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Temperature Effect on Phenol Extraction from Water Using Mixed Solvents

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Experimental measurements are reported for the equilibrium distribution of phenol between water and three mixed solvents: octanol–isopropyl ether, benzene–isopropyl ether, and octanol–butyl acetate. The temperature of investigation ranges between 15 and 60 °C. A two-term Redlich–Kister equation can be used to represent the distribution coefficients of phenol in terms of the mixed solvent composition. The temperature effect on the distribution coefficients is satisfactorily correlated with a van't Hoff relation.

Introduction

Polar solvents are generally more efficient in extracting phenol from water than are nonpolar solvents. However, polar solvents are usually more soluble in water and are more expensive. Economic and solubility considerations encourage the dilution of polar solvents with nonpolar ones. Phenol is undissociated in the organic phase and is polar. Hence, a polar solvent is favored because of its similarity with phenol. These considerations led to the investigation of the mixed solvents (I) 1-octanol–*n*-butyl acetate, (II) 1-octanol–isopropyl ether, and (III) benzene–isopropyl ether, in which the nonpolar solvents are octanol and benzene while *n*-butyl acetate and isopropyl ether are the polar ones. The solvents II and III are studied for the first time; however, solvent I has been measured at 25 °C only (*7*). The above pure solvents are widely used in industry and are biodegradable. The conclusions of Medir and MacKay (*7*) were taken into account for the preference of ester–alcohol mixtures for extracting phenol from water. Among the most recent work on extraction of phenol with mixed solvents, those of Nakagawa (*8*), of Korenman (*5*), and of Medir (*7*) may be mentioned. In this work, the partition of phenol between water and mixed solvents is measured over the entire range of mixed solvent composition at temperatures between 15 and 60 °C.

Experimental Section

The aqueous and mixed solvent phases were equilibrated in 250-mL Erlenmeyer flasks held in a constant-temperature bath within ±0.2 °C of the selected temperature. The systems were brought to equilibrium by gentle agitation with Teflon-coated magnetic stirrers. Following a 2-h agitation, the samples were allowed to stand for 4 h for phase separation. Known volumes of samples from the aqueous phase were withdrawn and analyzed for phenol concentration by UV spectroscopy.

Systems I and II were measured in a UV Perkin-Elmer Coleman 124 spectrophotometer at a wavelength of 270 nm with 5-cm (long) optical cells. Coabsorbance of benzene near the wavelength of 270 nm prevented the measurement of phenol for system III. In this case, the method of 4-aminoantipycin (4-AAP) described by Weiss (*9*) together with a Baush-Lomb Spectronic 70 spectrophotometer was used to determine the concentration of phenol. Measurements were made at a wavelength of 510 nm with 2-cm width optical cells. This method also served to measure the phenol content below 5 mg/L. The concentrations obtained by both methods agree within the experimental error.

At equilibrium, the amount of phenol transferred to the organic phase was found from the difference between the initial and equilibrium mass of phenol in the aqueous phase. The concentration of phenol in each phase was then calculated by a knowledge of the volumes of both phases at equilibrium. The distribution coefficients reported here are defined by $K = C_o/C_a$ in which C_o and C_a represent respectively the organic and aqueous phenol concentration in mg/L. Reagent grade chemicals were used without further purification.

Results

The measured distribution coefficients of phenol between water and mixed solvents, K, at different temperatures are reported in Table I with corresponding volume fraction of the polar solvent, ϕ_2. The value of each point is based on a set of at least three determinations. The average value of the mean deviation of the measured distribution coefficients, in percent, is also listed for each isotherm. Bath temperature variations of ±0.2 °C did not result in any important changes in the measurements of K.

No significant changes in K values of the mixed solvents were observed for phenol equilibrium concentrations varying between 50 and 250 mg/L. This observation has also been reported for pure solvents (*1*, *6*, *10*).

The different synergistic behavior at 25 °C on each mixed solvent is shown in Figure 1, while Figure 2 illustrates the net effect of synergism. The influences of temperature on the net effect of synergism are plotted in Figures 2–5. The solid lines traced on Figures 1–5 were obtained with values calculated with a van't Hoff equation in which the enthalpy of extraction, ΔH, and the change of entropy, ΔS, are represented by simple polynomials in volume fraction. A two-parameter Redlich–Kister equation was used to establish the ΔH and ΔS as functions of equidistant ϕ_2.

