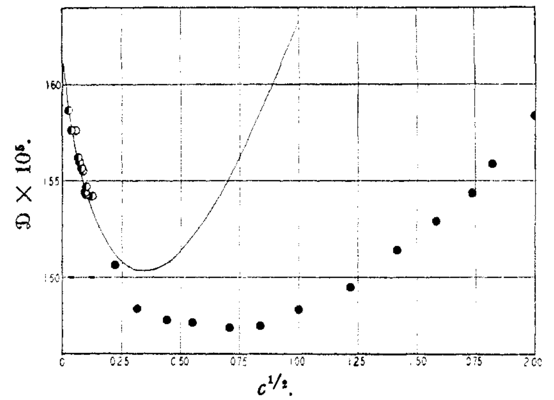

Fig. 1.—The diffusion coefficient of sodium chloride at 25° from conductance and diaphragm cell measurements. The curve represents the theoretical calculation according to equations (1) to (6): ◐, conductance; ●, diaphragm cell; —, theory.

deed, the agreement with the theory of our results on potassium chloride up to 0.3 to 0.5 molar concentration was entirely unexpected. A more normal condition occurs with the diffusion coefficients of lithium and sodium chlorides. As an illustration, the diffusion coefficient of sodium chloride up to 4 molar has been plotted against $\sqrt{c}$ in Fig. 1. The half-linked circles are our results and the dots represent values at high concentrations recently obtained by Stokes[8] who has developed an improved diaphragm cell method. His cell was calibrated by using the results of Harned and Nuttall[1] on potassium chloride. The experimental values approach the theoretical curve (represented by the solid line) as the concentration decreases. If the lowest point of Stokes at 0.05 molar is correct, then a curve through his results should coincide with the theoretical curve somewhat below 0.04 molar.

Summary

1. The differential diffusion coefficients of lithium and sodium chlorides from 0.001 to 0.01 molar concentrations have been determined by the conductance method.

2. Excellent agreement with the theoretical computation is obtained at these concentrations. Recent diaphragm cell measurements indicate that departure from the theoretical predictions will begin to occur in the neighborhood of 0.02 to 0.04 molar concentration.

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[8] Stokes, THIS JOURNAL, **72**, 763 (1950); **72**, 2243 (1950).

NEW HAVEN, CONN. RECEIVED JULY 5, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Differential Diffusion Coefficient of Potassium Nitrate in Dilute Aqueous Solutions at 25°

BY HERBERT S. HARNED AND ROBERT M. HUDSON

Values of the differential diffusion coefficients of lithium, sodium and potassium chlorides[1,2,3] at concentrations between 0.0005 and 0.015 molar have been shown to conform to the theory of Onsager and Fuoss.[4] On the other hand, values of the diffusion coefficient of calcium chloride at these low concentrations deviated considerably from the theoretical prediction.[5] Apart from the fact that calcium chloride is an unsymmetrical electrolyte, one might correlate the above nonconformity with theory with the anomalous behavior of the cation transference number of calcium chloride.[6] Although the equivalent conductance of this salt approaches the Onsager theory as the concentration approaches zero, the cation transference number lies considerably above the theoretical prediction and, at concentrations at which it has been determined, does not appear to approach the theoretical estimation.

The cation transference number of potassium nitrate behaves similarly to that of the calcium ion since it lies above the theoretical prediction. The equivalent conductance of this salt approaches the limiting law from below, a fact which has been interpreted as indicating slight ionic association. Since this behavior is different from that of the chlorides of lithium, sodium and potassium, we thought that possibly the diffusion coefficient of potassium nitrate might disagree with theory in a manner similar to that of calcium chloride.

Experimental Results and Theoretical Calculations.—In the determination of the diffusion coefficient by the conductometric method, it is assumed that the difference in conductances at the bottom and top electrodes is proportional to the difference in salt concentrations at these two electrodes. That no appreciable error is caused by this assumption is proved by the data in Table I which were derived from the conductance measurements of Shedlovsky.[7] In Table I, the specific conductances, L_1 and L_2, at round concentrations, c_1 and c_2, are recorded. In the last column, the

TABLE I

SPECIFIC CONDUCTANCES OF POTASSIUM NITRATE AT 25°

c_1	$L_1 \times 10^3$	c_2	$L_2 \times 10^3$	$(L_1 - L_2)/(c_1 - c_2)_{c_1 + c_2 = 0.011}$
0.01	1.3578	0.001	0.1418	0.1351
.009	1.2285	.002	.2810	.1354
.008	1.0955	.003	.4187	.1354
.007	0.9621	.004	.5558	.1354
.006	0.8276	.005	.6922	.1354

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[1] Harned and Nuttall, THIS JOURNAL, **71**, 1460 (1949).

