Subscripts

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

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

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Solubility of Anthracene and Anthraquinone in Some Pure and Mixed Solvents

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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

	refract. index		density	
compd	expt	ref *10*	expt	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

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Table II. Experimental Solubility of Anthracene (AN) and Anthraquinone (AQ) in Three Solvents and a Mixture, in g/kg of Solvent

		303.0 K	308.0 K	312.8 K	317.4 K	322.8 K
N,*N*-dimethylformamide	AN	13.3414	16.9352	19.9337	22.5539	27.1358
	AQ	2.0787	3.7332	5.4112	8.3659	13.6541
1,4-dioxane	AN	11.1643	12.6048	14.5024	16.5275	19.2823
	AQ	3.8009	5.9384	8.4405	13.4158	20.0383
1,4-dioxane–ethylene glycol						
10% dioxane	AN	0.4953	0.7050	0.7657	1.2237	1.6041
	AQ	0.1168	0.1182	0.1997	0.3844	0.7234
30% dioxane	AN	1.9269	2.4651	3.0255	3.7318	4.8402
	AQ	0.3251	0.4931	0.8059	1.2322	2.1827
50% dioxane	AN	3.3961	4.3959	5.6025	5.7551	8.4246
	AQ	0.8281	1.3273	2.0526	3.1316	5.3573
70% dioxane	AN	6.4209	7.7195	8.6412	9.9135	12.2087
	AQ	1.6886	2.7737	4.6108	6.4365	11.4146
90% dioxane	AN	9.7938	11.5050	12.6514	14.6899	11.0495
	AQ	2.8700	4.5933	7.1968	11.0495	17.0963

ethylene glycol[a]	AN	0.4384 (338.0)	0.7955 (352.0)	1.0680 (360.0)	1.5346 (371.0)	2.3934 (384.0)	3.3500 (397.0)	6.5100 (419.4)	8.5000 (433.0)
	AQ	0.8400 (351.4)	1.9722 (371.2)	3.0471 (387.8)	5.0252 (406.6)	8.2125 (416.8)			

[a] Temperatures (K) in parentheses.

Table III. Parameters and Correlation Coefficient for Eq 2

	anthracene			anthraquinone		
solvent	*a*	*b*	r^2	*a*	*b*	r^2
ethylene glycol	0.0104	1.3098	0.9995	0.0429	1.2279	0.9951
1,4-dioxane	0.1612	0.7751	0.9989	398.5566	2.0863	0.9990
N,*N*-dimethylformamide	0.3738	0.9586	0.9975	721.1463	2.3115	0.9987
1,4-dioxane–ethylene glycol mixture						
10% dioxane	18.3637	5781.7697	0.9834	37.9161	12345.4156	0.9986
30% dioxane	15.5228	4505.5596	0.9995	29.9358	9425.4237	0.9984
50% dioxane	16.0445	4486.8083	0.9991	30.0476	9167.0606	0.9995
70% dioxane	11.9820	3067.3408	0.9960	31.2737	9316.8166	0.9987
90% dioxane	10.3808	2449.9722	0.9950	31.1648	9135.1833	0.9999

of anthraquinone in the product of a process could give rise to some operating problems.

Data of solubility can be used to estimate the activity coefficients through the equilibrium relationship (*7*)

$$\ln \gamma_2 x_2 = -\frac{\Delta H_t}{RT}\left(1 - \frac{T}{T_t}\right) + \frac{\Delta C_p}{R}\left(\frac{T_t}{T} - 1 - \ln \frac{T_t}{T}\right) \qquad (1)$$

An ideal solubility value can be obtained by taking $\gamma_2 = 1$. For calculations the ΔH_t and T_t values at the triple point have been substituted for the enthalpy of fusion and the normal melting temperature. Moreover, the last term in eq 1 has litttle effect on the results and has therefore been omitted. In Figure 1 the experimental solubility x_2 and the ideal calculated values x_i are compared.

In nearly all the cases, the experimental solubilities are lower than the calculated values for ideal solubilities and show positive deviations from ideal solutions ($\gamma > 1$), calculated from eq 1. From the linear character of deviations in Figure 1 an equation of the type

$$\ln x_2 = a + b \ln x_i \qquad (2)$$

can be fitted by the least-squares method, and the parameters *a* and *b* are shown in Table III.

***Mixed Solvents*.** In Table II the solubilities of AN and AQ in mixtures of ethylene glycol and 1,4-dioxane are given. In the temperature range studied, 303–322.8 K, the solubility values depart considerably from that calculated supposing ideal behavior, in particular for anthraquinone solubility, while for anthracene this difference decreases sharply with the increase of dioxane solvent mixture. This nonideal behavior of the system due to the partial molar excess enthalpy and the excess entropy of mixing is important and makes the analysis of temperature dependence difficult. Nevertheless, the solubilities of solids in binary systems could be generally fitted to an equation similar to that of the ideal form (*8*, *9*)

$$\ln x_2 = \frac{\Delta S_2^{M}}{R}\left(\frac{T_m}{T} - 1\right) \qquad (3)$$

but with the entropies and transition temperatures replaced by different values obtained by the least-squares method. Correlation coefficients calculated from eq 3 result between 0.980 and 0.999, the fitness being shown graphically in Figure 2 with solubility expressed as grams per kilogram. No deviation from linearity is observed; that it occurs could be indicative of a change in composition or structure of solid. For solutions with 90, 70, 50, 30, and 10% 1,4-dioxane, values for ΔS (calculated

