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Specific Solvation of Electrolytes in Binary Solvent Systems¹

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The extensive data on the association of $n\text{Bu}_4\text{N}^+\text{Br}^-$ ions in binary solvent systems are re-examined and the deviations from linearity of the $\log K_A$ versus $1/D$ plot rationalized in terms of specific interaction between the electrolyte species and one or other component of the solvent system. Those characteristics of both the electrolyte and solvent species which determine whether the system can be approximated by the "sphere in continuum" model are discussed.

Introduction

Over the past few years Fuoss and co-workers have carried out extensive studies of the conductance of quaternary ammonium salts in binary solvent systems with wide variation of the bulk dielectric constant of the solvent medium. The main purpose of these studies has been to test and refine the various forms of the conductance equation for electrolytes in solution and to gain a further insight into the precise molecular structure of the electrolyte species in solution. Although recognizing the inherent inadequacy of the "sphere in continuum" model and admitting the possibility of the role of selective solvation of the electrolyte species in several papers, these authors have based most of their interpretations upon the "sphere in continuum" model. In certain instances where the electrolyte-solvent system has been specifically chosen to approximate the model most closely, e.g., $n\text{Bu}_4\text{N}^+\text{B}^-(\text{C}_6\text{H}_5)_4$ in $\text{CH}_3\text{CN}-\text{CCl}_4$, an excellent fit of the experimental data to the linear relationship between $\log K_A$ and $1/D$ has been obtained as required by the "sphere in continuum" model, i.e., $\log K_A = \log K_A^0 + e^2/2.303aDkT$. While there are other consequences of the "sphere in continuum" model which are amenable to experimental test, it is this linear relationship between the association constant and reciprocal dielectric constant that will be considered primarily in this paper.

Our main interest lies initially in those systems which show deviations from linearity since it is through observation of these deviations that one might hope to assess the principal inadequacies of the "sphere in continuum" model. In the majority of systems studied so far, these deviations have been relatively minor and although, as noted above, Fuoss and co-workers have considered the possibility of selective solvation as an explanation they have been cautious in ascribing too much significance to deviations which might be an artifact of computation.² Their analytical techniques have now reached such a point of refinement, however, that the frequent appearance of these minor deviations coupled with at least one example of gross deviation³ encourages a re-examination of the data as a whole in some detail in the hope of finding a rationale for the deviations based on selective solvation or related phenomena. Furthermore, several papers^{4,5} have appeared very recently reporting studies of very similar systems by techniques other than conductance which provide strong evidence for selective solvation which was not available to Fuoss and co-workers at the time of their earlier reports. It is upon this recent work and a re-examination of the extensive data of Fuoss and co-workers that this present analysis is based.

$n\text{Bu}_4\text{N}^+\text{Br}^-$ in Various Binary Solvent Systems.—Although the conductance studies of Fuoss and co-

workers have ranged over a wide selection of quaternary ammonium salts in binary solvents we will direct our attention, in the first instance, to the salt $n\text{Bu}_4\text{N}^+\text{Br}^-$. In subsequent sections of this paper reference will be made to some of the other salt systems. The $n\text{Bu}_4\text{N}^+\text{Br}^-$ salt warrants detailed attention since conductance studies have been carried out in several solvent systems: $\text{EtOH}-\text{CCl}_4$,⁶ $\text{H}_2\text{O}-\text{dioxane}$,⁷ $\text{C}_6\text{H}_5\text{NO}_2-\text{MeOH}$ ²; and infrared spectral studies have been reported in $\text{C}_6\text{H}_6-\text{MeOH}$ ^{4b} and $\text{CCl}_4-t\text{BuOH}$.⁵

In Fig. 1 $\log K_A$ versus $1/D$ plots are shown for $n\text{Bu}_4\text{N}^+\text{Br}^-$ in all three binary solvent systems so far reported. Several qualitative features are immediately obvious from these plots.

The three pure solvent points H_2O , MeOH and EtOH describe an excellent straight line and the $\text{EtOH}-\text{CCl}_4$ solvent mixture points show only minor deviations from this line. On the basis of the "sphere in continuum" model such a linear relationship would be expected since the particular molecular form of the components of the solvent have no significance in a "continuum" picture of the solvent medium. A similar linear dependence of association constant of $n\text{Bu}_4\text{N}^+\text{ClO}_4^-$ on $1/D$ for pure solvents has recently been reported.^{4a} Although less directly related, it should be noted that the activation energies of solvolysis of *t*-butyl chloride in H_2O , MeOH and EtOH are also linearly related to $1/D$ while the activation energies in mixtures of these solvents deviate markedly from the line described by the pure solvent systems.⁸ This observation has been interpreted previously as evidence for the "non-continuum" character of the solvation shell of the reacting species in the two component solvent systems.

