Vapor−Liquid Equilibrium in *m*-Xylene + Cyclohexanol at 19.99 and 94.93 kPa

Barbara E. Światek and Stanisław K. Malanowski*

Instytut Chemii Fizycznej PAN, Kasprzaka 44, 01-224 Warszawa, Poland

The vapor−liquid equilibrium (VLE−pressure, temperature, and composition of coexisting vapor and liquid phases) was directly determined by an ebulliometric method for the system *m*-xylene + cyclohexanol. An azeotrope was found. The experimental results were correlated by means of an equation of state (AEOS) that is capable of reproducing VLE for associating and reacting systems, over a wide range of pressure and temperature, with an accuracy close to the experimental uncertainty.

Introduction

This work is part of an ongoing investigation of the phase equilibria for systems of industrial interest. The data for the investigated system *m*-xylene + cyclohexanol cannot be predicted with sufficient accuracy from pure component properties or by semiempirical methods, such as that based on a group contribution concept like ASOG[1] or UNIFAC.[2]

Experimental Section

Chemicals. Cyclohexanol (CA registry no. 108-93-0) was purchased from P.O.Ch. Gliwice, as a laboratory reagent of purity > 99.0%. A purity > 99.2% (by mass) was found by GLC. The main impurity was cyclohexanone. The content of water, determined by GLC analysis, was <0.01 mass %. *m*-Xylene (CA registry no. 108-38-3) was purchased from Z.D. Chemipan, as a physicochemical standard of purity > 99.9%. A purity > 99.95% by mass of pure compound was found by GLC. The content of water, determined by GLC analysis with a thermal conductivity detector and a glass 2.5 m by 3 mm i.d. column filled with Chromosorb 101 (60/80 mesh), was <0.01 mass %.

Vapor Pressure. The vapor pressure data for cyclohexanol were reported by Goodwin and Newsham,[3] Sipowska and Wieczorek,[4] Gierycz et al.,[5] and finally Ambrose and Ghiasse.[6] The differences between the values of these authors are up to 1.5% of *P*. Our results are closest to those of Gierycz et al. The correlation results are given in Figure 1.

The vapor pressure data for *m*-xylene reported by Forziati et al.[7] in 1947 are in good agreement with our measurements and with the enthalpy of vaporization measured by Osborne and Ginnings.[8] Later measurements by Park and Gmehling[9] lead to similar values, except that their random errors are 2 orders of magnitude higher. Pressures measured in this work lay within the experimental error of the data of Osborne and Ginnings (deviations of *P* below 0.05%, Figure 2).

The vapor pressure data are represented by means of the Antoine equation

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

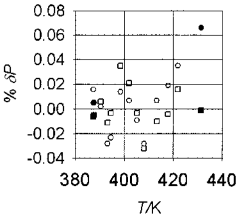

Figure 1. Deviations of cyclohexanol saturation pressure data from the Antoine correlation (■) and AEOS (●) equations: solid symbols, this work; hollow symbols, Gierycz et al.[5]

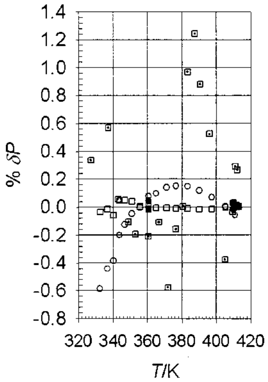

Figure 2. Deviations of *m*-xylene saturation pressure data from the Antoine correlation (■) and AEOS (●) equations: solid symbols, this work; hollow symbols, Forziati et al.;[7] dotted symbols, Park and Gmehling.[9]

where *p* is the pressure, *T* is the temperature, and *A*, *B*, and *C* are adjustable parameters. In addition, to obtain a good representation of isobaric VLE data for systems containing one associating component, the AEOS equation of state[10] was used.

