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Permalink
https://escholarship.org/uc/item/7x96208b

Journal
Journal of the Electrochemical Society, 140(8)

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Publication Date
1992-08-01

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials Sciences Division

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ABSTRACT

The restricted diffusion method was used to measure the differential diffusion coefficient of sulfuric acid in water at 25°C for the concentration range from 0.3 to 7.5 molar. The concentration gradients of diffusing species were observed by Rayleigh interferometry. Experimental transport data are analyzed with concentrated solution theory of electrolytes in order to elucidate macroscopic transport characteristics of sulfuric acid in terms of specific binary interactions in solution. Results indicate that the transport properties of sulfuric acid are determined by the hydrogen ion-water molecule interaction.

Introduction

Aqueous sulfuric acid is an economically important chemical reagent. It is one of the largest volume chemical commodities, finding uses in fertilizer production, petroleum refining, extraction of metals from their ores, production of inorganic pigments, pickling of iron and steel, synthesis of surface–active agents, and as a reactant in the lead-acid storage battery.

Recently, Armenta-Deu et al.[1] measured the diffusion coefficient of sulfuric acid at high concentration in order to improve the performance of the lead-acid battery. They determined the diffusion coefficient of sulfuric acid by using a rectangular tank to check the concentrations at different depths with time. Their measurements lacked accuracy and reproducibility. On the other hand, Leaist measured the diffusion coefficient in dilute concentrations by the conductometric method.[2] Savino and Vitagliano measured the diffusion coefficient up to 4.8 M by Gouy interferometry.[3] Tiedemann and Newman treated the transient

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discharge behavior of a lead-acid cell mathematically.[4] In the field of concentrated solutions, Newman, Bennion, and Tobias developed mass–transport theory.[5] And Newman and Chapman showed accuracy and repeatability between measurements and theory by using Rayleigh interferometry in a stagnant diffusion cell.[6] Nisancioglu and Newman successfully measured the diffusion coefficient of nitric acid over a wide range of concentration with an error of 0.2 % using the same optical method.[7]

We report the results of measuring diffusion coefficients of sulfuric acid up to 7.5 molar concentration by an optical method and discuss the transport properties of sulfuric acid.

Theory

Mass transport in concentrated solution.——— A generalized description of transport in concentrated electrolytic solutions can be given by a set of flux equations of the form

$$c_i \nabla \mu_i = \sum_{j \neq i} K_{ij} (v_j - v_i) = RT \sum_{j \neq i} \frac{c_i c_j}{c_T \mathcal{D}_{ij}} (v_j - v_i), \qquad (1)$$

where μ_i is the electrochemical potential of species i and $\mathcal{D}_{ij}$ are the fundamental binary transport coefficients defined by these equations. Eq.1 may be regarded as a force balance between the driving force $c_i \nabla \mu_i$ acting on species i and the opposite drag exerted by species j on i. It is also consistent with the principles of irreversible thermodynamics. Further discussion is given by Newman *et al.*,[5] Newman,[8] Chapman,[9] and Newman and Chapman.[6]

Eq.1 can be inverted to obtain explicit expressions for the fluxes in a binary system, thus defining a thermodynamic diffusion coefficient $\mathcal{D}$

$$\mathcal{D} = \frac{\mathcal{D}_{0+} \mathcal{D}_{0-} (z_+ - z_-)}{z_+ \mathcal{D}_{0+} - z_- \mathcal{D}_{0-}}, \qquad (2)$$

which is related to the normally measured differential diffusion coefficient by

$$D = \mathcal{D} \frac{c_T}{c_0} \left(1 + \frac{d \ln \gamma}{d \ln m} \right), \qquad (3)$$

where γ is the mean molal activity coefficient and m is the molality. The quantity D is the diffusion coefficient that is directly measurable by the restricted diffusion method. Another property, which can be measured independently by experiment, is the transference number

$$t_+^0 = 1 - t_-^0 = \frac{z_+ \mathcal{D}_{0+}}{z_+ \mathcal{D}_{0+} - z_- \mathcal{D}_{0-}}, \tag{4}$$

where the superscript ^{0} denotes reference to the solvent velocity. Finally, the solution conductivity, κ, is related to the binary coefficients $\mathcal{D}_{ij}$ by the equation

$$\frac{1}{\kappa} = -\frac{RT}{c_T z_+ z_- F^2} \left(\frac{1}{\mathcal{D}_{+-}} + \frac{c_0 t_-^0}{c_+ \mathcal{D}_{0-}} \right). \tag{5}$$

In a completely dissociated solution, ion-ion and ion-solvent interactions of the binary type will be dominant in determining the macroscopic characteristics of transport even at high concentrations. The binary coefficients $\mathcal{D}_{ij}$ are of fundamental and physical importance in forecasting the quantitative aspects of ionic transport in electrolytic solutions, whereas the measured quantities D, t_+^0, and κ are complicated, as can be inferred from Eq.3 to Eq.5, by a combination of different binary interactions and depend on the equilibrium properties of the system.

