Diffusion in Aqueous Nitric Acid Solutions

The restricted diffusion method is employed to measure the differential diffusion coefficients of nitric acid in water at 25°C for the concentration range 0.033 to 9.25 molar. The concentration gradients of diffusing solutions are observed by Rayleigh interference optics.

Experimental transport data are analyzed within the framework of the concentrated solution theory of electrolytes in order to elucidate the macroscopic transport characteristics of nitric acid in terms of specific binary interactions in solution. The results indicate that the transport properties of nitric acid are largely determined, as in other strong acids, by the hydrogen ion-water molecule interaction.

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SCOPE

The analysis of mass transfer problems in electrochemical systems, whether they are macroscopic design problems or theoretical studies on a microscopic basis, requires accurate values of the transport properties of electrolytic solutions. Theoretical work on the microscopic scale, for example, the Debye-Hückel theory, usually attempts to predict the transport properties from molecular considerations. Extensions of the Debye-Hückel theory have provided a firm basis for dilute solutions of electrolytes, and one might seek to find a uniform treatment of the diffusion coefficient, transference number, and electrical conductivity. This prompts one to seek systems with rather complete sets of data for all these properties as well as the thermodynamic properties.

Another incentive is to explore the specific binary interactions which combine to determine the apparent transport properties of an electrolytic system and with this experience predict the behavior of different systems with similar binary interactions. This also leads to the final objective of predicting properties of multicomponent solutions using data for only the binary solutions of their solutes.

The nitric acid-water system is chosen for the present study because it is a very common electrolyte employed in electrochemical systems with complete data reported in the literature on its conductivity, transference number, and thermodynamic properties. Missing data for the diffusion coefficients are measured here over a wide concentration range using the restricted diffusion method of Harned and French (1945) as recently improved by Newman and Chapman (1973). The complete set of data is then analyzed to investigate the nature of binary interactions determining the system behavior.

CONCLUSIONS AND SIGNIFICANCE

The differential diffusion coefficients of nitric acid in water at 25°C are measured between 0.033 and 9.25 molar, thereby rendering more complete the literature data for the transport properties of this system. Statistical analysis of the experimental data suggests a maximum error of 0.2% in the measured diffusion coefficient.

Experimental data for transport properties, such as the conductivity, transference number, and the diffusion coefficient, express a resultant behavior due to a combination of simple and basic interactions between various species constituting the electrolytic system. The transport theory for concentrated electrolytes, as discussed by Newman et al. (1965), provides a useful basis for deducing a set of transport coefficients $\mathcal{D}_{ij}$ for the specific binary interactions between the solute ions and the solvent molecules from an analysis of a complete set of experimental data.

Application of the theory to the experimental results for nitric acid indicates that the hydrogen ion-water interaction is a major factor in governing the diffusion process in this system next to the long range electrostatic interactions of oppositely charged ions. The results can be interpreted in terms of several different types of interactions which act in opposing directions. In dilute solutions, the hydrogen ion has a high mobility due to rapid proton transfer among the water molecules. At the same time, the high degree of solvation of the hydrogen ion effects a more orderly structure within the solvent medium, which tends to increase with rising hydrogen ion concentration. An opposing effect becomes discernable with increasing number of nitrate ions, which need to locate themselves between solvated hydrogen ions, thereby interfering with the development of a more orderly matrix and also with the proton-jump mechanism of the hydrogen ions. The results also suggest the beginnings of ionic association at about 4 molar in support of more firm evidence gathered from spectroscopic investigations.

The present method of analysis provides another perspective in investigating the nature of transport and ionic interactions in electrochemical systems along with other commonly used methods, such as the treatment of equilibrium properties and direct studies of the measured transport properties. It can be applied without much difficulty to a number of binary systems, for which adequate data are already available. The outcome should be fruitful in broadening the understanding of nonequilibrium processes in binary and multicomponent electrolytic systems.

The restricted diffusion method for the measurement of differential diffusion coefficients of binary solutions was first developed by Harned and French (1945), based on the dilute-solution theory of electrolytes. Newman and Chapman (1973) have improved the method recently both in theory and experimental technique to include concentrated binary systems and nonelectrolytes as well. The new theory corrects the equations of Harned and French for variable physical properties, which may be significant in both dilute and concentrated solutions, and non-zero solvent velocity which is particularly important in concentrated systems. The experimental method, in its improved form, employs Rayleigh interferometry to visualize the concentration gradients in the diffusion cell in contrast to the conductometric method of Harned and French, which is limited to dilute solutions of electrolytes only.

