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## Interactions in Ionic Solutions. The Effect of Electrolytes on the Infrared Spectra of Some Hydrogen-Bonded Compounds

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The effect of several electrolytes on the vibrational spectra of some hydrogen-bonded compounds—methanol, 1-butanol, *t*-butanol, *N*-methylacetamide—in dilute benzene solution is examined. The results are interpreted in terms of hydrogen bond formation to the anion of the electrolyte ion pair. This "solvation" increases with the anion charge density and is absent for picrate ion. The frequency of the absorption maximum is interpreted in terms of the O-H group as an harmonic oscillator. The addition of Bu<sub>4</sub>NBr to 1-butanol, *t*-butanol and *N*-methylacetamide reduces dimerization in these compounds while simultaneously anion solvation increases. A detailed spectral study of the Bu<sub>4</sub>NBr-MeOH-C<sub>6</sub>H<sub>6</sub> system, combined with previously obtained dielectric data (*J. Am. Chem. Soc.*, **82**, 1296 (1960)) yields  $n = 1$  for the ion pair solvation number, the equilibrium constant for ion pair solvation and  $\Delta H^0 = -6.7$  kcal. and  $\Delta S^0 = -13.6$  e.u. for hydrogen bond formation in agreement with commonly accepted values for this process. Some quadrupole solvation also occurs.

## Introduction

Evidence is steadily accumulating, that, although many properties of electrolytic solutions can be interpreted in terms of a continuum model for the solvent, others cannot. In the former category lie the success of the Debye-Huckel theory and its recent extensions by Fuoss and Onsager,<sup>3</sup> the application of this theory to ionic association<sup>4</sup> and the Denison-Ransey<sup>5</sup> treatment of ion pairing which correctly predicts the dependence of the ion pair association constant on solvent dielectric constant.

Attempts to account quantitatively for the molecular features of the solvent have been most vigorous as applied to aqueous solutions. We refer here only to the "iceberg" theory of Frank and Evans,<sup>6</sup> ionic number theories<sup>7</sup> and X-ray structure determinations of ionic solutions.<sup>8</sup>

Quantitative studies of ion-molecule interactions in low dielectric solvents have been rare, although it is of course recognized that these occur. For example, Gilkerson's<sup>9</sup> treatment of ion pairing includes the ionic solvation energy, but the theory has not been widely applied, partly because of the difficulties in assigning numerical values to some of the parameters.

The study of molecule-molecule interactions in solution is considerably further advanced, thanks in large part to the availability of infrared spectrometers, but this tool seems not to have been applied extensively to the electrolyte problem. A naive first look at the problem would lead one to argue that if a molecule becomes attached to an ion, thereby losing some of its rotational degrees of freedom, this should be detectable as a decrease in intensity of the corresponding rotational line. Because of collisional processes in solution, sharp lines are not observed (in contrast to the gas phase) in the far infrared. Moreover, the problems

of absorption of the weak radiation by atmospheric water vapor are very severe in this region. One is thus restricted to the study of vibrational lines in the near infrared.

The hydrogen bond in alcohols has been well studied and is also of interest for electrolytes since a number of studies have dealt with systems containing alcohols.<sup>10-14</sup> In this work we report on the effect of a number of electrolytes on the infrared spectra of some hydrogen-bonded compounds—mainly alcohols—when both are dissolved in dilute solution, and an application of the technique to the study of solvation equilibria in the system Bu<sub>4</sub>NBr-MeOH-C<sub>6</sub>H<sub>6</sub> which had previously been studied by a dielectric method. Some preliminary results have been published elsewhere.<sup>15</sup>

The line found most useful is the sharp fundamental for the OH stretching vibration. This was first noted in alcohols by Freymann.<sup>16</sup> Errera and Mollet<sup>17</sup> also observed the sharp OH band in the 3600 cm.<sup>-1</sup> region. This band is non-linear with concentration and was assigned to the OH stretching mode of the monomer. Some lower bands in the 3300 cm.<sup>-1</sup> region also were noted. These bands increase in intensity with increasing concentration and consequently were assigned to the OH stretching vibrations of H-bonded molecules. Subsequently, Fox and Martin,<sup>18</sup> Liddel and Wulf<sup>19</sup> and Pauling<sup>20</sup> recognized that the results could be explained in terms of chemical equilibria and that the infrared spectrum can facilitate the study of molecular complexes involving hydrogen bonds. Tsuboi<sup>21</sup> and Tsubomura<sup>22</sup> have shown that an equilibrium between a proton donor and a proton acceptor in an "inert" solvent can be studied by observing the OH frequency. For such a system as O-H . . . X, the energy of the hydrogen bond was found to be between 1 to 8 kcal./mole depending on the nature of X. The best and most

