around each bond of 200°, calculated from Debye's modification of the Kuhn equation, instead of the 360° for free rotation. Since the intrinsic viscosity is proportional to R_s^3 it is about 39 times larger than would be expected for a polystyrene molecule having free rotation.

Summary

Molecular dimensions for polystyrene fractions in benzene have been obtained from viscosity and light scattering data. It was found that the root mean square of the distance between the ends of the molecule is approximately equal to the diameter of the molecular sphere needed for the explanation of viscosity. Evidence for the absence of appreciable branching or cross-linking in the polystyrene fractions was obtained. Polystyrene molecules in benzene were found to be much stiffer than would be expected from a free rotation model. This stiffness is responsible for the relatively high viscosities of polystyrene solutions.

RECEIVED DECEMBER 17, 1948

[CONTRIBUTION FROM THE METCALF LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XXXVIII. The Distribution of Hexadecylpyridonium Chloride between Water and Nitrobenzene at 25°

BY PHILIP F. GRIEGER[1] AND CHARLES A. KRAUS

I. Introduction

The purpose of the present investigation was to determine the distribution of a long chain electrolyte between water and a slightly soluble organic liquid of relatively high dielectric constant, and thereby to test (by a method apparently hitherto untried) the validity of certain ideas which are currently held to be true, concerning aqueous long chain electrolyte solutions. Hexadecylpyridonium chloride was chosen as the salt because its critical concentration in water is convenient for the purpose of this work. Nitrobenzene was chosen as the reference liquid because its solubility in water is low (about 0.2% by weight), its dielectric constant is relatively high (34.5) and especially because considerable information was available on the conductance of long chain salts in this solvent.

Previous measurements made in this Laboratory on long chain electrolytes in nitrobenzene indicate that the activity product of simple ions can be evaluated from a knowledge of the conductance of these solutions.[2] Then, from distribution and conductance measurements, the activity product of simple ions in water saturated with nitrobenzene can be established and, in turn, the concentration product of simple ions in the aqueous solvent can be approximated. In the light of this information, another test can be made of the two leading hypotheses on long chain electrolyte solutions: (I) complete dissociation of the electrolyte at concentrations less than critical; (II) association of the electrolyte (to form one or more polyionic species) at concentrations greater than critical. The experimental results presented here are consistent with these two hypotheses.

In the distribution experiments concentrations were determined conductometrically; it was found that significantly precise measurements could be made at concentrations approaching 10^{-4} N, or well below the critical concentration, 5.8×10^{-4} N.

Although the solubility of nitrobenzene in water is low, the conductance of hexadecylpyridonium chloride in water saturated with nitrobenzene differs significantly in the neighborhood of the critical concentration (and below) from the conductance of this salt in pure water. Hence, the distribution results reported here must be regarded as appertaining specifically to the solvent: water saturated with nitrobenzene.

Conventions.—Salt concentrations are given in moles per liter of solution, exclusively. Quantities that refer to the water phase are designated by primes, while quantities that refer to the nitrobenzene phase are not specially marked. In some instances where only the water phase is under consideration (and no ambiguity can result), the water phase quantities have not been primed.

II. Experimental

Apparatus and Procedure.—The methods used in determining the conductance of the solutions have been adequately described in earlier papers of this series.[3]

The distribution measurements were made in a cell similar to those used in previous conductance work in this Laboratory, except that a side chamber (large enough to hold all the nitrobenzene in the system) was sealed to the cell near its base. By manipulating the cell, it was possible to place either the water or nitrobenzene layer in contact with the electrodes. It was found that equilibrium could be established (as judged by the constancy of the resistances of the separate phases) within a reasonable time, usually one or two days, by moving the cell in such a way that the liquids were caused to pass slowly through each other. By careful mixing, foam and emulsion formation were practically eliminated. The electrodes of the cell were lightly platinized.

The distribution experiments were carried out simply, as follows: after weighing the cell dry, nitrobenzene and then

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[2] H. L. Pickering, Thesis, Brown University (1947).