Discussion

The three mixed solvents exploited in this work are illustrated in Figure 1 at 25 °C. Our data for the system octanol–butyl acetate compares favorably with those of Medir and MacKay (*7*). The values of K pass through a broad maximum for the mixed solvents containing octanol. Although the values of the distribution coefficients in the system benzene–isopropyl ether never reach a maximum with respect to both pure solvents, it shows considerable deviation from the line joining the pure solvent K values. Because of this deviation as seen in Figures 2–5, the mixed solvent coefficients cannot be represented by the simple relation

$$K = \sum \phi_i K_i \tag{1}$$

In fact, this relation holds in very few cases, like in the mixed solvent benzene–butyl acetate (*7*). For systems which show strong association between phenol and mixed solvents, a correction term, ΔK, may be included in eq 1.

$$K = \sum \phi_i K_i + \Delta K \tag{2}$$

The sign of ΔK is positive for the systems investigated in this

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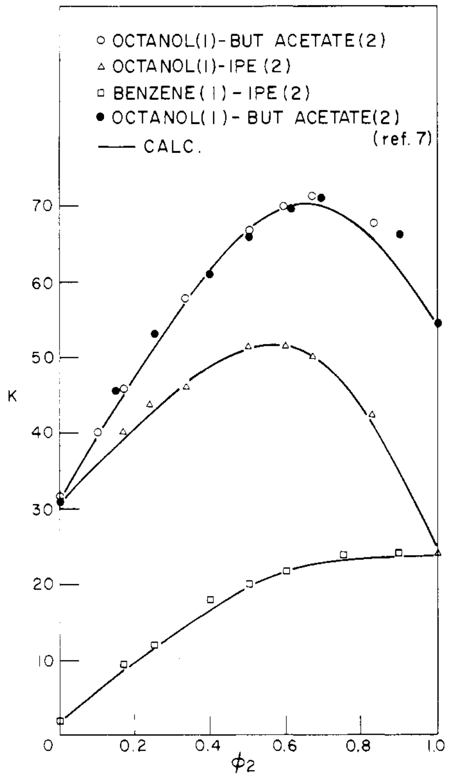

Figure 1. Distribution coefficients of phenol in mixed solvents at 25 °C.

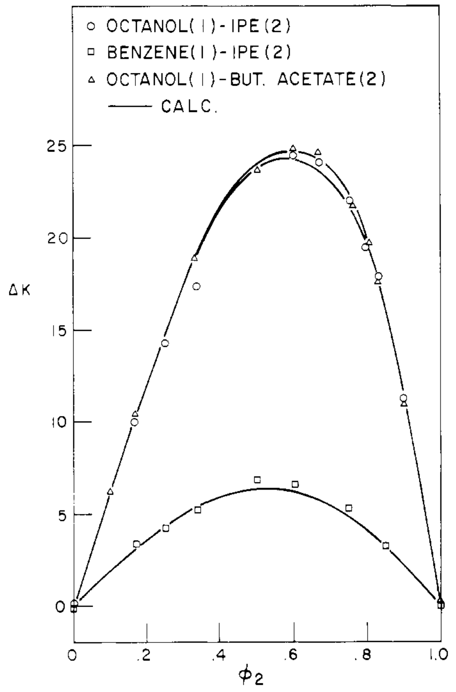

Figure 2. Net synergistic effect at 25 °C.

work; however, negative values of ΔK have been reported in the mixed solvent chloroform–carbon tetrachloride (*5*).

The property change of the mixed solvent ΔK defined by eq 2 can be seen as the difference between the mixture partition coefficient (real property) and the sum of the pure component partition coefficient (ideal property). This property of mixtures, giving considerable changes in distribution coefficient, has been termed the synergistic effect (*2*).

Although the values of K in the solvent octanol–butyl acetate are much greater than those of octanol–isopropyl ether, the net effect of synergism over the whole mixed solvent composition range is similar for both systems. The values of ΔK at 25 °C calculated with eq 2 in terms of mixed solvent composition are shown in Figure 2. This result suggests further investigation concerning the synergistic behavior in a family of mixed solvents constituted of polar solvents with a reference nonpolar solvent. Hence the prediction of K values for new systems may be envisaged from a knowledge of pure solvent properties and ΔK values of a family of mixed solvents.

