J. Indian Chem. Soc.,
Vol. LX, January 1983, pp. 42-46

Ionic Equilibria of Electrolytes in Dioxane-Water Mixtures : Potentiometric Studies of Barium, Zinc and Cadmium Chloride

U. C. MISHRA, K. C. SINGH and P. K. DAS*

Department of Chemistry, Ravenshaw College, Cuttack-753 003

Manuscript received 21 August 1979, revised 27 October 1981, accepted 7 November 1981

The dissociation constants of barium chloride (K_2), zinc chloride (K_2) and cadmium chloride (K_1 and K_2) have been studied in 10, 20, 30 and 40% (w/w) dioxane-water mixtures at 25, 30, 35, 40 and 45° in presence of HCl from potentiometric studies. Barium chloride and zinc chloride are found to be completely dissociated upto 0.1 ionic strength (except $ZnCl_2$ in 40% dioxane). The thermodynamic quantities ($\Delta G°$, $\Delta H°$ and $\Delta S°$) for $CdCl_2$ and for $ZnCl_2$ (in 40% dioxane) have been calculated at 25°.

INVESTIGATION of cells of the type :

$$\text{Pt. } H_2(1\text{ atm}) \left|\begin{matrix}HCl(m_1) \text{ dioxane } (X)\% \\ MCl_2(m_2) \text{ water } (Y)\%\end{matrix}\right| AgCl\text{-}Ag \quad ...(I)$$

has not been done so far in aquo-organic solvents, specially in dioxane-water mixtures. Lately Prasad and coworkers[1,2] have studied similar cells using quinhydrone and calomel electrodes in aqueous solutions for $BaCl_2$ and $CdCl_2$, and found $BaCl_2$ to be completely ionised upto 0.03 *M* in aqueous solution and have determined both K_1 and K_2 for $CdCl_2$. In the present investigation the cell (I) was studied for $BaCl_2$ and $ZnCl_2$ (i.e. M = Ba or Zn) in 10, 20, 30 and 40% dioxane-water mixtures at 25, 30, 35, 40 and 45°. The above cell was studied earlier[3] for $CdCl_2$ in 20% dioxane-water mixture at 35, 40 and 45°. This work has been extended to cover different solvent compositions i.e. 10, 30 and 40% dioxane-water mixtures in the temperature range 25-45° and the results are reported in this paper.

Experimental

Barium chloride (BDH, AR) and cadmium chloride (GR) were recrystallised and dried at 110°. The stock solution of these salts were prepared. Barium, cadmium and chloride contents were estimated gravimetrically. A stock solution of zinc chloride (BDH, AR) was prepared and desired quantity of HCl (Khalbaum) was added to maintain the *p*H at 4.0 to prevent hydrolysis[4]. Zinc and chloride contents were estimated gravimetrically. The other experimental procedures regarding preparation of electrodes, setting up of the cell etc. were the same as described earlier[5]. A Tinsley vernier potentiometer (accuracy ± 0.01 mV), with a matching galvanometer, was used for potential measurements. Duplicate readings were taken in each case and those which did not agree within ± 0.01 mV were rejected. The emf readings of the cell I after correction to 1 atm pressure in the usual way are reported in Table 1.

Results and Discussion

Emf of cell I is given by

$$E = E° - k \log [H^+][Cl^-] - k \log f_{H^+} f_{Cl^-} \quad ... (1)$$

where $E°$ is the standard potential of the cell, k equals 2.3026 RT/F and f's are respective activity coefficients.

The Guggenheim equation[6] for activity coefficient is

$$-\log f_{H^+} f_{Cl^-} = \frac{2A\sqrt{I}}{1+\sqrt{I}} - CI \quad ... (2)$$

where 'I' is the ionic strength of the solution, 'A' the Debye-Huckel constant and 'C' is an empirical constant which takes into account the ion-size parameter, dielectric constant, etc. It has already been noted that the Guggenheim equation (eqn. 2) can be applied satisfactorily to solutions of these solvents (dioxane-water mixtures)[7,8]. Substituting equation (2) in equation (1) and rearranging one gets

$$E + k \log [H^+][Cl^-] - \frac{2kA\sqrt{I}}{1+\sqrt{I}} = E° - kCI \quad ... (3)$$

