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Evaluation of Some Prediction Models for the Determination of Physicochemical Constants of Dialkylphosphoric Acids

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ABSTRACT

Some semitheoretical models for the determination of physicochemical constants of di-2-methylnonylphosphoric acid (DMNPA) and di-2-ethylhexylphosphoric acid (DEHPA) are evaluated. Dissociation constants (pK_a) for the two dialkylphosphoric acids have been estimated by using the modified Hammett equation. The pK_a values are also estimated by an interpolation method based on the Born equation. Distribution equilibrium between water and some kinds of organic solvents has been studied for DMNPA and DEHPA. The dimerization constants (K_2) and distribution constants (K_D) for the two dialkylphosphoric acids are predicted by using Leggett equation and Kamlet-Taft solvatochromic parameters. The linear solvation energy relationship model can be applied to the approximation of $\log K_2$ and $\log K_D$ for DMNPA and DEHPA in different organic solvents.

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Key Words: Prediction model; Dissociation constant; Dialkylphosphoric acid; Hammet equation; Distribution constant.

INTRODUCTION

Acidic organophosphorus compounds have been used extensively for the extraction of many metal ions because of highly selective and effective reagents.[1–3] Among them, dialkylphosphoric acids have been recognized to be very useful for mutual separation of transition or rare earth metal ions from aqueous media.[4–10] Furthermore, it has also been demonstrated that the extraction behavior of metal complexes can be correlated with physicochemical properties of extractants and organic solvents used. Therefore, we have investigated such equilibrium constants of extractants as aqueous acid dissociation constant (K_a), dimerization constant (K_2) in organic solvent, and distribution constant (K_D) between the organic and aqueous phase. However, it is particularly difficult to determine K_a values of organophosphorus acid compounds with relatively long chains in water because of their low solubilities.

In this article, we studied the validity of Hammet and Born relations to determine the dissociation constants (pK_a) value of di-2-methylnonylphosphoric acid (DMNPA) and di-2-ethylhexylphosphoric acid (DEHPA) in water. Recently, DMNPA has been paid much attention in the solvent extraction of metal ions.[9,10] The extraction of DMNPA and DEHPA is also studied to predict the K_2 and K_D values for some organic solvents. The equation we propose here is based on Kamlet-Taft solvatochromic parameters and Leggett model.

EXPERIMENTAL

Reagents and Apparatus

We used DEHPA (above 95% in purity) purchased from Tokyo Kasei Chemical Industry Co Ltd., Tokyo, Japan, without further purification. The DMNPA (above 96% in purity) was kindly supplied by Daihachi Chemical Industry Co Ltd., Osa, Japan. Ethanol, heptane, n-Dodecane, toluene, chloroform, and 1-octanol of reagent grade (Wako Pure Chemical Industry Co Ltd., Tokyo, Japan) were used as organic solvents. The other reagents were of analytical reagent grade.

The pH was measured using a TOA-DKK Model IM-55G pH-meter fitted with a Model GST-5721C glass electrode (TOA-DKK Electronics Co Ltd., Tokyo, Japan).

Procedures

Potentiometric Determination of pK_a

The dissociation constants of DEHPA and DMNPA were determined by a potentiometric titration. A mixed solution of ethanol-water containing the corresponding acid was titrated with 0.10 mol/dm^3 NaOH. The pH meter was used for the potentiometric measurement.[11]

Two-Phase Potentiometric Determination of K_2 and K_D

A volume of 18.0 cm^3 distilled water and 20.0 cm^3 phosphoric acid in organic solvent were placed into a 50-cm^3 centrifuge tube. A potentiometric two-phase titration was carried out while maintaining both the neutralized fraction constant and phase ratio equal to unity. This was achieved by successively adding 0.2 cm^3 of 1×10^{-2} mol/dm^3 NaOH into mixture.[12] The two phases were mixed well and then were centrifuged for enough time until reaching the complete equilibration. The pH value of the aqueous phase was measured.

RESULTS AND DISCUSSION

Dissociation Constants of Dialkylphosphoric Acids

As mentioned previously, the pK_a values of dialkylphosphoric acids as extractants are very important parameters to elucidate the extraction processes of metal complexes. Because DEHPA and DMNPA are considerably insoluble in water, however, the conventional methods to determine pK_a are inapplicable to the two dialkylphosphoric acids. The two estimation methods, based on the so-called Hammett and Born relations, were evaluated for the determination of the pK_a values.

Kabachnik proposed the emprical equation, based on Hammett relation, for pK_a values of some organophosphonic ester and phosphoric acids in 50% ethanol-water solution, introducing the substituent polar constant σ_ϕ to explain the structure-reactivity of phosphorus-based ligand.[13–15] However, the long chain alkylphosphorus compounds show low solubilities even in 50% (v/v) ethanol-water solution, which prevent determining accurate pK_a values.