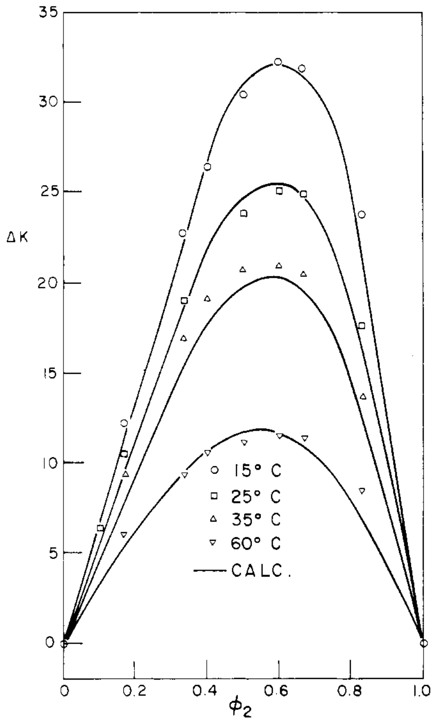

Figure 3. Temperature effect on ΔK for octanol (1)-butyl acetate (2).

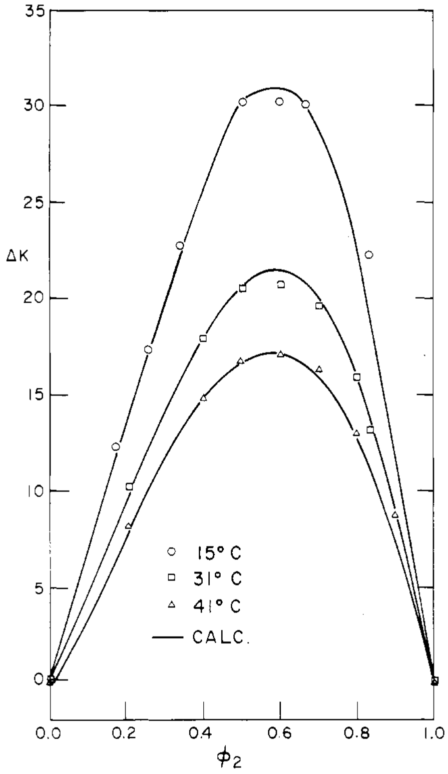

Figure 4. Temperature effect on ΔK for octanol (1)-isopropyl ether (2).

The temperature effects on the distribution coefficient change of the mixed solvents are plotted in Figures 3–5. At any tem-

Table I. Distribution Coefficients for the Mixed Solvents

	288.16 K		298.16 K		304.16 K		308.16 K		314.16 K	
	ϕ_2	K	ϕ_2	K	ϕ_2	K	ϕ_2	K	ϕ_2	K
octanol (1)–isopropyl ether (2)	0.00	33.10	0.00	31.40	0.00	29.10	0.00	28.00	0.00	27.20
	0.17	44.60	0.17	40.30	0.20	37.75	0.17	34.90	0.20	33.50
	0.25	49.00	0.25	44.00	0.40	43.95	0.30	39.00	0.40	38.10
	0.33	54.10	0.33	46.30	0.50	45.62	0.33	40.00	0.50	38.80
	0.50	60.30	0.50	51.40	0.60	45.31	0.50	43.65	0.60	38.40
	0.60	60.15	0.60	50.30	0.70	43.45	0.60	43.10	0.70	36.70
	0.67	59.50	0.67	50.40	0.80	39.00	0.67	41.70	0.80	32.50
	0.83	50.90	0.83	42.10	0.83	36.20	0.83	34.00	0.90	27.40
	1.00	27.90	1.00	24.00	1.00	21.83	1.00	19.75	1.00	17.66
r		1.58%		1.47%		1.12%		1.20%		0.94%

	288.16 K		298.16 K		308.16 K		318.16 K		333.16 K	
	ϕ_2	K	ϕ_2	K	ϕ_2	K	ϕ_2	K	ϕ_2	K
octanol (1)–butyl acetate (2)	0.00	33.10	0.00	31.40	0.00	28.00	0.00	25.80	0.00	23.30
	0.17	49.50	0.10	40.00	0.17	40.80	0.17	36.00	0.17	31.30
	0.33	64.00	0.17	45.70	0.33	51.50	0.33	44.70	0.33	36.40
	0.40	69.50	0.33	57.90	0.40	55.00	0.40	47.30	0.40	38.25
	0.50	76.00	0.50	66.40	0.50	58.50	0.50	50.10	0.50	40.00
	0.60	80.20	0.60	69.80	0.60	60.65	0.60	52.10	0.60	41.50
	0.67	81.50	0.67	71.10	0.67	61.60	0.67	52.80	0.67	42.00
	0.83	77.50	0.83	67.60	0.83	58.10	0.83	50.50	0.83	41.00
	1.00	58.00	1.00	53.80	1.00	47.75	1.00	42.20	1.00	34.40
r		1.77%		2.88%		2.18%		2.89%		1.91%

