V. Summary

1. The distribution of hexadecylpyridonium chloride between water and nitrobenzene at 25° has been determined. The simple ion activity product in water divided by the simple ion activity product in nitrobenzene is 9.00×10^{-4}.

2. The conductance of hexadecylpyridonium chloride in water, water saturated with nitrobenzene, nitrobenzene and nitrobenzene saturated with water, has been determined at 25°.

3. In water saturated with nitrobenzene, the breakpoint in Λ comes at 5.7 to 5.8×10^{-4}. In pure water, Λ passes through a slight maximum starting approximately at 6.7×10^{-4}.

4. The ion pair dissociation constant in nitrobenzene has been evaluated by the Fuoss method. $k = 1.19 \times 10^{-2}$ in nitrobenzene saturated with water, while in pure nitrobenzene, k is only about one-half that, namely, 4.26×10^{-3}.

5. The calculated sample ion activity ratio is constant at concentrations less than 5.8×10^{-4}, but increases at higher concentrations. This indicates that at concentrations less than critical, the salt is completely dissociated in the water phase. The value of the critical concentration determined in this way is in good agreement with that determined from the Λ-$\sqrt{C}$ plot.

6. An estimate has been made of the simple ion concentration product at concentrations greater than critical. An attempt has been made to calculate the state of the system on the assumption that only one complex species exists at concentrations greater than critical.

PROVIDENCE, R. I. RECEIVED SEPTEMBER 18, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Differential Diffusion Coefficient of Potassium Chloride in Aqueous Solutions

BY HERBERT S. HARNED AND RALPH L. NUTTALL

In a recent article,[1] we described in detail an apparatus and technique for the determination of the diffusion coefficients of electrolytes by means of conductance measurements. Values of the diffusion coefficient of potassium chloride at concentrations from 0.001 to 0.01 N at 25° were reported. The results at 25° have been extended to higher concentrations[2] and determinations in the dilute concentration range have also been made at 20 and 30°. The present communication contains the new results and a summary of all the results with emphasis on their theoretical computation.

TABLE I

THE DIFFUSION COEFFICIENTS OF POTASSIUM CHLORIDE IN AQUEOUS SOLUTION AT 20, 25 AND 30°

c is concn. in moles per liter, $\mathbf{D} \times 10^5$

c	20° Observed	Theoretical	c	25° Observed	Theoretical
0.00000		(1.7652)	0.00000[a]		(1.9958)
.00125	1.736[c]	1.734	.00125[a]	1.961	1.960
.00248	1.7245[c]	1.7235	.00194[a]	1.954	1.953
.00367	1.719[d]	1.716	.00325[a]	1.943	1.943
.00451	1.709[c]	1.712	.00585[a]	1.931	1.929
.01121	1.6885[d]	1.690	.00704[a]	1.924	1.924
	30°		.00980[a]	1.918	1.915
			.01261[b]	1.908	1.907
0.00000		(2.2334)	.02654[c]	1.879	1.883
.00326	2.172[c]	2.173	.03992[c]	1.877	1.870
.00650	2.154[c]	2.155	.04620[c]	1.872	1.866
.00896	2.146[d]	2.145	.05450[d]	1.860	1.861
.01236	2.139[d]	2.133	.06074[d]	1.856	1.858
			.1298[e]	1.838	1.840
			.3323[e]	1.842	1.839
			.5276[e]	1.852	1.853

Electrode areas: [a] 2 × 0.2 cm.^{2} [b] 2 × 0.1 cm.^{2} [c] 1 × 0.2 cm.^{2} [d] 1 × 0.1 cm.^{2} [e] circle, 1 mm. diameter.

Experimental

All the determinations are included in Table I. The manipulation and technique was the same as previously described. However, five kinds of cells which differed in containing electrodes of different areas were employed. Four of them had rectangular electrodes of areas indicated in the table and the fifth circular electrodes of millimeter diameter.

