[CONTRIBUTION NO. 1237 FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

Electrolyte–Solvent Interaction. VI. Tetrabutylammonium Bromide in Nitrobenzene–Carbon Tetrachloride Mixtures[1]

BY HUSSEIN SADEK[2] AND RAYMOND M. FUOSS

RECEIVED JULY 9, 1954

Tetrabutylammonium bromide in nitrobenzene (dielectric constant $D = 34.7$) is only slightly associated to ion pairs (reciprocal association constant $K = 0.018$). As carbon tetrachloride is added to the solvent, the conductance curves become steeper, thus indicating increased formation of ion pairs; at carbon tetrachloride mole fraction $x_2 = 0.50$ where D is 15.7, K equals 0.00048. To an extremely poor first approximation, the decrease in K as D diminishes can be described in terms of the conventional sphere-in-continuum model to represent the ions in the solvent; the effective ion size a computed from the experimental values of K changes from 2.1×10^{-8} cm. in nitrobenzene to 3.4×10^{-8} at $x_2 = 0.50$, instead of remaining constant. A more realistic model is proposed which leads to a constant value of a. It is assumed that continuum theory may be used for interionic distances ranging from infinity down to where there is one layer of solvent molecules between an anion and a cation; approach to this distance is described by a formal mass action constant $K(D)$. Rearrangement of the solvated pair by expulsion of the intervening solvent is assumed to be a discrete stepwise process, described by a constant k. Then the constant measured by conductance is $K(D)/(1 + k)$. The value of a computed from $K(D)$ remains constant at 4.25×10^{-8}, independent of solvent composition.

Introduction

The following "sphere-in-continuum" model has conventionally been used to describe electrolytic solutions: the solvent is assumed to be a continuum, characterized electrostatically by its macroscopic dielectric constant and hydrodynamically by its macroscopic viscosity, while the ions are assumed to be charged spheres. The center-to-center distance a of ions of opposite charges can be calculated, using the model, from the mass action constant K which describes ion association. Values of individual radii can be computed from limiting conductances Λ_0 by means of Stokes law, providing one single ion conductance in the solvent under consideration is known. Both Λ_0 and K can conveniently be determined from conductance data in the range of low concentrations when K is less than the order of 10^{-2}; when $K > 0.01$, its value is uncertain due to the unknown magnitude of c and $c \log c$ terms in the mobility. Consideration of a variety of electrolytic systems shows that the above model is frequently a good approximation: for example, slow moving ions (small Λ_0) usually are less associated (larger K) than fast ones, and both of these superficially unrelated facts are consistent with the same sequence of ionic sizes. Similarly, knowing Λ_0 in one solvent permits estimation of Λ_0 in another solvent of known viscosity by means of Walden's rule, while the change of K can be calculated solely from Coulomb's law, using a fixed value of a and a variable value of the dielectric constant D. On the other hand, probably as many cases are known where calculations based on the model fail to reproduce experimental observations; still more disconcerting is the fact that we are unable to predict when the model will work and when it will fail.

Investigation of a given electrolyte in a variety of solvents, both pure and in mixtures with each other, promises to give useful suggestions regarding improvement of the model to give a better approximation to physical reality. The purpose of this paper is to present conductance data for tetrabutylammonium bromide in mixtures of nitrobenzene and carbon tetrachloride, and to consider the results from the above point of view. As a preliminary remark, it must be emphasized that what is sought is an improvement in the model which will be physically plausible and which simultaneously will permit explicit calculation; it is conceded as a triviality that any set of experimental data can be reproduced numerically if enough empirical constants are introduced into a set of arbitrary functions.

As we shall show later, the continuum model leads to a distance of nearest approach a which depends on the composition of the solvent. By using the continuum model to describe the approach of a cation and an anion up to molecular distances, and then assuming that the expulsion of the last layer of solvent molecules from between the ions of an incipient pair is a discrete stepwise process, we can derive a distance of nearest approach which remains constant (at 4.25×10^{-8} cm. for this system) while K changes by a factor of about 40.

Experimental

Nitrobenzene was purified by washing successively with 1 N sulfuric acid, saturated sodium bicarbonate solution and water. After drying over calcium chloride, it was vacuum distilled as recommended by Witschonke and Kraus.[3] Our best product had a specific conductance κ_0 of 7×10^{-11}. Carbon tetrachloride was shaken with sodium bicarbonate and then distilled from alumina. Tetrabutylammonium bromide was from laboratory stock.

