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The Diffusion Coefficient at 25° of Potassium Chloride at Low Concentrations in 0.25 Molar Aqueous Sucrose Solutions

BY HERBERT S. HARNED AND JOSEPH A. SHROPSHIRE

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The diffusion coefficient of potassium chloride at concentrations between 0.004 and 0.025 molar in 0.25 molar sucrose solutions at 25° has been determined. Comparison with theoretical predictions has been made. The activity coefficient of potassium chloride has been determined from the diffusion coefficients. The limiting equivalent conductance of potassium chloride in the sucrose solution has been measured.

The conductometric method has been employed extensively to determine the diffusion coefficients of electrolytes of different valence types at low concentrations in water at 25°.[1] For the primary purpose of investigating the effects of varying viscosity and dielectric constant, the diffusion coefficient of potassium chloride at low concentrations in the medium sucrose–water has been determined. The results have been compared with those calculated by the theory of Onsager and Fuoss.[2]

Experimental Procedure and Results

Sucrose, dried over sodium hydroxide pellets, and dried potassium chloride were weighed and diluted to the required volumes in preparing the solutions. Due to the length of time required for the diffusion measurements, two parts per million of mercuric chloride were added to the solution to inhibit bacterial action.

The conductometric method for diffusion coefficient measurements is simplified if it is found that the difference in specific conductances between solutions of two concentrations is proportional to the difference in these concentrations. Conductance measurements were made to test this proportionality and to obtain the equivalent conductance of potassium chloride at infinite dilution in the 0.25 M sucrose solution. The extrapolated equivalent conductance was then employed to evaluate the limiting ionic conductances which are required for the theoretical computations. These results also were used to determine the final concentrations in the diffusion cell.

The conductance measurements were carried out in a suitable dilution cell in an oil thermostat. Since the solvent sucrose solution cannot be obtained in as high a degree of purity as that of conductivity water, corrections for solvent conductivity are much larger than in the usual aqueous solution investigations. Consequently, the results in this three-component system cannot be expected to equal in precision those obtained in the more usual case of a salt in water. However, the experimental consistency was such that a good estimate of the limiting conductance was obtained by employing the Onsager limiting theoretical equation.

The equivalent conductances read at round concentrations from a plot of Λ *versus* $c^{1/2}$ are given in Table I. The limiting value was found to 126.0 which is 0.4% lower than the value interpolated from the results of Stokes and Stokes.[3] Table II contains the specific conductances and values of the coefficient $(l'' - l')/(c'' - c')$. This conductance concentration coefficient varies somewhat but the variation is small. Consequently, in computing the diffusion coefficient from the conductance measurements, we have adopted the usual procedure of substituting the difference in conductance at the bottom and top of the cell for the concentration difference.[4]

TABLE I

EQUIVALENT CONDUCTANCE OF POTASSIUM CHLORIDE IN 0.25M SUCROSE SOLUTIONS AT 25°

c	Λ	c	Λ
0.002	122.78	0.014	118.43
.004	121.57	.016	118.03
.006	120.66	.018	117.66
.008	119.97	.020	117.31
.010	119.38	.030	115.89
.012	118.87	.040	114.78
Λ° = 126.00			

TABLE II

SPECIFIC CONDUCTANCE–CONCENTRATION COEFFICIENT FOR POTASSIUM CHLORIDE IN 0.25M SUCROSE SOLUTIONS

c''	$L'' \times 10^3$	c'	$L' \times 10^3$	$(L'' - L')/(c'' - c')$
0.02	2.34620	0.002	0.24556	0.1167
.018	2.11788	.004	.48628	.1165
.016	1.88848	.006	.72396	.1165
.014	1.65802	.008	.95976	.1164
.012	1.42644	.010	1.19380	.1163

Consistent results were obtained in this three-component system at concentrations of potassium chloride from 0.005 to 0.03 molar. Many attempts to obtain precise results at concentrations of salt less than 0.005 were not successful. In general, good results in these more viscous solutions were more difficult to attain than those previously achieved in aqueous solutions. The factors which caused this difficulty are obscure. The observed diffusion coefficients are recorded in the last column of Table III.

