Electrical Conductance and Viscosity of the Solvent System $MnSO_4$ in Water–Glycol at 25°[1a]

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Abstract: Measurements of electrical conductance at 25.00° of $MnSO_4$ in mixtures of H_2O–ethylene glycol up to 77 wt % of glycol are presented. The data have been analyzed by the Fuoss–Onsager theory as well as by a revised form of this theory. The two equations give reasonable fitting with consistent results for the association constants and limiting conductivity. Correlations between the thermodynamic parameters K_A, the hydrodynamic radii, and the dielectric constant of the solvent give reasonable values for the collision constant a. The sphere in a continuum model and the Fuoss–Onsager theory give a satisfactory description of the conductance of these highly viscous systems.

Transport theories like electrical conductance have been treated largely as functions of the dielectric constant for 1:1[2] and 2:2 electrolytes.[3] Very few data appear in the literature for the viscosity effect on conductance. Tests of the current theories for 1:1 electrolytes like KCl,[4a] Et_4N picrate,[4b] and Bu_4NBr[5] have been given very good results in a range of viscosity up to 10 poises. These studies are important because hydrodynamic and thermodynamic information is obtained through the ionic mobilities and the association constants. There is another basic aspect of interest. During the association process, according to Eigen,[6] the ions go through a diffusion-controlled process during their approach followed by desolvation of the ions. The first step of the association should then be viscosity dependent. This has been proven for $MgSO_4$[7] and $ZnSO_4$[8] in H_2O–glycol. To the authors' knowledge, no conductance data exist for polyvalent electrolytes in solvents of high viscosity besides some old measurements of James.[9]

In order to study the transport properties of highly charged electrolytes in viscous solvents, measurements of electrical conductance of $MnSO_4$ in H_2O–glycol at 25° have been made in this laboratory and are presented here.

Experimental Section

Materials. Water used for conductance was deionized water purified by passing it through a double Barnstead ion-exchange column (organic material exchange and mixed cation–anion exchange). The conductance of this water was monitored by measuring the conductance during the collection. The value was $<1 \times 10^{-6}$ ohm^{-1} cm^{-1} at room temperature.

KCl used for the cell calibration was reagent grade and was recrystallized three times from conductance water. It was then dried *in vacuo* at 200° (10^{-2} mm) for more than 1 week.

$MnSO_4$ was Baker reagent. It was recrystallized twice from conductance water and dried at 105° to the crystal form $MnSO_4 \cdot H_2O$.

Ethylene glycol (Fisher Reagent) was distilled under vacuum at 1–3 mm in an all-glass apparatus, collecting only the central portion.

Preparation of the Solutions. The solvent mixtures were prepared by weight and divided into two portions, one to prepare a 10^{-2} *M* stock solution of $MnSO_4$ and the other to fill the conductance cell. The stock solution was prepared by weight from $MnSO_4 \cdot H_2O$ and the prepared solvent. Its concentration was determined by cation exchange followed by analysis of the acid by tham[10] solutions. In order to improve the precision of the analysis, microburets were used and pH determination by a Leeds and Northrup pH meter (Model 7405) was performed. The pH meter had an expandable scale that allowed a precision of pH reading of $\pm 5 \times 10^{-3}$ pH unit. In this way a precision of ±0.05% between duplicate runs was obtained in the analysis of the stock solution.

The stock solution of $MnSO_4$ was syphoned into a weight buret and added to the solvent in the conductance cell after thermal equilibration of the solvent and determination of its resistance. "Concentration" runs were therefore performed. Generally the chosen concentrations went from 2–3 $\times 10^{-4}$ to 30–60 $\times 10^{-4}$ *M*. For each run from five to seven successive concentrations were prepared and their electrical resistance measured. The weight buret was weighed on a Mettler H6 balance to within ±0.1 mg.

