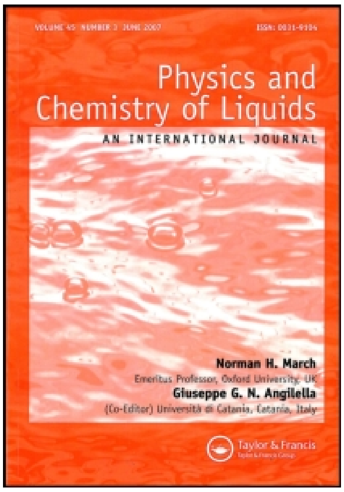

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Isothermal Phase Equilibria in the Binary Mixtures of some Polar Compounds

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ISOTHERMAL PHASE EQUILIBRIA IN THE BINARY MIXTURES OF SOME POLAR COMPOUNDS

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The simple and accurate gas chromatographic method proposed by us for the measurement of isothermal phase equilibrium has been used to study eight binary mixtures of different types of polar compounds such as: aliphatic alcohols (methanol, ethanol, propanol, butanol and pentanol), ketones (acetone and methyl-iso-butyl ketone), ethylacetate and chlorobenzene. The results of the present work on the binary mixtures of: acetone with methanol, and ethylacetate with methanol, ethanol and *n*-propanol are in good agreement with literature data.

Keywords: Activity coefficient; aliphatic alcohols; ketones; ethylacetate; chlorobenzene

INTRODUCTION

In continuation of our studies on isothermal phase equilibria of binary mixtures using gas chromatographic techniques [1, 2] this study on the binary mixtures involving different types of polar compounds has been taken up. The eight systems presently investigated are formed from: aliphatic alcohols (methanol, ethanol, *n*-propanol, *n*-butanol and *n*-pentanol), ketones (acetone and methyl-iso-butyl ketone), ethylacetate and chlorobenzene.

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EXPERIMENTAL

Solvents and Solutes

Analar/Spectroscopic grade: methanol, ethanol, *n*-propanol, *n*-butanol, *n*-pentanol, acetone, methyl-iso-butyl ketone, ethylacetate and chlorobenzene, procured from M/s E. Merck, Darmstadt (FRG), are used in the present study. While the other compounds have been used without further purification, *n*-butanol and *n*-pentanol are purified further by drying over a molecular sieve and calcium chloride and distillation.

No significant second peaks have been observed when the compounds have been injected to the chromatograph with the object of ascertaining the purity. As an additional check, the refractive-index and density of the substance have been measured at 293.15 K. The physical property values compare favourably with the literature data [3–6] as shown in Table I.

Support Material

Chromosorb – *W*(40/60), procured from Alltech, Arlington Heights, Illinois (USA) is employed as the support material. A stainless steel column, 60.96 cm long and 6.35 mm i.d. has been chosen to provide for: the ease of handling, filling and removal of the material as well as proper separation. The support material is initially dried for 3 to 4 hrs

TABLE I Comparison of the refractive-index and density of the pure liquids used in this literature data at 293.15 K

Substance	*Refractive-index*		*Density, g/ml*	
	This work	*Literature Source*	*This work*	*Literature Source*
Methanol	1.3287	1.3286 [3]	0.7916	0.7915 [3]
Ethanol	1.3618	1.3614 [4]	0.7904	0.7905 [3]
n-Propanol	1.3854	1.3856 [3]	0.8036	0.8036 [3]
n-Butanol	1.3995	1.3993 [3]	0.8097	0.8096 [3]
n-Pentanol	1.4100	1.4099 [3]	0.8145	0.8144 [3]
Acetone	1.3565	1.3591 [6]	0.7855	0.7857 [6]
Methyl-iso-butyl ketone	1.3967	1.3962 [4]	0.7975	0.7978 [4]
Chlorobenzene	1.5242	1.5241 [5]	1.1058	1.1057 [5]
Ethylacetate	1.3712	1.3716 [6]	0.9017	0.9021 [6]

in an oven at 373 ± 5 K. A known mass of the dry support material is soaked in an excess quantity of the stationary phase being used for the experiments. The vessel containing the support material soaked in the stationary phase is kept in a cold environment (a refrigerator) overnight. The solvent in excess of the desired percent loading, is removed by bubbling pure nitrogen gas. The coated support material is then filled inside the column. The column is installed inside the oven of the Model 5840A Hewlett Packard make microprocessor controlled gas chromatograph.

