Vapor−Liquid Equilibrium for Phenol + α-Methyl Benzyl Alcohol and 2-Ethoxyethanol + *n*-Butyl Formate[†]

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The saturation pressure of α-methyl benzyl alcohol (358 to 398) K and *n*-butyl formate (313 to 359) K was measured by an ebulliometric method. The vapor−liquid equilibrium (p, T, x, y) at (353.15, 373.15, and 393.15) K was measured by the ebulliometric method for the systems phenol + α-methyl benzyl alcohol and at (333.15, 343.15, and 353.15) K for 2-ethoxyethanol + *n*-butyl formate. The experimental vapor pressures were correlated with the Antoine and AEOS equations, whereas VLE was correlated with AEOS equation of state.

Introduction

This work is part of an ongoing investigation of the phase equilibrium for systems of industrial interest sponsored by Project 805 of the Design Institute for Physical Property Data (DIPPR) of the American Institute of Chemical Engineers. In this work, we report part of the experimental measurements that have been made under Project 805(B)/96. The only available VLE data are for phenol + α-methyl benzyl alcohol[1] and were determined at constant pressure. Data for 2-ethoxyethanol + *n*-butyl formate have not been reported in the literature, and results cannot be predicted with sufficient accuracy either by using pure component property data or using a semiempirical method, e.g., based on a group contribution concept such as ASOG[2] or UNIFAC.[3]

Experimental Section

Chemicals. Phenol (CAS Reg. No. 108-95-2) was described previously (Chylinski et al.[4]). α-Methyl benzyl alcohol (CAS Reg. No. 98-85-1) was supplied by Fluka (purum >98%). The compound was distilled at subambient pressure in a 40 theoretical plate laboratory column. The purity of collected fractions was checked by gas liquid chromatography (GLC) with flame ionization detector (FID) on the nitroterephthalic acid modified poly(ethylene glycol) (FFAP) 30 m long capillary column, and those fractions of purity better than 99.5 mol % were collected and used for vapor pressure measurements. The water content detected as above was lower than 0.01 mol %. 2-Ethoxyethanol (CAS registry no. 110-80-5) was described previously (Antosik et al.[5]). Butyl formate (CAS Reg. No. 592-84-7) was purchased from Merck in a synthesis grade (purity better than 98% by GLC.) was analyzed by GLC on the same FFAP capillary column. A 96% purity was found. The product was distilled at subambient pressure. The bottom product of purity better than 99.5%, with water content less than 0.01%, was used for the measurements. During the measurements at 353 K, some signs of decomposition or reaction were observed, confirmed by a new peak in the GLC analysis.

Table 1. Saturation Pressure of the Pure Compounds

α-methyl benzyl alcohol		butyl formate	
T/K	P/kPa	T/K	P/kPa
358.41	1.033	313.16	7.978
362.36	1.296	318.33	10.194
366.37	1.613	323.32	12.787
371.46	2.112	328.57	16.079
377.83	2.909	333.14	19.501
382.98	3.728	343.14	29.103
387.28	4.557	353.14	42.242
393.34	5.985	358.67	51.345
398.01	7.325		

Vapor Pressure. When processing VLE data, the most crucial data are the saturation pressures of the pure components. Data for α-methyl benzyl alcohol were reported by Dreisbach and Shrader[6] and for butyl formate by Nelson,[7] by Dreisbach and Shrader,[6] and by Usanovich and Dembickijj.[8] The predicted and correlated data for all components, except for α-methyl benzyl alcohol, are reported in the Daubert and Danner monograph.[9] Because there are discrepances between these data, the vapor pressure data of pure compounds were also measured in this work. The arrangement for VLE measurements was used. The modified Świętosławski's ebulliometer (Rogalski and Malanowski[10]) and the previously described (Antosik et al.[5]) experimental procedure were used. The estimated accuracy of the pressure measurement was ±10 Pa and that of temperature was ±10 mK. The ITS-90 was used to report temperature. The results obtained are given in Table 1. The vapor pressure measurements for phenol[4] and 2-ethoxyethanol[5] were reported previously.