Theoretical Calculations[3]

Onsager and Fuoss[4] have developed a theory for the variation of the diffusion coefficient of electrolyte with its concentration. For 1:1 electrolytes, their final equation is

$$\mathbf{D} = 16.629 \times 10^{10} T \left(\frac{\overline{M}}{c}\right)\left(1 + c\,\frac{\partial \ln y_\pm}{\partial c}\right) \quad (1)$$

where

$$\left(\frac{\overline{M}}{c}\right) \times 10^{20} = 1.0748 \left(\frac{\lambda_1^0\lambda_2^0}{\lambda_1^0 + \lambda_2^0}\right) - \frac{22.148}{\eta_0 (DT)^{1/2}}\left(\frac{\lambda_1^0 - \lambda_2^0}{\lambda_1^0 + \lambda_2^0}\right)^2 \frac{\sqrt{c}}{1 + A'\sqrt{c}} + \frac{9.304 \times 10^7}{\eta_0 (DT)^2}\, c\phi\,(A'\sqrt{c}) \quad (2)$$

$\mathbf{D}$ is the diffusion coefficient (cm.^{2} sec^{-1}), D the dielectric constant, T the absolute temperature, c the electrolyte concentration in moles per liter, η_0 the viscosity of the medium and λ_1^0, λ_2^0 are the equivalent conductances at infinite dilution.

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(1) Harned and Nuttall, THIS JOURNAL, **69**, 737 (1947); see also Harned and French, *Ann. N. Y. Acad. Sci.*, **46**, 267 (1945).

(2) Harned and Nuttall, *Ann. N. Y. Acad. Sci.*, in press.

(3) In this part, we have employed the symbols of Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, p. 178–180. See also Harned, *Chem. Rev.*, **40**, 461 (1947).

(4) Onsager and Fuoss, *J. Phys. Chem.*, **37**, 2689 (1932).

TABLE II

DATA EMPLOYED IN THEORETICAL CALCULATIONS

T	D [7]	η_0 [8]	λ_1^0 [9]	λ_2^0 [9]	a [10]	$2B$ [10]	$S_{(f)}$ [10]
293.16	80.36	10.087×10^{-3}	66.24	68.56	3.8	0.0182	0.5046
298.16	78.54	8.949×10^{-3}	73.52	76.34	3.8	.0213	.5092
303.16	76.75	8.004×10^{-3}	80.766	84.176	3.8	.0260	.5141

These expressions reduce to the Nernst limiting equation

$$D_0 = 17.873 \times 10^{-10} T \left(\frac{\lambda_1^0 \lambda_2^0}{\lambda_1^0 + \lambda_2^0}\right) \qquad (3)$$

when c equals zero. To evaluate the term containing the activity coefficient, $y_{\pm}$, on the mole per liter scale, which expresses the effect produced by the gradient of the chemical potential, we have employed the equation

$$\left(1 + c\,\frac{\partial \ln y_{\pm}}{\partial c}\right) = 1 - \frac{1.1514\, S_{(f)}\sqrt{c}}{(1 + A'\sqrt{c})^2} + 4.605\, Bc - c\psi(d) \qquad (4)$$

where

$$\psi(d) = \frac{\dfrac{\partial d}{\partial c} + 0.001\,(2M_1 - M_2)}{d + 0.001\,(2M_1 - M_2)c} \qquad (5)$$

In these equations $A'\sqrt{c} = \kappa a = \kappa \mathring{a} \times 10^{-8}$, where a and $\mathring{a}$ represent the mean distances of approach of the ions in centimeters and Ångström units, respectively, and κ is the Debye and Hückel reciprocal distance. $S_{(f)}$ is the limiting function of the Debye and Hückel theory and B an empirical constant. M_1 and M_2 are the molecular weights of the solvent and solute respectively.[4]