Equipment. The conductance cell was of the erlenmeyer type with lightly platinized electrodes. The cell constant was slightly dependent upon the specific conductivity of the solution and was determined by measurements with aqueous KCl solutions using the equation of Fuoss, *et at.*,[11] for the calibration. The cell constant values were expressible by the equation $K = 0.1790 + 4X_s$, where X_s is the specific conductivity of the solution. The individual values are presented in Table I.

Table I

C_{KCl}, $M \times 10^4$	K, cm^{-1}
2.8047	0.17898
5.7615	0.17914
10.256	0.17928
17.935	0.17969
22.277	0.17976
32.777	0.18007
42.090	0.18038

The bridge was a General Radio Type 1605-AS5 impedance comparator with a bridge arm constructed according to Janz.[12]

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[1] (a) This work is part of the thesis of Paul Hemmes in partial fulfillment of the requirements of the degree of Doctor of Philosophy; (b) National Science Foundation Kirk Fellow of the Polytechnic Institute of Brooklyn; (c) on leave of absence from the University of Rome.

[2] J. E. Lind and R. M. Fuoss, *J. Phys. Chem.*, **65**, 999 (1961).

[3] G. Atkinson, *et al.*, *J. Am. Chem. Soc.*, **83**, 1570, 3759 (1961); **84**, 721 (1962); **86**, 7 (1964).

[4] (a) F. Accascina and S. Petrucci, *Ric. Sci.*, **29**, 1640 (1959); **30**, 808 (1960); (b) *ibid.*, 30, 1164 (1960).

[5] F. Accascina, A. D'Aprano, and M. Goffredi, *ibid.*, **34**, 63, 151, 433 (1964).

[6] M. Eigen and L. DeMaeyer in "Techniques of Organic Chemistry," Vol. VIII, Part II, A. Weissberger, Ed., John Wiley and Sons, Inc., New York, N. Y., 1963.

[7] S. Petrucci, *J. Phys. Chem.*, 71, 1174 (1967).

[8] F. Fittipaldi and S. Petrucci, *ibid.*, 71, 3414 (1967).

[9] J. C. James, *J. Chem. Soc.*, 153 (1951).

[10] L. Meites, "Handbook for Analytical Chemistry," McGraw-Hill Book Co., Inc., New York, N.Y., 1963, p 334.

[11] J. E. Lind, J. J. Zwolenic, and R. M. Fuoss, *J. Am. Chem. Soc.*, **81**, 1557 (1959).

The addition of a 0.01-ohm decade resistor was made to improve the zero reading. The bridge assembly could reach a $\Delta R/R = 0.01\%$ or less.

The four-leads technique was used[12] to eliminate lead resistances. The thermostat was a 15-gal tank of oil stirred by an induction motor using a Bailey proportional thermoregulator (Model 124) with an infrared lamp as a heating device. This lamp was kept outside the tank to avoid overheating effects due to thermal inertia. Cooling water was provided by a Forma (Model 2095-2) cooling bath system kept at 22 ± 0.1°. The room was thermoregulated at 22 ± 1° and humidity controlled. In this way a precision of 25.00 ± 0.01° was obtained in the temperature during the runs.

The temperature was measured by a Mueller bridge (Leeds and Northrup) with a platinum thermometer as a sensor device. The calibration of the Pt thermometer was made by the National Bureau of Standards with a certified table.

The zero readings of the Mueller bridge were made by an electronic galvanometer (Leeds and Northrup) as a suspended mirror-galvanometer was judged unsuitable because of existing vibrations in the building. In this way an accuracy of ±0.005° was obtainable in the temperature readings.

The solution in the cell was magnetically stirred at a rate of 1-2 revolutions per second. The entire assembly was hooked to a common ground.

Measurements of resistance were made at 1000, 2000, 5000, and 20,000 cps (after thermal equilibration and constancy of the resistance within ±0.01% for at least 0.5 hr). Plots of R *vs.* f for the solvent and R *vs.* $1/\sqrt{f}$ for the solutions were constructed giving generally linear plots. For the solution the percentage change ($\Delta R/R\%$) with the frequency was within 0.1% in the range 10,000–300 ohms.