[2] Harned and Blake, Jr., *ibid.*, **72**, 2265 (1950).

[3] Harned and Hildreth, *ibid.*, **73**, 650 (1951).

[4] Onsager and Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

[5] Harned and Levy, THIS JOURNAL, **71**, 2781 (1949).

[6] Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1950, pp. 163–164.

[7] Shedlovsky, THIS JOURNAL, **54**, 1411 (1932).

coefficient $(L_1 - L_2)/(c_1 - c_2)$ where $(c_1 + c_2)$ equals 0.011 is given. We note that this coefficient is constant within very narrow limits as c_1 approaches c_2.

The observed and theoretically calculated diffusion coefficients are compiled in Table II. By substituting the values:

$T = 298.16$; $D = 78.54$[8]; $\eta_0 = 8.949 \times 10^{-3}$; $\lambda_1^0 = 73.52$[9]; $\lambda_2^0 = 71.44$[9]; $A' = 1.14$; $2B = -0.1250$; and $\mathcal{S}_{(f)} = 0.5091$

TABLE II

OBSERVED AND CALCULATED DIFFERENTIAL DIFFUSION COEFFICIENTS OF POTASSIUM NITRATE IN WATER AT 25°

c	$\mathfrak{D} \times 10^5$ obsd.	$\mathfrak{D} \times 10^5$ calcd.	$\mathfrak{D}' \times 10^5$
0.0000	...	1.9308	(1.9308)
.000904	1.902	1.900	1.933
.00121	1.894	1.895	1.928
.00163	1.887	1.891	1.927
.00221	1.891	1.885	1.937
.00259	1.873	1.882	1.921
.00268	1.878	1.882	1.927
.00403	1.869	1.872	1.929
.00452	1.868	1.869	1.930
.00503	1.877	1.866	1.942
.00515	1.857	1.865	1.923
.00538	1.872	1.864	1.939
.00600	1.868	1.861	1.938
.00728	1.856	1.855	1.932
.00868	1.847	1.849	1.929
.00919	1.855	1.847	1.939
		Mean	1.9314

in the theoretical equations,[3,10] we obtain for potassium nitrate solutions at 25°

$$\mathfrak{D} = 4.9581 \times 10^{13}\,(\overline{M}/c)\left(1 + c\,\frac{\partial \ln y_\pm}{\partial c}\right) \quad (1)$$

$$(\overline{M}/c) \times 10^{20} = 38.943 - 0.00333\,\frac{\sqrt{c}}{(1 + 1.14\sqrt{c})} + 18.960c\phi(1.14\sqrt{c}) \quad (2)$$

$$\left(1 + c\,\frac{\partial \ln y_\pm}{\partial c}\right) = 1 - \frac{0.5862\sqrt{c}}{(1 + 1.14\sqrt{c})^2} - 0.2879\,c - c\psi(d) \quad (3)$$

The values of empirical constants, A' and B, used in the thermodynamic term, were obtained by fitting the activity coefficient data of Robinson and Stokes[11] to the equation

$$\log y_\pm = -\frac{0.5091\sqrt{c}}{1 + A'\sqrt{c}} + 2Bc - \log(1 + 0.03603m) \quad (4)$$

over the concentration range of 0.1 to 0.5 molal. The term $c\psi(d)$ was evaluated from the computations of Gibson and Kincaid[12] from which the density can be expressed by

$$d = 0.997 + 0.0630c - 0.00229c^{3/2} \quad (5)$$

and the density term by

$$\psi(d) = \frac{-0.002c - 0.00344c^{3/2}}{0.997 - 0.00203c - 0.00229c^{3/2}} \quad (6)$$

The limiting equation for the diffusion coefficient of potassium nitrate at 25° becomes

$$\mathfrak{D} \times 10^5 = 1.9308 - 1.1319\sqrt{c} \quad (7)$$

Comparison of the results in the second and third columns of Table II indicate good agreement with the theory although a few of the results differ from the theory by ±0.5%. The nature of these deviations is shown in Fig. 1 in which $\mathfrak{D} \times 10^5$ is plotted against the molar concentration, c. Since the observed results show positive and negative deviations from the theory, we may conclude that the discrepancies are due to experimental error. The last column of Table II contains the function, $\mathfrak{D}' = (\mathfrak{D}_0 - \mathfrak{D})_{\text{theo.}} + \mathfrak{D}_{\text{obs.}}$. We note that the mean value of this quantity over all the experimental results is very nearly equal to $\mathfrak{D}_0$, the limiting Nernst value of the diffusion coefficient, a fact which is evidence in favor of the theory.

