Diffusion Coefficient of Aqueous Nitric Acid at 25°C as Function of Concentration from 0.1 to 1.0M

HSI-SHENG YEH and GEORGE B. WILLS[1]
Chemical Engineering Department, Virginia Polytechnic Institute and State University, Blacksburg, Va. 24061

A diaphragm cell method was employed to determine the integral diffusion coefficient of nitric acid in aqueous solution at 25° C over a concentration range from 0.1 to 1.0*M*. Differential diffusion coefficient data was calculated from the integral data by a stepwise regression method.

Nitric acid has been commonly used in the laboratory and in commercial manufacturing both as a chemical reagent and as a raw material; surprisingly enough, relatively few transport data for nitric acid have been published. For example, the usual references for electrolytes, such as books by Harned and Owen (*5*), Robinson and Stokes (*9*), and the International Critical Tables (*6, 7*), have far fewer entries for nitric acid than for hydrochloric acid. It was not until 1964 that Haase *et al.* (*3, 4*) published detailed results on electrical conductivity and transference number for nitric acid. While Arrhenius (*1*) studied the diffusion of nitric acid in 1892, the only available diffusion coefficient data are at 20° C and are listed in reference (*7*), dated 1933. For a 0.5*M* solution diffusing into pure water, reference (*7*) lists an integral coefficient of 2.58 × 10^{-5} cm^2/sec at 20° C. This study would predict an integral coefficient of about 2.8 × 10^{-5} cm^2/sec.

During a mass transfer study, accurate diffusion coefficient data for nitric acid were needed as a function of concentration up to 1.0*M* at 25° C. An experimental determination of the diffusion coefficient for such a system was undertaken.

EXPERIMENTAL METHOD

Integral diffusion coefficient data for aqueous nitric acid were determined by the diaphragm cell method (*11*). The diaphragm cell designed and used was based, with modification, on the principle suggested by Stokes (*11*). Experimental procedures employed will be briefly described here since details on the construction of the apparatus and procedures can be found elsewhere (*14*).

The diaphragm cell previously described in reference (*14*) was used throughout the course of the nitric acid experiments. The stirring rate was held at a constant speed of 10 rpm. The problem of the "minimum" stirring rates has been discussed by Dullien and Schemilt (*2*). Wide ranges of values, varying from 3 rpm (*10*), 25 rpm (*11*) to 100 rpm (*2*) or even 125 rpm (*8*), have been reported for the "minimum" stirring rates needed. Certainly, the stirring speed must be such that the contents of each cell chamber are kept essentially uniform, but in addition, it is desirable to reduce the stagnant liquid film on the faces of the diaphragm to a point where they offer negligible resistance to diffusion in comparison to that of the diaphragm capillaries. Here, using the data of Stokes (*11*), we would predict that the stagnant film resistance to mass transfer was 2–3% of the total resistance. No error is introduced, providing this stagnant film thickness does not vary from system to system. A significant variation in the film thickness for the systems studied here seems unlikely since there was only a modest variation in the Reynolds numbers, the variable controlling the film thickness. The close checks with known electrolytes of differing properties previously reported (*14*) thus serve as an indication of the adequacy of the stirring rate used in the present experiment.

The constant temperature bath was maintained at 25° ± 0.05° C as measured by a thermometer standardized against a precision National Bureau of Standards certified thermometer.

The runs were of 19–36 hr duration, depending on the electrolyte involved. The cell was calibrated with a 0.1*M* KCl aqueous solution (*13*). The KCl used was Fisher certified reagent; the HNO_3 used was Fisher chemical reagent. All were used without further purification. Freshly boiled distilled water, cooled in a tight container, was used throughout the experiments.

ANALYSIS

Nitric acid samples were analyzed by volumetric titration with alkali to a phenolphthalein end point.

Table I. Experimental Diaphragm Cell Integral Diffusion Coefficients, $\bar{D}$, *vs.* Initial Concentration for HNO_3 in Aqueous Solution at 25° C

