

Conductometric study of ion-pair formation in aqueous solutions of potassium pyrosulphate at different temperatures

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The thermodynamic association constant (K_A) for KS_2O_7^- ion-pair has been determined at four different temperatures, e.g. 298.15, 303.15, 308.15 and 313.15 K, in aqueous medium using Shedlovsky and Fuoss-Kraus extrapolation techniques. The thermodynamic functions for the process of ion-pair formation have been evaluated and discussed.

In continuation of our study on the determination of association parameters (Λ_0 and K_A)¹ of a number of 1:1 and 1:2 electrolytes in aqueous and different aquo-organic solvent systems from conductance data, the present work aims at determining the conductivity values of potassium pyrosulphate in water at 298.15, 303.15, 308.15 and 313.15 K to examine the validity of Shedlovsky and Fuoss-Kraus conductance equations in evaluating the association parameters in aqueous medium. The thermodynamic parameters for the process of ion-pair formation have been evaluated.

Experimental

Potassium pyrosulphate (E. Merck) of GR grade was used as such. Conductivity water ($K = 1 \times 10^{-6} \text{ S cm}^{-1}$) was used for preparing potassium pyrosulphate solutions. Conductance measurements were made on a digital reading conductivity meter (Systronics, Type 304) with a sensitivity of 0.1% and a dipping type conductivity cell with platinized electrodes (cell constant, 1 S cm^{-1}). The experiment was repeated several times with different concentrations of potassium pyrosulphate. All measurements were carried out in water thermostat maintained at appropriate temperatures varying within $\pm 0.05 \text{ K}$. The conductivities of salt solutions were always corrected for the contribution of the solvent (e.g. water) conductivity.

Results and discussion

The values of molar conductivity, Λ at any molar concentration, c (mol dm^{-3}) have been computed from the corrected conductivity data. An

auxiliary function, Λ' was calculated using the relation²,

$$\Lambda' = (\Lambda + Ac^{1/2}) / (1 - Bc^{1/2}) \quad \dots (1)$$

where A and B are the Onsager constants and were estimated by means of usual equations³ and by using the values of viscosity and dielectric constant of water at 298.15, 303.15, 308.15 and 313.15 K available in the literature³.

Approximate value of molar conductivity at infinite dilution [Λ_0 (approx)] was obtained by linear extrapolation of the auxiliary function Λ' as a function of $c^{1/2}$,

$$\Lambda' = \Lambda_0 (\text{approx}) - Sc^{1/2} \quad \dots (2)$$

where S is the Onsager slope. This value of Λ_0 (approx) was used to determine the Onsager slope S as follows:

$$S = 82.4 (DT)^{-1/2} \eta^{-1} + 8.20 \times 10^5 (DT)^{-3/2} \Lambda_0 (\text{approx}) \quad \dots (3)$$

where D is the dielectric constant of water, η is the coefficient of viscosity and T is the temperature. Using the values of D and η of water available in literature² at different temperatures, the value of S was estimated by Eq. (3).

Using these S and Λ_0 (approx) values, Z , $S(z)$ and α (the degree of dissociation) values were calculated by the following equations.

$$Z = S(\Lambda C)^{1/2} / \Lambda_0^{3/2} \quad \dots (4)$$

$$S(z) = 1 + Z + Z^2/2 + Z^3/8 \quad \dots (5)$$

Table 1—Values of the limiting molar conductivity, Λ_0 ($S\ cm^2\ mol^{-1}$) for $K_2S_2O_7$ in water at different temperatures

$T(K)$	S-technique			FK-technique		
	$a^0 = 0$	$= q$	$= 2q$	$a^0 = 0$	$= q$	$= 2q$
298.15	812.73 $\pm$ 40.18	809.78 $\pm$ 40.04	807.91 $\pm$ 39.95	812.59 $\pm$ 40.08	809.66 $\pm$ 39.94	807.79 $\pm$ 39.85
303.15	867.65 $\pm$ 44.56	864.28 $\pm$ 44.39	862.15 $\pm$ 44.28	867.49 $\pm$ 44.45	864.14 $\pm$ 44.29	862.01 $\pm$ 44.18
308.15	921.88 $\pm$ 48.80	918.08 $\pm$ 48.61	915.68 $\pm$ 48.49	921.70 $\pm$ 48.69	917.91 $\pm$ 48.50	915.52 $\pm$ 48.38
313.15	978.86 $\pm$ 53.38	974.58 $\pm$ 53.15	971.88 $\pm$ 53.01	978.65 $\pm$ 53.26	974.39 $\pm$ 53.03	971.70 $\pm$ 52.89

