composition. The values were obtained by varying the value of the interaction until a minimum in the pressure and composition predictions was achieved. The values were 0.06 ± 0.01 for the ethylcyclohexane–hydrogen sulfide pair and 0.02 ± 0.01 for the *n*-propylcyclohexane–hydrogen sulfide pair.

The sums of differences in bubble point pressures and vapor phase compositions at the optimum δ_{ij} value are presented in Table III. The arithmetic mean of the positive and negative pressure and vapor composition differences are also given in the table. The number of positive and negative points are indicated. Zero differences were considered positive for the averaging process.

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Glossary

a	constant in equation of state
i, j	molecular species
K	equilibrium ratio, y/x
m	pertaining to a mixture
P	pressure
T	temperature
x	mole fraction in liquid phase
y	mole fraction in vapor phase
δ	binary interaction parameter

Registry No. Hydrogen sulfide, 7783-06-4; ethylcyclohexane, 1678-91-7; *n*-propylcyclohexane, 1678-92-8.

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Phenol Recovery from Water Effluents with Mixed Solvents

Magda Medir,[†] Antoni Arriola, Donald Mackay,[‡] and Francesc Giralt*

Departament de Química Tècnica, Facultat de Ciències Químiques, Universitat de Barcelona, Tarragona, Catalunya, Spain

The infinite-dilution distribution coefficients of phenol between water and six solvent mixtures—*n*-butyl acetate–*n*-octane, and isopropyl ether with *n*-butyl acetate, 1-octanol, benzene, carbon tetrachloride, and *n*-octane—have been determined at 25 °C. Such mixed solvent systems may be useful for phenol extraction from water in industrial processes. The mixtures exhibit negative and positive nonlinear distribution coefficient–volume fraction relationships. Maximum mixture distribution coefficients are obtained with approximately equivolume mixtures of isopropyl ether with 1-octanol.

Introduction

The aqueous effluents of petroleum refineries and plants processing petrochemicals, phenolic resins, and fossil fuels frequently contain phenol or phenolic compounds with concentrations reaching several percent (*1*). Phenol concentrations of about 2 mg/L affect organoleptic properties and are toxic to marine fauna (*2*). Such effluents may be treated by destructive oxidation processes or the phenols may be recovered by a suitable separation process such as solvent extraction. Recovery may be economically attractive because the quantity of phenols in effluents of a catalytic cracking plant can reach 100–200 kg/day (*3*). The comparative study carried out by Earhart et al. (*4*) concerning the recovery of phenol in aqueous effluents with concentrations over 50 ppm shows that liquid–liquid extraction is the most economic nondestructive process. The application of liquid–liquid extraction to waste water treatment has been reviewed by Kiezyk and Mackay (*5*), Earhart et al. (*4*), Bailey et al. (*6*), Little (*7*), and Mackay and Medir (*8*, *9*). Earhart et al. (*10*) have suggested an extraction process with two solvents. In a first stage a nonvolatile polar solvent such as butyl acetate is used to extract most of the phenol and in a second a nonpolar volatile solvent (isobutylene) recovers the remaining phenol and the dissolved polar solvent which has entered the aqueous phase.

The factors which influence the selection of solvents for phenol extraction have been discussed by Kiezyk and Mackay (*11*). The most important single factor is a favorable solvent–water distribution coefficient, which is a fundamental property of the solvent–solute–water system. It has been shown that mixed solvents can be more effective in phenol extraction than pure solvents, as has been subsequently discussed by Nakagawa et al. (*12*), Korenman (*13*, *14*), Medir and Mackay (*15*), and Gravelle and Panayiotou (*16*).

In this work data are presented for pure and mixed systems involving two solvents frequently used in phenol extraction processes, butyl acetate and isopropyl ether. Distribution coefficients at infinite dilution of phenol between water and mixtures of butyl acetate and isopropyl ether, butyl acetate and octane, isopropyl ether and octanol, isopropyl ether and benzene, isopropyl ether and carbon tetrachloride, and isopropyl ether and octane have been experimentally determined.

Experimental Part

To determine phenol distribution coefficients a two-liquid phase system was equilibrated by gently shaking the mixture of 50 mL of aqueous phenol solution of known concentration with 10 or 25 mL of pure or mixed solvent in a 250-mL Erlenmeyer flask in a water bath at 25 ± 0.1 °C. It was found by concentration–time measurements that an equilibration time of 24 h was sufficient to establish equilibrium. After shaking, the samples were allowed to stand for 2 h to allow phase separa-

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[†] Escola Universitària del Professorat d'EGB, Universitat de Barcelona, Tarragona, Catalunya, Spain.
[‡] Department of Chemical Engineering and Applied Science University of Toronto, Toronto, Ontario, Canada.