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 has been shown by Pfohol et al.[11]

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

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* To whom correspondence should be addressed. E-mail: skm@ichf.edu.pl.

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Table 1. Pure Component Properties

Cyclohexanol

Antoine (kPa/K)	A	B	C	q	r
	6.0161296	1231.997	126.2361	3.51	4.27

AEOS	T'_c/K	P'_c/atm	ω'	$\Delta H°$/(J mol^{-1})	$\Delta S°$/(J mol^{-1} K^{-1})	$\Delta C_p°$/(J mol^{-1} K^{-1})
	641.5308	42.9783	0.34182	−17.36382	−86.432	−102.172

m-Xylene

Antoine (kPa/K)	A	B	C	q	r
	6.13942831	1465.8696	57.6397	3.54	4.66

AEOS	T'_c/K	P'_c/atm	ω'	$\Delta H°$/(J mol^{-1})	$\Delta S°$/(J mol^{-1} K^{-1})	$\Delta C_p°$/(J mol^{-1} K^{-1})
	621.29	36.49	0.3141			

general, depends on the nature of the associating compound. An equilibrium mixture of associated species is treated as a mixture of nonreacting polymeric aggregates.

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

$$z = z^{(\mathrm{ph})} + z^{(\mathrm{ch})} - 1 \tag{2}$$

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.[12]

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

where $a(T)$, b, and c are generalized as 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 the behavior of such compounds as alcohols, phenols, ketones, amines, pyridine bases, and other similar compounds.[10] In the Mecke−Kempter model, all subsequent association constants are equal. This leads to the following term for the chemical contribution:

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

The complete equation of state for an associating compound (eq 3) has the following characteristic parameters: the standard enthalpy ($\Delta H_{ii}°$) and entropy ($\Delta S_{ii}°$) 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 adjustable parameters with vapor pressure and liquid density as a function of temperature. The values of the parameters, including heat capacity (C_p), are given in Table 1. The temperature dependence of the association constant can be expressed by assuming that $\Delta H_{ij}°$ and $\Delta S_{ij}°$ of association are linearly dependent on temperature (the appropriate values of C_p are given in Table 1),

$$\ln K_{ij} = \frac{-\Delta H°(T_0) + \Delta C_p° T_0}{RT} + \frac{1}{R}[\Delta S°(T_0) - \Delta C_p° - \Delta C_p° \ln T_0] + \frac{\Delta C_p°}{R}\ln T \tag{5}$$

The determination of pure component parameters is a 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 $z^{(\mathrm{ph})}$ and $z^{(\mathrm{ch})}$ terms is correct, that is, that the effects of association and nonspecific interactions on the compressibility factor are correctly divided. In principle, this can be accomplished by using physically meaningful values of the association parameters $\Delta H_{ii}°$ and $\Delta S_{ii}°$ (Table 1).

The correlation results for pure component vapor pressures by means of both equations are given in Figures 1 and 2. There is almost no difference between the correlation abilities of the two equations. In the case of *m*-xylene, some systematic deviations are observed for the Forziati et al.[7] data.

VLE Measurements. The vapor−liquid equilibrium measurements were made with an ebulliometer,[13] enabling the sampling of the liquid phase and vapor condensate without interruption of boiling. The P, T, x, y method described by Rogalski and Malanowski[14] was used. Temperature was measured with Roberteau mercury-in-glass adjustable thermometers, calibrated after each series of measurements using an H. Tinsley and Co. Mueller bridge (type 4772) with a platinum resistance thermometer (type 5187SA), calibrated to class I by NPL (Teddington, U.K.), according to the IPTS-68. The estimated uncertainty is $|\delta T|/\mathrm{K} = 0.01$. Pressure was measured by the comparative method proposed by Świętosławski[15] (measurement of water boiling temperature with a second ebulliometer, connected to the same pressure stabilizing system and equipped with a calibrated Roberteau thermometer). The estimated uncertainty is $|\delta P|/\mathrm{Pa} = 3$. All results are reported in IPTS-68. The results can be recalculated to IPS-90, for the temperature range 360−435 K, according to the formula $T_{90} = T_{68} + 0.045437 - 0.0001917T_{68}$ derived from Preston-Thomas data.[16]

