

## Thermodynamics of Ion-Association in Aqueous Solutions of Calcium Phthalate & Terphthalate Using Ion-Selective Electrode Technique

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Stoichiometric ( $K$ ) and thermodynamic ( $K_A$ ) association constants of calcium phthalate and terphthalate have been determined at different temperatures (25°, 35° and 45°C) and ionic strengths (0.15, 0.20, 0.25 and 0.30 mol dm<sup>-3</sup>). The desired ionic strength is maintained by the addition of tetramethylammonium chloride. The  $K_A$  values decrease in the order phthalate > terphthalate > benzoate. This indicates that substitution of -COOH group in benzoate increases the tendency of the resulting anion to associate. The  $K_A$  value is less when -COOH group is in *ortho* position (as in phthalate) as compared to that in *para* position (as in terphthalate). It is concluded that  $pK_a$  values and Hammett  $\sigma$  function can be successfully used to predict the association behaviour of calcium phthalate and terphthalate.

In an earlier investigation<sup>1</sup>, we reported the results of study on the ion- association between the sodium ions and various aromatic ligands in aqueous solutions. Amongst these ligands, phthalate and terphthalate ions were found to associate appreciably with sodium. We consider that a similar study with calcium phthalate and terphthalate, in the presence of NaCl as ionic strength fixer is likely to throw light on the correlation between the effect of substituent (carboxylic group) on the benzoate and its association with Ca ions. In an earlier paper<sup>2</sup> we studied the effect of position and number of hydroxy groups on the benzoate ion and its association with Ca and Mg. Also the applicability of Hammett  $\sigma$ - function in interpreting association of phthalate and terphthalate ion with calcium was examined<sup>2,3</sup>.

### Materials and Methods

The potential measurements were made with a Radiometer model pH M62 digital pH-mV meter equipped with divalent cation membrane electrode (Orion model 92-93) in junction with single junction electrode (Orion model 90-01). These two electrodes were immersed in a double-jacket cell thermostated at the desired temperature.

Sodium salts of phthalic acid and terphthalic acid were prepared from AR grade chemicals the other salts used, viz. calcium chloride (Cambrian) and tetramethylammonium chloride (BDH) were of extra pure quality. Stock solutions of sodium phthalate and terphthalate and calcium chloride were prepared in deionised doubly distilled water and standardised by

flame photometry and ion exchange methods respectively.

The divalent electrode was calibrated using standard calcium chloride solution as a reference for the corresponding calcium phthalate and terphthalate. Tetramethylammonium chloride was used to keep the ionic strength constant for both the reference and investigated solutions. Linear calibration curves were obtained for the plot of e.m.f. against log activity of the corresponding ion<sup>4</sup>.

Several measurements at each ionic strength were carried out at the desired temperature to get average values for the stoichiometric constants. The measurements were carried out at 25°, 35° and 45°C. Calcium phthalate and terphthalate were obtained by mixing the corresponding sodium salts with calcium chloride in 1:1 molar ratio. However, the concentration of calcium phthalate and terphthalate never exceeded 0.2M to ensure the formation of 1:1 ion-pair only.

### Mathematical Approach

The association of Ca<sup>2+</sup> with phthalate and terphthalate can be mono- or bi- dentate depending on the experimental conditions. Earlier we have noted the association between sodium ion and phthalate or terphthalate ions<sup>1</sup>. The mathematical model described herein takes into account the mono- binding of phthalate and terphthalate with Ca<sup>2+</sup> (see Eq. 1). This correction is considered necessary for meaningful results. In Eq. (1) M<sup>2+</sup> is Ca<sup>2+</sup> or any other divalent ion and A<sup>2-</sup> represent phthalate and terphthalate.



The stoichiometric association constant is then given by Eq. (2).

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$$K_{(MA)} = \frac{[MA]}{[M^{2+}]_f \cdot [A^{2-}]_f} \quad \dots (2)$$

where  $[MA]$  is the concentration of the ion-pair;  $[M^{2+}]_f$  the concentration of the free metal ion; and  $[A^{2-}]_f$  the concentration of the free ligand ions.

