

# Salts of the Group IIA Metals Dissolved in Nonaqueous or in Mixed Solvents

## Conductance Study of Some Chlorides, Perchlorates, Nitrates, Sulfates, and Acetates Dissolved in Methanol

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Conductance data for methanol solutions of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Be}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ ,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Ca}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Sr}(\text{ClO}_4)_2$ , or  $\text{Sr}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  at 20° and 45° C. are reported. For all salts except  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Sr}(\text{ClO}_4)_2$ , and  $\text{Sr}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  the ratio,  $R$  (= molar conductance at 45° C./molar conductance at 20° C.), is independent of the salt concentration. For  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $R$  is less than one.  $\text{Sr}(\text{ClO}_4)_2$  and  $\text{Sr}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  systems have the same  $R$  values. Also described are the linear relations between the specific conductance and salt concentration for each salt at each temperature studied.

DAWSON AND KEELY (1) studied the conductivity and viscosity of methanol solutions containing  $\text{MgCl}_2$ ,  $\text{SrCl}_2$ ,  $\text{SrBr}_2$ ,  $\text{SrI}_2$ , or  $\text{BaCl}_2$  at 0° and 20° C. They found that for salt concentrations below 0.001*N* the equivalent conductance is linear in the square root of the alkaline earth halide concentration. At higher salt concentrations, significant deviations occur.

de Maine and McAlonie (7) found that for some chlorides of calcium, chromium, manganese, iron, and copper dissolved in methanol, the ratio,  $R$  (= Molar Conductance at 45° C./Molar Conductance at 20° C.) is independent of the salt concentration for each salt.  $R$  values for the three hydrates of cobalt (II) chloride (5, 7), and for two hydrates of each of nickel chloride (7, 8), ferrous chloride (7), calcium chloride (7), and cupric chloride (7) are all independent of the number of waters of hydration and the salt concentrations. For  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$  dissolved in methanol (9)  $R$  values are independent of the salt concentrations, up to 1.021 moles/liter for tin (II), and to 0.500 moles/liter for tin (IV). Within experimental error,  $R$  values are independent of the tin valency. Average  $R$  values for  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  dissolved in methanol (3) are  $0.851(\pm 0.011)$ ,  $1.229(\pm 0.012)$ , and  $1.203(\pm 0.007)$ , respectively. For  $\text{ZnCl}_2$  in methanol (7)  $R$  varies continuously with salt concentration, and all  $R$  values are less than one. For  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  solutions containing more than 0.500 moles/liter,  $R$  values increase which has been attributed to reversible formation of a non-conducting polymeric species (9).

Plots of the molar conductance *vs.* the square root of the salt concentration for all the salts mentioned above show the characteristic deviations from linearity found for polyvalent-univalent salts (1, 7). Plots of the specific conductance *vs.* the salt concentration at a fixed temperature yield two intersecting straight lines with a well-defined point of inflexion (4, 8, 9).

Here are reported conductance data at 20° and 45° C. for thirteen salts of the alkaline earth metals dissolved separately in methanol.

### EXPERIMENTAL

Fisher spectroanalyzed grade methanol was purged with Matheson anhydrous nitrogen (extra dry) immediately

before use. The salts and the concentration ranges studied at both 20° and 45° C. are given in Table I. Triplicate analyses of either the chlorine (10) or metal (11) contents of each salt showed that actual and theoretical compositions agreed to within one per cent.

Solutions with the desired salt concentrations were made as described previously (4, 6). Electrical resistances of all solutions were measured at 20° and 45° C. with a General Radio Company Impedance Bridge (type 1650A) using Leeds and Northrup cells with constants between 0.1000 and 23.00. Duplicates of selected solutions for each salt showed that resistances were easily reproduced to within two per cent. No changes in the resistance of these solutions were observed even after six hours.

### RESULTS

All data reported in this paper were processed with an IBM 650 digital computer using a recently developed integrated system of Fortran programs (2). Incorporated into these programs are corrections for temperature-density-volume changes and instruction for the rejection of all sets of conjugate information in which the specific conductivity (input information) is less than a preselected number of times ( $A$ ) greater than the conductivity of the solvent itself. This operation has been called the "Fail-Safe Procedure." For this work,  $A$  was chosen equal to one hundred. Molar conductances for the salts themselves are calculated and the "Self-Judgment Principle" is used to determine whether or not the input information (in this case specific conductivities and concentrations) is described by (i) the Onsager equation, or (ii) the equation: Specific Conductance = (salt concentration times constant) plus constant, to within a preselected "Instrument Reliability Factor" (here set equal to two per cent). Finally all  $R$  values are computed.

The results obtained by the computer analyses of the new data are summarized as follows.

The data do not fit the Onsager equation to within the limit of reproducibility (two per cent) even for a limited concentration range. Plots of the molar conductance *vs.* the square root of the salt concentration show the characteristic deviations from linearity found for all except univalent-univalent salts dissolved in MeOH or MeOH- $\text{CCl}_4$ . In Figure 1, selected data are used to illustrate this point.

