Glossary

A	characteristic parameter for the salt in the Jones–Dole equation
B	characteristic parameter for the solvent in the Jones–Dole equation
C	the concentration of KI in the NFM–water mixture, $cm^3\ mol^{-1}$
M	molecular weight of KI
n_{D0}	refractive index of the solvent (NFM–water mixture)
n_D	refractive index of the solution of KI in the NFM–water mixture
V_ϕ	apparent molar volume, $cm^3\ mol^{-1}$
V_ϕ^∞	apparent molar volume at infinite dilution
R_D	apparent molar refractivity
R_D^∞	apparent molar refractivity at infinite dilution
ρ_0	density of the NFM–water mixture, g cm^{-3}
ρ	density of the solution of KI in the NFM–water mixture, g cm^{-3}
η_0	viscosity of the NFM–water mixture, cP
η	viscosity of solutions of KI in the NFM–water mixture, cP
NFM	*N*-formylmorpholine

Registry No. NFM, 4394-85-8; KI, 7681-11-0; water, 7732-18-5.

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Vapor–Liquid Equilibria for the Systems Hexane–Aniline and Hexane–Benzene–Aniline at Atmospheric Pressure

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Isobaric vapor-liquid equilibria at 101.325 kPa have been measured for the systems hexane–aniline and hexane–benzene–aniline. The measured data for the binary system hexane–aniline, along with published data for hexane–benzene and benzene–aniline, were correlated using Wilson, nonrandom two-liquid (NRTL), and UNIQUAC equations. The binary parameters, thus determined, were used to predict the ternary vapor-liquid equilibria (VLE) for the system hexane–benzene–aniline in good agreement with the measured data. The use of the UNIFAC group contribution method is also seen to provide a good estimation of both binary and ternary VLE data. For the partially miscible hexane–aniline system the mutual solubility data are also presented.

Introduction

The knowledge of vapor–liquid equilibria (VLE) is essential for the design of various separation processes like distillation, evaporation, and adsorption. The separation of benzene from a typical hexane–benzene mixture representing light naphtha poses a problem in the petroleum industry. The present study was taken up to examine the suitability of aniline as a solvent for the separation of this model mixture. Isothermal VLE data for ternary hexane–benzene–aniline at 20 °C (*1*) and isobaric data for hexane–benzene (*2*) and benzene–aniline (*3*) systems are reported at 101.325 kPa. Isothermal VLE data for the partially miscible hexane–aniline binary from 0 to 67.5 °C (*4*, *5*) and isobaric from 74.13 to 97.46 kPa (*6*) are also available in the literature. All three binaries are nonazeotropic (*7*). The mutual solubility data for the binary hexane–aniline are reported from 16.5 to 59.6 °C and from 41.17 to 65.85 °C by Keyes and Hildebrand (*8*) and by Drucker (*9*), respectively.

In the present study the VLE data for the binary hexane–aniline and the ternary hexane–benzene–aniline were determined at 101.325 ± 0.07 kPa of pressure and correlated by using Wilson (*10*), nonrandom two-liquid (NRTL) (*11*), and UNIQUAC (*12*) equations. The results have also been compared with those calculated from the UNIFAC group contribution method (*13*–*15*).

Experimental Section

Materials. The sources of the chemicals are given in Table I. The purity of hexane and benzene was checked by gas chromatography. Aniline was vacuum distilled, and the heart cut collected was used in the study. The properties of these chemicals compared to those reported in the literature (*16*) indicate a minimum purity of 99% (Table I).

Apparatus and Procedure. The VLE studies for the binary and ternary systems were carried out in a modified Smith and Bonner type still (*17*) equipped with a magnetic stirrer. The equilibrium vapor temperatures *t* were measured by a mercury-in-glass thermometer having an accuracy of ±0.05 °C and subsequently corrected (*18*) for the exposed stem.

The pressure in the system was maintained at 101.325 ± 0.07 kPa with the help of a regulated air supply through a water column connected to a water manometer. The phases were equilibrated for 4 h before about 2 cm^3 of vapor sample was withdrawn in an iodine flask for analysis.

Since there is a wide difference in the boiling points of hydrocarbons and aniline, the amount of aniline in the vapor phase was expected to be small. A titration method (*19*) was, therefore, used for its determination. A known amount of the condensed vapor sample was titrated against standard perchloric acid using crystal violet as indicator. During titration the sample was vigorously stirred with the help of a magnetic stirrer. For the ternary system the samples were divided into two parts. The first part as well as vapor samples in the case of the binary were analyzed for aniline by the titration method,

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Table I. Normal Boiling Points t_b, Densities ρ and Refractive Indices n of the Chemicals

		t_b/°C		ρ(20 °C)/(g cm^{-3})		n(D, 20 °C)	
components	source	exptl	lit. (*16*)	exptl	lit. (*16*)	exptl	lit. (*16*)
hexane	Prolabo, France	68.70	68.74	0.6594	0.65937	1.3749	1.37486
benzene	Glaxo Labs, India	80.1	80.1	0.8789	0.87901	1.5011	1.50112
aniline	BDH, India	184.5	184.40	1.0220	1.0217	1.5862	1.58638