The present paper reports an application of the restricted diffusion method to aqueous nitric acid solutions at 25°C in order to complement already available transport data on this system (Chapman and Newman, 1968). Aqueous nitric acid is a commonly known electrolyte of engineering interest in industry and the laboratory. Yet, accurate data for the diffusion coefficients of this system appear to be lacking in the literature even though data for other transport properties of interest, such as the transference number and the electrical conductivity, are somewhat complete in a wide concentration range (0 to about 10 molar). The diffusion coefficients were measured in this range to obtain a complete set of transport property data to effect a quantitative study of the transport mechanism in aqueous nitric acid systems with the application of the theory for concentrated electrolytes.

THEORETICAL BACKGROUND

A generalized description of transport in concentrated (as well as dilute) electrolytic solutions can be given by a set of flux equations of the form

$$c_i \nabla \mu_i = \mathrm{RT} \sum_j \frac{c_i c_j}{c_T \mathcal{D}_{ij}} (\underline{v}_j - \underline{v}_i) \qquad (1)$$

where μ_i is the electrochemical potential of species i and $\mathcal{D}_{ij} (= \mathcal{D}_{ji})$ are the fundamental binary transport coefficients defined by these equations. Equation (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. (1965), Newman (1967 and 1973), Chapman (1967), and Newman and Chapman (1973).

As a consequence of inversion of Equation (1) to obtain explicit expressions for the fluxes in a binary system (Newman, 1967), a thermodynamic diffusion coefficient is defined, namely,

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

which is related to the 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 which is directly measurable by the restricted diffusion method. Another property, which can be measured independently by experiment, is the transference number

$$t_+^0 = 1 - t_-^0 = \frac{z_+ \mathcal{D}_{0+}}{z_+ \mathcal{D}_{0+} - z_- \mathcal{D}_{0-}} \qquad (4)$$

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

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

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 thus of fundamental and physical importance in depicting 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 Equations (3) to (5), by a combination of different binary interactions and also depend on the equilibrium properties of the system.

RESTRICTED DIFFUSION METHOD

Newman and Chapman (1973) treated the decay of a one-dimensional concentration gradient at large times in a column of solution of height a. An important result of that analysis is

$$\Delta c = c\left(\frac{a}{6}\right) - c\left(\frac{5a}{6}\right)$$
$$= \sqrt{3} A_1 e^{-Dt(\pi/a)^2} + B e^{-3Dt(\pi/a)^2} + \ldots \qquad (6)$$

where Δc is measured between points one-sixth of the overall length from each end of the liquid column. The coefficients A_1 and B depend on the initial conditions, and B is also a function of the concentration derivatives of solution properties. The column height a actually varies over the period of diffusion due to the nonzero volume change on mixing. Newman and Chapman (1973) have shown, however, that this variation is in effect negligible and 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 Equation (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 $-D\pi^2/a^2$. Such a plot is shown in Figure 1 for nitric acid. The concentration dif-

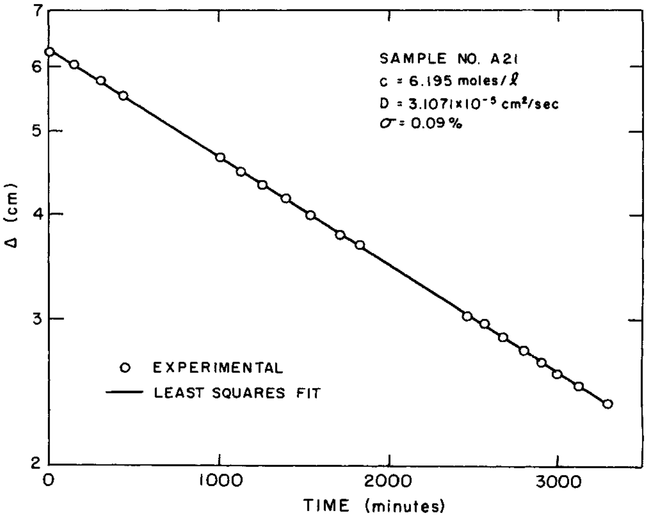

Fig. 1. Typical fringe displacement data with respect to time. σ is the mean standard deviation of the least squares fit.