[3] Evers and Kraus, THIS JOURNAL, **70**, 3049 (1948); Pickering, Thesis, Brown University, 1947.

water were added, the cell being weighed after each addition. The liquids were mixed and the conductance of each phase was determined. In general, the solvent conductances were: aqueous phase, 10^{-6}; nitrobenzene phase, 1 to 2 × 10^{-8}. A known quantity of salt was added (either as concentrated nitrobenzene or water solution) and the liquids were mixed and allowed to stand, alternately, until the resistances became constant (to less than a part per thousand). The experimental observables were, then: the specific resistance of each phase, the weight of nitrobenzene, water and salt in the system. All measurements reported here were made at 25 ± 0.01°.

Solvents.—Water[3] of specific conductance 1 × 10^{-6} was used. The nitrobenzene was purified by Dr. H. L. Pickering.[2] Its specific conductance was less than 10^{-9}.

Salt.—Hexadecyl alcohol (m. p., 47.3°) was fractionally distilled at reduced pressure (about 1 mm.), (m. p., 49.1°). This was converted into the iodide as described by Evers.[3] It was fractionally distilled at reduced pressure (m. p., 22.8°). Hexadecylpyridonium iodide was prepared from this as described by Evers.[3] It was recrystallized from isopropyl alcohol plus ether and then from acetone. Hexadecylpyridonium chloride was prepared by metathesis of the iodide with silver chloride in absolute ethanol. The chloride was recrystallized twice from acetone to which a little ethanol was added. This preparation was carried out by Dr. G. L. Brown.[4] The conductance of this salt was determined in water; its conductance was unchanged by one more crystallization from acetone plus ethanol.

III. Experimental Results

In Table I (and Fig. 1) are presented values of the equivalent conductance, Λ, as a function of the square root of concentration, $\sqrt{C}$, for hexadecylpyridonium chloride in water and water saturated with nitrobenzene. In the latter case, the measurements were made in the presence of a small amount (about 0.1% by weight) of excess nitrobenzene. The method of computing Λ in this case is described below.

TABLE I

CONDUCTANCE OF HEXADECYLPYRIDONIUM CHLORIDE IN WATER AND WATER SATURATED WITH NITROBENZENE AT 25°

$100\sqrt{C}$	Λ	$100\sqrt{C}$	Λ
A. Water			
1.186	92.7	2.999	89.84
1.377	91.8	3.126	89.01
1.924	90.48	3.339	85.07
2.274	89.92	3.466	82.56
2.424	89.69	3.785	75.88
2.572	89.39	4.196	68.92
2.693	89.86	4.674	62.89
2.709	90.01	5.316	56.75
2.861	89.96		
B. Water Saturated with Nitrobenzene			
1.225	90.8	2.372	89.50
1.746	90.36	2.567	86.36
1.838	90.51	2.999	77.87
2.049	90.22	3.295	73.20
2.284	89.82	3.962	64.95

In Table II (and Fig. 2), Λ is given as a function of $\sqrt{C}$ for hexadecylpyridonium chloride in nitrobenzene and nitrobenzene saturated with water. In the latter case, the measurements were also made in the presence of a small amount (about 0.1% by weight) of excess water. The method of computing Λ in this case is described below.

TABLE II

CONDUCTANCE OF HEXADECYLPYRIDONIUM CHLORIDE IN NITROBENZENE AND NITROBENZENE SATURATED WITH WATER AT 25°

$100\sqrt{C}$	Λ
A. Nitrobenzene	
0.9168	29.73
1.355	28.95
1.767	28.03
2.385	26.62

$100\sqrt{C}$	Λ	$100\sqrt{C}$	Λ
B. Nitrobenzene Saturated with Water			
1.565	30.27	3.821	27.02
1.986	29.72	4.046	26.65
2.244	29.38	4.410	26.07
2.611	28.83	4.930	25.30
2.948	28.34	5.213	24.85
3.254	27.88	5.474	24.46
3.568	27.39		

