alcohol > 1-butanol > *sec*-butyl alcohol > *tert*-butyl alcohol. A comparison of γ's and G^E obtained from Wilson parameters with those computed by using the UNIFAC model (*6*) indicates that the UNIFAC method provides a reasonable estimate of the solution behavior. In the case of 1,2-dichloroethane + *tert*-butyl alcohol, the properties are not predicted on the basis of UNIFAC model as the interaction parameters for methyl groups in *tert*-butyl alcohol are not available.

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Glossary

x	mole fraction in liquid phase
y	vapor composition
T	temperature, K
t	temperature, °C

Greek Letters

γ	activity coefficient
Λ	Wilson parameter

Subscripts

1	1,2-dichloroethane
2	isomeric butanols

Superscripts

G^E	excess Gibbs free energy

Registry No. *n*-Butyl alcohol, 71-36-3; isobutyl alcohol, 78-83-1; *sec*-butyl alcohol, 78-92-2; *tert*-butyl alcohol, 75-65-0; 1,2-dichloroethane, 107-06-2.

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Isobaric Vapor–Liquid Equilibria for Binary Mixtures of Ethylbenzene and *p*-Xylene with Dimethylformamide

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Isobaric vapor–liquid equilibrium data for the systems ethylbenzene–dimethylformamide and *p*-xylene–dimethylformamide were obtained at 760 mmHg pressure by using a vapor recirculating type of equilibrium still. Both the systems form minimum-boiling azeotropes. The activity coefficient data were tested for thermodynamic consistency by the methods of Herrington, Black, and Norrish and Twigg and correlated by the van Laar, Wilson, and Redlich–Kister equations.

Introduction

Petroleum fractions, especially from the catalytic reforming processes, are sources of C_8 aromatics. Mixtures of C_8 aromatics containing xylene and ethylbenzene are difficult to separate into pure components as the isomers are close boiling, having a relative volatility close to unity. *p*-Xylene and ethylbenzene form the closest boiling pair with about 2 °C difference in the boiling points. Knowledge of vapor–liquid equilibria between ethylbenzene or *p*-xylene and different classes of compounds will be of importance in the development of alternative distillation processes for their separation. Isobaric vapor–liquid equilibrium data were obtained for the systems ethylbenzene–dimethylformamide and *p*-xylene–dimethylformamide at 760 ± 2 mmHg pressure by using a vapor recirculating type of equilibrium still. Experimental data for these systems have not been reported in the literature.

Experimental Section

Ethylbenzene from British Drug House, England, *p*-xylene from Riedel, Germany, and dimethylformamide, also from Riedel, were first dried by keeping over anhydrous magnesium sulfate for 48 h with occasional shaking. Ethylbenzene and *p*-xylene were further dried with metallic sodium whereas dimethylformamide (DMF) was dried with phosphorus pentoxide for extreme desiccation (*1*). The dried and filtered materials were further purified by distillation in a glass column described elsewhere (*2*). Ethylbenzene and *p*-xylene were distilled at the prevailing atmospheric pressure whereas dimethylformamide was distilled under vacuum. The vacuum was adjusted to collect the purified sample at 78 °C. Table I summarizes some of the physical properties of the reagents used.

A modified version of the equilibrium still described by Rao and co-workers (*6*) was used for obtaining the vapor–liquid equilibrium data. The equilibrated mixtures were analyzed at 35 ± 0.1 °C by density measurements. Density measurements were made with a pycnometer calibrated with conductivity water. Triplicate density measurements were identical within ±0.0003 g/mL.

The samples were maintained at the temperature of analyses in an ultrathermostat (Metrimpex, Hungary). The temperature was controlled to within ±0.1 °C by means of a "merc-to-merc" magnetically adjusted thermoregulator supplied by the

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Table I. Physical Properties of Pure Compounds

		ethylbenzene	*p*-xylene	dimethylformamide
normal bp, °C	exptl	136.20	138.40	152.90
	lit. (*3*, *4*, *5*)	136.19	138.40	153.00
density *d*(*t*), mg/mL	exptl	0.8497 (35 °C)	0.8433 (35 °C)	0.9345 (35 °C)
	lit. (*3*)	0.8583 (30 °C)	0.8523 (30 °C)	0.9445 (25 °C)
refractive index	exptl	1.4910 (30 °C)	1.4908 (30 °C)	1.4228 (35 °C)
	lit. (*3*)	1.4905 (30 °C)	1.4905 (30 °C)	1.4269 (25 °C)

