Table III. Parameters of Eq 2 for Ions in Water-Acetamide Mixtures

ion	$B_{i,v}$	$-B_{i,s(0)}$	a	$\Delta = \left[\frac{1}{n}\sum_{i=1}^{n}(B_i^{calcd} - B_i^{exptl})^2\right]^{1/2}$
		Water		
Na^+	0.0835			
K^+/Cl^-	0.0570	0.0984	0.01745	0.000 36
Cs^+	0.0474	0.1214	0.01577	0.000 31
Br^-	0.0340	0.1305	0.02239	0.000 43
I^-	0.0150	0.1448	0.01598	0.001 00
		5.10 mol % $AcNH_2$		
Na^+	0.1141			
K^+/Cl^-	0.0957	0.1078	0.0167	0.000 34
Cs^+	0.0848	0.1269	0.0162	0.000 31
Br^-	0.0706	0.1374	0.0215	0.000 63
I^-	0.0373	0.1442	0.0169	0.000 69
		11.55 mol % $AcNH_2$		
Na^+	0.1270			
K^+/Cl^-	0.1156	0.1114	0.0188	0.000 23
Cs^+	0.1127	0.1330	0.0164	0.000 30
Br^-	0.0864	0.1351	0.0220	0.000 56
I^-	0.0492	0.1485	0.0169	0.000 70
		23.36 mol % $AcNH_2$		
Na^+	0.1358			
K^+/Cl^-	0.1347	0.1133	0.0205	0.000 50
Cs^+	0.1333	0.1309	0.0188	0.000 55
Br^-	0.0998	0.1398	0.0233	0.000 46
I^-	0.0562	0.1503	0.0170	0.000 79

are negative. In the case of aqueous solutions the $B_{i,s(0)}$ values as absolute values are larger than $B_{i,v}$ values. From this it follows that the addition of acetamide to water reduces the difference between $B_{i,v}$ and $B_{i,s(0)}$; however, the $B_{i,s(0)}$ values increase only a little. Moreover, it is noticed that the coefficient $B_{i,s(0)}$ as absolute value increases with increasing ionic radii. The facts observed lead one to conclude that the I^- ion has the largest breaking effect on the structure of water-acetamide mixture. The effect of temperature on $B_{i,s}$ (parameter a) decreases with increasing ionic radii.

Glossary

A	viscosity coefficient, $(dm^3\ mol^{-1})^{1/2}$
B	viscosity coefficient, $dm^3\ mol^{-1}$
dB/dT	temperature coefficient of B, $dm^3\ mol^{-1}\ deg^{-1}$
$B_{i,v}$	positive contribution due to size and shape of solvated ion
$B_{i,s}$	negative contribution related to destruction of solvent structure by ion
a	parameter of eq 2

Registry No. NaCl, 7647-14-5; NaI, 7681-82-5; KCl, 7447-40-7; KBr, 7758-02-3; CsI, 7789-17-5; acetamide, 60-35-5.

Literature Cited

(1) Stokes, R. H.; Mills, R. *International Encyclopedia of Physical Chemistry and Chemical Physics*; Pergamon: New York, 1965; Vol. 3.
(2) Kaminsky, M. *Z. Phys. Chem. (Munich)* **1955**, *5*, 154.
(3) Kaminsky, M. *Z. Phys. Chem. (Munich)* **1956**, *8*, 173.
(4) Kaminsky, M. *Z. Phys. Chem. (Munich)* **1957**, *12*, 206.
(5) Kaminsky, M. *Discuss. Faraday Soc.* **1957**, *24*, 171.
(6) Stokes, R. H.; Mills, R. *Viscosity of Electrolytes and Related Properties*; Pergamon: New York, 1965.
(7) Woldan, M. *Z. Phys. Chem. (Munich)* **1986**, *150*, 201.
(8) Woldan, M. *J. Chem. Eng. Data* **1985**, *30*, 479.
(9) Woldan, M. *Z. Phys. Chem. (Leipzig)* **1988**, *269*, 628.
(10) Woldan, M. *Rev. Roum. Chem.* **1988**, *33*, 125.
(11) Jones, G.; Dole, M. *J. Am. Chem. Soc.* **1929**, *51*, 2950.
(12) Kraeft, W. D.; Einfeldt, J. *Z. Phys. Chem. (Leipzig)* **1968**, *237*, 267; *Z. Phys. Chem. (Leipzig)* **1968**, *239*, 415.
(13) Krumgalz, B. S. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1275.
(14) Frank, M. S.; Wen, W. Y. *Discuss. Faraday Soc.* **1957**, *24*, 133.