The conductances and distribution ratios were computed by successive approximation in the following way. The conductance in nitrobenzene saturated with water and in the presence of a small excess of water was determined: κ was plotted against concentration, where concentration was computed on the assumption that the water phase contained no salt. A similar plot was made for water saturated with nitrobenzene. The first approximation to the distribution ratio was computed from the specific conductances of the two phases, using the plots described above to establish concentration as a function of conductance. The concentrations in the conductivity experiments were then corrected by taking into account the amount of salt that was present in the small excess water phase in the nitrobenzene saturated with water experiments, and in the small excess nitrobenzene phase in the water saturated with nitrobenzene experiments, using the first approximation distribution ratios. The Λ values in Tables I and II were computed using these corrected concentrations.

The densities of the solutions were assumed to be equal to those of the pure solvents. The densities of water and water saturated with nitrobenzene were assumed to be the same (0.9971). The density of nitrobenzene was taken as 1.999.[5] The density of nitrobenzene saturated with water was found to be 1.1979.

The solubilities of water in nitrobenzene solutions of hexadecylpyridonium chloride and of nitrobenzene in water solutions of this salt were not precisely determined but solubilities were approxi-

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(4) G. L. Brown, Thesis, Brown University, 1947.

(5) Walden and Birr, *Z. physik. Chem.*, **163A**, 281 (1932).

mated which were good enough to permit of accurate calculation of the distribution ratio.[6]

In Table III (and Fig. 4, curve 1), the ratio: (salt concentration, water phase)/(salt concentration, nitrobenzene phase) is given as a function of salt concentration water phase. The ratios were obtained as follows: the concentration of the nitrobenzene phase was determined from its conductance, the concentration of the water phase was determined by difference from a knowledge of the weights of salt, of nitrobenzene and of water in the system. In making this calculation, it was assumed that the solubility of water in nitrobenzene is 0.2% by weight and that the solubility of nitrobenzene in water is 0.2% by weight.

The concentration in the water phase was also determined directly by measuring its conductance. The distribution ratios so obtained are not presented here, but they are in satisfactory agreement with the ones listed in Table III, considering that the solvent correction for the water phase is about one hundred times the corresponding correction in the nitrobenzene phase. The ratios determined directly are higher in every case (corresponding to an undercorrection for solvent conductance). In the dilute end, they differ from those given in Table III by about 3%; in the concentrated end, by about 1%.

The uncertainty introduced by lack of precise measurements on the solubilities of nitrobenzene in water and *vice versa* is slight. Thus, in the experiment at $C' = 3.590 \times 10^{-4}$, if it is assumed that the liquids have zero solubility in each other, a value of C'/C is computed that is only 0.3% lower than the value listed in Table III.

For the nitrobenzene saturated with water phase, salt concentration was determined as a function of specific conductance using the empirical equation

$$C = 3.210 \times 10\kappa + 1.349 \times 10^{5}\kappa^{2} - 2.12 \times 10^{8}\kappa^{3} \quad (1)$$

For twenty concentrations between 2×10^{-4} and 3×10^{-3}, the mean deviation between observed and calculated values of C is 0.093%, the largest deviation being 0.2%. In determining the ratios directly, a large scale plot of C' as a function of κ for water saturated with nitrobenzene was used.

In column 3 of Table III are also given values of the ratio of activity products $C'f'/C\alpha f$ in water and nitrobenzene. These values will be discussed below.

