

Studies on the Application of the Quinhydrone Electrode in Formamide. III* The Ionization Constants and Related Thermodynamic Quantities of Phthalic Acid from E.M.F. Measurements at Different Temperatures

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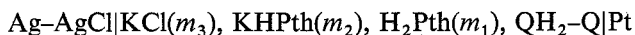
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Abstract

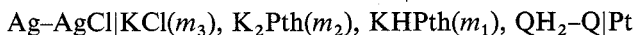
The first and second ionization constants of phthalic acid have been determined, in formamide, at temperatures ranging from 5° to 45°C at 5° intervals, with the help of cells without liquid junction using quinhydrone and silver-silver chloride electrodes. By means of the Bjerrum equation, the distance r between the acidic groups has been estimated in formamide at different temperatures.

Introduction

In a previous communication,¹ we reported the first and the second ionization constants of phthalic acid in formamide at 25° from the study of cells



and



In the present investigation, we have extended the studies to different temperatures, and now report the results over the temperature range 5-45°C. The distance r between the carboxylic groups has been estimated at different temperatures by using the Bjerrum equation for this solvent.

Experimental

The purification of materials needed for the e.m.f. measurements and preparation of the various solutions has been described in our earlier articles.^{1,2}

The cell measurements were carried out with electrodes prepared and set up as described earlier.³

Results and Discussion

A summary of e.m.f. data at 5° and 45° is given in Tables 1 and 2, for the first and second ionizations, respectively. Similar experimental values were obtained at each of the 5° temperature intervals throughout the range. As usual, values of K'_{1a} and K'_{2a} were calculated with the help of equations (1) and (2), and the ionization

* Part II, *Aust. J. Chem.*, 1973, 26, 115.

¹ Nayak, B., and Dash, U. N., *Aust. J. Chem.*, 1973, 26, 115.

² Dash, U. N., and Nayak, B., *Indian J. Chem.*, 1970, 8(7), 659.

³ Nayak, B., and Dash, U. N., *Aust. J. Chem.*, 1973, 26, 111.

Table 1. Determination of $-\log K_{1a}$ of phthalic acid in formamide

$$X \equiv [E - E^0(\text{Ag-AgCl}) + E^0(\text{QH}_2\text{-Q})]; \quad M \equiv m'(\text{H}^+)[m_2 + m'(\text{H}^+)]/[m_1 - m'(\text{H}^+)]$$

$10^2 m_1$ (mol/kg)	$10^2 m_2$ (mol/kg)	$10^2 m_3$ (mol/kg)	$-E$ (V)	$\frac{XF}{2 \cdot 303RT}$	$10^5 m'(\text{H}^+)$ (mol/kg)	$-\log M$	$2A \times$ $(\mu d_0)^{1/2}$	$10^2 \mu$	$-\log K_{1a}$
Temperature 5°C									
0.863	0.737	2.814	0.1873	5.851	6.124	4.2432	0.1163	3.558	4.3595
0.728	0.745	3.015	0.1818	5.953	4.868	4.2966	0.1198	3.765	4.4164
0.611	0.646	3.486	0.1845	5.902	4.797	4.2879	0.1255	4.137	4.4134
1.315	1.267	3.227	0.1868	5.860	5.781	4.2500	0.1309	4.500	4.3809
0.830	0.854	4.387	0.1963	5.682	6.563	4.1633	0.1414	5.248	4.3047
1.526	1.305	3.957	0.2007	5.608	8.835	4.1162	0.1417	5.271	4.2579
1.463	1.189	6.113	0.2101	5.438	8.964	4.1414	0.1669	7.311	4.3083
1.806	1.765	6.235	0.2031	5.564	6.543	4.1910	0.1746	8.007	4.3656
1.836	1.582	8.464	0.2149	5.348	8.318	4.1406	0.1956	10.054	4.3362
									$-\log K_{1a}$ (extrapolated) 4.39 ± 0.03
Temperature 45°C									
0.313	0.397	1.963	0.1489	5.896	8.162	3.9650	0.1009	2.368	4.0659
1.559	1.392	3.520	0.1692	5.576	10.540	4.0198	0.1455	4.923	4.1653
1.120	1.121	4.611	0.1753	5.479	10.330	3.9776	0.1571	5.742	4.1347
0.898	0.999	5.457	0.1714	5.540	7.759	4.0567	0.1667	6.464	4.2234
1.812	1.760	4.795	0.1787	5.425	11.540	3.9447	0.1681	6.567	4.1128
0.864	0.890	6.381	0.1771	5.450	8.354	4.0573	0.1768	7.279	4.2341
3.224	2.920	4.847	0.1837	5.346	14.180	3.8874	0.1830	7.781	4.0704
									$-\log K_{1a}$ (extrapolated) 4.06 ± 0.06

