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K. T. Valsaraj[a]; L. J. Thibodeaux[a]; Xiao-Y. Lu[a]
[a] DEPARTMENT OF CHEMICAL ENGINEERING LOUISIANA, STATE UNIVERSITY BATON, ROUGE, LOUISIANA

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Studies in Batch and Continuous Solvent Sublation. III. Solubility of Pentachlorophenol in Alcohol–Water Mixtures and Its Effects on Solvent Sublation

K. T. VALSARAJ,* L. J. THIBODEAUX, and XIAO-Y. LU
DEPARTMENT OF CHEMICAL ENGINEERING
LOUISIANA STATE UNIVERSITY
BATON, ROUGE, LOUISIANA 70803

Abstract

The solubility of pentachlorophenol (PCP) in pure water and alcohol–water mixtures at pH = 2.5 and 5.0 at 25°C are reported. The use of the two-suffix Margules equation and UNIFAC to predict these effects is ascertained. The implications of these observations with respect to the solvent sublation of PCP in the presence of alcohol resulting from the redissolution of the organic solvent is also described.

INTRODUCTION

Pentachlorophenol (PCP) is often used as a fungicide and is a significant soil and water contaminant near wood-preservation sites. It is highly toxic and a suspected carcinogen (*1*). The behavior of PCP is influenced considerably by the pH of the solvent phase and has been discussed in detail by Schwarzenbach and coworkers (*2*). The behavior of PCP with respect to different processes for removal from the aqueous phase by way of adsorption on solid phases, liquid–liquid extraction, solvent sublation, and foam flotation has been the focus of several investigations (*2–5*).

In solvent sublation and solvent extraction processes it is important to understand the effects of organic cosolvents upon the aqueous phase solubility of PCP. The removal of PCP can be drastically altered if small amounts of cosolvents are present in the aqueous phase or if redissolution of the organic solvent occurs; these aspects have been addressed in our laboratory recently (*4*). It is well known that neutral hydrophobic compounds are solubilized in the aqueous phase to a large extent by cosolvents

*To whom correspondence should be addressed.

such as alcohols, ketones, colloidal micellar phases, and dissolved organic macromolecules (*6–10*).

Solubility data for hydrophobic aromatic compounds of environmental significance are sparse, although recent work in this regard are worthy of note (*8*, *11–13*). It has also been shown by several investigators that conservative predictions of aqueous solubilities of hydrophobic organic compounds in mixed solvents are possible by means of semiempirical thermodynamic models such as UNIQUAC, NRTL, UNIFAC, and Margules equations (*14*, *15*).

Pentachlorophenol and other chlorophenols are unique in that they display different degrees of hydrophobicity depending on the pH of the aqueous phase they are in. At pH values less than pK_a, they exist as neutral hydrophobic compounds, whereas at pH values larger than their pK_a, they exist as ionic, phenolate salts capable of being solubilized to a high degree in the aqueous phase. This tendency imparts unique properties as far as their speciation between liquid phases (in solvent extraction) and adsorption on solid phases (on sediments, soils, etc.) from the aqueous phase are concerned. Thus, one should expect similar effects of pH on the aqueous solubility of PCP in the presence of cosolvents. This paper describes our experiments on the effects of alcohols and pH on the aqueous solubility of PCP, and our study of the prediction of these effects using thermodynamic models, such as Margules equation, and semiempirical models, such as UNIFAC.

EXPERIMENTAL

Chemicals

The pentachlorphenol used was 99% pure, supplied by Aldrich Chemicals. The organic solvents used had the following purities: methanol (99.9%, HPLC grade, Mallinckrodt), ethanol (200 proof, Midwest Solvents Co.), and isopropanol (99%, HPLC grade, Mallinckrodt). The water used was distilled for all experiments.

Preparation of Saturated Solutions

Saturated solutions were prepared by equilibrating excess amounts of PCP with pure distilled water or pre-mixed combinations of solvents in 160 mL glass bottles provided with silicone-lined rubber septum and crimp caps. The total volume of liquid phase was 100 mL in all cases. pH was adjusted by using 1 *N* sulfuric acid or 1 *N* sodium hydroxide. The flasks were mixed for 1 week or more on a shaker bath maintained at 25 ± 0.5°C. These conditions and mixing time were observed to be enough for attaining equilibrium solubilities in water–alcohol mixtures.