	288.16 K		298.16 K		308.16 K		313.16 K	
	ϕ_2	K	ϕ_2	K	ϕ_2	K	ϕ_2	K
benzene (1)–isopropyl ether (2)	0.00	2.00	0.00	2.22	0.00	2.45	0.00	2.55
	0.20	12.00	0.17	9.30	0.20	8.78	0.20	8.50
	0.40	19.40	0.25	11.90	0.40	14.03	0.40	12.80
	0.50	22.70	0.40	17.65	0.50	16.40	0.50	14.70
	0.67	25.80	0.50	20.00	0.67	18.80	0.60	16.10
	0.75	27.00	0.60	21.80	0.75	19.60	0.70	17.46
	0.90	27.80	0.75	23.80	0.80	19.72	0.80	17.61
	0.95	27.60	0.90	23.90	0.90	19.75	0.90	17.80
	1.00	27.90	1.00	24.00	1.00	19.75	1.00	18.03
r		0.83%		0.99%		0.66%		0.87%

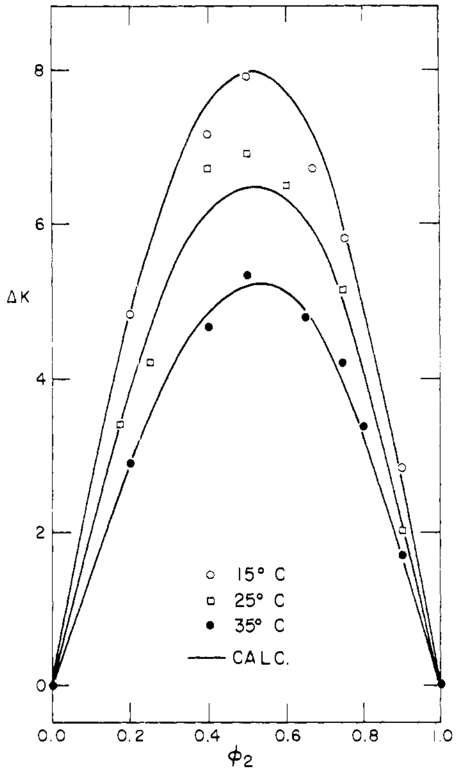

Figure 5. Temperature effect on ΔK for benzene (1)–isopropyl ether (2).

perature, the K values of the mixed solvent benzene–isopropyl ether show symmetry around $\phi_2 = 0.5$ while those containing octanol show asymmetry with maximum values at $\phi_2 \simeq 0.65$. An increase in temperature reduces the values of K or ΔK over the entire range of mixed solvent composition. It should be noted that this effect is reversed in the system containing benzene in which the isopropyl ether volume fraction is less than 0.05. This particularity is seen in Table III where the measured K values are reported for the pure solvents in terms of the temperature. The behavior for benzene in which K is proportional to temperature has also been reported (*1*,*6*).

Data Reduction

Data reduction is facilitated by using a semiemperical correlation for K based on the van't Hoff equation.

$$\ln K = \Delta S/R - \Delta H/RT \qquad (3)$$

This equation has been used to correlate the effect of temperature on pure solvent phenol distribution coefficients (*6*) and can be employed to yield thermodynamic properties such as the heat of extraction in a mixed solvent, ΔH, and the entropy change, ΔS. A plot of $\ln K$ vs. $1/T$ yielded a straight line indicating the constancy of the slope $\Delta H/R$ provided the mixed solvent composition is fixed. The coefficients of the polynomial representing ΔH and ΔS in terms of ϕ_2 are listed in Table II with the correlation coefficients, h. The enthalpy of extraction reported in the literature (*6*) for the pure solvents octanol, butyl acetate, and benzene are respectively −1.41, −1.8, and +1.7

Table II. Enthalpy and Entropy of Extraction as a Function of Volumetric Fraction

	octanol (1)–isopropyl ether (2)		octanol (1)–butyl acetate (2)		benzene (1)–isopropyl ether (2)	
F^a	$10^{-3}\Delta H$	ΔS	$10^{-3}\Delta H$	ΔS	$10^{-3}\Delta H$	ΔS
a	−1.4931	1.8365	−1.5573	1.603	1.8290	7.6731
b	−4.4059	−12.5297	−2.5985	−4.0943	16.9041	57.1844
c	+2.5364	10.2263	−0.7112	−5.0789	−5.7178	−22.6272
d	+0.1802	−3.8563	+2.6127	7.9131	0	0
e	0	0	0	0	−16.9246	−49.8081
f	0	0	0	0	0.8032	3.4237
h	0.9984	0.9997	0.9975	0.9963	0.99999	0.99995

[a] F, $10^{-3}\Delta H$ or ΔS; *a–e*, coefficients of the polynomial F; h, correlation coefficient; $F = a + b\phi_2 + c\phi_2^2 + d\phi_2^3 + e\phi_2^{1/2} + f\phi_2^4$ for $0 < \phi_2 < 1.0$, where $\phi_2 = V_2/(V_1 + V_2)$. In eq 3, $R = 1.987$ and T is in Kelvin.

