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Phthalic Acid as a Reagent in Inorganic Qualitative Analysis of Metal Ions. Part III. Thermodynamics of the Protonation of Phthalate Ion in Aqueous Sodium Perchlorate Solutions

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The protonation constants of phthalate ion were determined potentiometrically as functions of the ionic strength in aqueous sodium perchlorate solutions within the temperature range from 15 to 35 °C. The thermodynamic values ($K°_n$) of the protonation constants were evaluated by fitting the experimental data to semitheoretical equations. The values of the free energies, enthalpies, entropies, and heat capacities of the protonation equilibria were calculated on the basis of the thermodynamic values of the protonation constants. On the basis of the obtained data and our experience, phthalic acid was concluded to be well suited for use as a group reagent and a buffering agent, within wide ionic strength and temperature limits, for solutions in the inorganic qualitative analysis of metal ions.

The protonation of the phthalate ion in aqueous solutions has been studied several times before,[1-12] but generally the protonation constants were evaluated at one ionic strength and temperature only. An exception from this general tendency is the work of Hamer *et al.*[9-10] where the thermodynamic quantities were also considered.

In the present paper the protonation of the phthalate ion was studied potentiometrically in aqueous sodium perchlorate solutions. The determination of the protonation constants at different temperatures made it possible to estimate the thermodynamic quantities as well.

EXPERIMENTAL

Reagents and solutions. Phthalic acid was a product of E. Merck, designed for use in chromatography. The acid was dried in a desiccator. By potentiometric titration with a known sodium hydroxide solution its alkalimetric purity was found to be 99.64 %. Potassium biphthalate, sodium chloride, sodium hydroxide, mercurous chloride, mercury, and perchloric acid were all guaranteed reagents of E. Merck. Potassium biphthalate was dried in a desiccator and sodium chloride at 150 °C. Sodium perchlorate was an anhydrous product of G. Frederic Smith Chemical Co. The salt was dissolved in water. pH of the solution was adjusted with sodium hydroxide to 7. The solution was allowed to stand one day and filtered through a glass-sinter (G4). The filtrate was made neutral with perchloric acid so that it consumed no sodium hydroxide against phenolphthalein. The concentration of the solution (~4 M) was determined by evaporating 5 ml aliquots to dryness at 140 °C and, on the other hand, using cation exchanger (Ionentauscher E. Merck) and titrating the obtained perchloric acid solution with sodium hydroxide. The water used was distilled, deionized and carbon dioxide-free.

About 0.1 M sodium hydroxide solution was prepared diluting a Titrisol solution (E. Merck) under nitrogen atmosphere in a carbon dioxide tight titration equipment from Pyrex-glass. The concentration of the solution was determined by potentiometric titrations of weighed amounts of potassium biphthalate.

A dilute (0.1 M) perchloric acid solution was prepared from conc. acid (70 %) and its concentration was determined by potentiometric titrations with the known sodium hydroxide solution. The obtained solution was used to prepare the reference buffer solutions of 0.005 M.

The concentrations of the stock solutions are given in Table 1. The compositions of the solutions used in connection with the titrations are given in Table 2.

Sodium chloride was added as solid, the other reagents as stock solutions to the solutions

Table 1. The concentrations of the stock solutions used (20 °C). $[\mathrm{HClO_4}]=0.1003$ M.

I	M $\mathrm{NaClO_4}$	M NaOH
0.040	4.013	0.09945
0.250	4.013	0.09943
0.500	4.013	0.09961
1.000	4.013	0.09971
2.000	6.437	0.10038

prepared. In the preparation of the solutions at 20 °C guaranteed measuring flasks, burettes and pipettes were used. The temperature expansion of the solutions was assumed to be that of pure water and relative density values of water were used[13] to correct the volumes to the desired temperature.

Apparatus. The titration vessels (200 ml) were of Pyrex glass with gas tight covers equipped with inlets for glass and reference electrodes, burette and nitrogen gas. The nitrogen gas was washed and thermostated before inlet to the titration vessel. The water thermostat, where the titrations were performed, was held constant within ±0.01 °C. The titrated solution was stirred magnetically. The glass electrode was a Beckman type, No. 41260 and the reference calomel electrode of the immersion type. The potentiometer was a Radiometer PHM 4. The potentials were read to ±0.2 mV.