Analysis

Samples from the alcohol–water mixtures were taken, acidified with a drop of 1 *N* sulfuric acid and diluted appropriately in a 50/50 mixture of methanol and water, and PCP absorbance at 214 nm were measured on a Hewlett-Packard HP 8452A Diode Array UV-Visible Spectrophotometer. Acidified solutions guaranteed that PCP was quantified as neutral molecules for UV determination. Concentrations of PCP were obtained from calibration curves of the UV detector response at 214 nm. Interferences from solvent peaks at 214 nm were checked by monitoring their UV spectra. No interferences were observed in these analyses. pH was monitored using a Corning Model 250 pH-ionalyser.

RESULTS AND DISCUSSIONS

At least two or more experimental replicates were used to measure the solubilities of PCP in alcohol–water mixtures. Each replicate was analyzed twice, and an average value was obtained. The mean aqueous solubility of PCP at two different pH values, viz., 2.5 ± 0.1 and 5.0 ± 0.3, were observed to be 8 ± 2 and 32 ± 3 mg/L, respectively, at 25°C. These values are compared with reported literature values in Table 1. There is considerable disagreement between these literature values, and it appears that most of it results from inappropriate control of pH and/or temperature. Except for the values reported by Bevenue and Beckman (*1*), none of the authors reported at what pH these values were obtained. In addition, there is very little information on the vapor pressure or Henry's constant for PCP from which to obtain estimates of PCP solubility. Speece and coworkers (*16*) used a molecular topology concept to determine Henry's constant and then used it to predict an aqueous solubility of 41 mg/L at 25°C. Bevenue and Beckman (*1*) reported a value of 14 mg/L at a pH = 3.0 at 20°C, which agrees more closely with our value of 8 ± 2 mg/L at a

TABLE 1
Comparison of Aqueous Solubility of PCP from Various Sources

Source	Aqueous solubility (mg/L)
Bevenue and Beckman (*1*)	14 at 20°C at pH = 3.0
	19 at 30°C
Wallin et al. (*18*)	30 at 50°C
Ehrenfeld et al. (*17*)	80 at 25°C
Nirmalakhandan and Speece (*16*)	80 at 25°C (calculated)
	41 at 25°C (predicted)
This work (at 25°C)	8 ± 2 at pH = 2.5 ± 0.1
	32 ± 3 at pH = 5.0 ± 0.3

pH = 2.5 at 25°C. Ehrenfeld et al. (*17*) and Nirmalakhandan and Speece (*16*), who reported experimental values of 80 mg/L at 25°C, do not give the original source, and hence their values are suspect.

Figure 1 illustrates the influence of organic cosolvents (methanol, ethanol, and isopropanol) upon the aqueous solubility of PCP at two different pH values, viz., 2.5 ± 0.1 and 5.0 ± 0.3, at 25°C. In general, all the cosolvents were found to increase PCP solubility in water at mole fractions of 0.01 and greater. The solubilities are reported as mole fraction values of PCP and are given in Table 2. It was observed that the influence of alcohols upon the aqueous solubility was larger at pH = 2.5 than at pH = 5.0. At pH = 5.0 the ratio of phenolate/neutral phenol concentration is 2.0 while at pH = 2.5 this ratio decreases to 6.3×10^{-3}, indicating that at the lower pH all PCP exists as neutral molecules of high hydrophobicity. pK_a of PCP is reported to be 4.7 (*2*). These figures indicate that the presence of alcohols does not influence the aqueous solubility of already hydrophilic phenolate ions as much as the highly hydrophobic neutral PCP molecules. It has been reported that the aqueous solubility of phenolate ions in pure water at pH = 8.0 increases to as much as 4000 mg/L (mole fraction = 2.7×10^{-4}) (*1*). Under such pH conditions the ionic strength of the solution may play a larger role in the solubility of phenolate species.