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- (2) Electrochemistry Section, National Bureau of Standards, Washington 25, D. C.
- (3) R. M. Fuoss and L. Onsager, *J. Phys. Chem.*, **61**, 668 (1957).
- (4) Cf. R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience Publishers, Inc., New York, N. Y., 1959.
- (5) J. T. Denison and J. B. Ramsey, *J. Am. Chem. Soc.*, **77**, 2615 (1955).
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- (20) L. Pauling, *ibid.*, **58**, 94 (1936).
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- (22) H. Tsubomura, *J. Chem. Phys.*, **23**, 2130 (1955).

direct method of obtaining such bond energies would be to study the vibration of OH with respect to X. However this mode appears at about 60 microns.<sup>23</sup> In this region solutions are rather difficult, if not impossible, to study with the ordinary methods usually employed in such determinations.

### Experimental

**Apparatus.**—All spectral measurements were made with a Perkin-Elmer Model 21 double beam spectrophotometer. The instrumental conditions varied with the cells employed. When 2.5 mm. NaCl cells were used, the conditions were: resolution, 980X2; gain, 6.0; response, 1; pen speed, 11; source current, 0.60 amp.; chart expansion, 1 cm./micron; speed, 2 min./micron. With 1.0 mm. cells: resolution, 980; gain, 6.5; and source current 0.50 amp.; the chart expansion, speed, etc., were the same for both. The instrument was calibrated by using the NaCl wave length standard test run for the 2.673 micron water peak. The temperature was controlled to  $\pm 1.5^\circ$  for all measurements.

**Materials.**—The preparation of tetrabutylammonium bromide and tetrabutylammonium picrate has been described previously.<sup>14</sup>

**Tetrabutylammonium nitrate** was prepared from the corresponding iodide by titrating with silver nitrate. Its melting point was  $120 \pm 0.5$  which agrees well with the literature value<sup>24</sup> of  $118^\circ$ .

**Tetrabutylammonium chloride** was prepared in a manner similar to the bromide, but HCl was employed as the acid. In this case, the melting point was found to be  $92 \pm 1.0$ . This salt is very hygroscopic, making it difficult to handle.

**Tetrabutylammonium formate** was prepared in an analogous manner by titrating the hydroxide with formic acid. The salt was recrystallized three times at  $-10^\circ$  from ethyl acetate. This salt was even more hygroscopic than the chloride. The final purification was done by zone melting the salt 15 times in a closed system. A melting point of  $67 \pm 2.0^\circ$  was obtained for the salt.

**N,N-Dimethylaniline hydrochloride** was prepared by treating a benzene solution of reagent N,N-dimethylaniline with dry HCl. The precipitated salt was recrystallized from ethyl acetate. A melting point of  $90 \pm 0.5^\circ$  compared favorably with that of the literature.<sup>25</sup>

**Silver perchlorate** was obtained from G. F. Smith Co. in the reagent anhydrous grade. This was heated to  $70^\circ$  under a vacuum for two days before using.

**Benzene**<sup>26</sup> and **methanol**<sup>27</sup> were purified by the methods described in the respective references.

**N-Methylacetamide** was obtained from Eastman Kodak Co., as reagent grade and no further purification was conducted.

**Normal butyl alcohol** and **tert-butyl alcohol** were obtained from Fisher Scientific Co. as reagent grade and employed directly with no further purification.

**Preparation of Solutions.**—All solutions were initially prepared by weight, using dilution techniques. In this fashion it was possible to obtain five significant figures in the concentration. The method later was abandoned because of the high instrumental error ( $\pm 0.5\%$  transmittance) and all subsequent solutions were made up volumetrically.

