STUDIES OF THE DIASTEROISOMERIC EFFECT.

PART I. THE SOLUBILITIES OF (+) AND (−) TRIS-1 : 10-PHENANTHROLINE RUTHENIUM II PERCHLORATES IN SOLUTIONS CONTAINING OPTICALLY ACTIVE IONS.

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Manuscript received, August 31, 1955. Read, October 5, 1955.

In order to account for the movement of the equilibrium between the enantiomeric forms of a complex inorganic ion in solution in the presence of another optically stable ion—the so-called phenomenon of “first order asymmetric (Turner and Harris, 1948) transformation”—the concept of “configurational activity” was put forward (Dwyer, Gyarfas and O'Dwyer, 1951). If \( a^+ \) and \( a^- \) represent the equal activities of the labile dextro and laevo ions in the racemic mixture, then in the presence of another optical ion it was suggested that \( a^+ \), \( a^- \) and the equilibrium moves until the activities are again equal. As a result, the concentrations of the antipodes become unequal with a consequent net dextro or laevo rotation. Since the solubilities of simple salts of optical forms are equal, it follows that in their saturated solutions \( a^+ = a^- \). The addition of an extraneous optically active ion, if it affects the activities differently, should consequently change the solubilities of the antipodal forms unequally if they are not labile.

Tris-1 : 10-phenanthroline ruthenium II perchlorate is a suitable optically active complex salt, since the optical forms are stable and have a solubility of only \( 1.5 \times 10^{-3} \) M at 25° C. The (+) tartrates and (+) bromcamphorsulphonates are both very soluble in water. Suitable optically stable, colourless inorganic anions or organic cations were not available.

APPARATUS AND EXPERIMENTAL PROCEDURE.

Tris-1 : 10-phenanthroline ruthenium II perchlorate was resolved as described previously (Dwyer and Gyarfas, 1949). The active perchlorates were crystallized several times from hot water by the addition of sodium perchlorate and finally twice from distilled water. The optical forms crystallized well in small prisms of uniform size and had \( [\alpha]_{D}^{20} = \pm 1330^\circ \). Ammonium (+) bromcamphorsulphonate was crystallized from water using decolourizing charcoal to remove a slight yellow tint, and dried at 100° C. Sodium potassium (+) tartrate tetrahydrate A.R. was used without purification. Solubilities were determined in the apparatus of Campbell (1930). However, adsorption of the ruthenium compound on the glass wool filter was found to lead to low or erratic results and ultimately a small sintered glass filter was substituted. Samples of the saturated solution, 3–4 mls., were usually taken after equilibration at 25° ±0.02° for 20–24 hours. The concentration of the ruthenium compound was determined with a Spekker Photoelectric Colorimeter using Ilford blue filter 603, and a calibration curve prepared from an aqueous solution of the (+) perchlorate. In the range 0.025 to 0.05 g./100 ml. the calibration curve was
almost a straight line, and the volumes of the various samples were arranged so that the centre of this straight line portion was used.

Since the difference in the solubilities of the (+) and (—) forms was frequently close to the experimental error, all operations were carefully standardized. In order to check for colour purity of the optical forms, a number of solutions of each were compared. No systematic difference was noted, the maximum variation being ±0·1%.

It was found that addition of ammonium (+) bromcamphorsulphate to solutions of the ruthenium compound caused a shift in the absorption maximum towards the blue, leading to an apparent increase in concentration. In 0·25% solution, the maximum concentration in the diluted solutions, this led to the same error of 2% for either optical form. From a second curve, all concentrations were corrected for this effect. Ammonium β-naphthalene sulphonate also caused a similar absorption shift but sodium chloride and sodium potassium (+) tartrate were without effect.