Received for review June 4, 1987. Revised June 14, 1988. Accepted July 20, 1988.

Isobaric Vapor-Liquid Equilibrium for the Cumene-Phenol System

Emilio Cepeda,* Cristina González, and Jose M. Resa

Departamento de Química Técnica, Colegio Universitario de Alava, Apartado 450, Vitoria, Spain

Isobaric vapor-liquid equilibrium data for the cumene-phenol system were obtained at 13.33, 53.33, and 101.33 kPa pressures by using a vapor recirculating type of equilibrium still. The system forms a minimum-boiling azeotrope at atmospheric pressure. The activity coefficient data were tested for thermodynamic consistency by the methods of Herington, Black, and van Ness and correlated by the Norrish and Twigg, van Laar, and Wilson equations.

Introduction

Cumene can be converted to phenol and acetone via cumene hydroperoxide (*1*). In this process, the result is a mixture of cumene, phenol, and acetone. Cumene free of phenol is required for recycling to the cumene oxidation stage because the presence of phenol is detrimental for the oxidation. For the separation of this mixture, fractional distillation can be used, but the data in the literature for vapor-liquid equilibrium on this system are conflicting. Lecat (*2*) and Norrish and Twigg (*3*) did not find an azeotropic point at atmospheric pressure. In contrast, a patent (*4*) lists an azeotrope of 0.97 mole fraction cumene.

Table I. Physical Properties of the Pure Compounds: Density, Refractive Index, and Boiling Point

	ρ, g/cm^3		n_D		T_B, K	
	obsd	ref *6*	obsd	ref *6*	obsd	ref *6*
cumene (T = 298.15 K)	0.8574	0.8575	1.4889	1.4889	425.54	425.54
phenol (T = 318.15 K)	1.0542	1.0545	1.5400	1.5402	454.96	454.98

In the present paper, the vapor-liquid equilibrium of the cumene-phenol system was measured in order to clarify the different results at 13.33, 53.33, and 101.33 kPa. Furthermore the composition of the azeotrope at 101.33 kPa was determined by using a packed column.

Experimental Section

Chemicals. Cumene was supplied by Merck, and phenol was supplied by PANREAC. They are analytical-grade reagents and were purified by distillation in a laboratory column. Physical properties of these components are listed in Table I along with their literature values.

Apparatus and Procedure. The still used to obtain vapor-liquid equilibrium data was an Othmer modified vapor-liquid

0021-9568/89/1734-0270$01.50/0 © 1989 American Chemical Society

Table II. Refractive Index–Composition Data at 318.15 ± 0.1 K

mole fractn cumene	n_D	mole fractn cumene	n_D	mole fractn cumene	n_D
0.0000	1.5400	0.4979	1.5041	0.8927	1.4828
0.0511	1.5358	0.5955	1.4982	0.9469	1.4809
0.1016	1.5312	0.6977	1.4928	0.9803	1.4797
0.2021	1.5236	0.8116	1.4870	1.0000	1.4787

Table III. Vapor Pressures of Cumene

T, K	P, Torr	T, K	P, Torr	T, K	P, Torr
349.45	63.46	397.45	340.40	419.95	656.00
359.40	92.35	401.85	389.53	423.15	714.00
368.65	132.60	406.25	444.32	425.35	756.20
376.55	174.94	412.75	533.98	426.05	770.00
388.60	255.73	414.95	572.68	426.25	774.00
392.70	298.59				

equilibrium recirculation still (*5*). The vapor pressure of cumene was determined by using the same still without the condenser receiver.

