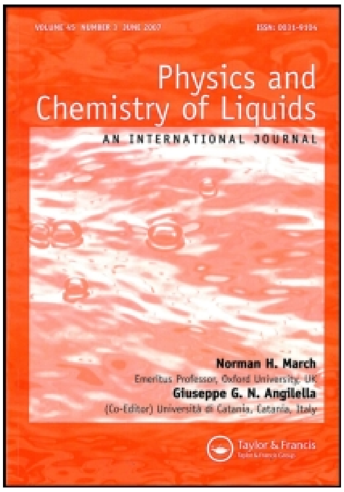

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Vapor-Liquid Equilibria for Chlorobenzene with Butan-1-ol, 2-Methylpropan-1-ol and 2-Methylpropan-2-ol at 94.6 kPa

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VAPOR-LIQUID EQUILIBRIA FOR CHLOROBENZENE WITH BUTAN-1-OL, 2-METHYLPROPAN-1-OL AND 2-METHYLPROPAN-2-OL AT 94.6 kPa

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Vapor-liquid equilibria at 94.6 kPa, over the entire composition range were measured for three binary systems - butan-1-ol(1) + chlorobenzene(2), 2-methylpropan-1-ol(1) + chlorobenzene(2), 2-methylpropan-2-ol(1) + chlorobenzene(2) - using a Swietoslawski type ebulliometer. The composition (x_1) *vs*. temperature (T) data were found to be well represented by Wilson model.

Keywords: Vapor-liquid equilibria; chlorobenzene; butan-1-ol

INTRODUCTION

This investigation on the vapor-liquid equilibria of the binary systems formed by chlorobenzene with butan-1-ol, 2-methylpropan-1-ol and 2-methylpropan-2-ol is in continuation of our previous studies on the phase equilibria of binary systems containing alcohols, hydrocarbons and halogenated organics. The butan-1-ol(1) + chlorobenzene(2) system was studied by: Artigas *et al.* [1], Arzhanov *et al.* [2], Dajoz *et al.*

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[3], Kormina *et al.* [4] and Rao *et al.* [5]; while the 2-methyl-propan-2-ol(1) + chlorobenzene(2) system was studied by: Rao and Rao [6] and the 2-methyl-propan-2-ol(1) + chlorobenzene(2) system was studied by Reddy and Rao [7].

EXPERIMENTAL SECTION

Materials

AR grade butan-1-ol, 2-methylpropan-1-ol and 2-methylpropan-2-ol supplied by SD's Fine Chemicals, Boisar (India) were dried over potassium carbonate and fractionally distilled twice. The middle fraction of the second distillation was stored in amber colored bottles for use in the experiments. Spectroscopic grade chlorobenzene procured from SD's Fine Chemicals, Boisar (India) was dried over calcium hydroxide and fractionally distilled twice. The middle fraction of the second distillation was stored in amber color bottles for use in the experiments.

Pycnometers, calibrated by determining the masses of pure mercury and double distilled water were used to measure the density of the pure liquids to within ± 0.001 g/mole. An Abbe type refractometer with sodium vapor lamp is used to measure the refractive index to within ± 0.00001 units.

For both the measurements, thermostats capable of maintaining the temperature to with in ± 0.01 K of the set value were used to maintain the temperature at 293.15 ± 0.01 K.

Based on a comparison of the density and refractive index presented in Table I, and absence of significant multiple peaks in the chromatograms (when the samples were injected to gas chromatographic colums normally used for the analysis of alcohols and chlorocarbons) the purity of the samples is expected to be 99.9%.

