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Electrolytic Behavior of Some Divalent Transition Metal Halides in Propylene Carbonate Solution

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The results of conductance measurements of cobalt(II) perchlorate, cobalt(II) chloride, cobalt(II) bromide, and zinc(II) bromide in propylene carbonate at 25 °C are reported. The conductance data for $Co(ClO_4)_2$ in PC has been analyzed by Fuoss–Edelson method. The anomalous conductance behavior of $CoCl_2$, $CoBr_2$, and $ZnBr_2$ in PC has been explained on the basis of equilibria $MX_2 \rightleftharpoons MX^+ + X^-$; $MX_2 + X^- \rightleftharpoons MX_3^-$; $MX^+ \rightleftharpoons M^{2+} + X^-$; and $MX^+ + MX_3^- \rightleftharpoons (MX_2)_2$. The equilibrium constants of $3MX_2 \rightleftharpoons M^{2+} + 2MX_3^-$; and $2MX_2 \rightleftharpoons (MX_2)_2$ equilibria for $CoCl_2$, $CoBr_2$, and $ZnBr_2$ in PC have been calculated in the present investigation. The conductance data of these divalent transition metal halide solutions show the existence of dimers in PC.

Divalent transition metal halides exhibit a variety of electrolytic behavior when dissolved in nonaqueous donor solvents e.g. acetonitrile,[1—4] *N*,*N*-dimethylformamide,[5,6] *N*,*N*-dimethylacetamide, and dimethylsulfoxide.[7] It is obvious that the differences between systems are due to the nature of the salts as well as the solvents. Inspection of literature shows divergence of opinion concerning the nature of the species formed in particular system. Libus and Grzybkowski[1,3,4] have explained the conductance behavior of $Co(NCS)_2$ and $CoCl_2$ in acetonitrile by equilibria $2Co(NCS)_2 \rightleftharpoons Co(NCS)^+ + Co(NCS)_3^-$ and $3CoCl_2 \rightleftharpoons Co^{2+} + 2CoCl_3^-$, respectively. Katzin[5] reported the solution equilibria of $CoCl_2$ in DMF solution as $2CoCl_2 \rightleftharpoons CoCl^+ + CoCl_3^-$. On the other hand, Grzybkowski and Pilarczyk[6] have reported that the dominating form of $CoCl_2$ in DMF solution is Co^{2+} and $CoCl_3^-$ species. The existence of neutral dimer has also been observed in $CoCl_2$–acetonitrile[8] system.

In the investigation of the electrolytic properties of the solution, conductance measurements may be the best source of quantitative information with several advantages. Studies of specific role of the dipolar aprotic solvents in view of the electrolytic behavior of divalent transition metal halides have been a subject of continued interest. In this respect, relatively very little attention has been directed towards propylene carbonate. The present work reports the electrolytic behavior of $Co(ClO_4)_2$, $CoCl_2$, $CoBr_2$, and $ZnBr_2$ in propylene carbonate in terms of solution equilibria at 25 °C.

Experimental

Materials. Commercially available 99% pure Fluka product was treated with *p*-toluenesulfonic acid ($2\ g\,dm^{-3}$) and was shaken well to remove any basic impurity. The supernatant liquid was then kept over dried 0.5 nm molecular sieves ($10\ g\,dm^{-3}$) for prolonged period of time with intermittent stirring. Thereafter, two successive distillations were carried out under reduced pressure in the presence of molecular sieves. Third distillation was carried out without any additive. The middle fraction boiling at 80 °C and 1 Torr pressure (1 Torr=133.322 Pa) was used in the present measurements. The specific conductivity of the purified solvent varied between $2—3\times10^{-8}\ S\,cm^{-1}$ at 25 °C. No water could be detected by GC analysis or Karl–Fischer titration. The purified solvent was stored in a sealed container fitted with an automatic burette in a dried N_2 gas atmosphere to prevent contamination with CO_2 and H_2O from the air. The solvent could be dispensed as desired under pressure of pure nitrogen gas. The purified PC was used within a week.

Hydrated cobalt(II) perchlorate (AR grade) was dissolved in purified PC and then method[9] was followed to prepare anyhydrous $Co(ClO_4)_2$ in PC. The water content of this solution was found to be negligible by titration with Karl–Fischer reagent. Anhydrous Cobalt(II) chloride, cobalt(II) bromide, and zinc(II) bromide were AR grade salts and were stored in a desiccator over P_2O_5. Stock solutions were prepared by dissolving weighed amounts of the substance in the desired volume of the solvent at room temperature. The individual solutions were analyzed by Standard EDTA titrations. The relative standard deviation of EDTA titration for these salts ranged from 0.1 to 0.15%. The working solutions were prepared by adding aliquots of stock solutions to a known volume of the solvent using a Gilmont ultramicroburette.