Stoichiometric association constant for the association of sodium with phthalate and terphthalate  $[Na^+ + A^{2-} \rightleftharpoons (NaA)^-]$  is given by Eq. (3)

$$K_{(NaA)^-} = \frac{[NaA]^-}{[Na^+]_f \cdot [A^{2-}]_f} \quad \dots (3)$$

In our further calculations following assumptions (i - iii) are made.

$$[M^{2+}]_T = [M^{2+}]_f + [M.A] \quad \dots (i)$$

$$[A^{2-}]_T = [A^{2-}]_f + [M.A] + [Na.A^-] \quad \dots (ii)$$

$$[Na^+]_T = [Na^+]_f + [Na.A^-] \quad \dots (iii)$$

From the above assumptions we can derive the following:

$$[A^{2-}]_f = [A^{2-}]_T - \{[M.A] + [Na.A^-]\} \quad \dots (iv)$$

$$[Na.A^-] = K_{(Na.A^-)} \cdot [Na^+]_f \cdot [A^{2-}]_f$$

$$\text{Therefore, } [Na.A^-] = [Na^+]_T - [Na^+]_f$$

$$\text{or, } [Na^+]_T - [Na^+]_f = K_{(Na.A^-)} \cdot [Na^+]_f \cdot [A^{2-}]_f$$

This leads to

$$[A^{2-}]_f = \frac{[Na^+]_T - [Na^+]_f}{K_{(Na.A^-)} \cdot [Na^+]_f}$$

Substituting the value of  $[A^{2-}]_f$  in Eq. (2) we get:

$$K_{(MA)} = \frac{[M^{2+}]_T - [M^{2+}]_f}{[M^{2+}]_f \cdot \{[Na^+]_T - [Na^+]_f / K_{(Na.A^-)} \cdot [Na^+]_f\}} \\ = \frac{K_{(Na.A^-)} \cdot [Na^+]_f \cdot \{[M^{2+}]_T - [M^{2+}]_f\}}{[M^{2+}]_f \cdot \{[Na^+]_T - [Na^+]_f\}} \quad \dots (4)$$

Since the experimental conditions permit the first association only to occur, the thermodynamic association constant ( $K_A$ ) can be calculated by Eq. (5).

$$K_A = K \cdot \frac{1}{f_{\pm}^2 [M^{2+}]} \quad \dots (5)$$

where  $K$  is the stoichiometric association constant and  $f_{\pm} [M^{2+}]$  is the mean activity coefficient of the corresponding metal.

#### Effect of hydrolysis

It is well known that both the anion and the cation of each of calcium phthalate and terphthalate can be

hydrolysed at specific pH range. However, hydrolyses of both cation and anion are neglected in the pH range of present study. This can be easily confirmed when we apply Eq. (6).

$$K_{corr} = K \left( 1 + \frac{[H^+]}{K_a} \right) \quad \dots (6)$$

where  $[H^+]$  is the concentration of the hydrogen ions in solution and  $K_a$  is the dissociation constant of the organic acids<sup>1</sup>.

#### Results and Discussion

In this work measurements were made at four ionic strengths (0.15, 0.2, 0.25 and 0.30 mol dm<sup>-3</sup>) and three temperatures (25°, 35° and 45°C) in tetramethylammonium chloride media. The association constants of calcium phthalate and terphthalate calculated by Eq. (4) are given in Table 1. The infinite dilution association constant ( $K_A$ ) is related to the stoichiometric constant by Eq. (5) and corrected for hydrolysis by means of Eq. (6). The values of  $K_A$  are given in Table 2. The thermodynamic parameters of association of Ca<sup>2+</sup> with phthalate and terphthalate at different temperatures are given in Table 2. For comparison, thermodynamic parameter for the association of Ca<sup>2+</sup> with benzoate<sup>2</sup> are also included in Table 2.

It should be pointed out that NaCl was not used to keep the ionic strength constant due to the association between Na<sup>+</sup> and phthalate and terphthalate ions<sup>1</sup>.

