K. and Spice, B., J. Chem. Soc. 406 (1952)

6. Keyes, D.B. and Hildebrand, J.H., J. Am. Chem. Soc. 39, 2126 (1917)

7. Duncan, W.A. Sheridan, J.P. and Swinton, F.L., Tans. Fara. Soc. 62, 1090 (1966)

8. Benjamin, L., J. Phys. Chem. 70, 3790 (1966)

9. Franks, F. and Smith, H.T., Trans. Fara. Soc. 63, 2586 (1967)

10. Millero, F.J., Rev. Sci. Instrum. 38, 1441 (1967)

11. Dorst-Hansen, W. Millero, F.J. Scheraga, H.A. Hunter, J.A. Gilman, W.S. and Johnson, S., U.S. Office of Saline water, Research and Development Progress Report No. 350, U.S. Govt. Printing Office, Washington D.C. 1968, 65 pp

12. Wirth, H.E., J. Am. Chem. Soc. 59, 2549 (1937)

13. Battino, R., Chem. Rev. 71, 1 (1971)

14. Washington, E.L. and Battino, R., J. Phys. Chem. 72, 4496 (1968)

15. Bauer, N. and Lewin, S.Z., "Physical Methods of Organic Chemistry", Vol. I, Part-1, 3rd ed. Edited by A. Weissberger, Interscience, New York, N.Y. 1959, 131 pp

16. Brown, I. and Ewald, A.H., Aust. J. Sci. Res. A4, 198 (1951)

17. Jain, D.V.S. Dhawan, R.K. and Tiwari, K.K., Indian J. Chem. 6, 511 (1968)

18. Hala, E. Pick, J. Fried, V. and Vilim, O., Vapour Liquid Equilibrium, 2nd Edition, 1967,Pergamon Press, Oxford

19. Ammer, H.H. Paxton, R.R. and Mathew, Van Winkle., Ind. Engg. Chem. 48, 142 (1956)

20. Pitzer, K.S. and Curl, R.F. (Jr)., J. Am. Chem. Soc. 79, 2369 (1957)

21. Black, C., Ind. Engg. Chem. 50, 391 (1958)

22. Black, C., A.I.Ch.E. J. 5, 249 (1959)

23. O'Connel, I.P. and Prausnitz, J.M., Ind. Engg. Chem. Proc. Des. Dev. 6, 245 (1967)

24. Boublikova, L. and Lu, B. C-Y., J. Appl. Chem. 19, 89 (1969)

25. Herington, E.F.G., Nature London, 160, 610 (1947)

26. Coulson, E.A. and Herington, E.F.G., Trans. Fara. Soc. 44, 629 (1948)

27. Redlich, O. and Kister, A.T., Ind. Engg. Chem. 40, 345 (1948)

28. Redlich, O. Kister, A.T. and Turngenst, C.E., Chem. Engg. Prog. Ser, 48 (2), 49 (1952)

29. McGlashan, M.L., J. Chem. Education, 40, 516 (1963)

30. Bourne, J.R., Chem. Engg. Sci. 19, 508 (1964)

31. Herington, E.F.G., J. Appl. Chem. 18, 285 (1968)

32. Dutta Choudhury, M.K., Indian J. Chem. 14A, 553 (1976)

33. Dulitskaya, K.A., Zh. Obshch, Khim, 15, 9 (1945)

34. Udovenko, V.V. Falkulinda, L.G. Zh. Fiz. Khim. 26, 1438 (1952)

35. Copp, J.L. and Everette, D.H., Disc. Fara. Soc. 15, 194 (1953)

36. Williamson, A.G. Scott, R.L. and Dunlap, R.D.,
J. Chem. Phys. 30, 325 (1959)

37. Williamson, A.G. and Scott, R.L.,
J. Phys. Chem. 64, 440 (1960)

38. Brown, I. and Fock, W., Aust. J. Chem. 14, 357 (1961)

39. Amaya, K. and Fujishiro, R., Bull. Chem. Soc. Japan
34, 1271 (1961)

40. McGlashan, M.L., Chapter 15, 321 pp. Experimental
Thermochemistry, Vol.II,(Edited by H.A. Skinner)
International Publishers,1962

41. Brown, I. and Fock, W., Aust. J. Chem. 14, 387 (1961)

42. Brown, I. Fock, W. and Smith, F. Aust. J. Chem.
17, 1106 (1964)

43. Adcock, D.S. and McGlashan, M.L., Proc. Roy. Soc.
226 A, 226 (1954)

44. Larkin, J.A. and McGlashan, M.L., J. Chem. Soc.
3425 (1961)

45. Savini, C.G. Winterhalter, D.R. Kovach, C.H. and
Van Ness, H.C., J. Chem. Eng. Data, 11, 40 (1966)

46. Winterhalter, D.R.& Van Ness, H.C.
J. Chem. Eng. Data, 11, 189 (1966)

47. Murakami, S. and Benson, G.C.,
J. Chem. Thermodyn. 1, 559 (1969)

48. Rose, V.C. and Strovick, T.S.
J. Chem. Eng. Data, 11(2), 143 (1966)

49. Stoesser, P. R. and Gill, S.T., Rev. Sci. Instrum.
38, 422 (1967)

50. Sturtevant, J.M. and Cyons, P.A., J. Chem. Thermodyn.
1, 201 (1969)

51. McGlashan, M.L. and Stoecki, H.F.,
J. Chem. Thermodyn. 1, 589 (1969)

52. Pathak, G. Katti, S.S. and Kulkarni, S.B.,
Indian J. Chem. 8, 357 (1970)

53. Dutta Choudhury, M.K. and Mathur, H.B.,
Indian J. Chem. 14A, 735 (1976)

54. Brown, I. Fock, W. and Smith, F.,
J. Chem. Thermodyn. 1 , 273 (1969)

55. Riddick, J.A. and Bunger, W.B.,
"Technique of Chemistry, Organic Solvents",
Wiley Interscience, Vol. II.(1970) New York

56. Timmermans, J., "Physico-chemical Constants of
Pure Organic Compounds", Elsevier Publishing
Company, Inc. (1950)

57. Griffiths, V.S., J. Chem. Soc. 1326 (1952)

....

III. RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

The results of the various excess thermodynamic properties namely V^E, G^E, H^E and S^E for isomeric butanols with n-heptane have been presented and discussed in this Chapter.

(a) VOLUME CHANGE ON MIXING :

The volume change on mixing of n, iso and sec-butanols with n-heptane were determined at 25°C while that of tert-butanol at 26°C throughout the concentration range. The results obtained are given in Table 10,11,12 and 13 for all isomeric butanols. The volume change on mixing V^E have been plotted as a function of x_1, the mole fraction of butanol in Fig. 14 for ready comparison.

Tressozanowicz and Benson[1] in 1977 also studied the volume change on mixing in case of n-butanol with n-heptane at 25°C. Their results are plotted in Fig. 15 along with our data. It is clearly seen that our results agree fairly well with their data throughout the concentration range.

The excess volumes V^E are fitted by a least square method into a series equation of the type.

$$V^E = Ax + Bx^2 + Cx^3 + Dx^4$$

where A,B,C and D are the constants and x is the mole fraction of butanol. The values of the constants calculated by computer (Honeywell 400) are tabulated in Table 14 along with standard deviation σ .

Table 10 : Volume change on mixing of n-butanol (1) and n-heptane (2) system at 25°C

Sr. No.	x_1 mole fraction of n-butanol	d_M	V^E (ml $mole^{-1}$)
1	0.0255	0.68109	0.0933
2	0.0506	0.68294	0.1401
3	0.0755	0.68482	0.1712
4	0.1063	0.68730	0.1890
5	0.1508	0.69105	0.2086
6	0.2110	0.69637	0.2255
7	0.2751	0.70241	0.2369
8	0.3420	0.70907	0.2357
9	0.4005	0.71542	0.2143
10	0.4999	0.72692	0.1822
11	0.5998	0.73955	0.1437
12	0.6746	0.75000	0.1061
13	0.7449	0.76045	0.0733
14	0.7999	0.76920	0.0509
15	0.8482	0.77730	0.0345
16	0.9010	0.78665	0.0188
17	0.9502	0.79581	0.0145

Table 11 : Volume change on mixing of iso-butanol (1) and n-heptane (2) system at 25°C

Sr. No.	x_1 mole fraction of iso-butanol	d_M	V^E (ml mole^{-1})
1	0.0510	0.68267	0.1441
2	0.1059	0.68662	0.2313
3	0.1504	0.69004	0.2801
4	0.2516	0.69841	0.3461
5	0.3483	0.70735	0.3713
6	0.4509	0.71790	0.3522
7	0.5464	0.72870	0.3103
8	0.6410	0.74057	0.2545
9	0.7498	0.75567	0.1780
10	0.8528	0.77162	0.1094
11	0.9502	0.78863	0.0361

Table 12 : Volume change on mixing of sec-butanol (1) and n-heptane (2) system at 25°C

Sr. No.	x_1 mole fraction of sec-butanol	d_M	V^E (ml mole^{-1})
1	0.0501	0.68270	0.1543
2	0.1035	0.68637	0.2845
3	0.1502	0.68986	0.3717
4	0.2024	0.69408	0.4409
5	0.3000	0.70261	0.5357
6	0.4025	0.71272	0.5704
7	0.5037	0.72389	0.5452
8	0.5974	0.73570	0.4611
9	0.6953	0.74919	0.3726
10	0.8015	0.76956	0.2576
11	0.8505	0.77390	0.1943
12	0.8976	0.78232	0.1254

Table 13 : Volume change on mixing of tert-butanol (1) and n-heptane (2) system at 26°C

Sr. No.	x_1 mole fraction of tert-butanol	d_M	V^E (ml mole^{-1})
1	0.0294	0.67982	0.1795
2	0.0523	0.68085	0.2920
3	0.1018	0.68360	0.4172
4	0.1504	0.68644	0.5400
5	0.2503	0.69294	0.7185
6	0.3467	0.69980	0.8635
7	0.4515	0.70820	0.9711
8	0.5508	0.71710	1.0195
9	0.6517	0.72762	0.9961
10	0.7503	0.73946	0.8648
11	0.8246	0.74985	0.6704
12	0.8509	0.75373	0.5999
13	0.8972	0.76110	0.4413
14	0.9499	0.77023	0.2119

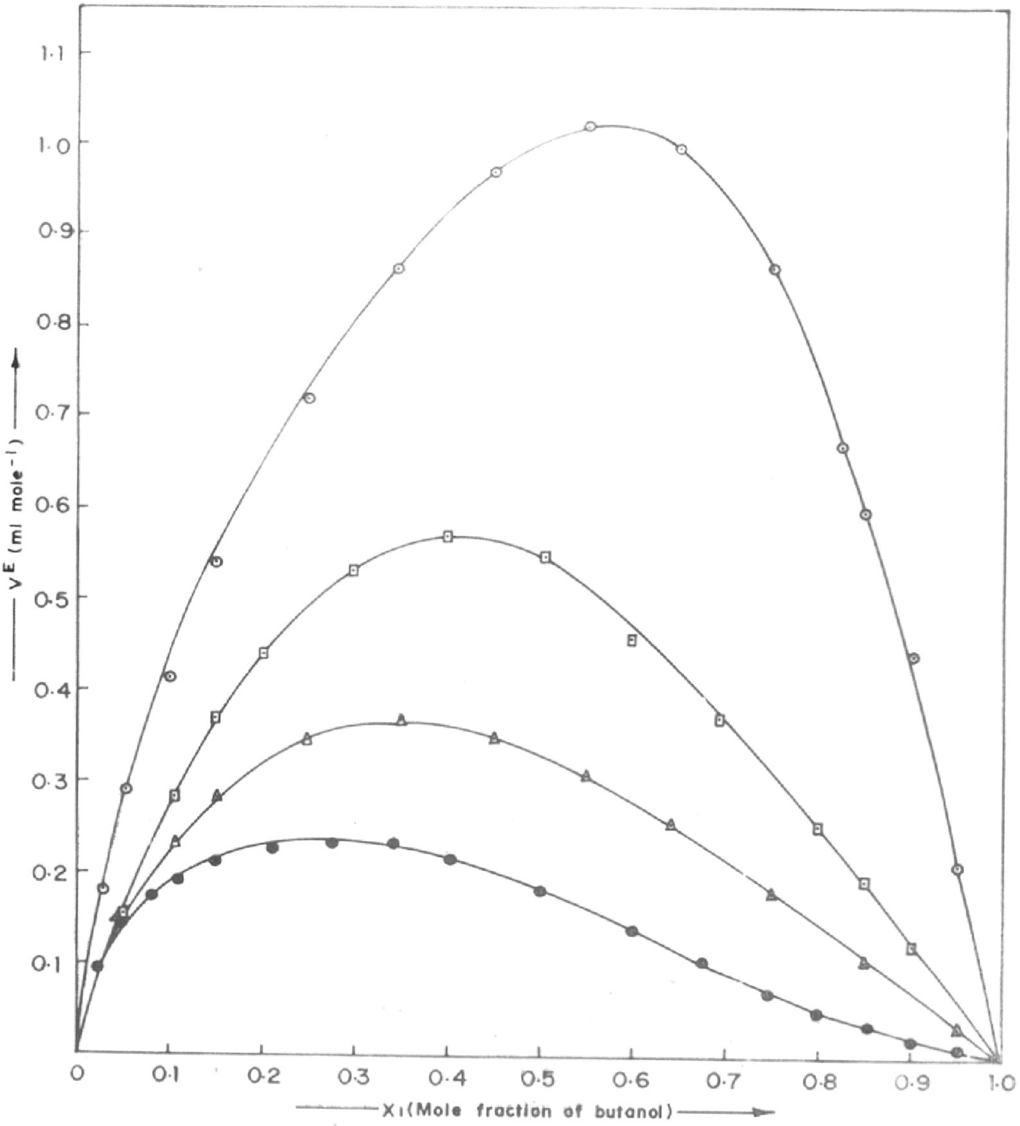


FIG. 14. VOLUME CHANGE ON MIXING OF isomeric BUTANOLS WITH n-HEPTANE AT 25°C

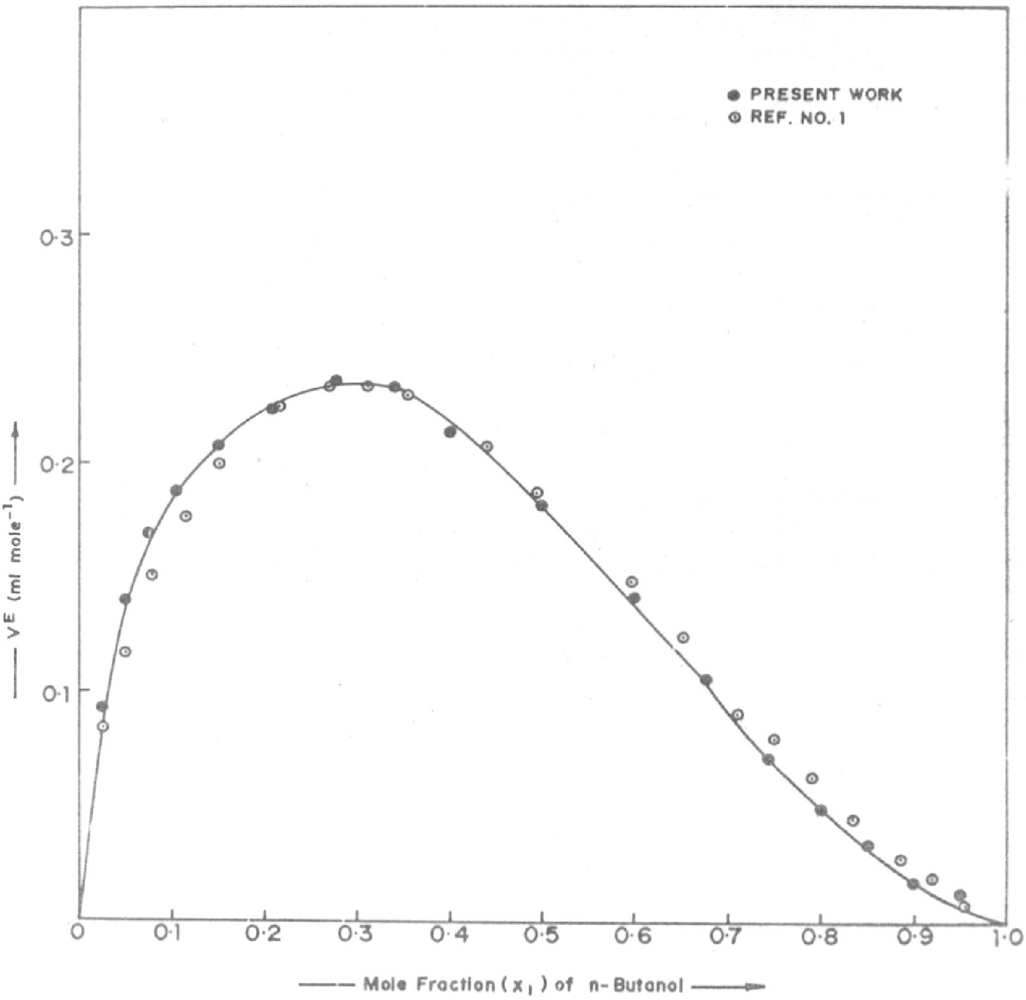


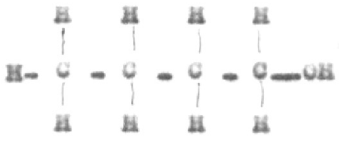
FIG.15. VOLUME CHANGE ON MIXING OF n-BUTANOL – n-HEPTANE MIXTURES AT 25° C

Table 14 : The least square constants of the relation between V^E and x_1 for isomeric butanols with n-heptane at 25°C

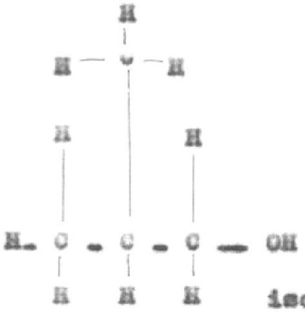
System	A	B	C	D	σ (Standard deviation)
n-butanol	0.08245	1.11984	-2.69571	1.43182	0.24×10^{-2}
iso-butanol	0.06011	1.19341	-3.54737	1.56835	0.41×10^{-2}
sec-butanol	0.01350	3.08509	-5.04582	1.95435	0.50×10^{-2}
tert-butanol	0.14608	2.54242	-0.47393	-2. 2264	0.83×10^{-2}

It is clear from Fig. 14 that V^E is positive throughout the concentration range for all the four systems. It is well established fact that aliphatic alcohols are strongly associated with hydrogen bonding and these species are broken on dilution with non-polar solvent. The positive excess volume change on mixing is therefore attributed to the dissociation of associated species of alcohols on dilution with n-heptane.

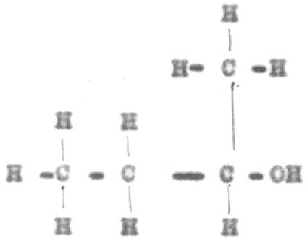
It is obvious that branching of the alkyl chain of alcohols has a considerable effect on the volume change on mixing. The change in magnitude and symmetry is observed among the curves with the branching of alcohols. The general structure of isomeric butanol is shown below.



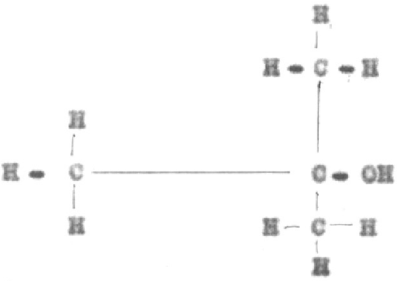
n-butanol



iso-butanol



sec-butanol



tert-butanol

The maximum shifts towards the higher mole fraction of the alcohol as the substitution of the methyl group shifts towards α- carbon atom. Thus the maximum volume change on mixing for n, iso, sec and tert butanols are obtained nearly at 0.275, 0.348, 0.40 and 0.55 mole fractions of the respective alcohols. Brown et al[2] have studied the volume change on mixing of isomeric butanols with benzene at 25°C. They also obtained the maxima at nearly the same mole fractions of alcohols.