Plots of the specific conductance *vs.* the salt concentration for each salt at each temperature showed a linear

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Table I. Sources of Materials, Concentrations, and Number of Samples Studied at 20° and 45° C.

Compound	Source	Grade	Conc. Range × 10 <sup>4</sup> (Moles/Liter)	No. of Samples
MeOH	Fisher	Spectroanalyzed	...	...
BaCl <sub>2</sub> ·2H <sub>2</sub> O	Fisher	Reagent	9.989-49.94	5
Be(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O	Fisher	Purified	8.992-1124	14
BeSO <sub>4</sub> ·4H <sub>2</sub> O	Fisher	Purified	82.60-1033	8
Ca(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	Baker	Reagent	6.476-1079	15
Ca(ClO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	G.F. Smith	Reagent	5.991-998.3	15
Mg(Ac) <sub>2</sub> ·4H <sub>2</sub> O	Fisher	Reagent	21.11-1056	11
MgCl <sub>2</sub> ·6H <sub>2</sub> O	Merck	Reagent	6.326-2108	17
Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	Fisher	Reagent	6.271-1045	15
Mg(ClO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	G.F. Smith	Reagent	18.79-2348	16
MgSO <sub>4</sub> ·7H <sub>2</sub> O	Mallinckrodt	Reagent	8.353-1043	16
SrCl <sub>2</sub> ·6H <sub>2</sub> O	Elmer	Purified	6.580-1096	15
Sr(ClO <sub>4</sub> ) <sub>2</sub>	G.F. Smith	Reagent	7.329-1222	15
Sr(ClO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	G.F. Smith	Reagent	4.899-816.5	15

relationship for a low (Figure 2) and a high (Figure 3) salt concentration range. Included in Figures 2 and 3 are some data rejected during application of the Fail-Safe and Self-judgment procedures.

For all salts except MgSO<sub>4</sub>·7H<sub>2</sub>O, BaCl<sub>2</sub>·2H<sub>2</sub>O, Mg-(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>·4H<sub>2</sub>O and the two strontium perchlorates, *R* is

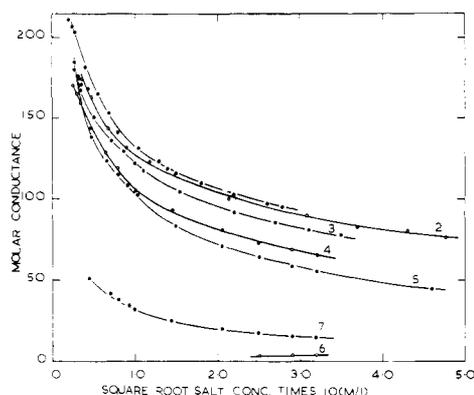


Figure 1. Molar conductance vs. square-root of the salt concentration at 20° C. for methanol solutions of Sr(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (Plot 1); Mg(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (2); Sr(ClO<sub>4</sub>)<sub>2</sub> (3); Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (4); MgCl<sub>2</sub>·6H<sub>2</sub>O (5); MgSO<sub>4</sub>·7H<sub>2</sub>O (6); and Mg(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>·4H<sub>2</sub>O (7).

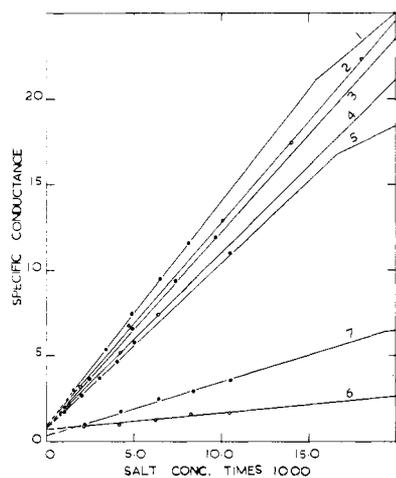


Figure 2. Specific conductance vs. salt concentration at 20° C. for methanol solutions of some alkaline earth salts. The salt represented by each plot is noted in the caption to Figure 1.

independent of the salt concentration to within the limits of experimental error. Because of their low solubility and conductivities insufficient acceptable data are available for MgSO<sub>4</sub>·7H<sub>2</sub>O and BaCl<sub>2</sub>·2H<sub>2</sub>O. However, for the sulfate, *R* is less than one. For Mg(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>·4H<sub>2</sub>O, Sr(ClO<sub>4</sub>)<sub>2</sub> and Sr(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, *R* appears to decrease linearly with the square root of the salt concentration (not shown). However, the maximum variation in *R* values for at least a 150-fold concentration range does not exceed eight per cent for each of the three salts. *R* values for the two strontium perchlorates appear to be identical (Table II).

In Table III, are given mean *R* values and the square-root-mean-square deviations for each salt. Also given are  $\Delta H$  values calculated with vant Hoff's equation using the mean values for *R*. The  $\Delta H$  values were calculated on the basis of a weak univalent-univalent electrolyte; and, although the actual behavior of these salts obviously differs from this simplest case, arguments based on the relative magnitudes are unaffected by this simplification.