Table II. Density-Composition Data at 35 ± 0.1 °C

ethylbenzene (1)-DMF (2)		*p*-xylene (1)-DMF (2)	
mole fraction ethylbenzene	density, g/mL	mole fraction *p*-xylene	density, g/mL
0.0000	0.9345	0.0000	0.9345
0.0449	0.9288	0.0485	0.9281
0.0635	0.9270	0.0681	0.9250
0.1336	0.9206	0.0910	0.9238
0.2061	0.9121	0.1343	0.9194
0.2908	0.9044	0.2120	0.9091
0.4101	0.8945	0.2931	0.9020
0.4510	0.8911	0.3804	0.8938
0.4810	0.8886	0.4315	0.8896
0.5750	0.8815	0.4722	0.8861
0.6032	0.8800	0.5837	0.8763
0.7217	0.8714	0.7167	0.8669
0.8365	0.8642	0.7747	0.8626
0.9300	0.8586	0.8732	0.8559
0.9605	0.8565	0.9249	0.8521
1.0000	0.8540	0.9619	0.8500
		1.0000	0.8480

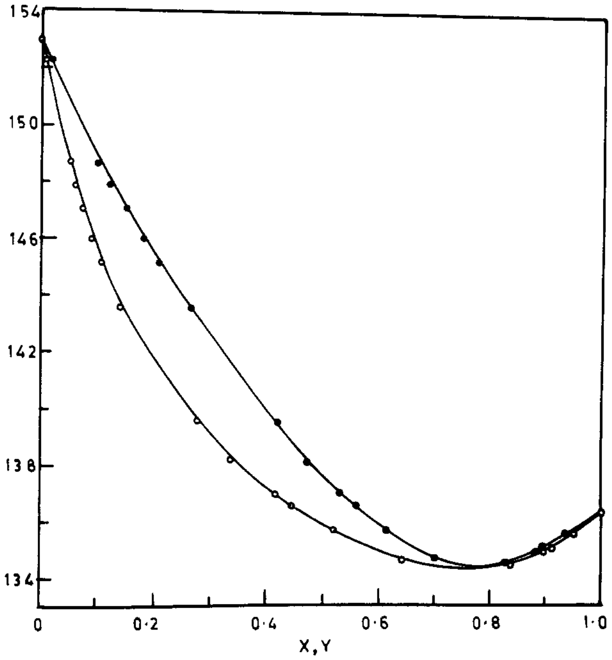

Figure 1. Boiling point-composition diagram for the ethylbenzene-dimethylformamide system at 760 ± 2 mmHg pressure.

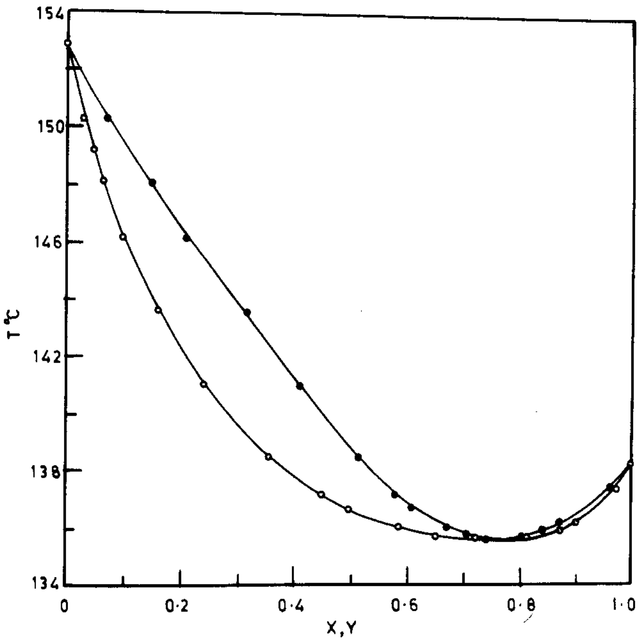

Figure 2. Boiling point-composition diagram for the *p*-xylene-dimethylformamide system at 760 ± 2 mmHg pressure.