TABLE I Comparison of density, ρ and refractive-index n_D of the substances used in the present work with the literature data of Riddick *et al.* [11]

	$(293.15\,K)/kg \cdot m^{-3}$		$n_D\ (293.15\,K)$	
Substance	*This work*	*Literature*	*This work*	*Literature*
Butan-1-ol	810.0	809.56	1.3992	1.39929
2-Methyl-propan-1-ol	802.0	801.60	1.3959	1.39591
2-Methyl-propan-2-ol	787.0	787.20	1.3877	1.3877
Chlorobenzene	1106.0	1106.30	1.5248	1.52481

Method

A swietoslawaski type ebulliometer very similar to the one described by Hala *et al.* [8] was used. The ebulliometer was connected to a vacuum pump and nitrogen gas cylinder, along with a closed end monometer to enable the measurement and maintenance of the total pressure of the system at the desired level to within ± 0.1 kPa of the desired value. The total pressure was maintained at 94.6 ± 0.1 kPa by adjusting the opening of the needle valve attached to the gas cylinder or the opening of the by pass line of the vacuum pump. The reading of the manometer and application of the needed corrective action were frequently carried out. A mercury – in glass thermometer, calibrated by means of point to point comparison with a platinum resistance thermometer certified by National Institute of Standards and Technology, Gaithersberg (USA) was used for the measurement of temperature to an accuracy of ± 0.1 k. The thermometer bulb was placed in a thermowell filled with mercury (located at the point in the apparatus where the gas-liquid mixture impinges it due to Cottrel effect). The mixture samples to be studied were prepared by weighing the required amounts of the two pure liquids and stirring them well before charging the mixture to the still. A Mettler balance, capable of recording weights to an accuracy of ± 0.0001 g was used to note all the masses. The heating rate was slowly increased and adjusted to produce the required drop rate of about 30 per minute in accordance with the suggestion of Hala *et al.* [8].

The technique of subjecting the mixture sample to the lowest pressure or highest temperature and reverting to ambient conditions several times *a priori*, was used to achieve and maintain the constancy of composition for the entire course of the experiment.

A chromatograph was used to verify the composition, both at the beginning and end of each experiment. The equilibrium temperature was recorded after steady state conditions, judged by the constancy of the equilibrium temperature and uniformity of the drop rate, could be maintained for atleast 30 min.

RESULTS AND DISCUSSION

The experimental composition (x_1) *versus* temperature (T) data summarized in Table II, were fitted to the Wilson model. The optimum

TABLE II The $x_1 - T$ measurements at 94.6 kPa

x_1	T/K	y_1	γ_1	γ_2
	Butan-1-ol(1) + Chlorobenzene(2) System			
0.0000	402.5	0.0000	5.5208	1.0000
0.1439	394.4	0.1488	1.5163	1.0759
0.2995	392.5	0.3855	1.1494	1.1586
0.4497	391.3	0.5107	1.0485	1.2206
0.5998	390.5	0.6403	1.0144	1.2206
0.7499	389.9	0.7744	1.0031	1.2911
0.9096	389.4	0.9100	1.0003	1.3066
1.0000	389.1	1.0000	1.0000	1.3116
	2-Methyl-1-propanol(1) + Chlorobenzene(2) System			
0.0000	402.5	0.0000	2.3104	1.0000
0.1488	391.7	0.3547	1.5434	1.0310
0.2989	387.6	0.4996	1.2458	1.0954
0.4491	385.0	0.6111	1.1110	1.1717
0.5994	383.1	0.7154	1.0455	1.2518
0.7496	381.5	0.8199	1.0143	1.3315
0.8999	380.2	0.9268	1.0019	1.4087
1.0000	379.4	1.0000	1.0000	1.4582
	2-Methyl-2-propanol(1) + Chlorobenzene(2) System			
0.0000	402.5	0.0000	2.2557	1.0000
0.0976	380.0	0.5178	2.0173	1.0079
0.1972	371.5	0.6734	1.7753	1.0334
0.2973	366.4	0.7489	1.5716	1.0785
0.3977	363.1	0.7955	1.4074	1.1466
0.4980	360.8	0.8296	1.2774	1.2433
0.5985	359.0	0.8582	1.1763	1.3773
0.6989	357.5	0.8855	1.0998	1.5630
0.7993	356.2	0.9150	1.0453	1.8240
0.8997	355.1	0.9510	1.0118	2.2005
1.0000	389.1	1.0000	1.0000	2.7647