Carrier Gas and Presaturation

Pure helium gas supplied by Indian Oxygen Limited, Special Gases Division, Bombay (India), is used as the carrier gas. The gas is initially presaturated by passing it through a specially designed presaturator described earlier [1]. Before entering the presaturator, the carrier gas is passed through the purifiers containing a molecular sieve and monganous dioxide to remove traces of moisture and oxygen likely to interfere with the functioning of the thermal conductivity detector, being used as the sensing element in the present work. Presaturated helium gas is run through the main column of the chromatograph at a constant ambient temperature of a value between 293 to 298 K. The gas is passed through the column for 10 to 15 minutes and its flow rate is recorded. The measurement of the flow rate is carried out using a soap-bubble flow meter to an accuracy of 0.05 ml/min. Three or four observations are made to calculate reliable values for the specific retention volume.

Actual Experiment

The injection port, detector and column temperatures of the chromatograph are set at the desired levels by means of the microprocessor. The injection port temperature is maintained 25 K above the boiling point of the solute, while the detector temperature is maintained 50 K above the boiling point of the solute. When the set conditions of the injection port, thermal conductivity detector and column temperature are reached, the system is ready for the experiment. Initially, a solute with a small retention time like diethylether is injected into the column. After elution of the corresponding peak, the column is removed from the oven and its weight recorded. The column is reinstalled in the oven and the same solute is injected again. The constancy of the retention time in such successive experiments helps in the measurement of the quantity of solvent present on the support material accurately. As the thermal conductivity detector is used in these investigations, the retention time due to dead volume caused by the porosity inside the column is detected by injecting one micro-litre of air. One microlitre of the solute is subsequently injected and its retention time noted.

RESULTS AND DISCUSSION

The values of the infinite dilution activity coefficients – γ_1^∞ and γ_2^∞ are calculated from the observed values of the retention times, flow rates and the other quantities measured employing the method described by Ashraf *et al.* [1]. The infinite dilution activity coefficients of the eight binary systems studied in this work are presented in Table II. The values of γ_1^∞ and γ_2^∞ are used to calculate the Wilson parameters Λ_{12} and Λ_{21} by the simultaneous solution of

$$\ln\gamma_1^\infty = -\ln\Lambda_{12} - \Lambda_{21} + 1 \tag{1}$$

$$\ln\gamma_2^\infty = -\ln\Lambda_{21} - \Lambda_{12} + 1 \tag{2}$$

TABLE II Infinite dilution activity coefficients and the Wilson parameters of the binary systems studied in the present work

Component 1	*Component 2*	*Temperature/K*	γ_1^α	γ_2^α	Λ_{12}	Λ_{21}
Acetone	Methanol	293	2.576	2.687	0.6084	0.5508
Methanol	Ethylacetate	313	2.888	4.275	0.6825	0.3214
Ethylacetate	Ethanol	313	3.242	2.963	0.4735	0.5714
Ethylacetate	*n*-Propanol	313	2.417	2.526	0.6362	0.5696
n-Pronanol	Methyl-isobutyl-ketone	313	2.056	1.803	0.5576	0.8633
Methyl-isobutyl-ketone	*n*-Pentanol	313	1.750	4.699	1.3336	0.1525
Methyl-isobutyl-ketone	Chlorobenzene	313	1.828	3.080	1.1124	0.2902
Methyl-isobutyl-ketone	*n*-Butanol	313	1.080	3.206	2.3144	0.8389

The Wilson parameters thus obtained are also noted in Table II and are used to calculate the activity coefficients from

$$\ln\gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 - \Lambda_{21}x_1}\right] \tag{3}$$

TABLE III Isothermal vapor-liquid equilibria predicted from infinite dilution activity coefficients