Table III. Correlations Used for the Estimation of Pure-Component Properties

component	temp range, °C	correlation	constants
	For Vapor Pressures		
DMF	132-154	RPME (*10*)	$a = 7.30667^a$ $G = 1.67133^a$ $K = 0.56282^a$
ethylbenzene	132-154	RPME (*10*)	$a = 7.10961^a$ $G = 1.63192^a$ $K = 0.55082^a$
p-xylene	132-154	RPME (*10*)	$a = 6.99718^a$ $G = 1.60944^a$ $K = 0.54257^a$
	For Second Virial Coefficients		
DMF	130-153	O'Connell (*11*)	$E = 0$
ethylbenzene	78-154	Pitzer and Curl (*12*)	
p-xylene	78-151	Pitzer and Curl (*12*)	
	For Liquid Molar Volumes		
DMF	130-153	surface tension (*13*)	
ethylbenzene	78-154	surface tension (*13*)	
p-xylene	78-151	surface tension (*13*)	

[a] Calculated.

same company. The estimated uncertainties in the measurements were composition, 0.004 mole fraction, temperature, 0.1 °C, and pressure, 2.0 mmHg. Table II gives the density-composition data. Figures 1 and 2 represent the boiling point-composition diagrams for the two systems ethylbenzene-DMF and *p*-xylene-DMF.

Results and Discussion

The liquid-phase activity coefficients were estimated from the experimental data taking into consideration the nonideality of the vapor phase and by employing the following equation (*7*, *8*)

$$\gamma_i = \frac{\pi y_i}{P_i^0 x_i} \exp\left[\frac{(\pi - P_i^0)(B_i - V_i)}{RT}\right]$$

Table III gives the correlations used for the estimation of pure-component vapor pressures, second virial coefficients, and

Table IV. Vapor–Liquid Equilibrium Data at 760 ± 2 mmHg Pressure

t, °C	x_1	Y_1	Y_1(calcd)	Z_1	Z_2	γ_1	γ_2
			Ethylbenzene (1)–Dimethylformamide (2)				
152.5	0.0100	0.0200		1.020	0.999	1.348	1.010
148.65	0.0500	0.0980		1.016	0.993	1.439	1.064
147.85	0.0600	0.1170		1.015	0.992	1.459	1.075
147.03	0.0750	0.1500		1.014	0.991	1.526	1.074
146.00	0.0900	0.1780		1.012	0.990	1.547	1.086
145.10	0.1050	0.2050	0.206[a]	1.011	0.998	1.562	1.094
143.55	0.1400	0.2650	0.258[a]	1.009	0.986	1.573	1.097
139.50	0.2750	0.4210	0.417[a]	1.004	0.980	1.408	1.146
138.15	0.3340	0.4700	0.470[a]	1.002	0.978	1.339	1.186
137.00	0.4130	0.5300	0.536[a]	1.001	0.977	1.258	1.232
136.55	0.4450	0.5600	0.560[a]	1.000	0.976	1.248	1.236
135.70	0.5200	0.6120	0.611[a]	0.999	0.975	1.193	1.291
134.70	0.6430	0.7000	0.687[a]	0.998	0.974	1.133	1.381
134.50	0.8350	0.8370	0.819[a]	0.998	0.973	1.048	1.633
134.90	0.8930	0.8860	0.872[a]	0.998	0.974	1.027	1.734
135.10	0.9100	0.9016	0.890[a]	0.999	0.974	1.020	1.777
135.60	0.9500	0.9418	0.937[a]	0.999	0.975	1.008	1.859
			p-Xylene (1)–Dimethylformamide				
150.30	0.0300	0.0680	0.085[b]	1.016	0.996	1.700	1.031
149.20	0.0450	0.1030	0.121[b]	1.014	0.994	1.761	1.037
148.10	0.0650	0.1480	0.165[b]	1.013	0.993	1.798	1.036
146.10	0.0980	0.2100	0.235[b]	1.010	0.990	1.775	1.050
143.60	0.1570	0.3150	0.311[b]	1.007	0.986	1.765	1.042
141.00	0.2370	0.4070	0.399[b]	1.003	0.982	1.611	1.070
138.45	0.3520	0.5100	0.495[b]	1.000	0.979	1.448	1.117
137.20	0.4480	0.5780	0.564[b]	0.998	0.977	1.331	1.170
136.75	0.4950	0.6050	0.595[b]	0.998	0.976	1.275	1.212
136.05	0.5850	0.6700	0.650[b]	0.997	0.976	1.217	1.257
135.70	0.6500	0.7020	0.687[b]	0.997	0.975	1.158	1.360
135.65	0.7200	0.7400	0.730[b]	0.996	0.975	1.103	1.485
135.68	0.8150	0.8020	0.791[b]	0.997	0.975	1.055	1.710
135.90	0.8700	0.8400	0.832[b]	0.997	0.975	1.030	1.954
136.23	0.9000	0.8700	0.861[b]	0.997	0.976	1.022	2.045
137.35	0.9700	0.9620	0.944[b]	0.999	0.977	1.019	1.930