Vapor Liquid Equilibrium. The vapor−liquid equilibrium measurements were made with sampling both the liquid phase and vapor condensate in the ebulliometer. The procedure and apparatus used were described earlier (Antosik et al.[5]). The results obtained are given in Table 2.

Analytical Method. The sample composition was determined by the GLC method with flame ionization detectors. An internal standard was used in the calibration procedure. A HP 5890 Series II gas chromatograph equipped with HP 3396 integrator and 2m Reoplex packed column

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[†] This contribution will be part of a special print edition containing papers reporting experimental results from the various projects of the Designs Institute for Physical Properties of the American Institute of Chemical Engineers.

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10.1021/je025566c CCC: $27.50

Table 2. Vapor Liquid Equilibrium Results

x_1	y_1	p/kPa	x_1	y_1	p/kPa	x_1	y_1	p/kPa
				Phenol (1) + α-Methyl Benzyl Alcohol (2)				
	T/K = 353.15			T/K=373.15			T/K=393.15	
0.0000	0.0000	0.760	0.0000	0.0000	2.301	0.0000	0.0000	5.934
0.2241	0.3264	0.785	0.0469	0.0539	2.305	0.0467	0.0570	5.966
0.3391	0.5288	0.877	0.0925	0.1139	2.316	0.0925	0.1174	6.008
0.4154	0.6655	0.956	0.1374	0.1839	2.348	0.1369	0.1868	6.085
0.5020	0.7800	1.072	0.1882	0.2729	2.385	0.1889	0.2763	6.194
0.5661	0.8437	1.168	0.2311	0.3416	2.442	0.2290	0.3414	6.315
0.6722	0.9214	1.368	0.2682	0.4036	2.498	0.2668	0.4056	6.438
0.7417	0.9526	1.523	0.3328	0.5177	2.617	0.3339	0.5287	6.746
0.8225	0.9763	1.695	0.4183	0.6634	2.840	0.4214	0.6674	7.262
0.8892	0.9885	1.845	0.4996	0.7669	3.121	0.5013	0.7545	7.863
0.9574	0.9962	1.972	0.5827	0.8437	3.454	0.5860	0.8380	8.574
1.0000	1.0000	2.037	0.6743	0.9113	3.881	0.6760	0.9048	9.494
			0.7512	0.9498	4.248	0.7433	0.9384	10.300
			0.8232	0.9693	4.649	0.8227	0.9634	11.140
			0.9007	0.9867	5.070	0.9012	0.9821	12.082
			0.9570	0.9951	5.361	0.9572	0.9931	12.700
			1.0000	1.0000	5.541	1.0000	1.0000	13.154
				2-Ethoxyethanol (1) + Butyl Formate (2)				
	T/K = 333.15			T/K=343.15			T/K=353.15	
0.0000	0.0000	19.504	0.0000	0.0000	29.103	0.0000	0.0000	42.241
0.0680	0.0312	18.993	0.0684	0.0328	28.390	0.1407	0.0726	41.121
0.1365	0.0547	18.501	0.1296	0.0560	27.627	0.2033	0.0842	39.987
0.2000	0.0713	17.861	0.1900	0.0753	26.754	0.2673	0.1064	38.805
0.3137	0.1070	17.053	0.2529	0.0984	25.929	0.3571	0.1369	36.876
0.3746	0.1259	16.435	0.4096	0.1440	24.241	0.4416	0.1646	34.976
0.4684	0.1536	15.471	0.4645	0.1615	23.409	0.5233	0.1896	32.912
0.6652	0.2332	12.964	0.5380	0.1923	22.141	0.5776	0.2165	31.403
0.7320	0.2746	11.894	0.6181	0.2178	20.573	0.6507	0.2485	29.192
0.7840	0.3222	10.906	0.6991	0.2723	18.700	0.7520	0.3259	25.806
0.8249	0.3791	10.070	0.7735	0.3323	16.763	0.8042	0.3740	23.755
0.8791	0.4708	8.842	0.8379	0.4171	14.899	0.8649	0.4752	21.089
0.9174	0.5715	7.866	0.8990	0.5360	12.911	0.9047	0.5741	19.114
0.9553	0.7145	6.774	0.9421	0.6782	11.196	0.9468	0.7023	16.949
0.9765	0.8050	6.145	0.9752	0.8324	9.785	0.9742	0.8401	15.289
1.0000	1.0000	5.300	1.0000	1.0000	8.646	1.0000	1.0000	13.623