Total Pressure/mm Hg	x_1	y_1	*Total pressure/mm Hg*	x_1	y_1
Acetone (1) + Methanol (2) System at 293 K			Methanol (1) + Ethylacetate (2) System at 313 K		
97.3	0.00	0.00	190.8	0.00	0.00
128.0	0.10	0.30	237.8	0.10	0.27
148.3	0.20	0.44	268.4	0.20	0.41
162.1	0.30	0.53	288.3	0.30	0.49
171.9	0.40	0.59	300.9	0.40	0.55
178.9	0.50	0.65	308.6	0.50	0.60
184.2	0.60	0.69	312.5	0.60	0.64
187.8	0.70	0.74	313.3	0.70	0.68
189.8	0.80	0.80	310.0	0.80	0.74
189.4	0.90	0.88	298.7	0.90	0.82
184.9	1.00	1.00	265.8	1.00	1.00
Ethylacetate (1) + Ethanol (2) System at 313 K			Ethylacetate (1) + *n*-Propanol (2) at 313 K		
134.2	0.00	0.00	52.2	0.00	0.00
170.1	0.10	0.28	86.3	0.10	0.45
189.9	0.20	0.40	110.2	0.20	0.61
201.6	0.30	0.48	127.8	0.30	0.69
208.8	0.40	0.53	141.2	0.40	0.74
213.2	0.50	0.58	152.1	0.50	0.88
215.5	0.60	0.63	161.3	0.60	0.82
215.7	0.70	0.68	169.5	0.70	0.86
213.0	0.80	0.75	177.1	0.80	0.90
205.8	0.90	0.84	184.3	0.90	0.94
190.8	1.00	1.00	190.8	1.00	1.00
n-Propanol (1) + Methyl-iso-butyl ketone (2) System at 313 K			Methyl-iso-butyl ketone (1) + *n*-Pentanol (2) System at 313 K		
43.7	0.00	0.00	7.3	0.00	0.00
48.8	0.10	0.19	13.9	0.10	0.52
52.0	0.20	0.30	19.7	0.20	0.70
54.1	0.30	0.39	24.9	0.30	0.79
55.4	0.40	0.47	29.4	0.40	0.84
56.2	0.50	0.54	33.1	0.50	0.88
56.5	0.60	0.60	36.3	0.60	0.90
56.4	0.70	0.68	38.8	0.70	0.92
55.7	0.80	0.76	40.7	0.80	0.94
54.3	0.90	0.87	42.4	0.90	0.96
52.2	1.00	1.00	43.7	1.00	1.00

TABLE III (Continued)

Total pressure/mm Hg	x_1	y_1	*Total pressure/mm Hg*	x_1	y_1
Methyl-iso-butyl ketone (1) + Chlorobenzene (2) System at 313 K			*n*-Butanol (1) + Methyl-iso-butyl ketone (2) System at 313 K		
26.4	0.00	0.00	17.7	0.00	0.00
31.3	0.10	0.24	20.7	0.10	0.23
35.3	0.20	0.39	23.8	0.20	0.41
38.6	0.30	0.50	27.0	0.30	0.54
41.2	0.40	0.58	30.2	0.40	0.65
43.1	0.50	0.65	33.4	0.50	0.74
44.6	0.60	0.70	36.4	0.60	0.80
45.5	0.70	0.76	39.2	0.70	0.86
45.9	0.80	0.81	41.5	0.80	0.90
45.7	0.90	0.88	43.2	0.90	0.94
43.7	1.00	1.00	43.8	1.00	1.00

$$\ln\gamma_2 = \ln(x_2 + \Lambda_{21}x_1) + x_1\left[\frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} - \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2}\right] \quad (4)$$

at regular intervals of the liquid phase composition to facilitate the construction of the phase diagrams.

The total pressure at each point is calculated from

$$P_{\text{total}} = \gamma_1 x_1 P_1^{\text{sat}} + \gamma_2 x_2 P_2^{\text{sat}} \quad (5)$$

where P_1^{sat} and P_2^{sat} are the saturated vapor pressures of the pure components 1 and 2. The values of the vapor pressure are calculated from the Antoine constants given in Reid *et al.* [7]. At equilibrium, the fugacity of the first component in the vapor phase

$$f_1^v = y_1 \phi_{1v} P_{\text{total}} \quad (6)$$

is equated to the fugacity of the first component in the liquid phase

$$f_1^l = x_1 \gamma_1 P_1^{\text{sat}} \quad (7)$$

As the present set of experiments are carried out at the atmospheric pressure, the vapor phase imperfection coefficient ϕ_{1v} is assumed to be unity, enabling us to calculate the vapor phase composition from

$$y_1 = x_1 \gamma_1 P_1^{\text{sat}} / P_{\text{total}} \tag{8}$$

Plots of x_1 versus y_1 are drawn for the eight binary systems studied in the present work in Figures 1 to 8. Literature data have also been