Table II. Experimental VLE Data for Hexane (1)–Aniline (3) at 101.325 kPa: Temperature t, Liquid-Phase Mole Fraction x_1, and Vapor-Phase Mole Fraction y_1

t/°C	x_1	y_1	t/°C	x_1	y_1
150.2	0.0150	0.6250	73.20	0.5200	0.9862
136.4	0.0250	0.7600	73.15	0.7146	0.9878
116.0	0.0530	0.8870	72.15	0.8126	0.9893
90.0	0.1100	0.9600	71.50	0.8650	0.9906
79.5	0.1685	0.9766	70.70	0.9093	0.9916
75.7	0.2099	0.9807	69.80	0.9532	0.9936
74.1	0.2735	0.9831	69.10	0.9786	0.9961
73.25	0.3790	0.9842			

Table III. Experimental VLE Data for Hexane (1)–Benzene (2)–Aniline (3) at 101.325 kPa: Temperature t, Liquid-Phase Mole Fraction x_i, and Vapor-Phase Mole Fraction y_i

t/°C	x_1	x_2	y_1	y_2
79.0	0.1858	0.1386	0.8079	0.1743
81.5	0.1533	0.1724	0.7495	0.2301
84.0	0.1225	0.0925	0.8257	0.1488
84.6	0.1224	0.2066	0.6707	0.3035
89.0	0.1011	0.1155	0.7745	0.1949
91.4	0.0928	0.0702	0.8318	0.1332
93.0	0.0802	0.1374	0.6937	0.2686
94.0	0.0602	0.2741	0.4433	0.5188
95.6	0.0760	0.0880	0.7671	0.1887
100.8	0.0297	0.3063	0.2735	0.6805
102.0	0.0610	0.1045	0.6955	0.2523
105.6	0.0392	0.1832	0.4707	0.4673
113.8	0.0308	0.1395	0.4780	0.4310
114.0	0.0194	0.2042	0.2763	0.6355
122.8	0.0154	0.1557	0.2910	0.5800

as mentioned above. The second part of the ternary vapor sample was washed with water for aniline content, and the hydrocarbon portion after water washing was analyzed by using a calibrated refractive index–composition chart prepared at 20 °C. The accuracy of analysis was found to be within ±0.5% as checked with synthetic mixtures while for hydrocarbons it was found to be within ±0.2%.

The mutual solubilities of hexane and aniline were determined in a sealed Pyrex glass tube using the procedure described by Johnson and Francis (*20*).

Results and Discussion

The experimental VLE data for the binary hexane–aniline and the ternary hexane–benzene–aniline systems are reported in Tables II and III, respectively. The mutual solubility data for hexane–aniline are given in Table IV and presented in Figure 1 along with the binary VLE data. The reported (*21*) aniline point for hexane (69.1 °C) also fits well on the solubility envelope. From Figure 1 it is clear that, as the solubility envelope and the bubble point line do not overlap each other, the VLE data measurements are well in the single-phase region. The VLE data for hexane–benzene and benzene–aniline were taken from the literature (*2*, *3*).

The experimental data of all three binaries were correlated by Wilson, NRTL, and UNIQUAC equations using Nelder–Mead's extended simplex optimization technique (*22*).

The binary parameters so obtained were used to predict the ternary data by using ternary forms of these equations. It was observed that NRTL, Wilson, and UNIQUAC equations are nearly equally suitable to correlate the binary data and also to predict the ternary VLE. The NRTL equation seems to be the best for the ternary with root mean square deviation (RMSD) in vapor-phase composition (mole fractions) of the order of 0.012 (hexane), 0.013 (benzene), and 0.0079 (aniline). The binary parameters are not reported here as these are already reported (*23*–*25*) and found comparable.

The equilibrium data have also been predicted for ternary hexane–benzene–aniline and its constituent binaries by the UNIFAC group contribution method. The parameters used for the prediction were taken from the literature (*15*). It was observed that the prediction by UNIFAC for the three binaries and the ternary was nearly as accurate as the NRTL equation.

Table IV. Mutual Liquid–Liquid Solubility Data for Hexane (1)–Aniline (3): Temperature t and Mole Fraction x_1

t/°C	x_1	t/°C	x_1	t/°C	x_1
59.5	0.2161	70.0	0.5187	56.4	0.7975
67.2	0.3082	67.9	0.6175	37.8	0.1114
69.8	0.4376	63.8	0.7160	37.0	0.9053

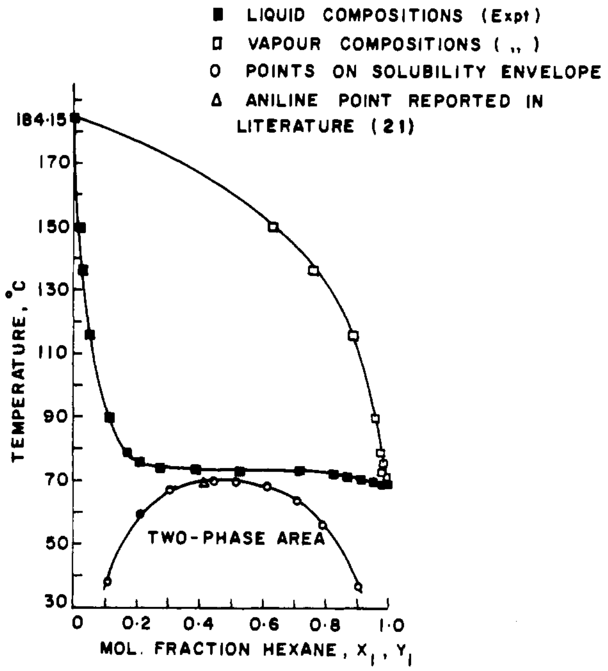

Figure 1. Temperature–composition phase diagram for hexane (1)–aniline (3) at 101.325 kPa.