Densities, viscosities, dielectric constants and refractive indices of mixtures of nitrobenzene and carbon tetrachloride were measured at 25.00°. Apparatus and methods were the same as those used in the work on methanol-carbon tetrachloride mixtures.[4] The results are shown in Table I,

$$P = (D - 1)(2D + 1)V_{12}/9D$$

$$V_{12} = (x_1M_1 + x_2M_2)/\rho$$

where w_2 is weight % of carbon tetrachloride and x_2 is its mole fraction. Figure 1 shows the dependence of viscosity, polarization P and volume V_{12} on mole fraction where D is dielectric constant at 200 kilocycles, and ρ is densities. Deviation functions similar to those for the MeOH–CCl_4 mixtures were employed to interpolate for the properties of the mixtures used in the conductance experiments. The properties of the mixtures of nitrobenzene and carbon

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[2] Du Pont Postdoctoral Research Fellow, 1953–1954, at Yale; on academic study leave from the University of Alexandria, Egypt. Grateful acknowledgment is made for a travel grant by the Fulbright Exchange Program.

[3] C. R. Witschonke and C. A. Kraus, THIS JOURNAL, **69**, 2472 (1947).

[4] H. Sadek and R. M. Fuoss, *ibid.*, **76**, 5897 (1954).

TABLE I

PROPERTIES OF NITROBENZENE–CARBON TETRACHLORIDE MIXTURES

w_2	x_2	ρ	$100\,\eta$	n_D	D
0.00	0.0000	1.1977	1.839	1.5501	34.69
10.04	.0820	1.2291	1.723	1.5453	31.11
23.09	.1937	1.2722	1.579	1.5345	26.79
35.87	.3092	1.3170	1.443	1.5255	22.23
46.65	.4117	1.3568	1.331	1.5160	18.94
57.35	.5183	1.3984	1.226	1.5063	15.30
71.41	.6666	1.4561	1.103	1.4917	10.86
85.81	.8287	1.5187	0.986	1.4761	6.25
100.00	1.0000	1.5839	0.911	1.4572	2.25

tetrachloride are much simpler than those of mixtures of alcohols with carbon tetrachloride. There is some contraction on mixing: the specific volume deviation reaches a minimum of −0.0030 at about $x_2 = 0.50$. The molecular polarization is nearly linear in volume fraction, and both dielectric constant and viscosity curves show little structure.

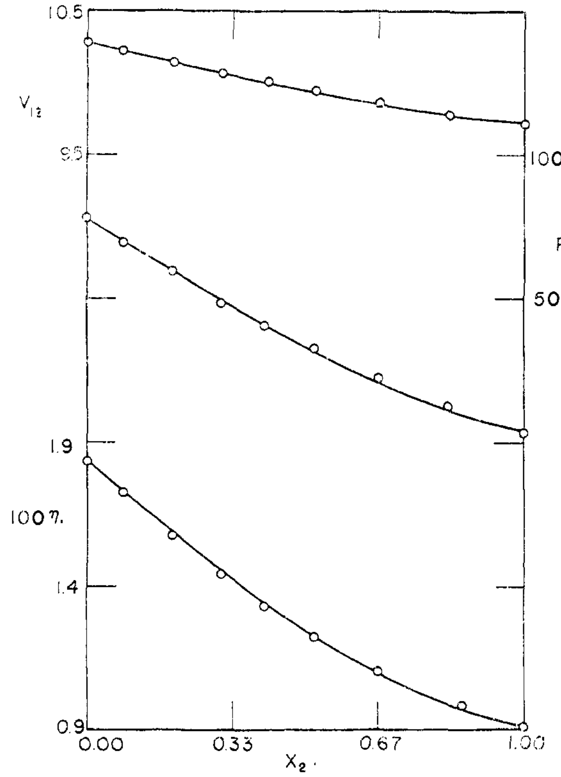

Fig. 1.—Properties of nitrobenzene–carbon tetrachloride mixtures at 25°: top, molar volume; center, molar polarization; bottom, viscosity.