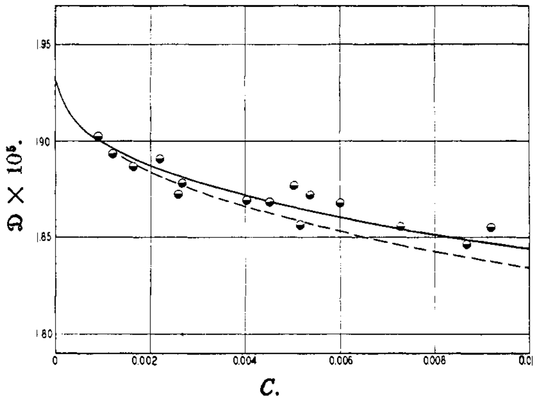

Fig. 1.—The diffusion coefficient of potassium nitrate in dilute aqueous solutions at 25°. The solid curve represents the theoretical results. The dashed curve represents $\mathfrak{D}$ in the theory after omission of the electrophoretic effect.

It is instructive to consider the details of the above calculation. In Table III, the contribution of the various terms in equations (2) and (3) are recorded while the density term has been omitted since its contribution is very small at these low concentrations. As shown by the second column, the contribution of the second term on the right of equation (2) is negligible. This result is due to the fact that this term involves the square of the difference in ionic conductances over the square of their sum, which for potassium nitrate is a small quantity. The variation of the electrophoretic term given in the fourth column is caused

TABLE III

DETAILS OF THE CALCULATION

c	(1)	(2)	$(\overline{M}/c) \times 10^{20}$	$\left(1 + c\,\frac{\partial \ln y_\pm}{\partial c}\right)$	$\mathfrak{D} \times 10^5$	$\mathfrak{D}_M \times 10^5$
0.0000	0.0000	0.0000	38.943	1.0000	1.9308	1.9308
.001	.0001	.0415	38.984	.9824	1.8989	1.8969
.003	.0002	.0955	39.039	.9707	1.8788	1.8742
.005	.0002	.1388	39.082	.9631	1.8661	1.8595
.01	.0003	.2176	39.161	.9499	1.8443	1.8341

(1) Negative of the second term on right of equation (2). (2) $\phi(1.14\sqrt{c})$ term. $\mathfrak{D}_M$ is the diffusion coefficient calculated by neglecting the variation of mobility term, $(\overline{M}/c) \times 10^{20}$, *i.e.*, by keeping this term constant and equal to its limiting value, 38.943.

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[8] Wyman, *Phys. Rev.*, **35**, 613 (1930).

[9] MacInnes, Shedlovsky and Longsworth, THIS JOURNAL, **54**, 2758 (1932).

[10] Harned, *Chem. Revs.*, **40**, 461 (1947).

[11] Robinson and Stokes, *Trans. Faraday Soc.*, **45**, 612 (1949).

[12] Gibson and Kincaid, THIS JOURNAL, **59**, 25 (1937); ref. (6), p. 253.

by the contribution of the third term on the right of equation (2), and this variation from 0 to 0.01 molar amounts to about 0.5%, which is one-tenth of the variation of the thermodynamic term over the above concentration range. The difference between the values in the last columns of the table equals the contribution of the mobility term. In Fig. 1, the dashed curve is the plot of $\mathfrak{D}_M \times 10^5$. The solid curve appears to represent the actual results somewhat better than the dashed curve. However, it would be a mistake to conclude categorically that such evidence confirms the correctness of the mobility term.

Summary

1. The differential diffusion coefficient of potassium nitrate in water at 25° from 0.001 to 0.01 molar has been determined by the conductometric method.

2. The results are in agreement with theory within the experimental error.

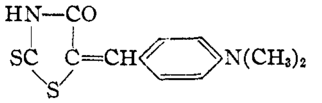
NEW HAVEN, CONN. RECEIVED JULY 5, 1950

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Ionization Constants of *p*-Diethylaminobenzylidenerhodanine

BY E. B. SANDELL AND J. J. NEUMAYER

Feigl[1] prepared *p*-dimethylaminobenzylidenerhodanine in 1928 and used it for the detection of silver.