Measurements. For both protonation equilibria the measurements were made at eleven points of the titration curve. For K_2 the potentials were measured from 4 to 6 ml and for K_1 from 14 to 16 ml of 0.01 M sodium hydroxide added in increments of 0.2 ml. At least two titrations were performed at each temperature and the results were combined to calculate the K_n values. The system was checked against a perchloric acid solution (0.005 M in $\mathrm{HClO_4}$) at the beginning and at the end of every titration. The starting volume of the titrated solutions was 100 ml at 20 °C. The pH (= $-\log[\mathrm{H^+}]$) values were calculated from the measured potentials.[14] To minimize the possible diffusion potentials the cell system used in the potentiometric titrations was of the type:[15]

$$\begin{array}{l|l||}\text{Glass} & 100\text{ ml}\\ \text{electrode} & 0.01\text{ M }\mathrm{C_8H_6O_4}\\ & 0.01\text{ M NaCl}\\ & (I-0.01)\text{ M }\mathrm{NaClO_4}\end{array}$$

$$\left|\begin{array}{l}0.01\text{ M NaCl}\\ (I-0.01)\text{ M }\mathrm{NaClO_4}\end{array}\right|\mathrm{Hg_2Cl_2},\ \mathrm{Hg}$$

RESULTS AND DISCUSSION

The protonation equilibria of the phthalate ion in aqueous solutions may be briefly expressed as follows:

$$\mathrm{L^{2-}+H_3O^+\rightleftharpoons HL^-+H_2O} \qquad (1)$$

$$\mathrm{HL^-+H_3O^+\rightleftharpoons H_2L+H_2O} \qquad (2)$$

The corresponding protonation constants

$$K_1=[\mathrm{HL^-}]/[\mathrm{L^{2-}}]\,[\mathrm{H^+}] \qquad (3)$$

$$K_2=[\mathrm{H_2L}]/[\mathrm{HL^-}]\,[\mathrm{H^+}] \qquad (4)$$

were calculated by iteration from the equations:

$$\log K_1=\mathrm{pH}-\log\{(Y-C+[\mathrm{H^+}]YK_2)/(2C-Y)\} \qquad (5)$$

$$\log K_2=\mathrm{pH}-\log\{Y/[C-Y+(2C-Y)/K_1[\mathrm{H^+}]]\} \qquad (6)$$

where $Y=C_\mathrm{B}+[\mathrm{H^+}]$ and C and C_B are the total concentrations of phthalic acid and the added sodium hydroxide, respectively, in the titrated solutions. The expressions are easily derived by taking into account the total concentrations and neglecting $[\mathrm{OH^-}]$.

The equations consider the effect of the overlapping of the protonation equilibria.

Table 2. The compositions of the solutions used in connection with the titrations (20 °C).

Titrant 0.1 M NaOH 0.01 M NaCl M $\mathrm{NaClO_4}$	I	Reference electrode 0.01 M NaCl M $\mathrm{NaClO_4}$	Reference buffer 0.005 M $\mathrm{HClO_4}$ 0.01 M NaCl M $\mathrm{NaClO_4}$	Studied solution 0.01 M $\mathrm{C_8H_6O_4}$ 0.01 M NaCl M $\mathrm{NaClO_4}$
0.030	0.040	0.030	0.025	0.030
0.240	0.250	0.240	0.235	0.240
0.490	0.500	0.490	0.485	0.490
0.990	1.000	0.990	0.985	0.990
1.990	2.000	1.990	1.985	1.990

Table 3. The potentiometric titration data of phthalic acid in aqueous sodium perchlorate solutions at 15 and 20 °C.

