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Liquid-Liquid Distribution Study of the Dissociation of Perchloric, Nitric, and Picric Acids in Polar Organic Solvents

Tatsuya SEKINE,* Tohru YOSHIKATA, and Takashi SAITOU
Department of Chemistry, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162

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The liquid-liquid distribution equilibria of perchioric, nitric, and picric acids between water and 4-methyl-2-pentanone or 4-methyl-2-pentanol have been determined at 298 K by measuring the concentrations of the anions in the two phases by spectrophotometry. The distribution ratio always increased on increase of the acid concentration; this was explained in terms of an increase in the degree of association of the acids in the organic phase. It was concluded from the analysis of the distribution data that the dissociation constant of perchloric acid was the highest and the value of picric acid was higher than that of nitric acid in 4-methyl-2-pentanone. The dissociation constant of picric acid was also higher in 4-methyl-2-pentanol than that of nitric acid; it was similar to that of perchloric acid. The differences of the dissociation constants were larger in 4-methyl-2-pentanone than in 4-methyl-2-pentanol.

In a previous study of solvent extraction of several mineral acids into 4-methyl-2-pentanone (MIBK), it was found that the shape of the extraction curve as a function of the acid concentration was appreciably different for different acids.[1] Several factors in the liquid–liquid system could be responsible for this and the difference in the dissociation of the acid in the organic phase might be one of the reasons. In order to learn further details of this problem, the liquid–liquid distribution ratio of perchloric, nitric, and picric acids between water and 4-methyl-2-pentanone or 4-methyl-2-pentanol has been measured as a function of the acid concentration and the extraction constant. The dissociation constant in the organic solvents were also calculated for these acids.

Experimental

The solvents and the acids were of reagent grade. The solvents were washed first with 0.5 mol dm^{-3} perchloric acid and then twice with water. They were then washed twice with 0.5 mol dm^{-3} sodium hydroxide solution and water. The solvent was finally washed several times with water. The concentrations of the stock solutions of the acids were determined by titration with standard sodium hydroxide solution. A 6 cm^3 portion of an aqueous acid solution and the same volume of the solvent were placed in a stoppered glass tube (capacity 20 cm^3). The two phases were vigorously agitated by a mechanical shaker for 15 min and centrifuged. A portion was pipetted from each phase and each was transferred separately into another tube.

The distribution ratio of picric acid was determined as follows. A 5 cm^3 portion of an aqueous 0.01 mol dm^{-3} solution of tetrabutylammonium chloride was added to the tube containing the equilibrated organic phase and the two phases were agitated for about 5 min in order to exchange the proton of the extracted picric acid with the tetrabutylammonium ion and thus all the picrate in the organic phase was in the anionic form whose optical density was higher than that of the acid form. Since the acid concentration in the aqueous phase was always lower than 1×10^{-4} mol dm^{-3} (its pK_a is 0.3[2]), this acid should be completely in the dissociated form. The amount of picrate was determined from the optical absorption of the organic phase thus obtained at 364 nm ($\varepsilon=1.50\times10^4$ in 4-methyl-2-pentanol) or 375 nm ($\varepsilon=1.80\times10^4$ in 4-methyl-2-pentanone). The amount of picrate ions in the equilibrated aqueous phase was also determined from the absorption at 355 nm ($\varepsilon=1.45\times10^4$ in aqueous solutions).

The distribution ratio of perchloric and nitric acid was determined as follows. A 5 cm^3 portion of water was added to the tube containing the equilibrated organic phase. The two phases were agitated in order to back-extract the acid and then centrifuged. A 4 cm^3 portion of the aqueous phase was transferred to another tube and a 1 cm^3 portion of 1×10^{-3} mol dm^{-3} solution of Crystal Violet and a 5 cm^3 portion of chlorobenzene were added. The two phases were vigorously agitated for 5 min and centrifuged. When the acid concentration was high, the amount extracted was large. In such a case, the washed solution was diluted with water before the dye and the solvent were added and a 4 cm^3 portion of the resulted solution was treated in the same manner as above. The optical absorption of the organic phase was measured at 596 nm. The apparent molar absorption coefficient after this treatment was 1.06×10^5 for perchloric acid and 3.35×10^4 for nitric acid. When the distribution ratio was low, the acid in the aqueous phase at equilibrium was calculated from the amount initially present in the aqueous phase and that extracted into the organic phase. In other cases, the aqueous phase was treated in the manner described above in order to determine the acid concentration. When the acid concentration was higher than 0.1 mol dm^{-3}, however, titration with a standard barium hydroxide was also employed for the determination of the acid in both phases. The water content in the organic phase was determined by a Karl-Fischer titration.