The conductance data are summarized in Table II, where Λ is equivalent conductance and c is concentration in equivalents per liter. The various systems are identified by the weight % of carbon tetrachloride above each set of data. Solvent conductance κ_0 was subtracted from observed conductance after extrapolating to infinite frequency[5] to eliminate polarization. For the mixtures, κ_0 varied from 1.8×10^{-9} to 5.3×10^{-8}; the maximum correction was 0.11%.

Discussion

The conductance data were extrapolated by Shedlovsky's method[6] in order to obtain values of the limiting conductances and reciprocal association constants K. (As pointed out elsewhere,[7] we prefer to describe the K's as reciprocal association constants rather than as dissociation constants. The latter term implies that the primary event in ionic equilibria is dissociation of a neutral entity, while we now have ample evidence which shows that strong electrolytes exist only as ions at all concentrations in all solvents. The ions may, however, associate to non-conducting pairs, provided the energy relationship is favorable.) Our values of Λ_0 and K for tetrabutylammonium bromide in pure nitrobenzene (33.25 and 0.018) agree fairly well with other values in the literature: Witschonke and Kraus,[3] 33.48 and 0.016; Sadek and Fuoss,[8] 33.07 and 0.022. As carbon tetrachloride is added to nitrobenzene, the dielectric constant of the mixture decreases, and we therefore expect an increase in extent of ion association at a given concentration. That this occurs is readily seen in Fig. 2, where Λ/Λ_0 is plotted against the square root of concentration. (In order to avoid confusion, the curves are displaced vertically; all have the ordinate scale shown on the left except the lowest one, where one ordinate unit as drawn corresponds to 0.25 in Λ/Λ_0 instead of 0.10, the scale for the upper five curves.) In nitrobenzene, the conductance curve is slightly concave down, corresponding to moderate association; at $c = 10^{-4}$, the curve is about 0.5% below the theoretical tangent. As the carbon tetrachloride content increases, the curves become progressively steeper at a given concentration and an inflection point appears in the curve. These various structures all reduce to straight lines when the appropriate combination of association and mobility effects are plotted.[9]

TABLE II

CONDUCTANCE OF TETRABUTYLAMMONIUM BROMIDE IN NITROBENZENE–CARBON TETRACHLORIDE MIXTURES

$10^4 c$	Λ	$10^4 c$	Λ
0.00 = w_2		31.13	
2.574	31.78	1.455	33.89
3.635	31.43	1.953	33.41
5.000	31.06	2.652	32.86
7.043	30.57	3.866	32.04
10.016	29.95	5.475	31.12
9.96		45.76	
1.438	32.72	1.464	33.51
2.075	32.41	2.077	32.46
2.905	32.08	2.838	31.39
3.968	31.70	4.260	29.79
5.224	31.34	6.455	27.97
21.67		56.28	
1.986	33.17	1.508	30.50
2.783	32.70	2.201	28.65
3.931	32.09	3.155	26.77
5.787	31.28	4.682	24.63
8.410	30.33	6.868	22.51

One marked contrast is immediately apparent between polar–non-polar mixtures in which methanol and nitrobenzene are the polar components.

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(5) J. C. Nichol and R. M. Fuoss, *J. Phys. Chem.*, **58**, 15 (1954).

(6) T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

(7) F. M. Sacks and R. M. Fuoss, *J. Electrochem. Soc.*, **99**, 483 (1952).

(8) H. Sadek and R. M. Fuoss, THIS JOURNAL, **72**, 301, 5803 (1950).

(9) R. M. Fuoss and T. Shedlovsky, *ibid.*, **71**, 1496 (1949).

