

Electrolytic Behaviour of Transition Metal Bromides in Acetonitrile Solution

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The molar conductivities for MnBr_2 , CoBr_2 , and ZnBr_2 in acetonitrile solution have been determined at 25 °C. Unlike perchlorates, the divalent transition metal bromides exhibit a variety of electrolytic behaviour, as shown by their molar conductivity curves. The properties of the solutions are discussed and interpreted in terms of the formation of the complex electrolytes.

Of the classical electroanalytical methods, conductometry was used in the early stages of investigation of solute-solvent interactions. As the conductivity of a solution depends in part on the number of ions present and in part on their mobility, measurements can provide information on the co-ordination states of the solutes. However, the more complicated the system, the less suitable are conductometric methods for its characterization. The analysis of conductance results for co-ordination compounds and the interpretation of such data in terms of formation constants of individual complexes appear to be impossible at the present stage of development of the theory. None of the extended conductance equations widely used for symmetrical electrolytes can be used for such a system. The more rigorous treatment proposed by Lee and Wheaton¹ and developed successfully by Pethybridge² gives satisfactory results for unsymmetrical electrolytes in non-aqueous systems. However, it is rather difficult to use this theory for systems involving more than three different ionic species. In the investigation of solutions containing more than two complexes conductometry may at best be a source of qualitative information.

Analysis of conductance results led Libuś³ to the conclusion that the dissolution of anhydrous $\text{Co}(\text{NCS})_2$ in acetonitrile is accompanied by the co-ordinative disproportionation reaction (1) ($L = \text{solvent}$), producing a complex electrolyte consisting of



a pseudo-octahedral cation and a pseudo-tetrahedral anion. In a previous paper⁴ I have shown that a moderately concentrated solution of NiBr_2 in acetonitrile (L) is an equilibrium mixture of the $[\text{NiBrL}_5]^+\text{Br}^-$ and $[\text{NiBrL}_5]^+[\text{NiBr}_3\text{L}]^-$ complex electrolytes, differing in structure and properties. As the concentration increases, the transformation (2) gradually occurs. The ions present in the solution are $[\text{NiBr}_3\text{L}]^-$, $[\text{NiBrL}_5]^+$, and Br^- . The equilibrium (3) takes

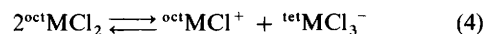


place in an acetonitrile solution of CoCl_2 and the resulting solution may be considered as an equilibrium mixture of the $[\text{CoL}_6]^{2+} + 2[\text{CoCl}_3\text{L}]^-$ complex electrolyte and the electrically neutral co-ordination form, $[\text{CoCl}_2\text{L}_2]$.^{5,6}

It should be noted that the above mentioned equilibria are accompanied by simple ionization processes controlling the electrolytic properties of the salts in the most diluted solutions.

The formation of the pseudo-tetrahedral complex anions in NN -dimethylformamide (dmf) solutions of MnCl_2 , FeCl_2 , CoCl_2 , NiCl_2 , and CuCl_2 was shown by Katzin⁷ and, using

his original notation, ascribed to the co-ordination disproportionation reaction (4), also producing a complex electrolyte.



However, in my opinion the properties of the solutions cannot be rationalized in terms of one type of equilibrium only. In recent reports from this laboratory it has been shown that the dominating form of CoCl_2 in dmf solution is the $[\text{CoL}_6]^{2+} + 2[\text{CoCl}_3\text{L}]^-$ complex electrolyte,⁸ while the equilibrium suggested by Katzin⁷ is responsible for the electrolytic properties of the NiCl_2 solution.⁹

It is evident now that the electrolytic properties of the divalent transition metal chlorides and bromides in strongly polar donor solvents may be rationalized in terms of a relatively small number of modes of ionization. The conductometric results may be considered as a starting point for further analysis, being an indication of the type of equilibrium taking place in the system studied.

The present work was undertaken in order to compare the electrolytic properties of the divalent transition metal bromides dissolved in acetonitrile. In previous papers I reported the results of the spectrophotometric studies of the solution equilibria of NiBr_2 ⁴ and CoBr_2 ¹⁰ in acetonitrile.

Experimental

Purification of reagent grade acetonitrile was carried out according to the method recommended by Coetzee *et al.*,¹¹ using, in succession, CaH_2 and P_2O_5 . The solvent was finally distilled through a fractionating column. Specific conductivity of the final material varied in the range $(0.8-2.0) \times 10^{-7} \text{ S cm}^{-1}$.

