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Articles

Vapor−Liquid Equilibrium in Phenol + 2-Ethoxyethanol at 363.15 to 383.15 K

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The vapor−liquid equilibrium (VLE−pressure, temperature, and composition of coexisting vapor and liquid phases) was directly determined by the ebulliometric method for the system formed by 2-ethoxyethanol with phenol. An azeotrope has been found. The experimental results were correlated by means of an equation of state (AEOS) that is capable of reproducing the VLE for associating and reacting systems over a wide range of pressure and temperature with accuracy similar to the experiment uncertainty. Such results are hard to obtain with equations representing activity coefficients.

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. This paper reports experimental measurements that have been made under Project 805(B)/95.

The data for the investigated system phenol + 2-ethoxyethanol cannot be predicted with sufficient accuracy from pure component properties or by semiempirical methods, such as those based on a group contribution concept like ASOG[1] or UNIFAC.[2]

Experimental Section

Chemicals. 2-Ethoxyethanol (CA registry no. 110-80-5) was described previously (Antosik et al.[3]).

Phenol (CA Registry No. 108-95-2) was purchased from Z. D. Chemipan, as a physicochemical standard of purity better than 99.9%. A purity better than 99.95% by mass of pure compound was found by GLC. The content of water, determined by GLC analysis with a thermal conductivity detector on a glass 2.5 m by 3 mm column filled with Chromosorb 101 (60/80 Mesh), was less than 0.01 mass %.

Vapor Pressure Measurements. In the processing of VLE data the most crucial data are the saturation vapor pressures of pure components. Hence, the vapor pressure data of pure compounds were measured in this work. The same arrangement as for the VLE measurements was used, namely a modified Świętosławski[4] ebulliometer and the earlier described[3] experimental procedure. The only modification was that liquid phenol (heated to above its melting temperature) was introduced to the ebulliometer. The estimated accuracy of the pressure measurement was ±10 Pa, and that of the temperature measurement was ±10 mK on the ITS-90 scale.

Table 1. Saturation Vapor Pressures

phenol		2-ethoxyethanol	
T/K	P/kPa	T/K	P/kPa
363.13	3.416	313.35	1.792
363.15	3.424	319.05	2.492
363.18	3.430	324.73	3.409
363.70	3.521	328.28	4.124
373.15	5.541	333.15	5.304
373.20	5.552	343.10	8.631
378.17	6.965	353.14	13.623
383.14	8.663	363.15	20.720
383.15	8.667	373.15	30.756
390.90	11.998	383.15	44.635

VLE Measurements. The vapor−liquid equilibrium measurements were made with the ebulliometer, enabling the sampling of the liquid phase and the vapor condensate. The procedure and apparatuses used were described earlier.[3]

Analytical Method. The sample composition was determined by GLC with a flame ionization detector (FID). A calibration procedure with an internal standard was used. A HP 5890 Series II gas chromatograph with an HP-17 capillary column and an HP 3396 integrator was used.

Results

Vapor Pressure. The results obtained are given in Table 1. Biddiscombe and Martin[5] and Dreisbach and Shrader[6] have published values for phenol, and Pick et al.[7] has published values for 2-ethoxyethanol. In addition, critically evaluated and recommended by DIPPR[8] parameters for the vapor pressure equation are available. The comparison of vapor pressure measurements with those published in the literature is given for phenol in Figure 1 and for 2-ethoxyethanol in Figure 2. The agreement with literature data is satisfactory. Some systematic deviations from the equation recommended by DIPPR are observed for both substances (Figures 1 and 2).