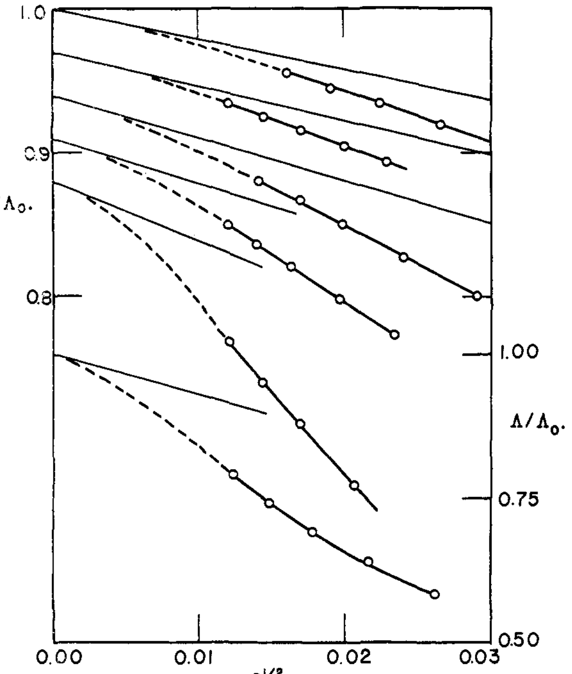

Fig. 2.—Reduced conductance curves: top curve, Λ/Λ_0 for nitrobenzene; bottom curve (ordinate scale to right), w_2 = 56.28.

When non-polar liquid is added to an electrolytic solution in methanol (at constant electrolyte concentration), association initially decreases, while initial addition of non-polar solvent to nitrobenzene solutions causes an immediate increase in association at a given concentration.

The values of K obtained from the slopes of the extrapolation plots are shown as a function of x_2 in Fig. 3. At mole fraction x_2 = 0.5074, the dielectric constant is reduced to 15.69, where K was found to be 4.77×10^{-4}. If this value of K is compared with values for tetrabutylammonium bromide in other solvent mixtures at about the same dielectric constant ($K = 14.0 \times 10^{-4}$ at D = 15.31 in MeOH–CCl_4; $K = 24 \times 10^{-4}$ at D = 15.70 in MeOH–C_6H_6), it is immediately evident that association occurs to a considerably higher extent in the $C_6H_5NO_2$–CCl_4 mixtures than in the mixtures of alcohols with other solvents. In terms of the sphere-in-continuum model, this simply means that the spheres electrostatically equivalent to the ions of the salt are smaller in nitrobenzene than in the alcohols. Now the initial ions are, of course, the same in both solvent systems. Solvation of ions by the compact highly polar methanol molecules would account for the difference in the behavior of the ions in solution, provided the additional assumption is made that methanol of solvation is retained in the ion pair. The ion size computed from the value of K in nitrobenzene is 2.11×10^{-8} cm. This is considerably smaller than the values found in the methanol systems and suggests that the ions are not solvated in nitrobenzene–carbon tetrachloride mixtures.

But the model is not quantitatively satisfactory: the value of a calculated from K varies systematically with the composition of the mixed solvent, as shown in Fig. 3. This result can be interpreted in one of several ways. In the first place, we might assume that solvation increases as the amount of carbon tetrachloride in the mixture increases, and therefore the effective ion size increases. This explanation requires that the solvate shell remain intact in the ion pair. It is, however, difficult to propose a plausible structure for a stable solvate. The alternative is to question the model; its most vulnerable point appears to be the continuity of the solvent, because both of the ions of tetrabutylammonium bromide should be representable as spheres. When an anion and a cation are at distances of the order of some tens of molecular diameters apart, the macroscopic dielectric constant of the mixed solvent certainly is a good approximation in calculating the potential energy of the two ions of an incipient pair, but as the mutual distance approaches several molecular diameters, the approximation must fail because solvent molecules will be polarized (by induction and/or orientation) by the intense ionic fields. It is, however, precisely the range of *small* distances which contributes most to the integral which relates a, D and K. According to the above argument, we should then treat D as a function of distance, which decreases from the macroscopic value of D at large r to something of the order of the square of the index of refraction as r becomes small.

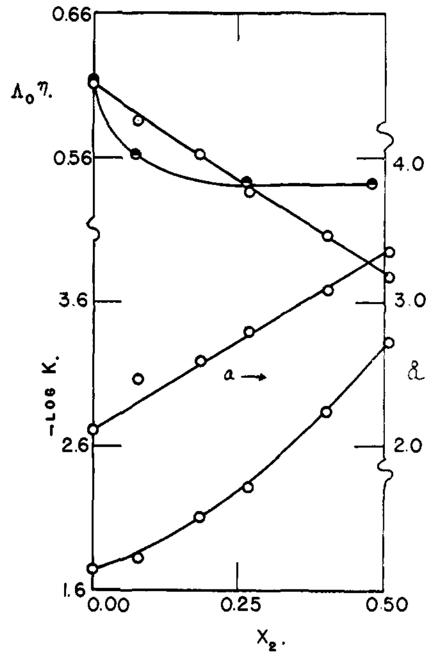

Fig. 3.—Properties of tetrabutylammonium bromide in nitrobenzene–carbon tetrachloride mixtures.