Figure 1 also indicates that the solubilizing power of alcohols at both pH values increase in the order: methanol < ethanol < isopropanol. This

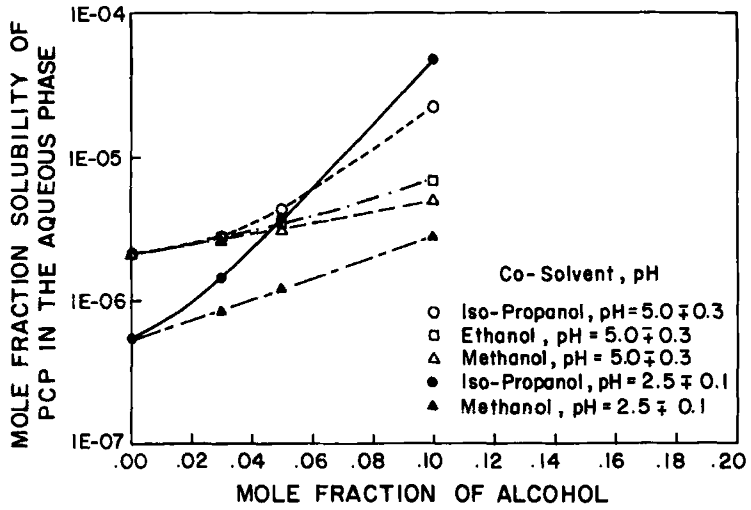

FIG. 1. Mole fraction solubilities of PCP in the presence of cosolvents at pH = 2.5 ± 0.1 and 5.0 ± 0.3 at 25°C.

TABLE 2
Mole Fraction Solubilities of PCP in Alcohol–Water Mixtures

Cosolvent	pH	Alcohol mole fraction	PCP mole fraction
None	2.5 ± 0.1	—	5.42×10^{-7}
	5.0 ± 0.3	—	2.16×10^{-6}
Methanol	2.5 ± 0.1	0.03	8.42×10^{-7}
		0.05	1.22×10^{-6}
		0.10	2.82×10^{-6}
Isopropanol	2.5 ± 0.1	0.03	1.41×10^{-6}
		0.05	3.76×10^{-6}
		0.10	4.59×10^{-5}
Methanol	5.0 ± 0.3	0.03	2.6×10^{-6}
		0.05	3.2×10^{-6}
		0.10	5.0×10^{-6}
Ethanol	5.0 ± 0.3	0.03	2.8×10^{-6}
		0.05	3.4×10^{-6}
		0.10	6.9×10^{-6}
Isopropanol	5.0 ± 0.3	0.03	2.7×10^{-6}
		0.05	4.4×10^{-6}
		0.10	2.2×10^{-5}

is the same order of increasing hydrogen bonding capability of alcohols with water. Several earlier investigators reported similar effects on the solubilities of other nonpolar hydrophobic compounds such as naphthalene (*8*), dichlorobenzene, and endrin (*7*).

The effect of alcohols on the PCP solubility follows closely the predictions of the two-suffix Margules equation as described by Mackay et al. (*19*). The equation is

$$\ln R_s = X_3[A_{12} - A_{13} + A_{23}] = X_3\overline{A} \qquad (1)$$

where R_s denotes the ratio of mole fraction solubility of PCP with the cosolvent present to the mole fraction solubility of PCP in pure water. X_3 is the cosolvent mole fractions. A_{12}, A_{13}, and A_{23} are interaction parameters between PCP (1), water (2) and cosolvents (3). $\overline{A}$ is an average value of the interaction parameter. The above equation predicts that if $\ln R_s$ is plotted against X_3, a linear relationship should be observed with slope $\overline{A}$; this was indeed observed for the case at pH = 2.5, as shown in Fig. 2. The slope was larger for isopropanol than for methanol, as predicted (*19*). However, this type of relationship was not observed at pH = 5.0 and is unlikely since the Margules equation will not be applicable to ionic systems such as phenolate ions at pH = 5.0.

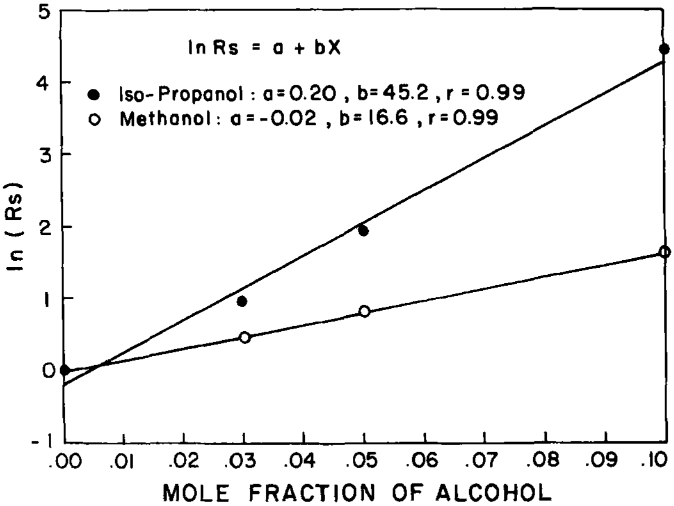

FIG. 2. Plot for the two-suffix Margules equation.