Table 2. Determination of $-\log K_{2a}$ of phthalic acid in formamide

$$X \equiv [E - E^0(\text{Ag-AgCl}) + E^0(\text{QH}_2\text{-Q})]$$

$10^2 m_1$ (mol/kg)	$10^2 m_2$ (mol/kg)	$10^2 m_3$ (mol/kg)	$-E$ (V)	$\frac{XF}{2 \cdot 303RT}$	$-\log \frac{m_1 m_3}{m_2}$	$2A \times$ $(\mu d_0)^{1/2}$	$10^2 \mu$	$-\log K_{2a}$
Temperature 5°C								
1.070	0.137	3.757	0.0597	8.164	0.5325	0.1413	5.238	7.7728
0.578	0.487	4.189	0.0224	8.839	1.3035	0.1540	6.228	7.6895
1.154	0.086	5.470	0.0830	7.741	0.1343	0.1619	6.882	7.7686
1.012	0.261	5.350	0.0498	8.345	0.6830	0.1650	7.145	7.8270
1.380	0.398	6.982	0.0698	7.982	0.6160	0.1907	9.556	7.5567
1.586	0.430	7.032	0.0730	7.923	0.5860	0.1942	9.908	7.5293
								$-\log K_{2a}$ (extrapolated) 8.10 ± 0.09
Temperature 45°C								
1.295	0.385	2.389	0.0180	7.973	1.0949	0.1443	4.839	7.0224
1.070	0.137	3.757	0.0603	7.303	0.5325	0.1501	5.238	6.9206
1.154	0.086	5.470	0.0750	7.069	0.1343	0.1721	6.882	7.1068
2.102	0.280	4.179	0.0475	7.506	0.5036	0.1750	7.121	7.1774
1.586	0.430	7.032	0.0602	7.305	0.5860	0.2065	9.908	6.9255
1.171	0.110	9.953	0.0902	6.828	-0.0251	0.1978	11.454	7.0509
								$-\log K_{2a}$ (extrapolated) 7.05 ± 0.10

Table 3. Values of pK_{1a} and pK_{2a} for phthalic acid in formamide at different temperatures

	5°	10°	15°	20°	25°	30°	35°	40°	45°
pK_{1a}	4.39	4.31	4.31	4.28	4.21	4.23	4.34	4.26	4.06
	± 0.03	± 0.06	± 0.03	± 0.02	± 0.02	± 0.02	± 0.02	± 0.04	± 0.06
pK_{2a}	8.10	7.73	7.74	7.51	7.72	7.42	7.69	7.42	7.05
	± 0.09	± 0.02	± 0.03	± 0.05	± 0.01	± 0.06	± 0.09	± 0.10	± 0.10

Table 4. Estimated values of r of phthalic acid in formamide at different temperatures

	5°	10°	15°	20°	25°	30°	35°	40°	45°
r (Å)	0.73	0.80	0.79	0.85	0.78	0.87	0.82	0.89	0.95
ΔpK_a	3.70	3.42	3.43	3.23	3.50	3.19	3.35	3.16	2.99
K_{1a}/K_{2a}	5012	2630	2692	1698	3177	1549	2239	1445	977.2

constants of phthalic acid, K_{1a} and K_{2a} , were found by the method^{1,3-5} of extrapolating the auxiliary functions, K'_{1a} and K'_{2a} , given by¹

$$\log K'_{1a} = -2A(\mu d_0)^{1/2} + \log \frac{m'(\text{H}^+)[m_2 + m'(\text{H}^+)]}{m_1 - m'(\text{H}^+)} \quad (1)$$

and

$$-\log K'_{2a} = \frac{[E - E^0(\text{Ag-AgCl}) + E^0(\text{QH}_2 - \text{Q})]F}{2 \cdot 303RT} + \log \frac{m_1 m_3}{m_2} + 2A(\mu d_0)^{1/2} \quad (2)$$

to $\mu = 0$, respectively, the symbols in these equations having their usual significance. The values of $E^0(\text{Ag-AgCl})$ and of $E^0(\text{QH}_2 - \text{Q})$ at different temperatures needed for the calculations were obtained from the empirical equations^{6,7}

$$E^0_t(\text{Ag-AgCl}) = 0.19839 - 9.3857 \times 10^{-4}(t - 25) + 1.2190 \times 10^{-6}(t - 25)^2$$

and

$$E^0_t(\text{QH}_2 - \text{Q}) = 0.71382 - 0.6666 \times 10^{-3}(t - 25) + 2.990 \times 10^{-6}(t - 25)^2$$

The values of d_0 at different temperatures were obtained from the empirical equation available in the literature⁸ and those of the Debye-Hückel constant A were either obtained from the literature⁶ or were calculated in the molal scale by the usual method using the exact values of the density,⁸ dielectric constant⁹ etc. of formamide.

A plot of $\log K'_{1a}$ and $\log K'_{2a}$ against the corresponding μ at each temperature should yield a straight line and intercept $\log K_{1a}$ and $\log K_{2a}$, respectively. Extrapolation of $\log K'_{1a}$ and $\log K'_{2a}$ to corresponding zero ionic strengths was done by the method of least squares. Values of $\text{p}K_{1a}$ and $\text{p}K_{2a}$ are shown in Table 3.

The effect of temperature on $\text{p}K_{1a}$ and $\text{p}K_{2a}$ values appears to be irregular, although with the increase of temperature there is a general tendency for these values to decrease slightly.

The distance r between the carboxylic groups was calculated from the Bjerrum equation as described earlier.¹ The values have been presented in Table 4 along with other data obtained in formamide. The values of r show an irregularity with change of temperature. A comparison of the present data with the corresponding values in water is difficult because of the lack of relevant data in water at all temperatures. However, available data at 25°C in water¹ (1.66 Å compared with the value in formamide of 0.78 Å) show the failure of the Bjerrum equation in the case of phthalic acid,¹ and point to the fact that, in changing the solvent from water to formamide, the second ionization constant of the acid is depressed more than the first.

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⁷ Sahu, D. K., Ph.D. Thesis, Indian Institute of Technology, Kharagpur, India, 1972, p. 155.

⁸ Smith, G. F., *J. Chem. Soc.*, 1931, 3257.

⁹ Leader, G. R., *J. Amer. Chem. Soc.*, 1951, **73**, 856, 5731.