TABLE III

DISTRIBUTION COEFFICIENTS, C'/C, AND ACTIVITY COEFFICIENTS, $C'f'/C\alpha f$, FOR HEXADECYLPYRIDONIUM CHLORIDE BETWEEN WATER AND NITROBENZENE AT 25°

$10^4C'$	C'/C	$C'f'/C\alpha f$	$10^4C'$	C'/C	$C'f'/C\alpha f$
0.795	0.280	0.302	5.133	0.229	0.298
.922	.280	.305	5.378	.229	.301
1.034	.283	.309	5.626	.228	.301
1.188	.280	.309	5.695	.228	.301
1.417	.276	.308	5.968	.234	.311
1.729	.266	.302	6.606	.250	.330
2.608	.254	.300	6.958	.261	.348
3.590	.244	.300	9.773	.349	.468
4.665	.233	.298	15.23	.517	.692
4.899	.230	.297			

IV. Discussion

1. Conductance in Aqueous Solution.—As shown in Fig. 1, the equivalent conductance, Λ, for hexadecylpyridonium chloride in water and water saturated with nitrobenzene, is nearly the same at concentrations less than critical (with nitrobenzene present), namely, 5.8×10^{-4}. At concentrations greater than this in pure water, Λ passes through a slight maximum before falling off rapidly. In pure water, the critical (rise) point lies at 6.7×10^{-4} slightly higher than the break in the presence of nitrobenzene. In water saturated with nitrobenzene, Λ decreases sharply at 5.8×10^{-4}. In Fig. 1, the water saturated with nitrobenzene curve has been drawn with 5.8×10^{-4} as the critical concentration; actually, a somewhat lower value, as low as 5.7×10^{-4}, might have been chosen.

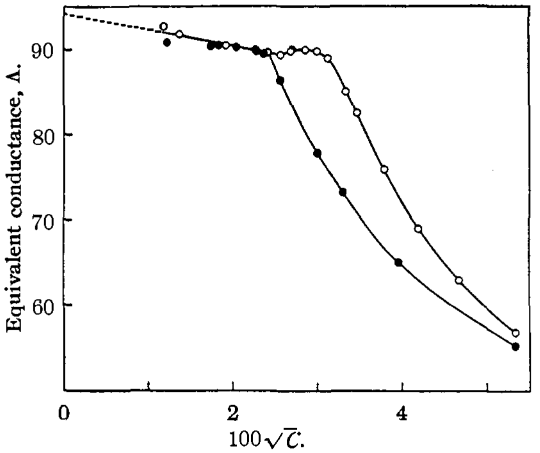

Fig. 1.—Conductance at 25° of hexadecylpyridonium chloride in: open circles, water; solid circles, water saturated with nitrobenzene.

The value of Λ_0, as determined by extrapolation, lies between 93 and 94, which corresponds to 17 or 18 for the limiting conductance for hexadecylpyridonium ion. This value is about the same as

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[6] To a large quantity of nitrobenzene solution, for example, small weighed amounts of water were added. The mixtures were agitated and allowed to stand until the conductance after each addition of water was constant. Saturation was judged visually and by the form of the conductance *vs.* water content plot. Thus, at a salt concentration of $1.3 \times 10^{-3}\ N$, the solubility of water was judged to be 2.5 mg./g. soln., and at a salt concentration of 5.7×10^{-3}, 2.3 mg./g. soln. Similarly, in water at a salt concentration of 1.1×10^{-4}, the solubility of nitrobenzene was judged to be 2 mg./g. soln., and at a salt concentration of 1.2×10^{-3}, 1.9 mg./g. soln. The solubility of nitrobenzene in pure water is about 2 mg./g. water. Gross and Saylor, THIS JOURNAL, **53**, 1744 (1931), give 1.78 mg./g. water at 15° and 2.05 mg./g. water at 30°. While the solubility of nitrobenzene doubtless increases with increasing salt concentration, this effect is so small that it may be neglected.

that approximated for the octadecyltrimethylammonium ion.[7]

2. Dissociation Constant in Nitrobenzene.—The properties of hexadecylpyridonium chloride are greatly modified on addition of water up to saturation. This will be evident on inspection of Fig. 2 in which values of Λ are plotted against $\sqrt{C}$ for solutions in nitrobenzene in the absence and presence of water to saturation.