Experimental method

Model of restricted diffusion.——— Restricted diffusion refers to diffusion in a vertical cell closed at both ends as shown in Figure 1. Accurate binary coefficients can be measured by observing isothermal diffusion in such a cell at long times. Newman and Chapman[6] treated the decay of a one-dimensional concentration gradient at large times in a column of solution of height a, which is shown in Figure 1. An important result of that analysis is
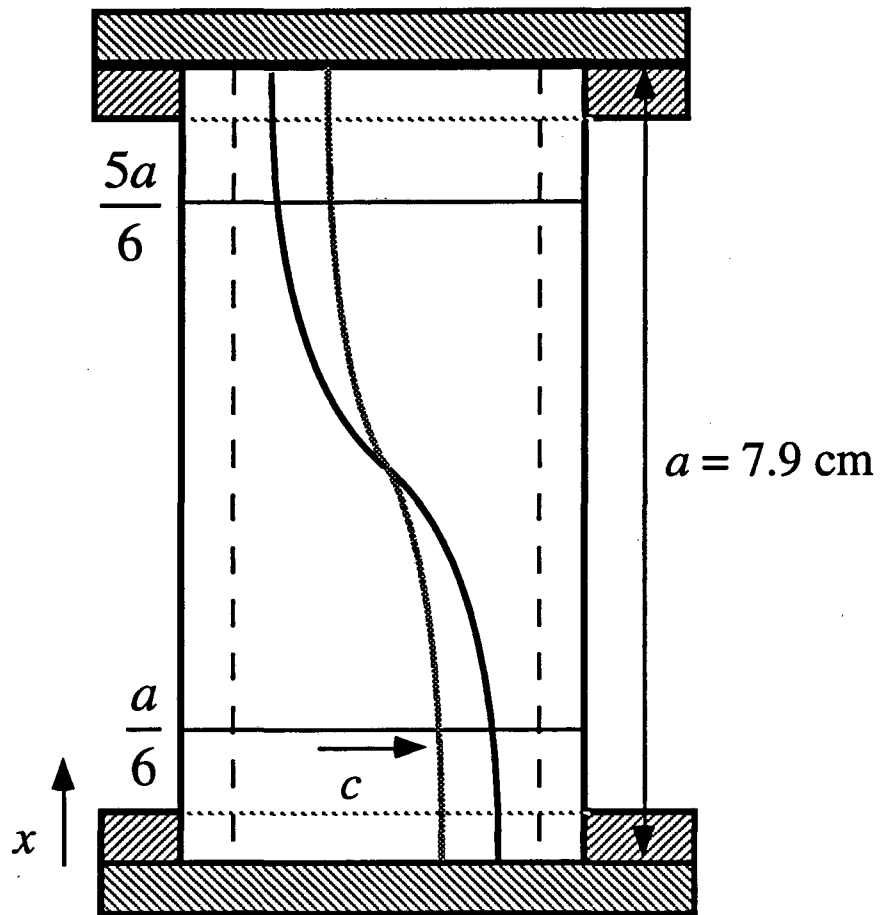
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Figure 1. Sketch of the optical diffusion cell.
The cell was made of quartz and immersed in a
temperature controlled water bath that was filled
with 30% ethylene glycol solution.

$$\Delta c = c\left(\frac{a}{6}\right) - c\left(\frac{5a}{6}\right) = \sqrt{3}A_1 e^{-Dt(\pi/a)^2} + A_2 e^{-3Dt(\pi/a)^2} + \cdots , \quad (6)$$

where Δc is measured between points one-sixth of the overall length from each end of the liquid column. The coefficients A_1 and A_2 depend on initial conditions, and A_2 is also a function of the concentration derivatives of solution properties. The column height, a, actually varies over the period of diffusion because of changing volume on mixing. Newman and Chapman[6] and Chapman[9] have shown that this variation is in effect negligible and that the column height can be taken to be the same as the length of the diffusion cell.

At sufficiently large times, the higher order exponential terms in Eq.6 become negligible as compared to the first term, and an experimental plot of $\ln(\Delta c)$ versus time is linear with a slope of $-D\pi^2/a^2$. Figure 3 shows such a plot for sulfuric acid. The concentration difference Δc was measured by Rayleigh interferometry. This technique serves to record the refractive–index profile along the liquid column at a given time in the form of interference fringes. Since the refractive index varies linearly with concentration over a small concentration range, the displacement (Δ) of a fringe on the photograph is proportional to Δc for a small concentration gradient.

The measurements of fringe displacements were made when Δc was about 0.5 molar or less. At larger concentration differences, the bending fringes are too close together to be measured on the picture. Initially, the boundaries were formed for Δc values in the range one-half to one molar; with higher density differences it is easier to form a sharp boundary, and the system stabilizes faster against convection, vibration, or any other disturbances caused during the preparation stage. The decay of this boundary required one to five days before Δc could be measured. Such time lapse was necessary to ensure that higher order terms in Eq.6 had become negligible before measurements were made.

Materials.—— Baker analyzed sulfuric acid was used without further purification. Stock solutions of acid were made up from deionized, doubly-distilled water. At the end of a

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diffusion run, the concentration was determined by using titration with standardized 0.1 N NaCl solution to the phenolphthalein end point.

Experimental apparatus.——— A schematic of the experimental apparatus is shown in Figure 2. Diffusion experiments were performed on a Perkin-Elmer Model 238 Electrophoresis Apparatus. This apparatus embodies an optical chamber and camera. The bath is constructed so that the diffusion cell can be mounted in alignment with the optical path. It is equipped with a centrifugal pump to stir the bath fluid and a cooling plate connected to an air–cooled refrigeration system. We added a 160-watt bayonet heater and a YSI temperature probe Model 404, both attached to a YSI Model 72 proportional temperature controller. The bath temperature was read on a mercury thermometer. The controller system regulated the bath at 25.0±0.1°C. The mercury–vapor lamp emits a monochromatic light beam of wavelength 546.1 nm. A multipoint source slit is positioned in front of the lamp in order to intensify and space the interference patterns equally. The converging lens projects the beam through the solution and reference components of the cell. The interference patterns formed by two slits placed behind the cell are focused on the screen and spread along a horizontal line.

