

for Li^+ , Na^+ , K^+ and Mg^{2+} are 1.67, 1.05, 0.75 and 3.08 respectively). According to hole model^{6,7}, the enthalpy of hole formation, the rate determining step, depends on the surface tension (γ) of the melt through the relation (2).

$$H_h = 4\pi r^2(\gamma - T\bar{c}_r/\partial T) \quad \dots(2)$$

Since the surface tension of the melt would be governed by the interionic forces in the medium, the above dependence of E_h on the average cationic field appears to be consistent with the model.

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References

- GAUR, H. C., MEHTA, O. P. & JAIN, S. K., *Indian J. Chem.*, **9** (1971), 570.
- GAUR, H. C. & JAIN, S. K., *Indian J. Chem.*, **9** (1971), 860.
- GAUR, H. C. & JAIN, S. K., *Indian J. Chem.*, **10** (1972), 624.
- GAUR, H. C. & JAIN, S. K., *J. chem. Engng Data*, **17** (1972), 200.
- GAUR, H. C. & JAIN, S. K., *J. chem. Engng Data*, **21** (1976), 284.
- FURTH, R., *Proc. Cambridge phil. Soc.*, **37** (1941), 281.
- BOCKRIS, J. O'M., CROOK, E. H., BLOOM, H. & RICHARDS, N. E., *Proc. R. Soc. London*, **A225** (1960), 558.

Ion-pair Formation Studies : Part III — Ion-pair Formation in Aqueous Solutions of Potassium & Ammonium Dichromates

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The possibility of ion-pair formation in aqueous solutions of potassium and ammonium dichromates has been investigated conductometrically. The thermodynamic association constants have been estimated to be 5.7 ± 0.3 (at 25°), 3.8 ± 0.2 litre mole⁻¹ (at 35°) for KCr_2O_7 and 7.5 ± 0.4 (at 25°), 5.7 ± 0.3 (at 35°) for $\text{NH}_4\text{Cr}_2\text{O}_7$. The limiting ionic conductances of $\text{Cr}_2\text{O}_7^{2-}$ are 60.36 ± 0.11 at 25° and 71.27 ± 0.11 ohm⁻¹ g equiv⁻¹ cm² at 35°. Thermodynamic parameters, ion-size parameters and Bjerrum's parameters are also reported.

IN our earlier papers^{1,2} we have reported the formation constants of some ion-pairs in aqueous solutions of peroxydisulphate ion from conductivity studies. Walden³ on the basis of his conductivity studies of aqueous solutions of $\text{K}_2\text{Cr}_2\text{O}_7$ simply pointed out that it behaves as a 2-1 type of electrolyte. Watkins and Jones⁴ have estimated the degree of dissociation of $\text{Na}_2\text{Cr}_2\text{O}_7$ in aqueous solutions from conductometric studies. In view of these meagre studies on dichromates it was a thorough investigation of the interest to study the ion-pair formation in aqueous solutions of dichromate ion from conductance measurements of dilute solutions of potassium and ammonium dichromates which show deviations from Onsager's equation⁵. The results presented in this note have been accounted for in terms of ion-pair formation.

Equivalent conductivities (accuracy $\pm 0.05\%$) of aqueous solutions of potassium dichromate (AR, Pfizer) and ammonium dichromate (AR, BDH) were determined as described earlier at 25° and 35° in the concentration range 6×10^{-4} to $20 \times 10^{-4} M$. The dielectric constant, viscosity of water and limiting ionic conductances of K^+ and NH_4^+ ions in water at 25° and 35° were taken from the literature^{6a,b}.

The association constants were calculated by plotting equivalent conductivities against the square roots of the molar concentration i.e., \sqrt{m} to obtain the approximate values of equivalent conductivities at infinite dilution ($\Lambda^\circ_{\text{approx}}$). These values of $\Lambda^\circ_{\text{approx}}$ were used to calculate the theoretical slopes (S) in Onsager's limiting equation⁵:

$$\Lambda_{\text{exp}} = \Lambda^\circ - Sm^{1/2}$$

the $\Lambda_{\text{exp}} + Sm^{1/2}$ values were then plotted against m to get a more accurate value of Λ° .