VLE. The results of measurements obtained for the equilibrium pressure (P/kPa), temperature (T/K), and mole

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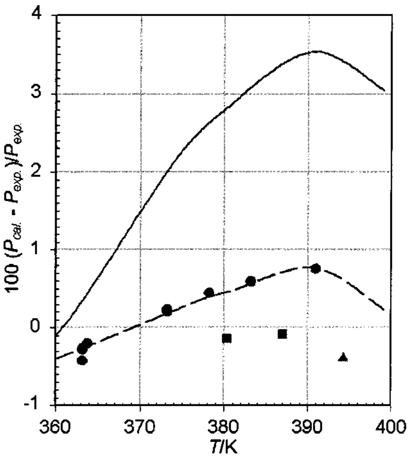

Figure 1. Deviation of phenol saturation pressure data correlated by the AEOS equation of state (parameters Table 5) from correlation with the Antoine equation (dotted line, parameters in Table 4), the DIPPR recommendation (solid line),[8] and experimental data: ●, our own; ▲, Biddisombe and Martin;[5] ■, Dreisbach and Shrader.[6]

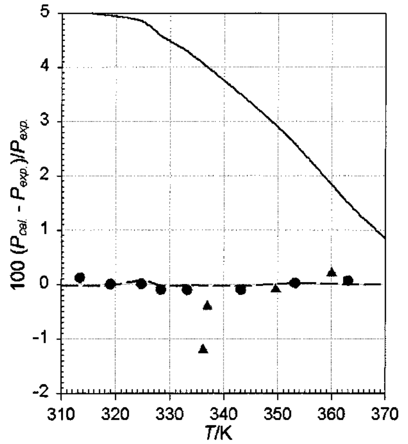

Figure 2. Deviation of 2-ethoxyethanol saturation pressure data correlated by the AEOS equation of state (parameters Table 5) from correlation with the Antoine equation (dotted line, parameters in Table 4), the DIPPR recommendation (solid line),[8] and experimental data: ●, our own; ■, Pick et al.[7]

fraction of component 1 in the liquid (x_1) and vapor (y_1) phases are listed in Table 2 and given in Figure 3. There are no literature data available for comparison.

Azeotropes. The negative azeotropes have been found. The azeotropic parameters are given in Table 3 and in Figure 4.

Correlation

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

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

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

The root-mean-square deviations (RMSDs) of a property (p or y_1) are calculated from the equation

$$\mathrm{RMSD}(p) = \sqrt{\frac{\sum_{i=1}^{n}(p_i^{\mathrm{calcd}} - p_i^{\mathrm{exptl}})^2}{n}} \tag{2}$$

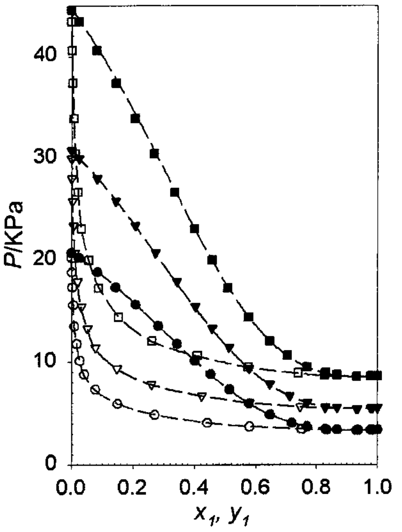

Figure 3. Vapor−liquid equilibrium in the system phenol with 2-ethoxyethanol: solid symbols, x_1; hollow symbols, y_1; lines, prediction and correlation (no difference) with the AEOS equation. Experimental data: ●, T/K = 363.15; ▲, T/K = 373.15; ■, T/K = 383.15.

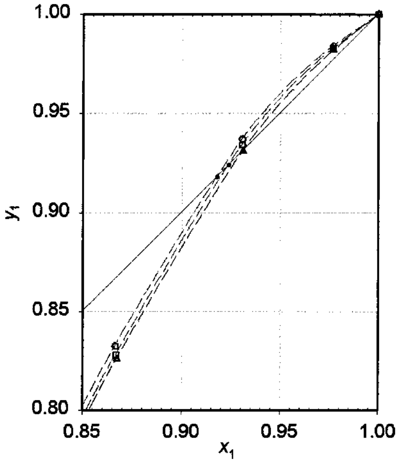

Figure 4. Azeotropic composition (x_1^{az}) calculated from the AEOS equation. Experimental data: ●, T/K = 363.15; ▲, T/K = 373.15; ■, T/K = 383.15.

where n is the number of experimental points, p_i^{calcd} is the property calculated at point number i, and p_i^{exptl} is the property measured at point number i.