Theoretical Calculations

The calculation of the diffusion coefficient, $\mathfrak{D}$, was made in the usual way by use of the equation

$$\mathfrak{D} = 2000RT(\overline{\mathfrak{M}}/c)(1 + c\partial \ln y_{\pm}/\partial c) \qquad (1)$$

where $(\overline{\mathfrak{M}}/c)$ is the mobility term and the term in the second parentheses on the right is the thermodynamic one. The mobility term was computed by the equations given by Harned and Owen.[5] For evaluation of the thermodynamic term, it was assumed that a good approximation for the activity coefficient in these dilute solutions could be attained by the Debye–Hückel equation

$$\log y_{\pm} = -\frac{\mathcal{S}_{(f)}\sqrt{c}}{1 + A'\sqrt{c}} \qquad (2)$$

or

$$1 - c\frac{\partial \ln y_{\pm}}{\partial c} = 1 - \frac{1.154\mathcal{S}_{(f)}\sqrt{c}}{(1 + A'\sqrt{c})^2} \qquad (3)$$

The values obtained by this procedure are listed in the next to last column of Table III. In the absence of transference number data, the limiting transference numbers of the ions in the sucrose solutions were assumed to be identical with those in water. Upon this assumption and our value for

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[1] A complete bibliography is given in H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Edition, Reinhold Publ. Corp., New York, N. Y., 1958, p. 701.

[2] L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **34**, 2689 (1932).

[3] J. M. Stokes and R. H. Stokes, *ibid.*, **60**, 217 (1956).

[4] See H. S. Harned and R. L. Nuttall, THIS JOURNAL, **69**, 736 (1947).

[5] Ref. 1, p. 121, 122. Equations (4-4-19), (4-4-20) and (4-4-21).

TABLE III

THEORETICAL AND OBSERVED DIFFUSION COEFFICIENTS OF POTASSIUM CHLORIDE IN 0.25M AQUEOUS SUCROSE SOLUTIONS AT 25°

c	$\overline{\mathfrak{M}}'/c \times 10^{20}$	$\overline{\mathfrak{M}}''/c \times 10^{20}$	$\overline{\mathfrak{M}}/c \times 10^{20}$	$\mathfrak{D}_M \times 10^5$	$\mathfrak{D} \times 10^5$ Calcd.	$\mathfrak{D} \times 10^5$ Obsd.
0.00473	0.0003	0.1015	33.946	1.6185	1.623	1.617
.00486	.0003	.1034	33.947	1.618	1.622	1.611
.00953	.0004	.1617	34.006	1.599	1.607	1.592
.01030	.0004	.1699	34.014	1.597	1.605	1.601
.01077	.0004	.1748	34.018	1.595	1.603	1.604
.01985	.0006	.2542	34.098	1.574	1.586	1.588
.02380	.0006	.2810	34.125	1.568	1.581	1.572

$\lambda_+{}^0 = 61.82$; $\lambda_-{}^0 = 64.18$; $A' = 1.264$; $a^0 = 3.8$; $\mathcal{S}_{(f)} = 0.5285$; $\eta_0 = 0.1124$; $D = 76.60$; $T = 298.16$; $R \times 10^7 = 8.3144$; $\mathfrak{D}_0 = 1.678 \times 10^{-5}$; $\mathcal{S}_{(D)} = 1.098 \times 10^{-5}$.

the limiting equivalent conductance of the salt, the equivalent ionic conductances listed at the bottom of the table were computed. The distance parameter $\mathring{a}$ was taken to be 3.8 Å. The other quantities required for the calculation are also included at the bottom of the table. The fifth column of the table, designated $\mathfrak{D}_M$, was obtained by neglecting the variation of $(\overline{\mathfrak{M}}/c)$ with concentration. The difference between the values in columns (5) and (6) is the theoretical contribution of electrophoresis.