For barium chloride (M = Ba), linear graphs are obtained when the L.H.S. of equation (3) is plotted against 'I', from which $E°$ and 'C' are found out and are given in Tables 2 and 3, respectively. The $E°$ and 'C' values so computed agree well with those obtained from the study of a similar cell taking HCl alone as the electrolyte in the cell I[5,7], in all the solvent compositions studied. This suggests that barium chloride is completely dissociated in 10, 20, 30 and 40% dioxane-water

TABLE 1—EMF (IN V) OF THE CELL I

$[MCl_2]_T$	$[HCl]_T$	Temperature °C 25	30	35	40	45
			M=Ba			
10% Dioxane						
0.004	0.002	0.49876	0.50034	0.50163	0.50295	0.50401
0.006	0.003	0.47922	0.48044	0.48140	0.48250	0.48318
0.008	0.004	0.46534	0.46637	0.46713	0.46795	0.46850
0.010	0.005	0.45467	0.45551	0.45613	0.45673	0.45711
0.020	0.010	0.42158	0.42188	0.42193	0.42203	0.42191
0.030	0.015	0.40196	0.40205	0.40178	0.40168	0.40117
20% Dioxane						
0.004	0.002	0.48976	0.49075	0.49171	0.49245	0.49292
0.006	0.003	0.47040	0.47110	0.47182	0.47225	0.47236
0.008	0.004	0.45673	0.45722	0.45769	0.45792	0.45786
0.010	0.005	0.44618	0.44651	0.44681	0.44688	0.44669
0.020	0.010	0.41346	0.41327	0.41302	0.41264	0.41188
0.030	0.015	0.39411	0.39352	0.39299	0.39231	0.39122
30% Dioxane						
0.004	0.002	0.48002	0.48094	0.48167	0.48217	0.48254
0.006	0.003	0.46100	0.46168	0.46221	0.46244	0.46241
0.008	0.004	0.44763	0.44813	0.44841	0.44842	0.44837
0.010	0.005	0.43729	0.43764	0.43781	0.43765	0.43736
0.020	0.010	0.40511	0.40509	0.40489	0.40420	0.40343
0.030	0.015	0.38588	0.38564	0.38527	0.38425	0.38317
40% Dioxane						
0.004	0.002	0.46656	0.46636	0.46676	0.46686	0.46625
0.006	0.003	0.44822	0.44775	0.44791	0.44756	0.44694
0.008	0.004	0.43521	0.43458	0.43453	0.43411	0.43318
0.010	0.005	0.42523	0.42445	0.42422	0.42367	0.42264
0.020	0.010	0.39401	0.39285	0.39227	0.39114	0.38973
0.030	0.015	0.37515	0.37376	0.37294	0.37150	0.36986
			M=Zn			
10% Dioxane						
0.004	0.0020	0.49373	0.50029	0.50160	0.50297	0.50400
0.005	0.0025	0.48794	0.48932	0.49045	0.49163	0.49253
0.006	0.0030	0.47915	0.48042	0.48139	0.48244	0.48318
0.007	0.0035	0.47172	0.47214	0.47375	0.47465	0.47528
0.008	0.0040	0.46532	0.46635	0.46710	0.46795	0.46850
0.009	0.0045	0.45968	0.46062	0.46132	0.46205	0.46250
0.010	0.0050	0.45462	0.45548	0.45068	0.45675	0.45712
20% Dioxane						
0.004	0.0020	0.48972	0.49075	0.49170	0.49244	0.49293
0.005	0.0025	0.47906	0.47992	0.48070	0.48128	0.48158
0.006	0.0030	0.47038	0.47110	0.45156	0.47221	0.47236
0.007	0.0035	0.46308	0.46366	0.46421	0.46454	0.44460
0.008	0.0040	0.45674	0.45725	0.45770	0.45791	0.45786
0.009	0.0045	0.45120	0.45160	0.45195	0.45210	0.45200
0.010	0.0050	0.44620	0.44652	0.44680	0.44687	0.44668
30% Dioxane						
0.004	0.0020	0.47998	0.48096	0.48171	0.48220	0.48255
0.005	0.0025	0.46956	0.47035	0.47090	0.47130	0.47150
0.006	0.0030	0.46100	0.46166	0.46214	0.46214	0.46240
0.007	0.0035	0.45388	0.45440	0.45476	0.45490	0.45481
0.008	0.0040	0.44765	0.44820	0.44840	0.44844	0.44836
0.009	0.0045	0.44229	0.44260	0.44293	0.44280	0.44263
0.010	0.0050	0.43740	0.43778	0.43794	0.43781	0.43750
40% Dioxane						
0.004	0.0020	0.46747	0.46731	0.46777	0.46786	0.46744
0.005	0.0025	0.45741	0.45711	0.45739	0.45736	0.45677
0.006	0.0030	0.44923	0.44879	0.44898	0.44882	0.44811
0.007	0.0035	0.44230	0.44183	0.44193	0.44158	0.44082
0.008	0.0040	0.43636	0.43577	0.43575	0.43542	0.43454
0.009	0.0045	0.43112	0.43050	0.43044	0.42998	0.42906
0.010	0.0050	0.42643	0.42570	0.42557	0.42506	0.42407

(Table 1 Contd.)