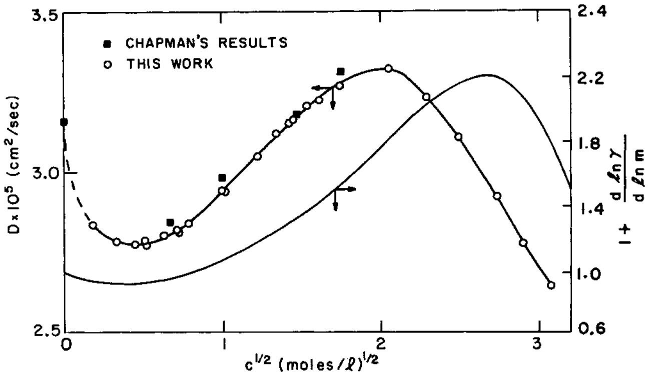

Fig. 2. The measured diffusion coefficient and the activity-coefficient factor of nitric acid in water at 25°C.

ference 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 short concentration range, the displacement (denoted by Δ) of a fringe on the photographic film is proportional to Δc for a small concentration gradient. Newman and Chapman (1973) reproduce photographs of fringe patterns.

The measurements of fringe displacements were made when Δc was about 0.4 molar and less. At larger concentration differences, the bending fringes are too close together to be resolved on the film [see Figure 2, Newman and Chapman (1973)]. 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 reasonably sharp boundary, and the system stabilizes faster against convection or any other disturbances caused during the preparation stage. The decay of this boundary required one to three days before resolvable Δ measurements could be effected. Such a time lapse was also necessary to ensure that the higher order terms in Equation (6) had become negligible before measurements were made.

The fringe displacement data were fitted to a straight line (see Figure 1), and the mean standard deviation of the measured points from the fitted line gave a good estimate of the error associated with each diffusion coefficient. This estimate, however, does not include any errors introduced by the measurement of concentration at the end of a diffusion run nor of the height of the cell.

Final concentrations of solutions were determined by titration with standardized 0.1 molar sodium hydroxide solution to the phenolphthalein end point. Since the diffusion coefficient varies rather gradually with concentration in concentrated solutions (by about 0.1% for 1% change in concentration), a more precise analytical method was deemed unnecessary.

The present method is not very accurate in very dilute solutions because the fringe displacements are smaller and therefore harder to measure with sufficient precision. For this case, Harned's (1945) conductometric technique would definitely be more suitable.

Additional details on the experimental method are given by Newman and Chapman (1973) and by Nisancioglu (1969).

RESULTS AND DISCUSSION

The differential diffusion coefficients of nitric acid were measured at various concentrations ranging from 0.033 to 9.25 molar, and these results and the estimated error associated with each are listed in Table 1. For all values included, the error lies below 0.2% as suggested by Newman and Chapman (1973) as the expected tolerance of the present method, except for the smallest concentration attempted. The results are plotted against concentration in Figure 2 along with some preliminary measurements reported by Chapman (1967). The thermodynamic factor in Equation (3) is also shown.

The differential diffusion coefficient is found to go through a minimum at about 0.2 molar, increase to a maximum value at around 4 molar, and then decrease continuously at higher concentrations. As can be seen in Figure 2, this behavior is more or less determined by the concentration dependence of the activity coefficient. This information, as it is, is then quite limited in conveying the mechanism of transport in nitric acid. Therefore, specific binary interactions between the dissociated molecules of the electrolyte and the solvent molecules need be singled out to obtain a clearer picture. The binary coefficients $\mathcal{D}_{ij}$ were calculated for this purpose from Equations (2) to (4) using data compiled by Chapman and Newman (1968) for the measured thermodynamic and transport properties of various electrolytes. Chapman (1967) has also conducted an extensive study on the transport properties of a number of electrolytic systems.

