

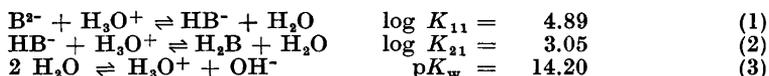
Equilibrium Studies on Phthalate Ions

On the Association between *o*-Phthalate Ions and Protons in 3 M (Na)ClO₄

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The association between *o*-phthalate ions and protons has been studied in 3 M (sodium) perchlorate medium at 25°C in the pH range 2.5–10.0 by electrometric titration using a glass electrode. The total *o*-phthalate concentration *B* had values between 0.001 and 0.055 M. The experimental data *Z* (average number of protons bound to one B²⁻) were plotted as a function of log [H₃O⁺]. After comparison with theoretical curves the following equilibrium constants were obtained for solutions in 3 M (sodium) perchlorate:



o-Phthalic acid has been the subject of extensive studies as being a substance of considerable interest not only from a technical point of view. The data reported in literature about the physical and chemical properties of this acid will give a good basis for studies on complex formation of dibasic acids now in progress at this Laboratory. As far as such studies with solutions are concerned, they are best performed using a constant ionic medium. The association constants of the complexes between protons and *o*-phthalate ions do not seem to have been determined for the ionic medium used in this research, *viz.* 3 M (sodium) perchlorate. This article will report on a determination of these constants.

The first determination of the association constant K_{11} between protons and *o*-phthalate ions seems to have been made in 1889 by Ostwald.¹ A value for the second constant K_{21} was given in 1898 by Smith. Both authors applied conductivity measurements at 18°C and the values found are given in Table 1. In this table results obtained by some other investigators have also been listed. Most of the values given are obtained from measurements at non-specified ionic strength or are valid for ionic strengths approaching zero.

Table 1. Previous data on the association constants of *o*-phthalic acid.

Method	Temp.	Log K_{11}	Log K_{21}	Observer
conductivity	18	—	2.92	Ostwald (1)
»	18	—	2.90	Berthelot (2)
sucrose inversion	25	—	2.92	Trevor (3)
»	25	5.77	—	Smith (4)
partition	25	5.51	—	Chandler (5)
indicators	25	—	2.89	Salm (6)
conductivity	25	5.41	2.92	Chandler (5)
»	25	—	2.90	White and Jones (7)
kinetics	25	—	2.92	Rivett and Sidgwick (8)
CO ₂ absorption	25	5.74	—	Datta and Dhar (9)
conductivity	25	5.40	3.10	Topp and Davies (10)
potentiometric	18	5.40	2.92	Larsson (11)
»	18	5.41	—	Kuhn and Wassermann (12)
»	25	—	2.89	Kuhn and Wassermann (12)
»	20	5.34	—	Morton (13)
»	50	—	3.00	Ölander (14)
»	25	5.28	2.98	Maxwell and Partington (15)
galvanic cell	25	5.408	2.910	Hamer and Acree (16)

LIST OF SYMBOLS

- α normalized concentration of the free ligand.
- B total concentration of *o*-phthalic acid = $[B^{2-}] + [HB^-] + [H_2B]$.
- E measured emf in mV.
- $E_{0a} = E - 59.16 \log [OH^-] - E_j$.
- $E_{0n} = E + 59.16 \log h - E_j$.
- E_j liquid junction emf.
- H total analytical excess concentration of hydrogen ions assuming no hydrolysis.
- h concentration of protons = $[H_3O^+]$.
- K_{11} the equilibrium constant for reaction (1).
- K_{21} the equilibrium constant for reaction (2).
- K_w the ionic product of water.
- $R = (K_{11}/K_{21})^{1/2}$.
- Z the average number of protons bound to one B^{2-} .