Results

Table II contains the results for concentration c of $MnSO_4$ (moles/l.) and equivalent conductance Λ (ohm^{-1} cm^2 $equiv^{-1}$) for the systems investigated; X_{glycol} means the mole fraction of glycol. At least one decimal figure in excess of the one allowed by the sensitivity of the method is reported in order to avoid round-off errors in future recalculations by others from these data.

Table II also contains the interpolated values of density, dielectric constant D, and viscosity η from the literature values.[13] The concentration data reported with an asterisk are above the range $\kappa a = 0.2$ (with $a = 5$ A), that is, above the range where the theory should be valid.[14]

Discussion

The Conductance Equations. The conductance data have been analyzed by the "1959" equation for associated electrolytes[14]

$$\Lambda = \Lambda_0 - S\sqrt{c\gamma} + Ec\gamma \log c\gamma + Jc\gamma - K_A c\gamma f_\pm^2\Lambda \tag{I}$$

by a 7090/7094 IBM computer program.

Equation I is a three-parameter equation in Λ_0, the equivalent conductance at infinite dilution, J, the coefficient of the linear term, and K_A, the association constant. The other symbols in eq I are the same as used by Fuoss in his monograph[14] adapted properly to 2:2 electrolytes by the introduction of the valencies Z^+ and Z^-.

Table II. Conductance Results at 25° of $MnSO_4$ in Water–Glycol Mixtures

10^4c^a	Λ
$X_{glycol} = 0.00$, $\rho = 0.9970_7$ g/cc, $D = 78.54$, $\eta = 0.0089_1$ poise	
2.7577	121.03
7.4441	111.74
10.855	107.34
14.780	103.27
22.353	97.34_0
$X_{glycol} = 0.0991$, $\rho = 1.0328$ g/cc, $D = 71.25$, $\eta = 0.0170$ poise Glycol = 27.26 wt %	
2.7833	62.51_3
6.2094	57.90_9
10.877	53.64_9
16.188	50.30_4
22.405	47.75_5
37.254	43.13_0
54.983*	39.69_5
$X_{glycol} = 0.2993$, $\rho = 1.0732$ g/cc, $D = 60.7$, $\eta = 0.0407$ poise, Glycol = 59.51 wt %	
4.1954	21.32_7
9.1409	18.35_2
17.555	15.64_1
25.909	14.14_6
39.740*	12.60_3
50.097*	11.82_2
71.565*	10.70_6
$X_{glycol} = 0.4990$, $\rho = 1.0924$ g/cc, $D = 53.1$, $\eta = 0.0725$ poise, Glycol = 77.43 wt %	
3.0373	10.088
5.8293	8.451
10.188	7.165
15.642	6.273
20.740	5.736
28.309	5.190

[a] An asterisk designates that the value is above the range $\kappa a = 0.2$; see text.

The various coefficients then read for symmetrical electrolytes where $|Z_+| = |Z_-| = |Z| = Z$

$$S = a\Lambda_0 + \beta = \frac{0.8204 \times 10^6}{(DT)^{3/2}} Z^3\Lambda_0 + \frac{82.50}{\eta(DT)^{1/2}} Z^2$$

$$E = E_1\Lambda_0 - E_2 = \frac{6.7747 \times 10^{12}}{(DT)^3} Z^6\Lambda_0 - \frac{0.9977 \times 10^8}{\eta(DT)^2} Z^5$$

$$J = \sigma_1\Lambda_0 + \sigma_2 =$$

$$\left\{\frac{5.8844}{(DT)^3} \times 10^{12} Z^6 \left[h(b) + 0.9074 + \ln\left(\frac{\kappa a}{C^{1/2}}\right)\right]\right\} \Lambda_0 + \left[\frac{0.67683 \times 10^8}{\eta(DT)^2} Z^5 + \frac{0.38035 \times 10^{12}}{\eta(DT)} Z^3 a - \frac{0.86658 \times 10^8}{\eta(DT)^2} Z^5 \left(1.0170 + \ln \frac{\kappa a}{C^{1/2}}\right)\right]$$

where

$$h(b) = (2b^2 + 2b - 1)/b^3$$

$$b = \frac{16.708 \times 10^{-4}}{aDT} Z^2$$

$$\kappa = \frac{0.50294 \times 10^{10}}{(DT)^{1/2}} Z\sqrt{c}$$

$$-\log f_\pm^2 = \frac{3.6494 \times 10^6 Z^3\sqrt{c\gamma}}{(DT)^{3/2}(1 + \kappa a\gamma^{1/2})}$$

