Ion-Pair Formation in Aqueous Solutions of Potassium & Ammonium Persulphates

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Conductivities of potassium and ammonium persulphates in aqueous solutions were determined at 25° and 35° with a view to detecting and estimating the stability of the possible ion-pairs. The thermodynamic association constants were estimated to be 13·16 (at 25°), 16·66 litre mole⁻¹ (at 35°) for $KS_2O^-_1$ and 16·67 (at 25°), 21·64 litre mole⁻¹ (at 35°) for $NH_4S_2O^-_8$. The limiting mobilities of persulphate ion, viz. 86·41 ± 0·08 (at 25°) and 97·42 ± 0·1 ohm⁻¹ g equiv⁻¹ cm² (at 35°) have been evaluated independently. Thermodynamic parameters for the ion-pairs have also been evaluated.

POTASSIUM persulphate as a 2:1 electrolyte, similar to potassium sulphate, was reported first by Bredig[1] from the conductance measurements of the salt solutions. Moeller[2] made similar studies on ammonium persulphate. Ion-pair formation in strong electrolyte solutions is a well-known phenomenon. Chlebek and Lister[3] have recently concluded from a potentiometric study that ion pairs exist in potassium persulphate solution. They also studied its effect on the kinetics of oxidation of potassium ferrocyanide. Determination of electrical conductivities of dilute solutions offer a sensitive method for detecting ion-pair formation. In general, the differences between the theoretical electrical conductivities calculated from various equations[4-7] and the experimental conductivities could be explained in terms of ion-pair formation. From these differences in conductance values association constants of the possible ion-pairs were also calculated[8-11] by several workers. As persulphates are uni-bivalent electrolytes, ion-pair formation in their solutions is most likely. Moreover, persulphates are powerful oxidizing agents and the formation of ion-pairs could influence the kinetics of persulphate oxidations considerably. Hence, it is necessary to determine the ion-pair formation constants for a quantitative understanding of the kinetic data. This necessitated the present work in which the electrical conductivities of dilute solutions of potassium and ammonium persulphates were determined and the deviations from Onsager's equation[4] were accounted for in terms of ion-pair formation.

Materials and Methods

Potassium persulphate (E. Merck) and ammonium persulphate (Sarabhai Merck) of GR grade were used as such. For conductivity the salt solutions[6] were prepared fresh in conductivity water (sp. cond. 1×10^{-6} mho). The experimental set-up consisted of a conductivity bridge employing Jones[12,13] circuit, fabricated by ITL (India) along with a beat frequency oscillator (Philips type GM 2307), and an AF amplifier (RADART, type 201A) and

line voltage corrector (Russian, type π 71M). The final amplifier and null detector was a double beam oscilloscope (Philips, type PM 3230M/90). All conductance measurements were made at a frequency of 4 kHz. The conductance cell was constructed on the design described by Daggett et al.[14]. Temperature was maintained constant to within ±0·02°. All conductance values were corrected for solvent conductance. The overall accuracy of the measured equivalent conductivites was within ±0·05%.

Results and Discussion

Equivalent conductivities of potassium persulphate at 25° and 35° were plotted against $m^{1/2}$ where m is molar concentration. Approximate values of equivalent conductivities at infinite dilution ($\Lambda°$) were obtained from these plots. These values of $\Lambda°_{(approx)}$ were used to calculate the theoretical slopes (S) in Onsager's limiting equation[4]:

$$\Lambda_{exp} = \Lambda°_{(approx)} - Sm^{\frac{1}{2}} \qquad ...(1)$$

The limiting mobilities of K⁺ used for the calculation of Onsager's slope (S) were 73·50 and 88·21 ohm⁻¹ g equiv⁻¹ cm² at 25° and 35° respectively[15]. $\Lambda_{exp} + Sm^{\frac{1}{2}}$ was plotted against m to get the accurate values of $\Lambda°$. The values of $\Lambda°$ for potassium and ammonium persulphates along with the limiting mobilities of $S_2O_8^{2-}$ ion at 25° and 35° are given in Table 1.

