Diffusion Coefficient of Sodium Nitrate in Aqueous Solution at 25° C. as a Function of Concentration from 0.1 to 1.0M

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The integral diffusion coefficient of sodium nitrate in aqueous system was determined by the diaphragm cell method in the concentration range from 0.1 to 1.0M at 25° C. A stepwise regression method was employed to convert the integral data to differential diffusion coefficient data.

ACCURATE VALUES of the diffusion coefficient as a function of concentration are frequently needed in the study of mass transfer. Some experimental diffusion coefficient data can be found. For electrolytes, books authored by Harned and Owen (*2*) and Robinson and Stokes (*5*), and International Critical Tables (*4*) are the usual references. Yet, still as a rule rather than an exception, one cannot find the specific data one needs.

During a mass transfer study, there was a need of accurate data on the diffusion coefficient as a function of concentration up to 1.0*M* for sodium nitrate in aqueous solution at 25° C. However, no such set of data was available in the literatures, except that Harned and Shropshire (*3*) have reported experimental values for sodium nitrate up to 0.01*M* at 25° C. Therefore, experimental determination of the diffusion coefficient for such a system was undertaken.

EXPERIMENTAL METHOD

The diaphragm cell method was chosen for the determination of the integral diffusion coefficient (*6*).

APPARATUS

The diaphragm cell designed and used in the present work is shown in Figure 1. It was based on a principle suggested by Stokes (*6*) but with some modifications.

In the design here, the commonly used rubber stoppers and lubricated parts were eliminated. The trouble of adjusting "the thickness of the wire and the tube walls" such that "the stirrer in the upper compartment sinks while in the lower floats" (*6*) was also avoided by using two permanent magnetic stirring bars. The stirring rate was held at a constant speed of 10 r.p.m. instead of the commonly adopted "above critical" values. It was believed that, because of the relative nature of the diaphragm cell method, a constant speed was more desirable than an uncontrolled "above critical" speed. In addition, the stirrer was in contact with the surface of the diaphragm and this would be expected to give agitation comparable to a much higher stirring speed with a clearance between the stirrer and the surface.

The cell consists of cylindrical vessel *D*, divided into two compartments, upper and lower, by a fritted glass disk, *DP*. The cylindrical vessel was a piece of short borosilicate glass tubing with a 4.50-cm. inside diameter. The fritted glass disk was of fine porosity with nominal maximum pore size of 4.0 to 5.5 microns, a diameter of 4.0 cm., and a thickness of 0.35 cm. It had a total pore volume in the neighborhood of 2.0 cc.

The lower compartment was 4.50 cm. in diameter, 3.0 cm. in height, and contained 29.0 cc. The upper compartment was connected to the outer part of a 24/40 ground joint, *FH*, which is used as the seat for the inner part of the ground glass joint. There was a mark, *M*, on the upper cell.

Two capillary tubes, L_1 and L_2, of 0.114-cm. i.d. were connected to the lower compartment; L_1 was connected to the center of the bottom part of the lower compartment, with a Teflon stopcock attached near its end. L_1 served as the inlet as well as outlet to the lower compartment. The other capillary tube, L_2, with a short enlarged portion in the middle, was connected to the lower side of the lower compartment, with a Teflon stopcock near its end. L_2 served as outlet for air bubbles and as inlet for compressed air for the removal of the solution from the lower compartment. Both Teflon stopcocks were vacuum-tight and showed no detectable leak-

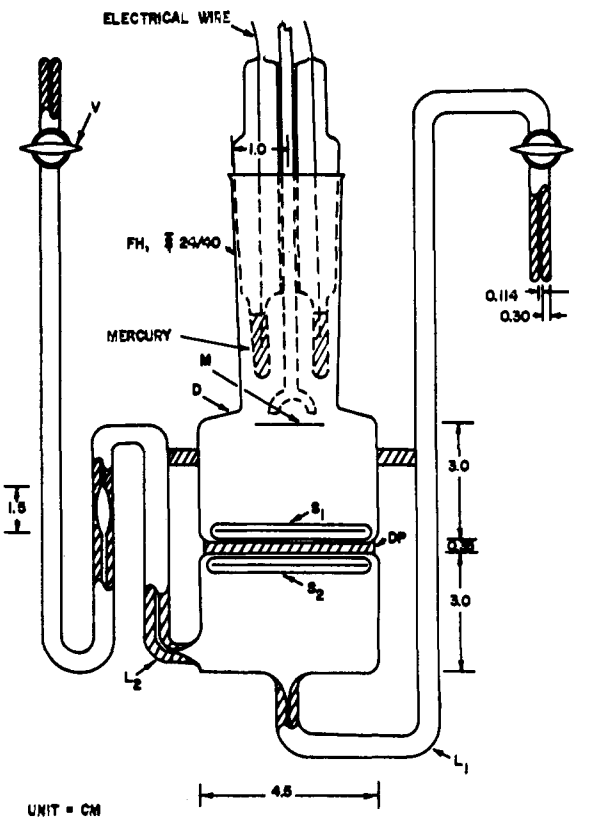

Figure 1. Diaphragm cell

age of solution under a vacuum of 60 mm. of Hg. Two such cells were constructed.

