Salts of Group IIA Metals Dissolved in Nonaqueous or Mixed Solvents

Conductance of Perchlorates and Nitrates Dissolved Separately in Primary and Secondary Aliphatic Alcohols

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New conductance data are reported for $Ca(ClO_4)_2 \cdot 6H_2O$, $Sr(ClO_4)_2 \cdot 6H_2O$, $Be(NO_3)_2 \cdot 3H_2O$, $Mg(ClO_4)_2 \cdot 6H_2O$, and $Mg(NO_3)_2 \cdot 6H_2O$ dissolved separately in *n*-propyl, isopropyl, *n*-butyl, isobutyl, *n*-amyl, and isoamyl alcohols at 20° and 45° C. For most systems, the ratio of molar conductance at 45° C. to molar conductance at 20° C. is linearly dependent on salt concentration; at both temperatures the plot of specific conductance *vs.* salt concentration is described by two intersecting lines. Plots of the salt concentration at the point of intersection *vs.* the dielectric constant at a fixed temperature for each salt yield a straight line. All data were processed by digital computer with programs which contain the self-judgment principle and allow the experimenter to determine compatibility of his data with a number of equations.

DESAI, NAIK, AND DESAI (*8*) observed that conductance data for chlorides, iodides, and nitrates of the alkali and alkaline earth metals dissolved in *n*-propyl alcohol do not fit the simple Onsager equation. The earlier data of Kraus and Bishop (*11*) for $Mg(NO_3)_2 \cdot 6H_2O$ and $Ca(NO_3)_2$ in *n*-propyl alcohol and *n*-propyl alcohol–water confirm this observation.

Van Rysselberghe *et al.* (*14, 15*) measured the conductance, Λ, 25° C. of $Mg(ClO_4)_2$ and $Ca(ClO_4)_2$ dissolved separately in acetone, nitromethane, and alcohols (methyl, *n*-propyl, and isopropyl). They found that the equation $\Lambda = \Lambda_0 - AC^{0.5}$, described the data for each salt-solvent system, even for relatively high salt concentrations, C. However, they noted that the parameters for this empirical equation are not predicted by the simple Onsager equation.

Lange (*12*) found that data for 560 strong electrolyte systems (which include salts of the alkali and alkaline earth metals dissolved in water, formic acid, acetonitrile, acetic anhydride, acetamide, sulfur dioxide, ammonia, hydrazine, methanol, and ethyl alcohol) fitted the equation, $1 - t_2 = AC^{0.5} + BC + \ldots\ldots$, with $t_2 = \Lambda/\Lambda_0$; A = Debye-Hückel-Onsager coefficient; and $B = -3.0 \times 10^{18}/(DT)^2 + K[(Z_cZ_a) - 1]$. Here D is the static dielectric constant of the solvent at the absolute temperature, T; Z_c and Z_a are the number of unit charges on the cation and anion; and K is a constant characteristic of the solvent.

For $MgCl_2$, $MgBr_2$, and MgI_2 dissolved separately in ethyl alcohol, Dawson and Golben (*2*) reported that the first-stage ionization is essentially complete. As the Kohlrausch plots did not yield straight lines, they suggested that the Debye-Hückel-Onsager equation was sensitive to valence changes. El-Aggan, Bradley, and Wardlaw (*9*) measured the conductance of some metal chlorides dissolved in ethyl alcohol and attributed discrepancies between their data and earlier work (*2*) to contamination of the alcohol by water.

For methanol solutions of some chlorides, nitrates, perchlorates, sulfates, and acetates of Be, Mg, Ca, Sr, and Ba plots of specific conductance *vs.* salt concentration at 20° and 45° C. yielded two intersecting straight lines (*1*). For each salt R (ratio of molar conductance at 45° to molar conductance at 20° C.) and the salt concentration at 20° C., denoted by C, are related thus: $R = R_0 + S.C.$ Usually S is zero, but for $MgSO_4 \cdot 7H_2O$, $BaCl_2 \cdot 2H_2O$,

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$Mg(C_2H_3O_2)_2 \cdot 4H_2O$, $Sr(ClO_4)_2$, and $Sr(ClO_4)_2 \cdot 6H_2O$ the slope is not zero. For $MgSO_4 \cdot 7H_2O$ R is less than unity. Similar results have been reported for nonaqueous solutions of iron-group chlorides, tin chlorides, cadmium salts, and rare earth salts, and these results together with spectral and viscosity data indicate that specific interactions between salt and solvent molecules determine the solution properties to a large degree.