The V^E vs x_1 curves (Fig. 14) suggest the probable stoichiometry of interaction. The maxima at 0.275 mole fraction of n-butanol in the first system indicates that n-butanol probably has a tetrameric association in pure liquid state. In the same way the maximum V^E at 0.55 mole fraction of tert-butanol indicates the possibility of predominance of dimeric species in pure liquid state. It may be noted that higher polymeric species decrease as the substitution of the methyl group approaches the α-carbon atom. This is in consistent with the observation that steric hindrance increases as we go from iso to sec to tert-butanol. Thus the magnitude of the volume change on mixing increases in the following order

tert-BuOH > Sec-BuOH > iso-BuOH > n-BuOH

Brown et al[2] have also noted the same trend for these alcohols.

It is clear that V^E in case of tert-butanol is 330% more than that it not only depends on the number of hydrogen bonds broken but also on the shape of the molecules. The n-butanol molecules are elongated and planner similar to those of n-heptane. 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-heptane these molecules are likely to be more random indicating higher V^E. The spherical tert-butanol molecules may also destroy the ordered alignment of n-heptane molecules.

The values of V^E/x_1x_2 vs x_1 were plotted and the extrapolated values of $x_1 \rightarrow 0$ and $x_2 \rightarrow 0$ are listed in Table 15. The values of partial molar excess volume $\bar{V}^E$ for n-butanol is 6.0 ml/mole that for n-heptane is 0.2 ml/mole. These values are in good agreement with the value obtained by Tresscsonowics and Benson[1] for the same system at 25°C. As seen from Table 15 the magnitude of partial molar excess volume $\bar{V}^E$ follows the trend as

tert-BuOH > sec-BuOH > iso-BuOH > n-BuOH

This trend is the same as obtained in the case of excess volumes.

The partial excess molar volume of n-heptane is affected by the structure and the shape of the alcohol molecules. In the case of n-butanol with straight alkly chain the value of $\bar{V}^E$ of n-heptane is 0.2 ml/mole whereas in the case of iso-butanol and sec-butanol the corresponding values are 0.7 and 1.0 ml/mole respectively. It may be noted that the shifting of the methyl substitution from β to α carbon atom of the alcohol makes a small change in symmetry accompanied by a small increase in $\bar{V}^E$ i.e. 0.3 ml/mole. The large value of $\bar{V}^E$ in case of tert-butanol i.e. 4.1 ml/mole is believed to be due to

Table 15 : Partial molar excess volume

System	$x_1 \rightarrow 0$ (ml mole^{-1})	$x_2 \rightarrow 0$ (ml mole^{-1})
n-butanol	6.0	0.2
iso-butanol	3.7	0.7
sec-butanol	3.4	1.0
tert-butanol	7.2	4.1
n-propanol	8.0	1.13*
iso-propanol	9.1	2.24*

* Ref No. 3 à 4

the presence of two methyl groups in α carbon atom of the alkyl chain.

Van Ness et al[3,4] have studied excess volumes of n- and iso- propanol with n-heptane at the same temperature. The results obtained by them on partial molar excess volumes have been tabulated in Table 15. On comparing the results obtained by them with our results, our analogy of more random distribution of n-heptane molecules due to mixing with spherical molecules seems to be reasonable.

Thus it seems that excess volumes mainly depend on hydrogen bond breaking and the structure and shape of alcohol molecules.

(b) EXCESS FREE ENERGY OF MIXING :

The excess free energy of mixing for all isomeric butanols with n-heptane were calculated from isothermal vapour liquid equilibrium data obtained at 55°, 65° and 75°C. The vapour liquid equilibrium data for n, iso, sec and tert-butanol systems at 55°, 65° and 75°C have been given in Tables 16,17, 18 and 19 as a function of liquid mole fraction x_1 of n-heptane and the corresponding mole fraction in vapour phase y_1. The x-y diagrams for each system at three temperatures are plotted in Fig. 16, 17,18 and 19. The pressure composition curves (P-x,y) for all the butanols are shown in Fig. 20,21,22,23,24 and 25 at different temperatures.

The x-y diagrams are 'S' shaped . P-x,y diagrams show the presence of azeotropes. The concentration at which the azeotropes were formed are listed in Table 20 for all the alcohols at various temperatures.

Table 16 : Vapour liquid equilibrium data of n-heptane (1) and n-butanol (2) system at 55°, 65° & 75°C

Sr. No.	Mole fraction of n-heptane in liquid x_1	Mole fraction of n-heptane in vapour y_1	P (in mm)	γ_1	γ_2	G^E J mole^{-1}
			At 55°C	$p_1 = 173$ mm	$p_2 = 45$ mm	
1	0.0055	0.1095	51.2	5.948	1.018	26
2	0.0503	0.5008	90.0	5.213	1.047	347
3	0.1083	0.6391	119.2	4.080	1.069	577
4	0.1482	0.6950	137.1	3.725	1.082	716
5	0.2432	0.7500	155.1	2.769	1.129	925
6	0.3432	0.7858	167.7	2.221	1.204	1079
7	0.4926	0.8104	176.2	1.674	1.448	1205
8	0.6415	0.8311	184.0	1.376	1.906	1188
9	0.7597	0.8411	186.8	1.194	2.717	1023
10	0.8268	0.8544	189.0	1.127	3.493	861
11	0.8758	0.8653	187.0	1.067	4.461	661
12	0.9303	0.8828	184.6	1.011	6.828	392
13	0.9596	0.9100	181.1	0.992	8.878	220

Table 16 continued

Sr. No.	Mole fraction of n-heptane in liquid x_1	Mole fraction of n-heptane in vapour y_1	P (in mm)	γ_1	γ_2	G^E J mole^{-1}
	At 65°C	p_1 = 253.4 mm		p_2 = 77.5 mm		
1	0.0245	0.2542	106.3	4.393	1.046	224
2	0.0645	0.4977	152.5	4.676	1.051	410
3	0.0750	0.5800	184.1	5.645	1.071	543
4	0.1504	0.6950	233.0	4.255	1.069	770
5	0.2008	0.7197	245.0	3.466	1.096	908
6	0.2542	0.7450	256.1	2.960	1.116	1005
7	0.3000	0.7555	262.0	2.602	1.167	1109
8	0.3750	0.7791	270.5	2.215	1.218	1184
9	0.4501	0.7918	276.1	1.913	1.331	1262
10	0.5344	0.7962	280.1	1.644	1.526	1299
11	0.6503	0.8150	284.6	1.404	1.917	1258
12	0.7212	0.8206	285.7	1.280	2.341	1167
13	0.7753	0.8241	285.0	1.193	2.841	1043
14	0.8317	0.8328	285.1	1.124	3.608	879
15	0.9000	0.8600	282.3	1.063	5.034	608
16	0.9435	0.8808	279.4	1.027	7.509	390
17	0.9799	0.9541	270.0	1.035	7.859	212

continued

Table 16 continued

Sr. No.	Mole fraction of n-heptane in liquid x_1	Mole fraction of n-heptane in vapour y_1	P (mm)	γ_1	γ_2	G^E J $mole^{-1}$
	At 75°C	p_1 = 361.3 mm		p_2 = 128.7 mm		
1	0.0462	0.3830	198.1	4.590	0.9926	225
2	0.0668	0.4634	232.7	4.500	1.106	378
3	0.1125	0.5700	288.4	4.062	1.076	644
4	0.1757	0.6600	347.0	3.604	1.098	877
5	0.2090	0.6842	367.4	3.329	1.125	997
6	0.2723	0.7222	389.3	2.852	1.147	1112
7	0.3755	0.7500	404.0	2.227	1.234	1252
8	0.4819	0.7718	412.0	1.820	1.390	1329
9	0.5389	0.7800	415.0	1.658	1.510	1339
10	0.6230	0.7899	416.7	1.457	1.776	1307
11	0.7201	0.7900	418.0	1.266	2.399	1200
12	0.8111	0.8105	418.5	1.153	3.212	938
13	0.8653	0.8208	413.6	1.081	4.210	757
14	0.9014	0.8355	409.0	1.046	5.222	589
15	0.9476	0.8674	404.8	1.003	7.843	323
16	0.9889	0.9456	385.0	1.017	14.340	133

Table 17 : Vapour liquid equilibrium data of n-heptane (1) and iso-butanol (2) system at 55°, 65° & 75°C

Sr. No.	Mole fraction of n-heptane in liquid x_1	Mole fraction of n-heptane in vapour y_1	P (in mm)	γ_1	γ_2	G^E J $mole^{-1}$
At 55°C		P_1 = 173 mm		P_2 = 70.4 mm		
1	0.0298	0.2720	93.6	4.965	0.994	114
2	0.0757	0.4461	120.1	4.106	1.020	338
3	0.1392	0.5724	148.6	3.538	1.042	576
4	0.2671	0.6768	180.0	2.635	1.119	932
5	0.3510	0.7057	190.0	2.205	1.214	1100
6	0.4314	0.7268	196.2	1.906	1.327	1198
7	0.5008	0.7340	200.0	1.690	1.501	1269
8	0.5611	0.7506	203.1	1.570	1.624	1279
9	0.6498	0.7633	206.0	1.395	1.960	1232
10	0.7047	0.7680	206.5	1.296	2.283	1164
11	0.7799	0.7811	207.0	1.195	2.898	1018
12	0.8755	0.8046	200.1	1.100	4.462	734
13	0.9089	0.8296	197.1	1.038	5.194	502
14	0.9733	0.9154	182.9	0.995	8.174	140

continued

Table 17 continued

Sr. No.	Mole fraction of n-heptane in liquid x_1	Mole fraction of n-heptane in vapour y_1	P (in mm)	γ_1	γ_2	G^E J $mole^{-1}$
	At 65°C	p_1 = 253.4 mm		p_2 = 119.8 mm		
1	0.0511	0.3346	175.3	4.507	1.023	275
2	0.1009	0.4707	208.1	3.819	1.023	438
3	0.1808	0.5811	248.7	3.152	1.054	697
4	0.2356	0.6230	264.4	2.758	1.080	837
5	0.2860	0.6507	276.5	2.479	1.119	955
6	0.3239	0.6676	283.0	2.298	1.151	1024
7	0.3754	0.6855	289.1	2.078	1.201	1095
8	0.4148	0.6951	293.6	1.936	1.264	1155
9	0.4690	0.7047	298.3	1.763	1.371	1218
10	0.5515	0.7199	304.0	1.561	1.570	1259
11	0.6006	0.7310	306.1	1.465	1.703	1242
12	0.6610	0.7425	308.5	1.362	1.936	1203
13	0.7538	0.7565	309.1	1.220	2.525	1061
14	0.8243	0.7703	305.8	1.123	3.305	858
15	0.8998	0.8073	298.2	1.053	4.742	568
16	0.9544	0.8509	289.9	1.016	7.841	307

continued

Table 17 continued

Sr. No.	Mole fraction of n-heptane in liquid x_1	Mole fraction of n-heptane in vapour y_1	P (in mm)	γ_1	γ_2	G^E J $mole^{-1}$
	At 75°C	p_1 = 361.3 mm		p_2 = 204.8 mm		
1	0.0465	0.2713	265.7	4.314	0.9988	165
2	0.0860	0.3871	309.3	3.865	1.007	356
3	0.1358	0.4705	348.3	3.342	1.035	559
4	0.1954	0.5527	385.4	3.013	1.037	725
5	0.2508	0.5908	402.6	2.618	1.064	833
6	0.3200	0.6254	418.0	2.254	1.114	965
7	0.3841	0.6480	428.7	1.994	1.185	1070
8	0.4489	0.6647	436.1	1.779	1.282	1146
9	0.5108	0.6800	442.5	1.623	1.399	1192
10	0.5505	0.6852	445.2	1.525	1.507	1207
11	0.6052	0.6982	449.0	1.426	1.658	1200
12	0.6512	0.7054	451.0	1.345	1.840	1175
13	0.7136	0.7200	454.1	1.285	2.140	1131
14	0.8307	0.7519	447.1	1.114	3.165	825
15	0.9186	0.8101	434.6	1.055	4.900	519
16	0.9586	0.8794	412.3	1.042	5.811	326

Table 18 : Vapour liquid equilibrium data of n-heptane (1) and sec-butanol (2) system at 55°, 65° & 75°C

Sr. No.	Mole fraction of n-heptane in liquid x_1	Mole fraction of n-heptane in vapour y_1	P (in mm)	γ_1	γ_2	G^E J mole^{-1}
	At 55°C	p_1 = 173 mm		p_2 =	104.6 mm	
1	0.0678	0.2979	139.6	3.555	1.002	240
2	0.1050	0.3810	156.1	3.276	1.028	406
3	0.1623	0.4616	173.0	2.843	1.058	589
4	0.2122	0.5261	185.9	2.663	1.064	699
5	0.2865	0.5663	196.6	2.242	1.136	878
6	0.3249	0.5809	200.4	2.066	1.182	951
7	0.4014	0.6052	205.9	1.791	1.291	1054
8	0.4590	0.6312	209.7	1.663	1.357	1086
9	0.4998	0.6403	211.5	1.379	1.445	1109
10	0.5492	0.6533	213.0	1.459	1.555	1109
11	0.58937	0.6650	214.5	1.395	1.662	1104
12	0.6263	0.6764	215.6	1.340	1.774	1083
13	0.6959	0.6978	215.7	1.239	2.035	995
14	0.7481	0.7111	213.1	1.168	2.319	894
15	0.8014	0.7288	211.5	1.108	2.744	770
16	0.8386	0.7508	209.8	1.081	3.077	675
17	0.9074	0.7881	206.8	1.035	4.495	464
18	0.9731	0.8990	188.2	1.003	6.722	148

Table 18 continued

Sr. No.	Mole fraction of n-heptane in liquid x_1	Mole fraction of n-heptane in vapour y_1	P (in mm)	γ_1	γ_2	G^E J $mole^{-1}$
	At 65°C	p_1 = 253.4 mm		p_2 =	174.4 mm	
1	0.0755	0.2706	229.7	3.253	1.035	338
2	0.1153	0.3592	247.1	3.039	1.022	413
3	0.1487	0.4082	260.2	2.815	1.032	508
4	0.2008	0.4731	278.0	2.581	1.045	634
5	0.2346	0.5001	288.0	2.415	1.072	730
6	0.2783	0.5360	299.3	2.268	1.098	829
7	0.3234	0.5582	308.1	2.090	1.145	928
8	0.3945	0.5868	315.2	1.843	1.224	1021
9	0.4592	0.6125	320.0	1.677	1.304	1069
10	0.5173	0.6270	321.7	1.531	1.414	1089
11	0.5501	0.6279	322.9	1.447	1.519	1100
12	0.5982	0.6403	324.8	1.365	1.654	1090
13	0.6503	0.6489	325.0	1.274	1.856	1048
14	0.7492	0.6643	323.0	1.125	2.460	882
15	0.8118	0.6931	319.1	1.070	2.959	728
16	0.8508	0.7313	313.1	1.058	3.209	616
17	0.8842	0.7533	307.5	1.030	3.730	503
18	0.9425	0.8229	296.8	1.020	5.208	317

continued

Table 18 continued

Sr. No.	Mole fraction of n-heptane in liquid x_1	Mole fraction of n-heptane in vapour y_1	P (in mm)	γ_1	γ_2	G^E J mole^{-1}
	At 75°C	p_1 = 361.3 mm		p_2 = 278.9 mm		
1	0.0748	0.2535	349.8	3.283	1.008	277
2	0.1373	0.3638	385.9	2.826	1.015	450
3	0.1882	0.4308	412.3	2.595	1.030	592
4	0.2433	0.4775	432.1	2.337	1.061	729
5	0.2983	0.5173	450.4	2.151	1.103	860
6	0.3452	0.5336	456.1	1.940	1.154	935
7	0.3891	0.5522	464.4	1.812	1.210	1007
8	0.4596	0.5838	472.0	1.648	1.288	1066
9	0.5022	0.5931	472.8	1.535	1.373	1079
10	0.5303	0.6031	475.0	1.485	1.425	1089
11	0.3344	0.6075	475.2	1.485	1.422	1086
12	0.5739	0.6176	475.9	1.407	1.517	1082
13	0.6193	0.6204	476.6	1.309	1.688	1060
14	0.6980	0.6425	470.4	1.191	1.979	949
15	0.7537	0.6624	466.3	1.127	2.272	846
16	0.7980	0.6823	458.5	1.079	2.557	724
17	0.8647	0.7275	446.7	1.035	3.201	542
18	0.9088	0.7723	434.2	1.017	3.859	400
19	0.9592	0.8570	410.3	1.011	5.125	223

Table 19 : Vapour liquid equilibrium data of n-heptane (1) and tert-butanol (2) system at 55°, 65° & 75°C

Sr. No.	Mole fraction of n-heptane in liquid x_1	Mole fraction of n-heptane in vapour y_1	P (in mm)	γ_1	γ_2	G^E J mole^{-1}
	At 55°C	p_1 = 173 mm		p_2 = 227.3 mm		
1	0.0998	0.2002	258.0	2.975	1.007	311
2	0.1592	0.2685	268.1	2.594	1.025	470
3	0.2012	0.3111	274.0	2.470	1.035	561
4	0.2422	0.3333	278.5	2.199	1.076	671
5	0.2812	0.3536	282.2	2.034	1.113	754
6	0.3653	0.4031	288.5	1.824	1.190	898
7	0.4213	0.4298	289.1	1.689	1.248	953
8	0.4496	0.4511	289.5	1.668	1.266	979
9	0.5144	0.4742	286.9	1.515	1.361	991
10	0.5666	0.4999	284.6	1.439	1.440	993
11	0.6060	0.5169	281.7	1.378	1.516	976
12	0.6863	0.5444	277.1	1.260	1.766	920
13	0.7604	0.5830	269.4	1.185	2.060	825
14	0.7948	0.5981	263.9	1.139	2.270	740
15	0.8496	0.6480	253.6	1.101	2.607	616
16	0.8865	0.6736	245.9	1.074	3.111	524
17	0.9144	0.7080	237.07	1.054	3.567	430
18	0.9626	0.7885	219.6	1.033	5.466	258

continued

Table 19 continued

Sr. No.	Mole fraction of n-heptane in liquid x_1	Mole fraction of n-heptane in vapour y_1	P (in mm)	γ_1	γ_2	G^E J mole^{-1}
	At 65°C	p_1 = 253.4 mm		p_2 = 365.1 mm		
1	0.0746	0.1477	393.6	3.047	0.992	212
2	0.1316	0.2140	407.5	2.614	1.008	371
3	0.2135	0.2880	423.9	2.232	1.048	584
4	0.2521	0.3136	430.2	2.086	1.076	676
5	0.3018	0.3432	435.7	1.932	1.119	778
6	0.3421	0.3684	440.1	1.847	1.153	853
7	0.3981	0.4026	445.0	1.755	1.205	944
8	0.4389	0.4151	441.6	1.629	1.256	960
9	0.5017	0.4426	437.8	1.507	1.337	980
10	0.5400	0.4595	433.6	1.440	1.391	979
11	0.5998	0.4873	428.0	1.357	1.496	964
12	0.6530	0.5071	422.4	1.280	1.638	934
13	0.7144	0.5374	413.2	1.213	1.828	872
14	0.7670	0.5616	403.9	1.156	2.078	791
15	0.8016	0.5818	396.1	1.124	2.283	723
16	0.8396	0.6108	385.0	1.096	2.541	637
17	0.8821	0.6487	372.2	1.072	3.036	539
18	0.9291	0.7083	347.9	1.040	3.923	374
19	0.9861	0.8477	297.6	1.003	8.959	96

continued

Table 19 continued

Sr. No.	Mole fraction of n-heptane in liquid x_1	Mole fraction of n-heptane in vapour y_1	P (in mm)	γ_1	γ_2	G^E J mole^{-1}
	At 75°C	p_1 = 361.3 mm		p_2 = 564.1 mm		
1	0.1066	0.1586	607.9	2.467	1.013	311
2	0.1486	0.2037	622.3	2.321	1.030	435
3	0.1888	0.2396	634.4	2.194	1.051	561
4	0.2296	0.2716	642.1	2.068	1.073	640
5	0.2674	0.2998	650.0	1.984	1.097	727
6	0.3123	0.3247	658.1	1.861	1.141	825
7	0.3510	0.3483	662.0	1.786	1.174	891
8	0.3999	0.3720	660.2	1.670	1.220	938
9	0.4771	0.3888	655.9	1.453	1.354	975
10	0.5238	0.4111	650.9	1.390	1.421	983
11	0.5936	0.4424	641.9	1.303	1.556	975
12	0.6389	0.4627	633.9	1.250	1.668	948
13	0.6997	0.4918	620.6	1.190	1.857	889
14	0.7482	0.5273	604.2	1.161	2.006	832
15	0.8244	0.5728	574.4	1.091	2.476	668
16	0.8938	0.6472	530.2	1.052	3.127	481
17	0.9439	0.7222	487.9	1.025	4.294	305
18	0.9861	0.8190	442.2	1.011	10.140	126