For comparison, the solubility of bis-2:2':2"-terpyridyl iron II perchlorate (Morgan and Burstall, 1930) was determined in ammonium (+) bromcamphorsulphonate. The cation of this deep purple salt carries the same charge as that of the ruthenium compound, is chemically analogous, of approximately the same size but is optically inactive. The concentration in the saturated solution was determined as before spectrophotometrically, using Ilford filter 605. An absorption shift was also noted with this compound in the presence of bromcamphorsulphonate ion.

**Experimental Results.**

The solubilities* shown in Tables I and II are the mean of at least six determinations for which the maximum deviation from the value quoted was ±0·3%. The mean activity coefficients were obtained in the usual way by extrapolating the solubility curve obtained with sodium chloride to I=0 to obtain the solubilities of either form as 1·65×10⁻³ M.

![Table 1](attachment:image)

*The values quoted previously (Turner and Harris, 1948) were obtained in the original apparatus of Campbell. Owing to an error, the signs of the antipodes were reversed.
Table II.
The Solubilities and Activity Coefficients in Solutions of Sodium Potassium (+) Tartrate.

<table>
<thead>
<tr>
<th>Concentration of NaKCl₃H₄O₆·4H₂O Molarity × 10⁻²</th>
<th>Solubility of (+) and (-) Ru(phosphor)₃(ClO₄)₂·2H₂O Molarity × 10⁻²</th>
<th>I₁₀₀</th>
<th>log S/S₀</th>
<th>f±</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.45</td>
<td>(+) 2.02</td>
<td>0.0666</td>
<td>0.0612</td>
<td>0.816</td>
</tr>
<tr>
<td></td>
<td>(-) 2.03</td>
<td>0.0667</td>
<td>0.0637</td>
<td>0.811</td>
</tr>
<tr>
<td>0.9</td>
<td>(+) 2.12</td>
<td>0.1091</td>
<td>0.0852</td>
<td>0.776</td>
</tr>
<tr>
<td></td>
<td>(-) 2.18</td>
<td>0.1095</td>
<td>0.0953</td>
<td>0.755</td>
</tr>
<tr>
<td>1.8</td>
<td>(+) 2.22</td>
<td>0.1731</td>
<td>0.1038</td>
<td>0.740</td>
</tr>
<tr>
<td></td>
<td>(-) 2.29</td>
<td>0.1734</td>
<td>0.1155</td>
<td>0.720</td>
</tr>
<tr>
<td>3.6</td>
<td>(+) 2.39</td>
<td>0.2645</td>
<td>0.1352</td>
<td>0.688</td>
</tr>
<tr>
<td></td>
<td>(-) 2.44</td>
<td>0.2651</td>
<td>0.1434</td>
<td>0.675</td>
</tr>
<tr>
<td>7.2</td>
<td>(+) 2.55</td>
<td>0.3967</td>
<td>0.1624</td>
<td>0.646</td>
</tr>
<tr>
<td></td>
<td>(-) 2.61</td>
<td>0.3970</td>
<td>0.1734</td>
<td>0.631</td>
</tr>
</tbody>
</table>

The results are expressed in the form (Fig. 1) used by Bronsted and La Mer (1924) in their studies of the solubilities of cobaltammines.

Text-fig. 1.
A. (+) Ru(phosphor)₃(ClO₄)₂·2H₂O in the presence of ammonium (+) bromcamphosphonate.
B. Theoretical slope (calculated from Debye-Huckel limiting law).
C. (-) Ru(phosphor)₃(ClO₄)₂·2H₂O in the presence of sodium potassium (+) tartrate.
D. (+) Ru(phosphor)₃(ClO₄)₂·2H₂O in the presence of sodium potassium (+) tartrate.
E. (+) Ru(phosphor)₃(ClO₄)₂·2H₂O in the presence of sodium chloride.
F. Fe(terpyridyl)₃(ClO₄)₂·H₂O in the presence of ammonium (+) bromcamphosphonate.
From the expression

$$\log \frac{S}{S_0} = AZ + Z - (I - I_0)$$  

(1)

derived from the simple Debye-Huckel Law, it was shown that the plot of \( \log \frac{S}{S_0} \) against \( I - I_0 \) was a straight line of slope \( AZ + Z - \) (where \( S \) and \( S_0 \) are respectively the molar solubilities in pure water, where \( I = I_0 \), and at ionic strength \( I, Z+, Z- \) are the ionic charges and \( A = 0.01 \)). Since large ions are involved, the extended expression

$$\log \frac{S}{S_0} = AZ + Z - \left( \frac{I}{1 + zBI^2} \right) - I_0$$  

(2)