Conductance data are reported for five salts of the alkaline earth metals dissolved separately in each of six aliphatic alcohols.

EXPERIMENTAL

Spectroanalyzed grade isoamyl, *n*-amyl, isobutyl, *n*-butyl, isopropyl, and *n*-propyl alcohols were saturated with Matheson "extra dry" nitrogen immediately before use. Frequent checks performed with an Aerograph Model A-90-P gas chromatograph (firebrick column and He carrier gas) showed less than 0.01% impurity in all solvents.

$Ca(ClO_4)_2 \cdot 6H_2O$, $Sr(ClO_4)_2 \cdot 6H_2O$, and $Mg(ClO_4)_2 \cdot 6H_2O$ were G. F. Smith Chemical Co. reagent grade. Fisher purified grade $Be(NO_3)_2 \cdot 3H_2O$ and reagent grade $Mg(NO_3)_2 \cdot 6H_2O$ were used. Triplicate analyses of the chlorine (*16*) or metal (*16*) showed that the actual and theoretical compositions agreed within 1%. The specific conductances of the pure solvents were measured at each temperature and good agreement with literature values (*10*) was found.

The preparation of solutions has been described (*1*), and Table I gives the concentration ranges over which data were collected at 20° and 45°C. (±0.01°). Electrical resistances were measured with a General Radio Co. impedance bridge (Type 1650A) as described (*1*). Duplicate samples for each salt-solvent system showed that measured values for solutions described as "stable" (Table I) were easily reproduced to within 2.0%, the "preselected limit of reliability" used in the calculations. This value was selected to increase the possibility that the data might fit, at least to this extent, some of the well-known conductance equations. Actual reproducibility for resistance measurements on solutions prepared at different times was between 0.10 and 0.50%. Data for the nine systems in which the measured resistance increased with time were not used in the calculations.

Table I. Experimental Details of Systems Studied

(Within each concentration range were samples of 18 distinct concentrations)

Salt	Alcohol (Solvent)	Salt Concn. Range × 10^4, Moles/Liter
$Ca(ClO_4)_2 \cdot 6H_2O$	Isobutyl	Time effect
	Isopropyl	Time effect
	Isoamyl	1.030–1030
	n-Propyl	1.029–1029
	n-Butyl	1.057–1057
$Sr(ClO_4)_2 \cdot 6H_2O$	*n*-Amyl	Time effect
	Isobutyl	Time effect
	n-Butyl	Time effect
	Isoamyl	Time effect
	n-Propyl	1.131–1131
	Isopropyl	1.030–1030
$Be(NO_3)_2 \cdot 3H_2O$	Isoamyl	1.158–1158
	n-Amyl	1.081–1081
	Isobutyl	1.169–1169
	n-Propyl	1.027–1027
	Isopropyl	1.079–1079
	n-Butyl	1.079–1079
$Mg(ClO_4)_2 \cdot 6H_2O$	Isobutyl	Time effect
	Isoamyl	1.038–1038
	n-Amyl	1.041–1041
	n-Propyl	1.028–1028
	n-Butyl	1.058–1058
	Isopropyl	1.116–1111
$Mg(NO_3)_2 \cdot 6H_2O$	*n*-Amyl	Time effect
	Isobutyl	Time effect
	Isoamyl	1.094–1094
	n-Propyl	1.092–1092
	n-Butyl	1.048–1048
	Isopropyl	1.051–1046

DATA PROCESSING METHOD

All conductance data were processed by a digital computer and new published methods (*5*, *6*). The actual salt concentration in each solution at each temperature is computed from the measured weights and/or volumes of the components and from the densities of solutions or liquid components at temperatures of sample preparation and of conductance measurement. The solutions were assumed to be ideal and densities of the pure solvents were obtained from the literature (*10*). This assumption of additive volumes results in an error of less than 0.35% (*3*).