Table III. Pure Component K Values and Redlich–Kister Coefficients

system	T, K	K_2	K_1	A	B	$\Sigma(K_{\text{exptl}} - K_{\text{calcd}})^2$
octanol (1)–isopropyl ether (2)	288.16	27.9	33.1	117.808	48.962	1.081
	298.16	24.0	31.4	93.638	39.459	0.721
	304.16	21.83	29.1	80.461	28.228	0.4699
	308.16	19.75	28.0	77.556	28.374	0.8588
	314.16	17.66	27.2	65.195	25.905	0.8396
octanol (1)–butyl acetate (2)	288.16	58.0	33.1	121.76	61.621	0.8174
	298.16	53.8	31.4	96.673	37.677	0.6942
	308.16	47.75	28.0	83.351	22.344	0.2790
	318.16	42.2	25.8	65.458	18.345	0.2217
	333.16	34.4	23.3	45.370	12.429	1.201
benzene (1)–isopropyl ether (2)	288.16	27.6	2.0	30.780	0.5136	0.1343
	298.16	24.0	2.22	27.593	3.166	0.6907
	308.16	19.75	2.45	20.848	3.243	0.1527
	313.16	18.03	2.55	17.918	0.6437	0.2414

kcal/mol. The values obtained by least-squares fitting of eq 3 are respectively −1.51, −2.22, and +1.83 kcal/mol while those calculated using the polynomial described in Table II are respectively −1.53, −2.25, and +1.83 kcal/mol.

The values of ΔH and of ΔS were obtained at equidistant values of ϕ_2 at corresponding distribution coefficients calculated with a two-parameter Redlich–Kister equation

$$\Delta K/\phi_1\phi_2 = A + B(\phi_1 - \phi_2) \tag{4}$$

in which ΔK is defined by eq 2. The volume fractions ϕ_2 and ϕ_1 are respectively those of the polar and nonpolar solvents. The parameters A and B were obtained at each temperature for each system by standard regression techniques. The results, listed in Table III, would give an almost perfect fit to the points shown in Figures 1–5 because of the low values of the sum of the squared deviations. The mutual interaction of temperature and composition for a given system is not considered by eq 4. On the other hand, the influence of the temperature on the distribution coefficient given by the van't Hoff equation is more soundly based on theoretical considerations.

The use of the polynomials for calculating ΔH and ΔS restrict eq 3 to a semiempirical relation. Some of the existing methods of data reduction of distribution coefficients for phenolic solutes between pure solvent and water have been studied in terms of normal boiling temperature (*1*), of solubility parameters (*4*), and of interfacial tension (*3*). The paucity of mixture property data renders impossible the prediction of mixed solvent K values. However, a judicious application of the theory of associated solutions applied to mixed solvents consisting of polar (*10*) and nonpolar solvents (*1*) together with appropriate mixing rules developed from a knowledge of some mixture physical properties may lead to the prediction of many phenolic solutes in mixed solvents. Furthermore, it has been shown that the free energy at 20 °C, $\Delta G = \Delta H - T\Delta S$, is a linear relation with molar volume of pure solvents (*6*). This approach applied to mixed solvents together with the associated solution theory for calculating activity coefficients of the solute may lead to useful results in predicting K values in mixed solvents as a function of the temperature.

Glossary

A,B	parameters defined by eq 4
C	concentration of phenol, mg L^{-1}
F	total function defined in Table II
$K = C_o/C_a$	distribution coefficient of phenol
r	average value of the mean deviation of the measured K, %
R	gas constant, cal g-mol^{-1} K^{-1}
T	absolute temperature, K
V	volume, mL
ΔH	enthalpy change, cal g-mol^{-1}
ΔK	excess distribution coefficient
ΔS	entropy change, cal g-mol^{-1} K^{-1}
ϕ	volume fraction

Subscript

i	pure solvent *i*
1	nonpolar solvent
2	polar solvent
o	organic phase
a	aqueous phase

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