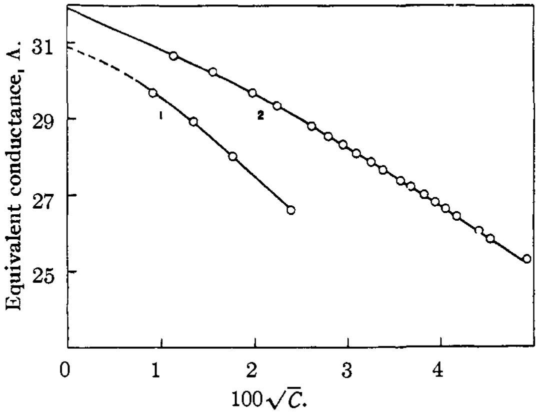

Fig. 2.—Conductance at 25° of hexadecylpyridonium chloride in: (1) nitrobenzene; (2) nitrobenzene saturated with water.

Fuoss plots[8] for the results of Table II are shown in Fig. 3. For hexadecylpyridonium chloride in nitrobenzene, $\Lambda_0 = 30.9$, $K = 4.26 \times 10^{-3}$; in nitrobenzene saturated with water, $\Lambda_0 = 31.9$, $K = 1.19 \times 10^{-2}$. In the latter case, the deviation from the straight line at $C = 3 \times 10^{-3}$ N (the highest nitrobenzene phase concentration in the distribution experiments) is positive and amounts to about 1%. The observed value of Λ, then, is about 1% lower[9] than that calculated using $K = 1.19 \times 10^{-2}$. Thus, α computed from $\alpha = \Lambda/\Lambda_0 f(Z)$ is about 1% lower than α calculated from $K = 1.19 \times 10^{-2}$.

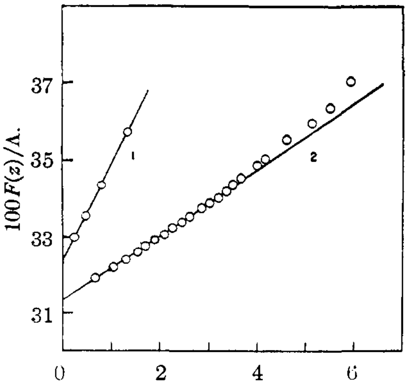

Fig. 3.—Fuoss plots for hexadecylpyridonium chloride in: (1) nitrobenzene; (2) nitrobenzene saturated with water.

3. Calculated Activity Product.—In what follows, let C be total salt concentration; C_+, C_-, a_+, a_-, the corresponding ion concentrations and activities; f, the mean activity coefficient; α, the degree of dissociation. Assume that simple positive and negative ions exist in both aqueous and nitrobenzene phases. For equilibrium in the system, it is necessary that

$$a'_+ a'_- / a_+ a_- = k \qquad (2)$$

where k is the distribution constant. If the electrolyte is completely dissociated in the water phase, then

$$C'f'/Cf\alpha = \sqrt{k} \qquad (3)$$

In Table III, columns 3 and 6, values of $C'f'/Cf\alpha$ are given as a function of C'.[10] This ratio is shown graphically in Fig. 4, curve 2; it is constant at concentrations less than 5.80×10^{-4} and increases (nearly linearly) with C' at higher concentrations. The critical concentration determined by this method is in good agreement with that derived from the Λ–$\sqrt{C'}$ plot. For the eleven (not all listed in Table III) determinations between $C' = 1.64 \times 10^{-4}$ and 5.80×10^{-4}, the activity ratio is 0.300 ± 0.001; for the seventeen (all) at concentrations less than 5.80×10^{-4}, the activity ratio is 0.302 ± 0.003. The constancy of the calculated activity ratio is consistent with hypothesis (I). In what follows, k is taken as 9.00×10^{-2}.