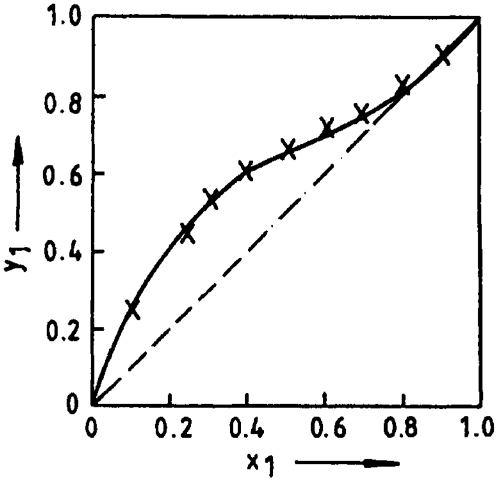

FIGURE 1 Equilibrium diagram for Acetone (1) + Methanol (2) system at 293 K (— This work, x Literature).

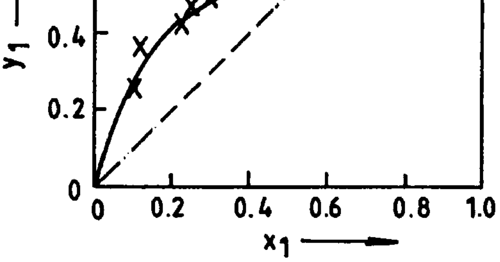

FIGURE 2 Equilibrium diagram for Methanol (1) + Ethylacetate (2) system at 313 K (— This work, x Literature).

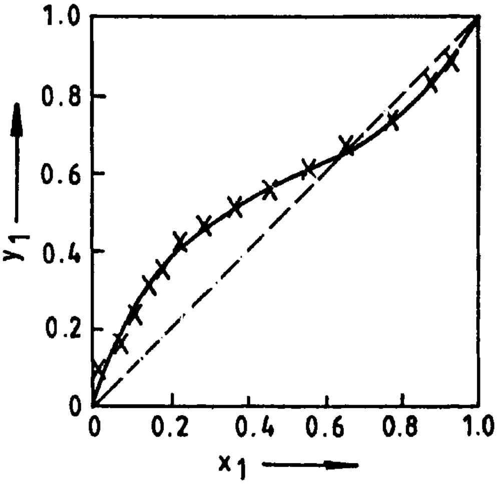

FIGURE 3 Equilibrium diagram for Ethylacetate (1) + Ethanol (2) system at 313 K (— This work, x Literature).

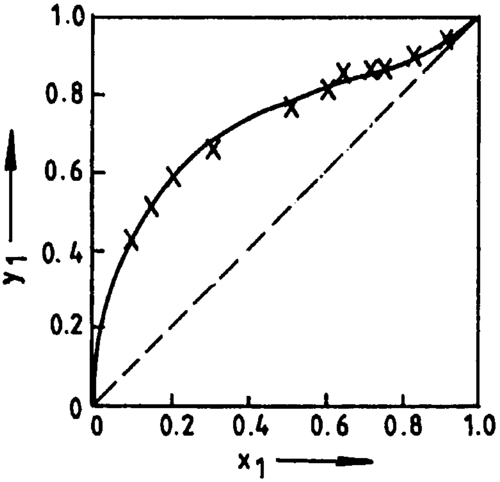

FIGURE 4 Equilibrium diagram for Ethylacetate (1) + *n*-Propanol (2) system at 313 K (— This work, x Literature).

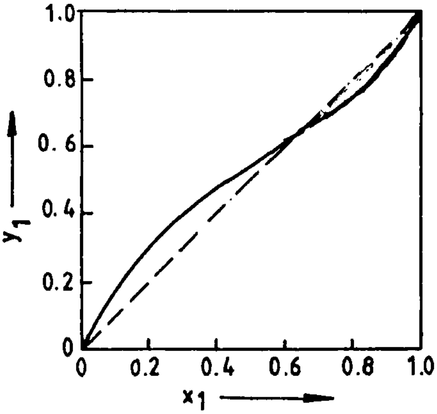

FIGURE 5 Equilibrium diagram for *n*-Propanol (1) + Methyl-iso-butyl ketone (2) system at 313 K (— This work).