Yuan's group studied the long-chain acidic organophosphorus compounds and proposed a new set of polar constants σ^P as an extension of the Kabachnik's constants to correlate with pK_a for dialkylphosphorus acids in 75% ethanol-water solution[16,17]:

$$pK_a = 1.32 - 1.76\sum \sigma^p \quad (25°C) \tag{1}$$

$$n = 38, \quad r = 0.9897,$$

where n and r represent the number of points and correlation coefficient, respectively. The estimated and experimental results obtained in 75% ethanol-water are given in Table 1. The polar constants of substitutes were calculated by using the Hammett equation proposed by Yuan's group. As seen from Table 1, the experimental values potentiometrically determined are slightly higher than the estimated ones, owing to different temperatures investigated. The temperature of this study is slightly higher than that reported by Yuan's group. The validity of the Hammett equation to estimate approximate pK_a values for dialkylphosphoric acid in ethanol-water mixture was assured.

One of the objectives of this study is to determine the pK_a values of the two dialkylphosphoric acids in water. Interestingly, Martinez et al. reported that the pK_a values of long-chain phosphinic compounds showed good correlation with the reciprocal of relative permittivity of mixture of ethanol and water by using the Born equation.[18] The pK_a values of DEHPA and DMNPA in different mixtures of ethanol-water, determined potentiometrically (Table 2), were plotted against the reciprocal of the relative permittivity for the ethanol-water mixtures (Fig. 1). As seen from Fig. 1, good correlations have been obtained for the two dialkylphosphoric acids. When the straight lines were interpolated to 12.8×10^{-3} (the point of water only), we could

Table 1. Polar constants of substituents and the estimated pK_a of dialkylphosphoric acids in 75% ethanol-water.

Acid	Substituent	σ^p	pK_a'	pK_a^*
DEHPA	i-$C_8H_{17}O$	−0.57 ± 0.05	3.45 ± 0.10	3.57 ± 0.06
DMNPA	i-$C_{10}H_{21}O$	−0.58 ± 0.05	3.36 ± 0.10	3.48 ± 0.08

pK_a' = Estimated by means of Hammett equation; pK_a^* = determined from this study.

Table 2. Dissociation constant of some dialkylphosphoric acids in ethanol-water mixtures at 27 ± 1°C.

$V_{ethanol}$:V_{water}	DEHPA	DMNPA
90:10	4.08 ± 0.03	3.92 ± 0.02
80:20	3.73 ± 0.04	3.59 ± 0.05
75:25	3.57 ± 0.06	3.48 ± 0.08
70:30	3.51 ± 0.05	3.41 ± 0.05
60:40	3.29 ± 0.03	3.18 ± 0.04

estimate the pK_a values in water: 2.75 ± 0.03 for DEHPA and 2.71 ± 0.02 for DMNPA, respectively. The estimated pK_a value for DEHPA in water gave better agreement with 2.79 of the corresponding value reported.[19]

In fact, the standard free energy of dissociation consists of the following two terms, an electrostatic one, which includes specific solute-solvent interactions, and solvation phenomena. When the electrostatic effects

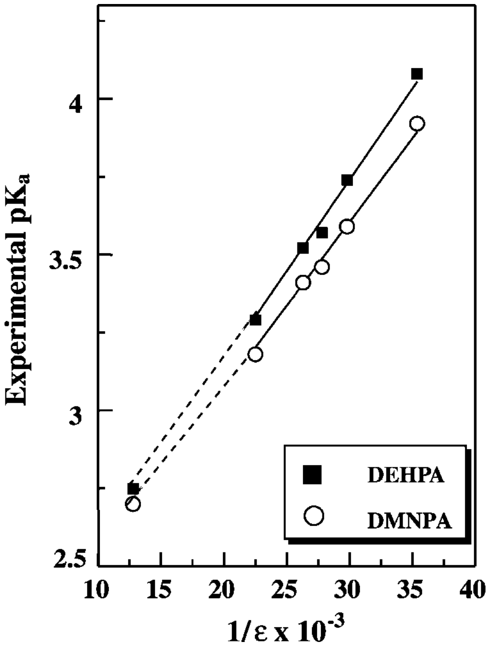

Figure 1. Experimental pK_a values against the reciprocal of permittivity.

predominate, a straight line should be obtained in the plot of pK_a vs. the reciprocal relative premittivity as it occurs with DEHPA investigated. Thus we can use this indirect method to estimate the pK_a value of long-chain dialkylphosphoric acid in water.

Dimerization Constants and Distribution Constants for Dialkylphosphoric Acids

It is well-known that dialkylphosphoric acids are present as dimers in nonpolar solvents and as monomers in polar ones, respectively.[20] The K_D and K_2 values for DEHPA and DMNPA between water and some organic solvents were determined, as shown in Table 3. Here we have attempted to obtain an empirical equation concerning the estimation of K_D for the two extractants between water and different organic solvents.

Taft et al. first formulated a linear free energy model for partitioning of a solute between two phases.[21] When one of the solvents is water, the formula can be expressed according to the following:

$$\log K_{1,2} = \alpha\delta_{H1}^2 + b(\pi_1^* - c\delta_1) + d_{\alpha 1} + e\beta_1 + f \tag{2}$$

where $K_{1,2}$ is the mole fraction distribution coefficient, δ_{H1}^2 is the molar cohesive energy density of the solvent, and π_1^*, α_1 and β_1 are the Kamlet-Taft solvatochromic parameters of the organic solvent, respectively. The constants a-f can be determined by the multiple linear regression, if distribution data are available. Recently, Leggett has proposed a modification of Eq. (2) by

Table 3. Distribution constants and dimerization constants in various two-phase extraction systems.