As $\text{K}_2\text{Cr}_2\text{O}_7$ and $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ are uni-bivalent electrolytes, the association equilibrium of the type $\text{M}^+ + \text{A}^{2-} \rightleftharpoons \text{MA}^-$



appears most likely in their solutions. If m is the molar concentration of the solution and ' α ' is the degree of dissociation of the ion-pair formed, then the concentrations of M^+ , A^{2-} and MA^- could be represented as $(1+\alpha)m$, αm and $(1-\alpha)m$ respectively. The thermodynamic association constant (K) is then given by Eq. (2):

$$K = \frac{[\text{MA}^-]}{[\text{M}^+][\text{A}^{2-}]} \cdot \frac{f_{\text{MA}}}{f_{\text{M}}f_{\text{A}}} \\ = \frac{(1-\alpha)}{\alpha(1+\alpha)m} \cdot \frac{f_{\text{MA}}}{f_{\text{M}}f_{\text{A}}} \quad \dots(2)$$

where f 's are the activity coefficients. The solution was considered as a mixture of completely dissociated uni-bivalent salt of molar concentration ' αm ' and a completely dissociated uni-univalent salt of concentration $(1-\alpha)m$. Hence

$$2\Lambda_{\text{exp}} = (1-\alpha)\Lambda_{1:1} + 2\alpha\Lambda_{2:1} \quad \dots(3)$$

where $\Lambda_{1:1}$ and $\Lambda_{2:1}$ are the theoretical equivalent conductivities of uni-univalent and uni-bivalent salts calculated from the Onsager's equation⁵. The limiting mobility of the ion-pair was calculated from relation (4)

$$\lambda_{\text{MA}^-}^\circ = 0.6\lambda_{\text{A}^{2-}}^\circ \quad \dots(4)$$

as suggested by Righellato and Davies⁷ from which $\Lambda_{1:1}$ was calculated. The ionic-strength (I) of the solution was calculated using the relation (5)

$$I = (1+2\alpha)m \quad \dots(5)$$

Activity coefficients were calculated using the Davies' equation⁸ (6)

$$-\log f_i = AZ_i^2 \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I \right) \quad \dots(6)$$

The method of successive approximation was used for calculating the degree of dissociation (α), ionic-strength (I), activity coefficient ($f_{\text{Cr}_2\text{O}_7^{2-}}$) and the association constant (K) for each concentration employed, as described in an earlier publication¹. TDC-12 computer was used for the above calculations. The computer programme replaced the

TABLE 1 — EQUIVALENT CONDUCTIVITY AND LIMITING MOBILITY OF ION-PAIR FOR POTASSIUM AND AMMONIUM DICHROMATES

Temp. °C	Λ° (ohm ⁻¹ g equiv. cm ²)	$\sigma\Lambda^\circ$	$\frac{1}{2}\lambda^\circ\text{Cr}_2\text{O}_7^{2-}$ (ohm ⁻¹ g equiv. ⁻¹ cm ²)
		$\text{K}_2\text{Cr}_2\text{O}_7$	
25	133.90 ± 0.07	0.01	60.40 ± 0.07
35	159.51 ± 0.08	0.02	71.30 ± 0.08
	$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$		
25	133.88 ± 0.07	0.01	60.33 ± 0.07
35	159.97 ± 0.08	0.02	71.24 ± 0.08

TABLE 2 — VALUES OF ASSOCIATION CONSTANT AND VARIOUS PARAMETERS FOR POTASSIUM AND AMMONIUM DICHROMATES

Temp.	K (litre mole ⁻¹)	a (Å)	b	ΔH° (kcal mole ⁻¹)	ΔG° (kcal mole ⁻¹)	ΔS° (e.u.)
		$\text{K}_2\text{Cr}_2\text{O}_7$				
25	5.7 ± 0.3	5.2	2.75		-1.0	-21.5
35	3.8 ± 0.2	5.9	2.43	-7.4	-0.8	-22.1
	$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$					
25	7.5 ± 0.4	4.7	3.06		-1.2	-12.7
35	5.7 ± 0.3	5.3	2.71	-5.0	-1.1	-12.7

graphical method by the numerical method of least squares and calculated the standard error in Λ° i.e. $\sigma\Lambda^\circ$ values also. From these values of association constants, the ion-size parameter (a) and Bjerrum's parameter (b) were calculated using Bjerrum's^{6c} expressions (7 and 8):