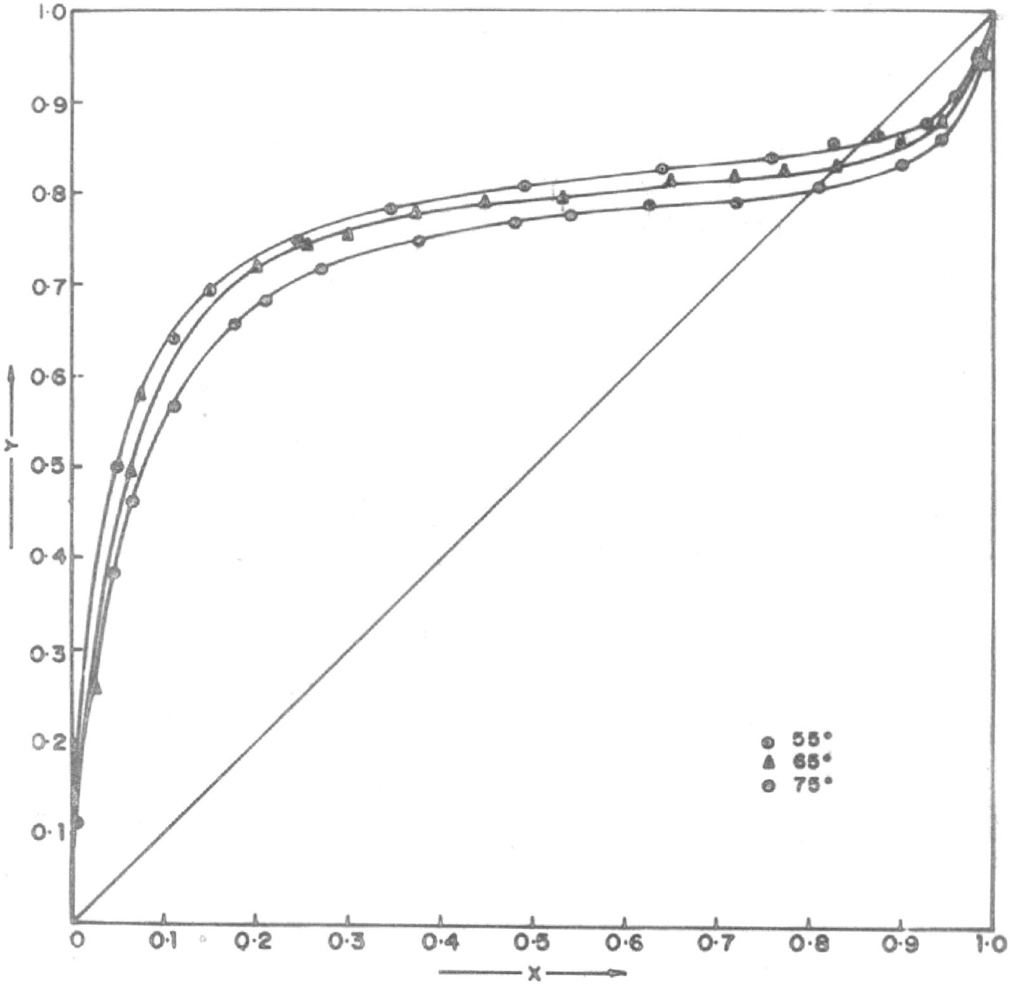


FIG.16. X-Y DIAGRAM FOR n-HEPTANE(1)—n-BUTANOL(2) SYSTEM AT 55°, 65° & 75°

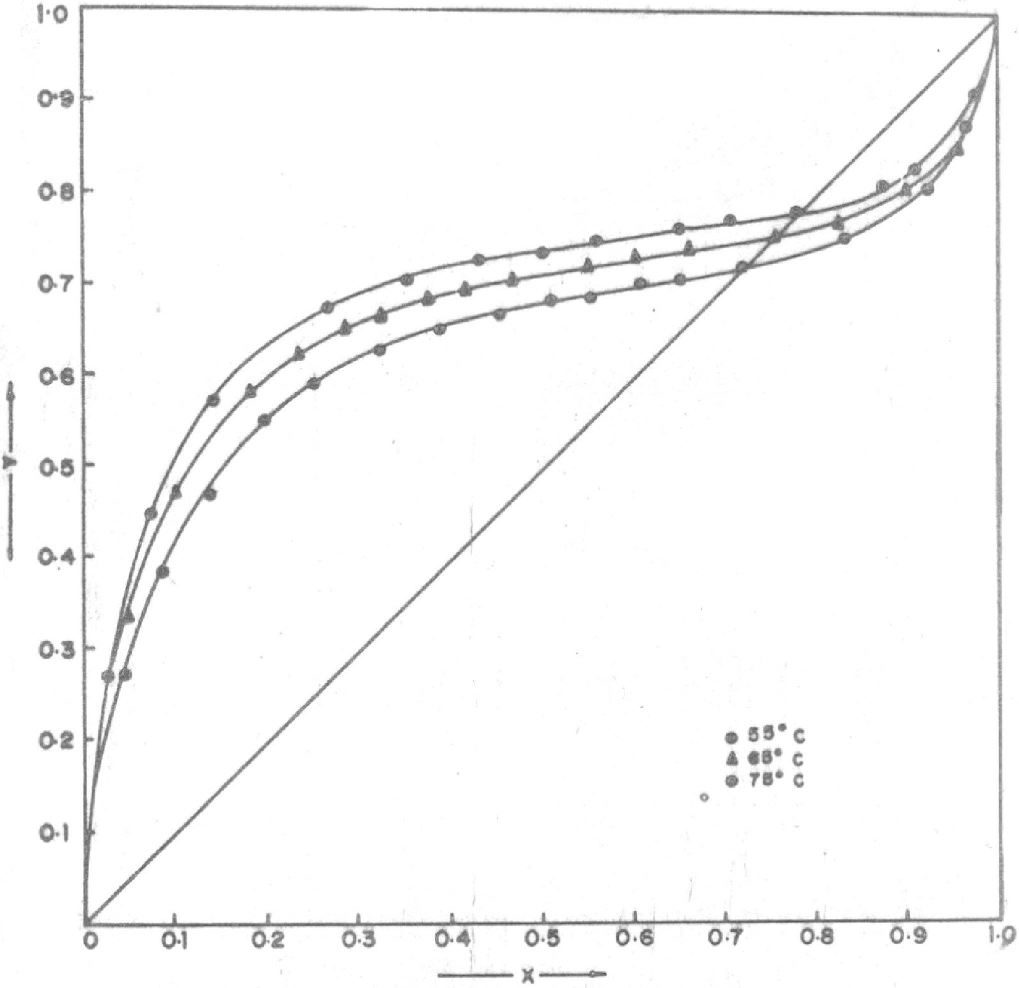


FIG. 17. X-Y DIAGRAM FOR n-HEPTANE (1) — iso-BUTANOL (2) SYSTEM AT 55°, 65° & 75° C

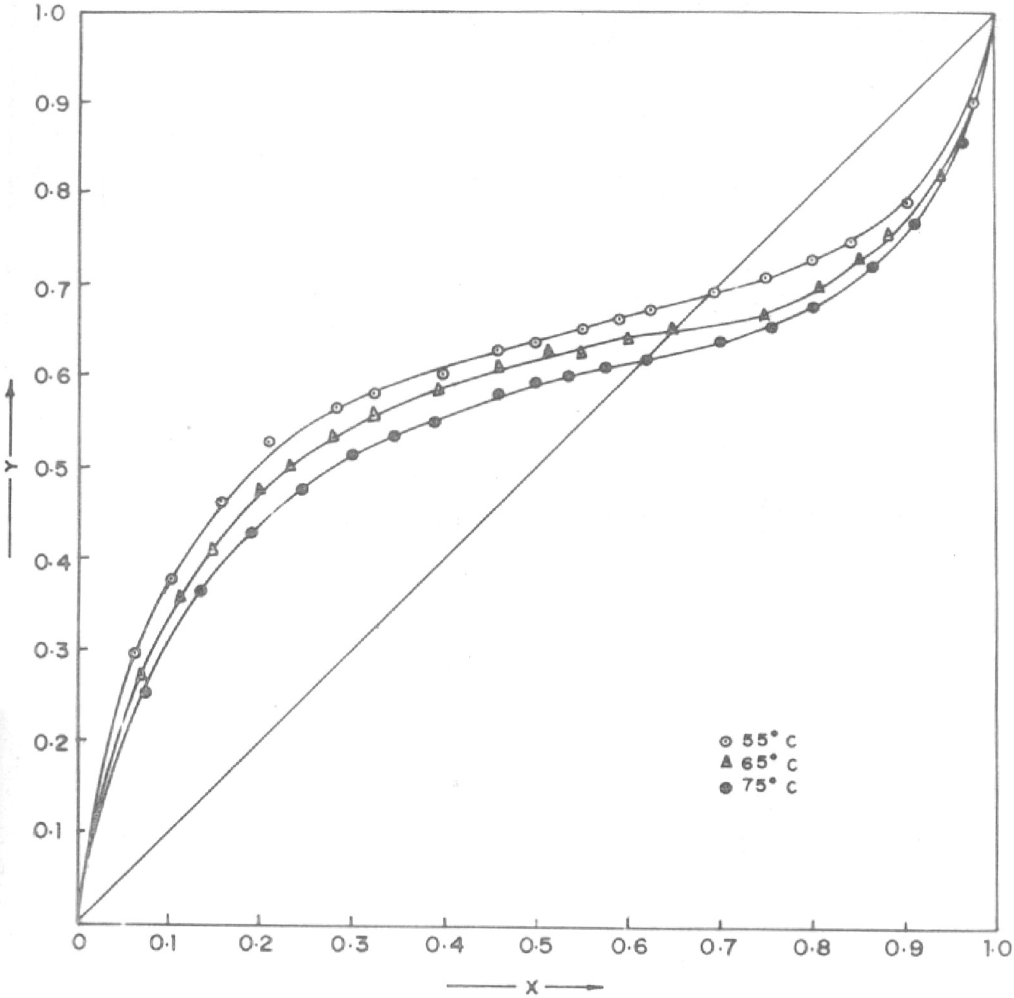


FIG.18. X-Y DIAGRAM FOR n-HEPTANE(1)—sec-BUTANOL(2) SYSTEM AT 55°,65° & 75° C

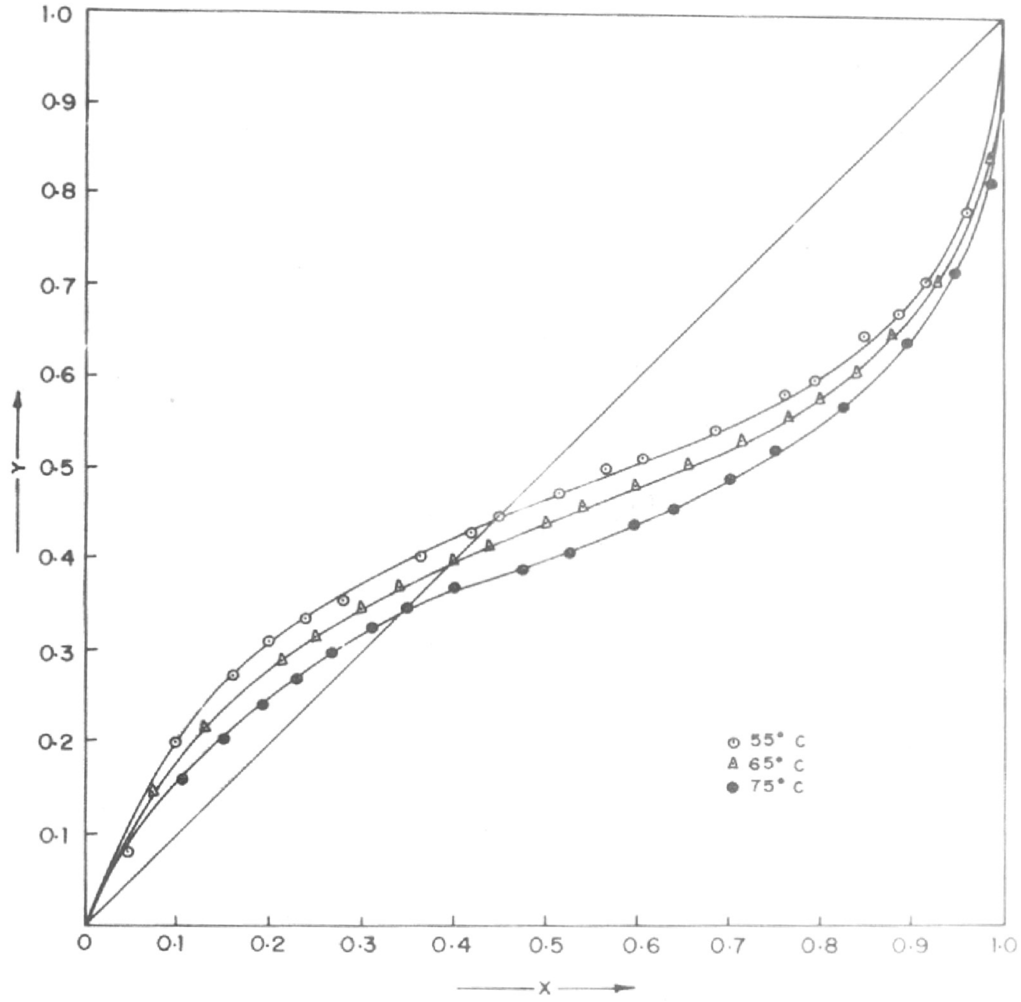


FIG.19. X-Y DIAGRAM FOR n-HEPTANE (I) — tert-BUTANOL (2) SYSTEM AT 55°, 65° & 75°C

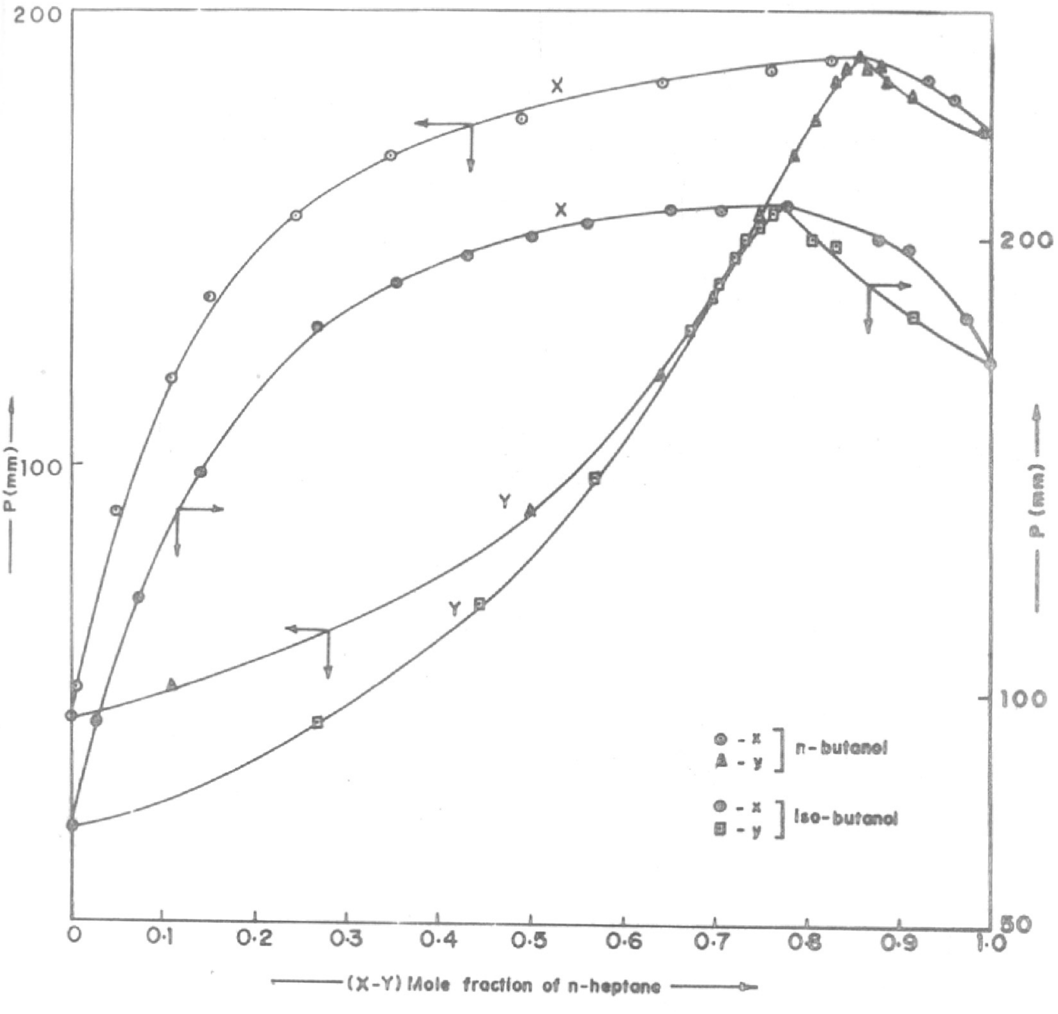


FIG.20. P-X,Y DIAGRAM OF n-HEPTANE (1) — n-BUTANOL (2) — Iso-BUTANOL(2) SYSTEM AT 55°C

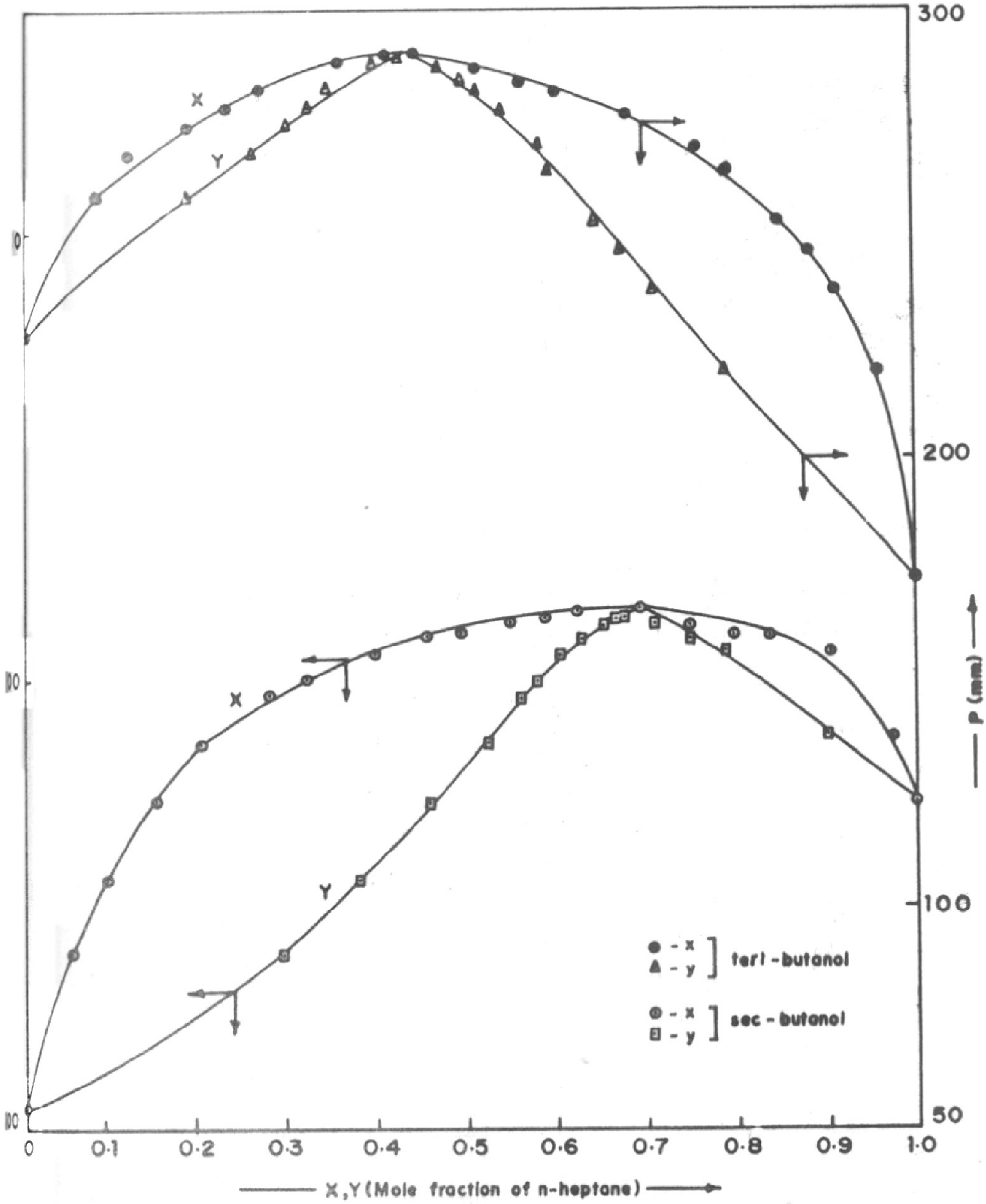


FIG. 21. P-X,Y DIAGRAM FOR n-HEPTANE (1) — sec-BUTANOL (2) — tert-BUTANOL(2) SYSTEM AT 55°C

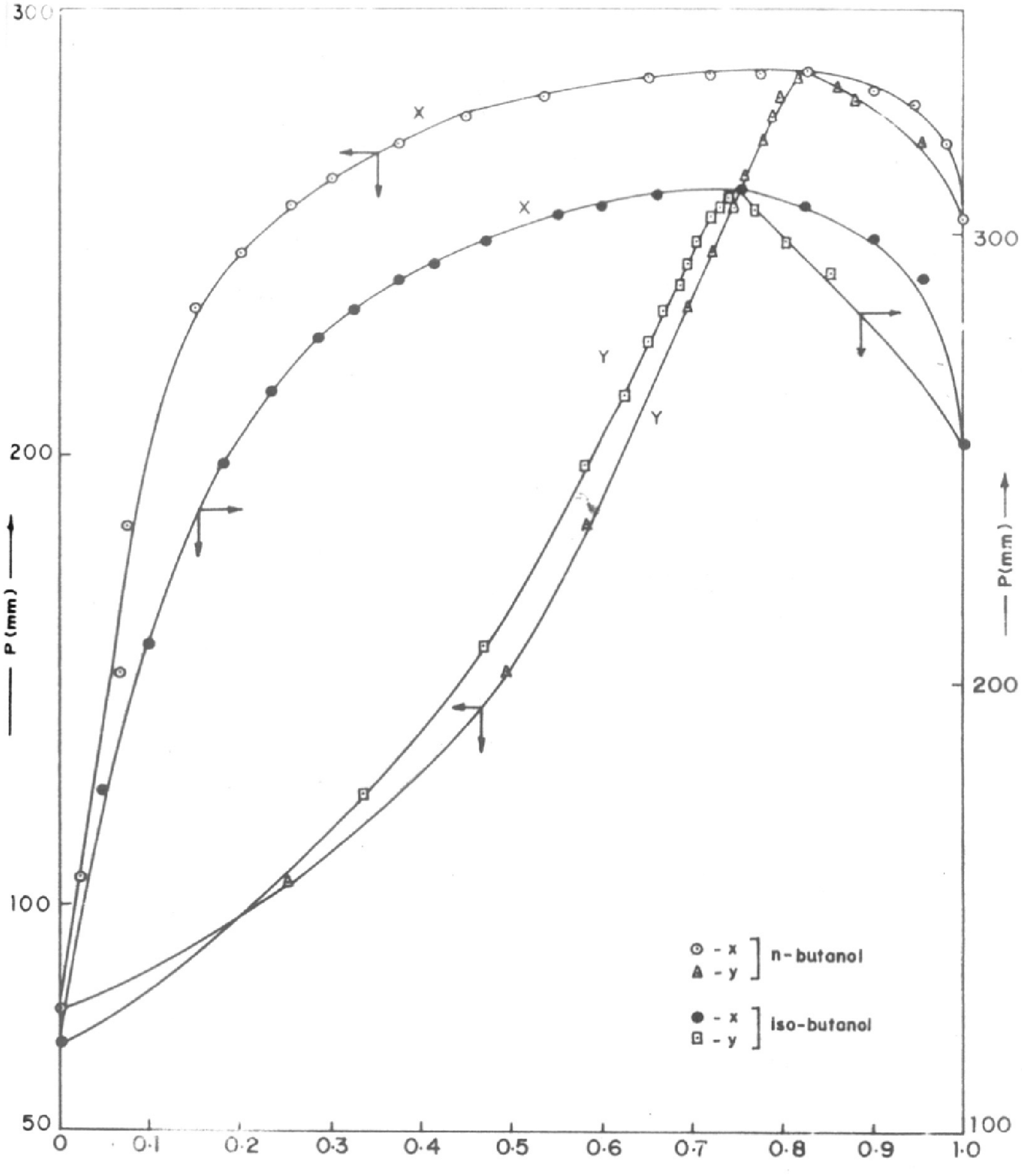