The pressures were measured with an accuracy of ±0.13 kPa, and the temperatures were measured by a mercury thermometer to within 0.1 K.

To verify the azeotropic composition at 101.3 kPa, a Pyrex glass column (30-mm o.d. and 100 mm long) packed with Dixon rings of 2 mm was used.

Analysis. Compositions of the liquid and condensed vapor samples were obtained from measurements of their refractive index at 318.15 K by using an Abbe type refractometer with an accuracy of ±0.0002.

Analysis was made by means of a carefully prepared calibration curve. The data were fitted to the equation

$$n_D = 0.02174x^2 - 0.0827x + 1.53975 \qquad (1)$$

with a correlation coefficient of 0.9999 and a standard deviation in the composition measurements of 0.0003 mole fraction. Table II shows the refractive index–composition values.

Results and Discussion

Because important differences were found among the literature values for the vapor pressure of cumene (*6–8*), they were measured experimentally. The experimental data agree with those of ref *6*. The results listed in Table III were fitted to the Antoine equation by the least-squares method. The Antoine constants used in this work are

	A	B	C
cumene	7.250 09	1671.459	230.000
phenol (*6*)	7.134 57	1516.072	174.569

The vapor–liquid equilibrium data for the system cumene–phenol at 13.33, 53.33, and 101.33 kPa are reported in Tables IV, V, and VI, respectively.

The activity coefficient at each data point was calculated by using

$$\gamma_i = y_i \phi_i P / x_i f_i{}^\circ \qquad (2)$$

where x_i and y_i are the liquid and vapor mole fractions, P is the pressure, γ_i is the fugacity coefficient, and $f_i{}^\circ$ is the fugacity in the standard state. Fugacity coefficients were calculated by means of a virial equation truncated after the second term:

$$\ln \phi_i = \frac{P}{RT}\left(2\sum^{j} y_j B_{ij} - B\right) \qquad j = 1, 2, \ldots n \qquad (3)$$

where B is the second virial coefficient, calculated by

$$B = \sum^{i}\sum^{j} y_i y_j B_{ij} \qquad i \text{ and } j = 1, 2, \ldots n \qquad (4)$$

where n is the number of components and B_{ij} represents interactions between molecules i and j. To predict the virial coefficients from available data, we used a method developed by Hayden and O'Connell (*9*). The values of the fugacity and activity coefficients are shown in Tables IV, V, and VI.

Table IV. Vapor–Liquid Equilibrium Data for the Cumene–Phenol System at 13.33 kPa

x_1	y_1	T, K	γ_1	γ_2	ϕ_1	ϕ_2
0.0000	0.0000	393.85	2.4135	1.0000	0.9929	0.9941
0.0983	0.4604	381.35	2.3006	1.0105	0.9911	0.9936
0.1737	0.5929	375.47	2.0995	1.0332	0.9904	0.9934
0.2653	0.6895	371.43	1.8313	1.0792	0.9899	0.9932
0.3239	0.7163	369.61	1.6408	1.1204	0.9897	0.9931
0.4077	0.7618	368.03	1.4832	1.1788	0.9895	0.9931
0.4721	0.7821	366.80	1.3650	1.2528	0.9893	0.9930
0.6017	0.8303	365.25	1.1923	1.4715	0.9891	0.9930
0.6990	0.8564	364.18	1.1068	1.6896	0.9890	0.9930
0.7739	0.8763	363.65	1.0603	1.9051	0.9889	0.9930
0.8719	0.9198	362.40	1.0200	2.2827	0.9887	0.9930
0.9222	0.9459	361.75	1.0076	2.5396	0.9886	0.9930
0.9653	0.9727	361.30	1.0016	2.8093	0.9886	0.9930
1.0000	1.0000	361.30	1.0016	3.0697	0.9886	0.9930