Titrant ml	pH 15 °C					20 °C				
4.00	2.807	2.778	2.774	2.796	2.849	2.803	2.780	2.773	2.782	2.859
4.20	2.826	2.796	2.791	2.817	2.872	2.824	2.800	2.793	2.804	2.880
4.40	2.847	2.820	2.818	2.837	2.895	2.846	2.822	2.816	2.823	2.900
4.60	2.868	2.840	2.839	2.858	2.919	2.867	2.844	2.837	2.847	2.926
4.80	2.892	2.872	2.861	2.884	2.944	2.890	2.866	2.859	2.870	2.948
5.00	2.914	2.894	2.884	2.904	2.968	2.914	2.888	2.881	2.893	2.973
5.20	2.937	2.917	2.907	2.928	2.991	2.937	2.911	2.906	2.919	2.996
5.40	2.961	2.940	2.931	2.952	3.016	2.962	2.936	2.930	2.941	3.020
5.60	2.984	2.963	2.955	2.977	3.042	2.985	2.962	2.957	2.967	3.045
5.80	3.007	2.987	2.978	3.003	3.068	3.010	2.986	2.976	2.990	3.070
6.00	3.031	3.012	3.005	3.030	3.093	3.037	3.012	3.003	3.015	3.099
14.00	4.790	4.637	4.565	4.533	4.599	4.808	4.627	4.557	4.524	4.601
14.20	4.823	4.670	4.599	4.565	4.631	4.841	4.662	4.592	4.555	4.636
14.40	4.859	4.701	4.630	4.596	4.663	4.876	4.694	4.625	4.587	4.664
14.60	4.891	4.735	4.661	4.626	4.695	4.912	4.727	4.657	4.622	4.697
14.80	4.925	4.769	4.691	4.658	4.730	4.946	4.760	4.691	4.654	4.729
15.00	4.962	4.799	4.726	4.691	4.762	4.978	4.795	4.726	4.685	4.763
15.20	4.996	4.833	4.759	4.721	4.795	5.013	4.827	4.759	4.718	3.793
15.40	5.030	4.868	4.790	4.756	4.830	5.047	4.862	4.795	4.752	4.827
15.60	5.065	4.902	4.824	4.794	4.864	5.080	4.897	4.826	4.785	4.862
15.80	5.100	4.936	4.860	4.824	4.897	5.115	4.930	4.862	4.820	4.898
16.00	5.137	4.973	4.895	4.858	4.936	5.153	4.965	4.896	4.856	4.932
Approx. *I*	0.05	0.25	0.50	1.00	2.00	0.05	0.25	0.50	1.00	2.00

Table 4. The potentiometric titration data of phthalic acid in aqueous sodium perchlorate solutions at 25 and 35 °C.

Titrant ml	pH 25 °C					35 °C				
4.00	2.801	2.785	2.776	2.788	2.856	2.808	2.793	2.786	2.804	2.883
4.20	2.820	2.806	2.797	2.807	2.878	2.829	2.814	2.805	2.826	2.903
4.40	2.841	2.828	2.818	2.828	2.900	2.851	2.834	2.825	2.846	2.925
4.60	2.863	2.849	2.839	2.851	2.924	2.874	2.857	2.845	2.865	2.945
4.80	2.886	2.871	2.862	2.874	2.948	2.897	2.876	2.867	2.887	2.967
5.00	2.910	2.894	2.885	2.897	2.968	2.919	2.901	2.889	2.909	2.991
5.20	2.932	2.918	2.908	2.921	2.995	2.942	2.924	2.910	2.932	3.014
5.40	2.955	2.942	2.931	2.945	3.016	2.968	2.945	2.935	2.955	3.038
5.60	2.979	2.964	2.955	2.970	3.045	2.992	2.969	2.959	2.978	3.063
5.80	3.005	2.989	2.980	2.994	3.071	3.018	2.994	2.982	3.002	3.090
6.00	3.032	3.016	3.005	3.019	3.098	3.044	3.019	3.006	3.027	3.117
14.00	4.789	4.622	4.556	4.523	4.597	4.812	4.625	4.556	4.525	4.611
14.20	4.823	4.653	4.591	4.556	4.629	4.847	4.658	4.589	4.558	4.642
14.40	4.857	4.690	4.625	4.587	4.662	4.881	4.693	4.622	4.592	4.675
14.60	4.889	4.723	4.658	4.620	4.693	4.914	4.724	4.656	4.623	4.706
14.80	4.922	4.757	4.690	4.653	4.727	4.943	4.759	4.689	4.657	4.739
15.00	4.958	4.790	4.724	4.686	4.760	4.980	4.791	4.722	4.690	4.772
15.20	4.991	4.824	4.756	4.718	4.792	5.013	4.825	4.754	4.723	4.805
15.40	5.025	4.856	4.791	4.752	4.826	5.048	4.860	4.788	4.758	4.838
15.60	5.059	4.891	4.827	4.787	4.861	5.082	4.892	4.822	4.791	4.872
15.80	5.095	4.924	4.860	4.820	4.894	5.116	4.925	4.857	4.824	4.908
16.00	5.128	4.962	4.895	4.856	4.930	5.150	4.960	4.889	4.859	4.942
Approx. *I*	0.05	0.25	0.50	1.00	2.00	0.05	0.25	0.50	1.00	2.00

Table 5. The calculated protonation constants of the phthalate ion at different ionic strengths and temperatures.