Since that time this compound, or its ethyl analog, has become an important reagent for the photometric determination of gold, silver, mercury and, indirectly, of cyanide. A knowledge of the ionization constants of the compound would be helpful in establishing the most favorable conditions for these procedures. The constants of the ethyl compound are reported in the present work.

Two equilibria have been found to exist in aqueous solutions of *p*-diethylaminobenzylidenerhodanine (HR)

$$\underset{\substack{\text{almost colorless}\\ \text{(very pale yellow)}}}{\mathrm{HR{\cdot}H^+}} \rightleftarrows \underset{\text{pink}}{\mathrm{HR}} + \mathrm{H^+}$$

$$\mathrm{HR} \rightleftarrows \mathrm{H^+} + \underset{\text{(yellow)}}{\mathrm{R^-}}$$

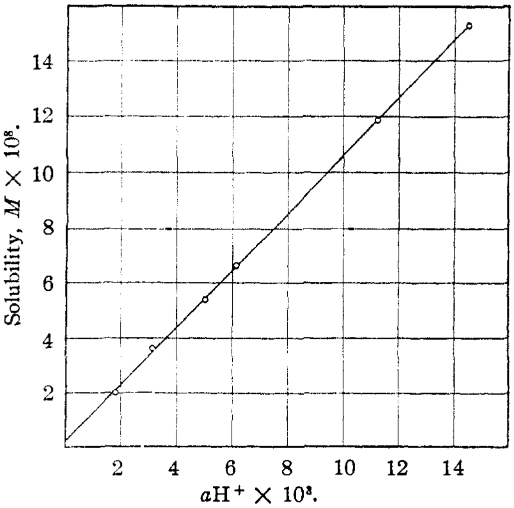


Fig. 1.—Solubility of *p*-diethylaminobenzylidenerhodanine in 20% ethyl alcohol solution on the acidic side of the isoelectric point.

The expressions for the respective ionization constants are

$$a\mathrm{H}^+[\mathrm{HR}]/[\mathrm{HR{\cdot}H^+}] = K_1 \qquad (1)$$

$$a\mathrm{H}^+[\mathrm{R^-}]/[\mathrm{HR}] = K_2 \qquad (2)$$

The values of these constants have been found by determining the solubility, S, of the substance as a function of the hydrogen-ion activity

$$\begin{aligned} S &= [\mathrm{HR}]_s + [\mathrm{HR{\cdot}H^+}] + [\mathrm{R^-}] \\ &= [\mathrm{HR}]_s + a\mathrm{H}^+[\mathrm{HR}]_s/K_1 + K_2[\mathrm{HR}]_s/a\mathrm{H}^+ \qquad (3) \end{aligned}$$

where $[\mathrm{HR}]_s$ is the concentration of the un-ionized form in the saturated solution.

The value of $[\mathrm{HR}]_s/K_1$ is given by the slope of the line representing the solubility in the acidic range (Fig. 1), where $[\mathrm{R^-}]$ may be considered negligible; the value of $K_2[\mathrm{HR}]_s$ is given by the slope of the line representing the solubility in the alkaline range (Fig. 2), where $[\mathrm{HR{\cdot}H^+}]$ is negligible. It then remains to determine $[\mathrm{HR}]_s$ to obtain K_1 and K_2. Evidently the most favorable acidity for determining $[\mathrm{HR}]_s$ from equation (3) is at or near that corresponding to minimum solubility (isoelectric point), where the ionized forms make the smallest contribution to the total solubility. The hydrogen ion activity at the isoelectric point is given by

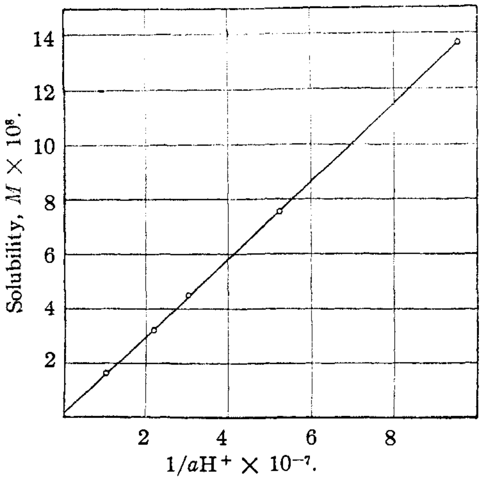


Fig. 2.—Solubility of *p*-diethylaminobenzylidenerhodanine in 20% ethyl alcohol solution on the basic side of the isoelectric point.

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[1] F. Feigl, *Z. anal. Chem.*, **74**, 380 (1928).