for Li⁺, Na⁺, K⁺ and Mg²⁺ are 1·67, 1·05, 0·75 and 3·08 respectively). According to hole model⁴, the enthalpy of hole formation, the rate determining step, depends on the surface tension (γ) of the melt through the relation (2).

\[ H'_A = 4\pi \sigma^2 (\gamma - T \sigma'/\gamma T) \]  

(2)

Since the surface tension of the melt would be governed by the interionic forces in the medium, the above dependence of \( H'_A \) on the average cationic field appears to be consistent with the model.

The authors thank the CSIR, New Delhi for financial assistance and a fellowship to S.K.J.

References


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

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Received 8 September 1976; accepted 3 November 1976

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 mol⁻¹ at 35° for K₂Cr₂O₇ and 7·5 ± 0·4 at 25°, 5·7 ± 0·3 at 35° for NH₄Cr₂O₇. The limiting ionic conductances of Cr₂O₇²⁻ are 60·36 ± 0·11 at 25° and 71·27 ± 0·11 cm² ohm⁻¹ g equiv⁻¹ cm² at 35°. Thermodynamic parameters, ion-size parameters and Bjerrum’s parameters are also reported.

In our earlier papers¹,² we have reported the formation constants of some ion-pairs in aqueous solutions of peroxydisulphate ion from conductometry studies. Walden⁶ on the basis of his conductivity studies of aqueous solutions of K₂Cr₂O₇ simply pointed out that it behaves as a 2-1 type of electrolyte. Watkins and Jones⁴ have estimated the degree of dissociation of Na₂Cr₂O₇ 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 ± 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 6x10⁻⁴ to 20x10⁻⁴ M. The dielectric constant, viscosity of water and limiting ionic conductances of K⁺ and NH₄⁺ ions in water at 25° and 35° were taken from the literature⁶b.

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 (\( \Lambda_{exp(approx.)}^\circ \)). These values of \( \Lambda_{exp(approx.)}^\circ \) were used to calculate the theoretical slopes (S) in Onsager’s limiting equation⁶:

\[ \Lambda_{exp} = \Lambda^\circ - Sm^{1/2} \]

the \( \Lambda_{exp} + Sm^{1/2} \) values were then plotted against \( m \) to get a more accurate value of \( \Lambda^\circ \).

As K₂Cr₂O₇ and (NH₄)₂Cr₂O₇ are uni-bivalent electrolytes, the association equilibrium of the type \( M²^+ + A²^- \rightleftharpoons MA²^- \) appears most likely in their solutions. If \( m \) is the molar concentration of the solution and \( \alpha \) is the degree of dissociation of the ion-pair formed, then the concentrations of \( M²^+ \), \( A²^- \) and \( MA²^- \) can be represented as \((1+\alpha)m\), \( \alpha m \) and \((1-\alpha)m \) respectively. The thermodynamic association constant (K) is then given by Eq. (2):

\[ K = \frac{[MA²^-]}{M²^+[A²^-]} f_M f_A \]

\[ = \frac{(1-\alpha)}{(1+\alpha)m} f_M f_A \]  

(2)

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

\[ 2\Lambda_{exp} = (1-\alpha)\Lambda_{A11} + 2\alpha\Lambda_{A21} \]  

(3)

where \( \Lambda_{A11} \) and \( \Lambda_{A21} \) are the theoretical equivalent conductivities of uni-univalent and uni-bivalent salts calculated from the Onsager’s equation⁶. The limiting mobility of the ion-pair was calculated from relation (4)

\[ \lambda_{MA²^-} = 0·6\lambda_{A²^-} \]  

(4)

as suggested by Righellato and Davies⁷ from which \( \Lambda_{A11} \) was calculated. The ionic-strength (I) of the solution was calculated using the relation (5)

\[ I = (1+2\alpha)m \]  

(5)

Activity coefficients were calculated using the Davies’ equation⁸

\[ -\log f_i = AZ_i \left( \frac{\sqrt{I}}{1+\sqrt{I}} \right) - 0·3I \]  

(6)

The method of successive approximation was used for calculating the degree of dissociation (\( \alpha \)), ionic-strength (I), activity coefficient (\( f_M \)) and the association constant (K) for each concentration employed, as described in an earlier publication⁴. TDC-12 computer was used for the above calculations. The computer programme replaced the
The authors wish to thank Shri P. Kishta Reddy and Shri A. Prakash Rao, Computer Centre, for their valuable assistance.

### Table 1 — Equivalent Conductivity and Limiting Mobility of Ion-pair for Potassium and Ammonium Dichromates

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Λ° (ohm⁻¹ g equiv.⁻¹ cm²)</th>
<th>aΛ°</th>
<th>∆H° (kcal mole⁻¹)</th>
<th>∆G° (kcal mole⁻¹)</th>
<th>∆S° (e.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>133.90 ± 0.07</td>
<td>0.01</td>
<td>60.40 ± 0.07</td>
<td>71.30 ± 0.08</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>159.51 ± 0.08</td>
<td>0.02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(NH₄)₂Cr₂O₇</td>
<td>133.88 ± 0.07</td>
<td>0.01</td>
<td>60.33 ± 0.07</td>
<td>71.24 ± 0.08</td>
<td></td>
</tr>
</tbody>
</table>

### Table 2 — Values of Association Constant and Various Parameters for Potassium and Ammonium Dichromates

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Λ° (litre mole⁻¹)</th>
<th>a (Å)</th>
<th>K₅Cr₂O₇</th>
<th>∆H° (kcal mol⁻¹)</th>
<th>∆G° (kcal mol⁻¹)</th>
<th>∆S° (e.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>5.7 ± 0.3</td>
<td>5.2</td>
<td>2.75</td>
<td>-1.0</td>
<td>-21.5</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>3.8 ± 0.2</td>
<td>5.9</td>
<td>2.43</td>
<td>-2.4</td>
<td>-22.1</td>
<td></td>
</tr>
<tr>
<td>(NH₄)₂Cr₂O₇</td>
<td>7.5 ± 0.4</td>
<td>4.7</td>
<td>3.06</td>
<td>-1.2</td>
<td>-12.7</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>7.5 ± 0.3</td>
<td>5.3</td>
<td>2.71</td>
<td>-1.1</td>
<td>-12.7</td>
<td></td>
</tr>
</tbody>
</table>

### References

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### Sorption of Nickel on Zeokarb 226 (NH₄⁺ form)

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Sorption of nickel on Zeokarb 226 (NH₄⁺ form) as a function of pH has been studied. The results show that nickel is initially sorbed as Ni⁺⁺ 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 baths, waste solutions, etc. However, there are apparent differences in the pH conditions of sorption. 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 (NH₄⁺ form). The nickel in the solution phase at equilibrium was determined either complexometrically or spectrophotometrically. 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 0.055 M nickel solution at pH...