[a] Calculated by van Laar equation. [b] Calculated by Redlich–Kister equation.

liquid molar volumes. These correlations gave a close fit (*9*) with the experimental pure component data from the literature.

Table IV gives the experimental t–x–y data, vapor-phase imperfection coefficients, and activity coefficients.

Both the systems formed minimum-boiling azeotropes. The ethylbenzene–DMF binary formed an azeotrope with a composition of 0.80 mole fraction ethylbenzene at 134.3 °C. The system *p*-xylene–DMF formed an azeotrope at 0.775 mole fraction *p*-xylene and 135.6 °C.

The data for both the systems were assessed for thermodynamic consistency by applying the Herrington (*14*, *15*), Black (*16*, *17*), and Norrish and Twigg (*18*) tests. The data satisfied the criteria of all the tests, thereby showing it to be thermodynamically consistent.

The activity coefficient data were fitted into the van Laar (*19*), Wilson (*20*), and Redlich–Kister (*21*) correlations. The constants in these correlations and the corresponding average absolute deviations of the activiy coefficients and the vapor compositions from the experimental values are given in Table V. The van Laar equation gave the best fit for the system ethylbenzene–DMF in the composition range 0.10–0.95 mole fraction ethylbenzene. For the system *p*-xylene–DMF, best fit was obtained by the Redlich–Kister equation in the composition range 0.10–0.90 mole fraction *p*-xylene. At concentrations lower than 0.1 mole fraction ethylbenzene or 0.1 mole fraction *p*-xylene none of the correlations could provide a satisfactory fit of the activity data.

Table V. Average Deviations and Correlation Constants

		av absolute error[a]		
correlation	constants	γ_1	γ_2	Y_1
	Ethylbenzene (1)–Dimethylformamide (2)			
van Laar	$A = 0.5102$			
	$B = 0.7857$	0.011	0.077	0.011
Wilson	$\Lambda_{12} = 0.6942$			
	$\Lambda_{21} = 0.7624$	0.030	0.087	0.031
Redlich–Kister	$B = 0.5466$			
	$C = -0.1000$			
	$D = 0.0833$	0.047	0.096	0.048
	p-Xylene (1)–Dimethylformamide (2)			
van Laar	$A = 0.6917$			
	$B = 1.1153$	0.015	0.036	0.014
Wilson	$\Lambda_{12} = 0.8677$			
	$\Lambda_{21} = 0.4768$	0.032	0.031	0.034
Redlich–Kister	$B = 0.8033$			
	$C = 0.0962$			
	$D = 0.0948$	0.017	0.013	0.018

[a] Error = (exptl − calcd)/exptl.

Glossary

B	gas-phase second virial coefficient, cm^3 mol^{-1}
P^0	pure-component vapor pressures, mmHg
R	gas constant
T	absolute temperature, K
t	system temperature, °C
V	pure-component liquid molar volume, cm^3 mol^{-1}
x	mole fraction in liquid phase
y	mole fraction in vapor phase
Z	vapor-phase imperfection coefficient
γ	activity coefficient
π	system pressure

Subscripts

1	more volatile component
2	less volatile component
calcd	calculated
exptl	experimental

Registry No. DMF, 68-12-2; *p*-xylene, 106-42-3; ethylbenzene, 100-41-4.