Initial lower cell concn, moles/liter	$\bar{D} \times 10^5$/ cm^2/sec	% Deviation, $[(\bar{D}_{exp} - \bar{D}_{cal})/\bar{D}_{exp}] \times 100$	C_{fu}, moles/liter	C_{fl}, moles/liter
0.0726	2.9840	1.14	0.0191	0.0535
0.0759	2.9744	0.95	0.0203	0.0557
0.1067	2.8657	−1.74	0.0275	0.0792
0.1109	2.9154	0.11	0.0287	0.0822
0.2002	2.8472	−0.38	0.0515	0.1488
0.2004	2.8906	1.14	0.0523	0.1480
0.2934	2.8111	−0.54	0.0746	0.2188
0.3043	2.7837	−1.44	0.0773	0.2269
0.4049	2.7953	−0.41	0.1058	0.2991
0.4201	2.8440	1.37	0.1094	0.3107
0.5196	2.8301	1.08	0.1348	0.3848
0.5376	2.7787	−0.74	0.1375	0.4000
0.7281	2.8101	0.09	0.1866	0.5414
0.7401	2.7927	−0.57	0.1926	0.5475
0.8645	2.8096	−0.48	0.2232	0.6414
0.9521	2.8521	0.56	0.2406	0.7115
0.9811	2.8435	0.10	0.2513	0.7297

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[1] To whom correspondence should be addressed.

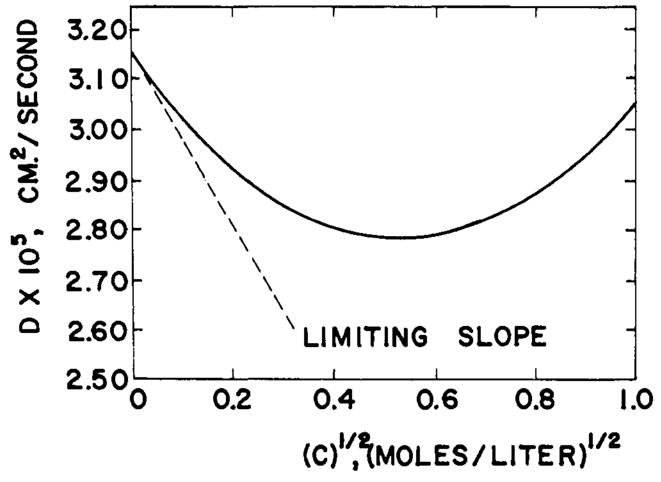

Figure 1. Observed differential diffusion coefficient for nitric acid in aqueous solution at 25° C

RESULT AND DISCUSSION

In all calculations, the well-known logarithmic formula (*12*), Equation 1, was used both for the cell constant, β, and for the diaphragm cell integral diffusion coefficients, $\bar{D}$, described in detail in reference (*9*).

$$\bar{D} = \frac{1}{\beta t} \ln \frac{C_{i,l} - C_{i,u}}{C_{f,l} - C_{f,u}} \tag{1}$$

In the calculation of the cell constants, the values for KCl tabulated by Stokes (*13*) were used. Four runs were performed for the determination of the β value. The 95% confidence interval for the cell constant is

$$0.3602 < \beta_{\text{av}} < 0.3645$$

Tabulation of the diaphragm cell integral diffusion coefficients for HNO_3 in aqueous solution at 25° C over a concentration range from 0.07 to 0.98 mole per liter is given in Table I. In all cases, the initial upper cell concentration, $C_{i,u}$, was zero. The average scatter of the data is ±0.78%. Also given in Table I are the final cell concentrations and the deviation of each experimental point from that calculated by Equation 2.

The series of approximation method as outlined by Stokes (*12*) was used in conjunction with a stepwise regression method to convert the experimental diaphragm cell integral diffusion coefficient data into differential diffusion coefficient data.

An equation form, such as Equation 2, was found to be the form which best represented the experimental data.

$$\bar{D} \times 10^5 = 3.1704 + 0.6736\,C - 1.0000\,(C)^{1/2} \tag{2}$$

Equation 3 can be used to calculate the corresponding differential diffusion coefficient data as a function of concentration.

$$D \times 10^5 = 3.1615 + 1.3000\,C - 1.4070\,(C)^{1/2} \tag{3}$$

Graphical presentation of Equation 3 is given in Figure 1 where the limiting slope, as calculated from the limiting Equation 4, and recorded as Equation 6-10-5 by Harned and Owen (*5*), is also included.

$$D = D_0 - \delta_D\,(C)^{1/2} \tag{4}$$

NOMENCLATURE

$C_{i,l}$ = average initial concentration for lower cell, moles/liter
$C_{i,u}$ = average initial concentration for upper cell moles/liter
$C_{f,l}$ = average final concentration for lower cell moles/liter
$C_{f,u}$ = average final concentration for upper cell moles/liter
$\bar{D}$ = diaphragm cell integral diffusion coefficient, cm²/sec
t = time, sec
β = cell constant

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RECEIVED for review May 18, 1970. Accepted October 2, 1970. Virginia's Water Resources Research Center acknowledges the support of this research project by the Office of Water Resources Research, Department of Interior, pursuant to Water Resources Act of 1964 (Public Law 88-379).