

몇 가지 혼합용매에서의 티오아세트산의 解離常數

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Dissociation Constant of Thioacetic Acid  
in Some Mixed Solvents

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Dissociation constant of thioacetic acid, which is insoluble in water, has been determined potentiometrically in the mixed solvents, such as methanol-water, acetone-water, and dimethylsulfoxide-water mixtures, with varying the mole fractions of organic solvents.

The results are discussed with the polarities of solvents and with the dissociation constant of acetic acid.

Experimental

Extra-pure grade reagents of thioacetic acid and sodium perchlorate were used without further purification. Methanol and acetone were purified by distillation, and dimethyl sulfoxide was purified in the previously reported manner.<sup>1</sup> The constant-boiling hydrochloric acid and stock solution of sodium hydroxide free from carbonate were used.

pH meter, Model Copenhagen Radiometer A/5, with Model GK 2311 C combined electrode was used. The calibration method of the electrode in the mixed solvent was the same as the

manner described previously.<sup>2</sup>

All solutions to be examined were maintained in the thermostatted bath at 25°C, and ionic strength was adjusted with sodium perschlorate at 0.1M.

Results and Discussion

The plots of dissociation constants versus the mole fractions of organic solvents give the straight lines as shown in Fig. 1. The empirical equations, between  $pK_a$  and the mole fraction of organic solvent, derived by the least square

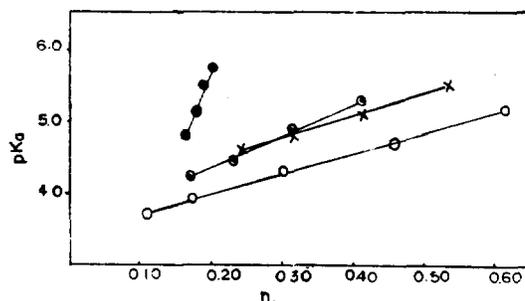


Fig. 1. Plot of  $pK_a$  vs. the mole fractions of the organic solvents at 25°C

○: Methanol, ×: Dimethylsulfoxide,  
⊙: Acetone, ●: Dioxane

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Table 1. Empirical formulas for dissociation constant of thioacetic acid with the mole fraction of organic solvent at 25°C and 0.1M of ionic strength.

Solvent	Empirical formula	Mole fraction
Methanol-water	$pK_a = 2.86n + 3.58$	$n = 0.06 \cdots \cdots 0.56$
Acetone-water	$pK_a = 4.33n + 3.71$	$n = 0.12 \cdots \cdots 0.36$
Dioxane-water	$pK_a = 23.3n + 2.27$	$n = 0.11 \cdots \cdots 0.18$
D. M. S. O. -water	$pK_a = 3.07n + 3.99$	$n = 0.19 \cdots \cdots 0.48$

method are presented in Table 1.

The extrapolated values of each straight line to the mole fraction of zero, or  $pK_a$  values put  $n=0$  into each empirical equation would be correspond to the dissociation constant of thioacetic acid in aqueous solution. The values extrapolated are close to 3.76 with deviation of six percent, except the dioxane-water solution. Since the  $pK_a$  value extrapolated is smaller than that of acetic acid at 25° C, it is convinced that thioacetic acid is clearly a stronger acid than acetic acid. This conclusion is explained by the greater atomic radius and the smaller electronegativity of sulfur atom, i.e., the weaker bond energy of S—H bond than that of O—H bond.

As shown in Fig. 2, the  $pK_a$  values increase linearly as the reciprocal values of the dielectric constants of the solutions<sup>3</sup> decrease. In acetone-water solution, however, this relation is not held in the solution having the smaller dielectric constant than 35. These results imply that the properties of the mixed solvents are depend on the polar nature only in the solvent having the greater dielectric constant than 35. From the facts that the  $pK_a$  values extrapolated do not have the same values and that the larger deviation is shown in the dioxane-water solution, the inherent properties of the organic

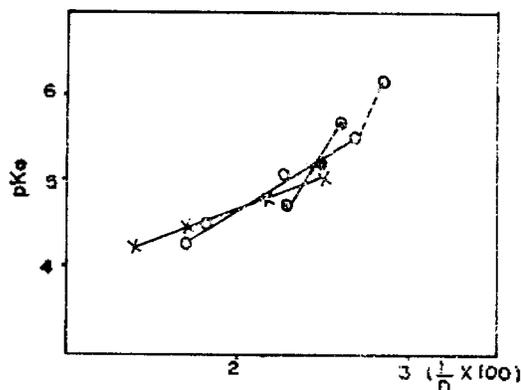


Fig. 2. Plot of  $pK_a$  vs. the reciprocal values of the dielectric constants of some mixed solvents at 25°C

×: Methanol, ○: Acetone, ⊙: Dioxane

molecules should be considered. Particularly it is obvious that some additional properties, such as ion-pairing other than the polar nature, become more important in the solutions having the smaller dielectric constant than 35 as elsewhere reported<sup>4</sup>.

#### Literature Cited

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