t °C	I	Mean log K_1	I	Mean log K_2
15	0.0573	4.967	0.0459	2.705
20	0.0572	4.985	0.0459	2.704
25	0.0570	4.963	0.0457	2.697
35	0.0569	4.984	0.0456	2.710
15	0.2675	4.804	0.2562	2.674
20	0.2672	4.796	0.2560	2.672
25	0.2668	4.791	0.2556	2.680
35	0.2661	4.791	0.2548	2.685
15	0.5177	4.722	0.5064	2.665
20	0.5173	4.720	0.5060	2.663
25	0.5166	4.719	0.5053	2.666
35	0.5150	4.715	0.5038	2.672
15	1.0182	4.682	1.0069	2.702
20	1.0173	4.677	1.0060	2.682
25	1.0160	4.677	1.0047	2.688
35	1.0129	4.681	1.0016	2.705
15	2.0193	4.724	2.0076	2.789
20	2.0175	4.745	2.0058	2.796
25	2.0150	4.733	2.0034	2.795
35	2.0090	4.743	1.9973	2.823

Table 6. The results of the fitting of the data in Table 5 to eqns. (7) and (8) at 25 °C.

I	A	α_1	B_1	Obs. log K_1	Calc. eqn. (7) log K_1
0.2668	0.5115[16]	1.4127	0.1690	4.791	4.792
0.5166				4.719	4.716
1.0160				4.677	4.679
2.0150				4.733	4.732

I	A	α_2	B_2	Obs. log K_2	Calc. eqn. (8) log K_2
0.2556	0.5115[16]	1.5875	0.1563	2.680	2.680
0.5053				2.666	2.665
1.0047				2.688	2.689
2.0034				2.795	2.795

log $K°_1 = 5.358$; log $K°_2 = 2.927$.

The experimental data of the determinations of the protonation constants are given in Tables 3 and 4 and the values of the constants calculated from these, in Table 5.

The data in Table 5 were fitted by the method of least squares to the semiempirical equations:

$$\log K_1 = \log K°_1 - \frac{4A\sqrt{I}}{1+\alpha_1\sqrt{I}} + B_1 I \qquad (7)$$

$$\log K_2 = \log K°_2 - \frac{2A\sqrt{I}}{1+\alpha_2\sqrt{I}} + B_2 I \qquad (8)$$

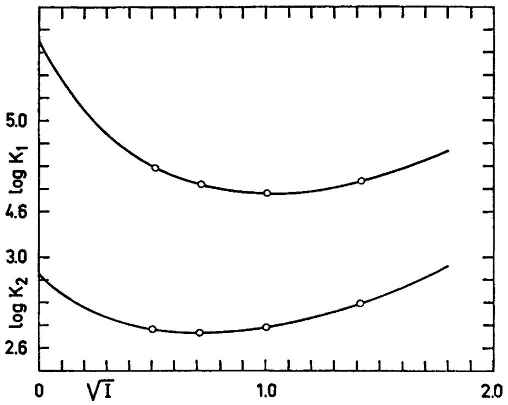

Fig. 1. The log K_1 and log K_2 values of the protonation constants of the phthalate ion in aqueous sodium perchlorate solutions as functions of the square root of the ionic strength at 25 °C.

at 25 °C only. The values of the constants of eqns. (7) and (8) obtained at 25 °C are given in Table 6 with the experimental and calculated values of the protonation constants. The constants at 25 °C were used to calculate the thermodynamic values of the protonation constants from eqns. (7) and (8) at the other temperatures. The results of these calculations are given in Table 7. In fitting the curve the values of the protonation constants at the lowest ionic strengths were disregarded, due to errors caused by diffusion potentials.

The log K_1 and log K_2 values of the protonation constants are represented as functions of the square roots of the ionic strength at 25 °C in Fig. 1.

As regards earlier studies of the protonation equilibria of the phthalate ion only the work of Hamer *et al.*[9,10] was carried out at different temperatures. The temperature range was from 0 to 60 °C and the ionic strength varied from about 0 to 0.55. Cells without liquid junctions were used. Further, Topp and Davies[2] evaluated the protonation constants at zero ionic strength. The results obtained by different workers are compared in Table 8.

In general the values of the protonation constants obtained by different workers are of the same order of magnitude. However, the present values are generally a little lower. This may be due to the liquid junction potentials in the measuring cells, if we assume the glass electrode to have functioned normally and that the error due to the potential measurements in log K_n values was about ±0.003 units. The determinations were made as consistent duplicate measurements and the stabilization of the systems at different titration points and temperatures was good.

