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Extraction of Phenol Using Trialkylphosphine Oxides (Cyanex 923) in Kerosene

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TECHNICAL NOTE

Extraction of Phenol Using Trialkylphosphine Oxides (Cyanex 923) in Kerosene

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INTRODUCTION

A group of extractants based on phosphine oxides have been reported as an alternative to conventional polar solvents for phenol liquid–liquid extraction. Among phosphoryl extractants, Cyanex 923 (a mixture of four trialkylphosphine oxides, alkyl = normal, C_6, C_8) has proved to combine high extraction efficiency and low water solubility (1, 2), obviating the necessity of removing the solvent from the aqueous raffinate, a need associated with the use of methyl isobutyl ketone and isopropyl ether, the solvents most widely employed for this application (3, 4).

Phosphoryl extractants are solvating extractants, and are known to form relatively strong and reversible hydrogen bonds with phenols (5, 6). The fact that most of these systems show a strong nonideality in the organic phase makes a general theoretical treatment of the equilibria almost impossible (7), leading to the necessity of obtaining a large number of data in order to describe the equilibria for design purposes.

In this work the effect of the concentration of phenol in the aqueous phase on the partition coefficient for phenol in Cyanex 923–kerosene/water systems is investigated at six different concentrations of the extractant in the organic phase: 1, 5, 10, 20, 50, and 70% v/v of Cyanex 923 in kerosene. The initial concentrations of phenol in the aqueous phase were in the 1000 mg/L < C_{PhOH} < 50,000 mg/L range.

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EXPERIMENTAL SECTION

Crystallized phenol (Fluka), 99.5% pure, was used to prepare the aqueous solutions. The extractant, Cyanex 923, was kindly obtained from Cytec (Canada). Commercial kerosene was used as the diluent of the organic phase. All aqueous solutions were prepared in ultrapure water obtained from a Milli-Q Plus water purification system (resistivity = 18.2 MΩ·cm).

Cyanex 923 is the commercial name of a mixture of four trialkylphosphine oxides, in which the alkyl groups are *n*-hexyl and *n*-octyl, with an average molecular weight 348 g/mol. The percentages of each phosphine oxide in the commercial extractant were given by Rickelton and Boyle (1):

$R_3P{=}O$	$R_2R'P{=}O$	$RR'_2P{=}O$	$R'_3P{=}O$
8%	31%	42%	14%

where R = $[CH_3(CH_2)_5]$ (normal hexyl) and R′ = $[CH_3(CH_2)_7]$ (normal octyl).

The physical properties of Cyanex 923 as supplied by the manufacturer (8) are given in Table 1.

Extraction equilibrium experiments were performed in closed glass tubes with a maximum capacity of 30 mL at 20 ± 1°C in a thermostated room. The initial concentration of phenol in the aqueous phase was in the $1000\ \text{mg/L} < C_{\text{PhOH}} < 50{,}000\ \text{mg/L}$ range. The concentrations of Cyanex 923 in the oil phase were 1, 5, 10, 20, 50, and 70% v/v (percentage in volume of the organic phase). The organic and aqueous phases were initially prepared in calibrated flasks. The experimental procedure involved

TABLE 1
Typical Physical Properties of Cyanex 923

Trialkyl phosphine oxides	93%
Appearance	Colorless mobile liquid
Specific gravity	0.88 at 25°C
Freezing point	−5 to 0°C
Viscosity	40.0 cP at 25°C 13.7 cP at 50°C
Flash point	182°C
Autoignition temperature	218°C
Vapor pressure	0.09 mmHg at 31°C
Solubility in water	10 mg/L
Solubility of water in Cyanex 923	8 w/o

measuring and adding to the glass tubes the proper volume of each phase according to the selected volume ratio. Volumetric ratios V_{AQ}/V_{ORG} between the aqueous and the organic phase ranging in proportions from 1/1 to 8/1 were investigated.

The glass tubes were then stoppered and attached to a rotatory stirrer (SBS, 5–150 rpm). The stirrer was set at a rotational speed of 60 rpm. The contact time was 1 hour. After this period, both phases were allowed to settle in separatory funnels and collected individually. The aqueous phases were centrifuged at 4000 rpm on an ALC 4235 centrifuge for further separation of the remaining organic residues. After centrifugation the aqueous phase was collected from the tube with a disposable syringe. All extraction experiments were conducted on a duplicate basis in order to obtain satisfactory reproducibility of the data.

The phenol concentration in the aqueous samples was determined by UV spectrophotometry after appropriate dilution. The Perkin-Elmer Lambda-2 spectrophotometer was set at $\lambda = 270$ nm. When the UV absorbance of the aqueous samples was under 0.1, alkaline determination (in 1 M NaOH) of the phenolate ion was performed, with the detector set at the optimum wavelength of $\lambda = 235$ nm. The UV absorbance of phosphine oxides is not referenced in the main literature sources. In order to check for any eventual interference, blank water samples were equilibrated with the organic phases at each of the Cyanex 923 concentrations. No UV absorption was detected in the equilibrated blanks.

RESULTS

The experimental results for the partition coefficient for phenol between the organic and the aqueous phase are plotted against equilibrium phenol concentrations as a function of the Cyanex 923 percentage in the organic phase in Fig. 1. The concentration-based partition coefficient, K, is calculated by

$$K = \left(\frac{(C_{AQ})_{\text{initial}} - (C_{AQ})_{\text{Equilibrium}}}{(C_{AQ})_{\text{Equilibrium}}}\right)\frac{V_{ORG}}{V_{AQ}} \tag{1}$$

where $(C_{AQ})_{\text{initial}}$ is the initial concentration of phenol in the aqueous phase, $(C_{AQ})_{\text{Equilibrium}}$ is the concentration of phenol in the aqueous phase at equilibrium, V_{ORG} is the volume of the organic phase, and V_{AQ} is the volume of the aqueous phase.