In the second stage of calculations, the salt concentrations and the specific conductances of the solvent and solution, plus factors, which define the reliability of each item of information, are used to compute the ordinates and the possible error arising from the possible data deviation for each equation to be tested. In the third stage, note is made of data points lying outside the zone of possible ordinate values. Values within the "zone" are used to compute the parameters of the equation and the related maximum possible deviations. Thus compatibility of data with an equation is tested to within preselected limits of experimental error.

In this project data compatibility was checked for seven, two-dimensional conductance equations (*5*):

$$\mu = \mu_0 - (A + B\mu_0)C^{0.5} \qquad (1)$$

$$\mu = A + BC^n \qquad (n \neq 0.5) \qquad (2)$$

$$\log_{10}\mu = A + B\log_{10}C \qquad (3)$$

$$K = A + BC \qquad (4)$$

$$K = A + BC^n \qquad (n \neq 1.0) \qquad (5)$$

$$\log_{10}K = A + B\log_{10}C \qquad (6)$$

$$R = A + BC \qquad (7)$$

where μ = molar conductance, K = specific conductance, C = salt concentration, R = ratio of molar conductance at 45° C. to molar conductance at 20° C., A and B = constants, and n is a specified real number.

RESULTS AND DISCUSSION

In the calculations, only values of the specific conductance more than 100 times the conductance of the pure solvent were used.

The conductance increase with time noted for nine salt-solvent systems (Table I) cannot be attributed to the presence of small undetected amounts of water or other contaminant in the solvent. Similar effects have been observed for $FeCl_3$ in methanol (*13*), where slow methanolysis of $FeCl_3$ yields H^+ and Cl^- and for $MnCl_2 \cdot 4H_2O$ in methanol-CCl_4 mixtures (*4*). In this latter system the rate of conductance increase is not changed by excluding light but is linearly dependent on the area of the platinized-platinum electrodes and the concentration of the salt. The role played by the CCl_4 has not been explained adequately. Information about the electrode surface during the reaction is needed for an adequate explanation of the observed conductance changes with time.

For systems in which the conductance remains unchanged with time, these new data are not compatible (within ± 2%) with Equations 1, 2, 3, 5, and 6. Plots of molar

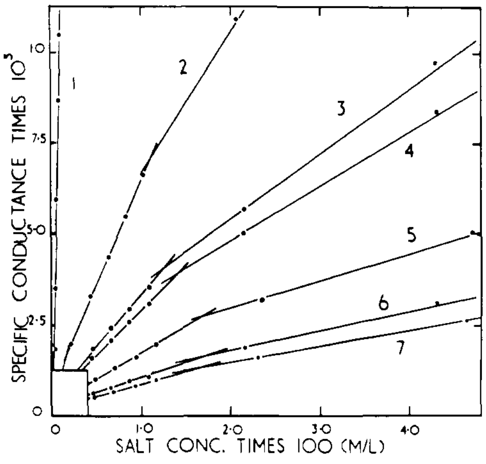

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Figure 1. Specific conductance of $Be(NO_3)_2 \cdot 3H_2O$ dissolved in solvent at 20° C. as a function of salt concentrations

Data points falling in small blank square are "unreliable"

▶

Figure 2. Salt concentrations at point of intersection, C_I, at 20° C. for $Be(NO_3)_2 \cdot 3H_2O$ vs. static dielectric constant of solvent