Figure 3 shows a logarithmic plot of the $\mathcal{D}_{ij}$ coefficients with respect to concentration, emphasizing their behavior at low concentrations. The quantity $\mathcal{D}_{+-}$, which represents the long range hydrogen ion-nitrate ion interaction, vanishes as the concentration approaches zero with a $\sqrt{c}$ dependence in accordance with the Debye-Hückel-Onsager theory for ion-ion interactions in dilute solution. As a consequence, the term $1/\mathcal{D}_{+-}$ becomes small as compared to $c_0 t^0_-/c_+ \mathcal{D}_{0-}$ in Equation (5) and is justifiably neglected in the dilute-solution theory of transport. The $\mathcal{D}_{+-}$ coefficient, however, is of an appreciable magnitude in concentrated solutions as can be inferred from Figure 3. It reaches a maximum value at about 4 molar and decreases rapidly at large concentrations probably due to increasing ionic association. Whether this is a Bjerrum-

TABLE 1. THE DIFFUSION COEFFICIENT OF NITRIC ACID IN WATER AT 25°C

c(moles/l)	$D \times 10^5$ (cm²/sec)	% error
0.033	2.835	0.38
0.110	2.782	0.19
0.199	2.774	0.13
0.256	2.786	0.05
0.265	2.780	0.11
0.414	2.805	0.07
0.499	2.815	0.05
0.515	2.806	0.07
0.629	2.837	0.06
1.006	2.939	0.08
1.020	2.939	0.04
1.505	3.045	0.05
1.797	3.119	0.11
2.030	3.148	0.06
2.090	3.158	0.18
2.375	3.203	0.17
2.586	3.224	0.06
3.039	3.268	0.10
4.187	3.317	0.08
5.253	3.233	0.08
6.195	3.107	0.09
7.450	2.921	0.07
8.40	2.778	0.07
9.25	2.642	0.08

type ion-pair formation or complexation of ions to form a new species, the outcome is a decrease in the conductance of the solution. As a result, conductivity data are sometimes used to make qualitative estimates about the microscopic state of a solution at high concentrations. Equation (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 4 compares the trends in $\mathcal{D}_{+-}$ and the conductivity with respect to concentration. The conductivity reaches its maximum at about 6 molar, whereas the maximum in $\mathcal{D}_{+-}$ suggests the onset of ionic association to be at about 4 molar.

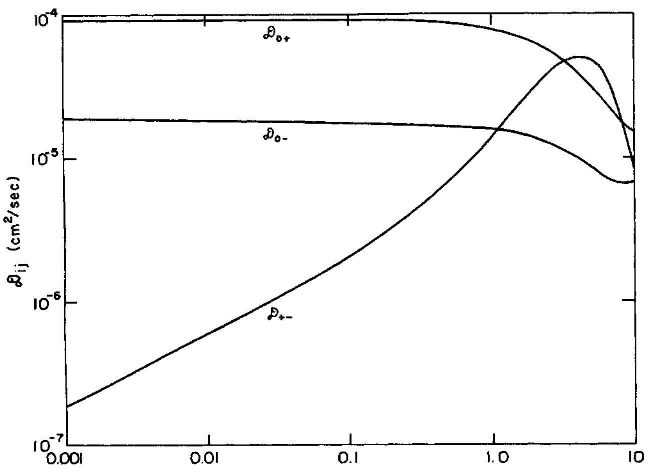

Fig. 3. The binary interaction coefficients of nitric acid in dilute solution.