EXPERIMENTAL

Apparatus

Electrodes: Glass electrode 41260, Beckman Instruments Inc., Fullerton, California.
 Ag, AgCl electrode prepared according to Brown.¹⁷
Potentiometer: PHM4c, Radiometer, Copenhagen, Denmark.
Salt bridge: The "Wilhem" type.¹⁸

Reagents

Nitrogen was purified by passing the gas through a tube containing activated copper on kieselguhr, at 180°C.¹⁹ It was further purified by passing it through 10 % sulfuric acid and through 10 % sodium hydroxide.²⁰

o-Phthalic acid, pro analysi from Merck was used without further purification.

Perchloric acid. The *p.a.* product from Merck was standardized against potassium hydrogen carbonate and thallium carbonate.

Silver perchlorate. Silver ions were eluted from a cation exchanger by means of a sodium perchlorate solution.

Sodium hydroxide. A 50 % solution was prepared from the commercial *p.a.* product from E. K. A., Bohus. Dilute solutions were prepared in a nitrogen atmosphere by filtering the 50 % stock solution through a G4 filter and diluting with deaerated water. The sodium hydroxide solutions were always stored in bottles of thick polythene under a nitrogen atmosphere. The solutions were standardized against standard perchloric acid.

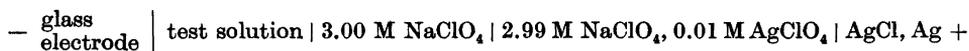
Sodium perchlorate from G. F. Smith was recrystallized twice, after which the chloride concentration was less than 10^{-6} M in 6 M sodium perchlorate. The solutions were analyzed by weighing, after evaporating to constant weight at 120°C.

Water was purified in an ion exchanger and then distilled once and finally, immediately before use, once more passed through an ion exchanger.

METHOD OF INVESTIGATION

This investigation was carried out as a number of potentiometric titrations, with the cell and the titration vessel in an oil thermostat bath at $25.00 \pm 0.03^\circ\text{C}$ and the whole equipment kept in a thermostated room at $25.0 \pm 0.2^\circ\text{C}$. In order to use concentrations instead of activities in the formula for emf and equilibrium constants, all solutions were made 3 M in respect of perchlorate by the addition of sodium perchlorate or perchloric acid. Due to the fairly small solubility of the acid (found²¹ to be 0.0425 moles per litre in pure water at 25°C) this investigation had to be limited to a maximum concentration of $B = 0.055$ M, which it was possible to obtain in alkaline solutions.

The cell investigated had the general composition:



In each titration the total *o*-phthalate concentration of the test solution was kept constant, while the pH was changed by adding sodium hydroxide or perchloric acid.

Using Nernst's formula, the emf of the cell can be expressed as

$$E = E_{0h} - 59.16 \log h + E_j \quad (\text{mV}) \quad (4)$$

$$E = E_{0a} + 59.16 \log [\text{OH}^-] + E_j \quad (\text{mV}) \quad (5)$$

depending on whether h or $[\text{OH}^-]$ is used as the independent variable in our calculations. Since the ionic mobility of the H_3O^+ and OH^- are much larger than that of other ions, the liquid junction potential, E_j , can be approximated as

$$E_j = k_1 h + k_2 [\text{OH}^-] \quad (6)$$

The ionic product of water was determined in separate potentiometric titrations by adding a solution of sodium hydroxide and sodium perchlorate to a solution

of perchloric acid and sodium perchlorate. The sum $(E + 59.16 \log h)$ was plotted as a function of h , and $(E - 59.16 \log [\text{OH}^-])$ as a function of $[\text{OH}^-]$. These functions were approximately linear as shown in Fig. 1. By extrapolation