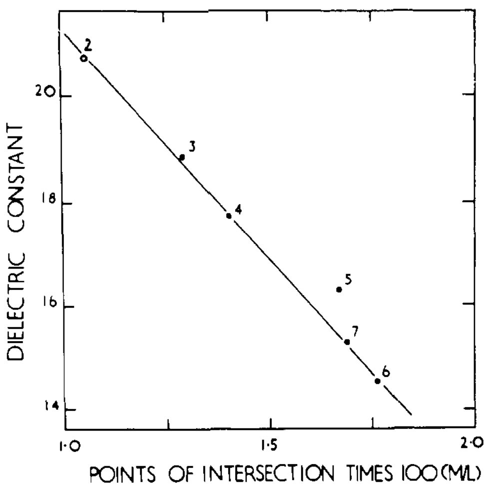

Table II. Intercepts (R_o), Slopes (S), and Maximum Permitted Errors (ΔR_o and ΔS) from Equation: $R = R_o + S \cdot C$

(G_1 = number of data points actually used to compute R_o, ΔR_o, S, and ΔS.
G = number of "reliable" data points remaining after application of instrument reliability factors).

Salt	Alcohol (Solvent)	S	$G_1 - G$	R_o	$\Delta R_o \times 100$	$\Delta S \times 100$
$Ca(ClO_4)_2 \cdot 6H_2O$	*n*-Propyl	0.653	15-18	1.413	10.8	3.762
	n-Butyl	0.446	15-18	1.287	10.1	2.491
	Isoamyl	2.021	5-5	1.079	9.9	11.2
$Sr(ClO_4)_2 \cdot 6H_2O$	*n*-Propyl	0.567	16-18	1.363	10.5	3.286
	Isopropyl	0.245	11-12	1.219	10.0	1.219
$Be(NO_3)_2 \cdot 3H_2O$	*n*-Propyl	1.797	15-18	1.410	10.8	10.3
	Isopropyl	0.930	14-14	1.185	9.9	5.086
	n-Butyl	0.536	15-17	1.247	10.1	2.988
	Isobutyl	2.090	10-10	1.159	9.8	11.6
	n-Amyl	1.802	7-7	1.058	9.7	9.964
	Isoamyl	1.961	5-5	1.076	9.7	11.0
$Mg(ClO_4)_2 \cdot 6H_2O$	*n*-Propyl	1.071	18-18	1.500	11.6	6.199
	Isopropyl	0.734	15-16	1.508	11.7	4.453
	n-Butyl	0.517	16-18	1.451	11.3	3.001
	n-Amyl	1.555	8-8	1.267	10.2	8.532
	Isoamyl	1.500	5-5	1.319	10.2	8.284
$Mg(NO_3)_2 \cdot 6H_2O$	*n*-Propyl	1.426	15-16	1.271	10.2	7.947
	n-Butyl	2.231	15-17	1.183	9.9	12.6
	Isoamyl	2.542	4-4	1.153	9.8	14.2
	Isopropyl	Almost all points were less than 100 times conductance of pure solvent.				

In *n*-amyl and isoamyl alcohol solutions of $Be(NO_3)_2 \cdot 3H_2O$ at 45° C. the lowest three and five data points were rejected by the fail-safe criterion because of increased solvent conductance at the higher temperature.

conductance *vs.* the square root of the salt concentration (Equation 1) showed negative curvature characteristic of weak electrolytes even for the perchlorates which show high conductance. The data are compatible with Equations 4 and 7. Typical plots of the specific conductance *vs.* salt concentration (Equation 4) for different solvents are shown in Figure 1. The parameters for the two linear portions of each plot were computed as described, and then the two equations were solved for the concentration at the intersection point, C_I. In these analyses only one or two of a maximum 18 "reliable" data points were rejected in applications of the self-judgment principle (7). Plots of C_I *vs.* the static dielectric constant of the solvent yielded single straight lines for each salt at each temperature (Figure 2).

Results of the compatibility tests of the data with Equation 7 are summarized in Table II. The linear relations between specific conductance (Equation 4) or molar conductance ratio (Equation 7) and salt concentration appear to describe virtually all conductance data for related systems, as noted in the literature. These relations are not predicted by equations derived with the basic assumption that average solvent properties (viscosity and dielectric constant) principally determine the ionic properties of a solution. The linear relation (Figure 2) between C_I and the solvent static dielectric constant suggests that specific interactions between solvent molecules themselves, or with un-ionized salt molecules, are of importance in ionization processes.