Typical fringe displacement data are shown in Figure 3. The fringe displacement data were fitted to a straight line, and the mean standard deviation of experimental points from a fitted line gives an estimate of the error associated with each diffusion coefficient. However, this estimate does not include any errors belonging to measurement of concentration at the end of the diffusion run or of the height of the cell.
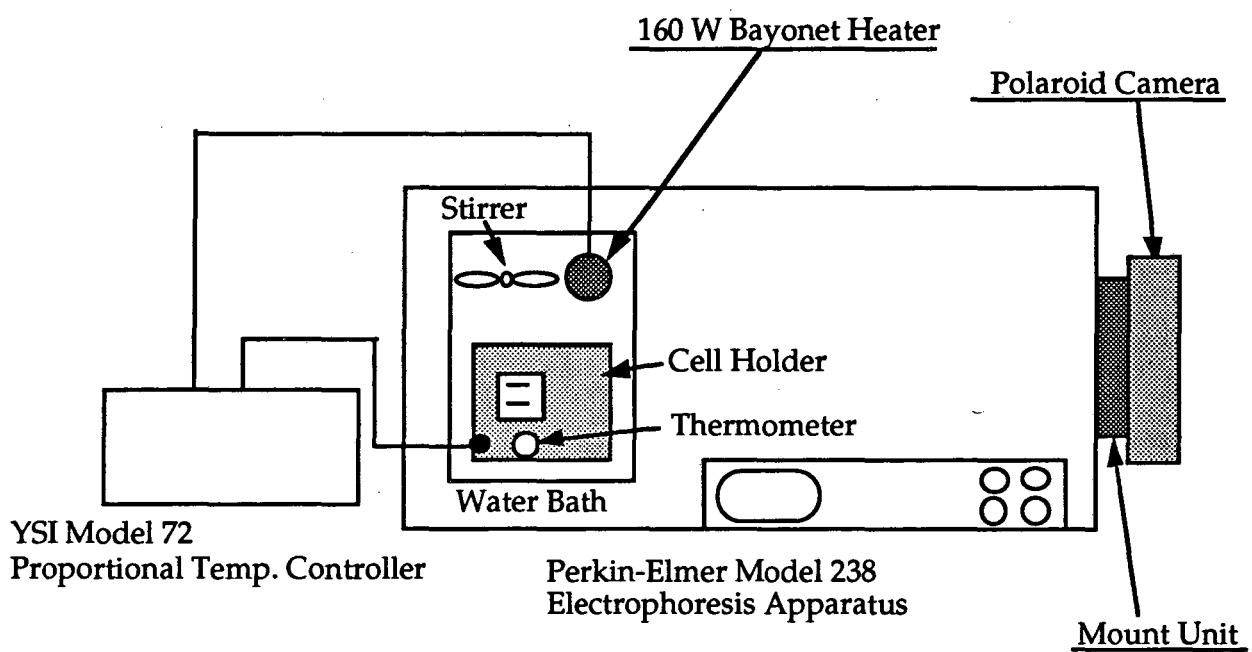
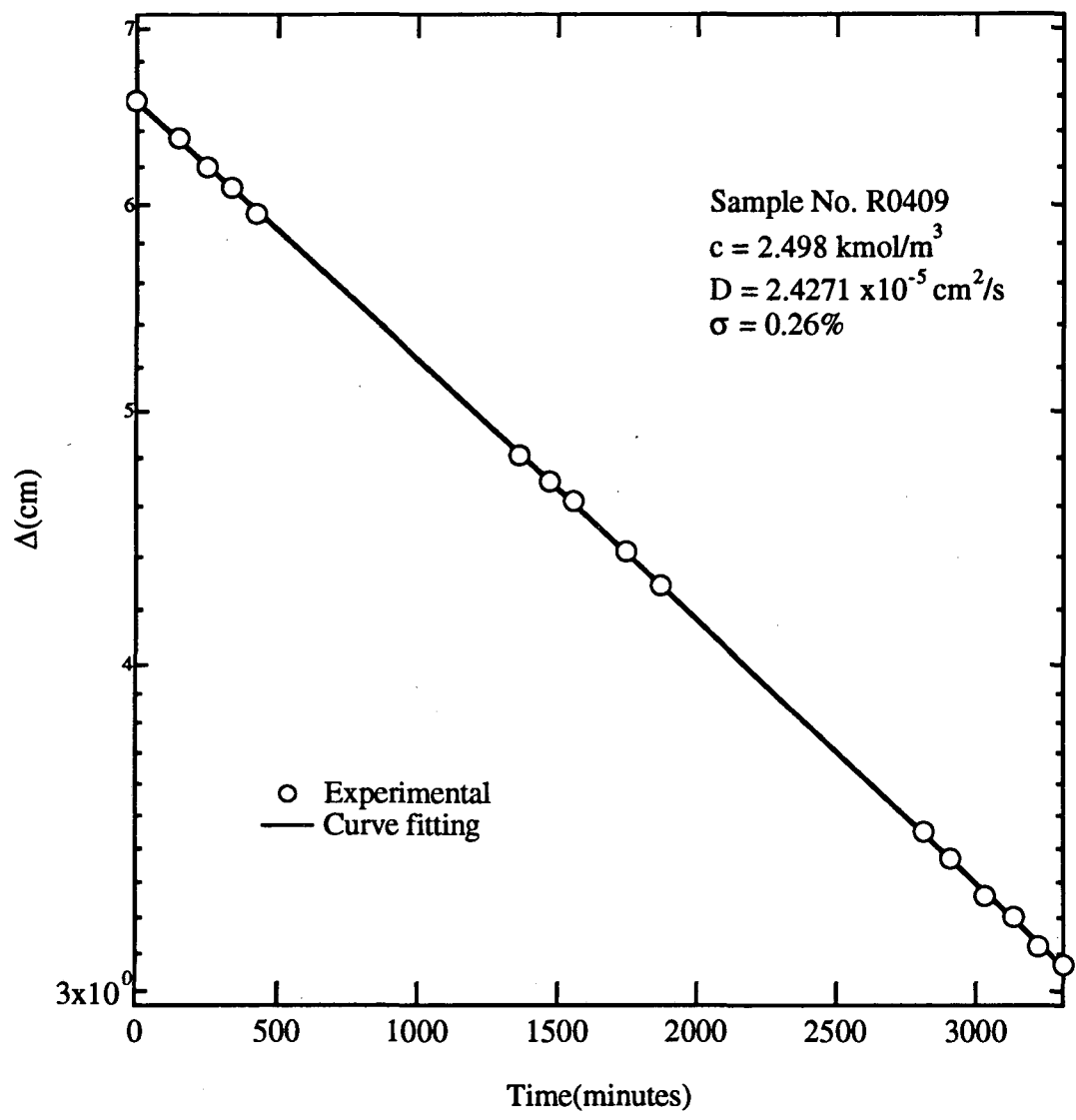Figure 2. Schematic of the experimental apparatus.