Conductance Measurements. The conductance measurements were carried out as described elsewhere.[10,11]

Conductance Data Analysis

The conductance data of $CoCl_2$, $CoBr_2$, and $ZnBr_2$ in propylene carbonate solution do not suggest the simple concentration dependence of the conductance. The conductance behavior of these salts in PC strongly indicates the typical solution equilibria for their observed results. The following equilibria are considered to account for their observed conductance behavior.

$$MX_2 \rightleftharpoons MX^+ + X^- \tag{1}$$

$$MX_2 + X^- \rightleftharpoons MX_3^- \tag{2}$$

$$MX^+ \rightleftharpoons M^{2+} + X^- \tag{3}$$

$$MX^+ + MX_3^- \rightleftharpoons (MX_2)_2 \tag{4}$$

Combining equilibria (1), (2), (3), and (1), (2), (4) gives the following set of equilibria

$$3MX2 \rightleftharpoons M^{2+} + 2MX_3^-\,;\, K_d = \frac{[M^{2+}][MX_3^-]^2 f_i f^2}{[MX_2]^3}, \tag{5}$$

$$2MX_2 \rightleftharpoons (MX_2)_2;\, K_D = \frac{[(MX_2)_2]}{[MX_2]^2}, \tag{6}$$

where MX_2=$CoCl_2$, $CoBr_2$, and $ZnBr_2$; K_d and K_D are dissociation and dimerization constants respectively, f_i and f are activity coefficients of M^{2+} and MX_3^- species respectively. The activity coefficients of all uncharged species are assumed to be unity.

Based on Eqs. 5 and 6 the total salt concentration, C_{MX_2}, can be written as

$$C_{MX_2} = [M^{2+}] + [MX_3^-] + [MX_2] + 2[(MX_2)_2]. \tag{7}$$

The equilibrium concentration of MX_3^-, MX_2, and $(MX_2)_2$ species can be expressed as

$$[MX_3^-] = 2[M^{2+}],$$

$$\text{(From charge-neutrality principle)} \tag{8}$$

$$[MX_2] = [M^{2+}]\left(\frac{4f_if^2}{K_d}\right)^{1/3}, \tag{9}$$

$$[(MX_2)_2] = K_D[M^{2+}]^2\left(\frac{4f_if^2}{K_d}\right)^{2/3}. \tag{10}$$

Combining Eq. 7 with Eqs. 8, 9, and 10, the total salt concentration, C_{MX_2}, is obtained in terms of $[M^{2+}]$, K_d and K_D.

$$C_{MX_2} = [M^{2+}]\left[3 + \left(\frac{4f_if^2}{K_d}\right)^{1/3} + 2K_D[M^{2+}]\left(\frac{4f_if^2}{K_d}\right)^{2/3}\right] \tag{11}$$

For an assumed range of values of $[M^{2+}]$, it is possible to simulate the corresponding values of C_{MX_2} using activity coefficients f_i and f, and a given set of values for K_d and K_D. The f_i and f are calculated by Debye–Hückel Law i.e. $\log f = -Az^2\sqrt{I}/(1.0+Ba\sqrt{I})$, where f is the activity coefficient of charged species; A and B are 0.685 and 0.363×10^8 respectively for PC at 25 °C; z is the charge of ionic species; I is the ionic strength of solution which is taken as $3[M^{2+}]$ and a is the ion-size parameter calculated from Stoke's Law.

Calculation of Molar Conductance (Λ_C). The molar conductance can be obtained from the equilibrium concentrations of all relevant ionic species and available estimates of their mobilities.

$$\Lambda_C = \frac{[M^{2+}]\lambda_{M^{2+}} + [MX_3^-]\lambda_{MX_3^-}}{C_{MX_2}}, \tag{12}$$

where $\lambda_{M^{2+}}$ and $\lambda_{MX_3^-}$ are molar conductances of M^{2+} and MX_3^- ions respectively. Combining Eqs. 8, 11, and 12 one gets

$$\Lambda_C = \frac{\lambda_{M^{2+}} + 2\lambda_{MX_3^-}}{3 + \left(\frac{4f_if^2}{K_d}\right)^{1/3} + 2K_D[M^{2+}]\left(\frac{4f_if^2}{K_d}\right)^{2/3}}. \tag{13}$$