Table V. Vapor–Liquid Equilibrium Data for the Cumene–Phenol System at 33.33 kPa

x_1	y_1	T, K	γ_1	γ_2	ϕ_1	ϕ_2
0.0000	0.0000	433.07	1.4344	1.0000	0.9805	0.9836
0.1965	0.5566	415.23	1.9583	1.0000	0.9747	0.9819
0.2360	0.5982	413.50	1.8453	1.0142	0.9742	0.9817
0.3253	0.6688	410.49	1.5962	1.0734	0.9733	0.9815
0.3667	0.6895	409.85	1.5018	1.1086	0.9731	0.9815
0.4325	0.7280	408.27	1.3809	1.1722	0.9726	0.9813
0.4769	0.7418	407.60	1.3152	1.2207	0.9724	0.9813
0.5095	0.7577	407.22	1.2728	1.2603	0.9723	0.9813
0.5894	0.7883	405.95	1.1824	1.3791	0.9719	0.9813
0.7300	0.8389	404.88	1.0561	1.7202	0.9716	0.9813
0.7719	0.8564	404.24	1.0290	1.8602	0.9714	0.9813
0.8028	0.8719	403.87	1.0135	1.9677	0.9712	0.9813
0.8944	0.9198	403.51	1.0000	2.1908	0.9711	0.9816
0.9580	0.9628	403.07	1.0000	2.0523	0.9710	0.9819
1.0000	1.0000	402.39	1.0000	1.7309	0.9708	0.9820

Table VI. Vapor–Liquid Equilibrium Data for the Cumene–Phenol System at 101.33 kPa

x_1	y_1	T, K	γ_1	γ_2	ϕ_1	ϕ_2
0.0000	0.0000	454.99	3.1443	1.0000	0.9695	0.9740
0.0570	0.2401	446.80	2.5427	1.0059	0.9655	0.9726
0.0717	0.2723	445.65	2.4344	1.0089	0.9649	0.9724
0.0932	0.3326	443.80	2.2988	1.0141	0.9640	0.9722
0.1871	0.4883	438.05	1.9024	1.0453	0.9614	0.9714
0.2209	0.5429	435.95	1.8038	1.0596	0.9605	0.9711
0.3444	0.6339	432.25	1.5261	1.1317	0.9588	0.9708
0.3667	0.6559	431.65	1.4845	1.1491	0.9586	0.9708
0.4514	0.7048	430.05	1.3438	1.2312	0.9578	0.9707
0.5178	0.7319	428.95	1.2524	1.3156	0.9573	0.9706
0.5859	0.7598	428.05	1.1761	1.4214	0.9569	0.9706
0.6159	0.7739	427.70	1.1480	1.4742	0.9568	0.9706
0.7049	0.8133	426.90	1.0827	1.6516	0.9564	0.9707
0.7163	0.8173	426.80	1.0761	1.6765	0.9563	0.9708
0.7497	0.8325	426.55	1.0588	1.7525	0.9562	0.9708
0.8282	0.8763	425.90	1.0285	1.9532	0.9558	0.9711
0.8564	0.8853	425.80	1.0205	2.0364	0.9558	0.9712
0.9036	0.9245	425.60	1.0100	2.1982	0.9557	0.9715
0.9387	0.9487	425.45	1.0044	2.3467	0.9556	0.9717
0.9678	0.9678	425.35	1.0013	2.4983	0.9555	0.9720
1.0000	1.0000	425.54	1.0000	2.7105	0.9556	0.9724

The thermodynamic consistency of the data was examined by using the point-to-point test originated by van Ness et al. (*10*) and modified by Fredenslund et al. (*11*) using a fifth-order Legendre polynomial. According to this test, the data point is considered consistent if the average absolute deviation in y is less than 0.01. The estimated standard deviations for vapor-phase compositions were 0.015 at 101.33 kPa and 0.01 at 53.33 and 13.33 kPa. The data for the three pressures were also assessed at thermodynamic consistency by applying the Herington (*12*, *13*) and Black (*14*) test. The data satisfied the

Table VII. Correlation Constants and Correlation Coefficients

		P, kPa		
		101.33	53.33	13.33
van Laar	A_{12}	0.9158	0.7399	1.0910
	A_{21}	0.9239	1.0047	1.2212
	r^2	0.9989	0.9991	0.9982
Norrish and Twigg	M	-1.7910	-1.9169	-2.1282
	C	1.7548	1.9316	2.2124
	r^2	0.9989	0.9991	0.9979
Wilson	Λ_{12}	0.5017	0.7065	0.5524
	Λ_{21}	0.6237	0.4600	0.4960
	σ	0.0267	0.0107	0.0115