The second and third terms on the right of equation (2) represent the effect of electrophoresis. Values of the function $\phi(\kappa a)$ or $\phi(A'\sqrt{c})$ are given in tabular form by Harned and Owen.[5,6] The values of the quantities employed in the computations are compiled in Table II. Upon introduction of these values in equations (1), (2) and (4), we obtain the numerical equations

$$20\,^{\circ}\text{C.}:\ D = 4.875 \times 10^{13}\left(\frac{\overline{M}}{c}\right)\left(1 + c\,\frac{\partial \ln y_{\pm}}{\partial c}\right) \qquad (6)$$

$$\frac{\overline{M}}{c} \times 10^{20} = 36.210 - \frac{0.00423\sqrt{c}}{1 + 1.245\sqrt{c}} + 16.62\, c\, \phi(1.245\sqrt{c}) \qquad (7)$$

$$\left(1 + c\,\frac{\partial \ln y_{\pm}}{\partial c}\right) = 1 - \frac{0.5810\sqrt{c}}{(1 + 1.245\sqrt{c})^2} + 0.0430\, c - c\psi(d) \qquad (8)$$

$$c\psi(d) = \frac{0.00990c - 0.00336c^{3/2}}{0.99823 + 0.00990c - 0.0024c^{3/2}} \qquad (9)$$

$$25\,^{\circ}\text{C.}:\ D = 4.958 \times 10^{13}\left(\frac{\overline{M}}{c}\right)\left(1 + c\,\frac{\partial \ln y_{\pm}}{\partial c}\right) \qquad (10)$$

$$\frac{\overline{M}}{c} \times 10^{20} = 40.253 - \frac{0.00573\sqrt{c}}{1 + 1.249\sqrt{c}} + 18.96c\, \phi(1.249\sqrt{c}) \qquad (11)$$

$$\left(1 + c\,\frac{\partial \ln y_{\pm}}{\partial c}\right) = 1 - \frac{0.5873\sqrt{c}}{(1 + 1.249\sqrt{c})^2} + 0.0490c - c\psi(d) \qquad (12)$$

$$c\psi(d) = \frac{0.00959c - 0.00348c^{3/2}}{0.99707 + 0.00959c - 0.00232c^{3/2}} \qquad (13)$$

$$30\,^{\circ}\text{C.}:\ D = 5.0412 \times 10^{13}\left(\frac{\overline{M}}{c}\right)\left(1 + c\,\frac{\partial \ln y_{\pm}}{\partial c}\right) \qquad (14)$$

$$\frac{\overline{M}}{c} \times 10^{20} = 44.3011 - \frac{0.00775\sqrt{c}}{1 + 1.253\sqrt{c}} + 21.47c\, \phi(1.253\sqrt{c}) \qquad (15)$$

$$\left(1 + c\,\frac{\partial \ln y_{\pm}}{\partial c}\right) = 1 - \frac{0.5919\sqrt{c}}{(1 + 1.253\sqrt{c})^2} + 0.0599c - c\psi(d) \qquad (16)$$

$$c\psi(d) = \frac{0.0094c - 0.0034c^{3/2}}{0.9957 + 0.0094c - 0.0023c^{3/2}} \qquad (17)$$

The values of $c\psi(d)$ were evaluated from the density computations of Scott[11] by means of the equations

$$d(20°) = 0.99823 + 0.04843c - 0.00224c^{3/2} \qquad (18)$$

$$d(25°) = 0.99707 + 0.04811c - 0.00232c^{3/2} \qquad (19)$$

$$d(30°) = 0.9957 + 0.0479c - 0.0023c^{3/2} \qquad (20)$$

Theoretical Considerations

A glance at Table I in which the results computed by the theoretical equations are tabulated reveals a remarkable agreement of experiment with theory at all three temperatures. This is illustrated by Fig. 1 where our results are represented by circles and the theoretical values by the curves B. At concentrations below 0.05 N, there is little doubt of the validity of the theoretical result. The agreement at the higher concentrations at 25° is unexpected. This may be partly due to a fortunate choice of salt and temperature since at 25° the relative viscosity of potassium chloride in water changes less than 0.3% over a concentration range from zero to 0.5 normal. Further, one would expect a deviation from theory due to the change in dielectric of the medium with increase in salt concentration.

The curves in Fig. 1 illustrate the nature of the theoretical calculation. Curve A is calculated from the limiting equation

$$D = D_0 - S_{(D)}\sqrt{c} \qquad (21)$$

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(5) Ref. 4, p. 130.

(6) Harned, *Chem. Rev.*, **46**, 461 (1947).