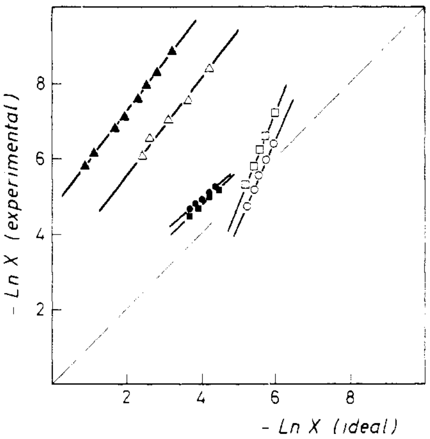

Figure 1. Discrepancy between experimental and ideal mole fraction solubilities calculated with eq 1. Solutes: filled symbols, AN; open symbols, AQ. Solvents: ○ and ●, 1,4-dioxane; △ and ▲, ethylene glycol; □ and ■, *N*,*N*-dimethylformamide.

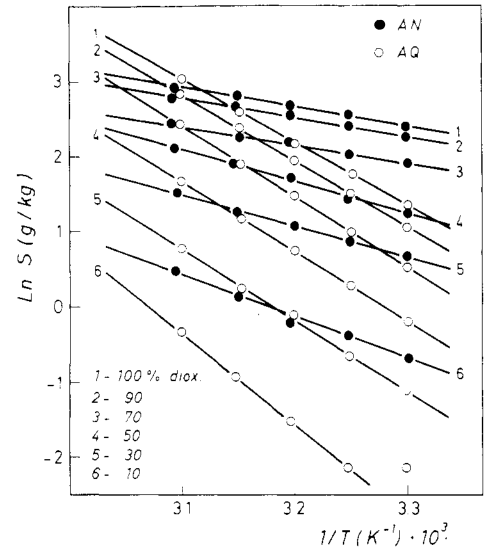

Figure 2. Solubility of AN and AQ in mixtures of 1,4-dioxane–ethylene glycol versus $1/T$.

Table IV. Entropy Variation Least-Squares Fitted Value ($-\Delta S$) Obtained from Eq 3 (J/(mol K))

	% 1,4-dioxane				
	90	70	50	30	10
AN	40.7	51.9	70.9	76.5	256.9
AQ	131.6	138.6	136.4	140.1	142.6

from eq 3) are shown in Table IV. An increasing departure from ideality at increasing concentrations of ethylene glycol is observed.

Ideal solubilities of AN and AQ in the solvent mixtures were calculated from the solubility in the pure solvents and from the molar fraction of each solvent in the mixed solvent by linear contribution. Compared with these ideal solubilities in the mixture, the experimental solubilities present positive deviations as shown in Figure 1 in pure solvents. Also good fitting of deviations to a linear relationship as in eq 2 is obtained. The constants a and b are recorded in Table III.

Glossary

ΔH	enthalpy of fusion of pure component, J/mol
ΔC_p	difference of molar specific heat between those of liquid and solid at fusion temperature, J/(mol K)
R	gas constant, J/(mol K)
S_2^M	Entropy, least-squares fitted value of eq 3, J/(mol K)
T	temperature, K
T_m	melting temperature, K
T_t	triple-point temperature, K
w	solubility on mass base, g/kg of solvent
x_2	experimental solubility in mole fraction
x_i	ideal solubility in mole fraction
γ	activity coefficient

Registry No. DMF, 68-12-2; anthracene, 120-12-7; anthraquinone, 84-65-1; dioxane, 123-91-1; ethylene glycol, 107-21-1.

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Novel Technique To Measure Equilibria of Supercritical Solvents and Liquid Mixtures

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A new flow method was developed to measure supercritical and near-critical phase equilibria. Equilibrium data for the carbon dioxide/ethanol/water system at 35 °C and 102.0 atm and the CO_2/2-propanol/water system at 25 °C and 81.6 atm and at 40 °C and 102.0 atm were determined by using this technique. The equilibria compared favorably with work reported previously.

Introduction

Since the commercialization of supercritical fluid (SCF) extraction processes in the late 1960s, interest in the separation technique has increased considerably. The sustained interest in supercritical extraction may be attributed to the unique advantages that the process offers, such as high mass-transfer rates, favorable selectivities, and low operating temperatures. These advantages can be coupled with the ready availability of nontoxic supercritical fluid solvents such as carbon dioxide.

When a supercritical extraction process is designed, a key parameter to consider is the phase equilibria of the operating systems. These equilibria determine the maximum separation possible for the process, the solvent/feed ratio (and hence the size of the extraction vessels), and the selectivity for the extracted solutes.

Although much past quantitative equilibrium work with supercritical fluids dealt with solvent/solid systems, quantitative equilibrium data for supercritical fluid/liquid systems have appeared often in the recent literature. This is probably due to improvements in experimental techniques.

Two approaches are used to measure supercritical fluid/liquid equilibrium: static and dynamic methods. With the static method, the components of interest are metered into a high-pressure viewing cell and agitated to establish equilibrium between the contacting phases (*1–3*). Mercury displacement is used to maintain the operating pressure while sampling. Another static technique that does not require sampling involves measuring cell loadings, determining phase volumes, and ob-

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