Figure 3. Typical fringe displacement data with respect to time. σ is the standard error of the least squares fit.

Results and discussion

The differential diffusion coefficient of sulfuric acid in water was measured at various concentrations ranging from 0.3 to 7.5 molar. These results and the estimated errors associated with each are listed in Table 1.

Table 1. Diffusion coefficients of sulfuric acid in water at 25°C.

Concentration (kmol/m^3)	Diffusion coefficient x10^5 (cm^2/s)	Standard error (%)
0.3243	1.7556	1.60
0.5223	1.8733	0.86
0.7591	1.9068	1.14
1.6218	2.1956	0.93
2.0012	2.1804	2.08
2.5063	2.4271	0.26
3.4971	2.7143	0.31
4.4196	2.7094	0.44
4.5045	2.6507	2.60
5.2075	2.6568	1.37
6.4516	2.1718	2.59
7.4508	1.1768	1.68

The measured diffusion coefficients are shown in Figure 4 along with diffusion coefficients measured by Leaist[2] and Savino and Vitagliano.[3] Leaist used a conductometric technique over the concentration range of 0.00035 to 0.2 molar. On the other hand, Savino and Vitagliano used Gouy interferometry to determine diffusion coefficients at
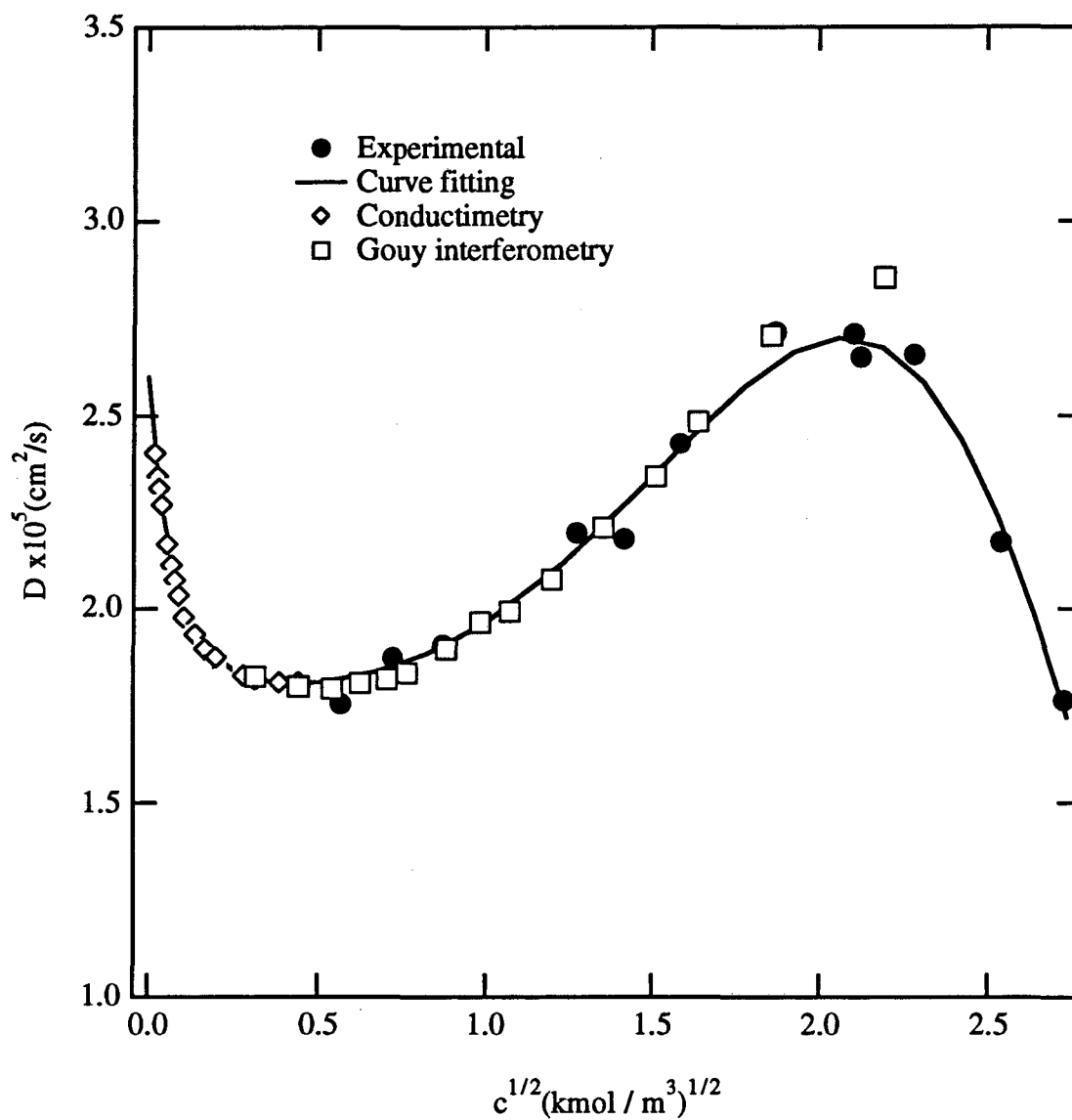
Figure 4. Comparison of the experimental diffusion coefficients to the results of other methods, and the fitting results at 25°C.