(7) Ref. 4, p. 112; (8) ref. 4, p. 128; (9) 25°: ref. 12, p. 172; Shedlovsky, THIS JOURNAL, **54**, 1423 (1932); Longsworth and MacInnes, *ibid.*, **60**, 3073 (1938); 20° and 30°: Zeldes, Dissertation, Yale University (1947); (10) ref. 4, p. 381; $S_{(f)}$ and B adjusted to universal constants given by Birge, *Rev. Mod. Phys.*, **13**, 233 (1941).

(11) Scott, *J. Phys. Chem.*, **35**, 2315 (1931).

where

$$S_{(\mathrm{D})} = \frac{3.754 \times 10^{-3}}{D^{3/2}T^{1/2}}\left(\frac{\lambda_1^0 - \lambda_2^0}{\lambda_1^0 + \lambda_2^0}\right) + \frac{3.683 \times 10^{-8}}{\eta_0\, D^{1/2}T^{1/2}}\left(\frac{\lambda_1^0 - \lambda_2^0}{\lambda_1^0 + \lambda_2^0}\right)^2 \quad (22)$$

At 25°, equation (21) becomes

$$\mathrm{D} \times 10^5 = 1.9958 - 1.170\sqrt{c} \quad (23)$$

Only at very great dilution does the experimental curve approach coincidence with the limiting law.

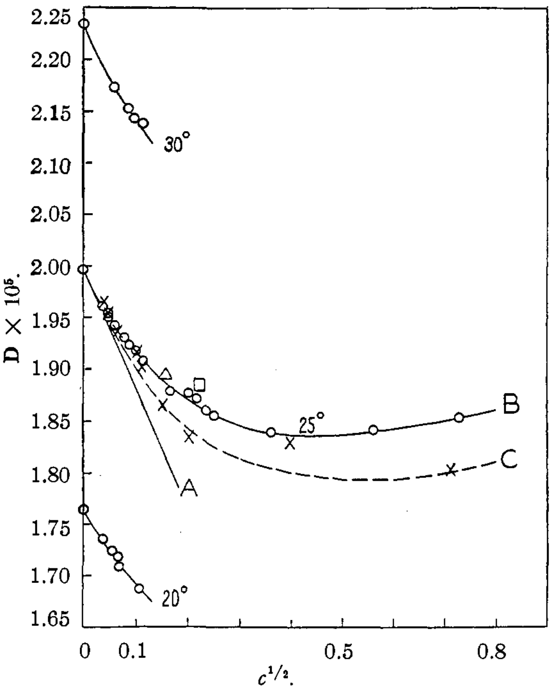

Fig. 1.—Diffusion coefficient of potassium chloride in water at 20, 25 and 30°: (1) circles represent observed results; (2) crosses represent diaphragm cell measurements; (3) triangle, Cohen and Bruins; (4) square, Lamm; A, limiting law by equations (21) and (22); B and solid curves at 20 and 30° represent the complete theoretical calculation according to equations (1), (2), (4) and (5); C, calculated by equation (24) which omits electrophoresis.

The dashed curve C was obtained from equation (1) by introducing the limiting value of $(\overline{M}/c)$ to give at 25°

$$\mathrm{D} = 4.958 \times 10^{13} \times 40.253 \times 10^{-20}\left((1 + c\,\frac{\partial \ln y_\pm}{\partial c}\right) \quad (24)$$

$$= 1.9958 \times 10^{-5}\left(1 + c\,\frac{\partial \ln y_\pm}{\partial c}\right)$$

Consequently, it represents the result obtained by neglecting the effect of electrophoresis. The deviation of this curve from the complete theoretical result represented by curve B is always greater than the deviations of the experimental points. Consequently, for this salt, our results appear to confirm the theory of the electrophoretic effect. It is interesting to note that since the mobilities of the potassium and chloride ions are so nearly equal the electrophoretic correction is due only to the third term in equation (2) involving $\phi(A'\sqrt{c})$.

Comparison with Results by Other Methods

The only other measurements at concentrations below 0.01 *N* which can be compared with ours, were obtained by the diaphragm cell method. Gordon[12] has calculated differential diffusion coefficients of potassium chloride from the data of McBain and Dawson,[13] Hartley and Runnicles[14] and his own experiments. These measurements[15] have been revised by Gordon by using a cell calibration which is based on our results below 0.01 *N* and are designated by crosses in Fig. 1. At low concentrations the agreement is very good but as the concentration increases their results are somewhat lower than ours.