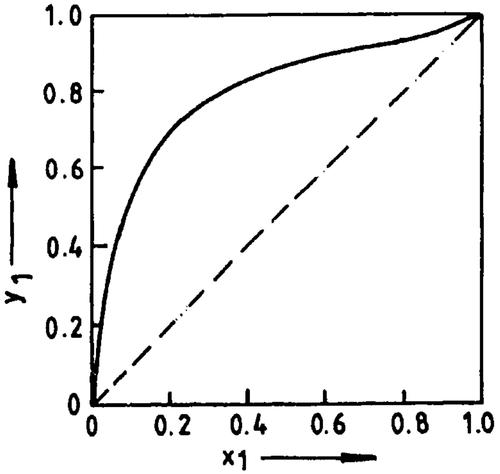

FIGURE 6 Equilibrium diagram for Methyl-iso-butyl ketone (1) + *n*-Pentanol (2) system at 313 K (— This work).

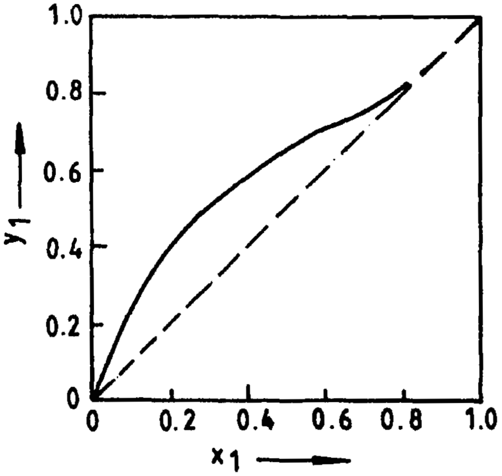

FIGURE 7 Equilibrium diagram for Methyl-iso-butyl ketone (1) + Chlorobenzene (2) system at 313 K (— This work).

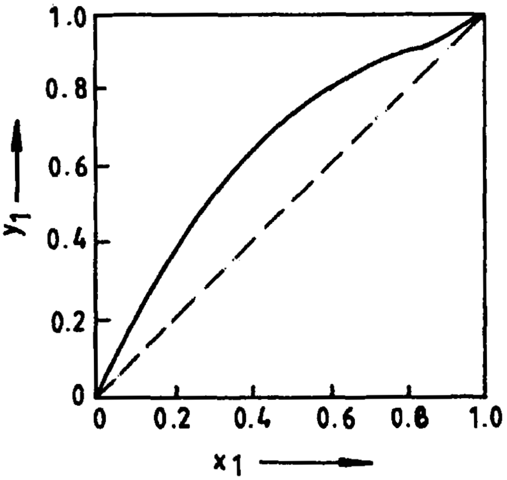

FIGURE 8 Equilibrium diagram for *n*-Butanol (1) + Methyl-iso-butyl ketone (2) system at 313 K (— This work).

plotted and marked as 'x' in the figures (Figs. 1 to 4) where data measured according to the conventional techniques has been published. It can be seen from Figures 1 to 4, that the agreement between the present work and the literature data [8, 9] is good.

References

[1] Ashraf, S. M., Ramakrishna, M. and Prasad, D. H. L. (1970). *Physics and Chemistry of Liquids* (in press).

[2] Ashraf, S. M. and Prasad, D. H. L. (1997). *Physics and Chemistry of Liquids* (Accepted).

[3] Monick, J. A. (1973). *Alcohols, their Chemistry, Properties and Manufacture*, Reinhold, London.

[4] Robert, C. W. (1987). *CRC Handbook of Physics and Chemistry*, 68th Edition, CRC Press, Boca Raton Florida.

[5] Driesbach, R. R. (1957). *Physical Properties of Chemical Compounds*, American Chemical Society Washington DC.

[6] *Alfa Catalog, Research Chemicals and Materials* (1981). Europian Edition, Karlsruhe.

[7] Reid, R. C., Prausnitz, J. M. and Sherwood, T. K. (1977). *The Properties of Gases and Liquids*, Third Edition, McGraw-Hill, New York.

[8] Morton, D. S. (1929). *J. Phys. Chem.*, **33**, 384.

[9] Murti, P. S. and Van Winkle, M. (1958). *Chemical Engineering Data Series*, **3**, 72.