Eq. 13 has been used to calculate the molar conductances of $CoCl_2$, $CoBr_2$, and $ZnBr_2$ solutions in PC for corresponding simulated salt concentrations (through Eq. 11). A series of plots of Λ_C vs. $C_{MX_2}^{1/2}$ were constructed with different sets of values for K_d and K_D over an assumed range of values of $[M^{2+}]$. The values of 37.34, 10.1, and 9.63 $S\,cm^2\,mol^{-1}$ are used in calculation (in Eq. 13) for $\lambda_{M^{2+}}$, $\lambda_{MCl_3^-}$, and $\lambda_{MBr_3^-}$, respectively. The value of limiting molar conductance of Co^{2+} ion ($\lambda^\circ_{Co^{2+}}$), i.e. twice the limiting equivalent conductance of Co^{2+} ion in PC, is found to be 37.34 $S\,cm^2\,mol^{-1}$ from the conductance data treatment of presently studied $Co(ClO_4)_2$ in PC. This value is used for $\lambda_{Co^{2+}}$ and $\lambda_{Zn^{2+}}$ in present calculation. It is considered that the limiting molar conductances of Co^{2+} and Zn^{2+} ions are about the same in PC by analogy with behavior in acetonitrile.[12)]

The values for $\lambda_{MCl_3^-}$ and $\lambda_{MBr_3^-}$ are taken as half of the $\lambda^\circ_{Cl^-}$ and $\lambda^\circ_{Br^-}$[13)] values in PC at 25 °C. It seems reasonable to use these values since the mobilities of X^- (Cl^-, Br^-) species are approximately reduced to half[14)] when it combines with neutral species (MX_2). In all cases, the variation of ion conductance with concentration has been ignored. In these calculations each variable (K_d and K_D) is changed in small increments or decrements in the direction which minimizes the error square sum i.e. $\sum(\Lambda_{obsd}-\Lambda_{cald})^2$ and the standard error of estimates (σ_Λ) is therefore $\sum(\Lambda_{obsd}-\Lambda_{cald})^2/(n-F)^{1/2}$, where n is the number of data points and F is the degree of freedom. The simulated data has been plotted in the form of Λ_C vs. $C_{MX_2}^{1/2}$ and compared with respective experimental plot. The specific set of constants (K_d and K_D) which provides the best agreement (least standard error of estimates) with the corresponding experimental one is considered as representative for a particular salt in PC.

Results and Discussion

Molar conductances, Λ_C ($S\,cm^2\,mol^{-1}$) are calculated from the solution resistivities after correcting for pure solvent contribution. Figure 1 shows plot of molar conductances against the square root of concentrations of cobalt(II) perchlorate in propylene carbonate at 25 °C and the corresponding experimental values are listed in

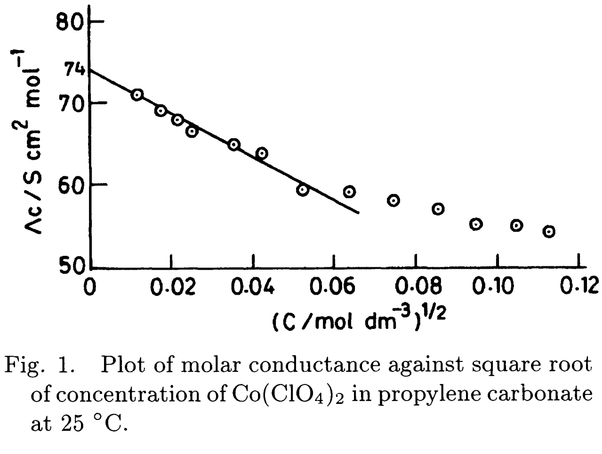

Fig. 1. Plot of molar conductance against square root of concentration of $Co(ClO_4)_2$ in propylene carbonate at 25 °C.