Statistical

In the present paper any species in the organic phase is denoted by a subscript "org" and that in the aqueous phase by lack of any subscript. Solvent extraction of an acid which dissociates in the aqueous phase may be written as;

$$\mathrm{H^+ + A^- \rightleftharpoons HA_{(org)}}$$

$$\begin{aligned} K_{\mathrm{ex}} &= \{\mathrm{HA}\}_{\mathrm{org}}\{\mathrm{H^+}\}^{-1}\{\mathrm{A^-}\}^{-1} \\ &= (\gamma_{\mathrm{HA}}^{\mathrm{org}})(\gamma_{\pm\mathrm{HA}})^{-2}[\mathrm{HA}]_{\mathrm{org}}[\mathrm{H^+}]^{-1}[\mathrm{A^-}]^{-1}, \end{aligned} \tag{1}$$

where $(\gamma_{\pm\mathrm{HA}})$ is the mean activity coefficient of the acid in the aqueous phase and $(\gamma_{\mathrm{HA}}^{\mathrm{org}})$ is the activity coefficient of the acid in the associated form in the organic phase. When the extracted acid also dissociates in the organic phase, the equilibrium may be written as;

$$\mathrm{HA_{(org)} \rightleftharpoons H^+_{(org)} + A^-_{(org)}}$$

$$\begin{aligned} K_{\mathrm{a(org)}} &= \{\mathrm{H^+}\}_{\mathrm{org}}\{\mathrm{A^-}\}_{\mathrm{org}}^{-1}\{\mathrm{HA}\}_{\mathrm{org}}^{-1} \\ &= (\gamma_{\pm\mathrm{HA}}^{\mathrm{org}})^2(\gamma_{\mathrm{HA}}^{\mathrm{org}})^{-1}[\mathrm{H^+}]_{\mathrm{org}}[\mathrm{A^-}]_{\mathrm{org}}[\mathrm{HA}]_{\mathrm{org}}^{-1}, \end{aligned} \tag{2}$$

where $(\gamma_{\pm HA}^{org})$ is the mean activity coefficient of the acid in the dissociated form in the organic phase. The distribution ratio of the acid in the absence of any other acids and salts of A^- may be written as;

$$\begin{aligned} D &= [HA]_{org,\,total}/[HA]_{total} \\ &= ([HA]_{org}+[H^+]_{org})/([HA]+[H^+]) \\ &= ([HA]_{org}+[A^-]_{org})/([HA]+[A^-]) \qquad (3) \\ &= (K_{ex}(\gamma_{\pm HA})^2(\gamma_{HA}^{org})^{-1}[A^-]^2 \\ &\quad +\sqrt{K_{a(org)}K_{ex}}(\gamma_{\pm HA})(\gamma_{\pm HA}^{org})^{-1}[A^-])/([HA]+[A^-]). \qquad (4) \end{aligned}$$

When the acid dissociation in the aqueous phase is complete, the distribution ratio may be given as;

$$\begin{aligned} D &= (\gamma_{\pm HA})^2(\gamma_{HA}^{org})^{-1}K_{ex}[A^-] \\ &\quad + (\gamma_{\pm HA})(\gamma_{\pm HA}^{org})^{-1}\sqrt{K_{ex}K_{a(org)}}. \qquad (5) \end{aligned}$$

The values of $(\gamma_{\pm HA})$ were taken from the literature.[3] When the material concentration in the organic phase is low, both of the activity coefficients (γ_{HA}^{org}) and $(\gamma_{\pm HA}^{org})$ can be taken as unity, Eq. 5 can then be rewritten as;

$$D = (\gamma_{\pm HA})^2K_{ex}[H^+] + (\gamma_{\pm HA})K_{ex}K_{a(org)}. \qquad (6)$$

From the values of D determined against $[H^+]$, the values of K_{ex} and $K_{a(org)}$ may be calculated on the basis of Eq. 6 by a successive approximation method using a least squares computer program.

Results and Discussion

Figures 1 and 2 give the log D *vs.* log $[H^+]$ plots of the acids. By the least squares calculation of these data, the extraction constant in Eq. 2 and the acid dissociation constant in the organic phase in Eq. 3 were obtained as listed in Table 1. The solid curves in Figs. 1 and 2 were calculated by Eq. 6 using the values of these constants.

As seen from Table 1, extraction constants of perchloric and nitric acid into 4-methyl-2-pentanol are higher than into 4-methyl-2-pentanone but that of picric acid is one order higher into the ketone. The increase in the slope of the plot on increasing the acid concentration can be explained in terms of the higher degree of association of the acid at higher concentration in the organic phase as seen from Eq. 5.

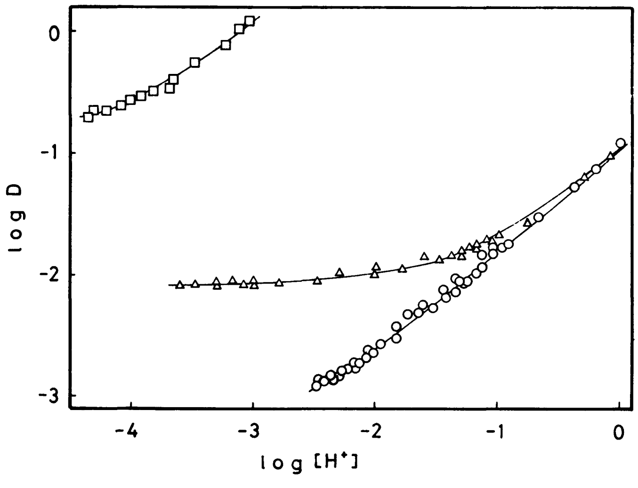

Fig. 1. The distribution ratio of acids as a function of their concentration in the equilibrated aqueous phase when solvent is 4-methyl-2-pentanone. Acids: perchloric acid (△), nitric acid (○), and picric acid (□). The solid curves were calculated by Eq. 6 using the value in Table 1.