Table 3. Correlation of Pure Components Vapor Pressure with the Antoine and AEOS Equations

		phenol[5]	α-methyl benzyl alcohol	2-ethoxyethanol[4]	n-butyl formate
temperature range/K		353−399	358−398	313−353	313−359
		parameters of Antoine equation (T/K, p/kPa)			
A		6.27771636	6.06504306	6.60812220	6.21077662
B		1520.6822	1466.6259	1570.7744	1344.6697
C		98.37	115.9906	66.1747	59.8694
RMSD(p)/Pa		2.81	2.18	1.86	7.59
		enthalpy of vaporization/kJ			
at T/K = 298.15	calc.	solid	75.22	49.61	40.10
	lit.			48.78[9], 48.21[11]	39.73[9], 41.25[12]
at normal boiling point	calc.	46.17	49.0	41.09	34.55
	lit.	47.36[9]		40.67[9]	35.95[9], 36.58[13]
		parameters of AEOS equation of state			
T'_c/K		646.36	604.25	576.456	584.28
p'_c/MPa		5.06	3.41	3.98	4.82
ω'_H		0.3972	0.4385	0.48469	0.3247
$-\Delta H^0$/kJ·mol^{-1}		15.33	22.79	2.70	
$-\Delta S^0$/J·mol^{-1}·K^{-1}		79.21	82.04	54.70	
$-\Delta C_p{}^0$/J·mol^{-1}·K^{-1}		10.39	−3.60	82.33	
errors: RMSD(p)/Pa		5.7	7.98	4.91	7.59

was used for mixtures containing 2-ethoxyethanol, and an HP-17 capillary column was used for systems with phenol.

Correlation

Vapor Pressure. The vapor pressure data were correlated by means of Antoine equation

$$\log (p/\text{kPa}) = A - \frac{B}{T/\text{K} - C} \tag{1}$$

where, p is pressure, T is temperature and A, B, and C are adjustable parameters.

The correlation results are summarized in Table 3.

The root-mean-square deviations of pressure (RMSD(p)/Pa) are calculated by

$$\text{RMSD}(p) = \sqrt{\frac{\sum_{i=1}^{n}(p_i^{\text{exp}} - p_i^{\text{calc}})^2}{n - m}} \tag{2}$$

where m is the number of adjustable parameters, n is the number of experimental points, p_i^{exp} is the pressure measured at point number i, and p_i^{calc} is the pressure calculated from eq 1 at point number i. The best evidence of the accuracy of the vapor pressure determination is calculation of the heat of vaporization from the measured vapor pressure and comparison with these obtained by a calorimetric method. This is also presented in Table 3. The calculated values exhibit small deviations from published calorimetric data. For α-methyl benzyl alcohol, there are no literature data available for comparison.

The investigated mixtures contain associating compounds. To properly represent such mixtures, a special treatment is necessary. In previous work,[4] it has been found that the AEOS (association + equation of state) equation of state is most suitable for representation of phase equilibria in the systems formed by associating or even chemically reacting compounds. In the AEOS model, the thermodynamic properties of an associated mixture are viewed as a result of chemical equilibrium between associated species and physical interactions between all, associated or inert, species existing in a mixture. The detailed formulas have been discussed by Antosik et al.[5] In the AEOS model, the thermodynamic properties of an associated mixture are viewed as a result of chemical equilibria between associated species and physical interactions between all, associated or inert, species existing in a mixture.