At higher concentrations, our results can be compared to those of Cohen and Bruins,[16] Lamm,[17] and Clack.[18] Cohen and Bruins used a layer analysis method by employing a four compartment cell and allowing a 0.1 *N* potassium chloride solution in the bottom compartment to diffuse into the other three compartments. The compartments were then separated and the solutions in each analyzed with the greatest care by the use of a liquid interferometer. The average concentration in the four compartments was 0.025 *N* and the mean diffusion coefficient was 1.674 × 10^{-5} cm.^{2}/sec. at 20°, or 1.893 × 10^{-5} cm.^{2}/sec. at 25°, if our estimate of the influence of temperature is employed. This value is shown by the triangle in Fig. 1. It is somewhat ambiguous since it is neither a true differential nor an integral diffusion coefficient. Hartley and Runnicles contended that it corresponds approximately to an integral diffusion coefficient for 0.06 *N* potassium chloride diffusing into water and it must correspond to a differential diffusion coefficient at a concentration close to the average concentration of 0.025 *N*. Lamm, using his optical scale method obtained a diffusion coefficient of 1.667 × 10^{-5} cm.^{2}/sec. at 20° for 0.1 *N* potassium chloride diffusing into water which corresponds to a value of 1.885 × 10^{-5} cm.^{2}/sec. at 25°. This is represented by the square in Fig. 1 at the mean concentration of 0.05 *N*. Both Cohen and Bruins' and Lamm's values compare favorably with ours. The results of Clack who employed a steady state optical method at 18.5° and at concentrations from 0.08 *N* to higher concentrations are about 4% lower than ours.

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(12) Gordon, *J. Phys. Chem.*, **5**, 522 (1937); *Ann. N. Y. Acad. Sci.*, **46**, 285 (1945).

(13) McBain and Dawson, *Proc. Roy. Soc.* (*London*), **A118**, 32 (1935).

(14) Hartley and Runnicles, *ibid.*, **A168**, 401 (1938).

(15) Harned, *Chem. Rev.*, **40**, 461 (1947).

(16) Cohen and Bruins, *Z. physik. Chem.*, **103**, 337 (1923).

(17) Lamm, *Nova Acta Reg. Sci. Upsala*, **IV**, 10(6) 1937.

(18) Clack, *Proc. Phys. Soc.* (*London*), **36**, 313 (1924).

This estimate was made by using the temperature coefficient obtained by us at low concentrations.

The effect of temperature is very marked. However, the relative change with concentration in dilute solution is almost independent of temperature. For a concentration of 0.01 N the ratio D/D_0 is 0.9593, 0.9591, and 0.9589 at 20, 25 and 30°, respectively.

Summary

1. Determinations of the diffusion coefficient of potassium chloride in water at 20°, 25° and 30° have been obtained by a conductance method previously described by us.[19]

2. In the region of concentration from 0.001 to 0.01 N, excellent agreement with the theory of Onsager and Fuoss is obtained, and the Nernst limiting law for electrolytic diffusion is confirmed.

3. Comparison of our results with those obtained by the diaphragm cell method, by layer analysis and by the optical scale method indicates good agreement considering the wide variety of mechanisms and theories of these methods.

[19] Ref. 1.

NEW HAVEN, CONN. RECEIVED NOVEMBER 16, 1948

[CONTRIBUTION NUMBER 700 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

The Heats of Dilution of Aqueous Solutions of Four Amino Acids at 25°[1]

BY L. S. MASON, W. F. OFFUTT[2,3] AND A. L. ROBINSON

Previous communications from this Laboratory have reported on the heats of dilution of aqueous solutions of glycine,[4] α- and β-alanine,[5] and four aminobutyric acids.[6] Examination of the results for these seven amino acids indicated that the structure of the organic radical was more important than the location of the amino group in determining the thermochemical properties studied.[6] The same conclusion was reached when the differential entropies of dilution of these same aqueous solutions were calculated.[7] Study of the heats of dilution of aqueous solutions of amino acids was continued to obtain further evidence affecting this conclusion. This paper reports results for α-amino-*n*-valeric acid, valine, norleucine and ε-aminocaproic acid.