$$K = \frac{4\pi N}{1000} \left(\frac{|Z_1 Z_2| e^2}{kT} \right)^3 Q_b \quad \dots(7)$$

$$b = \frac{|Z_1 Z_2| e^2}{DkTa} \quad \dots(8)$$

From the values of association constants at two temperatures the thermodynamic parameters ΔH° , ΔG° and ΔS° were calculated for the equilibrium (1). The values of Λ° , $\sigma\Lambda^\circ$ of potassium and ammonium dichromates alongwith the limiting conductances of $\text{Cr}_2\text{O}_7^{2-}$ ion at 25° and 35° are presented in Table 1. The association constants, Bjerrum parameter, ion-size parameter and thermodynamic parameters are tabulated in Table 2. From Table 1 it is evident that $\frac{1}{2}\lambda_{\text{Cr}_2\text{O}_7^{2-}}$ is 60.36 ± 0.11 at 25° and 71.27 ± 0.11 ohm⁻¹ g equiv.⁻¹ cm² at 35°.

The low values of association constants indicate that the potassium and ammonium dichromates are almost completely dissociated in dilute aqueous solutions used in the present work. These findings are similar to those of Watkins and Jones⁴ on aqueous solutions of sodium dichromate.

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References

- ANANTHA SWAMY, J. SETHURAM, B. & NAVNEETH RAO, T., *Indian J. Chem.*, (in press).
- ANANTHA SWAMY, J. SETHURAM, B. & NAVNEETH RAO, T., *Indian J. Chem.*, (in press).
- WALDEN, P., *Z. physik. Chemie*, **1** (1887), 529.
- WATKINS, C. & JONES, H. C., *J. Am. chem. Soc.*, **37** (1915), 2626.
- ONSAGER, L., *Phys. Z.*, **28** (1927), 277.
- ROBINSON, R. A. & STOKES, R. H., *Electrolytic solutions* (Butterworths, London), 1959, (a) 457, (b) 465, (c) 396.
- RIGHELLATO, E. C. & DAVIES, C. W., *Trans. Faraday Soc.*, **26** (1930), 592.
- DAVIES, C. W., *Ion association* (Butterworths, London), 1962, 41.

Sorption of Nickel on Zeokarb 226 (NH_4^+)

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Sorption of nickel on Zeokarb 226 (NH_4^+ form) as a function of pH has been studied. The results show that nickel is initially sorbed as Ni^{2+} which transforms to NiOH^+ with increase of loading. This provides an example of site sharing on a cation exchanger.

CARBOXYLIC acid exchangers are recommended for the recovery of nickel from electrolyte baths¹, waste solutions^{2,3}, etc.⁴⁻⁷. However, there are apparent differences in the pH conditions of sorption⁵⁻⁷. Hence sorption of nickel as a function of pH was studied by equilibrating varying amounts of the metal ion in 100 ml at different pH values (adjusted with ammonium chloride and ammonium hydroxide) with 0.25 g of Zeokarb 226 (NH_4^+). The nickel in the solution phase at equilibrium was determined either complexometrically⁸ or spectrophotometrically⁹. When the amount of nickel taken is small, its sorption is practically quantitative in the pH range of 6.0 to 9.0. Studied at higher concentrations, it is maximum at pH 7.5 and less on either side as against 7.0 (ref. 5) and 6.0-6.5 (refs. 6 and 7) recommended by earlier workers on similar exchangers with different ionic forms.

The sorption profile of nickel on a column was obtained by passing 0.05M nickel solution at pH

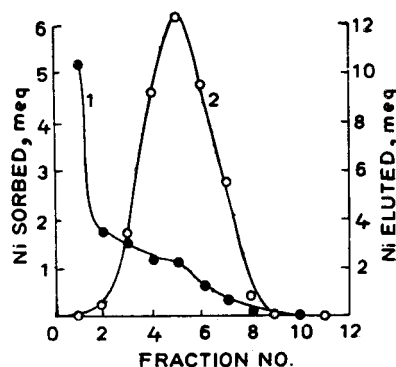


Fig. 1 — Sorption and elution of nickel from Zeokarb 226 (NH_4^+ -form) [Curve 1, resin capacity 5.93 meq. (fraction 50 ml); and curve 2, resin capacity 26.70 meq. (fraction 10 ml)]