FIG. 22. P-X,Y DIAGRAM FOR n-HEPTANE (1) — n-BUTANOL(2) — iso-BUTANOL(2) SYSTEM AT 65°C

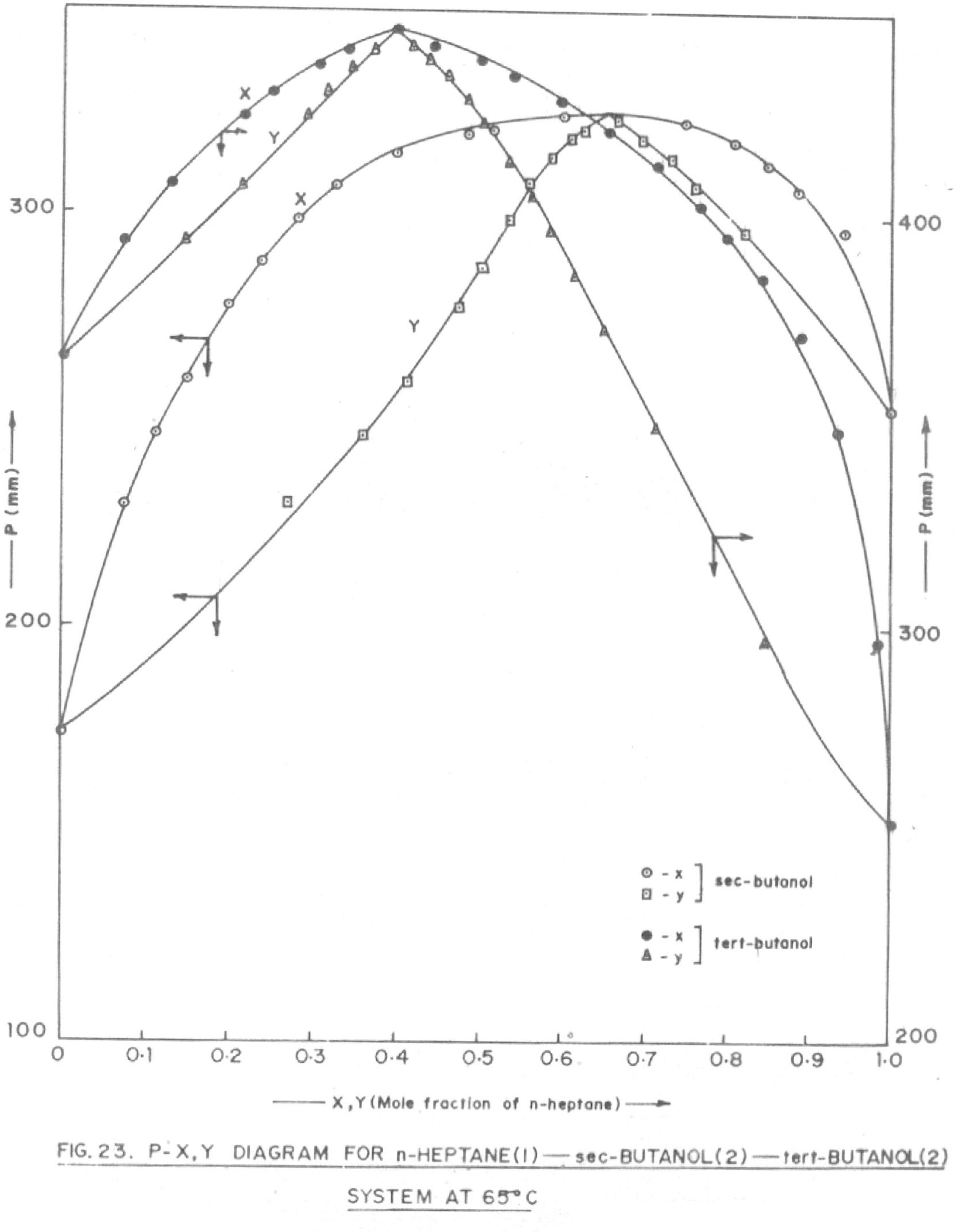


FIG. 23. P-X, Y DIAGRAM FOR n-HEPTANE(1) — sec-BUTANOL(2) — tert-BUTANOL(2) SYSTEM AT 65°C

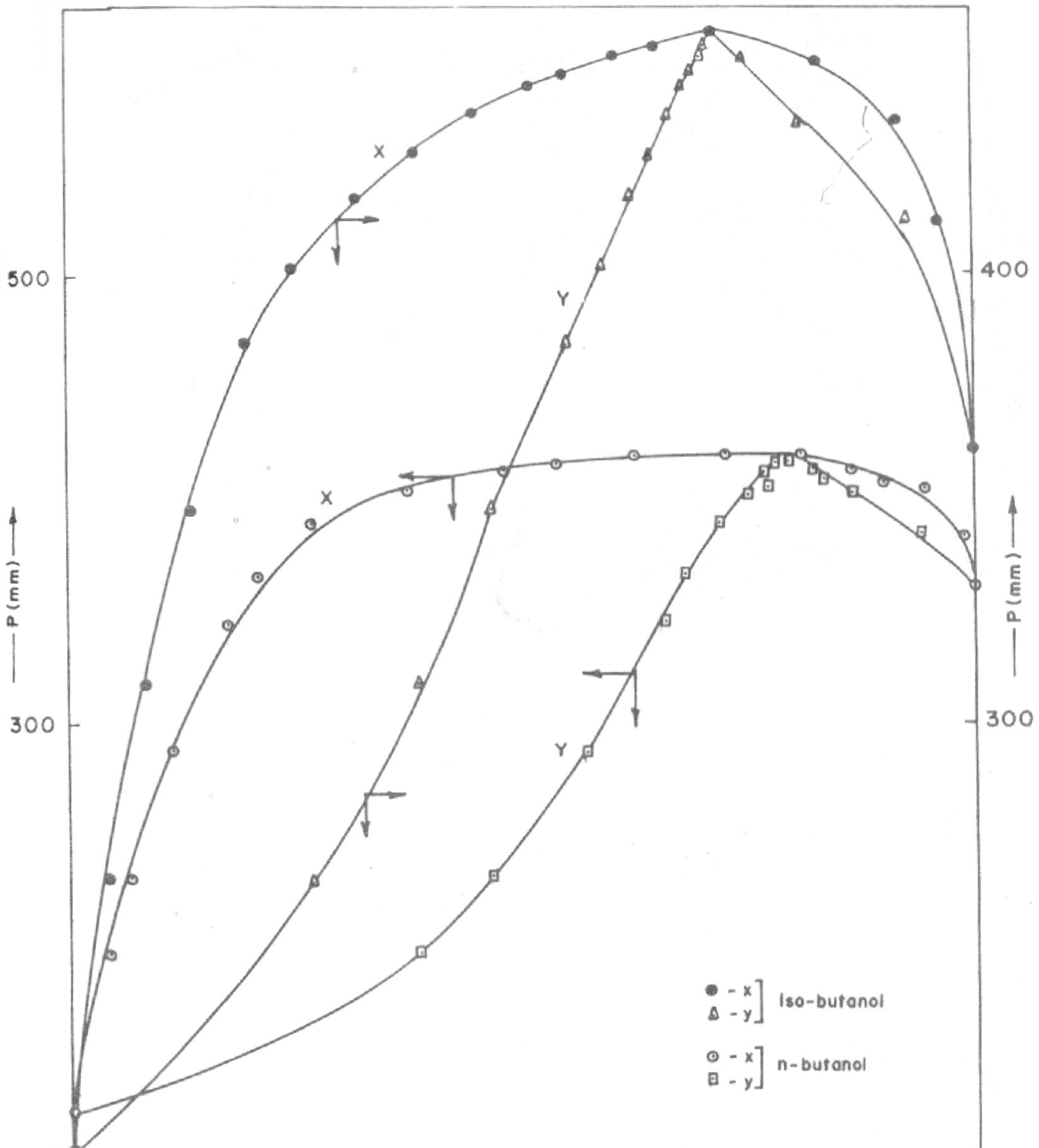


FIG. 24. P-X,Y DIAGRAM OF n-HEPTANE (1) — n-BUTANOL (2) & Iso-BUTANOL (2) SYSTEM AT 75°C

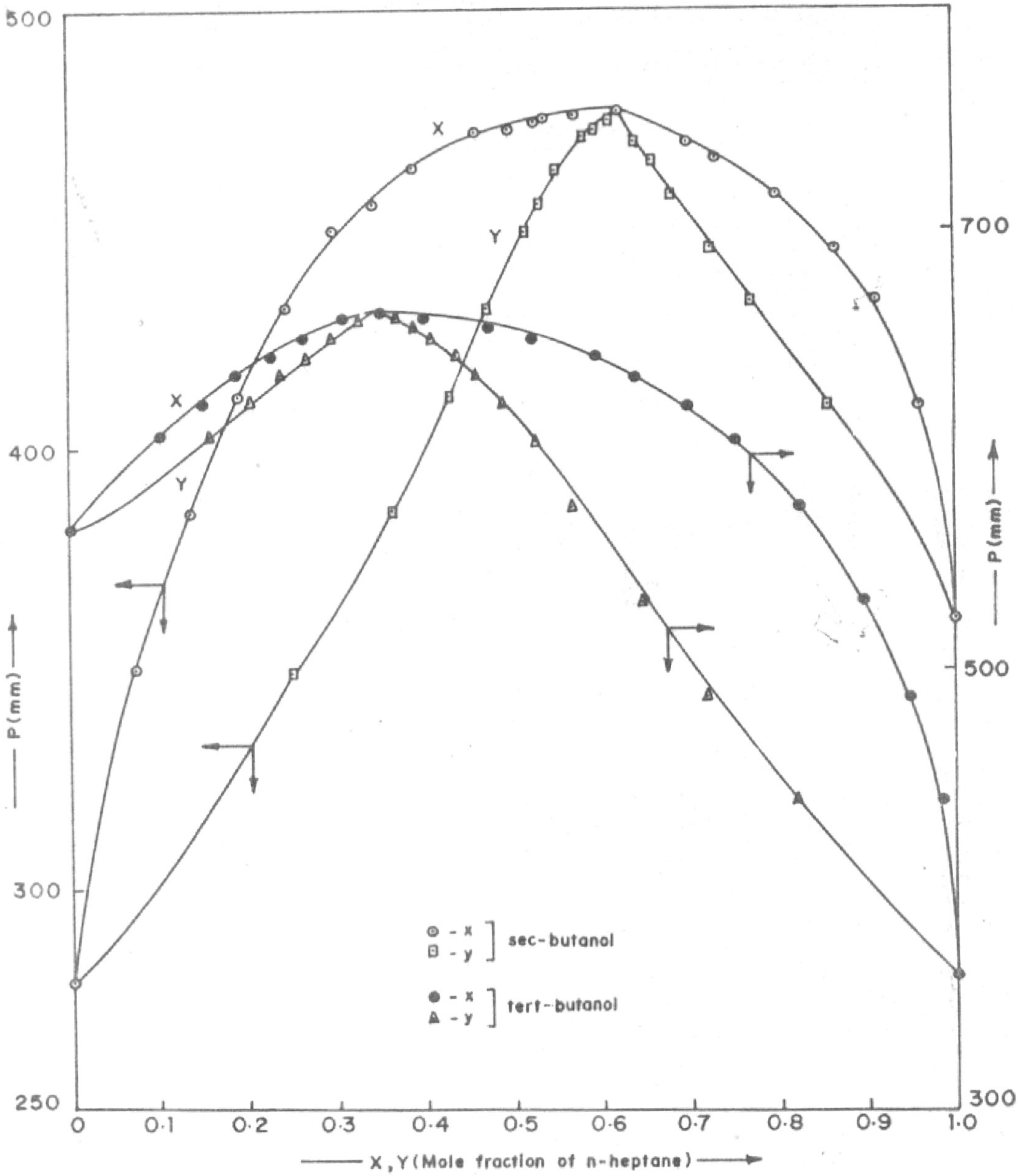


FIG.25. P-X,Y DIAGRAM FOR n-HEPTANE (1) — sec-BUTANOL (2) & — tert-BUTANOL (2) SYSTEM AT 75°C

Table 20 : Concentrations of n-heptane forming azeotropes at different temperatures in isomeric butanols

Systems	x_1 (mole fraction of n-heptane forming azeotropes)		
	55°	65°	75°
n-butanol	0.86	0.83	0 .81
iso-butanol	0.78	0.75	0.72
sec-butanol	0.70	0.65	0.62
tert-butanol	0.45	0.40	0.35