The deviation of the $\log K_A$ versus $1/D$ plot for the water-dioxane system from the line established by the pure solvent systems is evident in Fig. 1. The direction of the deviation is such as to suggest that the bulk dielectric constants of the dioxane-water mixtures used are too low and do not reflect the higher micro-dielectric constant in the immediate environment of the ionic species. Clearly if the micro-dielectric constant values in each solvent mixture were higher all of the dioxane-water points would be moved to lower values of $1/D$ than those dictated by bulk dielectric constant values and the dioxane-water line in Fig. 1 would be moved toward the line established by the pure solvents. Such an increase in the micro-dielectric constant value over the bulk value is in keeping with the displacement of the boat-chair equilibrium for dioxane toward the boat form under the influence of the coulombic field of the ionic species (see Fig. 2). Due to the opposition of the bond moments in the chair form the preponderance of this conformation in pure dioxane results in a low dielectric constant value. However, the preponderance of the boat form, with its bond moments acting together, in the solvation shell of the

(1) Presented in part at the 142nd Natl. Meeting of the American Chemical Society, Atlantic City, N. J., September 9, 1962.

(2) R. M. Fuoss and E. Hirsch, *J. Am. Chem. Soc.*, **82**, 1013, 1018 (1960).

(3) H. Sadek and R. M. Fuoss, *ibid.*, **72**, 301 (1950).

(4) (a) Y. H. Inami, H. K. Bodensch and J. B. Ramsey, *ibid.*, **83**, 4745 (1961); (b) J. Buffalini and K. H. Stern, *ibid.*, **83**, 4362 (1961).

(5) J. B. Hyné and R. M. Levy, *Can. J. Chem.*, **40**, 692 (1962).

(6) H. Sadek and R. M. Fuoss, *J. Am. Chem. Soc.*, **76**, 5902 (1954).

(7) P. L. Mercier and C. A. Kraus, *Proc. Natl. Acad. Sci. U. S. A.*, **41**, 1033 (1957).

(8) J. B. Hyné, *J. Am. Chem. Soc.*, **82**, 5129 (1960).

electrolyte species would result in an enhanced microdielectric constant value as required to account for the deviation of the dioxane-water line in Fig. 1 from the line established by the pure solvents. Such an argument is similar to that offered by Ramsey and co-workers^{4a} to explain the deviation of the point for $n\text{Bu}_4\text{N}^+\text{ClO}_4^-$ in 1,2-dichloroethane from the $\log K_A$ versus $1/D$ linear plot obtained for this salt in other pure solvents. Here, as in dioxane, 1,2-dichloroethane can exist in the *trans* or *gauche* forms and the equilibrium is displaced toward the *gauche* (higher D) in the immediate vicinity of the electrolyte species.

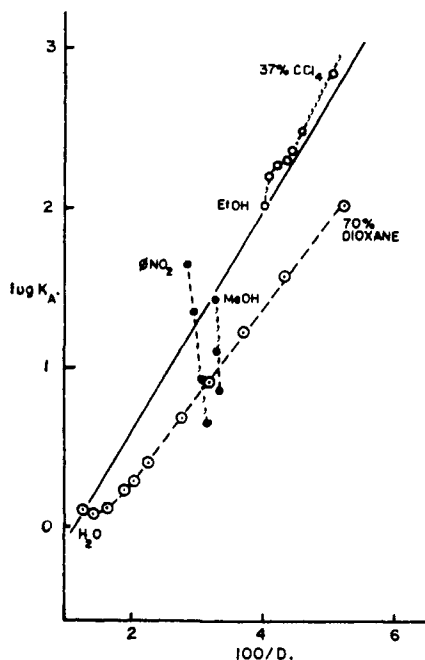


Fig. 1.— $\log K_A$ versus $1/D$ for $n\text{Bu}_4\text{N}^+\text{Br}^-$ in mixed solvents: \circ , H_2O to 70% dioxane- H_2O ; \bullet , MeOH to $\text{C}_6\text{H}_5\text{NO}_2$ (see ref. 3 for explanation of double point for MeOH); \circ , EtOH to 37% CCl_4 .

Further evidence for the claim that in the immediate vicinity of a charged center the boat-chair dioxane equilibrium is displaced in favor of the boat conformation is found again in solvolysis studies in mixed solvents.⁸ On the basis of differences in *bulk* dielectric constants of dioxane and water, the specificity of solvation by one solvent component of the partially ionic transition state in the solvolysis of alkyl halides in this solvent mixture should be much greater than that indicated by activation energy deviations (see ref. 8 for details). However, if the *bulk* dielectric constant of dioxane is much lower than that of the micro-dielectric constant of the dioxane near the ionic transition state, then the difference between the ability of the dioxane and water molecules to stabilize the developing charge will not be as great as that indicated by the difference in bulk dielectric constants of the two components.