In aqueous solutions, the acid strengths are in the order of perchloric acid>nitric acid>picric acid. The two mineral acids dissociate completely in their aqueous solutions. Picric acid is not a weak acid and its dissociation in aqueous solution is nearly complete over the concentration range of the present study. However, all of the acids are weak in these two organic solvents. Perchloric acid is always the strongest in both of the solvents but picric acid in 4-methyl-2-pentanol is as strong as perchloric acid. The difference in the strength of the acid is greater in 4-methyl-2-pentanone than in 4-methyl-2-pentanol and perchloric acid is weaker in the alcohol than in the ketone but the other two acids show an opposite tendency.

Several properties, such as the dielectric constant, solvation of the proton and anion, and interactions among the solvent molecules should affect the dissociation of the acid in these solvents. Furthermore, the solvents are saturated with water. It was found that the water content determined by Karl-Fischer titration was nearly constant except when the acid concentration in the aqueous phase was higher than 0.1 mol dm^{-3}. Above this an increase of water content was observed but the calculated values of K_{ex} and $K_{a(org)}$ were not affected whether or not the data obtained in this higher acid concentration range were included in the calculation.

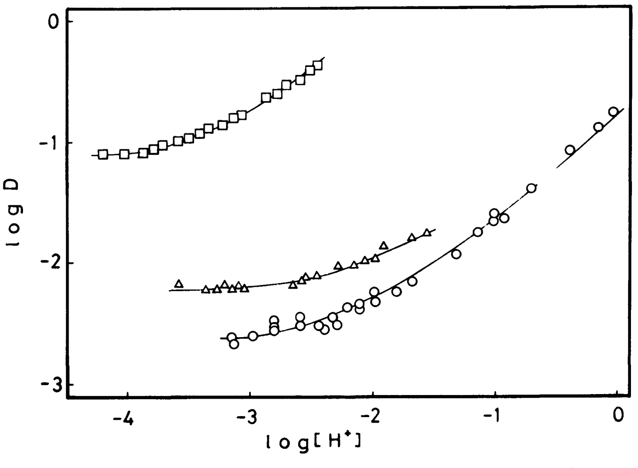

Fig. 2. The distribution ratio of acids as a function of their concentration in the equilibrated aqueous phase when solvent is 4-methyl-2-pentanol. Acids: perchloric acid (△), nitric acid (○), and picric acid (□). The solid curves were calculated by Eq. 6 using the value in Table 1.

Table 1. Extraction constant (Eq. 1) and acid dissociation constant (Eq. 2) in organic solvents

	4-methyl-2-pentanone		4-methyl-2-pentanol	
	$pK_{a(org)}$	$\log K_{ex}$	$pK_{a(org)}$	$\log K_{ex}$
Perchloric acid	3.5	−0.6	4.3	−0.2
Nitric acid	6	−0.6	4.8	−0.4
Picric acid	4.7	3.1	4.4	2.1

The association of strong acids in organic solvents have been extensively studied by conductimetry and potentiometry (for example Ref. 2 and Refs. 4 to 7 and also the references cited therein). Another approach to this problem is spectrophotometry which is however, applicable only when the optical absorption changes on acid dissociation as for picric acid.[5-6] The previous papers[5-7] observe that the strong acids which dissociated completely or nearly completely in aqueous solutions dissociated only partially in polar organic solvents. Furthermore the order of the dissociation in the solvents could be different from that in aqueous solutions and it could also be different in different organic solvents. For example, it was pointed out that the dissociation of picric acid was higher in dimethyl sulfoxide than of perchloric acid. This was explained in terms of the solvation of the former being stronger than that of the latter.[2]

In the present study, the solvents were saturated with water whereas in most of these previous studies, the solvents had been distillated and the water content should be much below saturation level. However, the tendency of the acid dissociation found in the present study is similar to that found previously. It can be pointed out that although the water content was different at different acid concentrations, a set of values of the two equilibrium constants could explain the results reasonably over a wide range of acid concentration.

There have been few quantitative studies of acid dissociation in organic solvents by liquid-liquid distribution methods. The present results indicate that this method is favorable for because even though the determination is done spectrophotometrically it can also be applied to those acids which have no strong optical absorption. If a dye of high molar extinction is used, it is possible to determine the equilibrium even when the acid concentration is low. However, it should also be noted that control of the water content in the solvent is not possible and several coexisting anions may interfere with the determination. Furthermore, the solvent should be water-immiscible and the anion should at least to some extent be extractable with a cationic dye.

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