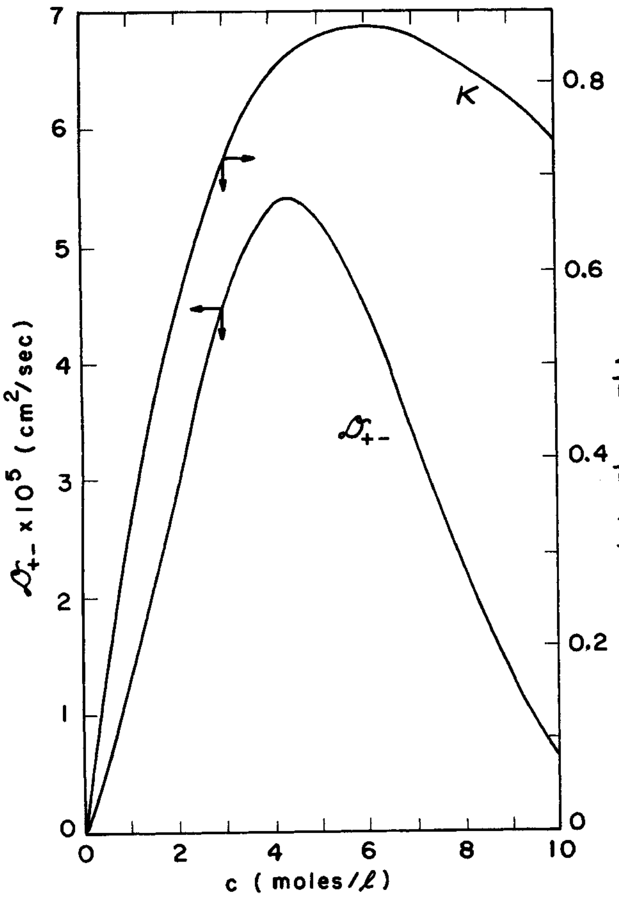

Fig. 4. The anion-cation interaction coefficient and the conductivity of nitric acid at high concentrations.

More conclusive results in this regard can be obtained by spectroscopic techniques. Redlich and Bigeleisen (1943) and later Hood et al. (1954) have studied the dissociation of nitric acid in aqueous solution with Raman and NMR spectroscopy respectively. Hood et al. report that nitric acid is about 90% dissociated at around 4 molar, and this drops monotonically to about 60% at 9 molar, confirming the increasing importance of ionic association above 4 molar.

The present analysis does not determine any specific mechanism for association 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 in concentrated nitric acid solutions with consideration of nondissociated species is out of context here because sufficient controversy exists as regards to the mechanism of dissociation as discussed by Mascherpa et al. (1969). Furthermore, the macroscopic framework of equations derived from the 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 consistent with the macroscopic model, but they lose their physical significance with increasing degree of ionic association.

The coefficients $\mathcal{D}_{0i}$ for the ion-solvent interactions remain roughly constant at small concentrations as compared to $\mathcal{D}_{+-}$. The coefficient for the hydrogen ion $\mathcal{D}_{0+}$ is considerably larger than the corresponding coefficient $\mathcal{D}_{0-}$ for the nitrate ion, demonstrating the relatively high mobility of the hydrogen ion in dilute aqueous solution. Both quantities, especially $\mathcal{D}_{0+}$, display increased concentration dependence at high concentrations. Another plot of the $\mathcal{D}_{0i}$ coefficients, this one on a linear scale against the square-root of concentration, is given in Figure 5 with the purpose of amplifying their behavior in concentrated solution. The thermodynamic diffusion coefficient $\mathcal{D}$ and the viscosity μ of the solution are also shown. The trend in $\mathcal{D}_{0+}$ in dilute solutions is governed by the fast proton-jump mechanism among the solvent molecules which results in the high mobility of the hydrogen ion (Robinson and Stokes, 1965). At the same time, the hydrogen ion is strongly structure-making because it carries a large charge relative to its size and therefore undergoes a high degree of solvation with water. With increasing concentration, the proton-jump mechanism is inhibited by the presence of larger numbers of nitrate ions which interfere with this structure, and $\mathcal{D}_{0+}$ decreases. The coefficient $\mathcal{D}_{0-}$ for the nitrate ion does not vary much in comparison to $\mathcal{D}_{0+}$. Analyses of transport data for various nitrate salts in aqueous solution by Chapman (1967) show an increase in $\mathcal{D}_{0-}$ with concentration before it drops again at higher concentrations as evidence to the structure-breaking tendency of the bulkier nitrate ion. This effect is not discernable from the present data, but it may have been obscured by the more dominant structure-making ability of the hydrogen ion. These observations are in qualitative agreement with the behavior of other strong acids in aqueous solution as discussed by Robinson and Stokes (1965) and by Chapman (1967).