Anhydrous CoBr_2 , MnBr_2 , and ZnBr_2 were prepared from the corresponding hydrates by drying under vacuum initially at 80 °C and then at 150 °C, followed by prolonged storing over P_2O_5 in a vacuum desiccator. The products were recrystallized from dry acetonitrile. These were dissolved in fresh solvent prior to taking measurements.

The stock solutions were analysed for metals by standard ethylenediamine- NNN' -tetra-acetate titrations as well as gravimetrically. Solutions for measurements were prepared by weighed dilutions. The concentrations were calculated using independently determined densities.

Details of the procedures were identical to those described previously.^{4,8} All the preparations and manipulations were performed in dry-boxes.

Results and Discussion

Figure 1 shows plots of the molar conductivities of MnBr_2 , CoBr_2 , and ZnBr_2 in acetonitrile at 25 °C and that of NiBr_2

Table. Molar conductivities of transition metal bromides in acetonitrile solution at 25 °C

$10^3 c /$ mol dm^{-3}	$\Lambda_m /$ $\text{S cm}^2 \text{ mol}^{-1}$	$10^3 c /$ mol dm^{-3}	$\Lambda_m /$ $\text{S cm}^2 \text{ mol}^{-1}$
MnBr₂			
0.2591	60.21	9.082	46.40
0.3350	58.15	10.008	45.96
0.3966	57.10	11.256	45.68
0.4768	56.23	13.185	45.15
0.5592	55.45	16.36	44.33
0.8152	54.12	18.74	43.76
1.0524	53.13	22.41	43.02
1.551	52.04	28.02	42.00
2.129	51.08	32.22	41.39
2.605	50.54	43.25	39.92
2.997	50.11	53.84	38.72
4.291	49.14	63.92	37.70
5.093	48.51	83.08	36.25
6.500	47.69	98.88	35.18
7.414	47.17	115.25	34.26
8.238	46.69	131.50	33.30
CoBr₂			
0.1274	57.60	3.169	51.31
0.2171	55.95	4.132	50.72
0.2848	54.95	5.322	50.10
0.4120	54.36	7.071	49.63
0.6731	53.85	8.969	48.68
0.8401	53.36	11.58	47.91
0.9160	53.37	13.50	47.33
1.284	52.59	15.71	46.83
1.697	52.24	18.43	45.78
2.243	51.74	21.57	45.24
		25.47	44.15
ZnBr₂			
0.6445	3.443	10.43	2.998
0.8883	3.360	13.54	2.995
1.438	3.174	16.95	3.008
1.941	3.065	21.11	3.012
2.405	3.072	28.01	3.023
2.568	3.070	34.93	3.047
3.658	3.032	45.66	3.067
4.965	3.009	55.34	3.094
7.032	3.023	65.82	3.100

reported previously.⁴ The experimental values are listed in the Table. The divalent transition metal bromides exhibit a variety of electrolytic behaviours in acetonitrile, as shown by the differences in the transport properties.

It has been shown by Libuš *et al.*^{12,13} that the divalent transition metal cations in acetonitrile, as well as in other strongly polar co-ordinating solvents, exist in the absence of co-ordinating anions as $[\text{M}(\text{CH}_3\text{CN})_6]^{2+}$ type solvato-complexes ($\text{M} = \text{Mn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{or Zn}^{2+}$). Moreover, their mobilities and abilities for outer-sphere association are essentially independent of the nature of the metal cation. As a consequence, solutions of the corresponding perchlorates and tetrafluoroborates display practically identical concentration dependences of the molar conductivity. The molar conductivity curve common for the corresponding tetrafluoroborates¹³ is indicated in Figure 1 for comparison.

Inspection of Figure 1 shows that the points for the bromides run well below the curve for the tetrafluoroborates, which are known to be strong electrolytes and only slightly associated. It should be noted that the limiting molar conductivities calculated for the bromides from known ionic conductivities^{13,14} vary within narrow limits (from 403.4 $\text{S cm}^2 \text{ mol}^{-1}$ for MnBr_2 to 408.4 $\text{S cm}^2 \text{ mol}^{-1}$ for NiBr_2), while the average