### Results

In pure liquid MeOH the O-H stretching vibration occurs at  $2.75\mu$  and the self-association (dimer) peak at  $3.0\mu$ .<sup>28</sup> In a moderately dilute solution ( $\sim 25 \times 10^{-3}M$ ) of methanol in a nonabsorbing, nonpolar solvent (benzene), both peaks are present, their intensity ratio depending on the total concentration. A plot of absorbancy *versus* total

concentration for both peaks has been published elsewhere.<sup>15</sup> The  $2.75\mu$  band becomes non-linear with increasing concentration because of dimer formation, but deviations from Beer's law are very slight up to  $30 \times 10^{-3}M$ .<sup>29</sup> If to a solution sufficiently dilute for the  $3.0\mu$  peak to be absent some electrolyte is added, this peak appears while the  $2.75\mu$  decreases. The exact position of the association<sup>30</sup> peak depends on the particular electrolyte added. This will be discussed later.

The extinction coefficient of free O-H was obtained from the straight line portion of an absorbancy *versus* concentration plot. At low concentration the  $3.0\mu$  peak is absent (in the absence of salt) and Beer's law holds for the  $2.75\mu$  peak. Then the extinction coefficient of the free peak is  $\epsilon_{free} = E_{free}/c_{free}l$  where  $l$  is the cell thickness and  $c_{free} = c_{total}$ . Our data give  $\epsilon_{free} = 5.07$ .

The extinction coefficient of the  $3.0\mu$  peak was determined in the same concentration range by adding salt ( $Bu_4NBr$ ). With an increasing salt concentration the  $3.0\mu$  peak steadily increases while the  $2.75\mu$  peak decreases until no further increase occurs at  $3.0\mu$  irrespective of the amount of salt added, provided the absorbancy of the salt is considered. This was done in two ways: by placing an equivalent concentration of salt in the reference side of the double beam instrument or by subtracting the absorbancy of the salt in this region by first running an absorbancy *vs.* concentration plot of the salt. The first method had the advantage in that the data were obtained directly but both methods were in excellent agreement. Since no further increase was observed in the  $3.0\mu$  region even though a large amount of salt was added, it could be assumed that  $c_{ass.} = c_{total}$  and since  $\epsilon_{ass.} = E_{ass.}/c_{ass.}l$  the extinction coefficient could be determined. Our data showed  $\epsilon_{ass.} = 10.0$ . The technique just outlined for the system  $Bu_4NBr-MeOH-C_6H_6$  was applied to this system at 25, 45 and  $60^\circ$  in an attempt to obtain thermodynamic data for the postulated solvation reaction in this system (see below), to a number of salts in  $MeOH-C_6H_6$ , and to a few systems containing salts and other hydrogen-bonded molecules: 1-butanol, 2-methyl-2-propanol and N-methylacetamide.

Table I shows the effect of  $Bu_4NBr$  on the absorbancy ratio  $R = (\log I_0/I)_{2.75\mu}/(\log I_0/I)_{3.0\mu}$  of MeOH in benzene at 25, 45 and  $60^\circ$  at three MeOH concentrations sufficiently low for the  $3.0\mu$  peak to be absent if salt is not present. The data show clearly the effect of added salt on lowering the concentration of free MeOH; this lowering is most pronounced at low MeOH concentration. For fixed solution composition an increase in temperature favors the free MeOH.

Similar results were obtained with  $Bu_4NCl$ ,  $Bu_4NNO_3$ , N,N-dimethylaniline hydrochloride,  $AgClO_4$ , and  $Bu_4NCO_2H$  at various  $MeOH-C_6H_6$  concentrations. The results are shown in Fig. 1 at one  $MeOH-C_6H_6$  concentration. They are all qualitatively similar although the effect of different salts on the  $[MeOH]_{ass.}/[MeOH]_{free}$  ratio

(29) U. Liddel and E. D. Becker, *Spectrochem. Acta*, **10**, 70 (1957).

(30) "Association" refers to methanol associated with the electrolyte as distinguished from "self-association" or "dimerization."

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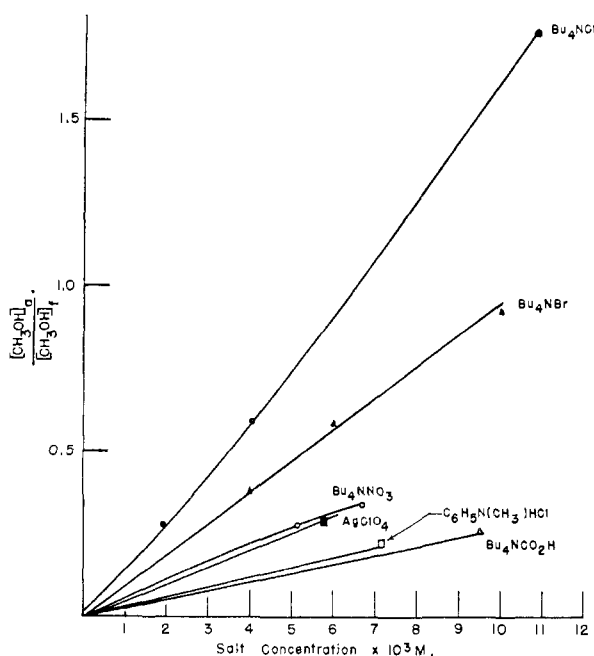