Table 1. Molar Conductance of Divalent Transition Metal Perchlorate and Halides in Propylene Carbonate Solution at 25 °C

	$10^3 C_{MX_2}$ mol dm^{-3}	Λ_c S cm ^{2} mol^{-1}	$10^3 C_{MX2}$ mol dm^{-3}	Λ_c S cm^2 mol^{-1}
$Co(ClO_4)_2$	0.1598	71.01	4.1898	58.91
	0.3294	68.98	5.5502	58.49
	0.4919	68.27	7.3901	57.28
	0.6497	66.58	9.0492	55.41
	1.2856	65.28	11.1032	54.78
	1.8996	64.68	12.9002	53.85
	2.8044	59.96		
$CoCl_2$	0.2194	10.76	3.0250	7.78
	0.4373	10.60	4.2982	7.24
	0.6536	10.24	6.1384	6.55
	0.8684	9.69	8.1946	5.97
	1.2933	9.40	10.5570	5.44
	1.7132	8.88	12.7160	5.16
	2.3298	8.80	15.9310	4.74
$CoBr_2$	0.1488	11.23	4.6240	6.71
	0.2483	11.22	6.4005	6.09
	0.4736	10.59	7.7610	5.74
	0.8541	9.79	9.2182	5.44
	1.2085	9.22	10.7680	5.17
	1.6080	8.68	12.9960	4.75
	2.2848	8.15	16.1290	4.84
	3.0056	7.42		
$ZnBr_2$	0.1543	6.95	2.3418	6.63
	0.3075	6.89	3.6796	6.46
	0.4595	6.84	5.5281	6.36
	0.6105	6.81	7.7370	6.21
	0.9093	6.75	9.6986	6.14
	1.2083	6.71	11.4520	6.05
	1.6380	6.69		

Table 1. The conductance data of $Co(ClO_4)_2$ in PC has been analyzed by Fuoss and Edelson method[15)] which evaluates the limiting equivalent conductance of $Co(ClO_4)_2$ and first step association constant (K_A) of equilibrium $Co^{2+} + ClO_4^- \rightleftharpoons CoClO_4^+$ in PC. This method has been critically analyzed by Pethybridge.[16)] Derived values of Λ_0 of $Co(ClO_4)_2$ and $\frac{1}{2}\lambda°Co^{2+}$ (limiting equivalent conductance of Co^{2+} ion) in PC are 37.10 and 18.67 S cm^2 mol^{-1} respectively and K_A is 101.2. Taking into account the known value of the limiting ionic conductance of ClO_4^- anion in PC[17)] at 25 °C, the limiting equivalent conductance of Co^{2+} cation in PC has been estimated. This value is useful in analyzing the conductance data of $CoCl_2$, $CoBr_2$, and $ZnBr_2$ in PC which are already described in previous section.

Figure 2 shows the plots of experimental and simulated data of molar conductance against square root of the concentration of $CoCl_2$, $CoBr_2$, and $ZnBr_2$ in PC at 25 °C. The experimental values are depicted in Table 1. Inspection of Figs. 1 and 2 shows that the points for $CoCl_2$, $CoBr_2$, and $ZnBr_2$ run well below the curve of $Co(ClO_4)_2$, which is known to be strong electrolyte and only slightly associated. It reflects that simple dissociation of these salts can not account for their observed conductance behavior and thus indicates the unusual solution equilibria leading to the formation of complex ionic species responsible for the drastic change in electrolytic behavior. As is seen from Fig. 2, the $CoBr_2$ in PC exhibits higher conductance value than others. The molar conductances of presently studied salts in PC display close similarity and vary within relatively very narrow range. The characteristic feature of the conductance behavior is a relatively very slight decrease in conductance with increasing concentration of studied salts in PC. The $ZnBr_2$–PC system shows peculiar conductance behavior of variation of the molar conductances within a very narrow limits (ca. 6.05—6.95 S cm^2 mol^{-1}) and the curve (Fig. 2) runs almost horizontally. This type of behavior is also exhibited by $ZnCl_2$ and $ZnBr_2$ in acetonitrile[3,18)] and $CoCl_2$ in *N,N*-dimethylacetamide.[19)]

The observed conductance behavior of the presently studied divalent transition metal halides i.e. $CoCl_2$, $CoBr_2$, and $ZnBr_2$ in PC is explicable on the basis