The following model is proposed as a tentative solution of the problem. Let us assume that an anion and a cation approach through a dielectric continuum up to a point where one layer of solvent molecules is between the ions. For this process of forming a solvated ion pair, we write the electrostatic equilibrium

$$A^+ + B'(+S) \rightleftharpoons ASB \qquad (1)$$

where S represents one or more solvent molecules. If a highly polar solvent is present, we may assume that solvent molecules accompany anion or cation or both, due to ion-dipole attraction; in any case, the concentration of solvent should not appear in the mass action equation which then is, with activities bracketed

$$[\mathrm{A}^+][\mathrm{B}'] = K_\mathrm{D}[\mathrm{ASB}] \tag{2}$$

Here K_D represents the formal dissociation constant[10] which can be expressed as a function of dielectric constant and average ion size in terms of a sphere-in-continuum model

$$K_\mathrm{D}^{-1} = (4\pi N/1000)(\epsilon^2/DKT)^3Q(b) \tag{3}$$

$$b = \epsilon^2/aDkT \tag{4}$$

where $Q(b)$ has been tabulated[10,11] and the other symbols have their conventional meaning. Then we make the additional assumption that in certain cases (in particular, in $\mathrm{PhNO_2}$–$\mathrm{CCl_4}$ mixtures) the solvent molecule is expelled

$$\mathrm{ASB} \rightleftarrows \mathrm{AB} + \mathrm{S} \tag{5}$$

$$[\mathrm{AB}][\mathrm{S}] = k[\mathrm{ASB}] \tag{6}$$

The symbol [S] in equation 6 means local concentration of polar solvent near the ion pair, and is assumed to be constant, independent of the bulk composition of the solvent mixture. (This assumption is analogous to selective concentrating of polar constituents near ions in the salting-out process.) For abbreviation, we set

$$k/[\mathrm{S}] = k_\mathrm{S} \tag{7}$$

In order to simplify the algebra, let us temporarily set interionic coefficients (activity and mobility) equal unity. Denoting $[\mathrm{A}^+] = [\mathrm{B}']$ by $c\gamma$ and using the stoichiometric relationship

$$[\mathrm{AB}] + [\mathrm{ASB}] = c(1 - \gamma) \tag{8}$$

Equations 2 and 6 may be combined to give

$$c\gamma^2/(1 - \gamma) = K_\mathrm{D}/(1 + k_\mathrm{S}) \tag{9}$$

It is evident that the constant K obtained by extrapolating the conductance data is therefore given by

$$K = K_\mathrm{D}/(1 + k_\mathrm{S}) \tag{10}$$

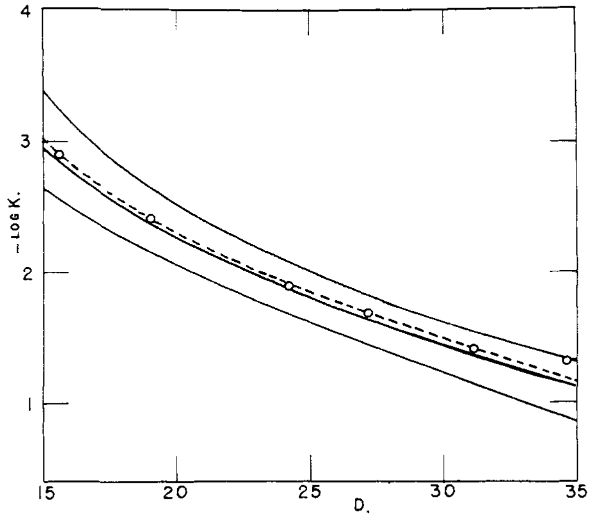

Fig. 4.—Graphical evaluation of k_S and a: solid curves $K(D, a)$ for a = 3.5 (top), 4.5 and 6.0 × 10^{-8} cm.; dotted curve, [$-\log K(D, 4.25) - 0.42$]; circles, ($-\log K_\mathrm{A}$).