$[MCl_2]_T$	$[HCl]_T$	Temperature °C 25	30	35	40	45
			M = Cd			
10% Dioxane						
0.003	0.0015	0.51552	0.51741	0.51904	0.52075	0.52215
0.004	0.0020	0.50194	0.50365	0.50506	0.50651	0.50764
0.005	0.0025	0.49151	0.49300	0.49431	0.49557	0.49655
0.006	0.0030	0.48297	0.48440	0.48555	0.48667	0.48750
0.007	0.0035	0.47482	0.47710	0.47814	0.47920	0.47992
0.008	0.0040	0.46965	0.47082	0.47181	0.46773	0.47335
0.009	0.0045	0.46415	0.46525	0.46612	0.46702	0.46760
0.010	0.0050	0.45932	0.46032	0.46110	0.46189	0.46235
0.020	0.0100	0.42825	0.42890	0.42932	0.42985	0.42995
0.022	0.0110	0.42396	0.42460	0.42493	0.42538	0.42545
0.024	0.0120	0.42005	0.42060	0.42090	0.42131	0.42131
0.026	0.0130	0.41640	0.41697	0.41722	0.41755	0.41755
0.028	0.0140	0.41311	0.41358	0.41382	0.41414	0.41407
0.030	0.0150	0.41005	0.41047	0.41065	0.41095	0.41082
20% Dioxane						
0.003	0.0015	0.50638	0.50776	0.50906	0.51011	0.51094
0.004	0.0020	0.49304	0.49417	0.49522	0.49612	0.49660
0.005	0.0025	0.48272	0.48369	0.48465	0.48532	0.48581
0.006	0.0030	0.47437	0.47521	0.47604	0.47660	0.47689
0.007	0.0035	0.46726	0.46804	0.46873	0.46931	0.46945
0.008	0.0040	0.46117	0.46188	0.46248	0.46290	0.46290
0.009	0.0045	0.45578	0.45639	0.45701	0.45727	0.45731
0.010	0.0050	0.45096	0.45151	0.45197	0.45222	0.45220
0.020	0.0100	0.42130	0.42145	0.42162	0.42154	0.42124
0.022	0.0110	0.41712	0.41729	0.41743	0.41722	0.41682
0.024	0.0120	0.41332	0.41340	0.41340	0.41330	0.41285
0.026	0.0130	0.40987	0.40942	0.41000	0.40970	0.40925
0.028	0.0140	0.40667	0.40672	0.40672	0.40642	0.40590
0.030	0.0150	0.40370	0.40365	0.40364	0.40324	0.40265
30% Dioxane						
0.003	0.0015	0.48347	0.48445	0.48534	0.48594	0.48642
0.005	0.0025	0.47328	0.47413	0.47482	0.47531	0.47557
0.006	0.0030	0.46495	0.46570	0.46628	0.46658	0.46679
0.007	0.0035	0.45794	0.45862	0.45905	0.45931	0.45935
0.008	0.0040	0.45196	0.45248	0.45286	0.45305	0.45296
0.009	0.0045	0.44660	0.44710	0.44738	0.44744	0.44729
0.010	0.0050	0.44191	0.44228	0.44251	0.44243	0.44230
0.020	0.0100	0.41355	0.44381	0.41332	0.41353	0.41311
0.022	0.0110	0.40948	0.40963	0.40958	0.40926	0.40880
0.024	0.0120	0.40578	0.40590	0.40584	0.40550	0.40502
0.026	0.0130	0.40248	0.40247	0.40235	0.40189	0.40133
0.028	0.0140	0.39929	0.39930	0.39911	0.39865	0.39805
0.030	0.0150	0.39633	0.39630	0.39620	0.39572	0.39507
40% Dioxane						
0.003	0.0015	0.48373	0.48383	0.48445	0.48485	0.48470
0.004	0.0020	0.47075	0.47060	0.47117	0.47134	0.47092
0.005	0.0025	0.46076	0.46050	0.46083	0.46088	0.46036
0.006	0.0030	0.45258	0.45219	0.45245	0.45236	0.45172
0.007	0.0035	0.44575	0.44526	0.44540	0.44517	0.44441
0.008	0.0040	0.43979	0.43926	0.43933	0.43901	0.43818
0.009	0.0045	0.43459	0.43396	0.43396	0.43355	0.43268
0.020	0.0100	0.40360	0.40272	0.40249	0.40180	0.40065
0.022	0.0110	0.39965	0.39870	0.39838	0.39778	0.39655
0.024	0.0120	0.39607	0.39505	0.39478	0.39401	0.39268
0.026	0.0130	0.39282	0.39165	0.39145	0.39062	0.38928
0.028	0.0140	0.38968	0.38877	0.38830	0.38738	0.38613
0.030	0.0150	0.38695	0.38585	0.38551	0.38446	0.38310