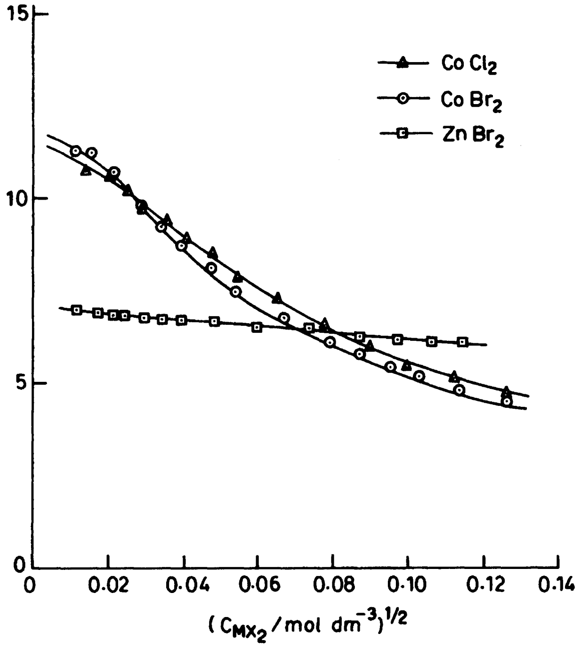

Fig. 2. Plot of molar conductance against square root of concentration of $CoCl_2$, $CoBr_2$, and $ZnBr_2$ in propylene carbonate. The symbols △, ○, and □ represent the experimental points and line (—) represents calculated curves for $CoCl_2$, $CoBr_2$, and $ZnBr_2$, respectively.

of solution equilibria (1) to (4). This underlying set of assumptions (equilibria (1) to (4)) makes clear that the concentrations of MX^+ and X^- species are negligible compared to the concentrations of other species involved in the system but it does not suggest that MX^+ and X^- species are completely absent. Based on the equilibria $3MX_2 \rightleftharpoons M^{2+}+2MX_3^-$, and $2MX_2 \rightleftharpoons (MX_2)_2$, an expression for the total salt concentration, C_{MX_2} (Eq. 11) and corresponding molar conductance, Λ_C (Eq. 13) has been derived to analyze the conductance data of studied salts in PC. The simulated plot of molar conductance against square root of concentration for a specific set of constants (K_d and K_D) for a particular salt in PC shows best agreement with the experimental one. It suggests the validity of the proposed solution equilibria to explain the observed conductance behavior of presently studied salts e.g. $CoCl_2$, $CoBr_2$, and $ZnBr_2$ in PC. It may be inferred from Eq. 5 that 3 moles of MX_2 salts in PC are consumed in forming 3 moles of ionic species (1 mole M^{2+} and 2 moles of MX_3^- species) instead of 9 moles of ionic species on simple dissociation as $MX_2 \rightleftharpoons M^{2+}+2X^-$. It seems reasonable that this mode of dissociation of these salts in PC is mainly responsible for very little decrease in conductance with increasing the concentration as observed in the present case especially for $ZnBr_2$ in PC. The derived values of dissociation constant (K_d) and dimerization constant (K_D) alongwith standard error of estimates (σ_Λ) for presently studied salts in PC at 25 °C are presented in Table 2. These divalent transition metal halides in PC show the tendency of dimerization as also observed in the case of cobalt(II) chloride in acetonitrile[8] and copper(II) chloride and copper(II) bromide in PC.[10] The bromide salts show the higher degree of dimerization than chloride salts in PC; however, zinc bromide in PC shows the lesser degree of dimerization than $CoCl_2$ and $CuCl_2$ (see Table 2). Equation 5 is similar to Libus and Puchalska coordinative disproportionation equilibria[20] as an explanation of electrolytic properties of some metal halides in nonaqueous solvents. The same equilibrium ($3[ZnCl_2(CH_3CN)_2]+2CH_3CN \rightleftharpoons [Zn(CH_3CN)_6]^{2+}+2[ZnCl_3(CH_3CN)]^-$) governs the electrolytic properties of $ZnCl_2$ and $ZnBr_2$ in acetonitrile.[3,18]

Table 2. The Derived Values of Dissociation Constant (K_d) and Dimerization Constant (K_D) for $CoCl_2$, $CoBr_2$, and $ZnBr_2$ in propylene carbonate at 25 °C

Salt	K_d	K_D	σ_Λ
$CoCl_2$	0.68	1200	0.0354
$CoBr_2$	0.96	1750	0.0518
$ZnBr_2$	3.01×10^{-2}	50	0.0385
$CuCl_2$[a]	1.5×10^{-2}	600	—
$CuBr_2$[a]	0.1	1000	—

a) Values from reference.[10]

In conclusion, it can be said that the observed conductance behavior of cobalt(II) chloride, cobalt(II) bromide, and zinc(II) bromide in propylene carbonate can be interpreted by the solution equilibria (1) to (4). The equilibrium constants (K_d and K_D) of $3MX_2 \rightleftharpoons M^{2+}+2MX_3^-$ and $2MX_2 \rightleftharpoons (MX_2)_2$ equilibria (derived from Eqs. 1, 2, 3, and 4) for $CoCl_2$, $CoBr_2$, and $ZnBr_2$ in propylene carbonate have been obtained in the present investigation.

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