Fig. 1.—Effect of various salts on the ratio  $[\text{CH}_3\text{OH}]_{\text{ass.}}/[\text{CH}_3\text{OH}]_{\text{free}}$ ;  $[\text{CH}_3\text{OH}]_{\text{tot.}} = 20 \times 10^{-3}$ ,  $25^\circ$ .

is different. An extreme case is  $\text{Bu}_4\text{NCl}$  which does not produce any association at all. As indicated previously<sup>15</sup> the order of effectiveness of salts in producing the association peak in MeOH is  $\text{Bu}_4\text{NCl} \ll \text{Bu}_4\text{NCO}_2\text{H} < \text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2\text{HCl} < \text{AgClO}_4 < \text{Bu}_4\text{NNO}_3 < \text{Bu}_4\text{NBr} < \text{Bu}_4\text{NCl}$ .

TABLE I

ABSORBANCY RATIOS OF MeOH WITH  $n\text{-Bu}_4\text{NBr}$  IN  $\text{C}_6\text{H}_6$  AT VARIOUS TEMPERATURES; CELL LENGTH = 2.5 MM.

$M_{\text{salt}} \times 10^3$	$M_{\text{MeOH}} = 2.50 \times 10^{-3}$		
	$R_{25^\circ}$	$R_{45^\circ}$	$R_{60^\circ}$
3.00	1.73	..	..
4.00	1.22	1.52	1.60
6.00	0.899	0.989	1.00
8.00	.617	.617	0.760
10.00	.414	.470	0.550
	$M_{\text{MeOH}} = 10.0 \times 10^{-3}$		
3.00	1.66	..	..
4.00	1.27	1.58	1.70
6.00	0.800	1.06	1.14
8.00	.483	0.731	0.87
10.00	.479	0.550	0.66
	$M_{\text{MeOH}} = 20.0 \times 10^{-3}$		
3.00	1.41	..	..
4.00	1.32	1.57	1.80
6.00	0.879	1.06	1.24
8.00	.680	0.822	0.95
10.00	.541	0.629	0.72

Tables II, III and IV show the effect of  $\text{Bu}_4\text{NBr}$  on three other hydrogen-bonded compounds— $n\text{-C}_4\text{H}_9\text{OH}$ , 2-methyl-2 propanol and N-methylacetamide. The actual wave lengths at which the peaks occur are somewhat different for the different compounds and have been shown. The absorbancies of *t*-butyl alcohol and *n*-butyl alcohols both indicate dimer peaks at 2.843 and 2.872 microns, respectively. These peaks disappear

with the addition of  $\text{Bu}_4\text{NBr}$ , which is indicative of dimer breakage. At the same time an enhancement of the band in the  $3.0\mu$  region is noticed. A steric factor is also evident with these two alcohols. With comparable salt concentrations the absorbancy ratios of free to associated is considerably greater for the tertiary alcohol.

TABLE II

ABSORBANCY OF  $n\text{-C}_4\text{H}_9\text{OH}$  IN BENZENE; CELL LENGTH = 1.0 mm.

$M_{\text{Bu}_4\text{NBr}} \times 10^3$	2.753 $\mu$	2.872 $\mu$	2.998 $\mu$
10.0	0.055	..	..
20.0	.110	0.0075	..
40.0	.160	.150	0.003
50.0	.253	.033	.007

Absorbancy ratio of  $n\text{-C}_4\text{H}_9\text{OH}$  with  $n\text{-Bu}_4\text{NBr}$  in benzene; molarity of  $\text{Bu}_4\text{NBr} = 16.14 \times 10^{-3}$ ; cell length = 1.0 mm.