The above may now be restated as follows: formation of a solvated ion pair is assumed to be describable by the sphere-in-continuum model, where the distance a represents center-to-center distance between ions which trap a solvent molecule between them. Then the solvate molecule is expelled by a discrete process described by the solvation constant k_S.

In order to test this hypothesis experimentally, we proceed as follows: the conductance data are plotted in the appropriate way to determine K (and Λ_0). Then ($-\log K$) is plotted on transparent graph paper against the dielectric constant D (or the composition of the solvent). Next, a series of a-values are chosen, the corresponding values of K_D are calculated for the experimental range of D values, and are plotted on the same scale as the constants derived from the conductance data. If K differs from K_D by a constant multiplier, it is possible to bracket the experimental K–D curve by a parallel pair of calculated K_D–D curves by vertical displacement at constant D. For the data of Table II, we find a = 4.25. Figure 4 shows a plot of ($-\log K_\mathrm{D}$) against D for a series of a values. The dotted curve is the experimental ($-\log K$)–D curve, displaced vertically by 0.42 log unit, the distance found by the graphical method described above. A numerical test of the method is included in Table III where K (calcd.) is K_D (calculated by equation 3 for a = 4.25) divided by 2.63 (= antilog 0.42). The agreement is excellent between the observed values of K_A from the conductance data and the computed values.

TABLE III

DERIVED CONSTANTS FOR TETRABUTYLAMMONIUM BROMIDE IN NITROBENZENE–CARBON TETRACLORIDE MIXTURES

x_2	D	K_A	K (calcd.)	Λ_0	$\Lambda_0\eta$
0.0000	34.69	0.018	0.024	33.25	0.611
.0813	31.13	.0148	.0145	33.92	.586
.1813	27.20	.0077	.0078	35.26	.563
.2656	24.23	.0048	.0046	36.06	.536
.4030	19.07	.00145	.00145	37.74	.506
.5074	15.69	.00048	.00048	38.61	.478

Until the hypothesis has been tested on a variety of systems, it is naturally impossible to decide whether the proposed model is a useful representation of the real physical system or whether the agreement between observed and calculated K-values is merely the arithmetical consequence of introducing one more empirical constant (k_S) into the equations. For the system at hand at least, the proposed mechanism has the virtue of producing a distance parameter which remains constant, independent of solvent composition, while the unmodified sphere-in-continuum model fails to give a constant effective ion size. In further support of the suggested model, we recall that the ion size calculated by assuming $K_\mathrm{D} = K_\mathrm{A}$ for tetrabutylammonium bromide in MeOH-$\mathrm{CCl_4}$ and EtOH-$\mathrm{CCl_4}$ mixtures[4,12] remained constant in the range of

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[10] R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 1019 (1933).

[11] N. Bjerrum, *Kgl. Danske Vidensk. Selskab.*, **7**, No. 9 (1926); correction, $Q(5)$ = 0.771.

[12] H. Sadek and R. M. Fuoss, THIS JOURNAL, **76**, 5902 (1954).

compositions where we believe the K-values to be reliable. It seems reasonable to expect that alcohol of solvation would be retained in an ion pair, due to the strong local field of the HO-dipole.

Finally, we consider the limiting conductances. As shown in Table III, they increase as the amount of carbon tetrachloride in the solvent mixture increases. The viscosity simultaneously decreases, but the two changes do not compensate each other as they would if Walden's rule were valid. As shown in Fig. 3, the product $\Lambda_0\eta$ decreases as x_2 increases. The change is the largest we have observed so far among the various mixtures investigated. For comparison, our data[8] for the salt in methanol–nitrobenzene mixtures are shown in Fig. 3 (half-shaded circles). The result may be stated in terms of a sphere-in-continuum model that the equivalent ion size increases as the carbon tetrachloride content increases; alternatively, assuming constant size of the ions, the ions encounter relatively greater frictional resistance in the carbon tetrachloride-rich mixtures. The first mechanism is consistent with selective solvation by nitrobenzene, as a consequence of the polar component of the mixture concentrating near the free ions as the bulk dielectric constant decreases.