Analytical Method. The sample composition was determined with a GLC (gas chromatograph: Wily Giede, type GCHF-18/2 with numerical integrator, thermal conductivity detector, and PEG-105 on Chromosorb P 60−80 mesh column). The estimated uncertainty is $|\delta x_1| = 0.002$; $|\delta y_1| = 0.005$.

Results

The properties of pure components are given in Table 1. The results of VLE measurements obtained for the equi-

Table 2. VLE in the System Cyclohexanol (1) + 1,3-Dimethylbenzene (2)

x_1	y_1	T/K	x_1	y_1	T/K
P/kPa = 94.925			P/kPa = 19.998		
0.0000	0.0000	409.85	0.0000	0.0000	360.60
0.0204	0.0207	409.74	0.0145	0.0137	360.59
0.0359	0.0353	409.76	0.0313	0.0276	360.62
0.0478	0.0458	409.77	0.0515	0.0422	360.65
0.0791	0.0717	409.94	0.2007	0.1098	361.50
0.2217	0.1642	410.73	0.3141	0.1434	362.51
0.3690	0.2425	412.20	0.4005	0.1692	363.52
0.4673	0.2960	413.54	0.4745	0.1949	364.54
0.6139	0.3910	416.22	0.5554	0.2304	366.10
0.6932	0.4574	418.22	0.6040	0.2568	367.19
0.7818	0.5521	420.59	0.6754	0.3052	368.82
0.8643	0.6737	424.38	0.7522	0.3774	371.20
1.0000	1.0000	431.27	0.8210	0.4742	375.43
			0.9144	0.6716	380.19
			1.0000	1.0000	387.51

librium pressure (P/kPa), the temperature (T/K), and the mole fraction of component 1 in the liquid (x_1) and vapor (y_1) phases are listed in Table 2. The only literature data available are at the constant pressure 6 kPa.[17]

Correlation. The results of measurements and available literature data[17] have been correlated with the Redlich−Kister and SSF equations with two to six adjustable parameters, the NRTL equation with three adjustable parameters, and the UNIQUAC and Wilson equations. The exact form of these equations was given previously.[18] The odd parameters of the SSF equation correspond to A_i, while even ones correspond to a_i. The correlation results are summarized in Table 3. The best results for single isobars were obtained with equations having a larger number of adjustable parameters (Redlich−Kister, SSF).

For correlation in larger intervals of pressure and temperature, the AEOS equation of state has been applied. The parameters of the AEOS equation obtained from pure component data (Table 1) were used unchanged for mixture calculations. The binary parameters a, b, and c of the Yu et al.[12] equation ($z^{(\mathrm{ph})}$ term) were calculated using the classical mixing rules

Table 3. Correlation of VLE[a]