Table 2—Values of K_A ($dm^3\ mol^{-1}$) of $KS_2O_7^-$ ion-pair in water at different temperatures

$T(K)$	S-technique			FK-technique		
	$a^0 = 0$	$= q$	$= 2q$	$a^0 = 0$	$= q$	$= 2q$
298.15	47.58 $\pm$ 4.86	45.24 $\pm$ 4.47	43.68 $\pm$ 4.32	47.38 $\pm$ 4.67	45.05 $\pm$ 4.44	43.51 $\pm$ 4.29
303.15	51.49 $\pm$ 5.28	48.92 $\pm$ 5.02	47.22 $\pm$ 4.85	51.28 $\pm$ 5.25	48.72 $\pm$ 4.99	47.03 $\pm$ 4.82
308.15	54.96 $\pm$ 5.82	52.18 $\pm$ 5.52	50.34 $\pm$ 5.33	54.73 $\pm$ 5.78	51.96 $\pm$ 5.49	50.14 $\pm$ 5.30
313.15	58.75 $\pm$ 6.40	55.73 $\pm$ 6.07	53.75 $\pm$ 5.86	58.51 $\pm$ 6.37	55.50 $\pm$ 6.04	53.53 $\pm$ 5.82

and

$$\alpha = \Lambda S(z)/\Lambda_0 \quad \dots (6)$$

where Λ and Λ_0 in Eqs (4) and (6) are Λ' and Λ_0 (approx) respectively.

Using this α value and the value D , the dielectric constant of water obtained from the literature⁴ at different temperatures, the values of $f_{\pm}$, the mean ionic activity co-efficient were evaluated by means of Eq. (7)

$$-\log f_{\pm} = \frac{1.824 \times 10^6 |z_+| z_- (DT)^{-3/2} [(1 + 2\alpha)c]^{1/2}}{1 + a^0 50.29 \times 10^8 (DT)^{-1/2} [(1 + 2\alpha)c]^{1/2}} \quad \dots (7)$$

with a^0 (the distance of closest approach of ions) = 0, q and $2q$, where z_+ and z_- are ion valencies and q is the Bjerrum critical distance and equals $z_+ z_- e^2 / 2DKT$ (the symbols have their usual meanings).

Using these initial values of $S(z)$ and $f_{\pm}$ (for $a^0 = 0, q$ and $2q$ separately) and of Λ (i.e. Λ' as obtained by Eq. (1)), the values of $1/\Lambda S(z)$ and $c\Lambda f_{\pm}^2 S(z)$ were calculated and plotted according to the following equation⁴ (i.e. Shedlovsky extrapolation technique)

$$\frac{1}{\Lambda S(z)} = \frac{1}{\Lambda_0} + \left(\frac{K_A}{\Lambda_0^2} \right) (c\Lambda f_{\pm}^2 S(z)) \quad \dots (8)$$

to get Λ_0 and K_A values from the intercept and slope, respectively. Using this new value of Λ_0 the

values of S , Λ (i.e. Λ' using Eq. (2)) and $f_{\pm}$ (with $a^0 = 0, q$ and $2q$), Z , $S(z)$, and α were further evaluated. The values of $1/\Lambda S(z)$ and $c\Lambda f_{\pm}^2 S(z)$ were again calculated and plotted according to Eq. (8) to yield better values of Λ_0 and K_A . The procedure was repeated using the new value of Λ_0 till the constancy in Λ_0 and K_A values appeared.

The conductance data were also analysed using the Fuoss-Kraus extrapolation technique⁵

$$F(z)/\Lambda = 1/\Lambda_0 + (K_A/\Lambda_0^2) (c\Lambda f_{\pm}^2 / F(z)) \quad \dots (9)$$

where

$$F(z) = (4/3) \cos^2[(1/3) \cos^{-1}(-3^{1/2} Z/2)]$$

$$\alpha = \Lambda/\Lambda_0 F(z)$$

and Z and $f_{\pm}$ were the same as defined in Eqs (4) and (7) respectively. The values of Λ_0 and K_A were estimated by following the iteration process, similar to that described in the case of Shedlovsky technique.

