The Protonation Constants of Diglycolic Acid in 0.1 M $(CH_3)_4NNO_3$ at 25 °C

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We recently studied the feasibility of various complex forming agents as possible detergent builders. In the course of this investigation some data with diglycolic acid were acquired with enough accuracy to warrant their publication.

Commercial diglycolic acid, recrystallized twice was dissolved in 0.1 M $(CH_3)_4NNO_3$, prepared from reagent grade quality. This medium was chosen in order to minimize the possibility of ion pair formation between ligand and medium cations. As titrant 0.1 M $(CH_3)_4NOH$, also that prepared from reagent grade chemicals, was used.

The titrations were performed as emf titrations using the standard technique and equipment developed by the Stockholm school.[1]

All measurements were made on 1 mM acid. Some preliminary titrations on 2 mM and 10 mM acids indicated no formation of polynuclear complexes in the dilute solutions used.

The experimental data were transformed into curves $Z(\lg h)$ where Z is defined by

$$Z = \frac{H-h}{B} = \frac{K_1h+2K_1K_2h^2}{1+K_1h+K_1K_2h^2} \qquad (1)$$

where

$h = [H^+]$ = hydrogen ion concentration as measured by a glass electrode calibrated in terms of hydrogen ion concentration in the ionic medium used.

H = Total concentration of protons from the diglycolic acid minus added OH^-.

B = Total concentration of diglycolic acid.

K_1 and K_2 the stepwise formation constants of HA^- and H_2A from the diglycolate anion.

The data were treated with three different methods. Firstly, the curves $Z(\lg h)$ were fitted to normalized curves $Z(\lg u)$ defined by

$$Z = \frac{u+2pu^2}{1+u+pu^2} \qquad (2)$$

where

$$u = K_1h; \qquad p = K_2/K_1 \qquad (3a,b)$$

Secondly, a least squares fit was made to the straight line

$$\frac{h(1-Z)}{Z} = \frac{1}{K_1} - K_2\frac{(2-Z)}{Z}h^2 \qquad (4)$$

which is obtained by rearrangement of eqn. (1).

Finally, the data were fitted by the least squares program LETAGROP.[2,3] The results are collected in Table 1, where also some literature values are given for comparison.

Since each method of treating the data corresponds to different ways of weighting the data,[4] it is satisfactory to note the good agreement between the three methods.

Unfortunately, the spread in the literature data does not warrant definite conclusions being drawn on the possibility of ion pairing to medium cations. The agreement between the present data and those of Yamasaki *et al.*[6,8] seems to indicate little ion pairing to alkali ions.

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Table 1. $\lg K_1$ and $\lg K_1K_2$ from some various ways of fitting the data $Z(h)$. Some literature values are also given.

Method	Medium	t °C	$\lg K_1$	$\lg K_1K_2$	Ref.
Graphical eqn. (2)	0.1 $(CH_3)_4NNO_3$	25	3.92	6.75	This work
Numerical eqn. (3)	0.1 $(CH_3)_4NNO_3$	25	3.95	6.74	This work
LETAGROP	0.1 $(CH_3)_4NNO_3$	25	3.94±0.01	6.75±0.01	This work
Average	0.1 $(CH_3)_4NNO_3$	25	3.94±0.02	6.75±0.01	This work
	0.1 KCl	30	4.03	6.93	5
	0.1	25	3.92	6.69	6
	0.1	20	4.11	7.17	7
	0.1 $NaClO_4$	25	3.92	6.69	8

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