equation	(1)	(2)	(3)	(4)	(5)	(6)	RMSD(P)/Pa	RMSD(P)/%	RMSD(y)
P/kPa = 94.925 (Own Data)									
R-K-2[b]	0.60649	−0.09831					352.2	0.37	0.0175
R-K-3[c]	0.60832	−0.10058	−0.02571				357.6	0.38	0.0178
R-K-4[d]	0.60425	−0.07985	−0.4119	−0.11023			311.8	0.33	0.0171
R-K-5[e]	0.59501	−0.08937	0.03258	−0.17946	−0.21662		261.5	0.28	0.0148
R-K-6[f]	0.58843	−0.14405	0.00784	0.05562	−0.37907	−0.47775	165.7	0.17	0.0113
NRTL[g]	−34128.66	28711.12	−0.2114				361.2	0.38	0.0206
UNIQUAC[h]	4602.40	−1882.80					405.3	0.43	0.0189
Wilson[i]	−13001.50	2704.14					370.6	0.39	0.0186
SSF-2[j]	0.57660	0.97700					849.5	0.89	0.0214
SSF-4[k]	0.52500	0.94531	0.089208	0.83039			440.7	0.46	0.0209
SSF-6[l]	0.65264	0.89476	0.030422	0.25729	−0.07233	0.47764	430.8	0.45	0.0219
AEOS[m]	0.0000						4249.3	4.48	0.0336
AEOS[n]	0.01942						462.8	0.49	0.0203
AEOS[o]	0.01840						517.9	0.55	0.0208
P/kPa = 19.998									
R-K-2[b]	0.91760	−0.22270					224.4	1.12	0.0090
R-K-3[c]	0.92469	−0.26623	0.058358				197.7	0.99	0.0080
R-K-4[d]	0.92354	−0.26325	0.061321	−0.021171			206.1	1.03	0.0082
R-K-5[e]	0.93026	−0.24025	−0.016538	−0.056708	0.22428		201.6	1.01	0.0100
R-K-6[f]	0.93904	−0.17493	0.056773	−0.50335	0.19615	0.79626	163.2	0.82	0.0147
NRTL[g]	17943.32	−1882.04	0.3362				194.4	0.97	0.0088
UNIQUAC[h]	9567.39	−4293.57					189.2	0.95	0.0082
Wilson[i]	−19974.02	3028.06					192.7	0.96	0.0087
SSF-2[j]	0.944	0.8656265					189.5	0.95	0.0076
SSF-4[k]	0.011945	1.26003	0.93317	0.86166			216.0	1.08	0.0087
SSF-6[l]	0.12225	−5.23743	0.94917	0.87396	0.01300	−0.06649	221.5	1.11	0.0192
AEOS[m]	0.0000						1245.1	6.23	0.0285
AEOS[n]	0.01739						283.6	1.42	0.0159
AEOS[o]	0.01840						293.3	1.47	0.0158
P/kPa = 6.0 (Literature[17] Data)									
R-K-2[b]	1.322 00	−0.12840					181.0	3.02	0.0755
R-K-3[c]	1.319 78	−0.25517	0.32366				73.8	1.23	0.0811
R-K-4[d]	1.330585	−0.27969	0.26914	0.129213			67.2	1.12	0.0834
R-K-5[e]	1.33738	−0.21901	0.14402	−0.0401	0.36729		43.4	0.72	0.0852
R-K-6[f]	1.337920	−0.22666	0.10281	0.0372	0.44605	−0.15110	43.3	0.72	0.0884
NRTL[g]	19647.77	11005.30	0.78549				87.7	1.46	0.0808
UNIQUAC[h]	4940.58	−144.64					178.5	2.97	0.0742
Wilson[i]	−17026.63	−3543.21					149.2	2.49	0.0759
SSF-2[j]	1.2400	0.9330					273.8	4.56	0.0635
SSF-4[k]	1.29055	0.96958	0.080382	−0.35729			165.8	2.76	0.0838
SSF-6[l]	0.84446	1.92936	1.2440	−0.84344	−0.65048	1.92936	58.6	0.98	0.0879
AEOS[m]	0.0000						827.3	13.79	0.0186
AEOS[n]	0.02502						156.2	2.60	0.0611
AEOS[o]	0.01840						288.6	4.81	0.0469

[a] The corrections for the vapor phase nonideality for the "γ/φ" method were calculated using data and equations supplied for second virial coefficients and liquid molar volume by Daubert and Danner.[20] [b] Redlich−Kister with two parameters. [c] Redlich−Kister with three parameters. [d] Redlich−Kister with four parameters. [e] Redlich−Kister with five parameters. [f] Redlich−Kister with six parameters. [g] NRTL with adjustable α. [h] UNIQUAC. [i] Wilson. [j] SSF with two parameters. [k] SSF with four parameters. [l] SSF with six parameters. [m] AEOS without adjustable parameters. [n] AEOS with one adjustable parameter. [o] AEOS with one predicted parameter.