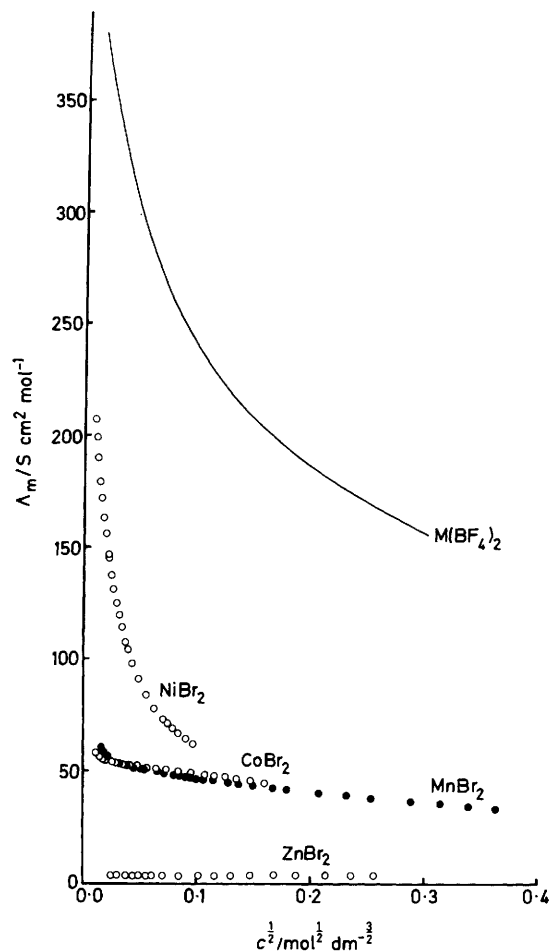


Figure 1. Dependences of molar conductivity on concentration for MnBr_2 , CoBr_2 , and ZnBr_2 (and NiBr_2 ⁴) in acetonitrile solution at 25 °C. The molar conductivity curve for the corresponding metal(II) tetrafluoroborate¹³ is also included

value for the tetrafluoroborates is 417.0 $\text{S cm}^2 \text{ mol}^{-1}$. Thus, the curve for the tetrafluoroborates provides a good approximation of the molar conductivity curve for the hypothetical strong electrolyte $[\text{M}(\text{CH}_3\text{CN})_6]^{2+} 2\text{Br}^-$. The relatively small differences arising from the difference in the mobilities of the anions are negligible, while the shape of the curve is more realistic than those resulting from calculations.

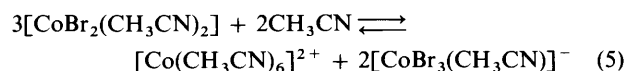
It is evident that the simple association of the solvato-complexes with the bromide anion cannot account for the conductivity properties of the metal bromides and complex formation is responsible for the drastic differences in the electrolytic behaviour within the whole range of concentrations.

As is seen from Figure 1, NiBr_2 shows the highest conductivity in acetonitrile solution of all the metal bromides. The most characteristic feature of the conductance behaviour of NiBr_2 is a rapid decrease in conductivity with increasing concentration at the lowest concentration range. It has been shown that this effect is related to the formation of the complex electrolyte $[\text{NiBr}(\text{CH}_3\text{CN})_5]^+ [\text{NiBr}_3(\text{CH}_3\text{CN})]^-$.⁴ As a result, 1 mole of the 1:1 electrolyte is formed instead of 2 moles of the formal $\text{Ni}^{2+} 2\text{Br}^-$ electrolyte and this transformation is responsible for the observed drastic decrease of molar conductance.

Further inspection of Figure 1 shows that the electrolytic behaviour of MnBr_2 and CoBr_2 is quite different from that of

NiBr₂. Moreover, the molar conductivities of the salts display close similarity and vary within relatively narrow limits (*ca.* 33–60 S cm² mol⁻¹). The highest values at the lowest concentration of MnBr₂ or CoBr₂ are somewhat lower than the lowest values obtained for NiBr₂ in the most concentrated solutions.

The observed behaviour of CoBr₂ in acetonitrile is a consequence of the more complicated system of complex formation equilibria. Acetonitrile solutions of CoBr₂ have been investigated spectrophotometrically^{15,16} and these studies have yielded good evidence for the existence of two pseudo-tetrahedral species, [CoBr₂(CH₃CN)₂] and [CoBr₃(CH₃CN)]⁻, besides the [Co(CH₃CN)₆]²⁺ solvento-cation in the solution. Analysis of the spectrophotometric results obtained in this laboratory¹⁰ led us to the conclusion that the reversible coordinative disproportionation equilibrium (5) determines the



electrolytic properties of CoBr₂ in acetonitrile solutions throughout a large range of concentration. It may be inferred from (5) that 3 moles of CoBr₂ are consumed in forming one mole of the [CoL₆]²⁺ + 2[CoBr₃L]⁻ complex electrolyte, the principal form the solute in more concentrated solutions. The simple dissociation of the [CoBr₂(CH₃CN)₂] complex, resulting in the liberation of a bromide anion and formation of the [CoBr(CH₃CN)₅]⁺ complex cation cannot be neglected for more dilute solutions.