The aqueous solubilities of neutral, hydrophobic compounds can be predicted on a semiempirical basis from the surface areas and volumes of individual groups comprising the molecules and their interaction energies (*15*). One such method is the so-called UNIFAC model (*14*, *15*). UNIFAC gives the activity coefficients of solutes based on the mole fractions of the components. The activity coefficient consists of a combinatorial part due to the differences in sizes and shapes of the molecules in a mixture and a resudual part due to energy interactions. All components in solution must be nonelectrolytes, nonpolymers, and condensable. For compounds that are solids at room temperature, such as PCP, the mole fraction solubility of the solute in water or in an alcohol mixture (X_1) can be obtained by using the equation (*15*, *20*)

$$X_1 = \frac{1}{\gamma_1} \exp\left[\frac{\Delta H_f}{R}\left(\frac{1}{T_m} - \frac{1}{T}\right)\right] \tag{2}$$

where γ is the activity coefficient (calculated by UNIFAC) and ΔH_f is the molar heat of fusion of the solute at its melting point, T_m. Mackey et al. (*19*) showed that for most compounds where the molar heat of fusion is not available, the above equation may be written as

$$X_1 = \frac{1}{\gamma_1}[-0.01(T_m - 298)] \tag{3}$$

where $\Delta H_f/RT_m$ was chosen as 6.8.

The UNIFAC program is first used to obtain γ_1 at infinite dilution of PCP in pure water (defined as $X_1 = 10^{-9}$), and the effect of PCP mole fractions on γ is ascertained. Figure 3 shows that γ_1 is independent of mole fraction up to $X_1 = 1 \times 10^{-4}$. This shows that for all the conditions encountered in the present experiments (where X_1 is less than 10^{-5}), UNIFAC predicts that γ_1 is not a function of X_1. Therefore, we can substitute γ_1^{∞}, the infinite dilution activity coefficient (obtained by setting $X_1 = 10^{-9}$ in UNIFAC) for γ_1 and compare them with the experimental values if the mole fractions are less than 10^{-5}.

It should be pointed out that UNIFAC predicts an infinite dilution activity coefficient of 1.3×10^{-8} which, when combined with $T_m = 463$ K, yields a mole fraction solubility, X_1 (UNIFAC), for PCP in pure water of 1.7×10^{-8} whereas the experimental value was 5.4×10^{-7}. This may partly be due to the arbitrary value of the heat of fusion used in obtaining Eq. (3). Thus, UNIFAC underpredicts the PCP solubility in water. We found that this trend is maintained in alcohol–water mixtures as well. However, the effect of alcohols on infinite dilution activity coefficients of PCP is vastly overpredicted. These are shown in Fig. 4 where the y-axis is defined as the ratio of infinite dilution activity coefficients $= \gamma_1^{\infty}(X_{\text{cosolvent}} \neq 0)/\gamma_1^{\infty}(X_{\text{cosolvent}} = 0)$, where $\gamma_1^{\infty}(X_{\text{cosolvent}} = 0)$ was evaluated at a solute mole fraction of 10^{-9} for UNIFAC predictions, and for the experiments the value of γ_1 was obtained from Eq. (3) and the ratio calculated. Measured cosolvent effects were much smaller than those predicted by UNIFAC. It is interesting to note that at least an order of magnitude