The present thermodynamic values of the protonation constants showed so little variation

Table 7. The thermodynamic values of the protonation constants of the phthalate ion calculated from eqns. (7) and (8) at different ionic strengths and temperatures.

t °C	A^{16}	I	log $K°_1$	Mean log $K°_1$	I	log $K°_2$	Mean log $K°_2$
15	0.5028	0.2675	5.360		0.2562	2.916	
		0.5177	5.352	5.348	0.5064	2.922	2.917
		1.0182	5.347		1.0069	(2.934)	
		2.0193	5.333		2.0076	2.914	
20	0.5070	0.2672	5.357		0.2560	2.916	
		0.5173	5.356		0.5060	2.922	
		1.0173	5.348	5.356	1.0060	2.917	2.920
		2.0175	5.362		2.0058	2.924	
25	0.5115	0.2668– 2.0150	–	5.358	0.2556– 2.0034	–	2.927
35	0.5211	0.2661	5.368		0.2548	2.937	
		0.5150	5.371		0.5038	2.941	
		1.0129	5.376	5.375	1.0016	2.951	2.948
		2.0090	5.387		1.9973	2.965	

Table 8. Comparison of the protonation constants of the phthalate ion determined by different workers.

°C	Ionic strength added salt	log K_1	log K_2	Method	Reference
15	→0	5.405	2.937	H, Ag–AgCl	9,10
15	→0	5.348	2.917	Glass electrode	This work
20	→0	5.405	2.943	H, Ag–AgCl	9,10
20	→0	5.356	2.920	Glass electrode	This work
25	→0	5.40	3.14	Conductivity	2
25	→0	5.408	2.950	H, Ag–AgCl	9,10
25	→0	5.358	2.927	Glass electrode	This work
25	0.1 (KNO_3)	4.92	2.76		3
25	0.1	4.92	2.76		4
25	0.1 ($NaClO_4$)	4.928	2.728		This work
25	0.15 ($NaClO_4$)	5.13	2.91		12
25	0.15 ($NaClO_4$)	4.871	2.705		This work
25	1.0 (KNO_3)	4.73	2.67		5
25	1.0 (KNO_3)	4.73	2.63		6
25	1.0 ($NaClO_4$)	4.679	2.688		This work
25	3.0 ($NaClO_4$)	4.89	3.05		7
25	3.0 ($NaClO_4$)	4.837	2.923		This work
35	→0	5.427	2.967	H, Ag–AgCl	9,10
35	→0	5.375	2.948	Glass electrode	This work

with temperature that the dependence was assumed to be linear according to the equation:

$$\log K^\circ_n = a + bT \tag{9}$$

On the basis of this assumption the thermodynamic quantities, the free energies, enthalpies, entropies, and heat capacities of the protonation equilibria of the phthalate ion were calculated from the following expressions:

$$\Delta G^\circ = -2.303\ R(aT + bT^2) \tag{10}$$

$$\Delta H^\circ = 2.303\ RbT^2 \tag{11}$$

$$\Delta S^\circ = 2.303\ R(a + 2bT) \tag{12}$$

$$\Delta C^\circ_p = 4.606\ RbT \tag{13}$$

where $R = 8.31433$ J K^{-1} mol^{-1} and T is the absolute temperature.

Fitting the mean values of log K°_1 and log K°_2 at different temperatures from Table 7 with the method of least squares to eqn. (9) gave for the constants a and b the following values:

	a	$b \times 10^3$
log K°_1	4.967	1.320
log K°_2	2.450	1.611

The values of the free energies, enthalpies and entropies were then calculated from eqns. (10)–(12). These are given for the first protonation equilibrium in Table 9 and for the second in Table 10.

The mean values of log K°_1 and log K°_2 from Table 7 are represented as functions of the absolute temperature in Fig. 2.

The effect of temperature on the protonation of the phthalate ion is very weak (Fig. 2, Table 7). The values of both protonation constants increase only slightly with temperature.