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(12) G. J. Janz and J. D. E. McIntyre, *J. Electrochem. Soc.*, **108**, 272 (1961).

(13) F. Accascina and S. Petrucci, *Sci. Tec.*, 3, 242 (1959).

(14) R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience Publishers, Inc., New York, N. Y., 1959.

Table III

X_{glycol}	1959 Fuoss equation[14] Λ_0	a_J	K_A	$\overline{\Delta\Lambda}$	1965 Fuoss equation[15] Λ_0	$a_{(L_2)}$	K_A	$\overline{\Delta\Lambda}$
0.00	133.54	5.1	146	0.113	133.51	4.3	136	0.108
0.10	71.16	5.8	280	0.216	71.14	4.6	260	0.150
0.30	28.58	4.9	854	0.268	28.62	3.9	844	0.069
0.50	17.00	6.4	4300	0.004	17.00	4.6	4230	0.008

Table III contains the results of the application of these data to eq I in terms of the parameters Λ_0, a_J, and K_A where a_J is the collision distance calculated from J.[14] The standard deviation $\overline{\Delta\Lambda}$ calculated from the differences $|\Lambda_{\text{calcd}} - \Lambda_{\text{measd}}|$ are also in Table III.

A similar calculation has been made using the 1965 version of the Fuoss-Onsager theory[15] which retains the full exponential term in the relaxation of the ionic atmospheric effects. These results are also tabulated in Table III.

The 1965 equation by Fuoss and Onsager does offer some better fitting than the 1959 equation ($\Delta\Lambda$, smaller and slightly more consistent a's). It was predicted[15] that at low dielectric constants the 1965 equation would give more consistent results. (Notice that for 2:2 electrolytes the dielectric constant is effectively reduced by a factor of 4 with respect to the predictions of Fuoss for 1:1 electrolytes.)

Thermodynamic Considerations. The Association Constant

In order to correlate the results of the association constants, the Fuoss equation[14,16] has been considered

$$K_A = \frac{4\pi N a^3}{3000}\exp\left(\frac{|Z_+Z_-|e_0^2}{aDkT}\right) \qquad \text{(II)}$$

where N is the Avogadro number, a is the collision distance, Z_+ and Z_- are the valencies of the two ions, e_0 is the electronic charge, D is the dielectric constant, k is the Boltzmann constant, and T is the absolute temperature. Examination of this equation and of its derivation[14,16] shows that it is composed of two factors, the preexponential term $K_0 = 4\pi N a^3/3000$, and the exponential term exp(b) with b the Bjerrum ratio $b = |Z_+Z_-|e_0^2/aDkT$. If the ions would be uncharged then $K_A = K_0$; therefore, K_0 is the association constant calculated on simply mechanistic grounds and was called the geometrical factor.[16] It should be noted that K_0 and exp(b) are mathematically in competition in terms of the parameter a. In fact K_0 increases with a and exp(b) decreases with increasing a. The product of the two functions passes through a minimum by increasing a.