The use of AEOS equation leads to the split of the compressibility factor into two parts

$$z = z^{(\mathrm{ph})} + z^{(\mathrm{ch})} - 1 \qquad (3)$$

where $z^{(\mathrm{ph})}$ and $z^{(\mathrm{ch})}$ are the physical and chemical contributions to the compressibility factor, respectively. The $z^{(\mathrm{ph})}$ contribution is equivalent to the equation of state for nonreacting monomeric species. In this work, it was calculated from the cubic equation of state of Yu et al.[14]

$$z^{(\mathrm{ph})} = \frac{v}{v-b} - \frac{a(T)v}{RT[v(v+c)+b(3v+c)]} \qquad (4)$$

where $a(T)$, b, and c are generalized functions of the critical temperature T_{c}, critical pressure P_{c}, and acentric factor ω of a pure component.

The $z^{(\mathrm{ch})}$ contribution is equal to the reciprocal mean association number (K) and depends on the association model applied. In this work, the linear Mecke−Kempter-type association model has been used. It well represents compounds such as alcohols, phenols, ketones, amines, pyridine bases, and others.[15] For pure compounds, this model leads to the equation:

$$z^{(\mathrm{ch})} = \frac{2}{1+\sqrt{1+4RTK/V}} \qquad (5)$$

The complete equation of state for an associating compound, eq 3, has five characteristic parameters: the standard enthalpy ($\Delta H°$) and entropy ($\Delta S°$) of association; the critical temperature (T'_{c}); the critical pressure (p'_{c}); and the acentric factor (ω') of a hypothetical monomeric compound with nonspecific interactions identical to those in the associating substance but incapable of forming associates. The values of parameters obtained by fitting the equation to vapor pressure data are given in Table 3. The temperature dependence of the association constant can be expressed by assuming that $\Delta H°$ and $\Delta S°$ of association are linearly dependent on temperature (the appropriate values of C_{p} are given in Table 3)

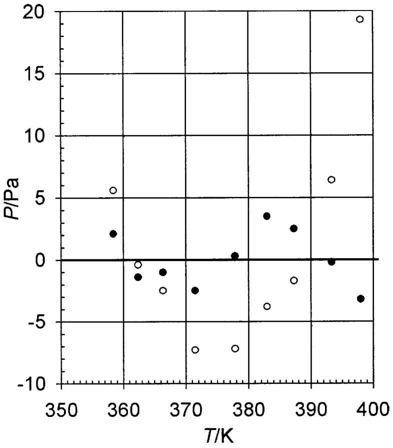

Figure 1. Deviations of experimental vapor pressure of α-methyl benzyl alcohol from the Antoine correlation (●) and the AEOS (○).

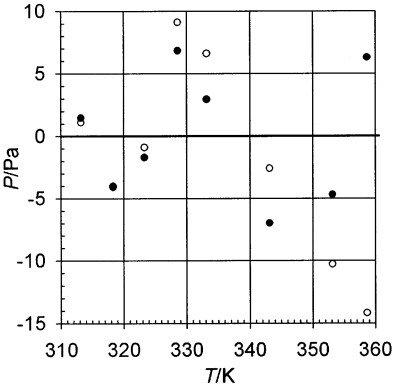

Figure 2. Deviations of experimental vapor pressure of butyl formate from Antoine correlation (●) and the AEOS (○).

$$\ln K_{ij} = \frac{-\Delta H°(T_{\mathrm{o}}) + \Delta C_{\mathrm{p}}^{\circ} T_{\mathrm{o}}}{\mathrm{R}T} + \frac{1}{\mathrm{R}}[\Delta S°(T_{\mathrm{o}}) - \Delta C_{\mathrm{p}}^{\circ} - \Delta C_{\mathrm{p}}^{\circ} \ln T_{\mathrm{o}}] + \frac{\Delta C_{\mathrm{p}}^{\circ}}{R} \ln T \qquad (6)$$

The results of correlation of pure components vapor pressures by means of AEOS equation are given in Table 3. A comparison of correlation of vapor pressure by Antoine and AeOS equations is shown in Figures 1 and 2. It is clear from these figures that there is no significant difference between the correlation ability of both equations. In both cases, the distribution of deviations is random.