TABLE 1 — EQUIVALENT CONDUCTIVITY AT INFINITE DILUTION AND THE LIMITING MOBILITY OF $S_2O_8^{2-}$

Temp. °C	$\Lambda°$ (ohm⁻¹ g equiv⁻¹ cm²)	$\frac{1}{2}\lambda°_{S_2O_8^{2-}}$ (ohm⁻¹ equiv⁻¹ cm².)
	$K_2S_2O_8$	
25	159·91 ± 0·08	86·41 ± 0·08
35	185·63 ± 0·10	97·42 ± 0·10
	$(NH_4)_2S_2O_8$	
25	159·90 ± 0·08	86·41 ± 0·08
35	186·03 ± 0·10	97·42 ± 0·10

The association constants of the ion-pairs were computed by a slightly modified method of Righellato and Davies[8]. As $K_2S_2O_8$ and $(NH_4)_2S_2O_8$ are uni-bivalent electrolytes, the association equilibrium of the type

$$M^+ + A^{2-} \rightleftharpoons MA^- \qquad ...(2)$$
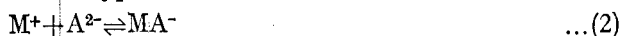
is most likely in their solutions. Further, association to form M_2A was neglected as the solutions were very dilute and the persulphates used were strong electrolytes. If m is the molar concentration of the solution and α the degree of dissociation of the ion-pair formed, then the concentrations of M^+ A^{2-} and MA^- are $(1+\alpha)$ m, αm and $(1-\alpha)$ m respectively. The thermodynamic association constant (K) may be given by Eq. (3):

$$K = \frac{[MA^-]}{[M^+][A^{2-}]} \cdot \frac{f_{MA}}{f_M f_A}$$
$$= \frac{(1-\alpha)}{(1+\alpha)\alpha m} \cdot \frac{f_{MA}}{f_M f_A} \qquad ...(3)$$

where f_M, f_A and f_{MA} are the activity coefficients of the species M^+, A^{2-} and MA^- respectively. The solution was considered as a mixture of a completely dissociated uni-bivalent salt of molar concentration αm and a completely dissociated uni-univalent salt of concentration $(1-\alpha)m$. Hence

$$2\Lambda_{exp} = (1-\alpha)\Lambda_{1:1} + 2\alpha\Lambda_{2:1} \qquad ...(4)$$

where $\Lambda_{1:1}$ and $\Lambda_{2:1}$ are the theoretical equivalent conductivities of uni-univalent and uni-bivalent salts calculated from Onsager's equation[4]. The limiting mobility of the ion-pair was calculated from the reaction

$$\lambda^o_{MA^-} = 0.6\ \lambda^o_{A^{2-}} \qquad ...(5)$$

as suggested by Righellato and Davies[8]. The ionic strength (μ) of the solution is given by the relation

$$\mu = (1+2\alpha)m \qquad ...(6)$$

Activity coefficients were calculated using the Davies[16] equation:

$$-\log f_i = AZ_i^2 \left(\frac{\sqrt{\mu}}{1+\sqrt{\mu}} - 0.3\mu \right) \qquad ...(7)$$

where

$$A = \frac{1.8246 \times 10^6}{(\epsilon T)^{3/2}} \qquad ...(8)$$

For example, the Λ^o for $K_2S_2O_8$ at 25° was found to be 159.91 ohm^{-1} g equiv^{-1} cm^2, which gives a value of 86.41 ohm^{-1} g equiv^{-1} cm^2 for the limiting mobility of persulphate ion. Using Eq. (6), the limiting mobility of the ion-pair $KS_2O_8^-$ was calculated as 51.85 ohm^{-1} g equiv^{-1} cm^2. These limiting mobilities give the expressions

$$\Lambda_{2:1} = 159.91 - 159.22\sqrt{\mu} \qquad ...(9)$$
$$\Lambda_{1:1} = 125.35 - 89.01\sqrt{\mu} \qquad ...(10)$$