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NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF RUTGERS UNIVERSITY]

Charge Reversal of Cationic Poly-4-vinylpyridine Derivatives in KBr Solutions[1]

BY ULRICH P. STRAUSS, NORMAN L. GERSHFELD AND HARRY SPIERA

RECEIVED JULY 12, 1954

A polysoap derived from poly-4-vinylpyridine by quaternizing 13.6% of the nitrogen with *n*-dodecyl bromide and the remainder with ethyl bromide ("13.6%"-polysoap) was found to be completely soluble in both dilute and concentrated KBr solutions, but partly insoluble in KBr solutions of an intermediate concentration range. Electrophoresis experiments showed that the polysoap was positively charged in dilute KBr solutions and negatively charged in concentrated KBr solutions. The precipitation region surrounded the isoelectric point. A considerably wider precipitation region was found in the case of a "28.5%"-polysoap. Poly-4-vinyl-N-ethylpyridinium bromide also became negative in concentrated KBr solutions, and its electrophoretic mobility values coincided with those of the "13.6%"-polysoap. However, this polyelectrolyte was completely soluble even at the isoelectric point. The electrophoretic mobility was insensitive to additions of hydrogen or barium ions, which indicated the absence of weakly and certain strongly acidic groups. Consequently, the charge reversal of the polyions was explained by the binding of bromide ions in excess of their stoichiometric equivalent. The results show that forces other than coulombic ones between polyions and their counter ions may play a role even in the case of so-called "strong" polyelectrolytes.

In the course of an investigation concerning the influence of electrolytes on polysoap behavior it was observed that a "13.6%"-polysoap[2] derived from poly-4-vinylpyridine is completely soluble in both dilute and concentrated aqueous potassium bromide solutions, but that there is an intermediate potassium bromide concentration region where the polysoap is partially insoluble. As one goes through this region which lies approximately between the KBr molalities of 0.35 and 1.80, the amount of polysoap which is insoluble gradually increases, comes to a maximum somewhere between the KBr molalities of 0.6 and 0.9, and then decreases. To obtain an understanding of this curious phenomenon, an investigation was undertaken.

While such an effect has not been reported previously for completely cationic polyelectrolytes, precipitation regions have been observed with polyampholytes in the neighborhood of their isoelectric points.[3–7] Therefore our polysoaps were tested for the possible presence of an isolectric point by electrophoresis measurements. The question of why the polysoap was only partially insoluble in the precipitation region also was investigated. Finally in order to cast further light on these problems it was decided to perform, whenever expedient, similar experiments with a "28.5%"-polysoap, a "37.9%"-polysoap, and a typical polyelectrolyte, poly-4-vinyl-N-ethylpyridinium bromide, all derived from the same parent poly-4-vinylpyridine as the "13.6%"-polysoap.

Experimental

The preparation of the "13.6%"-, the "28.5%"- and the "37.9%"-polysoaps[2] (our samples No. G 147, No. G 146 and No. G 145, respectively) and the poly-4-vinyl-N-ethylpyridinium bromide (our sample No. G 254) from poly-4-vinylpyridine (our sample No. G 13), D.P. $\approx$ 6000, has been described previously.[8]

The potassium bromide and the lithium bromide were C.P. products obtained from Coleman and Bell.

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[1] Part of these results will be contained in a thesis to be submitted by N. L. Gershfeld to the Graduate School of Rutgers University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Paper presented at the American Chemical Society Meeting, Division of Polymer Chemistry, New York, N. Y., September, 1954.

[2] In this paper, an "X%"-polysoap denotes a compound prepared from poly-4-vinylpyridine by quaternizing X% of the nitrogen with *n*-dodecyl bromide and nearly all of the remaining nitrogen with ethyl bromide.

[3] T. Alfrey, H. Morawetz, E. B. Fitzgerald and R. M. Fuoss, THIS JOURNAL, **72**, 1864 (1950).

[4] H. L. Wagner and F. A. Long, *J. Phys. Colloid Chem.*, **55**, 1512 (1951).

[5] T. Alfrey and H. Morawetz, THIS JOURNAL, **74**, 436 (1952).

[6] T. Alfrey, R. M. Fuoss, H. Morawetz and H. Pinner, *ibid.*, **74**, 438 (1952).

[7] A. Katchalsky and I. R. Miller, *J. Polymer Sci.*, **13**, 57 (1954).

[8] U. P. Strauss and N. L. Gershfeld, *J. Phys. Chem.*, **58**, 747 (1954).