## DISCUSSION

Arguments already advanced for the iron transition group metal salts (7) suggest that the constant *R* values,

Table II. *R* (= Molar Conductance at 45° C./Molar Conductance at 20° C.) for Sr(ClO<sub>4</sub>)<sub>2</sub> and Sr(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O in Methanol at the Concentrations Indicated

Sr(ClO <sub>4</sub> ) <sub>2</sub>			Sr(ClO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O		
Salt conc. × 10 <sup>4</sup> mole/liter	Molar conductance 20° C.	<i>R</i>	Salt conc. × 10 <sup>4</sup> mole/liter	Molar conductance 20° C.	<i>R</i>
7.329	180.7	1.329	4.899	211.9	1.336
9.772	174.4	1.313	6.532	207.4	1.312
12.22	172.4	1.298	8.165	203.6	1.309
12.22	170.1	1.302	8.165	203.2	1.302
24.43	150.1	1.286	16.33	180.8	1.284
48.86	136.0	1.272	32.66	164.9	1.257
73.29	128.2	1.252	48.99	153.0	1.252
97.72	121.6	1.256	65.32	145.6	1.262
122.2	118.3	1.245	81.65	141.9	1.253
122.2	116.1	1.242	81.65	141.3	1.253
244.3	104.5	1.232	163.3	122.7	1.248
488.6	91.9	1.220	326.6	110.0	1.234
732.9	84.9	1.225	489.9	102.2	1.228
977.2	80.8	1.203	653.2	97.7	1.224
1222.0	78.5	1.214	816.5	94.4	1.226
Average of 15 samples		1.259			1.265
Square-Root Mean					
Square Deviation		0.037			0.036
Max. Deviation		0.070			0.071

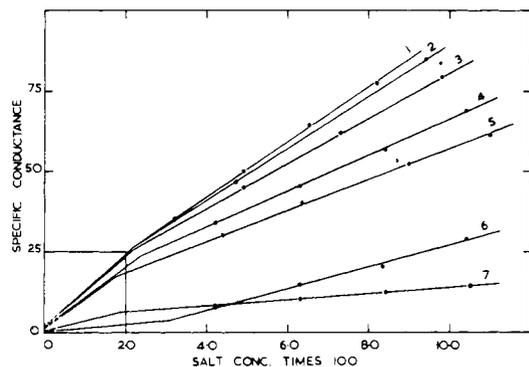
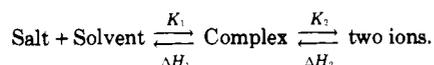


Figure 3. Specific conductance vs. salt concentration at 20° C. for methanol solutions of some alkaline earth salts. The salt represented by each plot is noted in the caption to Figure 1.

found for many salts, may arise from a consecutive reaction, thus:



Here the complex concentration is small and both ions may be solvated in the normal way.  $\Delta H_1 < 0$  and  $\Delta H_2 > 0$ .  $\Delta H$ , calculated from the average  $R$  values, would thus consist of two parts, ( $\Delta H_1$  and  $\Delta H_2$ ). If this occurs the negative  $\Delta H$  values found for methanol solution of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , (this work),  $\text{ZnCl}_2$  (7) and  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  (3) and the constant  $R$  values found for many salts can be understood. Models which assume ionization first, then solvolysis do not predict constant  $R$  values.

The two intersecting straight lines which describe specific conductance-concentration data can be understood assuming that a second consecutive ionization process predominates at low salt concentrations.

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Table III. Average values for  $R$  (= Molar Conductance at 45° C./Molar Conductance at 20° C.) for the indicated salts in methanol

( $\Delta H$  is the heat of ionization calculated with vant Hoff's equation with the assumption that only binary ionizations occur. Square-root-mean-square deviations for  $R$  and  $\Delta H$  are given in brackets)

Salt	$R$	$\Delta H$ (Kcal./Mole)
$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	...	...
$\text{Be}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	$1.220 \pm (0.024)$	$2.94 \pm (0.29)$
$\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$	$1.311 \pm (0.037)$	$4.01 \pm (0.41)$
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	$1.303 \pm (0.006)$	$3.92 \pm (0.07)$
$\text{Ca}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$	$1.282 \pm (0.030)$	$3.68 \pm (0.33)$
$\text{Mg}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}^a$	$1.150 \pm (0.041)$	$2.07 \pm (0.51)$
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	$1.269 \pm (0.018)$	$3.53 \pm (0.21)$
$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	$1.271 \pm (0.027)$	$3.55 \pm (0.31)$
$\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$	$1.315 \pm (0.001)$	$4.05 \pm (0.01)$
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}^b$	$0.745 \pm (0.024)$	$-4.36 \pm (0.47)$
$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$	$1.241 \pm (0.031)$	$3.20 \pm (0.37)$
$\text{Sr}(\text{ClO}_4)_2^a$	$1.259 \pm (0.037)$	$3.41 \pm (0.43)$
$\text{Sr}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}^a$	$1.265 \pm (0.036)$	$3.48 \pm (0.42)$

<sup>a</sup>  $R$  values not independent of salt concentration (see text).

<sup>b</sup> Average of two ratios.

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