Substituting Eqs. (9) and (10) in Eq. (4) we get

$$2\Lambda_{exp} = 125.35 - 89.01\sqrt{\mu} +$$
$$(194.47 - 229.43\sqrt{\mu})\alpha \qquad ...(11)$$

To start with α was assumed to be unity and the corresponding value of μ was calculated from Eq. (6). This value of μ was then substituted in Eq. (11) to obtain an improved value of α. Thus the

TABLE 2 — EQUIVALENT CONDUCTIVITY, ACTIVITY COEFFICIENTS AND THERMODYNAMIC ASSOCIATION CONSTANTS OF ION-PAIRS IN PERSULPHATES

$m \times 10^4$ (moles litre^{-1})	Eq. cond. (ohm^{-1} g equiv^{-1} cm^2)	α	$\mu \times 10^4$	$f_{S_2O_8^{2-}}$	K^o_{assocn} (litre mole^{-1})
		$K_2S_2O_4$ AT 25°			
20.00	144.32	0.9614	58.46	0.7223	14.17
17.14	145.51	0.9650	50.22	0.7381	14.60
15.00	146.58	0.9692	44.08	0.7511	14.33
13.33	147.44	0.9723	39.25	0.7623	14.22
12.00	148.21	0.9754	35.41	0.7720	13.78
10.91	148.83	0.9775	32.24	0.7805	13.66
10.00	149.44	0.9801	29.60	0.7879	13.02
9.23	149.89	0.9815	27.35	0.7949	12.97
8.57	150.38	0.9836	25.43	0.8011	12.24
8.00	150.76	0.9848	23.76	0.8085	12.02
7.50	151.08	0.9857	22.29	0.8117	12.01
7.06	151.40	0.9868	20.99	0.8164	11.68
6.66	151.61	0.9898	19.08	0.8210	12.31
					Av. 13.16
		$K_2S_2O_8$ AT 35°			
20.00	167.28	0.9480	59.92	0.8044	17.51
17.14	168.91	0.9513	49.75	0.8160	18.76
15.00	170.24	0.9573	43.72	0.8256	18.42
13.33	171.34	0.9621	38.98	0.8339	18.05
12.00	172.41	0.9676	35.22	0.8407	16.86
10.91	173.05	0.9695	32.06	0.8470	17.27
10.00	173.80	0.9730	29.46	0.8525	16.50
9.23	174.38	0.9753	27.23	0.8574	16.21
8.57	174.87	0.9770	25.32	0.8618	16.13
8.00	175.39	0.9793	23.67	0.8658	15.41
7.50	175.78	0.9807	22.21	0.8694	15.24
7.06	176.25	0.9830	20.94	0.8728	14.14
6.66	176.33	0.9817	19.74	0.8760	16.13
					Av. 16.66
		$(NH_4)_2S_2O_8$ AT 25°			
20.00	143.62	0.9525	58.10	0.7230	17.67
17.14	144.86	0.9569	49.94	0.7386	18.18
15.00	145.94	0.9612	43.84	0.7516	18.25
13.33	146.91	0.9656	39.07	0.7628	17.83
12.00	147.71	0.9691	35.26	0.7723	17.48
10.91	148.40	0.9720	32.12	0.7809	17.15
10.00	149.01	0.9747	29.49	0.7883	16.67
9.23	149.53	0.9768	27.26	0.7952	16.37
8.57	150.00	0.9788	25.35	0.8013	15.95
8.00	150.43	0.9806	23.69	0.8069	15.48
7.50	150.88	0.9829	22.24	0.8119	14.41
7.06	151.09	0.9829	20.94	0.8166	15.22
6.66	151.31	0.9829	19.75	0.8212	16.05
					Av. 16.67
		$(NH_4)_2S_2O_8$ AT 35°			
20.00	166.51	0.9324	57.30	0.8054	23.31
17.14	168.00	0.9384	49.31	0.8168	24.21
15.00	169.49	0.9460	43.38	0.8262	23.64
13.33	170.71	0.9521	38.71	0.8343	23.15
12.00	171.69	0.9568	34.96	0.8407	22.88
10.91	172.63	0.9616	31.89	0.8474	22.03
10.00	173.31	0.9645	29.29	0.8529	21.98
9.23	174.02	0.9680	27.10	0.8576	21.23
8.57	174.58	0.9704	25.20	0.8620	20.96
8.00	175.21	0.9739	23.58	0.8660	19.61
7.50	175.63	0.9755	22.13	0.8696	19.49
7.06	176.04	0.9772	20.86	0.8732	19.16
6.66	176.31	0.9778	19.68	0.8762	19.69
					Av. 21.64