A Teflon-covered permanent magnetic stirring bar, S_2, sealed into the lower compartment, stirred the lower compartment solution. Another Teflon-covered permanent magnetic stirring bar, S_1, was placed upon the upper face of the diaphragm, DP. S_2 was held beneath the lower face of the diaphragm by magnetic action. Both stirrers were rotated with a synchronous motor.

A 24/40 inner joint (Figure 1) served as the housing for the stirring rod, and the two extended legs served as the conductivity electrodes for measuring the conductivity of the upper solution during the diffusion process.

A glass stirring rod with a forked end (Figure 1) served as a means of rotating the stirrers. The other end of the glass rod went through the tube sealed inside the inner joint and was connected to a flexible connecting rod by a section of thick rubber tubing. This was then connected to the synchronous motor through an adaptor. A heavy-duty Hurst synchronous motor, operating at a constant speed of 10 r.p.m., was used for rotating the stirrer bars.

The constant temperature bath was maintained at 25° C. as measured by a standardized thermometer. The temperature was controlled to ±0.05° C.

PROCEDURES

The cell shown in Figure 1 was filled with an air-free solution of approximately known concentration and one end was connected to a vacuum to remove air from the diaphragm. After eliminating any bubbles formed, the cell was thermostated, and the solution in the upper compartment was replaced by pure solvent. The cell was run for a few hours and then the upper solution was replaced by pure solvent. The run was timed from this point, and proceeded for 15 to 50 hours. The compartments were then sampled at a known time. The first few cubic centimeters of sample from the lower compartment were discarded. The final solutions were analyzed.

The cell was calibrated by using a 0.1N KCl aqueous solution. In addition to the calibration and the sodium nitrate runs, extra runs were performed at various concentrations of some "known" electrolytes, such as sodium chloride, hydrochloric acid, and 0.9N potassium chloride, whose diaphragm cell integral diffusion coefficients have been reported explicitly or implicitly (*7*, *8*). The KCl used was Fisher certified reagent, the NaCl was Fisher laboratory chemicals, and the $NaNO_3$ was Baker analyzed reagent, all used without further purification. Freshly boiled distilled water cooled in a tight container was used throughout the experiments.

ANALYSES

The concentrations of samples from the KCl and NaCl runs were analyzed by both the Volhard method (without filtration) and determination of the corresponding electrical conductivity. The concentrations of the samples from the $NaNO_3$ runs were analyzed by both flame spectrophotometric techniques and determination of the corresponding electrical conductivity. Samples from the HCl runs were analyzed by volumetric titration with alkali to a phenolphthalein end point.

RESULTS AND DISCUSSION

The well-known logarithmic formula (*7*), Equation 1, was used in all calculations both for the cell constants, β, and for the diaphragm cell integral diffusion coefficients, $\overline{D}$.

$$\overline{D} = \frac{1}{\beta t} \operatorname{Ln} \frac{C_{i,l} - C_{i,u}}{C_{f,l} - C_{f,u}} \tag{1}$$

The values for KCl tabulated by Stokes (*8*) were used in the calculation of the cell constants. The values for β reported here are the averages of four runs.

The 95% confidence intervals for the cell constants are

$$0.2839 < (\beta_1)_{av} < 0.2896$$
$$0.3602 < (\beta_2)_{av} < 0.3645$$

for β_1 and β_2, respectively.

Several runs were performed at various concentrations of HCl, KCl, and NaCl. The resulting diaphragm cell integral diffusion coefficients compared favorably with the values given by Stokes (*7*, *8*), and thus serve as a check on the reliability of the data obtained in the present experiment. Table I summarizes such a comparison. These data are single determinations and the average scatter is ±0.42%.

The resulting diaphragm cell integral diffusion coefficients for $NaNO_3$ in aqueous solution at 25° C. over a concentration range from 0.06 to 1.08 mole per liter are tabulated in Table II. The average scatter in the data is ±1.78% and thus these data are less precise than those given in Table I, because of differences in the analytical methods. A very precise analysis was available for the salts and acids used to generate the data in Table I. The analytical methods available for $NaNO_3$ were less satisfactory and this is reflected in the precision of the data.

To convert the experimental diaphragm cell integral diffusion coefficients into differential diffusion coeffi-

Table I. Experimental and Published (*7*, *8*) Diaphragm Cell Integral Diffusion Coefficients at 25° C.