Results of conductometry are from Leaist,[2] and those of Gouy interferometry are from Savino and Vitagliano.[3]

concentrations from 0.1 to 4.8 molar. The differential diffusion coefficient is found to go through a minimum at about 0.2 molar, increase to a maximum value at around 4.0 molar, and then decrease continuously at higher concentrations. A fit of data is also shown.

$$D = \exp\left\{-10.56 - 0.37\left[1 - \exp\left(-12c^{1/2}\right)\right] - 0.11c + 0.29c^{3/2} - 0.0092c^2\right\}. \quad (7)$$

Data for the differential diffusion coefficient are of limited value in explaining the mechanism of transport in sulfuric acid solutions. Therefore it is necessary to consider the specific binary interactions between the dissociated molecules of the electrolyte and the solvent molecules. Fortunately, sulfuric acid can be treated as a binary system at high concentrations.[10] For this reason, the binary coefficients $\mathcal{D}_{ij}$ were calculated from Eq.2 to Eq.4 using data compiled by Chapman and Newman,[11] Zeleznik,[12] and Darling.[13] The data for thermal and transport properties were expressed with fitting functions that are shown in the Appendix.

Figure 5 shows a logarithmic plot of the $\mathcal{D}_{ij}$ coefficients versus concentration, emphasizing their behavior at low concentrations. The quantity $\mathcal{D}_{+-}$, which represents the long-range hydrogen ion-sulfate ion interaction, vanishes as the concentration approaches zero with a $\sqrt{c}$ dependence in accordance with Debye-Hückel-Onsager theory for ion-ion interactions in dilute solution. Consequently the term $1/\mathcal{D}_{+-}$ becomes small as compared to $c_0 t_-^0 / c_+ \mathcal{D}_{0-}$ in Eq.5 and is justifiably neglected in the dilute–solution theory of transport. The $\mathcal{D}_{+-}$ coefficient is of an appreciable magnitude in concentrated solutions as can be inferred from Figure 5. It reaches a maximum value at about 3.5 molar and decreases rapidly at large concentrations probably due to increasing ionic association. Irrespective of a Bjerrum type formation or complexion of ions to form a new species, the outcome is a decrease in the conductance of the solution. As a result, conductivity data are frequently used to make qualitative estimates about the microscopic state of a solution at high concentrations.
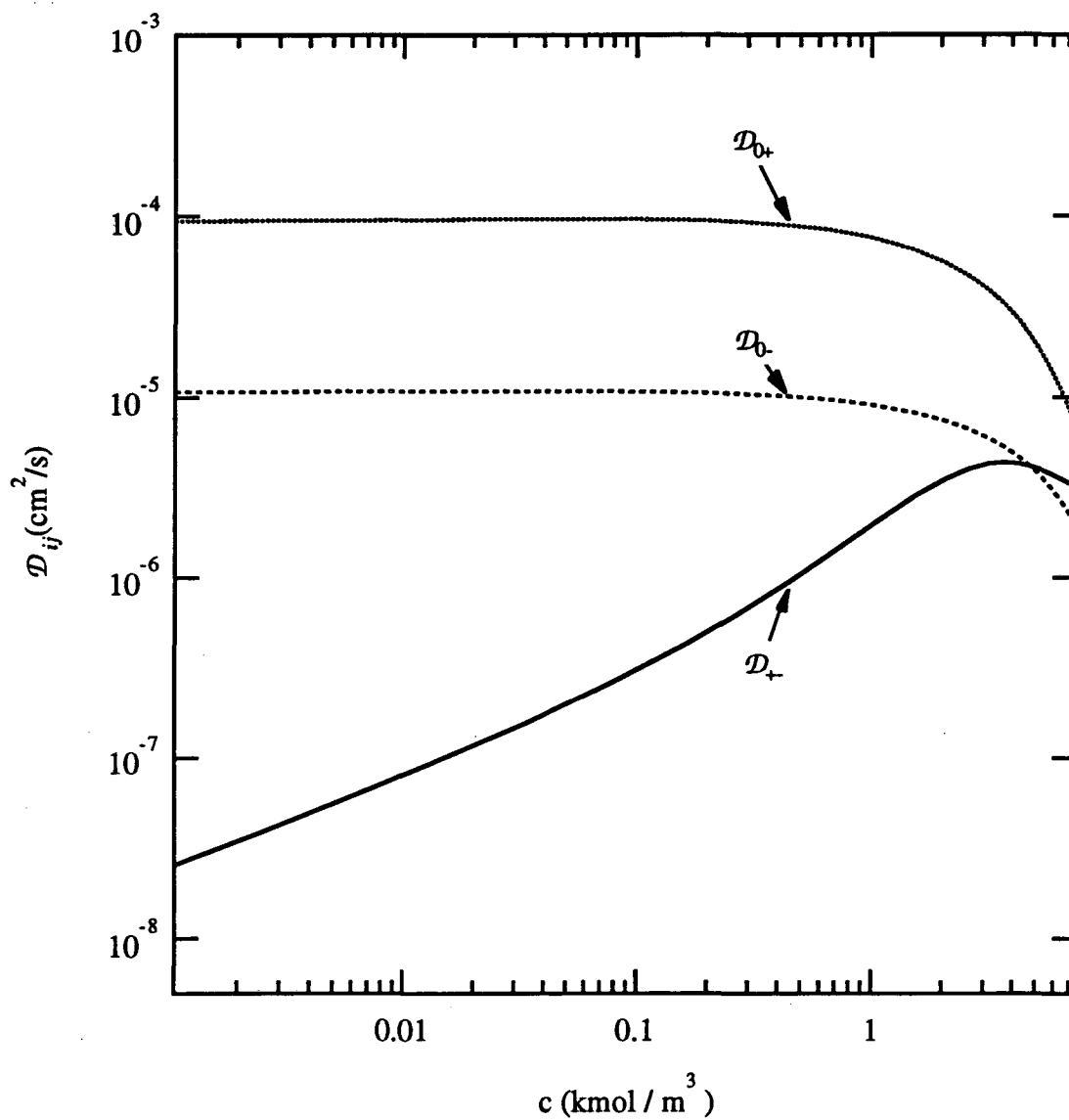
Figure 5. Multicomponent diffusion coefficients of H_2SO_4-H_2O at 25°C.