The results of the correlation are summarized in Table 4 and in Figures 1 and 2. The calculated enthalpies of vaporization from the vapor pressure measured in the course of this work show very small deviations from the values reported in the literature and obtained by the calorimetric method. For phenol some improvement of the calculated enthalpy of vaporization is observed when our data are combined with those of Biddiscombe and Martin[5] (Table 4). On the other hand it is known[5,9] that the Antoine equation is unable to represent the vapor pressure of phenol within experimental accuracy over a wide range of temperature.

The development of the equation of state methods[10,11] shows that these methods are able to reproduce the vapor pressure and VLE data, approaching the accuracy of the measurement. Another advantage of the equation of state method is the ability to reproduce with only one set of parameters binary VLE data in a wide range of pressure and temperature.

Table 2. VLE in the System Phenol (1) + 2-Ethoxyethanol (2)[a]

$T = 363.15$ K			$T = 373.15$ K			$T = 383.15$ K		
x_1	y_1	P/kPa	x_1	y_1	P/kPa	x_1	y_1	P/kPa
0.0000	0.0000	20.720	0.0000	0.0000	30.756	0.0000	0.0000	44.635
0.0257	0.0004	20.208	0.0255	0.0003	30.003	0.0254	0.0004	43.400
0.0843	0.0015	18.826	0.0837	0.0017	28.006	0.0829	0.0021	40.615
0.1433	0.0033	17.335	0.1434	0.0039	25.803	0.1437	0.0048	37.394
0.2085	0.0063	15.619	0.2068	0.0066	23.379	0.2072	0.0080	33.945
0.2827	0.0104	13.539	0.2731	0.0122	20.713	0.2688	0.0131	30.479
0.3433	0.0180	11.795	0.3425	0.0202	17.913	0.3355	0.0226	26.666
0.4013	0.0279	10.159	0.4024	0.0325	15.461	0.4000	0.0336	23.050
0.4527	0.0424	8.811	0.4578	0.0530	13.287	0.4581	0.0571	19.956
0.5140	0.0782	7.341	0.5131	0.0786	11.422	0.5087	0.0888	17.241
0.5792	0.1504	5.956	0.5786	0.1477	9.378	0.5768	0.1536	14.381
0.6470	0.2709	4.878	0.6462	0.2605	7.823	0.6475	0.2617	12.075
0.7185	0.4420	4.074	0.7119	0.4240	6.683	0.7053	0.4101	10.655
0.7684	0.5805	3.722	0.7689	0.5795	6.062	0.7687	0.5747	9.525
0.8291	0.7501	3.470	0.8292	0.7459	5.669	0.8287	0.7411	8.945
0.8667	0.8324	3.418	0.8670	0.8280	5.561	0.8675	0.8258	8.745
0.9308	0.9370	3.365	0.9307	0.9340	5.470	0.9311	0.9310	8.590
0.9770	0.9839	3.398	0.9772	0.9829	5.506	0.9772	0.9818	8.622
1.0000	1.0000	3.424	1.0000	1.0000	5.541	1.0000	1.0000	8.667

[a] Estimated errors of measurements: $\delta x_1 = \pm 0.002$; $\delta y_1 = \pm 0.003$; $\delta P/\mathrm{Pa} = \pm 10$; $\delta T/\mathrm{mK} = \pm 20$.

Table 3. Azeotropic Data

			azeotrope	
T/K	p_1°/kPa	p_2°/kPa	P_{az}/kPa	x_1^{az}
363.15 ± 0.01	20.72 ± 0.01	3.42 ± 0.01	3.36 ± 0.02	0.931 ± 0.003
373.15 ± 0.01	30.76 ± 0.01	5.54 ± 0.01	5.46 ± 0.02	0.924 ± 0.003
383.15 ± 0.01	44.64 ± 0.01	8.67 ± 0.01	8.51 ± 0.03	0.918 ± 0.003

