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Ionic Equilibria in Aqueous Solutions of the Chlorides of Magnesium, Calcium, Strontium and Barium

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The e.m.f. of the cells of the type,

$$\mathrm{Hg}\left|\begin{matrix}\mathrm{Hg_2Cl_2HCl\ (c_1)}\\ \mathrm{MCl_2(c_2)}\end{matrix}\right|\begin{matrix}\mathrm{HCl\ (c_1)}\\ \mathrm{MCl_2(c_2)}\end{matrix}\Bigg|\begin{matrix}\mathrm{HCl\ (c_1)\ Q.H.}\\ \mathrm{MCl_2(c_2)}\end{matrix}\Bigg|\mathrm{Pt}$$

where M stands for Mg, Ca, Sr or Ba have been measured at one or more temperatures and compared with the values calculated on the basis of complete dissociation of MCl_2. The difference is so small (some times even less than 0·1 mv) that we may safely conclude that the salts are completely dissociated in solutions having ionic strength upto 0·1.

Conductance[1,2] as well as vapour pressure[3,4] measurements indicate complete dissociation of chlorides of the alkaline earth metals in dilute aqueous solutions. We have measured the e.m.f. of the cells of the type,

$$\mathrm{Hg}\left|\begin{matrix}\mathrm{Hg_2Cl_2\ HCl\ (c_1)}\\ \mathrm{MCl_2(c_2)}\end{matrix}\right|\begin{matrix}\mathrm{HCl\ (c_1)}\\ \mathrm{MCl_2(c_2)}\end{matrix}\Bigg|\begin{matrix}\mathrm{HCl\ (c_1)\ Q.H.}\\ \mathrm{MCl_2(c_2)}\end{matrix}\Bigg|\mathrm{Pt}$$

where M stands for Mg, Ca, Sr or Ba and Q.H. for quinhydrone.

Only analytical grade chemicals and double distilled water were used. All solutions were made by mixing (*a*) stock solutions of the chloride concerned, in hydrochloric acid with (*b*) stock solutions of hydrochloric acid and by diluting with water to the appropriate volume at the experimental temperature. The concentrations of the various components of the stock solutions were determined or confirmed by standard analytical methods. $[\cdot]_T$ indicate stoichiometric concentration in gram moles per litre.

TABLE I

Composition of the Mixture of $BaCl_2$ and HCl		15°		25°		35°	
$[BaCl_2]_T$	$[HCl]_T$	Observed e.m.f.	Calculated e.m.f.	Observed e.m.f.	Calculated e.m.f.	Observed e.m.f.	Calculated e.m.f.
0.0040	0.0020	0.16190	0.16187	0.14745	0.14750	0.13380	0.13384
0.0080	0.0040	0.19453	0.19452	0.18120	0.18124	0.16865	0.16867
0.0120	0.0060	0.21345	0.21350	0.20080	0.20086	0.18884	0.18891
0.0160	0.0080	0.22684	0.22694	0.21468	0.21475	0.20313	0.20323
0.0200	0.0100	0.23723	0.23737	0.22548	0.22554	0.21423	0.21435
0.0240	0.0120	0.24576	0.24592	0.23425	0.23437	0.22327	0.22345
0.0280	0.0140	0.25299	0.25316	0.24167	0.24185	0.23098	0.23117

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TABLE II

Temperature 25°

Composition of the Mixture of MCl_2 and HCl		Observed e.m.f. (in volt)			Calculated e.m.f. (volt) assuming complete dissociation
$[MCl_2]_T$	$[HCl]_T$	$MgCl_2$	$CaCl_2$	$SrCl_2$	
0.0040	0.0020	0.14746	0.14742	0.14744	0.14750
0.0080	0.0040	0.18122	0.18112	0.18116	0.18124
0.0120	0.0060	0.20078	0.20076	0.20074	0.20086
0.0160	0.0080	0.21465	0.21466	0.21464	0.21475
0.0200	0.0100	0.22550	0.22545	0.22546	0.22554
0.0240	0.0120	0.23426	0.23420	0.23421	0.23437
0.0280	0.0140	0.24170	0.24165	0.24166	0.24185

DISCUSSION

The e.m.f. of the cell,

$$Hg\left|Hg_2Cl_2\ \begin{matrix}HCl\ (c_1)\\ MCl_2(c_2)\end{matrix}\right|\begin{matrix}HCl\ (c_1)\\ MCl_2(c_2)\end{matrix}\Bigg|\begin{matrix}HCl\ (c_1)\ Q.H.\\ MCl_2(c_2)\end{matrix}\Bigg|Pt$$

is given by the equation

$$E = E^\circ + \frac{2\cdot3026RT}{F}\log[H^+]\,[Cl^-] - \frac{2\cdot3026RT}{F}\left(\frac{2A\sqrt{\mu}}{1+\sqrt{\mu}} - \beta\mu\right) \quad .. \quad (1)$$

Assuming complete dissociation, ionic strength and concentrations are given by,

$$\mu = 3[MCl_2]_T + [HCl]_T,\ [H^+] = [HCl]_T$$

$$[Cl^-] = 2[MCl_2]_T + [HCl]_T$$

The values of E°, A and β are known[5] and μ is calculated as above. The value of E has been calculated from equation (1) and given in the tables. The calculated and the experimental values seldom differ by more than 0·1 mv, indicating that the salts are completely dissociated upto 0·1 ionic strength. Alternatively, if we assume that these salts are completely dissociated then it follows that the value of β is not effected by the composition of the ion atmosphere upto 0·1 μ.

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