$M_{\text{Bu}_4\text{NBr}} \times 10^3$	2.753 $\mu$	2.998 $\mu$	R
10.00	0.030	0.035	0.857
20.00	.065	.068	0.956
30.00	.097	.097	1.000
40.00	.133	.125	1.06
50.00	.165	.153	1.08

TABLE III

Absorbancy of 2-methyl-2-propanol in benzene

$M \times 10^3$	2.766 $\mu$	2.843 $\mu$	3.030 $\mu$
10.00	0.050	..	..
20.00	.093	..	..
30.00	.135	0.007	0.005
40.00	.175	.012	.007
50.00	.215	.017	.010

Absorbancy ratio of 2-methyl-2-propanol with  $n\text{-Bu}_4\text{NBr}$  in benzene; molarity of  $\text{Bu}_4\text{NBr} = 15.20 \times 10^{-3}$

$M \times 10^3$	2.766 $\mu$	3.032 $\mu$	R
10.00	0.025	0.025	1.00
20.00	.060	.045	1.33
30.00	.090	.065	1.38
40.00	.130	.085	1.53

TABLE IV

Absorbancy of N-methylacetamide in benzene; cell length = 1.0 mm.

$M \times 10^3$	2.895 $\mu$	2.980 $\mu$	3.10 $\mu$
10.00	0.067	0.006	0.006
20.00	.135	.114	.020
30.00	.205	.037	.037
40.00	.270	.060	.060
50.00	.330	.090	.090
60.00	.385	.125	.125

Absorbancy of N-methylacetamide with  $n\text{-Bu}_4\text{NBr}$  in benzene concentration of  $\text{Bu}_4\text{NBr} = 9.811 \times 10^{-3} M$ ; cell length = 1.0 mm.

$M \times 10^3$	2.895 $\mu$	2.980 $\mu$	3.10 $\mu$
10.00	0.060	0.005	0.030
20.00	.120	.017	.055
30.00	.180	.030	.080
40.00	.233	.040	.097
50.00	.285	.057	.112
60.00	.325	.075	.125

The association of N-methylacetamide presents some interesting results much similar to the alcohols. The compound alone gives a sharp band

at 2.895 $\mu$  and another at 2.980 $\mu$ . The first is attributed to the free N-H vibration and the second to the associated N-H. However, with the addition of Bu<sub>4</sub>NBr, the 2.895 and 2.980 $\mu$  bands decrease in intensity and a completely new band appears at 3.10 $\mu$ . This latter absorption we attribute to hydrogen bonding of the acetamide.

### Discussion

Using the extinction coefficients of free and associated MeOH the actual concentrations of these species can be calculated. Figure 1 shows the ratio for a fixed total MeOH concentration of  $20 \times 10^{-3}M$  as a function of salt concentration. The effectiveness of salt in favoring association is that indicated previously and increases roughly with the charge density of the anion. At high salt concentration these curves become non-linear because  $[\text{CH}_3\text{OH}]_{\text{free}} \rightarrow 0$  and the ratio  $[\text{CH}_3\text{OH}]_{\text{ass.}}/[\text{CH}_3\text{OH}]_{\text{free}} \rightarrow 0$ . Relevant in this connection, *i.e.*, to the nature of the structure giving rise to the spectral observations, is the correlation of the exact position of the absorption maximum for the associated MeOH with the anion radius. This is shown in Table V.

TABLE V  
EFFECT OF SALTS ON ABSORPTION MAXIMUM OF ASSOCIATED MeOH

Salt	Absorption max ( $\mu$ )	Anion radius <sup>a</sup> (Å.)
Bu <sub>4</sub> NCl	3.040	1.81
Bu <sub>4</sub> NBr	2.975	1.95
Bu <sub>4</sub> NCO <sub>2</sub> H	2.973	..
Bu <sub>4</sub> NNO <sub>3</sub>	2.925	2-2.5
C <sub>6</sub> H <sub>5</sub> N(CH <sub>3</sub> ) <sub>2</sub> HCl	2.925	..
AgClO <sub>4</sub>	2.900	3.0
Bu <sub>4</sub> NPi	...	5.10

<sup>a</sup> Van der Waals radius.