Table 4. Correlation of Pure Component Vapor Pressures with the Antoine Equation

	phenol		2-ethoxyethanol
	P^{sat}	P^{sat} + lit[a]	our own data
temp range/K	363−391	363−455	310−385
A	6.204 481 9	6.318 379 9	6.507 647 9
B	1480.581	1558.327	1519.460
C	102.026	93.658	70.409
errors: RMSD(p)/Pa	1.7	24.9	28.3
	Enthalpy of Vaporization/(kJ/mol)		
at T/K = 298.15			
calc from Antoine eq	solid phase	solid phase	49.79
lit.			48.78[8] 48.21[18]
at boiling point T/K =	454.65	455.00	407.92
calc from Antoine eq	46.90	47.07	40.75
lit.	47.36[8] 46.18[19]		41.22[8] 39.22[20]

[a] Biddiscombe and Martin.[5]

In previous work[12] it has been found the AEOS equation of state is most suitable for representation of phase equilibria in the systems formed by associating or even chemically reacting compounds.[13] The superiority of the AEOS equation over other EOSs in the representation of the pressure and molar volume (V) of mixtures containing phenol and its derivatives and also for pure associating compounds was proved by Pfohol et al.[14]

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 chemical equilibria are assumed to follow a simplified, yet plausible, association model, which, in general, depends on the nature of the associating compound. An equilibrium mixture of associated species is treated analogously to a mixture of nonreacting polymeric aggregates.

The use of the 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 and Lu and Iwai.[15]

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

where $a(T)$, b, and c are generalized as functions of the critical temperature T_c, the critical pressure P_c, and the acentric factor ω of a pure component.

Table 5. Correlation of Pure Component Vapor Pressures with the AEOS Equation of State

compound	T'_c/K	p'_c/bar	ω'_H	$-\Delta H°$/(kJ/mol)	$-\Delta S°$/[J/(mol K)]	$-\Delta C_p$/[J/(mol K)]	RMSD(p)/Pa
phenol	646.36	50.56	0.3972	15.334	79.21	10.39	5.7
2-ethoxyethanol	577.02	39.71	0.4900	2.3335	55.04	70.97	29.7

Table 6. Molecular Parameters and Critical Constants for Phenol[8] and 2-Ethoxyethanol[8]

compound	mol. wt	T_c/K	p_c/bar	V_c/(cm^3/mol)	Z_c	w	d_{20}/(g/cm^3)
phenol	94.113	694.25	61.30	229.0	0.243	0.4259	solid
2-ethoxyethanol	90.122	569.00	42.40	294.0	0.264	0.7582	0.929 45

Table 7. Parameters of the AEOS Equation and the Root-Mean-Square Deviation of Pressure (P) and Vapor Phase Composition (y) for the Binary Mixture Phenol + 2-Ethoxyethanol

	T/K	K_{12}	θ_{12}	RMSD(p)/Pa	RMSD(y)
Part 1. Correlation—K_{12} and θ_{12} Values Obtained by Direct Fit to Each Isotherm					
	363.15	1.9906×10^{-6}	−0.17494	104.0	0.0309
	373.15	2.2588×10^{-6}	−0.16769	126.2	0.0377
	383.15	2.4436×10^{-6}	−0.15734	286.5	0.0402
parameters (eq 11): $A =$		-6.2207×10^{-6}	−0.49508		
$B =$		2.26497×10^{-8}	8.8015×10^{-4}		
Part 2. Prediction—K_{12} and θ_{12} Values Computed for Each Isotherm by Eq 11					
	363.15	2.0045×10^{-6}	−0.17546	95.1	0.0312
	373.15	2.231×10^{-6}	−0.16666	155.4	0.0372
	383.15	2.4575×10^{-6}	−0.15785	261.4	0.0405

Table 8. Correlation of VLE of the Mixture Phenol + 2-Ethoxyethanol in the Temperature Range 263−283 K by Various Equations

equation	RMSD(p)/Pa	RMSD(y)	RMSD(T)/C	no. of adjustable binary parameters
AEOS	172.2	0.0364	0.0000	4
NRTL	63.9	0.0374	0.0791	9
UNIQUAC	124.1	0.0374	0.1564	6
Redlich−Kister	63.3	0.0373	0.0788	9