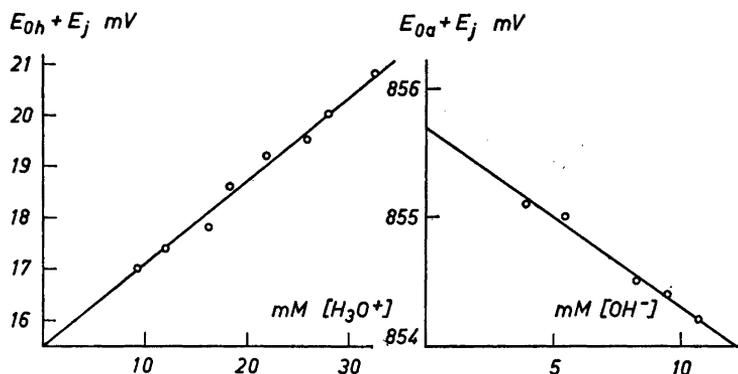


Fig. 1. $E + 59.16 \log h = E_{0h} + E_j$ as a function of $[\text{H}_3\text{O}^+] = h$ and $E - 59.16 \times \log [\text{OH}^-] = E_{0a} + E_j$ as a function of $[\text{OH}^-]$.

to $h = 0$ and $[\text{OH}^-] = 0$, the constants E_{0h} and E_{0a} were obtained and the ionic product of water in 3 M $(\text{Na})\text{ClO}_4$ at 25°C was determined as follows:

$$-\log K_w = \frac{E_{0a} - E_{0h}}{59.16} = \frac{855.7 - 15.5}{59.16} = 14.20$$

In the same ionic medium and at the same temperature Ågren²² obtained 14.15, and Ingri *et al.*²⁰ got 14.22.

From the slopes E_j/h and $E_j/[\text{OH}^-]$ in Fig. 1, we obtain $k_1 = 160$ and $k_2 = -140$ and thus

$$E_j = 160 h - 140 [\text{OH}^-] \quad (E_j \text{ in mV, } h \text{ and } [\text{OH}^-] \text{ in M})$$

The actual measurements on the cell were made in the pH-range 2.5–10.0. Normally the accuracy of glass electrodes decreases rapidly when pH increases over 8, but it was found that the electrode used (Beckman 41260) was fairly reliable even up to pH 10.0.

The accuracy of the measurements depends on the accuracy of the glass electrode and on the liquid junction potential. The former is estimated to be about ± 0.3 mV in the acid range and ± 0.5 mV at $8 \leq \text{pH} \leq 10$. The latter is, according to the formula (6), at most $+0.05$ mV in the pH-range $3.5 \leq \text{pH} \leq 10$ and it can thus be neglected in the calculations, compared to errors in the glass electrode. Within the pH-range $2.5 \leq \text{pH} \leq 3.5$ the accuracy of the measurements may be somewhat lower due to the influence of the rather high value of the liquid junction potential.

It this way the total inaccuracy of the measurements is estimated to be about ± 0.8 mV for solutions with $\text{pH} \leq 3.5$ and about ± 0.3 mV for $\text{pH} \geq 3.5$.

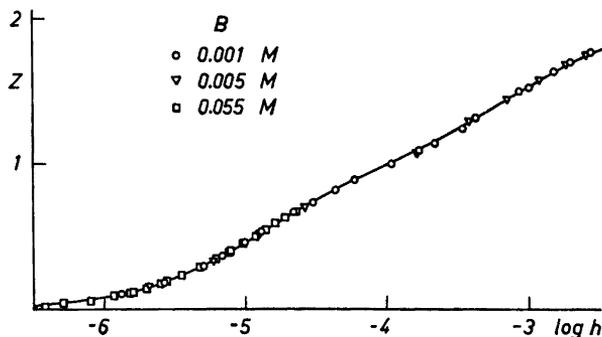


Fig. 2. Average number, Z , of protons bound to one B^{2-} as a function of $\log h$. The normalized curve $Z(\log a)_B$ has also been drawn using the relation $\log a = \log h + 3.97$ and $R = 8.3$.

To study if the solutions were at equilibrium during the measurements, a back titration was also carried out. The reversibility of the equilibrium was confirmed as the values of $Z(\log h)$ always fall on the same curve (cf. Fig. 2).

Table 2. Experimental data. Corresponding values of Z and $-\log h$ for *o*-phthalate ions at various total concentrations, B , at 25°C, 3 M (Na)ClO₄ medium.