mixtures at 25, 30, 35, 40 and 45° in the concentration range studied.

The data for $ZnCl_2$ were analysed in a similar manner. Linear plots were obtained according to equation (3) for zinc chloride in 10, 20 and 30% dioxane-water mixtures at 25, 30, 35, 40 and 45° within the concentration range studied. But a departure from linearity was observed in 40%

TABLE 2—VALUES OF E^0 OF THE CELL I

Wt. % dioxane	Temperature °C				
	25	30	35	40	45
10	0.21363	0.21030	0.20674	0.20320	0.19938
20	0.20305	0.19915	0.19516	0.19096	0.18652
30	0.19105	0.18695	0.18260	0.17810	0.17335
40	0.17420	0.16875	0.16395	0.15890	0.15315

TABLE 3—VALUES OF 'C' OBTAINED FROM CELL I

Wt. % dioxane	Temperature °C				
	25	30	35	40	45
10	0.5758	0.5846	0.6116	0.6144	0.6205
20	0.7862	0.8212	0.8178	0.8470	0.8712
30	1.1131	1.1083	1.0480	1.0907	1.1088
40	1.5805	1.5611	1.5820	1.6278	1.8299

TABLE 4—DISSOCIATION CONSTANT (K_2)

Wt. % dioxane	Temperature °C				
	25	30	35	40	45
10	0.00977	0.00955	0.00933	0.00912	0.00891
20	0.00851	0.00822	0.00790	0.00767	0.00741
30	0.00569	0.00550	0.00531	0.00513	0.00490
40	0.00260	0.00248	0.00237	0.00224	0.00211

TABLE 5—C' VALUES

Wt. % dioxane	Temperature °C				
	25	30	35	40	45
10	1.0	1.6	2.2	2.8	3.2
20	4.6	5.2	5.8	6.4	6.8
30	2.6	2.8	3.0	3.4	3.6
40	2.6	3.0	3.4	3.6	4.0

dioxane-water mixtures. This departure suggests the possibility of the formation of $ZnCl^+$. Similar results were also observed in the case of cadmium chloride in all the solvent mixtures studied suggesting the formation of $CdCl^+$ species. Binary electrolytes MCl_2 (M=Zn or Cd) dissociate in two stages as

$$MCl_2 \overset{K_1}{\rightleftharpoons} MCl^+ + Cl^-$$

and

$$MCl^+ \overset{K_2}{\rightleftharpoons} M^{2+} + Cl^-$$

The first stage of dissociation has been found to be complete for both $ZnCl_2$ (in 40% dioxane) and $CdCl_2$ (in all the solvent mixtures studied) upto $[MCl_2]_I = 0.01\ M$. The data for $ZnCl_2$ (in 40% dioxane) and $CdCl_2$ were treated in the manner of Prasad and coworkers[2] to study the 2nd stage dissociation. The dissociation constant for the 2nd stage dissociation, 'K_2', is given by

$$K_2 = \frac{[M^{2+}][Cl^-]}{[MCl^+]} \frac{f_{M^{2+}} f_{Cl^-}}{f_{MCl^+}} \quad \ldots (4)$$

Taking logarithm and using equation (2) for activity coefficients and rearranging, the equation (4) becomes

$$\log K_{A(2)} - \frac{4A\sqrt{I}}{1+\sqrt{I}} = \log K_2 - C'I \quad \ldots (5)$$

where $K_{A(2)} = \frac{[M^{2+}][Cl^-]}{[MCl^+]}$ and

$$C' = C_{M^{2+}} + C_{Cl^-} - C_{MCl^+}$$

The plots of L.H.S. of equation (5) against I gave linear graphs.