Eq.5 indicates that the conductivity, κ, depends both on the anion-cation and ion-solvent molecule interactions, and care is needed to interpret such data. Figure 6 compares the trends in $\mathcal{D}_{+-}$ and the conductivity with respect to concentration. The conductivity reaches its maximum at about 4 molar, whereas the maximum in $\mathcal{D}_{+-}$ suggests the start of ionic association to be at about 3.5 molar.

The present analysis does not determine any specific mechanism for association of sulfuric acid but suggests, rather successfully, an upper limit for the concentration below which the solution can be treated without much error as a completely dissociated binary system. A study of transport of sulfuric acid in concentrated solution with consideration of ion dissociation is not necessary because Pitzer[10] and Zeleznik[12] discussed and summarized the mechanism of dissociation sufficiently. The macroscopic framework of equations derived from concentrated solution theory is sufficient to treat transport problems without dependence on the microscopic degree of association. Hence, the calculated values of the $\mathcal{D}_{ij}$ coefficients are determined from macroscopic model, but they lose their physical significance with increasing degree of ionic association.

The coefficient $\mathcal{D}_{0i}$ for the ion-solvent interactions remains roughly constant at low concentration as compared to the $\mathcal{D}_{+-}$. The coefficient for the hydrogen ion $\mathcal{D}_{0+}$ is considerably larger than the coefficient for the sulfate ion $\mathcal{D}_{0-}$. Both quantities, especially $\mathcal{D}_{0+}$, show that the concentration dependence increases at high concentrations. Another plot is shown in Figure 7 with the purpose of amplifying the behavior of the $\mathcal{D}_{0i}$ coefficients in concentrated solutions. The thermodynamic diffusion coefficient, $\mathcal{D}$, and viscosity, μ, of the solution are also shown. The value of $\mathcal{D}_{0+}$ in the dilute region is governed by the proton–jump mechanism between solvent molecules, which results in the high mobility of hydrogen ion.[14] At the same time, the hydrogen ion is strongly structure making because it carries a large charge relative to its size and undergoes a high degree of solvation with water. With increasing concentration, the proton–jump mechanism is inhibited by the presence of larger number of anions that interfere with this structure, and $\mathcal{D}_{0+}$ decreases.
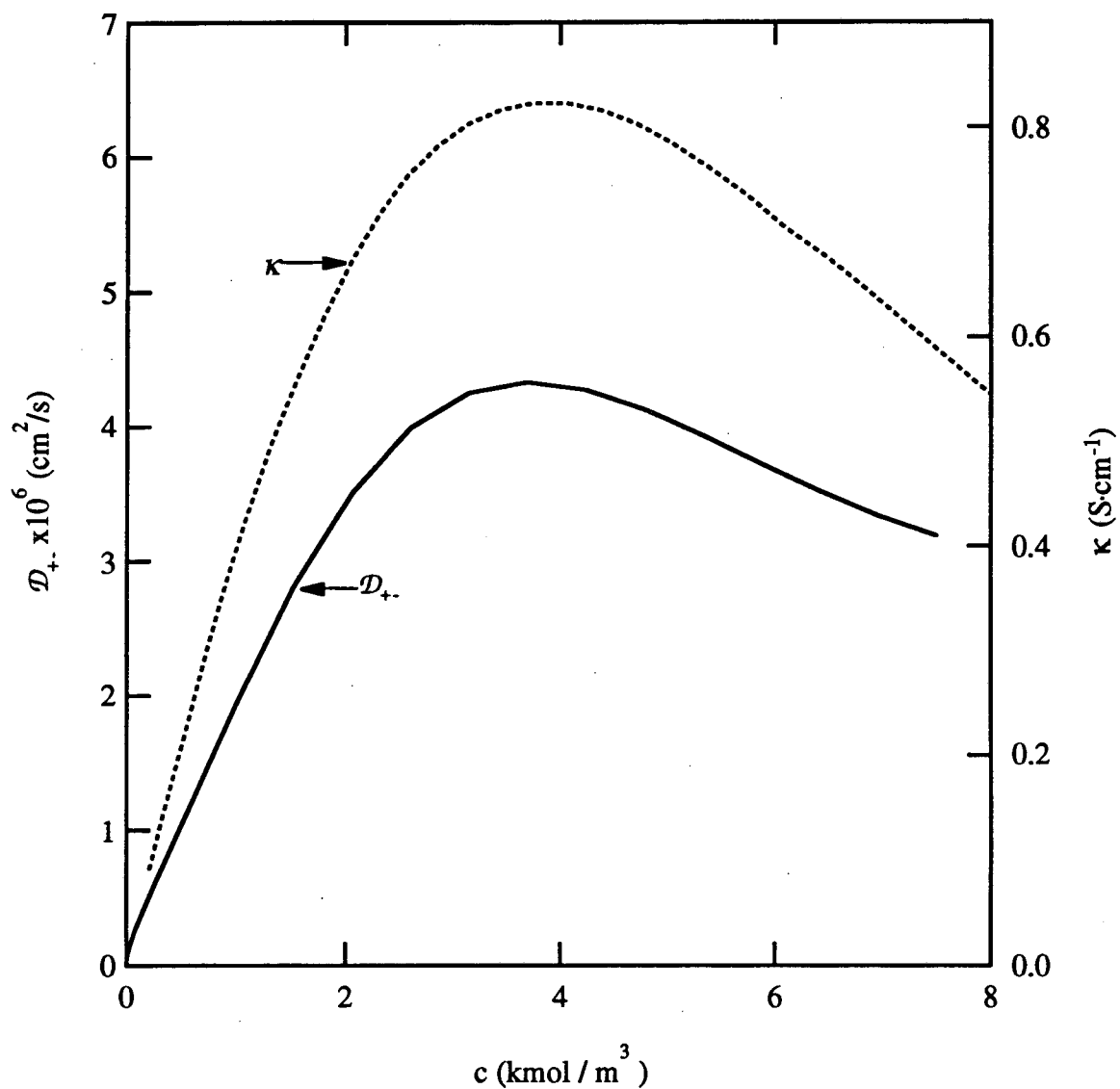
Figure 6. Anion-cation interaction coefficients and conductivity
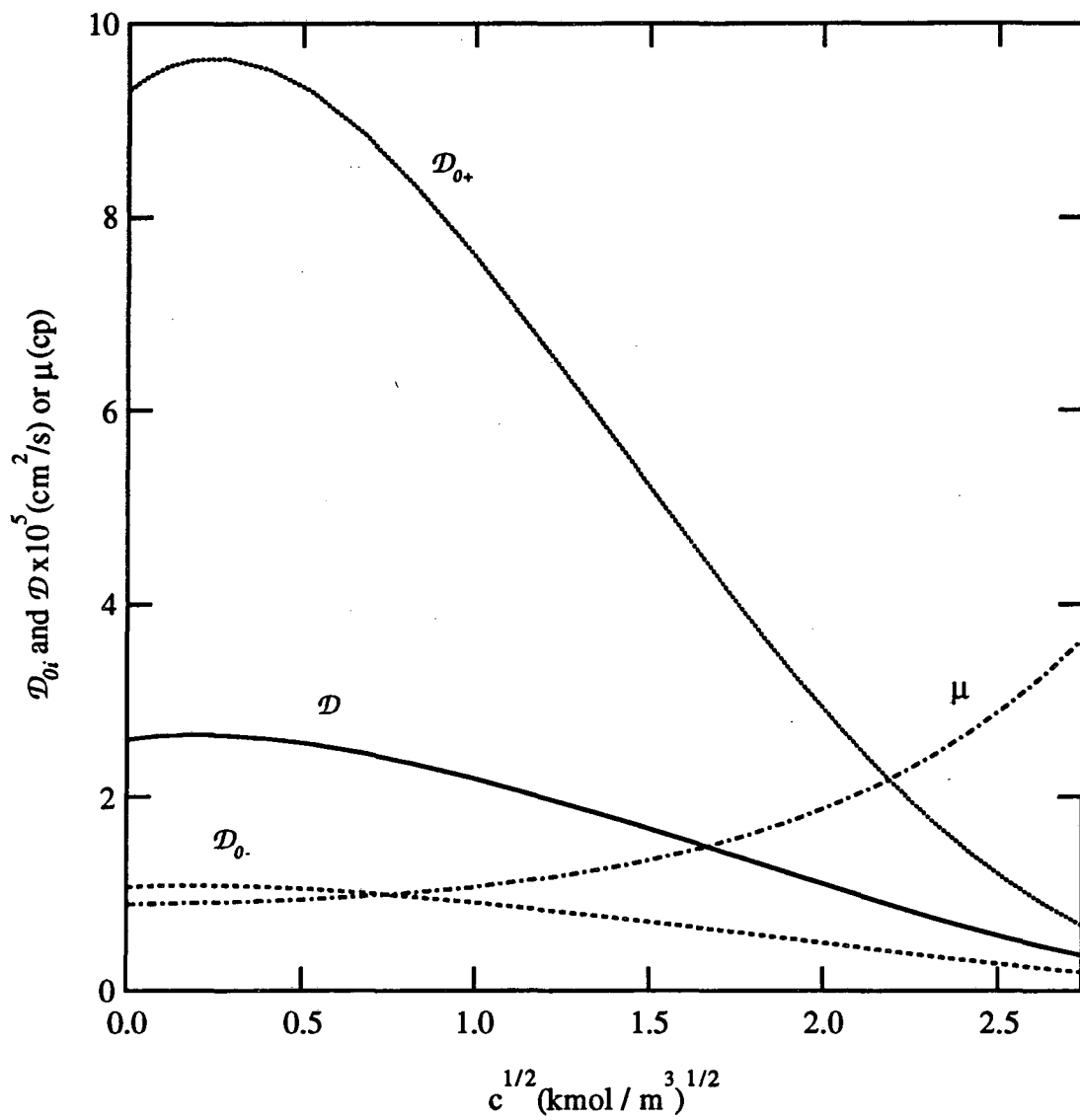of sulfuric acid at high concentration.