$B = 0.001\text{ M}$		$B = 0.005\text{ M}$		$B = 0.055\text{ M}$ back titr.	
Z	$-\log h$	Z	$-\log h$	Z	$-\log h$
1.766	2.573	1.742	2.603	0.001	8.117
1.692	2.717	1.677	2.741	0.008	7.028
1.634	2.830	1.572	2.930	0.013	6.760
1.521	3.024	1.441	3.155	0.015	6.689
1.493	3.073	1.287	3.421	0.021	6.544
1.310	3.377	1.069	3.786	0.028	6.412
1.138	3.469	0.886	4.223	0.041	6.282
1.135	3.661	0.696	4.579	0.059	6.092
1.085	3.775	0.507	4.899	0.083	5.923
0.996	3.966	0.324	5.222	0.106	5.810
0.897	4.228	0.146	5.685	0.112	5.785
0.814	4.368			0.134	5.697
0.729	4.527			0.169	5.600
0.664	4.664			0.179	5.560
0.526	4.890			0.228	5.442
0.456	5.009			0.285	5.318
0.361	5.166			0.340	5.208
0.290	5.301			0.392	5.110
0.171	5.570			0.396	5.103
0.100	5.879			0.450	5.007
0.005	6.464			0.496	4.926
				0.541	4.855
				0.583	4.786
				0.624	4.716
				0.664	4.645

TREATMENT OF DATA

By using eqns. (4) and (5) for the emf of the cell and the formula

$$Z = \frac{H-h + [\text{OH}^-]}{B} \quad (7)$$

we could for each point in the titration obtain the corresponding values of h and Z shown in Table 2. Plotting Z against $\log h$ gives Fig. 2. The points for different values of B all fall on the same curve which indicates that only mononuclear complexes exist in the concentration range investigated.

The shape of a curve $Z(\log a)_B$, where a is the normalized concentration of a free ligand (*cf.* Sillén²³) depends only on the value of the parameter R in the equation

$$Z = \frac{Ra + 2a^2}{1 + Ra + a^2} \quad (8)$$

where $R = (\beta_1^2/\beta_2)^{\frac{1}{2}}$

By comparing theoretical curves $Z(\log a)_B$ calculated for different values of R [in this investigation $\beta_1 = K_{11}$ and $\beta_2 = K_{11} \cdot K_{21}$] with the curve obtained in Fig. 2, the best fit between calculated and experimental curve was obtained for $R = 8.3$. From this follows:

$$\log K_{11} - \log K_{21} = \log (8.3)^2 \quad (9)$$

Then, as described by Sillén,²³ in order to determine the product $K_{11} \cdot K_{21}$ the normalized curve $Z(\log a)_B$ was moved along the $\log h$ axis of the experimental plot $Z(\log h)_B$ until the best fit was obtained. The value of $\log h$ corresponding to $\log a = 0$ was found to be -3.97 . We thus obtain:

$$\log K_{11} + \log K_{21} = -2(-3.97) \quad (10)$$

Eqns. (9) and (10) then give

$$\begin{aligned} \log K_{11} &= 4.89 \\ \log K_{21} &= 3.05 \end{aligned}$$

The limits of error of the constants are estimated to be about ± 0.05 , considering the influence of the inaccuracy inherent in the experimentally observed values and also in the treatment of the data.

From the experiments we thus obtain the following values of the association constants for complex formation between protons and *o*-phthalate ions in 3 M (Na)ClO₄ medium and of the ionic product of water in the same medium:

$$\begin{aligned} \log K_{11} &= 4.89 \\ \log K_{21} &= 3.05 \\ \text{p}K_w &= 14.20 \end{aligned}$$

The value of $\log K_{21}$ is in fair agreement with those published earlier as results from emf measurements (*cf.* Table 1). However, the values $\log K_{11}$ reported in the literature differ markedly from the result obtained in the present investigation. The choice of ionic medium applied in the experiments may be the cause of this difference.

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