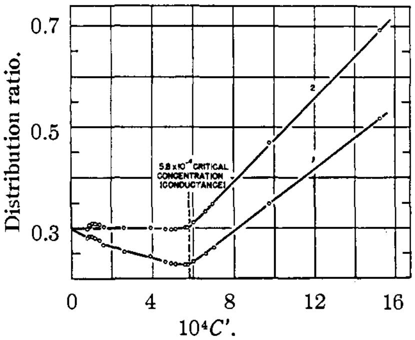

Fig. 4.—Distribution of hexadecylpyridonium chloride between water and nitrobenzene at 25°: (1) concentration ratio; (2) activity ratio.

4. Simple Ion Product at Concentrations Greater than Critical.[11]—In Table IV are listed, for water saturated with nitrobenzene, the simple ion activity product (Eq. (2)) and an estimate of the simple ion concentration product. The latter quantity has been computed using $\log_{10} f =$

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[7] Grieger and Kraus, This Journal, **70**, 3803 (1948), estimated 18 for the limiting conductance of octadecyltrimethylammonium ion.

[8] Using $Z = (0.7838\ \Lambda_0 + 44.64)\Lambda_0^{-3/2}\sqrt{\Lambda C}$; $\log_{10} f = -1.736 \sqrt{C\alpha}$

[9] The slope is 0.0820. The % deviation in Λ is approximately equal in magnitude (but slightly less) to the % deviation in the Fuoss plot.

[10] Values of $C'f'/Cf\alpha$ have been computed using $\log_{10} f' = -0.5065\sqrt{C'}$ (for f, see note 8) and $k = 1.19 \times 10^{-2}$.

[11] The primes have been omitted in Sections 4 and 5.

$-0.5065(C_+C_-)^{1/4}$. The values so obtained are uncertain, because the ionic strength of the solution is unknown, but they are probably not greatly in error. For example, if $\log_{10}f = -0.5065\sqrt{C}$ is used to estimate the activity coefficient, values of the simple ion concentration product are obtained that differ from those listed in Table IV by a few per cent. at most.

Also listed in Table IV, for convenience, are the quantities C_+C_-/C^2 and C_+C_-/C.

TABLE IV

SIMPLE ION ACTIVITY AND CONCENTRATION PRODUCT IN WATER SATURATED WITH NITROBENZENE AT CONCENTRATIONS GREATER THAN CRITICAL

$C \times 10^4$	$a_+ a_-$ $\times 10^7$	$\mathrm{C}_+ \mathrm{C}_-$ $\times 10^7$	C_+C_-/C^2	C_+C_-/C $\times 10^2$
5.968	3.13	3.31	0.929	5.55
6.606	3.33	3.52	.808	5.34
6.958	3.38	3.57	.737	5.13
9.773	3.66	3.89	.407	3.98
15.228	3.98	4.21	.182	2.77

The fact that C_+C_-/C^2 is less than unity, is consistent with the assumption of ion association at concentrations greater than critical (hypothesis II).

Since neither the simple long chain nor the gegenion concentrations can be larger than C, the quantity C_+C_-/C represents a lower limit on either simple ion concentration. This ratio falls off with increase in C, but at $C = 1.5 \times 10^{-3}$, the simple ion concentrations cannot be less than about one-fifth the total salt concentration.

5. Calculation for One Complex Species.[11]—If it is assumed that in the water phase there exist only simple ions and only complex species made up of i, long chain ions, and j, gegenions, then the three concentrations and i and j can be found from conductivity, distribution and transference data.[12] Let C be the salt concentration; C_+, C_-, and C_{ij} be the concentration of the simple long chain ion, the gegenion and the ij complex ion; u_+, u_-, and u_{ij}, the corresponding mobilities (cm./sec. per volt/cm.); κ, the specific conductance (ohm^{-1}cm.$^{-1}$); $p = C_+C_-$; and t_+, the cation transference number. Then, if $i > j$

$$10^3\kappa/N\kappa = \bar{\kappa} = C_+u_+ + c_-u_- + (i-j)(C_{ij}u_{ij})$$
$$t_+\bar{\kappa} = C_+u_+ + iC_{ij}u_{ij}$$

$$\begin{aligned} p &= C_+C_- \qquad (4)\\ C &= C_+ + iC_{ij}\\ C &= C_- + jC_{ij}\end{aligned}$$