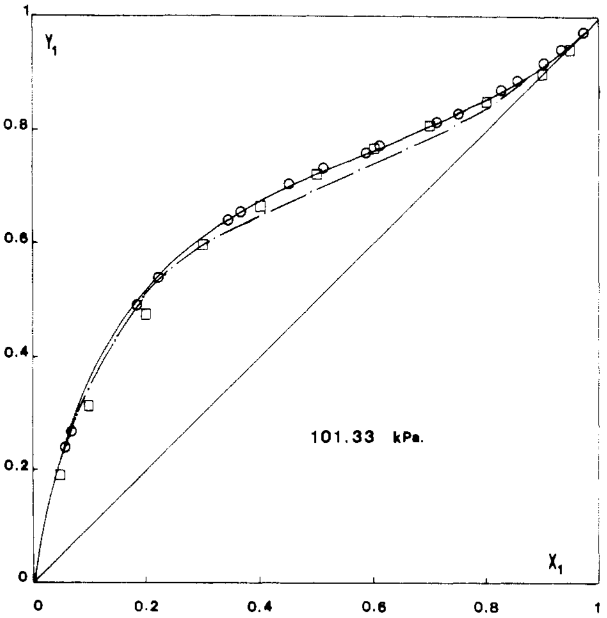

Figure 1. x-y phase equilibrium diagram for cumene (1)-phenol (2) at 101.33 kPa: (O) experimental data; (□) values obtained by means of UNIFAC method; (—) Norrish-Twigg's correlation; (-·-) Wilson's correlation.

criteria of all the tests, thereby showing them to be thermodynamically consistent.

The activity coefficient data were fitted into the Norrish and Twigg (*3*), van Laar (*15*), and Wilson (*16*) correlations. The constants in these correlations are given in Table VII. The Norrish and Twigg equation correlated the composition data properly, but the activity coefficients calculated with it are bigger than the experimental ones. Van Laar and Wilson's equations do not correlate the composition data so well. In Figures 1-3 the experimental values of composition and their fit to Norrish and Twigg and Wilson equations are plotted.

The activity coefficients have also been calculated by the UNIFAC method (*17*), which shows that the experimental values are lower than the predicted ones. This method predicts an azeotrope at 0.90 mole fraction cumene. A very different value from the experimental one was found by us at atmospheric pressure. Data obtained with this method are plotted in Figures 1-3.

The data for 101.33 kPa are different from those of Norrish and Twigg for all compositions (*3*). These authors and Lecat (*2*) do not indicate an azeotrope, but there is one indicated in a patent (*4*) at 101.33 kPa for $x = 0.974$ and $T = 422.15$ K. We found an azeotropic point for $x = 0.9678$ and $T = 425.35$ K, and the composition of this azeotrope was confirmed by use of a high-efficiency packed column.

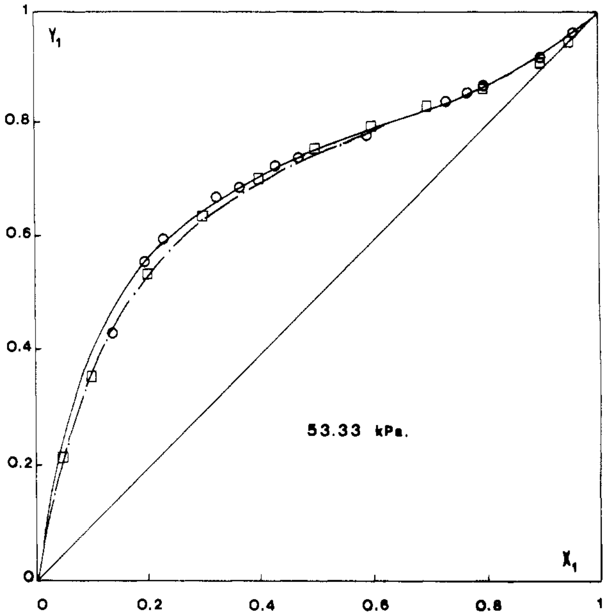

Figure 2. x-y phase equilibrium diagram for cumene (1)-phenol (2) at 53.33 kPa. Symbols as in Figure 1.