\((x \text{ is the average effective diameter of the ions, } B \text{ is a constant})\) is the more appropriate except at very low ionic strengths—but its use would not affect the conclusions reached. In approximately \( 5 \times 10^{-2} \text{M} \) solution of bromcamphorsulphonate the solubilities of the antipodes are equal; above this concentration the (+) form is the more soluble. No explanation can be advanced at this stage for the reversal of the solubilities.

\[ \text{Discussion of Results.} \]

It is evident that the solubilities of the (+) and (−) forms are different in the presence of the optically active electrolytes, and the curves (Fig. 1) do not follow the theoretical slope for Debye-Huckel interionic forces. Although with the tartrate ion the limiting slope \( (AZ + Z -) \) applies at approximately the same ionic strength as with sodium chloride, the slope at higher ionic strengths is too large for a large ion. Even at the lowest ionic strengths the slopes of the curves of the ruthenium and iron compounds in the presence of bromcamphorsulphonate ion are too great. Since the bis-2':2':2''-terpyridyl iron compound is not optically active this cannot be ascribed to a special form of interaction due to the optical activity. It is probable that these large cations are “salted in” by the bromcamphorsulphonate ion and to a lesser extent by the tartrate ion. The possibility that the properties of large ions are not treated adequately by Debye-Huckel interionic forces but that Van der Waals forces—especially the dispersion interaction component—may be important, has already been envisaged by Kortum (1936), who has ascribed absorption maxima shifts in electrolytic solutions of the type noted with the ruthenium and iron compounds in the presence of bromcamphorsulphonate ion, to the operation of these forces. A quantitative treatment of the lyotropic “salting in” of non-electrolytes by large ions, based primarily upon dispersion interaction forces, has been made by Bockris, Bowler-Reed and Kitchener (1951), but such a treatment does not appear to be available for purely electrolytic systems.

Van der Waals dispersion interaction forces between an optically active substance and the antipodal forms of another would not be identical, but since these forces decrease very rapidly with separation of the interacting units, they could contribute little to antipodal differentiation in dilute solution. If appreciable differentiation can occur in dilute solution without association, the only other component of Van der Waals forces that is available is the interaction between particles with an asymmetric distribution of charge. It is believed that the existence of such asymmetric electric fields is fundamentally associated with the phenomenon of optical activity. These fields, which are mirror image with respect to the antipodes, may arise from the asymmetry of the centre itself as in carbon and related atoms due to the arrangement of four different dipoles (Betti, 1930) or from the asymmetric distribution of charge over the ligands (Pauling, 1948) in complex inorganic compounds. Organic compounds exhibiting
molecular asymmetry without an asymmetric carbon atom belong to the latter category.

The electrical asymmetry of the antipodes of complex inorganic compounds in which the asymmetry is centred in a multi-charged ion may be considerable and Van der Waals interaction even with the weak fields due to the four different dipoles in an organic molecule could lead to considerable differentiation.

**SUMMARY.**

Measurements on the perchlorates of a pair of optical antipodes have shown that the solubilities are appreciably different in the presence of optically active electrolytes. The nature of the forces responsible for such differentiation—the "diastereoisomeric effect"—is discussed.

**ACKNOWLEDGMENTS.**

The authors are indebted to Dr. K. L. Sutherland and Professor D. P. Craig for criticism of the paper in draft.

**REFERENCES.**


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