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Table I. Infinite-Dilution Phenol Distribution Coefficients (K) between Pure and Mixed Solvents and Water at 25 °C

solv vol fraction	K, $(g/m^3)/(g/m^3)$	solv vol fraction	K, $(g/m^3)/(g/m^3)$
n-Butyl Acetate (1)–*n*-Octane (2)		Isopropyl Ether (1)–Benzene (2)	
0.00	0.11	0.00	2.21
0.20	4.64	0.20	9.87
0.40	12.5	0.40	15.4
0.60	23.0	0.60	17.4
0.80	36.0	0.80	19.6
1.00	54.4	1.00	18.5
Isopropyl Ether (1)–*n*-Butyl Acetate (2)		Isopropyl Ether (1)–Carbon Tetrachloride (2)	
0.00	54.5	0.00	0.44
0.20	49.4	0.20	5.41
0.44	42.4	0.41	9.16
0.59	38.2	0.60	12.3
0.80	29.8	0.80	16.2
1.00	18.5	1.00	18.5
Isopropyl Ether (1)–1-Octanol (2)		Isopropyl Ether (1)–*n*-Octane (2)	
0.00	31.0	0.00	0.11
0.20	38.9	0.20	2.30
0.40	43.0	0.41	4.81
0.59	46.1	0.60	7.78
0.80	42.3	0.80	12.3
1.00	18.5	1.00	18.5

tion and the phenol concentration in the aqueous phase was determined. During equilibration, pH was maintained between 5.8 and 6.0. The phenol content was determined by UV spectroscopy. Samples of the aqueous phase were diluted about 20 times in order to work within the range of Beer–Lambert's law. The phenol concentration was measured at a wavelength of 270 nm in a Beckman DK2A spectrophotometer using 5 cm path length silica cells with a slit width of 0.12 mm. The phenol distribution coefficient K was calculated as the ratio between the phenol concentration (g/m^3) in the organic and aqueous phases (y/x) after the system reached equilibrium. The final phenol concentration in the organic phase was determined from the initial and final phenol concentrations in the aqueous phase and the values of the initial and final volumes of the phases

$$y = (VX - v_a x)/v_0 \qquad (1)$$

The final equilibrated volumes of the aqueous and organic phases differed from the initial ones, due to the mutual solubilities of the phases. Final volumes were determined according to the method described by Medir and Mackay (*15*). In the determination of phenol distribution coefficients at infinite dilution, three to eight experiments were carried out with different initial phenol concentrations, ranging from 50 to 350 mg/L. The distribution coefficients were plotted vs. the final phenol concentration in the aqueous phase and the infinite-dilution or zero-concentration distribution coefficient was estimated by extrapolation of the least-squares regression of distribution coefficient with concentration. The standard error of the distribution coefficient was calculated to be 2%.

Results and Discussion

The phenol distribution coefficient data for single and mixed solvents are given in Table I. Figures 1–3 show that the distribution coefficients of phenol between water and mixed solvents consistently deviate positively from linearity except when *n*-octane is one of the components of the mixture, where the deviation is negative.

The distribution coefficient data plotted in Figure 1 and corresponding to the mixture *n*-butyl acetate–*n*-octane exhibit a

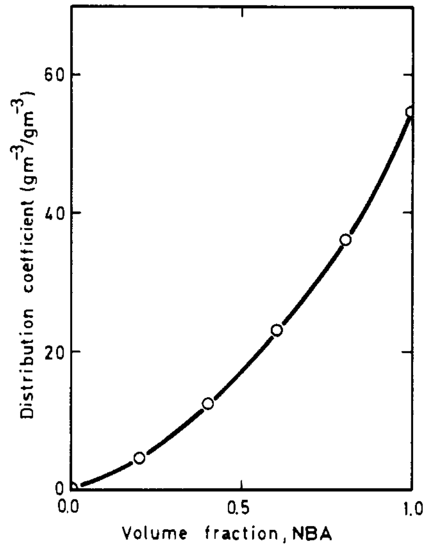

Figure 1. Phenol distribution coefficients between water and the mixture of *n*-butyl acetate with *n*-octane.

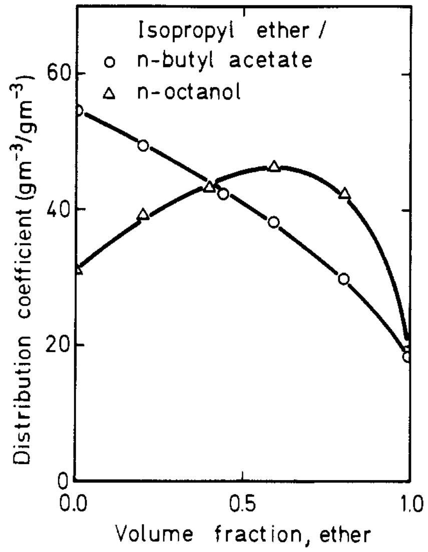

Figure 2. Phenol distribution coefficients between water and mixtures of isopropyl ether with *n*-butyl acetate and 1-octanol.