Vapor Liquid Equilibrium. The mixture phenol + α-methyl benzyl alcohol consists of two associating components, whereas 2-ethoxyethanol + n-butyl formate contains one associating compound. The continuous linear association Mecke−Kempter model with the following equation for the chemical term represents the self- as well as cross-association:

$$z^{(\mathrm{ch})} = \sum_{i=1}^{2}\left(2x_{Ai}/\left(1 + \sqrt{1 + 4RT\left(\sum_{j=1}^{2} K_{ji}x_{Aj}\right)/V}\right)\right) \qquad (7)$$

where K_{ij} is either the self-association constant (for $i = j$) or the cross-association constant (for $i \neq j$).

The parameters of the AEOS equation of state obtained from pure component data (Table 3) were used unchanged for mixture calculations. The binary parameters a, b, and c of Yu et al.[14] equation ($z^{(\mathrm{ph})}$ − term) were calculated using the classical mixing rules

Table 4. Binary Parameters of the AEOS Equation, RMSD(y_1) and RMSD(p)

T/K	$K_{12} \times 10^4$	θ_{12}	RMSD(y_1)	RMSD(p)/Pa
Phenol (1) + α-Methyl Benzyl Alcohol (2) − Correlation				
353.15	0.209882	−0.11853	0.0300	3.19
373.15	0.159518	−0.11058	0.0302	10.4
393.15	0.107887	−0.11199	0.0358	32.0
isobaric data by Smirnov at al.[1] 343−360	0.207160	−0.07984	0.0145	15.10
Phenol (1) + α-Methyl Benzyl Alcohol (2) − Prediction				
353.15	0.208775	−0.11762	0.0297	3.70
373.15	0.158237	−0.11387	0.0314	7.12
393.15	0.107699	−0.11012	0.0352	36.90
isobaric data by Smirnov at al.[1] 343−360	eq 11	eq 12	0.0339	23.58
2-Ethoxyethanol (1) + Butyl Formate (2) − Correlation				
333.15		0.013451	0.055628	334.75
343.15		0.011936	0.057078	488.25
353.15		0.018811	0.059093	346.57
2-Ethoxyethanol (1) + Butyl Formate (2) − Prediction				
333.15		0.0150	0.0533	266.77
343.15		0.0150	0.0533	299.47
353.15		0.0150	0.0636	627.55

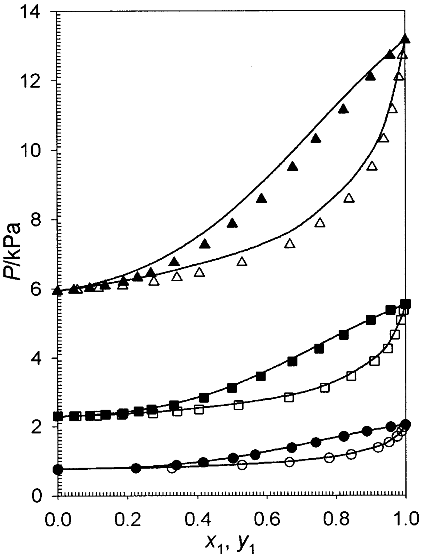

Figure 3. VLE for phenol (1) + α-methyl benzyl alcohol (2): ●, 353.15 K; ■, 373.15 K; ▲, 393.15 K. The lines represent a prediction with the AEOS equation of state; solid symbols represent experimental bubble points; and hollow symbols represent experimental dew points.

$$a = \sum_{i=1}^{2} \sum_{i=1}^{2} x_i x_j (1 - \theta_{ij}) \sqrt{a_i a_j} \tag{8}$$

$$b = \sum_{i=1}^{2} x_i b_i \tag{9}$$

$$c = \sum_{i=1}^{2} x_i c_i \tag{10}$$

These mixing rules contain only one binary adjustable parameter θ_{12}. The phenol + α-methyl benzyl alcohol consists of two polar compounds. In this case, better results were obtained with the cross association constant K_{12} calculated from binary data. The correlation results are summarized in Table 4 and in Figures 3 and 4.