TABLE 3 — ION-SIZE PARAMETER (a), BJERRUM'S PARAMETER (b) AND THERMODYNAMIC PARAMETERS FOR THE ION ASSOCIATION IN PERSULPHATES

Temp. °C	K°_{assocn} (litre mole^{-1})	b (cm^{-1})	a (Å)	ΔG° (kcal mole^{-1})	ΔH° (kcal mole^{-1})	ΔS° (cal deg^{-1} mole^{-1})
			$K_2S_2O_8$			
25	13·16	4·27	3·34	−1·53	4·31	19·59
35	16·66	4·91	2·94	−1·72		
			$(NH_4)_2S_2O_8$			
25	16·67	5·02	2·84	−1·67	4·76	21·57
35	21·64	5·51	2·62	−1·88		

values of α and μ were calculated by the method of successive approximations. Using these values of μ and α in Eqs. (7) and (3) the values of activity coefficient and thermodynamic association constant (K) of the ion-pair KS_2O_8 were calculated. The results are given in Table 2. Equations similar to Eq. (11) for $K_2S_2O_8$ at 35° and $(NH_4)_2S_2O_8$ at 25° and 35° are given below:

For $K_2S_2O_8$ at 35°:

$$2\Lambda_{exp} = 146·69 - 93·90\sqrt{\mu} + (224·57 - 236·64\sqrt{\mu})\alpha \quad \ldots(12)$$

For $(NH_4)_2S_2O_8$ at 25°:

$$2\Lambda_{exp} = 125·40 - 89·02\sqrt{\mu} + (194·52 - 229·46\sqrt{\mu})\alpha \quad \ldots(13)$$

For $(NH_4)_2S_2O_8$ at 35°:

$$2\Lambda_{exp} = 147·09 - 93·99\sqrt{\mu} + (224·97 - 236·73\sqrt{\mu})\alpha \quad \ldots(14)$$

The equivalent conductivities, association constants, etc. for $(NH_4)_2S_2O_8$ are given in Table 2.

According to Bjerrum[17], association constant may also be given by the expression

$$K_{assocn} = \frac{1}{K_{dissocn}} = \frac{4\pi N}{1000}\left(\frac{|Z_1 Z_2|e^2}{\epsilon Tk}\right)^3 Q_b \quad \ldots(15)$$

where

$$b = \frac{|Z_1 Z_2|e^2}{\epsilon kTa} \quad \ldots(16)$$

and a is ion-size parameter. From the values of association constant, Q_b were calculated. The values

of Bjerrum's parameter (b) corresponding to these Q_b values were calculated from standard tables[16]. Using these values of b in Eqs. (16) the values of ion-size parameter a were calculated (Table 3). Finally from the association constants obtained at two temperatures the thermodynamic parameters ΔH°, ΔG° and ΔS° were calculated for the process given by Eq. (2). The results are presented in Table 3. The limiting mobility of $S_2O_8^{2-}$ ion obtained in the present work at 25°, viz. 86·41 ohm^{-1} g equiv^{-1} cm^2 is comparable with the reported value[19] of 86 ohm^{-1} g equiv^{-1} cm^2. The association constant and thermodynamic parameters for $K_2S_2O_8$ are also in good agreement with those reported by Chlebek and Lister from a potentiometric study[3].

Acknowledgement

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