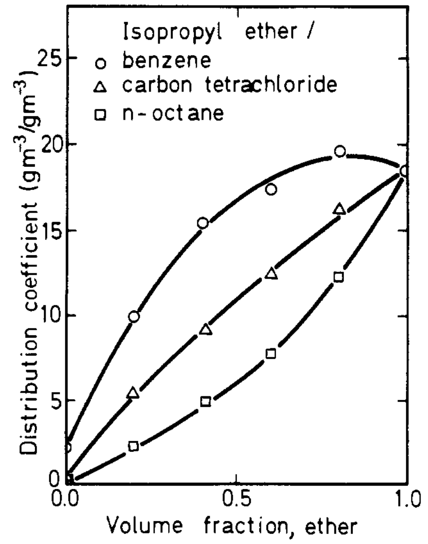

Figure 3. Phenol distribution coefficients between water and mixtures of isopropyl ether with benzene, carbon tetrachloride, and *n*-octane.

negative deviation from linearity amounting to approximately 30% less than the linear value at a *n*-octane volume fraction between 0.4 and 0.6. Medir and Mackay (*15*) showed previously that *n*-butyl acetate–benzene systems were approximately linear in behavior.

The solvent mixture isopropyl ether–1-octanol presented in Figure 2 shows a deviation of 96% above linearity for an ether volume fraction of 0.6. The present data show a maximum distribution coefficient value some 8% lower than that reported by Gravelle and Panaylotou (*16*). This behavior is similar to the one previously reported by Medir and Mackay (*15*) in a mixture of *n*-butyl acetate and 1-octanol, suggesting that ethers also have a significant capacity to reduce the self-association of alcohols and thus increase the concentration of the free hydroxyl groups. In both mixtures, 1-octanol–isopropyl ether and 1-octanol–*n*-butyl acetate, the positive deviation is greater for lower alcohol concentrations, the distribution coefficients being significantly greater than those of the pure solvents. Alcohol–ether mixtures thus appear to be very attractive for solvent extraction of phenol. Figure 2 also shows slight positive linearity in the phenol distribution coefficient for the mixture of isopropyl ether and *n*-butyl acetate, in which there is no maximum. This deviation is significantly smaller than that exhibited by mixtures of octanol and isopropyl ether.

The phenol distribution coefficient data corresponding to mixtures of benzene, carbon tetrachloride, and *n*-octane with isopropyl ether in Figure 3 are similar to those reported by Medir and Mackay (*15*) with mixtures of these three solvents and 1-octanol. The mixtures of isopropyl ether and benzene have positive deviations of about 60% for ether volume fractions between 0.4 and 0.6. This solvent mixture presents a maximum distribution coefficient for an ether volume fraction of 0.8, which was not observed by Medir and Mackay (*15*) in the mixture benzene–*n*-butyl acetate. Gravelle and Panaylotou (*16*) did not observe a maximum distribution coefficient for the system isopropyl ether–benzene, but a rather large positive deviation. The mixture isopropyl ether–carbon tetrachloride has only a slight positive deviation of 15%. Spencer (*17*) reported a complex formation between phenol and ether in carbon tetrachloride, through hydrogen bonding. The deviations of the systems formed by isopropyl ether and *n*-octane shown in Figure 3 are also negative, as was previously observed in Figure 1 for the mixture *n*-butyl acetate–*n*-octane. The negative deviations for the two *n*-octane mixtures amount to some 30%.

At present it is impossible to present or suggest a molecular thermodynamic interpretation for these data beyond the observation that there is a strong association between phenol and the ether or ester solvents which can apparently be enhanced if a third polar solvent such as octanol is present. The role of the octanol may be to disrupt the self-association of the ether or ester and make it more available for interaction with the phenol. Octanol is also an attractive cosolvent because of its low solubility in water and its low toxicity. Other alcohols may also be suitable. Other factors which play an important role in solvent selection and which have not been considered here include the following: the mutual miscibility characteristics of water and these solvents, the distribution behavior of other phenolic compounds and of other contaminants present in the water stream, the effects of pH and temperature, and the cost and recoverability of the solvents.

Conclusions

Of the mixed solvent systems studied here, that formed by isopropyl ether with 1-octanol is of primary interest for liquid–liquid extraction processes since it provides a large positive deviation from linearity. The isopropyl ether–benzene system also exhibits a large positive deviation but the pure benzene distribution coefficient is low and benzene also has toxicity disadvantages. Both systems which contain *n*-octane as a component have negative deviations. Isopropyl ether thus appears to be as good a solvent as *n*-butyl acetate when mixed with octanol for the extraction of phenol.

Glossary

y	final concentration in the organic phase, g/m^3
X	initial phenol concentration in the aqueous phase, g/m^3
x	final phenol concentration in the aqueous phase, g/m^3
K	distribution coefficient
V	initial volume of the aqueous phase, m^3
v_a	final volume of the aqueous phase, m^3
v_o	final volume of the organic phase, m^3

Registry No. Phenol, 108-95-2; *n*-butyl acetate, 123-86-4; *n*-octane, 111-65-9; isopropyl ether, 108-20-3; benzene, 71-43-2; carbon tetrachloride, 56-23-5; 1-octanol, 111-87-5; water, 7732-18-5.

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