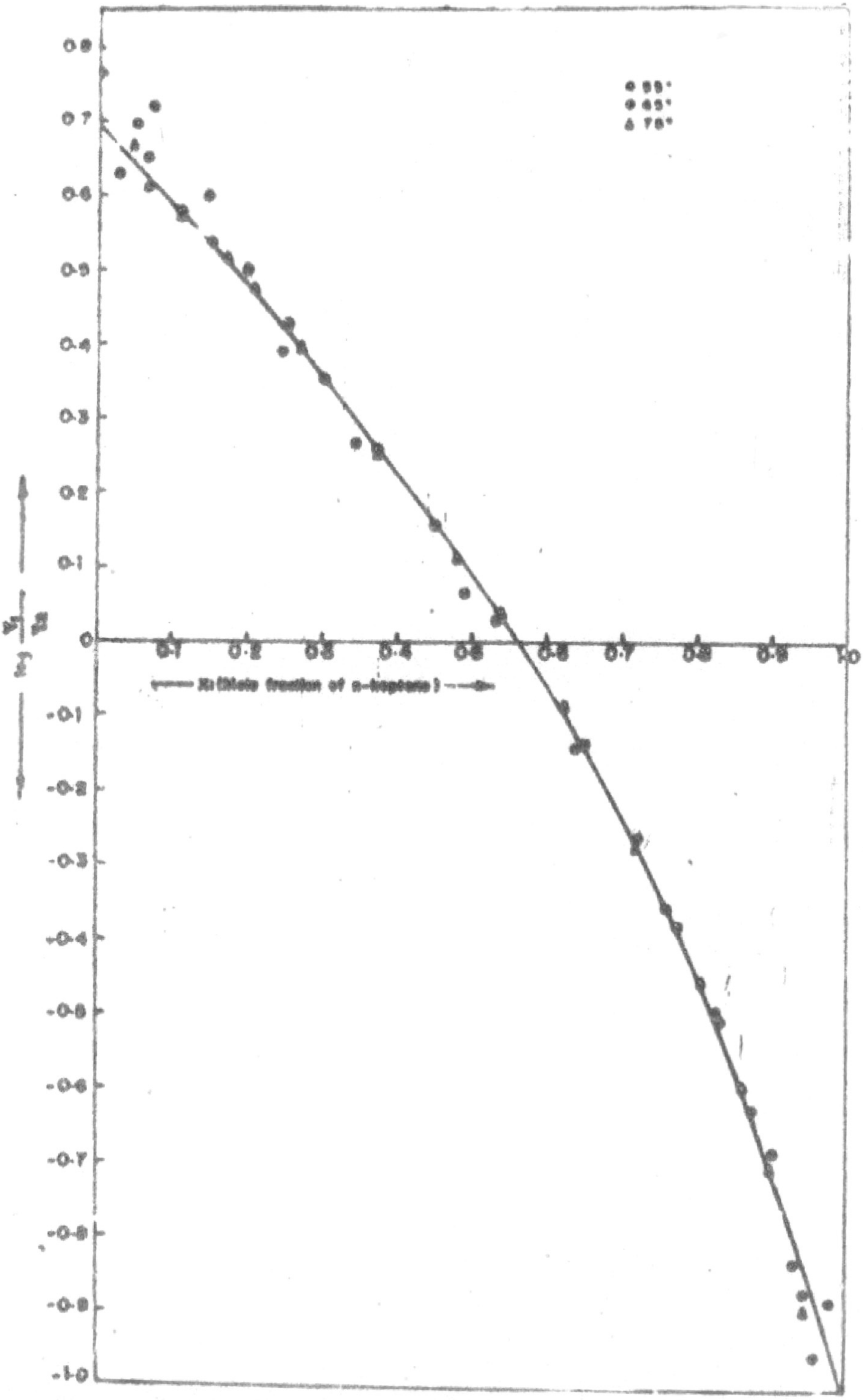


FIG. 26. THERMODYNAMIC CONSISTENCY TEST FOR n-HEPTANE(1)—n-BUTANOL(2) SYSTEM AT 55°, 65° & 75°C

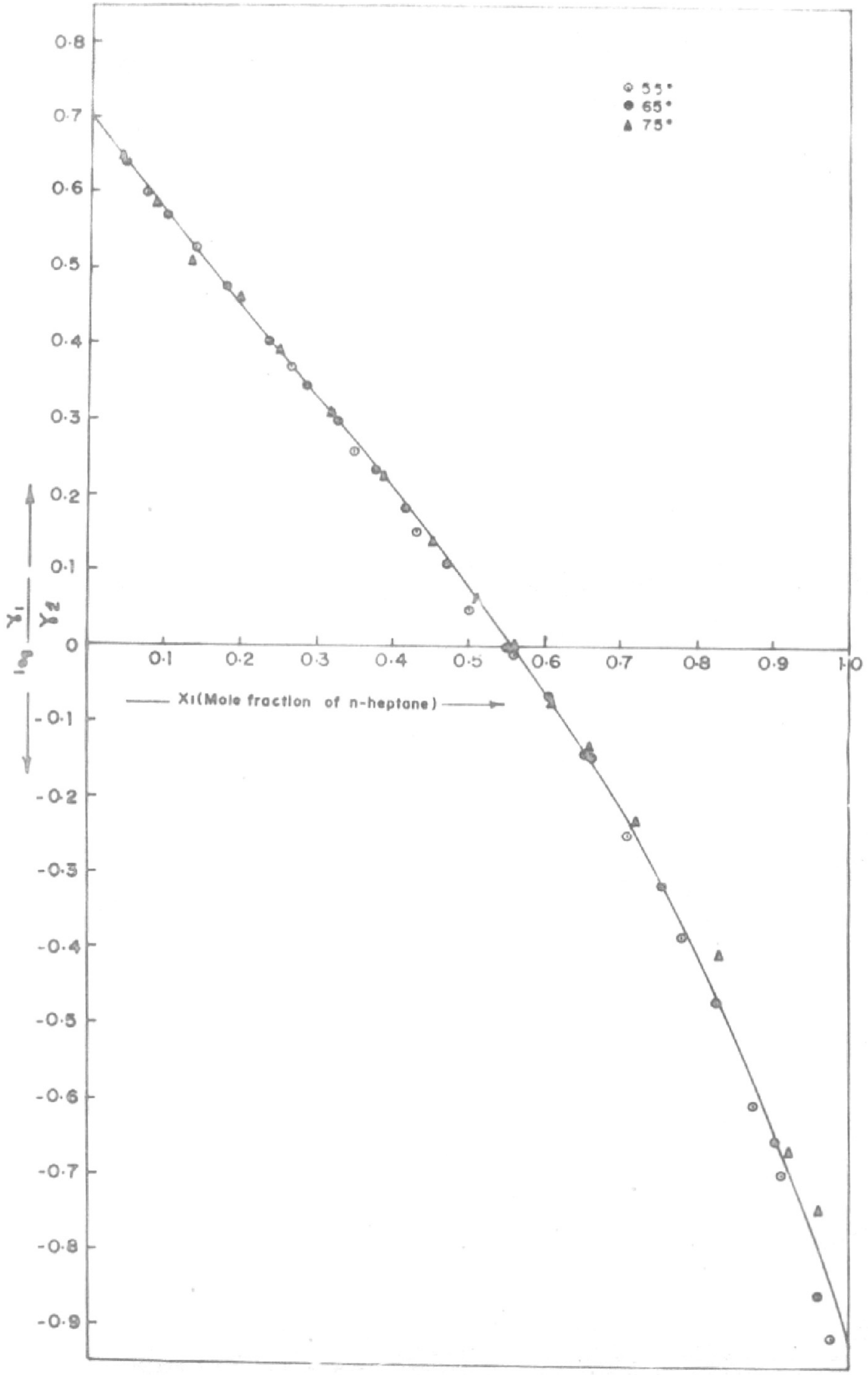


FIG. 27. THERMODYNAMIC CONSISTENCY TEST n-HEPTANE (I)—Iso-BUTANOL (2) SYSTEM AT 55°, 65° & 75°

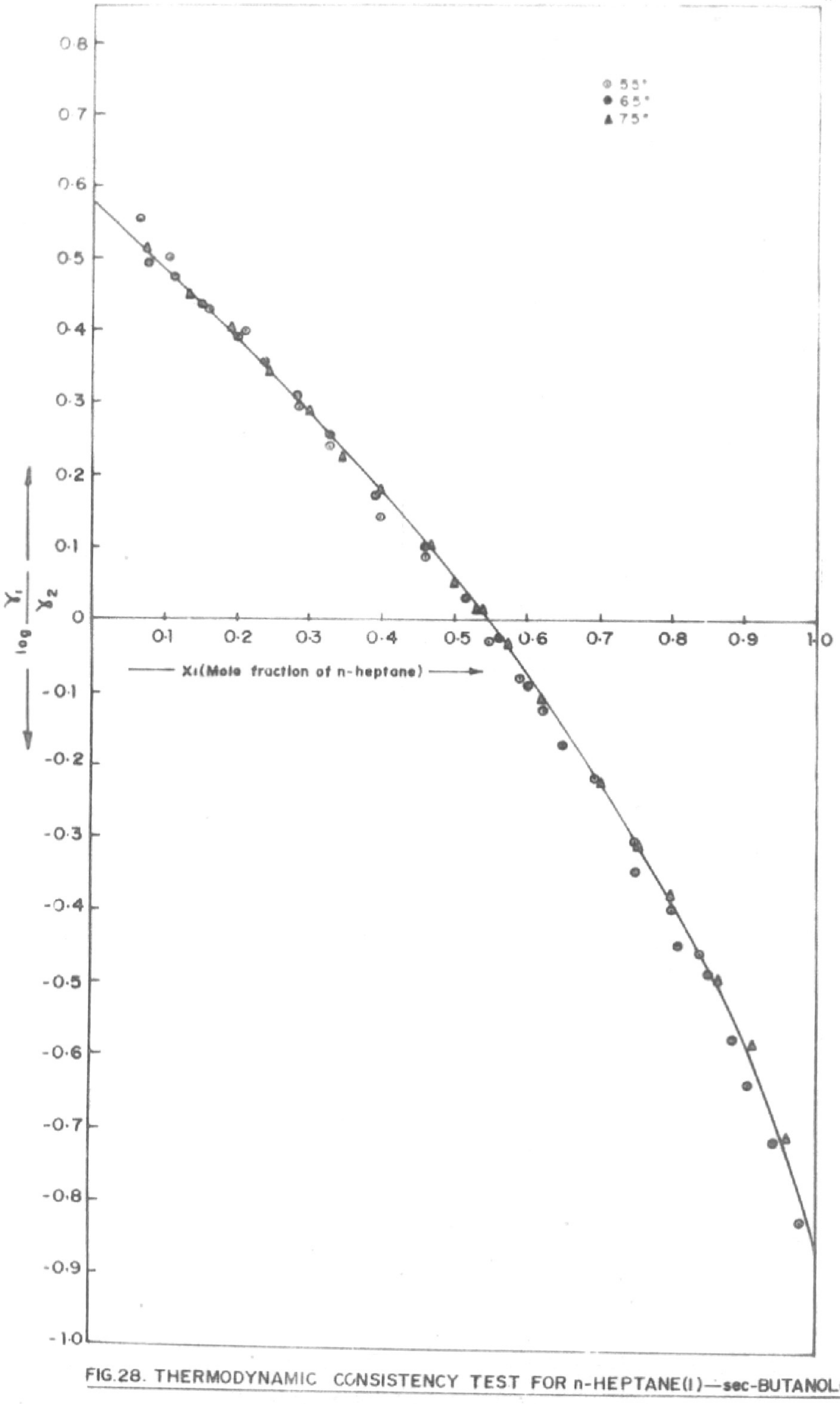


FIG.28. THERMODYNAMIC CONSISTENCY TEST FOR n-HEPTANE(1)—sec-BUTANOL(2) SYSTEM AT 55°, 65° & 75°

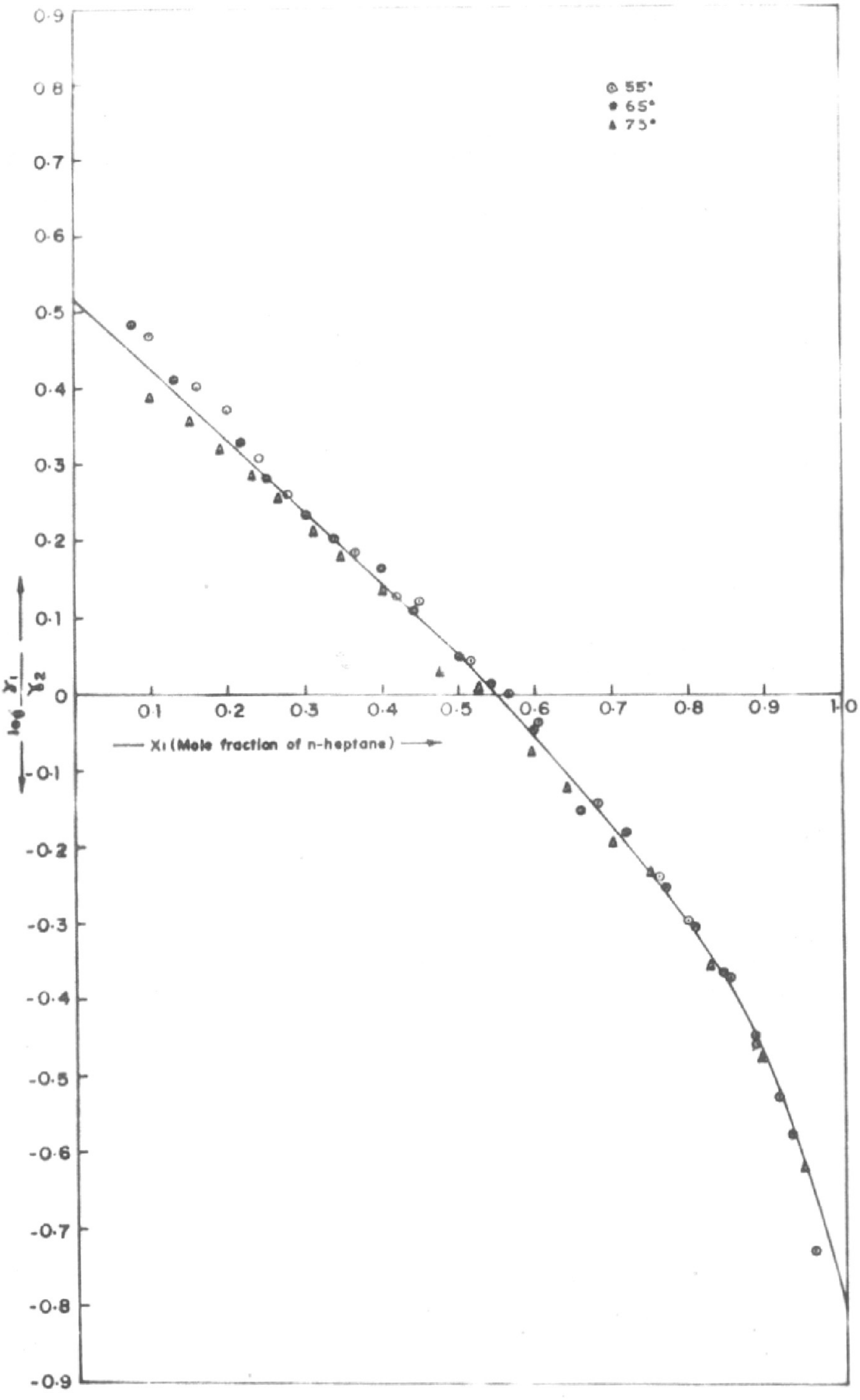


FIG. 29. THERMODYNAMIC CONSISTENCY TEST OF n-HEPTANE(1) — tert-BUTANOL SYSTEM AT 55°, 65° & 75°C

The accuracy of data was checked by Herington internal thermodynamic consistency test[5]. The plots of log γ_1/γ_2 vs x_1 for each butanol at these temperatures are shown in Fig. 26,27,28 and 29. The data were found to be consistent better than 2.2, 3.5, 1.9 and 2.1% for n, iso, sec and tert butanol systems respectively.

The values of excess free energy G^E were calculated by the equation 5 given in Chapter II (b). The G^E vs x_1 plots for n, iso, sec and tert-butanol systems have been shown in Fig. 30,31,32 and 33 at 55°, 65° and 75°C. The behaviour of G^E with x_1 for all isomeric forms of butanols at each temperature has been presented in Fig. 34, 35, 36 at 55°, 65° and 75°C respectively.

The applicability of Van Laar equation[6] to these systems may be indicated by plotting G^E/x_1x_2 vs x_1 curves which are nearly straight lines. The Van Laar constants A and B and σ, the standard deviation between observed vapour composition and calculated by Van Laar equation for isomeric butanols at 55°C are listed in Table 21.

The G^E can be well represented by Redlich Kister equation[7] of the type

$$G^E = RT\left[x_1(1-x_1)\sum_{n=1}^{5} A_n(1-2x_1)^{n-1}\right]$$

where x_1 is the mole fraction of n-heptane in liquid phase. The values of constants calculated by computer (Honeywell 400) are