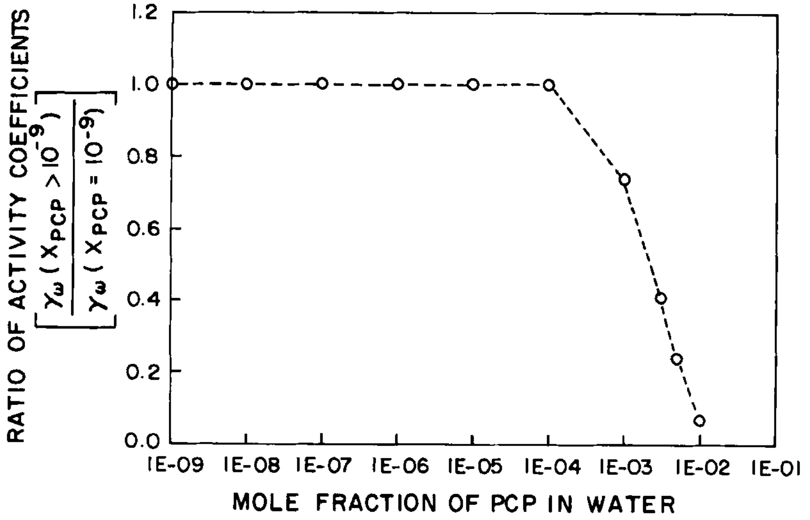

FIG. 3. UNIFAC prediction of PCP activity coefficient on PCP mole fraction in water.

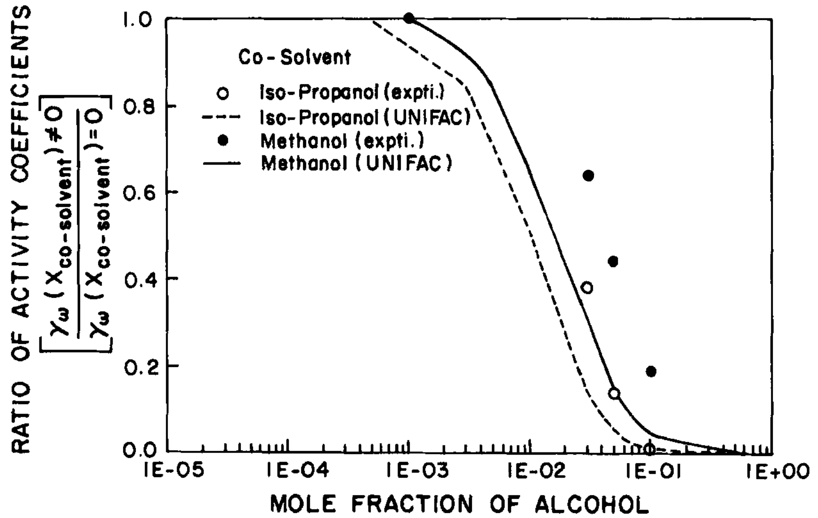

FIG. 4. UNIFAC prediction and experimental observations at pH = 2.5 of the effect of methanol and isopropanol on PCP activity coefficient in water–alcohol mixtures.

larger mole fractions of cosolvent than those predicted by UNIFAC were necessary to see significant cosolvent effects on PCP solubility. Thus UNIFAC may be considered a conservative model as have been previously observed for other chlorinated compounds (*6*). The qualitative UNIFAC observations that the effect would be more pronounced for cosolvents of higher hydrophobicity (e.q., isopropanol versus methanol) is valid, as can be seen from Fig. 4. Thus, although UNIFAC is a conservative model, it is easy to use, at least to obtain order of magnitude estimates of cosolvent effects, especially in those cases where accurate experimental data are unavailable.

In previous papers (*4, 21*) we showed that the solvent sublations of PCP into mineral oil and decyl alcohol are seriously effected by methanol, ethanol, and propanol in the aqueous phase. The trend of decreasing sublation efficiency with increasing chain length of the cosolvent followed the effect on PCP solubility as predicted by UNIFAC and as shown in the present experiments. Similar observations on the sublation of other compounds (*22, 23*) are also validated by our calculations. An additional aspect of significance is whether the redissolution of decyl alcohol (the solvent used for sublation) in the aqueous phase would seriously increase the PCP solubility and decrease its hydrophobicity and thereby decrease the PCP removal by sublation. Our determinations of PCP solubility in decyl-alcohol-saturated water (7 ± 1 mg/L at pH = 2.5 and 38 ± 3 mg/L at pH = 5.0) showed no significant enhancement as compared to its solubility in pure water. It appears that decyl alcohol, even at its saturation solubility of 4.3×10^{-6} mole fraction in water, therefore may not decrease the hydrophobicity of neutral PCP molecules, but it will compete with PCP molecules for adsorption sites on the air bubbles and may thus decrease the rate of removal of PCP from the aqueous phase.

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