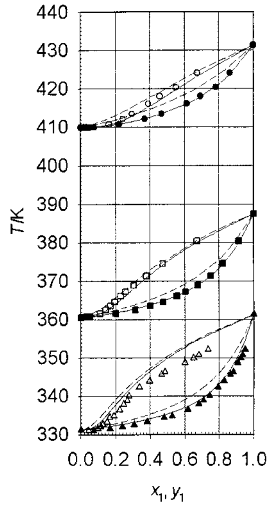

Figure 3. VLE in the system cyclohexanol + m-xylene: ●, this work at P/kPa = 19.998; ■, this work at P/kPa = 94.925; ▲, Comelli et al.[17] data at P/kPa = 6.0; solid symbols, bubble points; hollow symbols, dew points; solid line, correlation and prediction (θ_{12} = 0.0184); dotted line, prediction from pure component properties (θ_{12} = 0).

$$a = \sum_{i=1}^{2}\sum_{i=1}^{2} x_i x_j (1 - \theta_{ij})\sqrt{a_i a_j} \tag{6}$$

$$b = \sum_{i=1}^{2} x_i b_i \tag{7}$$

$$c = \sum_{i=1}^{2} x_i c_i \tag{8}$$

The AEOS equation has only one binary adjustable parameter θ_{12}.

The root-mean-square deviations [RMSD(p)] of a property p representing P or y_1 are calculated from the equation

$$\mathrm{RMSD}(p) = \sqrt{\frac{\sum_{i=1}^{n}(p_i^{\mathrm{calcd}} - p_i^{\mathrm{exptl}})^2}{n - m}} \tag{9}$$

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

The correlation has been carried out three ways. First, the results for each isobar were fitted separately. Then, the mean value of θ_{12} (0.0184) was calculated and y_1, T values were predicted for experimental x_1, P using this value, and finally y_1, T values were predicted from pure component properties (θ_{12} = 0). The results are compared in Table 2 and Figure 3. The differences between values obtained by direct correlation and by prediction with a constant value of θ_{12} are negligible. Systematic deviations in the composition of the vapor phase, both for correlation and prediction, are observed for the literature data. This is also observed for all equations representing the "γ/φ" method. The deviations of the measured data from the calculations with the AEOS equation with a constant θ_{12} (0.0184) are <2% for both pressure and composition.

Table 4. Azeotropic Parameters

x_1	P/kPa	T/K	δT/K	remarks
0.154	101.3	412.3	0.1	M. Lecat[19]
0.03	94.925	409.73	0.12	estimated from own measurements
0.017	19.998	360.58	0.02	
0.001	6.0	330.95	0.11	estimated from Comelli et al.[17.]

Azeotropes. A positive azeotrope, first reported by Lecat,[19] was observed. The azeotropic parameters are given in Table 4. These depend strongly on temperature. With a decrease of temperature, the cyclohexanol content decreases. At the lowest temperature, an almost tangent azeotrope is observed. The cyclohexanol content is much lower than that reported by Lecat, while the azeotropic depression remains the same.

Literature Cited

(1) Kojima, K.; Tochigi, T. *Prediction of Vapour-Liquid Equilibria by the ASOG Method*; Elsevier: Amsterdam, 1979.

(2) Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapour-Liquid Equilibria Using UNIFAC*; Elsevier: Amsterdam, 1977.

(3) Goodwin, S. R.; Newsham, D. M. T. Relative Volatilities of Mixtures of Cyclohexanol and Cyclohexanone in Pressure Range 30−750 mmHg. *J. Chem. Eng. Data* **1974**, *19*, 363−366.