To find out the real ionic concentration of various ionic species, the mean activity coefficient and K_2, the procedure adopted by Prasad and coworkers[1,2] was followed. The values of K_2 and C' obtained from the graph are given in Tables 4 and 5, respectively.

At higher concentrations i.e. above 0.01 M of $CdCl_2$, the first stage of dissociation was studied. K_1 is given by the expression

$$K_1 = \frac{[CdCl^+][Cl^-]}{[CdCl_2]} f_{Ca^{2+}} f_{Cl^-}$$

$$= K_{A(1)} f_{Ca^{2+}} f_{Cl^-} \quad \ldots (6)$$

Introducing the expression for activity coefficient, taking logarithm and rearranging, equation (6) becomes

$$\log K_{A(1)} - \frac{2A\sqrt{I}}{1+\sqrt{I}} = \log K_1 - C''I \quad \ldots (7)$$

where $C'' = C_{Ca^{2+}} + C_{Cl^-}$

The K_1 values obtained from the plot of the L.H.S. against I are given in Table 6.

TABLE 6—VALUES OF K_1

Wt. % dioxane	Temperature °C				
	25	30	35	40	45
10	0.219	0.207	0.193	0.176	0.168
20	0.119	0.111	0.102	0.098	0.089
30	0.050	0.045	0.042	0.039	0.038
40	0.025	0.024	0.022	0.020	0.019

The data have been utilised further to calculate the heat of ionisation ΔH^0 of the 2nd stage dissociation of $ZnCl^+$ and for both the dissociation processes of $CdCl_2$. The ΔG^0 and ΔS^0 values have also been calculated at 25°. The ΔH^0, ΔG^0 and ΔS^0 values are reported in Tables 7 and 8. It is seen that for $ZnCl^+$ and $CdCl_2$ both the dissociations are exothermic. For $CdCl_2$ the free energy increases with increase in dioxane content in the solvent mixture but the entropy change decreases with increase in dioxane content. Further, as the dioxane content of the solvent mixture is decreased the dissociation constant increases favouring association.

TABLE 7—THERMODYNAMIC PARAMETERS FOR THE PROCESS : $MCl^+ \rightleftharpoons M^{2+} + Cl^-$ AT 25°

Wt. % dioxane	$-\Delta H°$/KJ mol^{-1}	$\Delta G°$/KJ mol^{-1}	$-\Delta S°$/KJ^{-1}mol^{-1}
10*	3.724	11.46	51.04
20*	5.356	11.80	57.74
30*	5.941	12.80	62.76
40*	7.950	14.77	76.15
40**	11.590	9.58	70.92

* Data for M = Cd.
** Data for M = Zn.

TABLE 8—THERMODYNAMIC PARAMETERS FOR THE PROCESS : $CdCl_2 \rightleftharpoons CdCl^+ + Cl^-$ AT 25°

Wt. % dioxane	$-\Delta H°$/KJ mol^{-1}	$\Delta G°$/KJ mol^{-1}	$-\Delta S°$/KJ^{-1} mol^{-1}
10	10.125	3.77	46.44
20	10.711	5.27	53.56
30	11.380	7.41	63.18
40	12.929	9.12	74.06

Acknowledgement

One of the authors (U.C.M.) is grateful to University Grants Commission, New Delhi for financial assistance.

References

1. L. SHARMA, G. SAHU and B. PRASAD, *J. Indian Chem. Soc.*, 1968, **45**, 580.
2. G. SAHU and B. PRASAD, *J. Indian Chem. Soc.*, 1969, **46**, 233.
3. S. C. MOHANTY, U. C. MISHRA, K. C. SINGH and P. K. DAS, *J. Indian Chem. Soc.*, 1973, **50**, 302.
4. C. CORSARO and H. L. STEPHENS, *J. Electrochem. Soc.*, 1957, **104**, 512.
5. U. C. MISHRA and P. K. DAS, *Electrochim. Acta*, 1977, **22**, 59.
6. E. A. GUGGENHEIM, "Thermodynamics", 3rd Edn., North Holland Publication, Amsterdam, 1957, p. 357.
7. B. K. DAS, U. C. MISHRA and P. K. DAS, *Acta Ciencia Indica*, 1979, **50**, 175.
8. B. K. DAS, Ph. D. Thesis, Utkal University, 1978.