Figure 7. Ion-solvent interaction coefficients, thermodynamic diffusion
coefficient, and viscosity of sulfuric acid at high concentrations.

The coefficient $\mathcal{D}_{0-}$ for the sulfate ion does not vary much in comparison with $\mathcal{D}_{0+}$. These observations are in qualitative agreement with the behavior of other strong acids in aqueous solution as discussed by Robinson and Stokes[14] and by Chapman.[9]

From Figure 7, we note that the viscosity varies with concentration as strongly as any of the $\mathcal{D}_{ij}$ coefficients. This behavior supports the work of Gordon,[15] who attempted to correlate diffusion coefficients with the product $\mu\mathcal{D}_{0i}$ or $\mu\mathcal{D}$, which is assumed independent of composition and equal to its limiting value as the concentration vanishes.

Conclusion

The restricted diffusion method was used to measure the differential diffusion coefficients of sulfuric acid in water at 25°C for the concentration range from 0.3 to 7.5 molar. The concentration gradients of diffusing species were observed by Rayleigh interferometry. This method is an accurate and reliable way of measuring the differential diffusion coefficient.

Experimental transport data are analyzed with concentrated solution theory of electrolytes in order to elucidate macroscopic transport characteristics of sulfuric acid in terms of specific binary interaction in solution. Results indicate that the transport properties of sulfuric acid are determined by the hydrogen ion-water molecule interaction and support the work of Gordon, that is correlation of diffusion coefficients by assuming the product $\mu\mathcal{D}_{0i}$ or $\mu\mathcal{D}$ is independent of composition.

Acknowledgments

APPENDIX

Functions Used to Fit Thermodynamic and Transport Property Data of Sulfuric Acid Solution

      Experimental data on thermodynamic and transport properties were fitted to certain correlation functions by Chapman[9] in order to interpolate the experimental data to the concentration where calculation was made. We used a computer program to convert all available experimental data on the properties of sulfuric acid to a consistent set of units and fit them to these functions. The functions are given by

$$\rho = \exp\left(a_1 + a_2 c + a_3 c^{3/2} + a_4 c^2\right)$$
$$a_1 = -0.0029 \quad a_2 = 0.068 \tag{A-1}$$
$$a_3 = -0.0074 \quad a_4 = -0.00016$$

for densities,

$$\mu = \exp\left(b_1 + b_2 c^{1/2} + b_3 c + b_4 c^{3/2} + b_5 c^2\right)$$
$$b_1 = -0.12 \quad b_2 = 0.042 \quad b_3 = 0.091 \tag{A-2}$$
$$b_4 = 0.055 \quad b_5 = -0.0094$$

for viscosity,

$$t_+ = d_1 + d_2 c^{1/2} + d_3 c + d_4 c^{3/2} + d_5 c^2$$
$$d_1 = 0.81 \quad d_2 = 0.022 \quad d_3 = -0.037 \tag{A-3}$$
$$d_4 = 0.011 \quad d_5 = -0.0035$$

for cation transference numbers, Eq.7 for diffusion coefficients, and

$$P = \exp\left(f_1 + \frac{f_2 c^{1/2}}{1 + c^{1/2}} + f_3 c + f_4 c^{3/2} + f_5 c^2\right) \tag{A-4}$$

for equivalent conductance, $\mathcal{D}_{0i}$, $\mathcal{D}$, and $\mathcal{D}_{+-}/\sqrt{c}$.

Table A-1. Correlation function coefficients for thermodynamic and transport properties of aqueous sulfuric acid solutions at 25°C.

Property	f_1	f_2	f_3	f_4	f_5
Λ	6.063	-1.789	0.353	-0.264	0.0299
$\mathcal{D}$	-10.56	0.192	-0.364	0.136	-0.0384
$\mathcal{D}_{0+}$	-9.282	0.314	-0.458	0.138	-0.0400
$\mathcal{D}_{0-}$	-11.45	0.160	-0.331	0.121	-0.0328
$\mathcal{D}_{+-}/\sqrt{c}$	-14.09	0.563	1.456	-0.951	0.154

$$1 + \frac{d\ln\gamma}{d\ln m} = \exp\left(0.5g_2 \frac{c^{1/2}}{\left(1+c^{1/2}\right)^2} + g_3 c + 1.5g_4 c^{3/2} + 2g_5 c^2 + 3g_6 c^3\right) \qquad (A-5)$$

$$g_2 = -4.38 \quad g_3 = -0.089 \quad g_4 = 0.51$$
$$g_5 = -0.17 \quad g_6 = 0.0045$$

for activity coefficient factor.

LIST OF SYMBOLS

a height of diffusion cell, cm

A_n Fourier series coefficients defined by Eq.6

c concentration of electrolyte, mol/cm^3

c_i concentration of species i, mol/cm^3

c_0 concentration of solvent, mol/cm^3

c_T total solution concentration, mol/cm^3

D diffusion coefficient of electrolyte based on concentration driving force, cm^2/s

$\mathcal{D}$ diffusion coefficient of electrolyte for thermodynamic driving force, cm^2/s

$\mathcal{D}_{ij}$ diffusion coefficient for ion-ion, or ion-solvent interaction, cm^2/s

F Faraday's constant, 96,486 C/equiv

m molality of electrolyte, mol/kg

R gas constant, 8.314 J/mol·K

t time, s

t_i^0 transference number of species i with respect to the solvent

T absolute temperature, K

v_i velocity of species i, cm/s

z_i valence of species i

γ mean molar activity coefficient

Δ fringe displacement on photographic film, cm

κ conductivity of solution, S·cm^{-1}

Λ equivalent conductance of binary electrolyte, S·cm^2/ equiv

μ viscosity of solution, centipoise

μ_i electrochemical potential of species i, J/mol

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