(4) Sipowska, J. T.; Wieczorek, S. A. Vapour pressures and excess Gibbs free energies of (cyclohexanol + n-heptane) between 303.147 and 373.278 K. *J. Chem. Thermodyn.* **1984**, *16*, 693−699.

(5) Gierycz, P.; Rogalski, M.; Malanowski, S. Vapour-Liquid Equilibria in Binary Systems formed by N-Methylpirrolidone with Hydrocarbons and Hydroxyl Derivatives. *Fluid Phase Equilib.* **1985**, *22*, 107−122.

(6) Ambrose, D.; Ghiassee, N. B. Vapour pressures and critical temperatures and critical pressures of C5 and C6 cyclic alcohols and ketones. *J. Chem. Thermodyn.* **1987**, *19*, 903−909.

(7) Forziati, A. F.; Norris, W. R.; Rossini, F. D. Vapor pressures and boiling points of 60 API−NBS hydrocarbons. *J. Res. Natl. Bur. Stand. (U.S.)* **1949**, *43*, 555−563.

(8) Osborne, N. S.; Ginnings, D. C. Measurements of Heat of Vaporization and Heat Capacity of a Number of Hydrocarbons. *J. Res. Natl. Bur. Stand. (U.S.)* **194**7, *39*, 453−477.

(9) Park, S.-J.; Gmehling, J. Isobaric Vapor-Liquid Equilibrium Data for the Binary Systems 1,3,5-Trimethylbenzene/N-Formylmorpholine and m-Xylene/N-Formylmorpholine. *J. Chem. Eng. Data* **1989**, *34*, 399−401.

(10) Anderko, A.; Malanowski, S. K. Calculation of solid−liquid, liquid−liquid and vapor-liquid equilibria by means of an equation of state incorporating association. *Fluid Phase Equilib.* **1989**, *48*, 223−241.

(11) Pfohl, O.; Pagel, A.; Brunner, G. Phase equilibria in systems containing o-cresol, p-cresol, carbon dioxide, and ethanol at 323.15−473.15 K and 10−35 MPa. *Fluid Phase Equilib.* **1999**, *157*, 53−79.

(12) Yu, J. M.; Lu, B. C.-Y.; Iwai, Y. Simultaneous calculation of VLE and saturated liquid and vapor volumes by means of a cubic EOS. *Fluid Phase Equilib.* **1987**, *37*, 207−222.

(13) Rogalski, M.; Rybakiewicz, K.; Malanowski, S. K. Rapid and Accurate Method for Determination of Vapour-Liquid Equilibrium. *Ber. Bunsen Ges.* **1977**, *81*, 1070−1073.

(14) Rogalski, M.; Malanowski, S. Ebulliometers Modified for the Accurate Determination of Vapour-Liquid Equilibrium. *Fluid Phase Equilib.* **1980**, *5*, 97−112.

(15) Świętosławski, W. *Ebulliometric Measurements;* Reinhold: New York, 1945.

(16) Preston-Thomas, H. The International Temperature Scale of 1990 (ITS-90). *Metrologia* **1990**, *27* (3−10), 107.

(17) Comelli, F.; Francesconi, R.; Arcelli, A. Isobaric Vapour-Liquid Equilibrium and Liquid-Phase Enthalpy of mixing Data for the Binary Mixtures of m- and p-Xylene with Cycloxexanol. *Can. J. Chem. Eng.* **1988**, *66*, 644−50.

(18) Malanowski, S.; Anderko, A. *Modelling Phase Equilibria: Thermodynamic Background and Practical Tools*; Wiley: New York, 1992.

(19) Lecat, M. *Tables Azéotropiques, Vol. 1, Azéotropes binaires orthobares*; Edited by the author: Ucole-Bruxelles, 1949.

(20) Daubert, T. E.; Danner, R. P. *Physical and Thermodynamic Properties of Pure Chemicals*, Core Edition and Supplements 1−8; Taylor & Francis: London, 1998.

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