The characteristic feature of the concentration dependence of the molar conductivity is a relatively slight decrease with increasing concentration of CoBr₂. Such behaviour is due to the formation of ionic species in the solution, this effect compensating the decrease of the ionic mobility with increasing electrolyte concentration.

The spectrophotometric data reported previously¹⁰ were re-analysed in terms of the consecutive formation constants of the bromo-complexes of cobalt(II). In the calculations actually performed I used the equilibrium concentrations of the two pseudo-tetrahedral complexes of cobalt(II) determined for a series of solutions of CoBr₂ in acetonitrile at 25 °C. Taking into account the equations arising from material balance for the cation and anion, and assuming that variations in the activity coefficients follow the Debye-Hückel equation involving the

ion size parameter (B_a^0 , estimated as 3.4 from solvodynamic radii of the respective ions^{13,14}), I attempted to find the formation constants K_n , equation (6), where $n = 1, 2$, or 3 and Y_n is the

$$K_n = \frac{c_n}{c_{n-1}[\text{Br}^-]} \cdot Y_n \quad (6)$$

quotient of the respective activity coefficients. The resulting values of the formation constants of [CoBr(CH₃CN)₅]⁺, [CoBr₂(CH₃CN)₂], and [CoBr₃(CH₃CN)]⁻ are $(1.7 \pm 0.1) \times 10^3$, $(4.4 \pm 0.7) \times 10^3$, and $(4.4 \pm 0.6) \times 10^2$ dm³ mol⁻¹, respectively. The analogous sequence obtained previously⁴ for the consecutive bromo-complexes of nickel(II) is as follows: $K_1 = 1.6 \times 10^3$ dm³ mol⁻¹, $K_2 = 6.0 \times 10^2$ dm³ mol⁻¹, and $K_3 = 3 \times 10^3$ dm³ mol⁻¹ at 25 °C. The observed sequences, $K_1 < K_2 > K_3$ for bromo-complexes of cobalt(II) and $K_1 > K_2 < K_3$ for bromo-complexes of nickel(II), reflect the change in the co-ordination number of the central metal atom upon co-ordinating the second or third bromide anion, respectively. The formally neutral NiBr₂ complex comprises the [NiBr(CH₃CN)₅]⁺Br⁻ outer-sphere ion pair, while the corresponding dibromo-complex of cobalt(II) is the pseudo-tetrahedral [CoBr₂(CH₃CN)₂] co-ordination cluster. The structural difference arising from the known tendency of cobalt(II) towards a tetrahedral environment brings about the essential difference in the transport properties of NiBr₂ and CoBr₂ in acetonitrile solutions.

Figure 1 shows the close similarity of the molar conductivities of CoBr₂ and MnBr₂. This striking resemblance in the curves suggests a similar mode of ionization of the solutes in acetonitrile solutions. I infer that the similarity represents the same number and type of complex ions existing in the solutions. Thus, we can assume that MnBr₂ exists as the [Mn(CH₃CN)₆]²⁺ + 2[MnBr₃(CH₃CN)]⁻ complex electrolyte, analogous with the ionic co-ordination form of CoBr₂ in acetonitrile and CoCl₂ in dmf⁸ solutions. In the latter system a similar concentration dependence of the molar conductivities was observed.⁸

The most characteristic feature of the acetonitrile solutions of ZnBr₂ is a very low but distinct molar conductivity varying in very narrow limits (*ca.* 3.0–3.4 S cm² mol⁻¹). Figure 2 shows the molar conductance more precisely. The curve runs almost horizontally, exhibiting a very flat minimum at a concentration