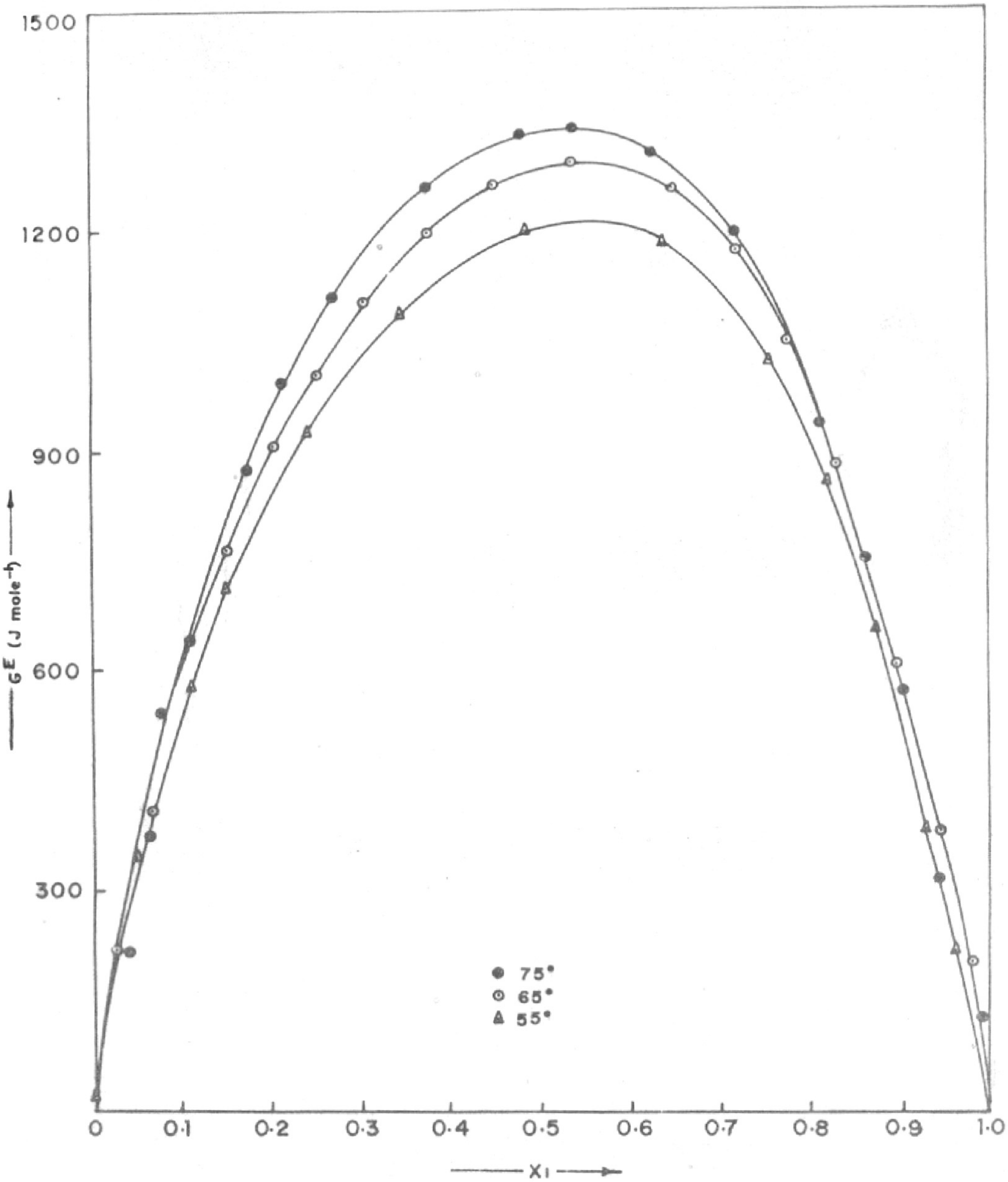


FIG. 30. EXCESS FREE ENERGY OF MIXING OF n-HEPTANE(1)—n-BUTANOL(2) SYSTEM AT 55°, 65° & 75°C

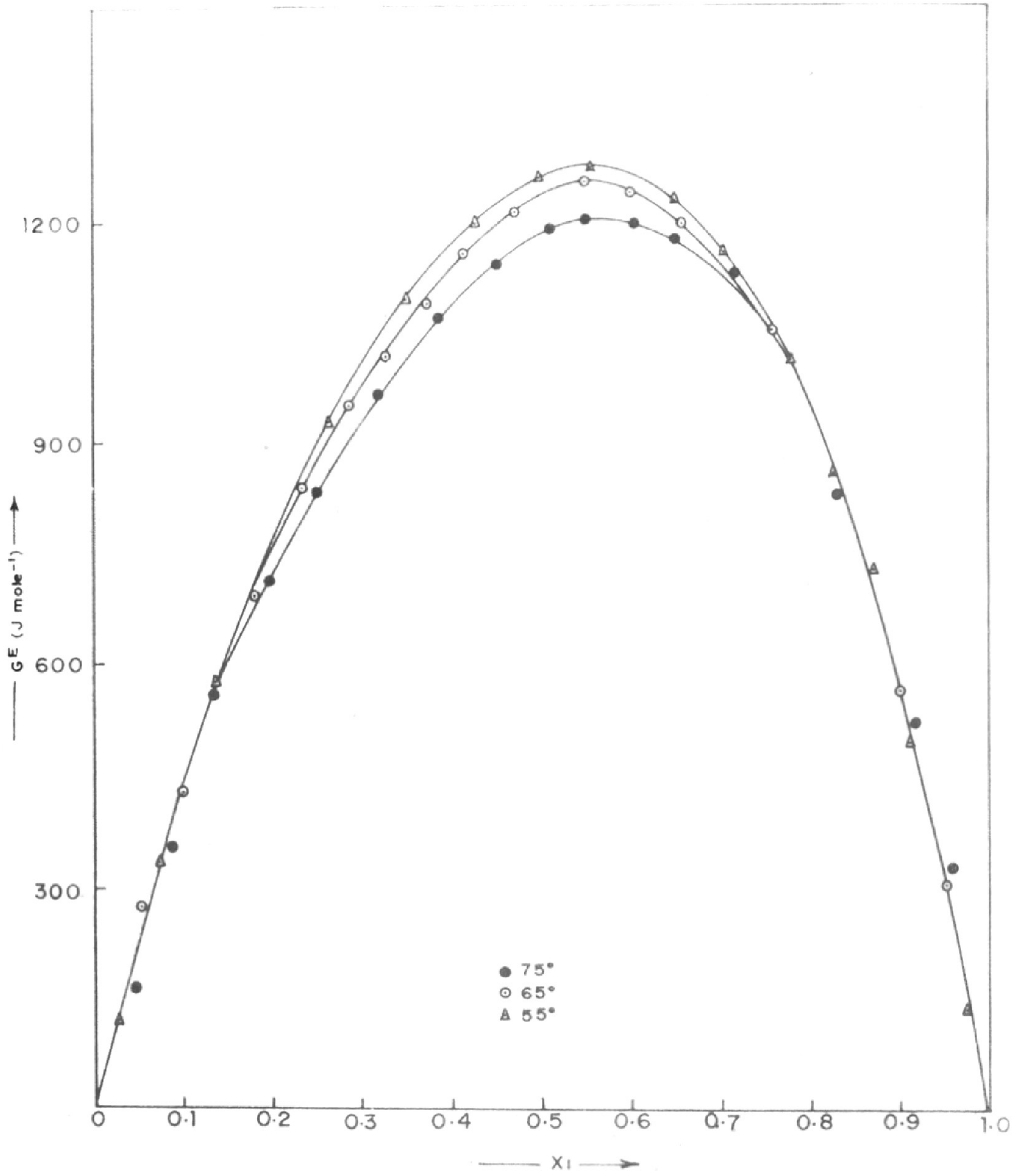


FIG. 31. EXCESS FREE ENERGY OF MIXING FOR n-HEPTANE(1) — iso-BUTANOL(2) SYSTEM AT 55°, 65° & 75° C

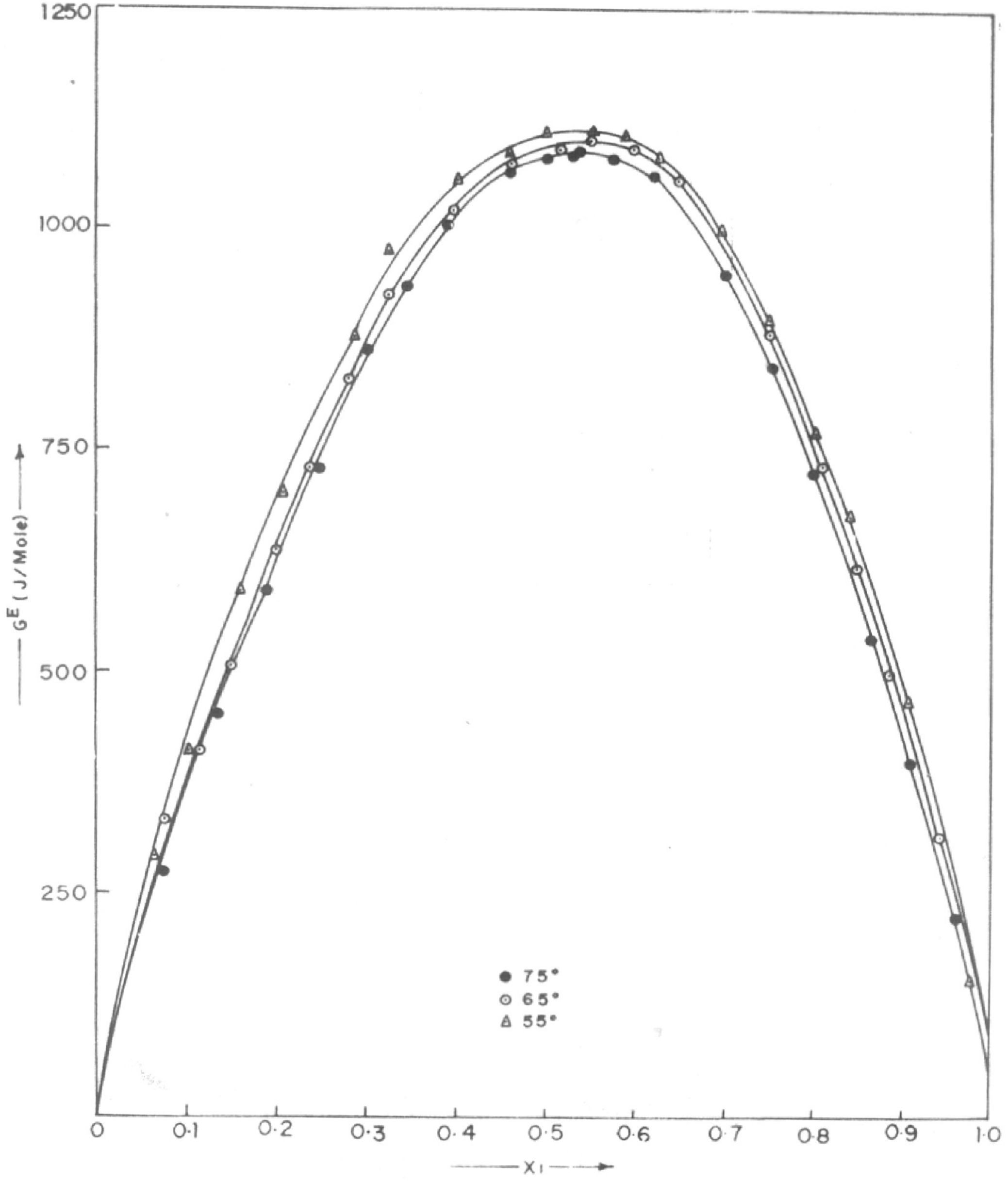


FIG. 32 EXCESS FREE ENERGY OF MIXING OF n-HEPTANE (1) — sec-BUTANOL(2) SYSTEM AT 55°, 65° & 75°C

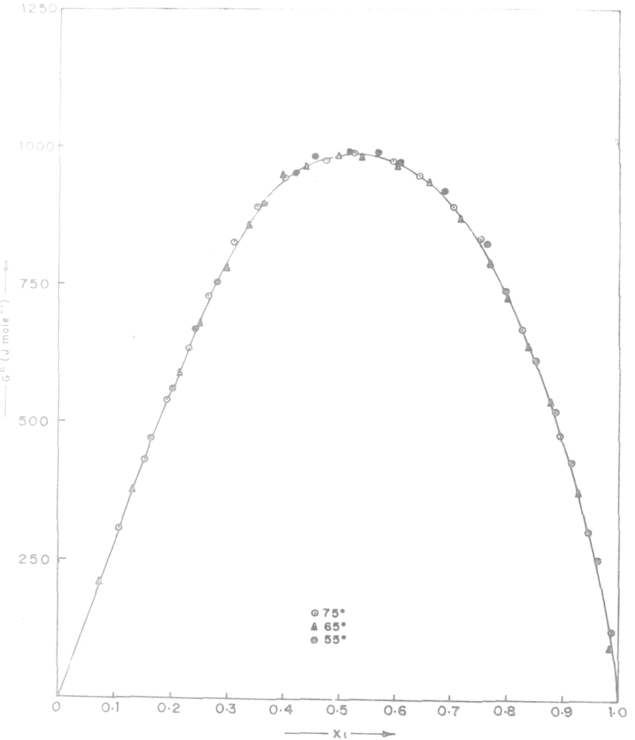


FIG.33. EXCESS FREE ENERGY OF MIXING n-HEPTANE(1) — tert-BUTANOL(2) SYSTEM AT 55°, 65° & 75°C

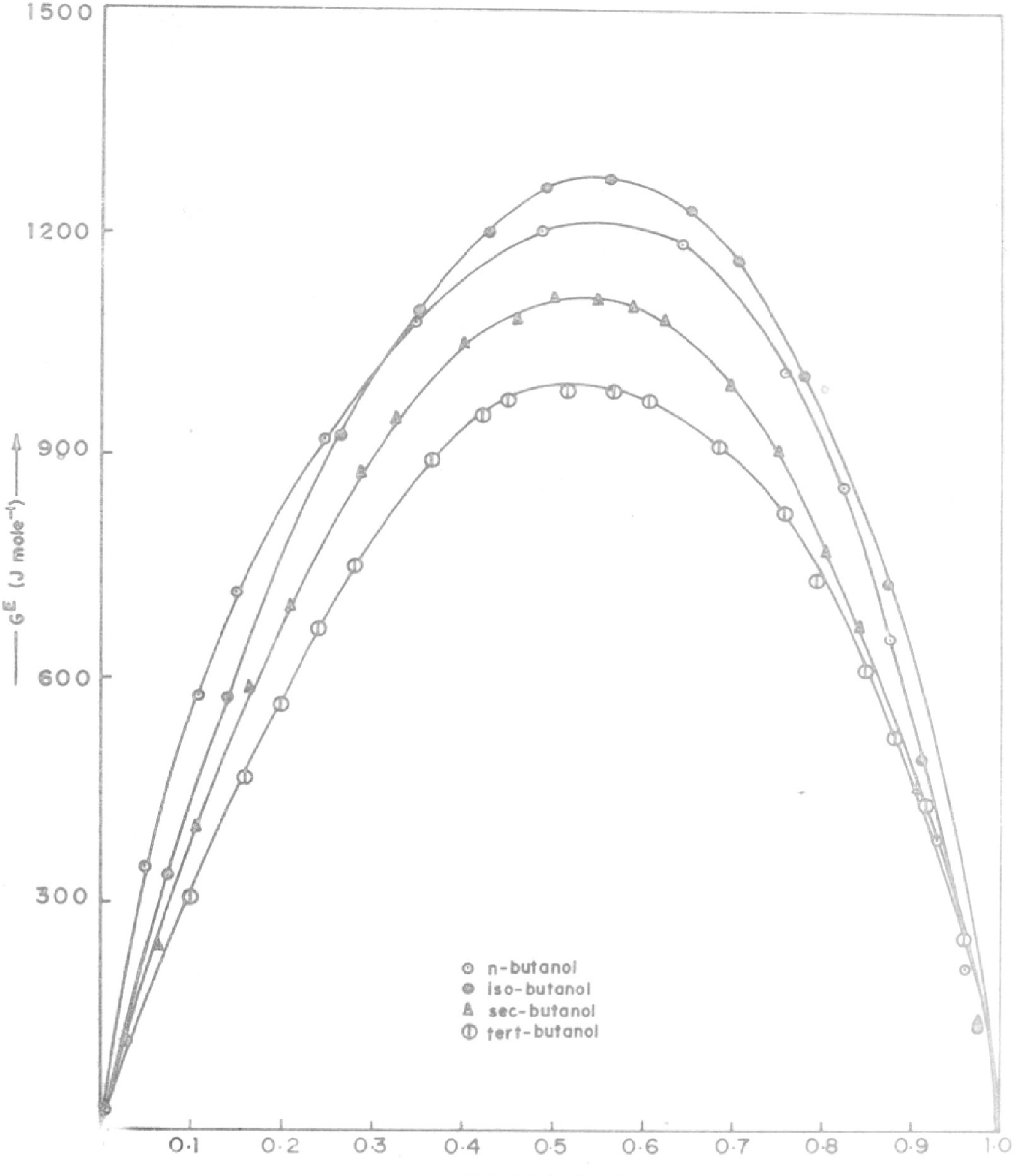


FIG. 34. EXCESS FREE ENERGY OF n-HEPTANE (1) — isomeric BUTANOLS (2) SYSTEMS AT 55° C

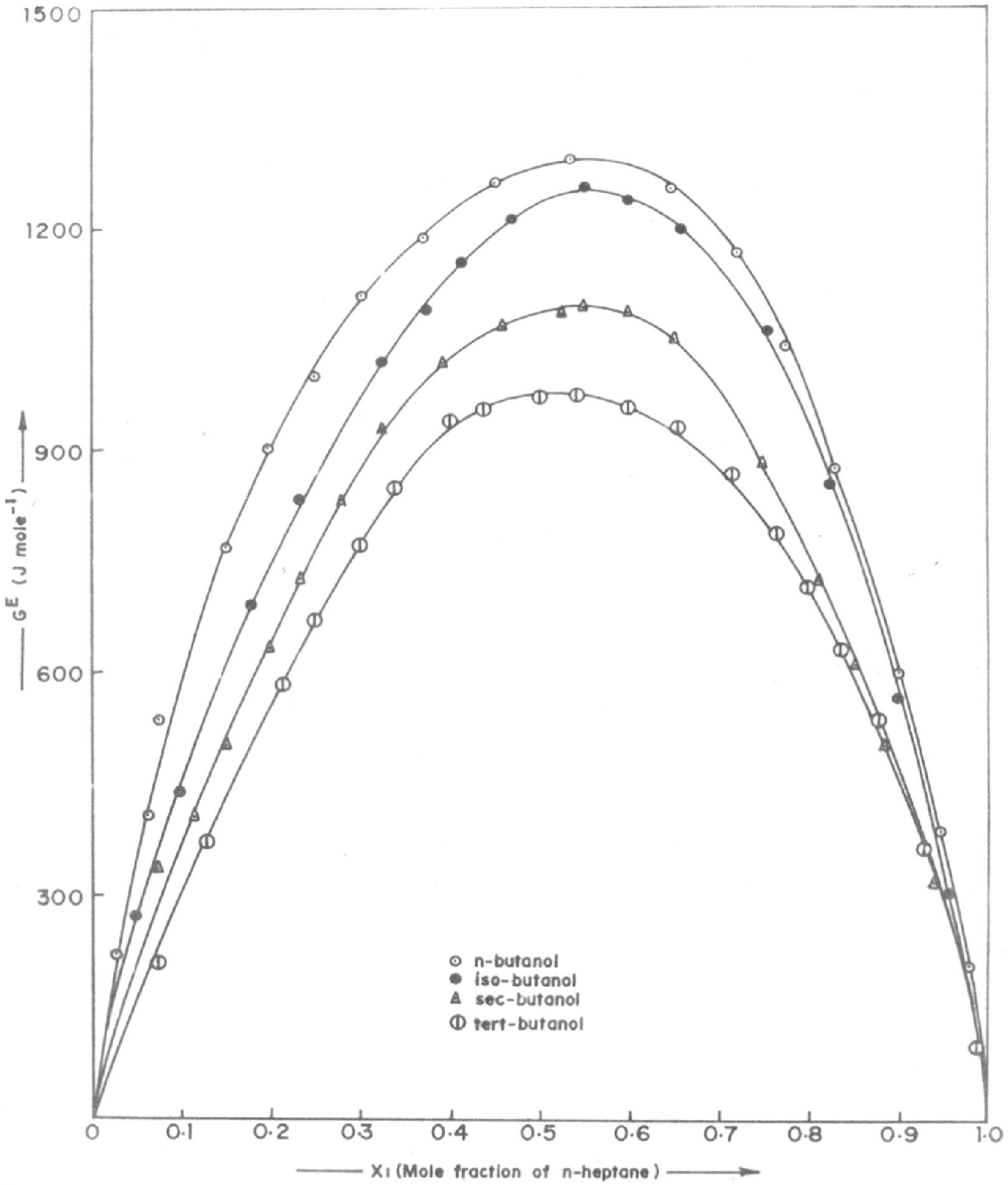


FIG. 35. EXCESS FREE ENERGY OF n-HEPTANE(1) — Isomeric-BUTANOLS (2) SYSTEM AT 65°C

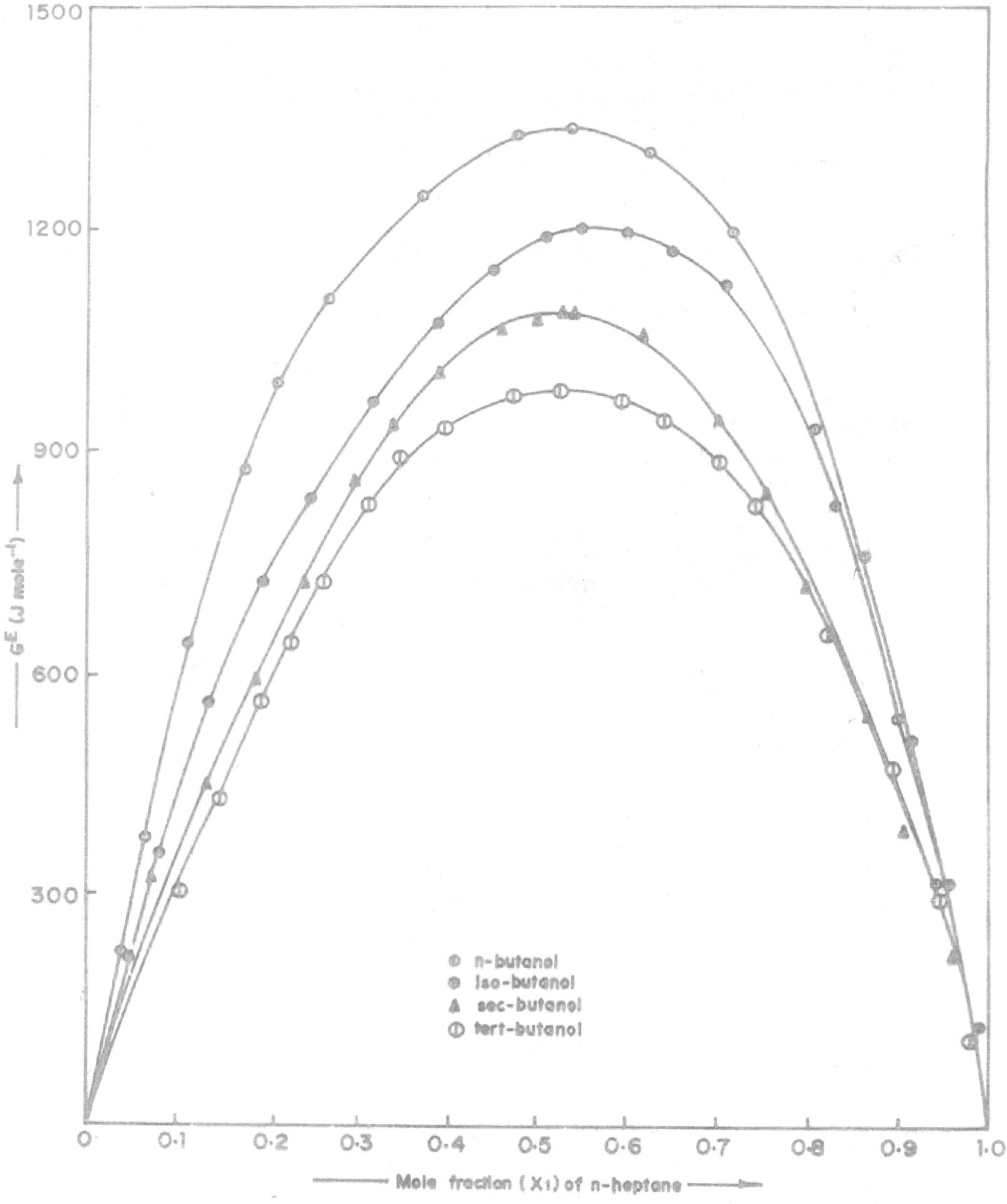


FIG. 36. EXCESS FREE ENERGY OF n-HEPTANE (1) — Isomeric-BUTANOLS (2) SYSTEM AT 75°C

Table 21 : Van Laar constants and standard deviation σ for isomeric butanols and n-heptane systems at 55°C

System	A	B	σ (Std.dev.in vapour composition)
n-butanol	0.7043	0.9375	0.0704
iso-butanol	0.6275	1.0006	0.0225
sec-butanol	0.6346	0.7324	0.0098
tert-butanol	0.5118	0.7889	0.0156

given in Table 22,23,24 and 25 along with standard deviation σ .