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Liquid–Liquid–Vapor Equilibria Behavior of Certain Ethane + *n*-Paraffin Mixtures

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Liquid–liquid–vapor phase equilibria for the binary mixtures ethane + *n*-docosane, *n*-tricosane, and *n*-tetracosane were studied and compared with earlier studies in the literature for the mixtures containing *n*-docosane and *n*-tetracosane. Solid–liquid–vapor phase equilibria were also studied for these binary mixtures. Compositions and molar volumes of the liquid phases in all the multiphase systems are reported. The study indicates a transition in the nature of the liquid–liquid–vapor locus between *n*-tricosane and *n*-tetracosane.

Introduction

There has been interest in the liquid–liquid–vapor (LLV) phase equilibria behavior of ethane with the homologous series of *n*-paraffins. Following up earlier studies of Kohn et al. (*1*), Specovius et al. (*2*) established that LLV immiscibility commences with *n*-octadecane and continues through at least *n*-eicosane. The LLV loci are terminated from below by a lower critical end point (LCEP, or L=L–V) and from above by a K point (L–L=V), often known as an upper critical end point (UCEP). Rodrigues and Kohn (*3*) identified similar LLV behavior for the mixture ethane + *n*-docosane, with the extent of the LLV locus increasing with the carbon number of the *n*-paraffin; although the K point moves slightly lower in temperature with increasing carbon number, the LCEP moves substantially lower at the same time.

In a little-known study, Patel (*4*) reported the behavior along the LLV locus for the mixture ethane + *n*-tetracosane. This locus differed from those of the lighter *n*-paraffins in that its lower terminus was a quadruple point (Q point, or SLLV), as would be expected with further increase of the carbon number. The Q point marks the intersection of the SLV locus with the LLV locus; since the SLV locus originates at the triple point of the heavy hydrocarbon, it will move upward in temperature with increasing carbon number, eventually intersecting the LLV locus. LLV immiscibility is finally lost with increasing carbon number when the SLV locus follows a path temperaturewise above the (potential) K point. The reader is referred to ref *5* for a discussion of the topography of multiphase systems in thermodynamic phase space.

In this paper we will report on the LLV behavior of ethane + *n*-docosane, *n*-tricosane, and *n*-tetracosane. The investigators have attempted to update the earlier studies on *n*-docosane and *n*-tetracosane, using components of improved purity. Peters et al. (*6*) recently reported some results (plots only) for the SLV loci of this homologous series, identifying *n*-tetracosane as the first *n*-paraffin to display a Q(SLLV) point. Our results herein confirm this.

Experimental Apparatus and Procedure

A detailed description of the experimental apparatus is given in an earlier paper by Fall and Luks (*7*). The procedure for performing LLV studies is presented by Fall et al. (*8*). The apparatus employs a stoichiometric approach wherein a known amount of *n*-paraffin is added to a visual (glass) equilibrium cell. (The volume of these cells is typically 7–8 mL.) Measured amounts of ethane gas are added to the cell from a high-pressure bomb. By careful mass balances, the moles of ethane in the liquid phases can be determined from "conjugate" measurements at a given temperature. Conjugate measurements involve two experimental runs in which one measurement has a large amount of L_1 relative to L_2 present. The second measurement has L_2 in excess. The vapor phase in all experiments is kept small and is assumed to be pure ethane due to the low volatility of the *n*-paraffins at the temperatures of interest. The termination points of the LLV loci are determined individually by straightforward visual observation.

Determination of a solid–liquid–vapor point is done by cooling a vapor–liquid system until crystals form and then slowly heating up the agitated system until only a trace of crystals remain. This procedure, combined with the vapor-phase assumptions stated above, permits determination of the liquid composition and molar volume, although care must be taken to ensure thermal and chemical equilibria at the crystal point.

Temperature is measured with a Pt-resistance thermometer to an estimated accuracy of ±0.02 K. Pressure is measured to ±0.07 bar with pressure transducers which are frequently