Registry No. Hexane, 110-54-3; benzene, 71-43-2; aniline, 62-53-3.

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Isobaric Vapor–Liquid Equilibria for Three Binary Systems of 2-Butanone with 3-Methyl-1-butanol, 1-Butanol, or 2-Butanol

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A new apparatus for measuring vapor–liquid equilibria was constructed. Vapor–liquid equilibria for the three binary systems of 2-butanone with 3-methyl-1-butanol, 1-butanol, or 2-butanol were measured with the present recirculation still at 100.00 kPa of pressure. The isobaric vapor–liquid equilibrium data obtained were correlated with an equation of state and with the Wilson equation.

Introduction

We have previously reported vapor–liquid equilibrium (VLE) data obtained with several types of ebulliometers for measuring boiling points (*1–5*).

In the present study, a new apparatus for measuring VLE was constructed. Isobaric VLE data for the three binary systems of 2-butanone with 3-methyl-1-butanol, 1-butanol, or 2-butanol were measured at 100.00 kPa. VLE data for those systems have been published previously by Miller et al. (*6*), Amick et al. (*7*), and Aristovich et al. (*8*). However, there are significant differences between these measurements (*6–8*).

The data were successfully correlated with our pseudocubic equation of state (*9–11*) and the Wilson equation (*12*), with vapor-phase corrections according to Hayden and O'Connell (*13*).

Experimental Section

The present experimental apparatus for measuring vapor–liquid equilibria is schematically shown in Figure 1. The recirculation still is entirely constructed by borosilicate glass. The main parts are a boiling still (B), two condensers (C), two cocks (K), an overflow tube (O), a condensate chamber (S), and a thermometer (T). The structure of the boiling still (B) is essentially the same as the previous ones (*1–5*). The amount of solution required is about 45 cm^3 per determination. The reliability of the present apparatus was confirmed for the methanol–water system at atmospheric pressure. The experimental data obtained agreed fairly well with the data of Uchida and Kato (*14*).

At the start of the experiments, cocks K_1 and K_2 are closed. A prepared solution is charged to the boiling still (B) from the top of the condenser. The boiling vapor–liquid mixture flashes to the thermometer well in the boiling still. The vapor is condensed and introduced to the condensate chamber (S). The condensed vapor in the condensate chamber (S) recirculates to the boiling still (B) through the overflow tube (O).

After attainment of steady state, equilibrium temperatures were measured with a Hewlett-Packard 2804A quartz thermometer calibrated by the triple point of water in a reference cell with an accuracy of ±0.01 K. The steady state was confirmed with the constancy of the equilibrium temperature of ±0.01 K. The atmospheric pressures were evaluated from the boiling point temperatures of water. In order to analyze equilibrium compositions, both samples of liquid and vapor phases were individually taken from cocks K_1 and K_2, respectively. The analysis of the equilibrium composition was carried out with a Hitachi GC-163 gas chromatograph equipped with a 3.0-m dioctyl sebacate (DOS) 25% chromosorb W column. Helium was used as a carrier gas with the flow rate of 25 cm^3/min. The column temperature was about 373.15 K, and the current on thermal conductivity detector (TCD) was 100 mA. The total reproducibility of the composition analysis was ±0.001 mole fraction.

Special-grade reagents were supplied by Wako Pure Chemical Industries, Ltd. 2-Butanone was used without further purification. 3-Methyl-1-butanol and 2-butanol were purified by fraction distillation in a 30-plate Oldershaw column. The physical properties of the materials used are listed in Table I.

Results

The experimental equilibrium temperatures were corrected from the raw data to those at 100.00 kPa of pressure, using the linear approximation of the derivatives of temperature with pressure for the mixture, similar to the previous work (*2*). The experimental isobaric VLE data are given in Tables II–IV and shown in Figures 2–4. For the 2-butanone + 3-methyl-1-butanol system, large differences were observed between the present data and those of Miller et al. (*6*), as shown in Figure 2. For the 2-butanone + 1-butanol system, substantial differences were observed between the present data and those of Aristovich et al. (*8*), as shown in Figure 3. For the 2-butanone + 2-butanol system, the present experimental data agreed fairly well with the data of Amick et al. (*7*), as shown in Figure 4. For this system, large differences were observed between the present data and those of Miller et al. (*6*).

The three-parameter pseudocubic equation of state previously proposed by us (*9–11*) and the Wilson equation (*12*) with

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