By far the most obvious of the deviations from linearity in the $\log K_A$ versus $1/D$ plots in Fig. 1 are the points for $n\text{Bu}_4\text{N}^+\text{Br}^-$ in nitrobenzene-methanol mixtures. The deviations here are of such a magnitude that there can be little question that the deviations are *not* due to an artifact of computation. Sadek and Fuoss³ have, in this case, already offered a selective solvation explanation for the observed behavior and Fuoss⁹ has suggested this explanation again as the possible reason for deviations from his Stokes radius equa-

tion $R = R_\infty + B/D + O(D^{-2})$. In view of the fact that the pure nitrobenzene point itself lies off the line described by the pure solvents in Fig. 1, while the methanol point does not, a reinterpretation of the observations is presented here including some of the arguments previously used by Sadek and Fuoss. On the basis of bulk dielectric constant and the pure solvent line in Fig. 1, the K_A value in nitrobenzene is too high.

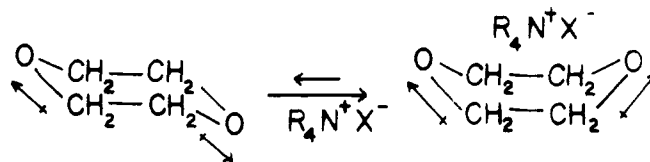


Fig. 2.

Consideration of the relative dimensions and charge distributions of the $n\text{Bu}_4\text{N}^+\text{Br}^-$ ion pair and the nitrobenzene molecule reveals that it is not improbable that the nitrobenzene acts as a sort of "template for the adsorption" of $n\text{Bu}_4\text{N}^+\text{Br}^-$ ion pairs, as shown in Fig. 3. Using Fuoss' values for the hydrodynamic radius of the two ions of the ion pair⁹ an approximate value of 4.9 Å. is obtained for the center to center distance in the ion pair. This distance compares very favorably with the approximate value of 4.2 Å. for the distance from the center of the aromatic ring to the oxygen atoms of the nitro group at which points one might assume the center of $\delta+$ and $\delta-$ charge in the dipolar nitrobenzene might be located. Some preliminary evidence for the validity of this picture has been found recently in this Laboratory through n.m.r. studies. Addition of $n\text{Bu}_4\text{N}^+\text{Br}^-$ to 10% solutions of nitrobenzene in carbon tetrachloride effects the chemical shift of the *meta* and *para* protons of the aromatic ring but not the *ortho* proton shift. Although the shifts are small, they are well outside the limits of error of measurement and support the postulate that this part of the aromatic ring is under the influence of the charge of the bromide ion. Further detailed studies of this phenomenon are being undertaken.

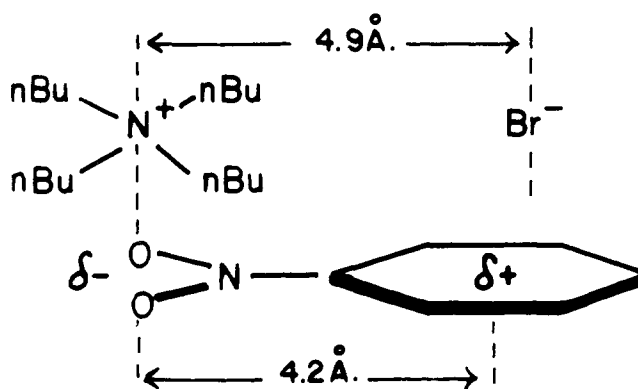
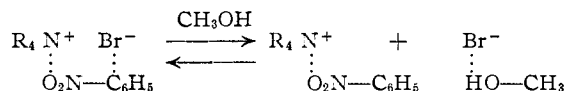


Fig. 3.

The nitrobenzene molecule therefore requires both a positive and a negative electrolyte species to satisfy its dipolar character and this requirement can be met by quaternary ammonium and bromide ions held in a relative position to one another which is essentially that of an ion pair. Consequently the bulk dielectric constant of nitrobenzene is not the sole factor determining the stability of ion pairs in pure nitrobenzene and the enhanced K_A value can be rationalized. Upon addition of small amounts of methanol there is compe-

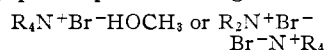
(9) R. M. Fuoss, *Proc. Natl. Acad. Sci. U. S.*, **45**, 807 (1959).

tion between the δ^+ aromatic ring and the methanol for the role of solvating the bromide ion. As has been suggested by both Buffalini and Stern^{4b} and Hyné and Levy⁵ on the basis of infrared investigations, Br^- in $n\text{Bu}_4\text{N}^+\text{Br}^-$ is specifically solvated by alcohol in alcohol-carbon tetrachloride solvents as reflected in the marked influence of added salt on the O-H stretching frequency of the alcohol. The precise nature of this Br^- -OH interaction is not clearly understood, but the evidence is sufficiently compelling to permit acceptance of the specific solvation argument. In the competition for Br^- between nitrobenzene and methanol the latter solvent species provides more effective solvation and the $\text{R}_4\text{N}^+\text{Br}^-/\text{C}_6\text{H}_5\text{NO}_2$ complex is broken down, thus reducing K_A as observed on addition of methanol.