Table 1—Stoichiometric Association Constants ( $K$ ) of Calcium Phthalate and Terphthalate using CaCl<sub>2</sub> as a Standard Solution in Aq Tetramethylammonium Chloride at Various Temperatures and Ionic Strengths

$\mu$ (mol dm <sup>-3</sup> )	$K$ (dm <sup>3</sup> mol <sup>-1</sup> )	
	Phthalate	Terphthalate
	Temp. = 25°C	
0.15	33.46	24.22
0.20	31.27	24.06
0.25	28.61	21.82
0.30	26.46	20.80
	Temp. = 35°C	
0.15	34.35	25.07
0.20	31.74	23.23
0.25	28.85	22.92
0.30	27.41	21.45
	Temp. = 45°C	
0.15	35.23	26.30
0.20	31.87	24.68
0.25	30.70	23.80
0.30	28.96	21.91

Table 2—Therodynamic Parameters of Association of Calcium Phthalate and Terphthalate at Different Temperatures

Temp. °C	$K_A$ ( $\text{dm}^3\text{mol}^{-1}$ )	$\Delta G^\circ$ ( $\text{kJmol}^{-1}$ )	$\Delta H^\circ$ ( $\text{kJmol}^{-1}$ )	$\Delta S^\circ$ ( $\text{kJK}^{-1}\text{mol}^{-1}$ )
Phthalate				
25	84.53	10.99	1.00	0.0403
35	86.33	11.41	1.00	0.0403
45	89.51	11.87	1.00	0.0405
Terphthalate				
25	63.54	10.28	1.34	0.0390
35	65.49	10.70	1.34	0.0391
45	68.30	11.16	1.34	0.0393
Benzoate				
25	21.0	7.52	2.103	0.0324
35	22.5	7.98	2.103	0.0327
45	23.8	8.36	2.103	0.0329

It is seen from Table 2 that  $K_A$  values decrease in the order phthalate > terphthalate > benzoate. The fact that  $K_A$  of both phthalate and terphthalate are larger than the benzoate indicates that the substitution of the carboxylic group in the benzoate does increase its tendency for association. However, if the COOH is in the *ortho*-position (as in phthalate) the  $K_A$  value is less than that when COOH is in *para* position (as in the terphthalate). Such a behaviour can be explained on the basis of  $pK_a$  values of the parent acids, which also show a similar trend. On this basis alone, both are expected to be more associated than the benzoate itself. However, in our earlier investigations<sup>2,3</sup> on the association of  $\text{Ca}^{2+}$  with a number of substituted benzoates, this explanation in the trend of  $K_A$  values (based on  $pK_a$  of the ligands) was not valid. We had to use another approach, i.e. Hammett  $\sigma$  - function to explain the trend in  $K_A$  values. The Hammett  $\sigma$  - function can be obtained from the equation:  $\sigma = \log$

 Table 3—Hammett Function ( $\sigma$ ) for Calcium Phthalate and Terphthalate

Salt (Substituent)	Temp. (°C)	$\sigma$
Phthalate ( <i>o</i> -COOH)	25	0.605
	35	0.584
	45	0.575
Terphthalate ( <i>p</i> -COOH)	25	0.481
	35	0.464
	45	0.458

$K/K_0$  where  $K$  is the association constant of Ca phthalate or terphthalate and  $K_0$  is that for the benzoate at the same temperature. According to Hammett the more negative or the smaller the  $\sigma$  the more dissociated or less associated is the salt. Table 3 gives the  $\sigma$  - values and it is obvious that the association should be greater in Ca phthalate than in Ca terphthalate at each temperature, in conformity with the experimental observation. Thus it is evident that  $pK_a$  and  $\sigma$  approaches can be used to predict the association behaviour of calcium phthalate and terphthalate.

It is also worth noting that for all the four salts investigated, the thermodynamic association constants increase with increase in temperature as is also evident from the sign of  $\Delta H^\ddagger$  values. This indicates that these association processes are endothermic ones, similar to the association of Ca and Mg salts studied before<sup>2,3</sup>.

#### References

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