Data in Fig. 1 show the strong dependency of the partition coefficient on the equilibrium concentration of phenol in the aqueous phase. A similar result was presented by Watson et al. (9) for the extraction of phenol with

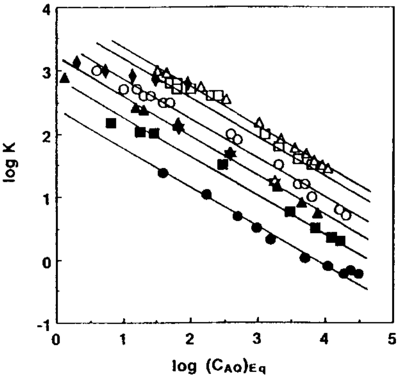

FIG. 1 Log of the partition coefficient against the log of the equilibrium concentration of phenol in the aqueous phase. Content of Cyanex 923 in the organic phase: (●) 1%; (■) 5%; (▲) 10%; (○) 20%; (□) 50%; and (△) 70%. (◆) 100% Cyanex 923 at 50°C, Watson et al. (9). (☆) 20% in a hollow fiber contactor, Urtiaga et al. (10).

undiluted, commercial grade Cyanex 923 at 50°C. The extraction isotherm reported by these authors is included in Fig. 1. It can be observed that increasing values of the distribution coefficient with decreasing phenol equilibrium concentrations were obtained in the 2 to 150 mg/L range of phenol, giving values up to 1300. The difference in the slope of the logarithmic scale can be assigned to the different temperatures of the equilibrium assays (the results of the present work were attained at 20°C).

Similarly, in previous work using 10% Cyanex 923 in kerosene for the nondispersive extraction of phenol in hollow fiber modules (10), analysis of the extraction courses yielded three values of the partition coefficient, which are also included in Fig. 1. Comparison of the two extraction isotherms indicates that both methods of contact lead to the same equilibrium conditions and, consequently, to similar partition coefficients for equivalent equilibrium phenol concentrations in the aqueous phase.

A linear relationship between log K and $\log(C_{AQ})_{Equilibrium}$ is seen for each concentration of Cyanex 923. The linear regression of the data provided satisfactory correlation coefficients (over 0.98), leading to similar values of the slopes (0.58–0.64) at the six experimental concentrations of Cyanex 923 in the organic phase.

Previous studies on the extraction capacity of Cyanex 923 can be found in the literature. Watson et al. (9) reported a comparison of Cyanex 923 with TOPO and isopropyl ether for phenol extraction to illustrate very favored overall economics for the use of Cyanex 923. Haesebroek et al.

(11) studied the solvent extraction separation of Nb and Ta, comparing a flow sheet using MIBK and a new flow sheet using Cyanex 923, and they noted that Cyanex 923 is a suitable alternative for MIBK for the simultaneous extraction and successive selective stripping of Nb and Ta. Studies on the regeneration of phenol-loaded Cyanex 923 by stripping with sodium hydroxide solutions have also been performed. Urtiaga et al. (10) reported the maintenance of the extraction efficiency of Cyanex 923 for long operation times involving five continuous cycles of extraction of phenol and reextraction with sodium hydroxide.

The advantage of using diluted Cyanex 923 as the extractant is that the viscosity of the extractant solution is small, making it easier to handle the extractant solution. In reference to this, Haesenbroek et al. (11) reported troublesome separation in the settling stage when undiluted Cyanex 923 was used due to the high loading capacity of the extractant. These characteristics suggest the suitability of using diluted Cyanex 923. However, when using low concentrations of the active extractant Cyanex 923 in the organic phase for the extraction of highly loaded aqueous phases, an important amount of the extraction yield is due to kerosene. This is the reason for the constant value of the partition coefficients in Fig. 1 (1% Cyanex 923) in the range of high concentrations of phenol at the equilibrium. Obviously, the low and constant value of the partition coefficient of phenol between kerosene and water, $K = 0.22$, determines this behavior (12).

CONCLUSIONS

In this work the effect of the concentration of phenol in the aqueous phase on the partition coefficient for phenol in Cyanex 923–kerosene/water systems is investigated at six different concentrations of the extractant in the organic phase: 1, 5, 10, 20, 50 and 70% v/v of Cyanex 923 in kerosene. Initial concentrations of phenol in the aqueous phase were in the 1000 mg/L $< C_{\mathrm{PhOH}} <$ 50,000 mg/L range.

The following conclusions are based on the results. The equilibrium concentration of phenol has a strong effect on the partition coefficient for phenol between trialkylphosphine oxides in kerosene and water, leading to an approximately linear dependency of the log of the partition coefficient K with the log of the concentration of phenol in the aqueous phenol at equilibrium. The higher the concentration of the extractant in the organic phase, the higher the extraction yield, yielding approximately parallel courses in the log K–$\log(C_{\mathrm{AQ}})_{\mathrm{Equilibrium}}$ plot for the six extractant concentrations investigated. These data are of special importance for design purposes, since the strong nonideality of the organic extractant Cyanex 923, included in the group of solvating extractants, makes a general theoretical treatment of the equilibria almost impossible. Moreover, a comparison of the actual study with previous data of the equilibrium obtained in a hollow fiber contactor leads to the conclusion that both contacting systems (dispersive and nondispersive extraction) lead to the same equilibrium conditions.

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