As the nitrobenzene component is depleted and solvent composition approaches pure methanol, R_4N^+ ions once again pair with Br^- resulting in an increase in K_A to a value which lies on the line established by the pure hydroxylic solvents in Fig. 1. Preliminary infrared spectral studies of solutions of $n\text{Bu}_4\text{N}^+\text{Br}^-$ in methanol-nitrobenzene solutions provide evidence for the preferred Br^- -HOCH₃ bonding in this system as methanol is added.

Deviations from the pure solvent line in Fig. 1 of points in the EtOH-CCl₄ sequence of solvents are sufficiently minor to be attributable to artifacts of computation. Such computational errors, however, are normally more common in the lower ranges of K_A values and are not to be expected where $K_A > 100$. Consequently, one is tempted to attribute some significance to the deviations noted at the ethanol end of the solvent composition range and in general to the fact that the deviations throughout the range are of a sign indicating higher than expected K_A values. The supporting infrared studies on $n\text{Bu}_4\text{N}^+\text{Br}^-$ in alcohol-carbon tetrachloride solvents⁵ are at the high CCl₄ end of the composition range, but clearly indicate that there is a marked tendency for the quaternary ammonium ion to form ionic aggregates with the bromide ion in order to exclude the low polarity CCl₄ from the centers of charge. While the positive nitrogen center is comparatively well shielded by four butyl groups, the bromide ion must acquire some solvation shielding and it has been suggested⁵ that this can be achieved by either pairing with the ammonium ion and solvating with methanol or by forming quadruplets and higher ionic aggregates.



Consequently, as the CCl₄ composition is enhanced there will be a tendency to ion-pair to a somewhat greater extent than predicted on the basis of bulk dielectric constant due to the specific solvation role played by the alcohol in the ion-pair.

Other Quaternary Ammonium Systems.—The foregoing analysis of the data presented in Fig. 1 has concentrated solely on the case of $n\text{Bu}_4\text{N}^+\text{Br}^-$ in binary solvent systems. Although no attempt will be made to enter into an equally detailed analysis of the behavior of other quaternary ammonium salts, a few remarks are warranted on the general manner in which these other systems fit the selective solvation interaction picture which has been presented.

The log K_A versus $1/D$ plots for almost all other tetra-*n*-butylammonium salts reported so far show only very minor deviations from linearity over considerable ranges of various binary solvent systems. Among the anions studied have been I^- ,^{2,10} NO_3^- ,² picrate^{2,12} and $(\text{C}_6\text{H}_5)_4\text{B}^-$.¹¹ The lack of major deviations in these cases would suggest that specific interaction with one or other component of the binary solvent mixtures is not significant when these anions are involved. This fits well with the observations of Buffalini and Stern^{4b,13} that the order of specific solvation demand of these ions in benzene-alcohol systems increases in the order, picrate < NO_3^- < Br^- < Cl^- . In those cases where some slight deviation from linearity was noted² nitrobenzene was one of the solvent components and deviation was most marked at high nitrobenzene composition. In view of the particular role suggested for nitrobenzene previously, it is hardly surprising that even with ions of low specific solvation demands, some deviation should be observed.

The extensive data on various quaternary ammonium tetraphenyl borides in acetonitrile-carbon tetrachloride mixtures all fit the log K_A versus $1/D$ linearity with remarkable precision.¹¹ As suggested by the authors of these studies, such systems approximate the "sphere in continuum" model most closely since the solute electrolyte species are very large compared with the solvent molecules. Furthermore, the excellent screen provided by the four phenyl groups in the boride ion reduces its demand for solvent screening markedly.

Conclusions

While it is clear that the role of selective solvation of electrolytes in binary solvent systems is still inadequately understood, the deviations from the predictions of the "sphere in continuum" model coupled with supporting evidence from infrared studies would indicate that in certain systems this role is a major one. Computational artifact does not appear to be an adequate explanation for the observed deviations, particularly when these deviations can be rationalized in terms of a model involving specific solute-solvent interactions. It is hoped that this analysis will aid in the design of experiments and the choice of systems to test further the role of selective solvation in determining the behavior of electrolytes in binary solvent systems.

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- (11) D. S. Berns and R. M. Fuoss, *ibid.*, **82**, 5585 (1960).
- (12) F. Accascina, A. D. Aprano and R. M. Fuoss, *ibid.*, **81**, 1058 (1959).
- (13) J. Buffalini and K. H. Stern, *Science*, **130**, 1249 (1959).