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Stabilization of Monoethanolamine Solutions in Carbon Dioxide Scrubbers

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Monoethanolamine (MEA), the regenerative absorbent used in CO_2 scrubbers aboard nuclear submarines, is now stabilized with a chelating agent, the monosodium salt of *N,N*-diethanolglycine (VFS). This inhibitor is not effective against oxidative degradation at 55° C. in the presence of procatalytic metals, particularly copper. Effective stabilization in the presence of copper is given by tetrasodium (ethylenedinitrilo)tetraacetate (EDTA). At 98° C., with small quantities of typical metal contaminants added, both VFS and EDTA are required for stabilization. The additive combination is ineffective at 138° and 149° C. with limited amounts of oxygen present. Pyrolytic stability of the formulation is adequate at these temperatures. VFS and EDTA are both true antioxidants for MEA in their own right. Their reactivity with peroxides, and their prevention of peroxide formation in oxidized MEA, suggest that their antioxidant activity results from an ability to interrupt an autocatalytic oxidation chain reaction. Less efficient additives did not prevent peroxide formation in MEA.

AN IMPORTANT specialized use of the regenerative absorbent monoethanolamine (MEA) is in carbon dioxide scrubbers for atmosphere purification aboard nuclear-powered submarines. The present study summarizes the factors influencing MEA degradation under conditions of submarine service, and the beneficial effect of certain chelate formers in reducing such degradation. Pertinent chemical properties of MEA have been reviewed (*4*).

On the assumption that metal contaminants, particularly iron, catalyzed oxidative breakdown of MEA, a chelating agent, the monosodium salt of *N,N*-diethanolglycine (*2*) (VFS), is now a required constituent of base stock MEA procured for submarine scrubber use (*3*).

EXPERIMENTAL

In service, scrubber solutions are in contact with stainless steel, and are exposed to temperatures from about 32° C. in the absorber to 138° C. in the stripper, and possibly 150° C. in contact with the stripper heaters. Experiments simulated a variety of conditions. Most of the aeration tests were conducted in glass cells at 55° C., permitting convenient measurement of the reaction products. At temperatures much above 55° C. corrosive attack on glassware was excessive, so stainless steel (Type 304) was employed. All cells were fitted with standard taper joints to accept water-cooled reflux condensers. The rate of air through the 300-ml. samples was 1 cc. per ml. of solution per minute. Ammonia evolution was monitored by passing the effluent air through 2% boric acid solutions, which were periodically titrated with strong acid. Total nitrogen was determined by Kjeldahl analysis, and peroxides by the iodine-thiosulfate method. All MEA used was redistilled and stored at 5° C. in evacuated sealed vials.

EFFECT OF AIR AND CARBON DIOXIDE

Carbon dioxide-free air passed through 4*N* MEA solutions at 55° C. for several days produced no perceptible degradation. Addition of 1% CO_2 to the air stream to simulate submarine atmospheric conditions, however, resulted in almost instantaneous degradation characterized by the production of ammonia and peroxide (Figure 1, *A*), the conversion of amine nitrogen to nonbasic forms (possibly cyclic condensation products) as shown in Figure 2, and gross discoloration of the fluid. All further references to MEA in this study imply the carbonated form unless otherwise indicated.

EFFECT OF VFS (NO METALS PRESENT)

Aeration-oxidation experiments at 55° C. with metal-free MEA solutions containing 1.5% VFS revealed no degradation during a 6-week period, indicating that the chelate was an efficient antioxidant in its own right—i.e., it plays a role in which metal deactivation has no part. The long useful life of the amine containing VFS also strongly suggests that VFS is not functioning as a short-term sacrificial additive.

VFS-PEROXIDE REACTION

Air oxidation of many compounds proceeds autocatalytically by a sequence of free radical reactions characterized by the initial formation of peroxides. Efficient antioxidants for such systems function by reacting with, and destroying, the peroxide intermediate, thus interrupting the reaction chain. The presence of peroxides in oxidized MEA solutions