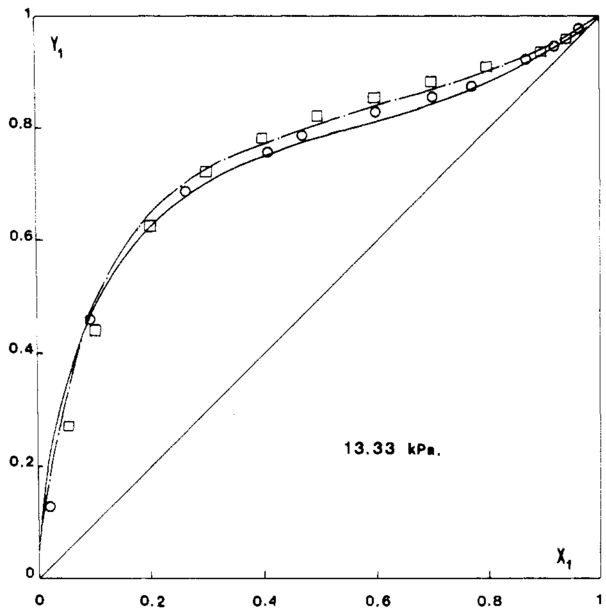

Figure 3. x-y phase equilibrium diagram for cumene (1)-phenol (2) at 13.33 kPa. Symbols as in Figure 1.

Glossary

A_{12}, A_{21}	constants in van Laar correlation
B	second virial coefficient, cm^3 mol^{-1}
f_i°	fugacity in standard state, kPa
M, C	constants in Norrish and Twigg equation
n	number of points
n_D	refractive index
P	pressure, kPa
r^2	correlation coefficient
R	gas constant, J/(mol K)
T	temperature, K
T_B	boiling point, K
x	liquid-phase mole fraction
y	vapor-phase mole fraction

Greek Letters

γ	activity coefficient
ϕ	fugacity coefficient
Λ_{12}, Λ_{21}	constants in Wilson model
ρ	density, g/cm^3
σ	average deviation $[\sum(y_{\text{exptl}} - y_{\text{calcd}})/n]$

Subscripts

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

Registry No. Cumene, 98-82-8; phenol, 108-95-2.

Literature Cited

(1) Weissermel, K.; Arpe, H. J. *Industrial Organic Chemistry*; Verlag-Chemie: Weinheim, 1973.
(2) Lecat, J. *Tables Azeotropiques*; L'auteur: Bruselles, 1949.
(3) Norrish, R. S.; Twigg, G. H. *Ind. Eng. Chem.* **1954**, *46*, 201.
(4) Dow Chemical Corp., unpublished data. Horsley, L. H. *Azeotropic Data III*; Gould, R. F., Ed.; American Chemical Society: Washington, DC, 1973.
(5) Mato, F.; Cepeda, E. *An. Quim.* **1984**, *80*, 338.
(6) Riddick, J.; Bunger, W. B. *Organic Solvents*; Wiley Interscience: New York, 1970.
(7) *Handbook of Chemistry and Physics*, 52nd ed.; Weast, R. C., Ed.; CRC Press: Cleveland, 1971.
(8) Reid, R. C.; Praustnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; MacGraw-Hill: New York, 1977.
(9) Hayden, J. G.; O'Connell, J. P. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209.
(10) Van Ness, H. C.; Byer, S. M.; Gibbs, R. E. *AIChE J.* **1973**, *19*, 238.
(11) Fredenslund, A. G.; Gmehling, J.; Rasmusen, P. *Vapor-Liquid Equilibria Using UNIFAC*; Elsevier: Amsterdam, 1977.
(12) Herington, E. F. G. *Nature (London)* **1947**, *160*, 610.
(13) Herington, E. F. G. *J. Inst. Pet.* **1951**, *37*, 457.
(14) Black, C. *Ind. Eng. Chem.* **1958**, *50*, 403.
(15) Van Laar, J. J. *Z. Phys. Chem.* **1929**, *185*, 35.
(16) Wilson, G. M. *J. Am. Chem. Soc.* **1964**, *86*, 127.
(17) Fredenslund, A.; Jones, R. L.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 1986-9.