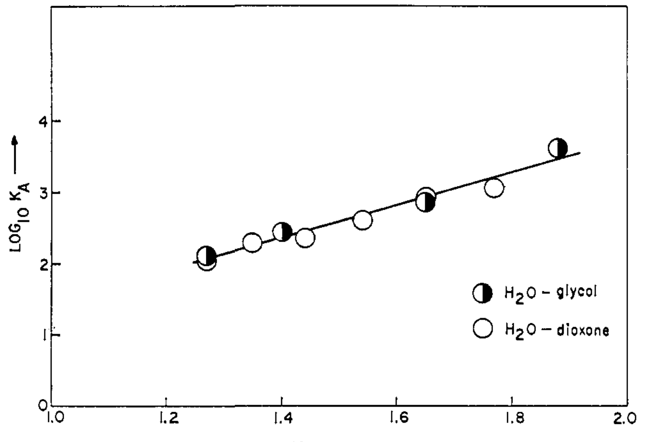

Figure 1. Plot of log K_A vs. $10^2/D$ for $MnSO_4$ in H_2O-glycol and H_2O-dioxane at 25°.

In Figure 1, log K_A is reported vs. $1/D$. From the slope of this graph the value of a can be calculated according to eq II. The value $a = (4.6 \pm 0.5) \times 10^{-8}$ cm is in fair accord with the average $a(L_2) = (4.4 \times 10^{-8}$ cm).[15] L_2 is the a dependent part of the L coefficient in the 1965 Fuoss-Onsager equation.[15] In Figure 1 the results of log K_A vs. $1/D$ are also reported for $MnSO_4$ in H_2O-dioxane.[3] These data lie on the same line (within experimental error) as the H_2O-glycol data.

The lack of specificity of behavior of the association of $MnSO_4$ in H_2O-glycol and in H_2O-dioxane suggests the predictions of the "ideality" of the thermodynamic properties of the above systems. This behavior is confirmed by measurements of ultrasonic absorption and its frequency dependence.[8]

Hydrodynamic Considerations. Ion-Solvent Relaxation Effects. In Figure 2, the "Walden rule" $\Lambda_0\eta$ is reported as a function of dielectric constant of the solvent. The behavior is ideal, within experimental error, since a horizontal line describes the data.

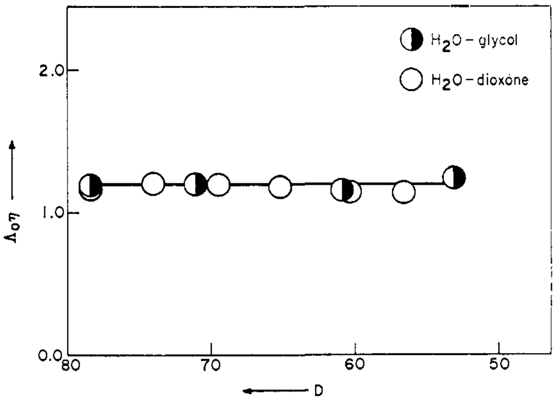

Figure 2. Plot of $\Lambda_0\eta$ vs. D for $MnSO_4$ in H_2O-glycol and in H_2O-dioxane at 25°.

The $MnSO_4$-H_2O-dioxane system[3] is identical in behavior. A calculation of the hydrodynamic radii

$$R_+ = \frac{F|Z_+|e_0}{6\pi n\lambda_0^+},\ R_- = \frac{F|Z_-|e_0}{6\pi\eta\lambda_0^-} \qquad \text{(III)}$$

has been tried. To calculate λ_0^+ and λ_0^- the value of

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(15) R. M. Fuoss and L. Onsager, *J. Phys. Chem.*, **69**, 2581 (1965).
(16) R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).

λ_0^- in water as $\lambda_0^- = 80.0$ has been taken. From $\Lambda_0 = 133.51$ one gets for the transport number at infinite dilution, $n_+^0 = 0.401$. Assuming n_+^0 to remain constant with glycol composition in the glycol mixtures, R_+ and R_- could be calculated.