The G^E is found to be positive throughout the concentration range for all alcohols at various temperatures. The high values of G^E may be attributed to the breaking of hydrogen bonds in self associated molecules of butanols. For a given temperature, the values of G^E decrease from n to tert butanol. This phenomena can be explained on the basis of idealised model given by Brown et al[2].

Alcohols are strongly associated due to hydrogen bonding and these hydrogen bonds are broken on dilution with n-heptane. As discussed by Brown et al the number of hydrogen bonds formed in such a mixture at a given mole fraction will be a function of w/KT and thus the number of hydrogen bonds broken will also be another function of w/KT where w is the Gibbs energy. The process of hydrogen bond breaking may depend on two factors- a) the hydroxyl group contribution hN (w/KT.C) abbreviated as Nh b) the change in the energy of interaction between the alkyl chains which are separated on breaking of hydrogen bonds. The values of hydroxyl group contribution Nh as calculated by the above workers for n, iso, sec and tert-butanols are 30.5, 29.0, 27.9 and 24.8 kJ mole^{-1}. If it is assumed that enthalpy (h) associated with breaking of hydrogen bonds is independent of the alcohol for a given value of w, it may be concluded that the value of w decreases from n to tert-butanol. The same behaviour has also been observed by us in the case of isomeric butanols with n-heptane binary mixtures. Hence it is clear that

Table 22 : Coefficients A_n along with standard deviation σ for relation between G^E and x_1 of n-heptane and n-butanol system at different temperatures

temp.	A_1	A_2	A_3	A_4	A_5	σ J $mole^{-1}$
55°	4717	-1115	2108	-1386	-154	19
65°	5143	-1244	1659	3384	3403	23
75°	5382	324	1770	-1500	-	35

Table 23 : Coefficients A_n along with standard deviation σ for relation between G^E and x_1 of n-heptane and iso-butanol system at different temperatures

temp.	A_1	A_2	A_3	A_4	A_5	σ J mole^{-1}
55°	5342	-1034	1709	-1285	148	13
65°	4936	-1272	643	1436	1447	10
75°	4730	- 832	1292	- 922	-	23

Table 24 : **Coefficients A_n along with standard deviation σ for relation between G^E and x_1 of n-heptane and sec-butanol system at different temperatures**

temp.	A_1	A_2	A_3	A_4	A_5	σ J mole^{-1}
55°	5757	-773	1419	-1240	856	12
65°	4372	-836	- 455	1760	1782	16
75°	4336	-602	- 551	744	756	7

Table 25 : Coefficients A_n along with standard deviation σ for relation between G^E and x_1 of n-heptane and tert-butanol system at different temperatures

Temperature	A_1	A_2	A_3	A_4	A_5	σ J mole^{-1}
55°	3970	-527	1391	-1028	1478	9
65°	3928	-439	200	-1124	-1120	9
75°	3958	-280	196	-1155	-1150	8

there is a pronounced effect on G^E of the isomers of butanols. Even if we consider on the basis of steric effect, we find that depending upon the decreasing values of Nh, fewer hydrogen bonds will be available for breaking from n to tert-butanol and hence a decrease in G^E values is expected. It was noted that such decrease was less visible at 55° where the values of G^E for n and iso butanols are nearly the same. This observation also agrees well with that of Brown et al[2].

It is seen from figures (30,31,32,33) that the values of G^E decrease with increase in temperature for all the systems studied except for n-butanol. The decrease in G^E with increase in temperature is expected due to decrease in associated species as reported by Vilcu and Cenoise[8]. In the case of n-butanol the values of G^E are found to increase with increase in temperature. Such a behaviour was confirmed by careful repetition of the experiments several times. However, Brown et al[2] have measured G^E in case of n-butanol with benzene at 25°, 35° and 45° and observed negligible change of G^E with temperature.

In the case of tert-butanol the effect of temperature on G^E is noticed practically negligible. The effect of temperature on G^E for all the systems at equimolar mixture has been presented in Fig. 37. It is obvious from the figure that all butanols except n-butanol show similar behaviour.

While accounting the temperature effect, it is noted that the change in temperature did not exhibit any shift in the maximum value of G^E. The maxima in G^E values for all alcohols were

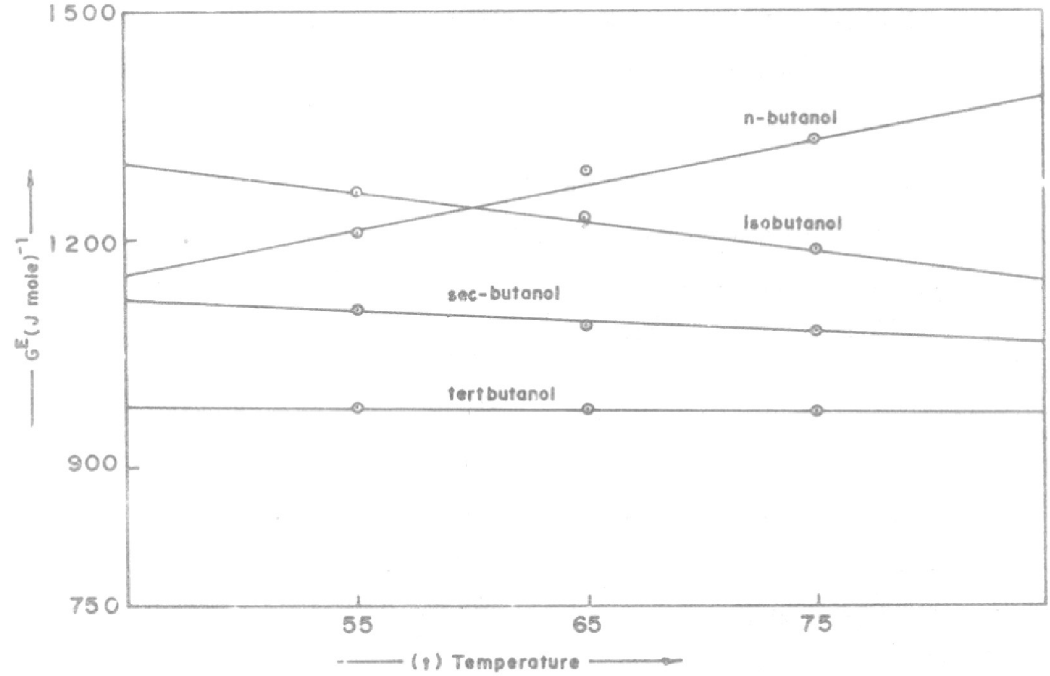


FIG.37. TEMERATURE DEPENDENCE OF FREE ENERGY AT EQUIMOLAR MIXTURE

obtained at nearly 0.55 mole fraction of n-heptane.

It is also observed that the substitution of methyl group in the alkyl chain of butanol does not show any effect on the maximum values of G^E at a particular temperature as they are obtained at the same mole fraction of n-heptane. Hence it is clear that there is no shifting of maxima towards high or low mole fraction range by substituting methyl groups.

Regarding the effect of temperature on azeotropes it can be seen from Table 20 that the concentration at which the azeotropes are formed does not change with temperature. This observation is also supported by Vilcu and Cenelse[8] in case of isobutanol and benzene at 45° and 55°C.

(c) EXCESS ENTHALPY OF MIXING :

The heats of mixing of n, iso, sec and tert-butanol with n-heptane were measured at 55° throughout the concentration range. The results on heats of mixing H^E as a function of mole fraction x_1 of butanol are presented in Table 26, 27, 28 and 29 along with the values of H^E/x_1x_2. The H^E vs x_1 plots are shown in Fig. 38. Huong Nguyen et al[9] have measured the heats of mixing of n-butanol-n-heptane system at the same temperature by isothermal dilution calorimeter. Their results along with our data are plotted in Fig. 39. It is seen that the values obtained by us are higher in the region x_1 0.2 than those reported by them. The heats of mixing results can be well represented by the equation[10]

Table 26 : Heats of mixing of n-butanol (1) and n-heptane (2) system at 55°C

Sr. No.	x_1 Mole fraction of n-butanol	H^E J mole^{-1}	H^E/x_1x_2 KJ mole^{-1}
1	0.0489	395	8.492
2	0.0820	528	7.013
3	0.1094	738	7.572
4	0.1182	809	7.762
5	0.1667	949	6.830
6	0.2030	1040	6.426
7	0.2545	1122	5.912
8	0.3027	1060	5.498
9	0.3991	1202	5.012
10	0.4019	1212	5.041
11	0.4952	1188	4.752
12	0.5462	1143	4.611
13	0.6150	1088	4.595
14	0.6561	1028	4.555
15	0.7070	930	4.491
16	0.7871	750	4.475
17	0.8279	627	4.401
18	0.8750	482	4.406
19	0.9146	357	4.570

Table 27 : Heats of mixing of iso-butanols (1) and n-heptane (2) system at 55°C

Sr.No.	x_1 Mole fraction of iso-butanol	H^E J mole^{-1}	H^E/x_1x_2 KJ mole^{-1}
1	0.0588	456	8.239
2	0.0765	568	8.042
3	0.0881	675	8.398
4	0.1033	735	7.733
5	0.1270	858	7.736
6	0.1276	840	7.546
7	0.1684	1015	7.249
8	0.2157	1137	6.719
9	0.2415	1215	6.634
10	0.2500	1213	6.469
11	0.3213	1302	5.971
12	0.3256	1268	5.775
13	0.3256	1323	6.023
14	0.3961	1345	5.624
15	0.4493	1353	5.469

continued

Table 27 continued

Sr.No.	x_1 Mole fraction of iso-butanol	H^E J mole^{-1}	H^E/x_1x_2 KJ mole^{-1}
16	0.4498	1362	5.503
17	0.4840	1344	5.381
18	0.5422	1320	5.317
19	0.5918	1248	5.165
20	0.6168	1236	5.228
21	0.6798	1104	5.071
22	0.7469	963	5.094
23	0.8021	801	5.049
24	0.8478	661	5.125
25	0.9085	415	4.990

Table 28 : Heats of mixing of sec-butanol (1) and n-heptane (2) system at 55°C

Sr. No.	x_1 Mole fraction of sec-butanol	H^E J mole^{-1}	H^E/x_1x_2 KJ mole^{-1}
1	0.0538	479	9.407
2	0.0769	615	8.662
3	0.1066	758	7.959
4	0.1289	892	7.943
5	0.1818	1054	7.085
6	0.2000	1152	7.199
7	0.2442	1255	6.799
8	0.2963	1350	6.473
9	0.3091	1347	6.307
10	0.3468	1400	6.179
11	0.4028	1434	5.960
12	0.4112	1446	5.971
13	0.4952	1442	5.768
14	0.4953	1431	5.723

continued

Table 28 continued

Sr. No.	x_1 Mole fraction of sec-butanol	H^E J mole^{-1}	H^E/x_1x_2 KJ mole^{-1}
15	0.5462	1396	5.630
16	0.6168	1350	5.711
17	0.6179	1335	5.654
18	0.6611	1264	5.641
19	0.7103	1152	5.598
20	0.7458	1064	5.612
21	0.8007	895	5.608
22	0.8557	708	5.732
23	0.9111	468	5.773

Table 29 : Heats of mixing of tert-butanol (1) and n-heptane (2) system at 55°C

Sr. No.	x_1 Mole fraction of tert-butanol	H^E J mole^{-1}	H^E/x_1x_2 KJ mole^{-1}
1	0.0585	471	8.552
2	0.0807	596	8.034
3	0.1020	706	7.708
4	0.1122	753	7.557
5	0.1333	833	7.210
6	0.1584	937	7.028
7	0.2030	1040	6.427
8	0.2488	1158	6.195
9	0.3077	1246	5.848
10	0.3489	1283	5.647
11	0.4108	1305	5.390
12	0.4413	1324	5.369
13	0.4976	1320	5.279

continued

Table 29 continued

Sr. No.	x_1 Mole fraction of tert-butanol	H^E J mole^{-1}	H^E/x_1x_2 KJ mole^{-1}
14	0.5679	1305	5.317
15	0.6511	1196	5.267
16	0.7244	1064	5.329
17	0.7862	900	5.353
18	0.8478	714	5.533
19	0.8798	626	5.918
20	0.9143	462	5.896

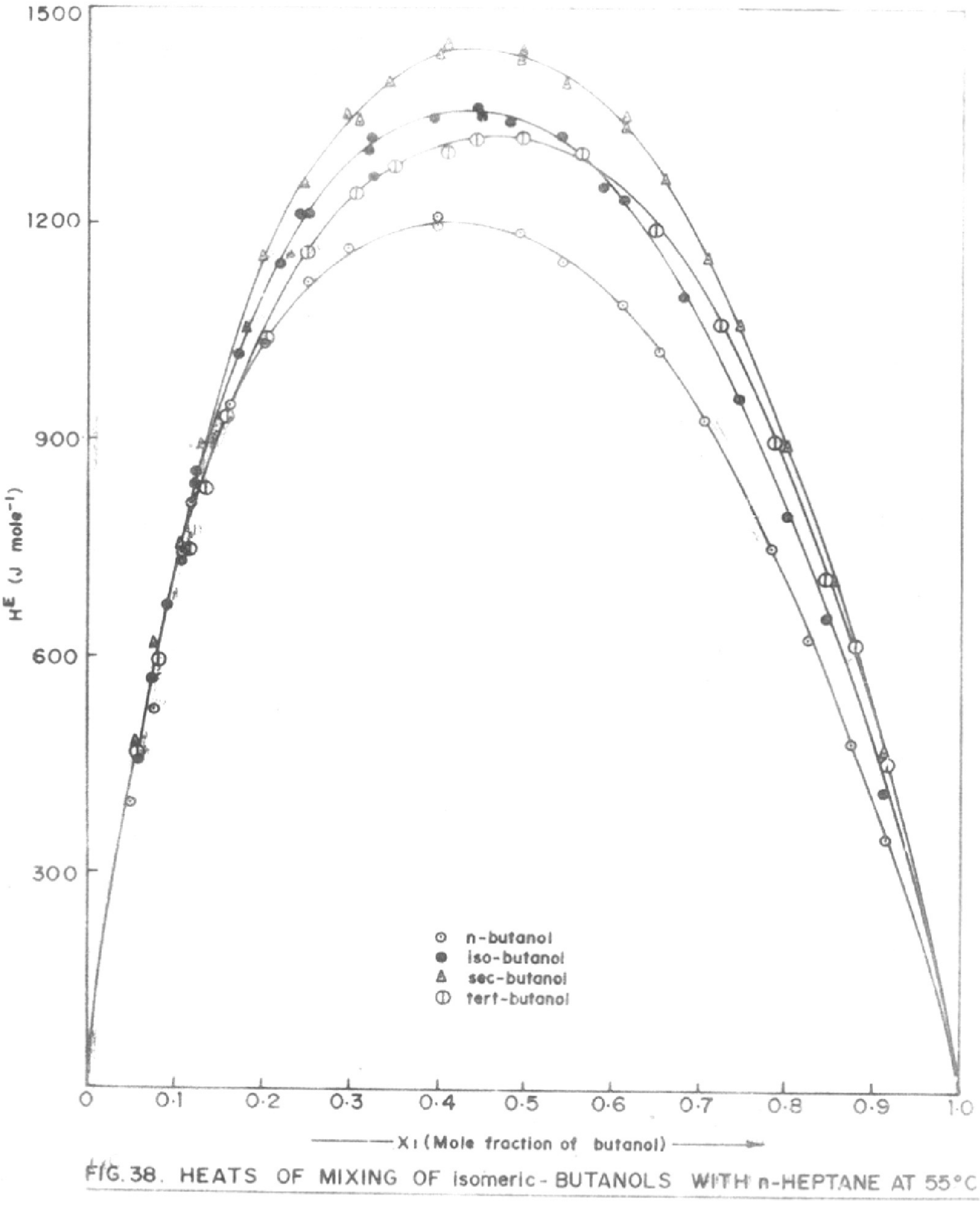


FIG. 38. HEATS OF MIXING OF isomeric-BUTANOLS WITH n-HEPTANE AT 55°C

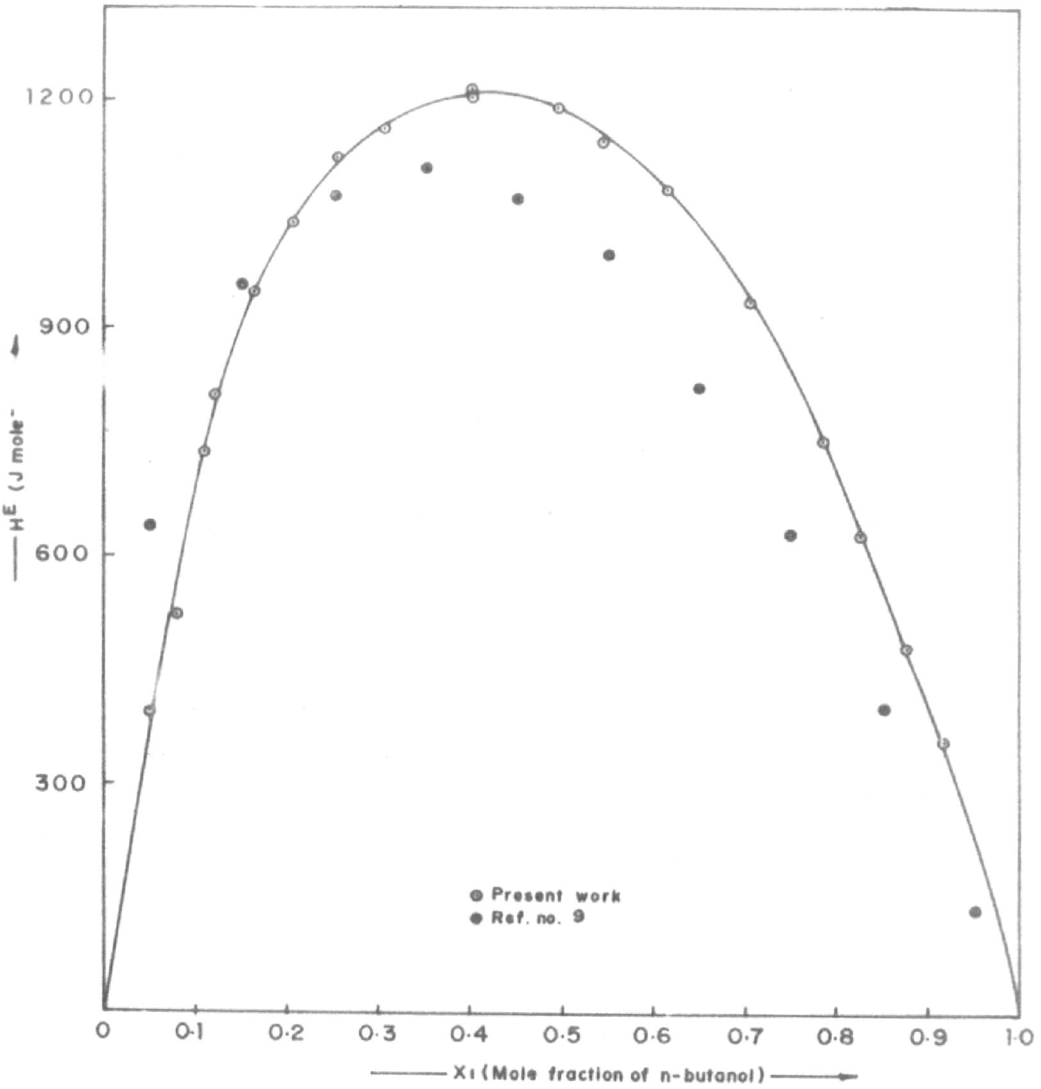


FIG.39. HEATS OF MIXING OF n-BUTANOL(1) — n-HEPTANE(2) SYSTEM AT 55°C

$$H^E = x_1(1-x_1) \sum_{n=0}^{2} A_n (2x_1-1)^n$$

where A_0 to A_2 are the constants and x_1 is the mole fraction of butanol. The values of constants A_n and standard deviation σ as calculated by a computer (Honeywell 400) are listed in Table 30.