	DEHPA		DMNPA	
Media	$\log K_D$	$\log K_2$	$\log K_D$	$\log K_2$
Heptane/water	3.04	3.54	4.10	4.01
Octane/water	2.66	4.02	3.78	4.23
Dodecane/water	2.33	4.33	3.24	4.70
Benzene/water	3.25	3.85	—	—
Toluene/water	3.01	4.36	4.70	3.24
Chloroform/water	4.90	2.40	5.25	4.07
1-Octanol/water	4.40	—	4.27	—

Table 4. Solvatochromic parameters of some organic solvents.

Solvent	X_w	π^*	β	α
Hexane	—	−0.04	0	0
Heptane	5.1×10^{-4}	−0.02	0	0
Octane	1.5×10^{-4}	0.01	0	0
Dodecane	6.9×10^{-5}	0.05	0	0
Chloroform	4.8×10^{-3}	0.58	0.10	0.20
Butylether	—	0.24	0.46	0
Benzene	2.7×10^{-3}	0.59	0.10	0
Toluene	1.7×10^{-3}	0.54	0.11	0
Xylene	—	0.47	0.12	0
Octanol	—	0.40	0.33	0.45

X_w = mole fraction of water in water-saturated solvent.

substituting the cavity term in δ^2_{H1} by terms in $\alpha\beta$, or $\alpha\beta$ and π^{*2}, where α, β, π^* are the solvatochromic values of the organic solvent[22,23]:

$$\log K_D = g\alpha + h\beta + i\pi^* + j\alpha\beta + k\pi^{*2} + 1 \qquad (3)$$

where the parameters g-l are constants. Using this modified equation, very good correlations were obtained for several solutes such as dimethylmethylphosphonate, phenol, aniline, and acetylacetone.

The effect of organic solvents on K_D for the extraction of DEHPA and DMNPA was investigated according to the Eq. (3) proposed by Leggett. The solvatochromic parameters of dry solvents shown in Table 4 were used.[23,24] The parameters for DEHPA and DMNPA, obtained from Eq. (3), are listed in Table 5.

Table 5. Parameters calculated for dialkylphosphoric acids.

Acid	g	h	i	j	k	l	σ	N
DEHPA	13.15	13.15	−10.35	−47.04	14.92	2.79	0.11	7
DMNPA	8.56	19.80	−12.34	−63.04	18.13	3.89	0.07	7

Table 6. log K_C for different dialkylphosphoric acids.

Dialkylphosphoric acid	log K_c	N-points
Diethyl	− 1.8 ± 1.0	5
Di-*n*-butyl	3.2 ± 0.6	9
Di-*n*-pentyl	6.3 ± 0.6	4
Di-*n*-hexyl	8.2 ± 0.7	5
Di-*n*-octyl	11.9 ± 0.7	9
Di-2-ethylhexyl	10.1 ± 0.8	6
Di-2-methylnonyl	12.5 ± 1.0	5

The linear solvation energy relationship model for DEHPA and DMNPA can be correlated to the Eq. (4) and (5), respectively.

$$\log K_D = 13.15\alpha + 13.5\beta - 10.35\pi^* - 47.04\alpha\beta + 14.92\pi^{*2} + 2.79 \quad (4)$$

$$\log K_D = 8.56\alpha + 19.8\beta - 12.34\pi^* - 63.04\alpha\beta + 18.13\pi^{*2} + 3.89 \quad (5)$$

As a general rule, the longer the alkyl chain of the organic substituents, the greater the distribution constant, regardless of organic solvents used. In fact, the log K_D value increased about 0.6 units for each $-CH_2$ added to the alkyl chain. On the other hand, the K_2 value increased as the number of carbon chain decreased. This agrees very well with the correlation $K_2K_D^2 = \text{const}$, which is called as a global constant (K_C). Obviously, the K_C value should be the same for a certain extractant in different solvents.[25] The log K_C values for some dialkylphosphoric acids are shown in Table 6, including the literature.[24,26,27] For the straight-chain dialkylphosphoric acids, the log K_C value increases about one unit for each $-CH_2$ added to the hydrocarbon chain. Thus we can easily get the approximated values of K_D and K_2 by using the correlated equation and log K_C.

CONCLUSION

Because long-chain dialkylphosphoric acids are sparingly soluble in water, the indirect methods based on the suitable Hammett and Born equations were suggested to obtain the pK_a values of DMNPA and DEHPA. The extraction of DMNPA and DEHPA into organic solvents was also studied to predict the physicochemical constants K_2 and K_D for some organic solvents. The equations based on Kamlet-Taft solvatochromic parameters and Leggett model were evaluated to determine the approximated values of K_2 and K_D for DMNPA and DEHPA.

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