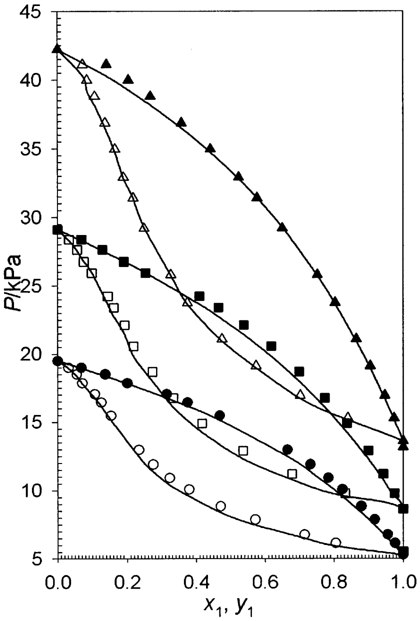

Figure 4. VLE for 2-ethoxyethanol (1) + n-butyl formate (2): ●, 333.15 K; ■, 343.15 K; ▲, 353.15 K; the lines represent a prediction with the AEOS equation of state; solid symbols represent experimental bubble points; and hollow symbols represent experimental dew points.

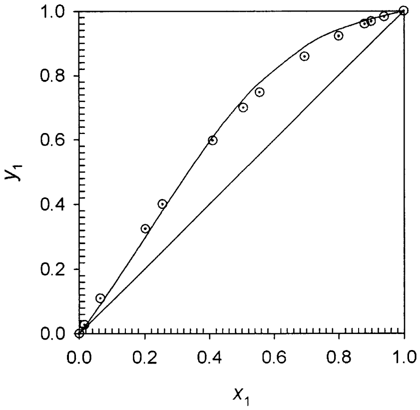

Figure 5. Isobaric VLE at 1.33 kPa (x_1-y_1, diagram) for phenol (1) + α-methyl benzyl alcohol (2); ○, Measurements by Smirnov et al.[1]; the lines represent a prediction with the AEOS equation of state; AEOS parameters were calculated from isothermal data reported in this paper.

For the system phenol + α-methyl benzyl alcohol, the temperature dependence of parameters K_{12} and θ_{12} has been calculated for the temperature range (330 to 400) K by linear regression from isothermal data reported in this paper

$$K_{12} = 1.10115 \times 10^{-4} - 2.5269 \times 10^{-7}\, T \tag{11}$$

$$\theta_{12} = -0.18379 + 1.8738 \times 10^{-4}\, T \tag{12}$$

The RMSDs for p and y_1 obtained with this prediction are given in Table 4. The literature data by Smirnov at al.[1] were also compared, and the results were given in Table 4 and in Figure 5. The results of prediction by AEOS with eqs 11 and 12 used for K_{12} and θ_{12} are very satisfactory. A comparison of all results leads to the conclusion that the correlated results are similar to those predicted with the temperature-dependent K_{12} and θ_{12} parameters.

In the system 2-ethoxyethanol + n-butyl formate, there is only one associating compound (2-ethoxyethanol) and thus only the θ_{12} parameter was adjusted. The correlation results are given in Table 4. For predictions a constant value ($\theta_{12} = 0.015$) was used.

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Received for review June 7, 2002. Accepted November 19, 2002. The authors thank the Steering Committee of the Project 805 of the Design Institute for Physical Property Data (DIPPR) of the American Institute of Chemical Engineers for selection of the systems and for financial support.

JE025566C