All the four systems were found to exhibit the endothermic heats of mixing. The high endothermic enthalpy of mixing may be attributed to the breaking of hydrogen bonds in self associated butanol molecules. The maximum value of H^E was observed in the case of sec-butanol. The sequence of H^E maxima as shown in Fig. 38 is the same as reported by Brown et al[2] for isomeric butanols with n-hexane. It is worth mentioning that sec-butanol has an asymmetric carbon atom and hence is optically active which may be responsible for its different behaviour among the four isomers. This probability has been mentioned by Woycicka et al[11] while studying the enthalpy of mixing of isomeric butanols with n-heptane in very dilute region at 30°C.

The maxima in all systems obtained remained in the range of 0.4 to 0.45 mole fraction. This indicates that there is little effect on the maxima by substituting methyl groups in the butanols studied. The H^E/x_1x_2 values presented in Table 26, 27, 28, 29 are plotted in Fig. 40 against x_1, the mole fraction of butanol. H^E *vs* x_1 plots give the energy change associated with the interaction of the two liquids while those

Table 30 : Coefficients A_n along with standard deviation σ for the relation between H^E & x_1 of butanol at 55°C

System	A_o	A_1	A_2	σ J mole^{-1}
n-butanol	4715	-1619	-2112	27.4
iso-butanol	5346	-1396	-1988	28.7
sec-butanol	5719	-1170	-2002	22.7
tert-butanol	5231	- 933	-2361	21.0

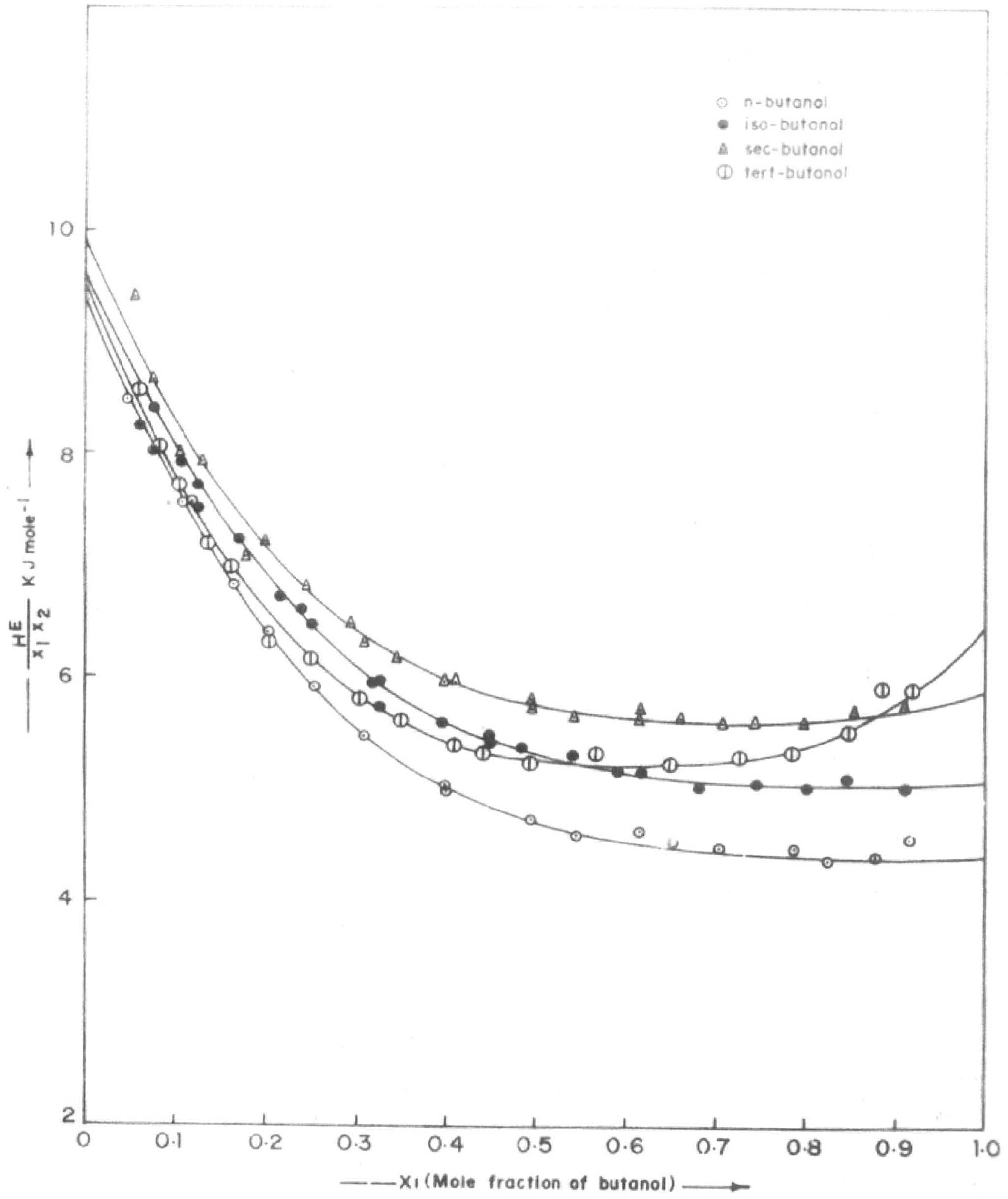


FIG. 40. $H^E/x_1 x_2$ Vs x_1 PLOTS FOR isomeric-BUTANOLS—n-HEPTANE SYSTEM

AT 55°C

H^E/x_1x_2 vs x_1 give the partial molar heats of mixing[12]. The curves of H^E/x_1x_2 vs x_1 when extrapolated to $x_1 \rightarrow 0$ give the partial molar enthalpy of mixing of the first component at infinite dilution while the extrapolated values at $x_2 \rightarrow 0$ is the partial molar enthalpy of mixing of the second component at infinite dilution. In the present investigation due to experimental difficulties our measurements could not be extended to the region of $x_1 < 0.05$ so it was not possible to get the accurate value of H^E/x_1x_2 at $x_1 \rightarrow 0$. Such values if obtained are the direct measure of hydrogen bond energies of isomeric butanols.

At low mole fractions of butanols where all hydrogen bonds are expected to break, the enthalpy of hydrogen bond breaking should be in the order of n > iso > sec > tert. This may be attributed to the steric effect of the isomeric butanols. It appears that tert-butanol would have maximum steric effect because of substitution of two methyl groups at the α-carbon atom followed by secondary butanol where one methyl group is attached to the α-carbon atom. The iso-butanol will have small steric effect due to substitution at β carbon atom. The enthalpy of self association of these isomers is therefore expected to decrease as n > iso > sec > tert. This trend is also supported by Geisler et al[13] on the basis of IR spectroscopic studies on these isomeric butanols.

However we could not confirm these trends since our experiments could not be carried out at $x_1 < 0.05$.

Table 31 : Values of TS^E at 55°C for isomeric butanols

x_1 Mole fraction of butanol	TS^E J mole^{-1}			
	n-butanol	iso-butanol	sec-butanol	tert-butanol
0.1	166	168	255	250
0.2	114	160	382	327
0.3	54	114	354	348
0.4	6	98	340	345
0.5	- 24	90	324	346
0.6	- 60	80	300	332
0.7	- 94	60	266	310
0.8	-138	42	210	298
0.9	-174	20	106	200

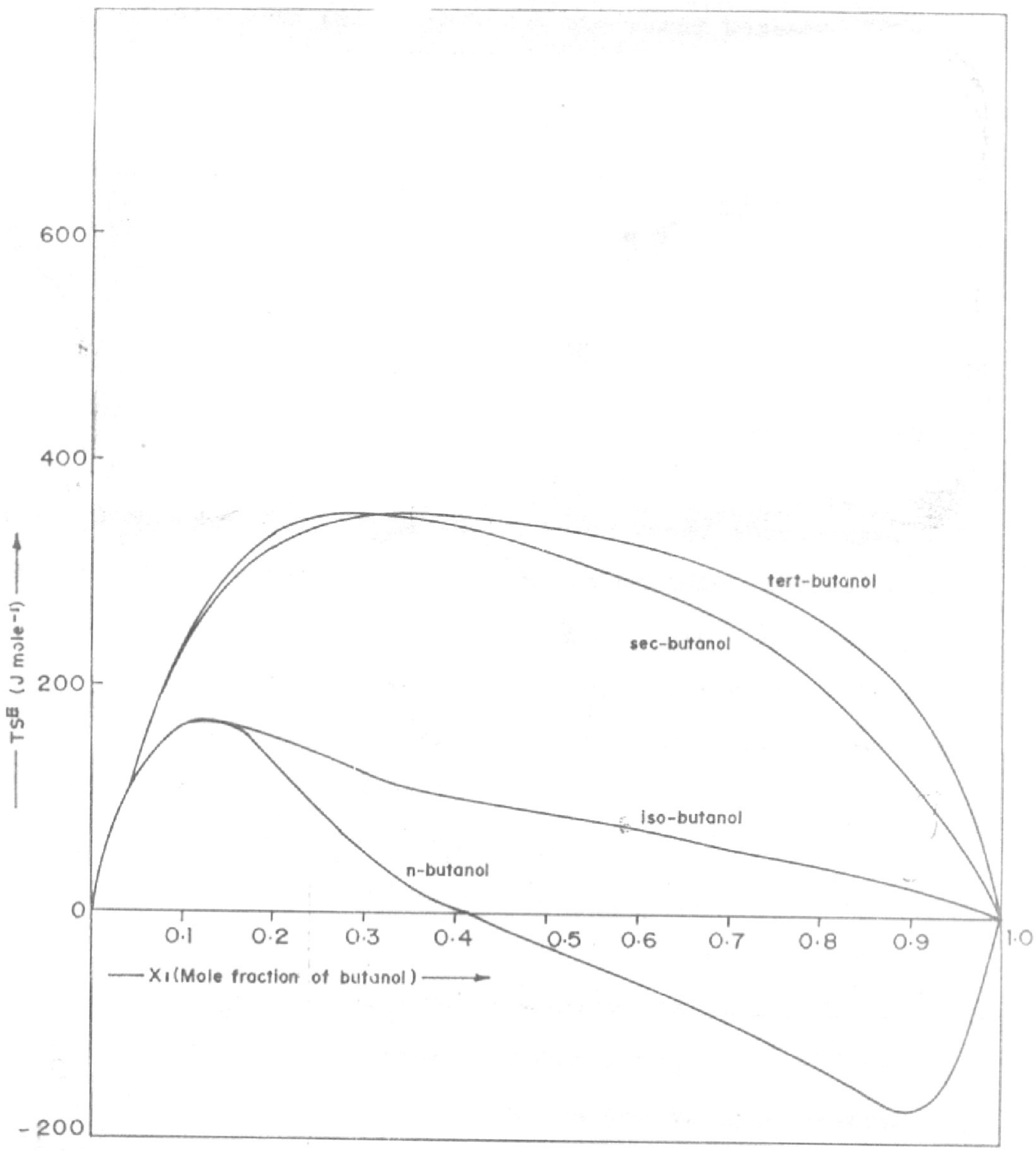


FIG. 41 EXCESS ENTROPY OF MIXING FOR Isomeric-BUTANOLS —n-HEPTANE SYSTEMS AT 55°C

At high mole fraction of butanol the reverse trend is observed due to crossing of the curves and the trend becomes

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

which is in agreement with Brown's observations.

The values of excess entropy $T\,S^E$ at 55°C have been calculated with the experimental G^E and H^E values presented in Table 16 and 26 respectively by the expression

$$G^E = H^E - TS^E$$

at known intervals of mole fractions. The calculated values of TS^E are presented in Table 31 as a mole fraction x_1 of butanol and are plotted in Fig. 41 for ready comparison. All systems except n-butanol are found to exhibit positive excess entropies throughout the concentration range. The positive excess entropies in the case of iso, sec and tert-butanols may be ascribed due to breaking of hydrogen bonds. The trend of excess entropy is found to be

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

The decrease from tert to iso-butanol may be due to decrease in steric hindrance.

In n-butanol case a 'S' shape curve is obtained. In this system at high mole fraction of butanol $(x_1 > 0.4)$ TS^E values are found to be negative which may be due to high restriction on translational and orientational movements which reduce the hydrogen bond breaking process and hence low entropy. The positive TS^E in the lower mole fraction region may be ascribed to the larger number of hydrogen bonds broken by means of which

Table 32 : Comparison of H^E values obtained calorimetrically and obtained from temperature dependence of G^E for iso and sec-butanol systems at 55°C

Sr. No.	Mole fraction of butanol	H^E exptl. J mole^{-1}	H^E cacd. J mole^{-1}	% deviation
		Iso-butanol		
1	0.25	1230	1176	4
2	0.35	1338	1600	19
3	0.40	1364	1600	17
4	0.45	1362	1600	17
5	0.50	1356	1692	25
6	0.60	1250	1600	28
		Sec-butanol		
1	0.3	1344	1702	26
2	0.4	1440	1466	2
3	0.5	1434	1428	nil
4	0.6	1355	1600	18
5	0.7	1181	1500	27
6	0.8	900	1125	25

there is greater freedom in orientational and translational movements. This in turn facilitates the increase in entropy of the system.

(d) CALCULATION OF H^E FROM TEMPERATURE DEPENDENCE OF G^E :

The values of H^E have been calculated for iso and sec-butanols by Gibbs Helmhots equation making use of the experimental G^E values at 55°, 65° and 75°C shown in Table 17 and 18. The calculated H^E values have been listed in Table 32 along with H^E values obtained calorimetrically for comparison. The H^E values could not be calculated in case of n-butanol system due to improper change in G^E with temperature, whereas tert-butanol did not exhibit any considerable change in G^E with temperature.

REFERENCES

1. Treszczanowicz, A.J. and Benson, G.C.,
   J. Chem. Thermodyn. 9, 1189 (1977)

2. Brown, I. Fock, W. and Smith, F.,
   J. Chem. Thermodyn. 1, 273 (1969)

3. Van Ness, H.C. Soczek, C.A. and Kochar, N.K.,
   J. Chem. Eng. Data, 12, 346 (1967)

4. Van Ness, H.C. Soczek, C.A. Peloquin, G.L. and
   Machado, R.L., 12, 217 (1967)

5. Herington, E.F.G., Nature London, 1602, 610 (1947)

6. Van Ness, H.C. "Classical Thermodynamics of
   Non-electrolyte Solutions", Pergamon Press,
   Oxford (1964)

7. Warycha, S., Z. Phys. Chemie, 258(5), 864 (1977)

8. Vilcu, R. and Gencise, Z.,
   Rev. Roum. Chim. 18 (3), 377 (1973)

9. Huong, T.N. and Ratcliff, G.A.,
   J. Chem. Eng. Data, 20, 252 (1975)

10. Arenosa, R.L. Menduina, C. Tardajos, G. and DiazPena, M.,
    J. Chem. Thermodyn. 11, 159 (1979)

11. Woycicka, M.K. and Kalinowska, B.,
    Bull. De La Acad. Polon. Des. Sci. Ser. Sci. Chim.
    25, 639 (1977)

12. Savini, C.G. Winterhalter, D.R. and Van Ness, H.C.,
    J. Chem. Eng. Data, 10, 168 (1965)

13. Geisler, G. Fruwert, J. and Seidel, H.,
    Spectrochim. Acta. 27(9)A, 1893 (1971)

……

... SUMMARY

SUMMARY

The present studies are concerned mainly with the changes in thermodynamic properties such as excess volume (V^E), excess free energy (G^E), excess enthalpy (H^E) and excess entropy (S^E) which occur on diluting the isomeric butanols with n-heptane. Such properties are useful in understanding the nature of the interactions among butanols and n-heptane. Various excess properties viz. V^E, G^E and H^E have been measured by using pyknometer, modified Jones colburn recirculating still and twin type calorimeter respectively.

The excess volumes of all the isomeric butanols with n-heptane have been determined at 25° except that of tert-butanol at 26°C. All the four systems show a positive excess volume throughout the concentration range. The excess volumes have been found to vary in the order of tert $>$ sec $>$ iso $>$ n-butanol. Thechange in magnitude and symmetry is observed among the curves with branching of alcohols. The maxima are shifted towards the higher mole fraction of the alcohol as the substitution of methyl group shifts towards carbon atom. The order of excess volume has been attributed to the breaking of hydrogen bonds of associated species of alcohols by dilution with n-heptane and more random distribution of n-heptane molecules.

Isothermal vapour liquid equilibrium data for isomeric butanols-n-heptane were obtained at 55°, 65° and 75°C. The excess free energy calculated from these data is found to be

positive throughout the concentration range for all systems at all the temperatures. The G^E decreases with the increase in temperature. At each temperature G^E decreases from n to tert-butanol. This decrease in free energy has been explained in terms of idealised model. The hydrogen bond breaking process is expected to depend on two factors, the hydroxyl group contribution and the interaction energy of alkyl chains. In all the systems azeotropes have been observed. The azeotropes and G^E maxima are independent of temperature.

Enthalpy of mixing measured at 55° is found to be positive throughout the concentration range which may be due to breaking of hydrogen bonds in self associated butanol molecules. In low mole fraction range of butanol the order of H^E/x_1x_2 vs x_1 curves is expected to be n $>$ iso $>$ sec $>$ tert while the reverse trend is observed at higher mole fractions. The excess entropy calculated from G^E and H^E values is positive throughout concentration range for all systems except n-butanol. In this case the 'S' shape curve is obtained which may be due to high restriction of translational and orientational movements.

H^E has been calculated from temperature dependence of free energy for iso and sec-butanol systems and compared with the experimental values.

BIBLIOGRAPHY

1. Molecular Thermodynamics of Fluid Phase Equilibria
   J.M. Prausnitz, Prentice-Hall Inc. New Jersey (1969)

2. Vapour Liquid Equilibrium
   E Hala, J. Pick, V. Fried and O. Vilin
   2nd Edition Pergamon Press (1967)

3. Heats of Mixing, Experimental Thermochemistry Vol. I & II,
   M.L. McGlashan, Interscience Publications New York (1962)

4. Regular and Related Solutions
   J.H. Hilderbrand, J.M. Prausnitz and R.L. Scott,
   Van Nostrand, Reinhold Company, New York (1970)

5. Chemical Thermodynamics
   I Prigogine and R. Defay
   Longmans Green & Company, London (1954)

6. Liquid and Liquid Mixtures
   J.S. Rowlinson 2nd edition Butterworth & Company,
   London (1969)

7. Classical Thermodynamics of Non-electrolyte Solutions
   H.C. Van Ness, Pergamon Press, Oxford (1964)

8. Mixtures
   E.A. Guggenheim, Clarendon Press, Oxford (1952)

9. Principles of Chemical Thermodynamics
   C.B. Reid. Reinhold Publishing Company, New York (1960)

....

LIST OF PUBLICATIONS

The entire work has been published in the form of following papers:

1. Volume change on mixing of isomeric butanols with n-heptane at 25°C
   Anil Kumar, S.D. Pradhan & S.S. Katti
   Proc. Indian. Acad. Sci. 88A, 249 (1979)

2. Isothermal vapour liquid equilibrium of isomeric butanols with n-heptane at 65°C
   Anil Kumar, & S.S. Katti
   Indian J. Technol. 18(2), 60 (1980)

3. Excess free energy of binary mixtures of isomeric butanols with n-heptane at 75°C
   Anil Kumar & S.S. Katti
   Indian J. Chem. (Section A) (In Press)

4. Excess thermodynamic properties of isomeric butanols with n-heptane at 55°C
   Anil Kumar, Gopal Pathak & S.S. Katti
   Proc. Indian Acad. Sci. (Accepted)

....