Wilson parameters were obtained by minimizing the objective function defined as

$$\phi = [(P_{\mathrm{cal}}/P_{\mathrm{expt}}) - 1]^2. \qquad (1)$$

The Nelder-Mead optimization technique described in detail by Kuester and Mize [9] was used. Vapor pressures needed in the calculations were computed from the Antoine constants collected from Reid *et al.* [10] and noted in Table III for ready reference. The equation represents the vapor pressure data available in the literature with an average absolute deviation of ±0.5%, in the ranges to temperature of interest to the present investigations. The pure liquid boiling

TABLE III The Antoine constants for $\ln(P/\mathrm{kPa}) = A - [B/(T/K) + C]$

Substance	*A*	*B*	*C*
Butan-1-ol	15.1988	3137.02	−94.4
2-Methyl-1-propanol	14.8538	2874.72	−100.3
2-Methyl-2-propanol	14.8373	2658.28	−95.5
Chlorobenzene	14.0503	3295.11	−55.6

TABLE IV Representation of the data by Wilson model

System	$[(\lambda_{12} - \lambda_{11})/R]/K$	$[(\lambda_{12} - \lambda_{22})/R]/K$	*Std. dev. in T/K*
Butan-1-ol(1) + Chlorobenzene(2) System	1087.4	−298.3	0.18
2-Methyl-1-propanol(1) + Chlorobenzene(2) System	534.1	−173.3	0.06
2-Methyl-2-propanol(1) + Chlorobenzene(2) System	187.8	199.9	0.03

TABLE V Comparison with literature data

System	*Source of data*	*Av. abs. dev. in* y_1
n-Butanol + Chlorobenzene	Arzhnov *et al.* (1976) – 760 mm Hg	0.116
	Dejoz *et al.* (1997) – 750 mm Hg	0.045
	Dejoz *et al.* (1997) – 150 mm Hg	0.072
	Rao *et al.* (1977) – 760 mm Hg	0.040
	Artigas *et al.* (1977) – 300 mm Hg	0.043
	Artigas *et al.* (1977) – 760 mm Hg	0.037
2-Methyl-1-propanol + Chlorobenzene	Rao *et al.* (1976) – 760 mm Hg	0.043
2-Methyl-2-propanol + Chlorobenzene	Reddy and Rao (1989) – 760 mm Hg	0.011

temperatures observed in the present work at 94.6 kPa were within the stated limits of the experimental accuracy of ±0.1 K of the values predicted by the Antoine equation. The density measurements of this work given in Table I were used as input to the derivation of the optimum Wilson parameters. The results of the representation of the observed phase equilibrium data by the Wilson model are summarized in Table IV. The Wilson model along with the parameters noted in Table IV, has been used to predict the vapor phase composition at the conditions of the literature phase equilibrium observations. A summary of the comparisons of the predicted values with the literature data is presented in Table V. The comparison and the plotting of the data in the form of a phase diagram (not given in the paper) indicates that:

(i) the agreement amongst different investigators for the *n*-Butanol + Chlorobenzene system is not satisfactory except for the case of the data of Artigas *et al.* [1] and Arzhnov *et al.* [2] at 760 mm Hg. The agreement of all the literature data with the present work is also not good, characteristically the disagreement is worse at lower concentration of the more volatile component,

(ii) for the iso-Butanol + Chlorobenzene system the vapor phase compositions can be predicted from the Wilson model with the constants predicted from the present set of observations at the points reported by Rao and Rao [6] with an average absolute deviation of 0.0425 units,

(iii) while the agreement between the present measurements and those of Reddy and Rao [7] on the tert-Butanol + Chlorobenzene system, for which the vapor phase compositions of Reddy and Rao [7] are predicted from the Wilson constants derived from the present set of measurements, are predicted with an average absolute deviation of 0.011 units, is found to be good.

In view of the care taken, and the good agreement of our measurements using the same method and apparatus with the literature data on several systems studied by us earlier, the data reported in this paper are expected to be reliable to within the stated limits of experimental error given for the measured variables.

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