For both protonation reactions ΔH° is positive, which indicates endothermic processes (Tables 9 and 10). The values of ΔS° are also positive and increase almost unobservably with increasing temperature within the tem-

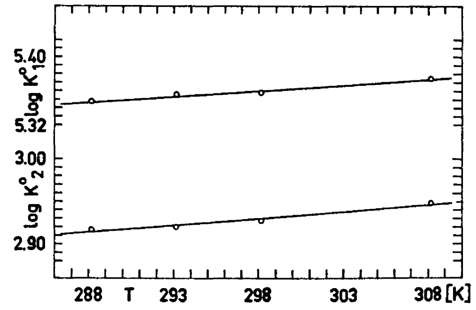

Fig. 2. The thermodynamic values log K°_1 and log K°_2 of the protonation constants of phthalate ion as functions of the absolute temperature.

Table 9. The calculated thermodynamic quantities of the first protonation equilibrium of the phthalate ion.

t °C	log K°_1 (eqn. (7))	log K°_1 (eqn. (9))	$-\Delta G^\circ$ (kJmol^{-1})	ΔH° (kJmol^{-1})	ΔS° (JK^{-1}mol^{-1})	$\left\|\frac{10^2 T\Delta S^\circ}{\Delta G^\circ}\right\|$
15	5.348	5.347	29.50	2.10	110	107
20	5.356	5.354	30.05	2.17	110	107
25	5.358	5.360	30.60	2.25	110	107
35	5.375	5.374	31.71	2.40	111	108
Mean at 15 – 35 °C			30.47 ± 0.70	2.23 ± 0.1	110 ± 1	107

Table 10. The calculated thermodynamic quantities of the second protonation equilibrium of the phthalate ion.

t °C	log K°_2 (eqn. (8))	log K°_2 (eqn. (9))	$-\Delta G^\circ$ (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J K^{-1}mol^{-1})	$\left\|\frac{10^2 T\Delta S^\circ}{\Delta G^\circ}\right\|$
15	2.917	2.914	16.08	2.56	64.8	116
20	2.920	2.922	16.40	2.65	64.8	116
25	2.927	2.930	16.73	2.74	65.3	116
35	2.948	2.946	17.39	2.93	66.1	117
Mean at 15 – 35 °C			16.65 ± 0.41	2.72 ± 0.1	65.3 ± 0.5	116

Table 11. The thermodynamic quantities of the protonation reactions of the phthalate ion previously obtained at the present temperatures.

t °C	$-\Delta G^\circ$ (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J K^{-1} mol^{-1})	$\Delta C^\circ p$ (J K^{-1} mol^{-1})	Ref.
The first protonation reaction					
15	29.812	−0.810	100.6	283.5	10
20	30.327	0.620	105.5	288.5	10
25	30.867	2.074	110.5	293.4	10
25	29.884	2.075	87.9	292.9	8
35	32.021	5.056	120.3	303.2	10
The second protonation reaction					
15	16.198	1.780	61.4	87.0	9
20	16.513	2.219	63.9	88.5	9
25	16.836	2.666	65.4	90.0	9
35	17.505	3.581	68.4	93.0	9

perature range used. These changes are in agreement with the opinion that the protonation of the phthalate ion is favored by temperature increase although the enthalpy changes are against this, because the increase of the entropy values due to the liberation of hydration water molecules of the reaction species. The values of ΔC°_p are also positive and increase with increasing temperature, but are very inaccurate and are not given.[17]

Hamer *et al.*[9,10] and Banerjee *et al.*[8] have determined previously the thermodynamic quantities of the protonation reactions of the phthalate ion. The latter evaluated the thermodynamic quantities of the first protonation reaction at 25 °C by extrapolation from potentiometric measurements in mixtures of ethylene glycol and water at different temperatures (5 – 45 °C). The results of these studies in the temperature range 15 – 35 °C are compared in Table 11.

Comparing our results in Tables 9 and 10 with the earlier ones in Table 11, they may be said to be of the same order of magnitude. The error in log K_n values when working with a glass electrode and a system with minimized liquid junction potentials may, however, easily be of the order of ± 0.02 unit. This means estimated inaccuracies of about ± 0.2 kJ mol^{-1} in ΔG°, ± 3 kJ mol^{-1} in ΔH° and ± 10 J K^{-1} mol^{-1} in ΔS° values or better.

On the basis of Table 8 and Fig. 1 and 2 it may be concluded that, within the temperature range of 15 to 35 °C, the protonation equilibria of the phthalate ion are fairly independent both of the nature of the neutral salts present, and of ionic strength in solution. This means that phthalic acid is, in these respects, well suited for use as a group reagent and a buffering agent in the usual precipitation conditions prevailing in the inorganic qualitative analysis of metal ions.[18]

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