The $z^{(ch)}$ 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 is well representing such compounds as alcohols, phenols, ketones, amines, pyridine bases, and other similar compounds.[16] For pure compounds this model leads to the equation

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

The complete equation of state for an associating compound (eq 3) has characteristic parameters: the standard enthalpy (ΔH°_{ii}) and entropy ΔS°_{ii} of association, both dependent on temperature, 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. These parameters were determined by fitting the equation to vapor pressure and liquid density data. The values of the parameters obtained, including the heat capacity (C_p), are given in Table 5. The temperature dependence of the association constant can be expressed by assuming that the ΔH°_{ii} and ΔS°_{ii} of association are linearly dependent on temperature (the appropriate values of C_p are given in Table 5):

$$\ln K_{if} = \frac{-\Delta H^\circ(T_0) + \Delta C^\circ_p T_0}{RT} + \frac{1}{R}[\Delta S^\circ(T_0) - \Delta C^\circ_p - \Delta C^\circ_p \ln T_0] + \frac{\Delta C^\circ_p}{R} \ln T \tag{6}$$

The determination of pure component parameters is the crucial step in the application of the AEOS equation. It is not sufficient to obtain a good fit to pure component data. It must also be ensured that the relative magnitude of the $z^{(ph)}$ and $z^{(ch)}$ terms is correct, that is, that the effects of association and nonspecific interactions on the compressibility factor are correctly divided. This can be, in principle, accomplished by using physically meaningful values of the association parameters ΔH°_{ii} and ΔS°_{ii} (Table 5).

The results of the correlation of pure component vapor pressures by means of the AEOS equation are given in Table 5 and Figures 1 and 2. To obtain an extended range of T, combined values, our own and those of Biddiscombe and Martin,[5] were used to obtain the AEOS parameters reported in Table 5. Auxiliary parameters are given in Table 6. The comparison of the correlation of vapor pressure by the Antoine and AEOS equations is given in Figures 1 and 2. It is visible from these figures that there is practically no difference between the correlation abilities of these equations. In both cases the distribution of errors is random.

VLE. The investigated mixture consists of two associating components whose self- as well as cross-association is represented by the continuous linear association model. For such a case, Anderko proposed[17] the following equation for the chemical term:

$$z^{(ch)} = \sum_{i=1}^{2} \frac{2x_{A_i}}{1 + \sqrt{1 + \dfrac{4RT(\sum_{j=1}^{2} K_{ji}x_{A_j})}{V}}} \tag{7}$$

where K_{ij} is either the self-association constant (for $i = j$) or the cross-association constant (for $i \neq j$). Equation 5 has been found to be very useful for mixtures containing alcohols, phenols, ketones, and amines.

The parameters of the AEOS equation of state obtained from pure component data (Table 6) were used unchanged for mixture calculations. The binary parameters a, b, and c of the Yu and Lu and Iwai equation (z^{ph} term) were calculated using the classical mixing rules:

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

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

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

These mixing rules contain only one binary adjustable parameter, θ_{12}. The mixture investigated consists of two polar compounds. In such cases, better results were obtained with the cross association constant K_{12} calculated from binary data. The correlation results are summarized in Table 7, Part 1.

The K_{12} and θ_{12} values given in Part 1 of Table 7 were fitted to the equation

$$K_{12}^{T} \quad \text{or} \quad \theta_{12}^{T} = A + BT \tag{11}$$

representing the temperature dependence of both parameters.

The values computed for each temperature are given in Part 2 of Table 7 together with the root-mean-square deviations of pressure and vapor-phase composition. Comparison of results leads to the conclusion that the correlated results are almost identical to those predicted with the temperature dependent K_{12} and θ_{12} parameters.

In Table 8 a comparison with the correlation by "gamma/phi" is given. The results are similar besides the fact that the "gamma/phi" method is representing only particular isotherms and there is no possibility of finding a reasonable temperature dependence of the adjustable parameters. In all cases some deviations in y are observed. The experimental results prove to be thermodynamically consistent within usual limits.

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