Comparison of the observed results with those calculated indicated a maximum error of about one per cent. of the diffusion coefficient. The nature of the deviations is seen more clearly from the curves in Fig. 1 which represent the calculated values of $\mathfrak{D}$, $\mathfrak{D}_M$ and the limiting equation of the theory. It is apparent from this figure that these results are not precise enough to prove the existence of the small electrophoretic contribution.

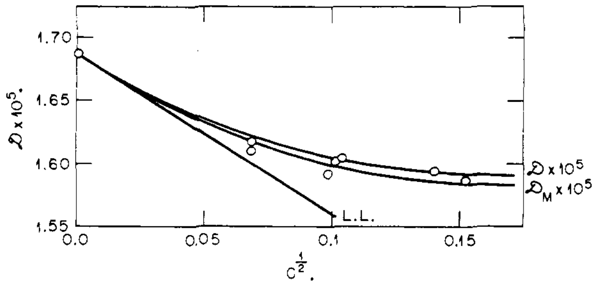

Fig. 1.—Observed and calculated diffusion coefficients.

The Activity Coefficient of Potassium Chloride in 0.25 M Sucrose Solutions

To determine the activity coefficient, $y_\pm$, the method[6] which employs the integral

$$\log y_\pm = -0.8686 \int_0^c \frac{\mathfrak{D}'}{c^{1/2}} \, dc^{1/2} \tag{4}$$

was adopted where the function $\mathfrak{D}'$ is given by

$$\mathfrak{D}' \equiv \frac{\mathfrak{D}}{1000\nu RT(\overline{\mathfrak{M}}/c)} - 1 \tag{5}$$

The limiting value of $\mathfrak{D}'/c^{1/2}$ is independent of the diffusion measurements and is given by the expression

$$\lim_{c\,=\,0} \left[\frac{\mathfrak{D}'}{c^{1/2}}\right] = -1.1513\mathcal{S}_{(f)} \tag{6}$$

where $\mathcal{S}_{(f)}$ is the theoretical slope of the Debye–Hückel equation for the logarithm of the activity coefficient. Table IV contains values of $\mathfrak{D}'/c^{1/2}$ at the concentrations designated and values of the activity coefficient at round concentrations, evaluated from the areas under the graph shown in Fig. 2.

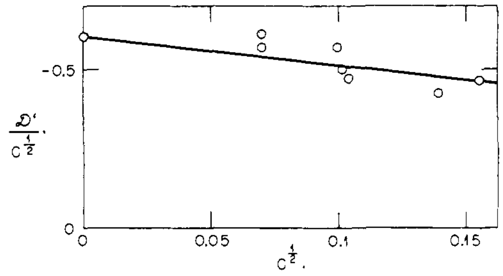

Fig. 2.—Graph for computing the activity coefficient.

Although the values of $\mathfrak{D}'/c^{1/2}$ are more scattered than those obtained in the majority of cases of salts in pure water, the graph as drawn to the exact limiting value yields activity coefficients which should be within the limit of one in the third decimal place.

TABLE IV

$D'/c^{1/2}$ AND MOLAR ACTIVITY COEFFICIENT $y_\pm$ OF POTASSIUM CHLORIDE IN 0.25M SUCROSE SOLUTIONS AT 25°

$c^{1/2}$	$-\mathfrak{D}'/c^{1/2}$	$c^{1/2}$	$-\mathfrak{D}'/c^{1/2}$
0.0000	0.598	0.1015	0.499
.0688	.574	.1038	.471
.0697	.613	.1409	.429
.0976	.572	.1543	.461
c	$y_\pm$	c	$y_\pm$
0.0000	1.000	0.005	0.922
.0005	.974	.010	.894
.001	.963	.015	.874
.002	.949	.025	.858

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[6] H. S. Harned, *Proc. Natl. Acad. Sci.*, **40**, 551 (1954).