As a final observation, one may note that the viscosity does not vary as strongly as any of the $\mathcal{D}_{ij}$ coefficients with respect to concentration. After the work of Gordon (1937), it is commonly attempted to correlate diffusion coefficients by assuming that the product $\mu\mathcal{D}_{0i}$ or $\mu\mathcal{D}$ is independent of composition and equals its limiting value

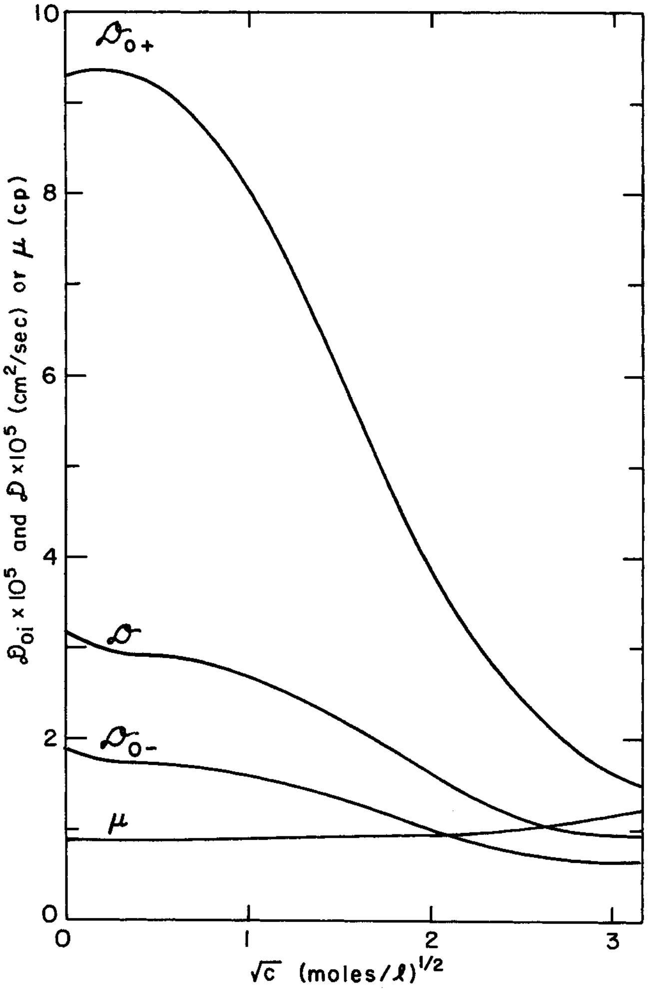

Fig. 5. The ion-solvent interaction coefficients, the thermodynamic diffusion coefficient, and the viscosity of nitric acid at high concentrations.

as the concentration vanishes. Bearman (1961) discusses from a statistical-mechanical basis the significance of this and similar assumptions involved in various theories of diffusion. This assumption works reasonably well over a wide concentration range for electrolytes which remain completely dissociated at high concentrations such as some of the alkali halides (Nisancioğlu, 1969; Newman, 1973). It does not appear to work, however, for strong acids such as nitric acid whose transport characteristics are complicated by the proton-jump mechanism in dilute solutions and ionic association in concentrated solutions.

Types of ionic interactions, which determine the thermodynamic and nonequilibrium properties of an electrolytic system, are quite complicated and call for further study. The transport theory of concentrated solutions is another means of attacking this problem, along with already established thermodynamic, conductometric, and spectroscopic methods, as it is applied to nitric acid here and to various other systems by Chapman (1967). Additional experimental data for the transport properties may be needed to meet this purpose. The restricted diffusion method is an accurate and reliable way of measuring the differential diffusion coefficient.

ACKNOWLEDGMENT

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NOTATION

a = height of restricted diffusion cell or of liquid column, cm
A_1, B = coefficients of series expression for concentration in restricted diffusion cell
c = concentration of binary electrolyte, mole/cm^3
c_i = concentration of species i, mole/cm^3
c_0 = concentration of solvent, mole/cm^3
c_T = total solution concentration, mole/cm^3
D = experimental (differential) diffusion coefficient of binary electrolyte, cm^2/s
$\mathcal{D}$ = diffusion coefficient of electrolyte for thermodynamic driving force, cm^2/s
$\mathcal{D}_{ij}$ = diffusion coefficient for binary interactions, cm^2/s
F = Faraday's constant, 96,487 C/equiv
m = molality of electrolyte, mole/kg
R = universal gas constant, 8.3143 J/mole-deg
t = time, s
t_i^0 = transference number of species i with respect to the solvent
T = absolute temperature, °K
$\underline{v}_i$ = velocity of species i, cm/s
z_i = valence of species i
γ = mean molal activity coefficient
Δ = fringe displacement on photographic film, cm
κ = conductivity of solution, ohm^{-1}-cm^{-1}
μ = viscosity of solution, centipoise
μ_i = electrochemical potential of species i, J/mole

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