Experimental

Apparatus and Method.—Except for minor changes, the calorimeter is the same as that used in previous investigations.[6] The thermopile had been sealed into the Dewar vessel, which comprises the calorimeter vessel, with wax, thus dividing the vessel into two watertight compartments. The junctions of the thermopile had been separated from the solutions in the calorimeter by a plastic coating, so that dilutions in organic solvents might be made if desired, two copper vessels were constructed, one for each half of the calorimeter, which conformed to the inner surface of the Dewar vessel and whose flat surfaces fitted snugly against the junctions of the thermopile. The interiors of these vessels could not be satisfactorily gold plated; instead, a plastic coating was baked on. This coating provided an electrical resistance greater than 10 megohms. Electrical resistance of 1000 megohms between the thermopile junctions and the copper vessels was furnished by sheets of mica of 0.04 mm. thickness.

The two electrical heaters were made by winding no. 40 Advance wire spirally around a glass tube. The wire was soldered to platinum nibs which lead through the wall of the tube to heavy copper leads. Several coats of a silicone resin were baked on over the wire for insulation from the solutions in the calorimeter.

The volumes of the monel metal dilution pipets were 10.36 (left) and 10.32 (right) ml. To maintain a constant dilution ratio of one to 100 in the two halves of the calorimeter, the twin calorimeters held 1036 and 1032 ml. of water, respectively.

The amino acid solutions were prepared immediately before each day's series of measurements to minimize bacterial action. Following each day's measurements, the calorimeter was rinsed with distilled water. The calorimeter was disinfected periodically with 10% formaldehyde solution.

Solutions were made up by volume. Concentrations were converted to molalities using the density data of Dalton and Schmidt[8] for valine and the data of Daniel and Cohn[9] for ε-aminocaproic acid. The densities of α-amino-*n*-valeric acid and norleucine solutions were determined by standard methods using specific gravity bottles. The results may be expressed by the following equations for 25°

α-Amino-*n*-valeric acid ($m < 0.6$) $d = 0.9971 + 0.0240\,m$

Norleucine ($m < 0.05$) $d = 0.9971 + 0.0188\,m$

It has been suggested[10] that atmospheric carbon dioxide dissolved in the dilution water may affect the heats of dilution of amino acids at low concentrations by disturbing their dissociation equilibria. This effect was not observed in the previous studies[4,5,6] of this series. A further test was made by performing dilutions with norleucine solutions using water in equilibrium with atmospheric carbon dioxide and with free access of the atmosphere to the interior of the calorimeter. Results were compared with runs made with carbon dioxide-free water (specific conductance 0.4×10^{-6} ohm^{-1} cm.$^{-1}$) and with the calorimeter sealed from the atmosphere. The results agreed within the limits of the experimental error.

Dilutions were made to the limits of solubility of the

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[1] This investigation was supported by the Buhl Foundation.

[2] The material of this paper is taken from the thesis submitted to the Graduate School, University of Pittsburgh, by W. F. Offutt, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1948.

[3] Present address: Operations Evaluation Group, Division of Industrial Cooperation of M. I. T., OEG, Room 3827 (CNO), Navy Department, Washington 25, D. C.

[4] W. E. Wallace, W. F. Offutt, and A. L. Robinson, THIS JOURNAL, **65**, 347 (1943).

[5] H. A. Benesi, L. S. Mason, and A. L. Robinson, *ibid.*, **68**, 1755 (1946).

[6] L. S. Mason and A. L. Robinson, *ibid.*, **69**, 889 (1947).

[7] A. L. Robinson, *J. Chem. Phys.*, **14**, 588 (1946).

[8] J. B. Dalton and C. L. A. Schmidt, *J. Biol. Chem.*, **103**, 549 (1933).

[9] J. Daniel and E. J. Cohn, THIS JOURNAL, **58**, 415 (1936).

[10] J. M. Sturtevant, *ibid.*, **62**, 3519 (1940).