XCVIII.—*The Molecular Conductivity of Cadmium Iodide in Acetonitrile.*

By Frederick Karl Victor Koch.

Cadmium iodide is of especial interest from the electrochemical point of view since both of its constituent elements show considerable residual valency in their compounds. The solutions of this salt therefore contain highly complex molecular and ionic species and have been the subject of considerable investigation (McBain, *Z. Elektrochem.*, 1905, **11**, 215).

The following results for the molecular conductivity of this compound in acetonitrile at 0° and 25°, and the calculated values of the temperature coefficients, not only furnish additional evidence of this complexity, but also allow certain general conclusions to be drawn as to the molecular state of cadmium iodide in these solutions.

Apparatus and Materials.—The bridge used was of the drum

type (Leeds and Northrup) and was 10 m. long, whilst the standard resistances were of the dial pattern (Cambridge and Paul). The alternating current was supplied by a valve oscillator, electromagnetically shielded from the rest of the apparatus. A variable condenser was placed in parallel with the standard resistance to balance the capacity of the conductivity cell. An excellent minimum was found (usually complete silence) and the readings could therefore be obtained with a high degree of accuracy.*

The conductivity cell was of the cylindrical type with vertical grey platinum electrodes and a ground-in stopper (Washburn, *J. Amer. Chem. Soc.*, 1916, **38**, 2431). The cell constant was determined by the method of Parker and Parker (*ibid.*, 1924, **46**, 312).

Acetonitrile (B.D.H.) was allowed to stand over solid potash for 2 or 3 days in order to remove acetic acid and moisture. It was then decanted on to calcium chloride and, after distillation, shaken with a very little phosphorus pentoxide for about a day. After a final distillation from the phosphorus pentoxide the product (b. p. 81·6°/760 mm.) had a specific conductivity of $0{\cdot}5—1{\cdot}0 \times 10^{-7}$ mho (Walden gives $\kappa = 0{\cdot}398 \times 10^{-6}$ mho).

Cadmium iodide (Analytical Reagent) was purified from iodine (which it contained in sufficient quantity to give yellow solutions in acetonitrile) by recrystallisation—once from conductivity water and twice from absolute alcohol. It was then dried over phosphorus pentoxide in a vacuum. Solutions of pure cadmium iodide in acetonitrile are colourless.

The most concentrated solution (approx. $N/10$) was made up by weight and the others, except the last three, by volume-dilution.

The following table, giving the specific conductivities of three of the intermediate solutions at 0°, which were made up by dilution from two different stock solutions of the same concentration, indicates the reproducibility of the results. (V indicates the volume of solvent containing 1 g.-mol. of cadmium iodide.)

	κ (mho).	
V (litres).	(1).	(2).
163·4	$1{\cdot}842 \times 10^{-4}$	$1{\cdot}858 \times 10^{-4}$
326·7	0·943 ,,	0·948 ,,
653·4	0·483 ,,	0·480 ,,

For the majority of the solutions, the error in Λ (which was calculated from the average specific conductivity) is estimated to be not greater than 0·5%. The values of Λ in the case of the three most dilute solutions are probably somewhat less certain owing to

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the increasing significance of the specific conductivity of the pure solvent.

The values for the density of acetonitrile used in calculating the dilutions were 0·8052/0° (Beilstein) and 0·7800/25° (this investigation).

The temperature coefficients are calculated by using the molecular conductivities at 0° and 25° of the same original solution, *i.e.*, a solution of the same weight-normal concentration.

At 0° ± 0·01°.			At 25° ± 0·01°.		
V (litres).	$\kappa \times 10^4$.	Λ.	V (litres).	$\kappa \times 10^4$.	Λ.
*10·21	24·05	24·57	*10·53	24·46	25·75
20·42	13·15	26·86	21·06	12·98	27·33
40·84	6·950	28·38	42·12	6·713	28·29
81·68	3·612	29·48	84·24	3·426	28·85
163·4	1·850	30·23	168·5	1·736	29·23
326·7	0·9454	30·87	337·0	0·8842	29·80
653·4	0·4815	31·46	673·9	0·4524	30·50
1321	0·2510	33·16	1363	0·2519	34·34
2696	0·1455	39·23	2788	0·1526	42·54
7816	0·05425	42·40	8069	0·06194	49·98

* Determination of the density of an approx. $N/10$-solution of cadmium iodide in acetonitrile has shown that if the dilution is expressed in terms of volume of solution instead of volume of solvent, the first values of Λ in the above table would both be increased by about 0·5%.

The temperature coefficients of the molecular conductivity calculated from the above data are: + 0·00192, + 0·000750, − 0·000127, − 0·000855, − 0·00132, − 0·00139, − 0·00122, + 0·00142, + 0·00338, and + 0·00715, for the ten dilutions, respectively.

The significant point is that the temperature coefficients of the molecular conductivity are positive in the most concentrated and in the most dilute solutions, but negative in the intermediate solutions. Similar anomalous behaviour has been observed by Franklin (*J. Physical Chem.*, 1911, **15**, 675) for solutions of potassium iodide in liquid sulphur dioxide.

Any complex molecular and ionic species in solution will tend to break up both with rising temperature and with increasing dilution. It seems, therefore, that in order to explain the anomalous changes in the temperature coefficient, it is necessary to assume the existence of *at least three* molecular (or complex ionic) species in solution, the intermediate one having the largest conductivity, owing either to its more extensive dissociation or to the greater mobility of its ions.

The molecular conductivity of the most dilute solution (V = 8069) at 25° is only 49·98, whilst the ionic conductivity of the iodine ion is 96 (Walden, " Elektrochemie nichtwässeriger Lö-

sungen," p. 186), so that the cadmium iodide cannot be regarded as completely dissociated even at a dilution of 8000 litres. It should be noted that the temperature coefficients of the molecular conductivity tend (for the last three solutions) with increasing dilution towards the value of the temperature coefficient of the fluidity of acetonitrile, *viz.*, 0·0113.

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