Received for review November 17, 1987. Revised June 13, 1988. Accepted August 12, 1988.

Solubility of Anthracene and Anthraquinone in Some Pure and Mixed Solvents

Emilio A. Cepeda and Beatriz Gomez

Departamento de Química Técnica, Colegio Universitario de Alava, Vitoria, Alava, Spain

Mario Diaz*

Departamento de Ingenieria Química, Universidad de Oviedo, Asturias, Spain

The solubilities of anthracene and anthraquinone in 1,4-dioxane, *N,N*-dimethylformamide, ethylene glycol, and ethylene glycol-dioxane mixtures have been measured for temperatures ranging from 303 to 323 K (338 to 433 K in ethylene glycol). The experimental solubilities as mole fractions, x_2, may be conveniently correlated with the ideal solubilities, x_i, by means of expressions of the form $\ln x_2 = a + b \ln x_i$. This is valid for the pure and mixed solvents with an accuracy of ±0.5%.

Introduction

Anthraquinone can be obtained by oxidation from purified cake anthracene (*1*). Studies of this oxidation were carried out in the liquid phase with several catalysts (*2-5*). For the selection of the solvent and in order to design the process, it is necessary to know the solubility of reagents and products in the solvent where the reaction is carried out. Glycols and, in some cases, mixtures to improve the properties are some of the solvents that have been proposed for this reaction. Solubilities cannot be obtained with precision from liquid-state theories.

In this work the solubility of anthracene and anthraquinone in three solvents of interest for the anthracene industrial oxidation and also in mixtures of 1,4-dioxane-ethylene glycol has been experimentally obtained in a temperature range of industrial importance. Relations with the ideal solutions prediction are analyzed with pure and mixed solvents, and the effect of temperature on the solubilities is tested.

Experimental Section

Materials. Anthracene (95%) obtained from Fluka was purified by the method of Takeuchi and Furusawa (*6*), and their purity was checked by high-temperature gas chromatography and found to be at least 99.5%. Ethylene glycol, 1,4-dioxane and *N,N*-dimethylformamide (Panreac p.a.) were used without further purification. The physical properties are shown in Table I.

Table I. Physical Properties of Pure Solvents at 298.16 K

compd	refract. index expt	refract. index ref *10*	density expt	density ref *10*
ethylene glycol	1.4306	1.4306	1.1102	1.1100
1,4-dioxane	1.4224	1.4224	1.0278	1.0280
N,N-dimethylformamide	1.4281	1.4282	0.9439	0.9440

Procedure. Solubilities were determined by equilibrating the solute with solvent in a 250-mL flask shaken in a carefully controlled (±0.05 K) thermostat. In previous experiments in which samples were withdrawn at various time intervals, no detectable concentration change was found after 3-5 contact hours. Equilibrium experiments at all temperatures were carried out for more than 12 h.

Analysis of the samples was done by liquid chromatography (Pye Unicam 4020) with a UV detector at 254 nm. Reference mixtures were prepared for calibration. The precision of the analyzing instruments in mole fraction is ±0.0002. All the solubility determinations were made in triplicate and precision was within ±2%.

Results and Discussion

Pure Solvents. The solubility values for anthracene in ethylene glycol (338-433 K), in *N,N*-dimethylformamide, and in 1,4-dioxane (303-323 K) are listed in Table II. Solubilities in ethylene glycol of both solutes are always smaller than in the other solvents. *N,N*-dimethylformamide is a better solvent for anthracene than for anthraquinone while with 1,4-dioxane the solubility of anthraquinone reaches that of anthracene when the temperature increases. Under some conditions the insolubility

0021-9568/89/1734-0273$01.50/0