

Discussion and results. Fig. 1a shows that all the crystals of PPO are hedritic. The micrograph of PPO in Fig. 1b shows that two different types of crystals, partly dendrites and partly spheres, are formed during the crystallization. In DSC analysis PPO gives only one endothermic peak at 507 K¹ whereas PPOO gives two peaks at

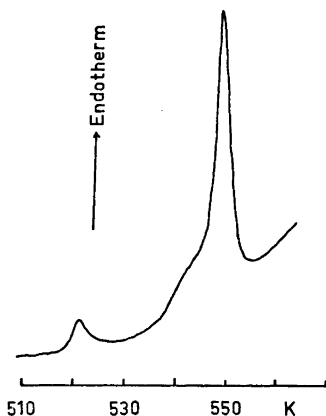


Fig. 2. DSC thermogram of PPOO. Endothermic peaks occur at 523 K and 549 K.

523 K and 549 K (Fig. 2). It can be assumed that these endothermic peaks of PPOO correspond to the two different crystalline forms.

The work is being continued.

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Dissociation Constants of Thiomalic Acid in Aqueous Potassium Chloride Solutions

OSMO MÄKITIE and
AULIS ILVONEN

Department of Chemistry, University of Helsinki, SF-00170 Helsinki 17, Finland

In connection with studies on metal complex formation by thiomalic acid, HOOC·CHSH·CH₂·COOH (mercaptosuccinic acid), the dependence of the dissociation constants of the acid on ionic strength with potassium chloride as the neutral salt was studied potentiometrically.

Table 1. Potentiometrically determined dissociation constants of thiomalic acid at 25°C. The calculated values were obtained by means of eqns. 4–6.

I	Observed	Calculated	
	pK ₁	pK ₁	pK ₁ ^o
0.005	3.375	3.372	3.435
0.203	3.231	3.235	3.429
0.504	3.214	3.220	3.428
1.003	3.249	3.238	3.445
2.004	3.306	3.310	3.430
	pK ₂	pK ₂	pK ₂ ^o
0.006	4.880	4.872	5.020
0.011	4.828	4.830	5.010
0.020	4.751	4.779	4.984
0.031	4.750	4.735	5.026
0.211	4.502	4.504	5.010
0.511	4.457	4.418	5.050
1.011	4.366	4.408	4.970
2.011	4.516	4.506	5.024
	pK ₃	pK ₃	pK ₃ ^o
0.012	10.872	10.848	11.167
0.018	10.763	10.791	11.115
0.030	10.678	10.707	11.114
0.038	10.718	10.664	11.198
0.219	10.212	10.254	11.102
0.519	10.051	10.036	11.159
1.020	9.918	9.906	11.155
2.019	9.870	9.876	11.138

The results of the determinations of the equilibrium constants:

$$K_1 = [\text{H}^+][\text{H}_2\text{L}^-]/[\text{H}_3\text{L}] \quad (1)$$

$$K_2 = [\text{H}^+][\text{HL}^{2-}]/[\text{H}_2\text{L}^-] \quad (2)$$

$$K_3 = [\text{H}^+][\text{L}^{3-}]/[\text{HL}^{2-}] \quad (3)$$

are listed in Table 1. The following Debye-Hückel equations were fitted to the data:

$$\text{p}K_1 = 3.43 - 1.018\sqrt{I}/(1 + 2.45\sqrt{I}) + \frac{0.10}{I} \quad (4)$$

$$\text{p}K_2 = 5.01 - 2.036\sqrt{I}/(1 + 1.52\sqrt{I}) + \frac{0.20}{I} \quad (5)$$

$$\text{p}K_3 = 11.14 - 3.054\sqrt{I}/(1 + 1.14\sqrt{I}) + \frac{0.19}{I} \quad (6)$$

The values $\text{p}K_1 = 3.26$, $\text{p}K_2 = 4.60$ and $\text{p}K_3 = 10.45$ at ionic strength 0.1 and 25°C can be calculated by means of these equations. Fig. 1 shows plots of $\text{p}(K^\circ/K)$ against the square root of ionic strength.

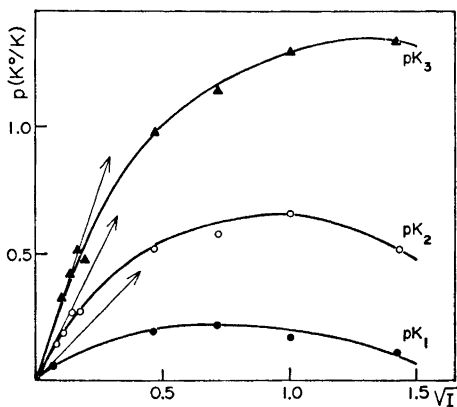


Fig. 1. $\text{p}(K^\circ/K)$ as a function of the square root of ionic strength.

The thermodynamic dissociation constants of thiomalic acid seem not to have been evaluated earlier. The $\text{p}K$ values at certain ionic strengths obtained in the present study differ somewhat from those reported in the literature, particularly in the case of $\text{p}K_1$ and $\text{p}K_3$. Cheney *et al.* obtained the values $\text{p}K_1 = 3.30$, $\text{p}K_2 = 4.94$, and $\text{p}K_3 = 10.64$ (at 25°C, ionic strength not specified) potentiometrically.¹ Lenz and Martell reported the values $\text{p}K_1 = 3.64$, $\text{p}K_2 = 4.64$ and $\text{p}K_3 = 10.37$ at ionic

strength 0.1, and the values 2.53, 4.44, and 9.73 at ionic strength 1.0 (KNO_3 , 25°C).² These values have been employed in several studies on metal complex formation with thiomalic acid.

The values $\text{p}K_1^\circ = 3.46$ and $\text{p}K_2^\circ = 5.10$ obtained for malic acid³ show that the acid strengths of the carboxyl groups of thiomalic acid are of the same magnitude as those of malic acid. Owing to the sulfhydryl group, the third dissociation constant of thiomalic acid has, however, a much higher value than the third dissociation constant of malic acid ($\text{p}K_3 = 14.3$)⁴ On the other hand, the carboxyl groups in succinic acid are clearly weaker ($\text{p}K_1^\circ = 4.21$ and $\text{p}K_2^\circ = 5.64$ at 25°C⁵).

Experimental. Thiomalic acid ("DL-mercaptosuccinic acid"), a reagent from British Drug Houses, Ltd., was purified by recrystallization from water. Dried potassium chloride was used as inert salt to adjust the ionic strengths of the solutions.

A Radiometer PHM 4d potentiometer connected to a Beckman glass electrode and an open liquid junction reference calomel electrode filled with saturated potassium chloride solution was used. Titrations of thiomalic acid solutions (2.0–5.0 ml of 10^{-2} M in 100 ml) with 0.1 M sodium hydroxide solution were carried out in a nitrogen atmosphere at 25°C. Apparent activity coefficient values were used to calculate the hydrogen ion concentrations.⁵

The values of the dissociation constants were evaluated from the titration data by the customary method. Titration data in the buffer range $c_{\text{NaOH}}:c_{\text{L}} = 0.4-0.75$ were used for the calculation of the first constant, those in the range 1.25–1.60 for the calculation of the second constant, and those in the range 2.25–2.75 for the calculation of the third constant. A computer programme was used to evaluate the values of these equilibrium constants when the first and second reactions overlapped.

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