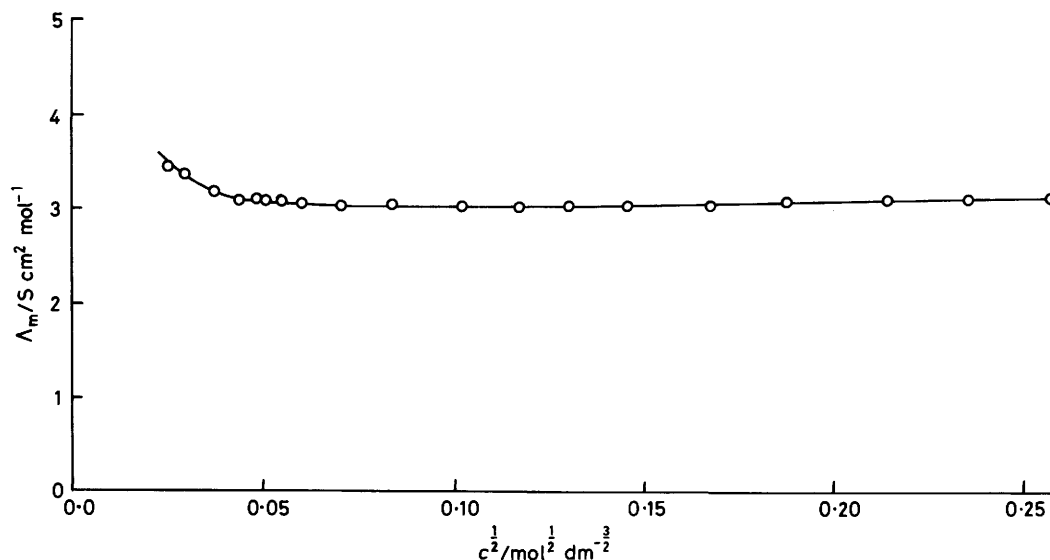
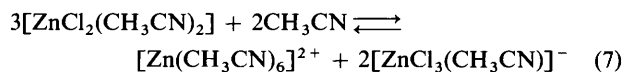


Figure 2. Dependence of molar conductivity on concentration for ZnBr₂ in acetonitrile at 25 °C

of 0.01 mol dm⁻³. The low value of the molar conductivity indicates the predominance of electrically neutral complexes of zinc(II) in the solutions. An almost identical curve for the molar conductivity of CoCl₂ in *NN*-dimethylacetamide (dma) solutions was reported by Kamińska and Uruska.¹⁷ On the basis of the spectrophotometric measurements the properties of the latter systems were explained in terms of the co-ordinative disproportionation equilibria strongly shifted to the left, *i.e.* to the [CoCl₂(dma)₂] complex, exhibiting a typical absorption spectrum. Co-ordination properties of cobalt(II) and zinc(II) are known to be rather similar. However, the tendency of zinc(II) to form tetrahedral complexes is markedly higher and the solid complexes [ZnCl₂(CH₃CN)₂] and [ZnBr₂(CH₃CN)₂] were obtained and studied.¹⁸ Moreover, the equilibrium (7) was



found to be responsible for the electrical conductivity of ZnCl₂ in acetonitrile.⁵ Thus I infer that the same equilibrium determines the electrolytic properties of ZnBr₂ in acetonitrile. It should be noted that other types of complex electrolytes, *e.g.* [Zn(CH₃CN)₆]²⁺[ZnBr₄]²⁻ or [ZnBr(CH₃CN)₅]⁺[ZnBr₃(CH₃CN)]⁻, cannot, *a priori*, be excluded. However, these co-ordination forms are less favourable in terms of the high tendency of zinc(II) to form tetrahedral structures.

Co-ordinative disproportionation equilibria were proposed by Libuś and Puchalska¹⁹ as an explanation of the electrolytic properties of some metal halides in non-aqueous solvents; Libuś²⁰ also presented a general scheme covering the majority of cases encountered in solutions of divalent transition metal salts involving unidentate anions. One of the factors determining the mode of ionization, *i.e.* the type of co-ordinative disproportionation equilibrium responsible for the electrolytic properties of the transition metal salts dissolved in donor solvents, is the relative stability of tetrahedral and octahedral complexes. The results show that the halides of nickel(II), known to prefer an octahedral environment, exist as the [NiXL₅]⁺X⁻ or [NiXL₅]⁺[NiX₃L]⁻ complex electrolytes (L = solvent molecule), while the halides of cobalt(II) exist mainly as the [CoXL₅]⁺[CoX₃L]⁻ or [CoL₆]²⁺2[CoX₃L]⁻ co-ordination

forms due to the preference of cobalt(II) for a tetrahedral structure. The extreme stability of tetrahedral complexes of zinc(II) appears to be responsible for the existence of the neutral [ZnX₂L₂] complexes in the solutions in the presence of a small amount of the [ZnL₆]²⁺2[ZnX₃L]⁻ complex electrolyte. Finally, a relatively small dependence of the mode of ionization on the nature of the solvent and of the anion should be pointed out.

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