These equations can be combined (without any assumption about u_{ij}) to give

$$\Lambda/\Lambda_+ = y + q\,\Lambda_-/y\Lambda_+ + ((q/y) - y)(-y + t_+\Lambda/\Lambda_+)/(1-y) \qquad (5)$$

where $y = C_+/C$, $q = p/C^2$, $\Lambda_+ = N\epsilon u_+$, $\Lambda_- = N\epsilon u_-$. Further, C_{ij}, i and j can be established if some rule is adopted for u_{ij}. Corresponding to $u_{ij} = u_+(i-j)/i^{1/3}$

$$i^{2/3} = (-y + t_+\Lambda/\Lambda_+)^2/(\Lambda(1/\Lambda_+) - y - q\Lambda_-/y\Lambda_+)(1-y) \qquad (6)$$

Once C_+ is found from Eq. (5), C_- comes immediately from $p = C_+C_-$; i can be obtained from Eq. (6) and then C_{ij} and j from the material balance equations in (4).

In Table V, the experimental quantities, Λ, p and t_+, are given for several round values of C, together with the five calculated quantities. Λ and p were taken from graphs of the data given here. The values of t_+ listed in Table V are estimates. Their basis is as follows. Hartley, Collie and Samis[13] found for hexadecylpyridonium bromide in water at 35°: $t_+ = 0.22$ at 7×10^{-4} N (critical concentration); $t_+ = 1.34$ at 3.2×10^{-3} N. It has been assumed, here, that t_+ is a linear function of concentration for hexadecylpyridonium bromide at 35° over the range 7×10^{-4} to 3.2×10^{-3} N. The same relation has been assumed for hexadecylpyridonium chloride in water saturated with nitrobenzene at 25° over the range 5.8×10^{-4} to 1.4×10^{-3} N and, further, that dt_+/dc is the same for both systems. In short, t_+ as given in Table V corresponds to

$$t_+ = 0.19 + 4.5 \times 10^2(C - 5.80 \times 10^{-4})$$

For the calculations listed in Table V, no attempt has been made to estimate the variation of Λ_+ and Λ_- with C. These calculations were made using $\Lambda_+ = 17$, $\Lambda_-/\Lambda_+ = 4.2$.

TABLE V

CALCULATED QUANTITIES ASSUMING ONE COMPLEX SPECIES

							No. of ions in complex species		Charge of complex species
$C \times 10^4$	Λ	$p \times 10^7$	t_+	$C_+ \times 10^4$	$C_- \times 10^4$	$C_{ij} \times 10^4$	Long chain i	Gegenions j	$i - j$
6.00	89.1	3.42	0.20	5.73	5.97	0.068	3.97	0.44	3.53
8.00	81.0	3.72	.27	5.36	6.94	.574	4.60	1.85	2.75
10.00	75.3	3.91	.34	4.90	7.98	.713	7.15	2.83	4.32
12.00	71.0	4.05	.40	4.68	8.65	.913	8.02	3.67	4.35
14.00	67.4	4.16	.48	4.48	9.29	1.026	9.28	4.59	4.69

As may be seen from Table V, the calculated long chain ion concentration decreases over the range in C tested while the gegenion concentration shows a sharper increase. The complex species concentration builds up as C increases; both i and j increase, but their difference over the range $C = 10^{-3}$ to $1.4 + 10^{-3}$ is roughly constant.

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(12) This calculation is similar to that given by van Rysselberghe, *J. Phys. Chem.*, **43**, 1049 (1939).

(13) Hartley, Collie and Samis, *Trans. Faraday Soc.*, **32**, 795 (1936).

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, D × 10^5

	20°			25°	
c	Observed	Theoretical	*c*	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

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

where

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

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).