All the calculations were carried out on PC-386-DX computer, and the results are shown in Tables 1 and 2, along with standard deviations.

The values of Λ_0 obtained for $K_2S_2O_7$ and that of pK_A for $KS_2O_7^-$ ion pair in association equilibrium $K^+ + S_2O_7^{2-} \rightleftharpoons KS_2O_7^-$ at the four different temperatures using both the Shedlovsky (S) and Fuoss-Kraus (FK) techniques were fitted by least-squares method to equations of the type^{3,6},

$$\Lambda_0 = a + bT \quad \dots (10)$$

and

Table 3—Values of the parameters a and b for Λ_0 and A , B and C for pK_A in water

	S-technique			FK-technique		
	$a^0=0$	$=q$	$=2q$	$a^0=0$	$=q$	$=2q$
a	-2481.2280 ± 0.7421	-2457.8220 ± 0.7252	-2443.2334 ± 0.7145	-2479.6544 ± 0.7391	-2456.5106 ± 0.7268	-2442.1614 ± 0.7143
$b \times 10^3$	11052.4 ± 2.4050	10964.0 ± 2.3496	10908.8 ± 2.3146	11047.8 ± 2.3946	10959.2 ± 2.3546	10904.8 ± 2.3146
A	1505.0382 ± 0.2731	1533.6111 ± 0.2689	1505.0382 ± 0.2731	1504.4883 ± 0.2731	1533.6111 ± 0.2689	1533.6111 ± 0.2689
$B \times 10^4$	-97165.06 ± 8.9815	-99016.42 ± 8.7996	-97092.06 ± 8.9387	-97147.06 ± 8.9815	-98998.42 ± 8.7996	-98966.62 ± 8.8015
$C \times 10^6$	10029 ± 2.9273	10402 ± 2.8815	10129 ± 2.9273	10129 ± 2.8600	10402 ± 2.8815	10442 ± 2.8815

Table 4—Thermodynamic quantities for KS_2O_7^- ion-pairs in aqueous medium at 298.15 K

	S-technique			FK-technique		
	$a^0=0$	$=q$	$=2q$	$a^0=0$	$=q$	$=2q$
ΔG^0 (kJ mol^{-1})	-9.57 ± 0.25	-9.44 ± 0.25	-9.36 ± 0.25	-9.56 ± 0.25	-9.44 ± 0.25	-9.35 ± 0.25
ΔH^0 (kJ mol^{-1})	10.30 ± 0.50	10.19 ± 0.50	10.13 ± 0.50	10.31 ± 0.50	10.19 ± 0.50	10.12 ± 0.50
ΔS^0 ($\text{J mol}^{-1}\text{K}^{-1}$)	67 ± 3	66 ± 3	65 ± 3	67 ± 3	66 ± 3	65 ± 3
$\Delta C_p^0 \times 10^2$ ($\text{kJ mol}^{-1}\text{K}^{-1}$)	6.91 ± 0.33	6.84 ± 0.33	6.80 ± 0.33	6.92 ± 0.34	6.84 ± 0.33	6.79 ± 0.33

$$pK_A = A/T + B + CT \quad \dots (11)$$

respectively where T is the temperature. The parameters a and b for Λ_0 and A , B and C for pK_A are recorded in Table 3 along with their standard deviations.

The various thermodynamic parameters for the association process of KS_2O_7^- ion pair in their standard states have been evaluated by means of usual relations⁷ and are given in Table 4 for 298.15 K only.

A perusal of Table 1 shows that the values of Λ_0 derived from both S and FK techniques with $a^0=0$, q and $2q$ for calculating activity coefficient are very close to each other.

Association constants (K_A) estimated from S and FK techniques taking $a^0=0$, q and $2q$ are recorded in Table 2. Our investigations of potassium pyrosulphate show a considerable ion pair formation. Of such cases deviations from the limiting Onsager and Debye-Huckel equations can be attributed almost wholly to the strong cation-anion electrostatic interaction.

A perusal of Table 4 shows that the ΔH^0 and ΔS^0 values for the association process are positive.

The more positive value for ΔS^0 indicates that the ions are hydrated. As observed, the standard change in heat capacity, Δc_p^0 for the association process is positive. Electrostatic interactions between ions and dipolar solvent molecules (e.g. water) would be expected to change the entropy and heat capacity of the system in the same direction, which is found to be in accord with our actual observations.

References

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