Solute	Initial Lower Cell Concn., Mole/L.	Diaphragm Cell Integral Diffusion Coefficient: $\overline{D}_{exptl} \times 10^5$ sq. cm./sec.	Diaphragm Cell Integral Diffusion Coefficient: $\overline{D}_{lit} \times 10^5$ sq. cm./sec	$\frac{\overline{D}_{exptl} - \overline{D}_{lit}}{\overline{D}_{lit}} \times 100$
NaCl	0.1020	1.5089	1.5119	−0.19
KCl	0.8910	1.8457	1.8510	−0.31
	0.8706	1.8433	1.8518	−0.46
HCl	0.3178	3.0383	3.0616	−0.76
	0.3214	3.0802	3.0620	−0.39

Table II. Experimental Diaphragm Cell Integral Diffusion Coefficient, $\overline{D}$, vs. Initial Concentration for $NaNO_3$ in Aqueous Solution at 25° C.

Initial Lower Cell Concn., Mole/L.	$\overline{D} \times 10^5$ Sq. Cm./Sec.
0.0628	1.4442
0.0999	1.3752
0.1060	1.4066
0.2168	1.4286
0.3082	1.3171
0.4112	1.2878
0.4204	1.2870
0.5337	1.2807
0.7226	1.3102
0.7301	1.3343
1.0109	1.2845
1.0785	1.3197

cients, the series of approximation method as outlined by Stokes (*7*) was used, except that a stepwise regression was used instead of a graphical method. This avoided the pitfall of "arbitrary assumptions concerning the degree of the power series used to describe the individual regions" (*1*). The stepwise regression will try various possible combinations of the possible forms of the equations to determine an equation which will best represent the experimental data. An equation form such as $\overline{D} \times 10^5 = b_0' + b_1'C + b_2'\sqrt{C}$ was the result of the finding, with $b_0' = 1.5764$, $b_1' = 0.3895$, and $b_2' = -0.6359$. The resulting differential diffusion coefficients as a function of concentration were calculated from $D \times 10^5 = b_0 + 2b_1C + 3/2\ b_2\sqrt{C}$ with $b_0 = 1.5700$, $b_1 = 0.3736$, and $b_2 = -0.6350$. This is presented graphically in Figure 2. Calculated data are compared with two experimental values from the literature in Table III.

In Figure 2, the limiting slope has been included. Such a slope was calculated from the limiting Equation 2, recorded as Equation 6-10-5 by Harned and Owen (*2*).

$$D = D_0 - \delta_{(D)}\sqrt{C} \qquad (2)$$

In the present work, the diaphragm cell method was used for $NaNO_3$ solutions of concentrations greater than $0.05N$ as suggested by Stokes (*6*). Table II reflects such a restraint, as the lowest concentration was greater than $0.06N$. Since a stepwise regression was used for the converting from the integral data in Table II to the differential data in Figure 2, it was convenient to obtain some differential values at 0.005 and $0.01M$ for comparison of the values obtained in this work to those obtained by Harned and Shropshire (*3*). Table III and Figure 2 indicate such a comparison.

Table III. Differential Diffusion Coefficient, D, for $NaNO_3$ in Aqueous Solution at 25° C.

Concn., Mole/L.	$D_{exptl} \times 10^5$ Sq. Cm./Sec.	$D_{lit} \times 10^5$ Sq. Cm./Sec.[a]	$\frac{D_{exptl} - D_{lit}}{D_{lit}} \times 100\%$
0.005	1.509	1.516	−0.59
0.01	1.483	1.498	−1.00

[a] (*3*).

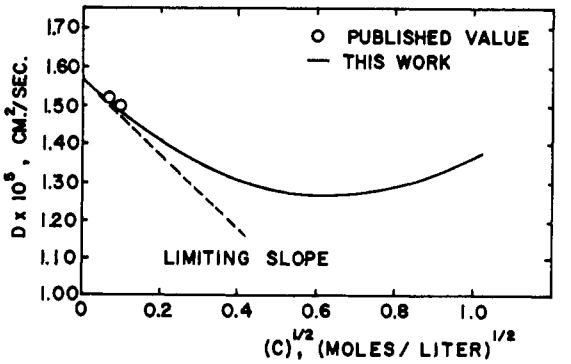

Figure 2. Observed differential diffusion coefficient for $NaNO_3$ in aqueous solution at 25° C.

NOMENCLATURE

$C_{i,l}$ = average initial concentration for lower cell, moles/l.
$C_{i,u}$ = average initial concentration for upper cell, moles/l.
$C_{f,l}$ = average final concentration for lower cell, moles/l.
$C_{f,u}$ = average final concentration for upper cell, moles/l.
$\overline{D}$ = diaphragm cell integral diffusion coefficient, sq. cm./sec.
D = differential diffusion coefficient, sq. cm./sec.
β = cell constant

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