The semiempirical equations

$$\begin{aligned} R_+D &= A + (R_+)_\infty D \\ R_-D &= A^1 + (R_-)_\infty D \end{aligned} \qquad \text{(IV)}$$

of Fuoss[17] (expressing the relaxation of the solvent dipoles orientation upon the passage of the ions) have been applied in Figure 3 for $MnSO_4$ with H_2O-glycol and H_2O-dioxane[3] where the products R_+D and R_-D are reported *vs.* D. The slopes give $(R_+)_\infty = 3.35 \times 10^{-8}$ cm and $(R_-)_\infty = 2.35 \times 10^{-8}$ cm, the hydrodynamic radii in a medium of infinite dielectric constant. In this medium no ion-solvent interaction could exist; therefore

$$(R_+)_\infty + (R_-)_\infty = a_\Lambda = 5.7 \times 10^{-8} \text{ cm}$$

in fair accord with $a_K = 4.6 \times 10^{-8}$ cm and $a(L_2) = (4.4 \pm 0.2) \times 10^{-8}$ cm.

Conclusion

The parameter a has been calculated through the interaction terms J[14] and L_2,[15] through the association constant K_A and the hydrodynamic radii, giving a consistent value (a_J having the most scattering as predicted) for two different solvent systems like H_2O-dioxane and H_2O-glycol. The viscosity and the dielectric constant of the solvent seem to suffice to describe the hydrodynamic and electrostatic properties of the above systems.

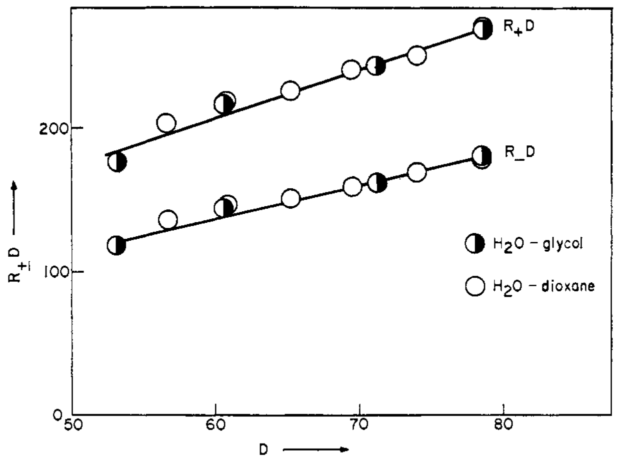

Figure 3. Plot of $R_\pm D$ *vs.* D for $MnSO_4$ in H_2O-glycol and in H_2O-dioxane at 25°.

The validity of formulas II and IV and the satisfactory fitting of the conductance equations to the conductance data lead to the conclusion that the sphere in a continuum model and the Fuoss-Onsager theory[14] hold physically and mathematically for these systems.

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[17] R. M. Fuoss, *Proc. Natl. Acad. Sci. U. S.*, **45**, 807 (1959).

The Hydrolytic Polymerization of Ferric Citrate. I. The Chemistry of the Polymer

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Abstract: The chemistry of ferric citrate at equal molar concentrations of iron and citrate has been examined by a variety of techniques including ultraviolet and visible spectrophotometry, glass-electrode measurements, and equilibrium dialysis. On titration with base, an anionic chelate, $FeCit^-$, is formed at low pH and then polymerizes in a buffer region at pH 8-9, which terminates at 3 base equiv per mole of iron. About 85% of the citrate dissociates from the polymer in the process. The polymer was isolated using the techniques of gel and membrane filtration. Electron microscopy shows the polymer particles to be spherical, with a diameter of 72 ± 9 A. Its molecular weight determined by its volume and density measurements is $2.1 \pm 0.1 \times 10^5$. The spheres appear to consist of an iron hydroxide core with citrate ions bound to the surface. The polymer may be a good model for the iron storage protein, ferritin.

Recently we have shown that the hydrolysis of ferric ion can lead to the formation of a high molecular weight soluble polymer.[2,3] This polymer has a molecular weight of approximately 1.5×10^5 and contains about 1200 iron atoms linked by hydroxy and oxy

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[1] (a) Princeton University. (b) Research Career Development Awardee, U. S. Public Health Service.

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[3] S. E. Allerton, J. Renner, S. Colt, and P. Saltman, *ibid.*, **88**, 3147 (1966).