A comparison of the several tetrabutylammonium salts shows clearly that the anion (rather than the cation) is primarily responsible for the effect; *e.g.*, no association is produced by Bu<sub>4</sub>NPi. This is also most consistent with the polarities of anions and hydrogen. Attempts to confirm this using picrates with small cations were unsuccessful because of the low solubility of these salts. A reasonable model for the associated structure is  $\text{A}^+ \text{X}^- \cdots \text{H}-\text{O}-\text{CH}_3$  where A<sup>+</sup> and X<sup>-</sup> represent cation and anion of the ion pair which is the predominant polar species in most of these solutions (*cf.* below). Evidence for hydrogen bonding by a number of proton donors to the anion of some quarternary ammonium halides also has been presented by Lund.<sup>31</sup> This also fits well the correlation of the absorption maximum with anion charge density shown in Table V. The O-H group can be regarded as an harmonic oscillator whose frequency is given by  $\nu = \frac{1}{2}\pi(k/\mu)^{1/2}$  where  $\mu$  is the reduced mass and  $k$  the force constant which increases as the interatomic O-H distance  $d$  decreases. The smaller the anion the greater will be its effect in stretching the O-H bond and consequently increasing  $d$ . This has the effect of lowering  $\nu$  or raising the wave length. Our reasons for implying that only one hydrogen bond per anion is formed are given in the next section.

(31) H. Lund, *Acta Chem. Scand.*, **12**, 298 (1958).

The influence of the cation on MeOH association can be seen from a comparison of the effects of Bu<sub>4</sub>NCl and C<sub>6</sub>H<sub>5</sub>(CH<sub>3</sub>)<sub>2</sub>HCl, the effect of the latter being considerably less. In that case intra-ion pair hydrogen bonding probably lessens the chloride hydrogen bonding to MeOH.

**The Bu<sub>4</sub>NBr-MeOH-C<sub>6</sub>H<sub>6</sub> System.**—Previous dielectric studies of this system<sup>14,32</sup> indicate that most of the electrolyte is present in the form of non-polar quadrupoles and polar ion pairs. (In these media the concentration of free ions and triple ions is very small by comparison.) The previously determined ion pair-quadrupole equilibrium constant  $K_{IQ}$  permits the calculation of ion pair concentrations in these solutions which we visualize provisionally as containing (in dilute solution in benzene) primarily Bu<sub>4</sub>NBr ion pairs some of whose anions are "solvated" by hydrogen-bonded MeOH molecules in an as yet unspecified number, Bu<sub>4</sub>NBr quadrupoles, perhaps similarly solvated, free MeOH, and a few ions and triple ions probably solvated. From the previously published  $K_{IQ}$  values<sup>32</sup> (interpolated for the MeOH concentrations of this work and extrapolated to 60°) and the spectral data, it is possible to calculate ion pair and associated MeOH concentrations for a number of fixed MeOH and salt concentrations. These are given in Table VI for 25°. Calculations at 45 and 60° also were made.<sup>33</sup>

TABLE VI  
CONCENTRATIONS OF Bu<sub>4</sub>NBr ION PAIRS AND MeOH IN Bu<sub>4</sub>NBr-MeOH-C<sub>6</sub>H<sub>6</sub><sup>a</sup> AT 25°

(A) [MeOH] <sub>total</sub> = $20 \times 10^{-3}$			
[Bu <sub>4</sub> NBr] <sub>tot.</sub> $\times 10^3$	[Bu <sub>4</sub> NBr] <sub>I.P.</sub> $\times 10^4$	[MeOH] <sub>ass.</sub> $\times 10^3$	[MeOH] <sub>ass.</sub> <sup>b</sup> [Bu <sub>4</sub> NBr] <sub>I.P.</sub>
3.00	0.661	4.48	6.8
4.00	0.783	5.50	7.0
6.00	1.05	7.25	6.9
8.00	1.23	8.47	6.9
10.00	1.41	9.60	6.8
(B) [MeOH] <sub>total</sub> = $10 \times 10^{-3}$			
3.00	0.561	2.31	4.1
4.00	.652	2.82	4.3
6.00	.820	3.84	4.7
8.00	.955	4.58	4.8
10.00	1.07	5.10	4.7
(C) [MeOH] <sub>total</sub> = $2.5 \times 10^{-3}$			
3.00	0.450	0.56	1.3
6.00	.650	0.90	1.4
8.00	.760	1.12	1.5
10.00	.850	1.29	1.5

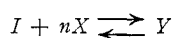
<sup>a</sup> All concentrations on the molarity scale. <sup>b</sup> Calculated by assuming that all the [MeOH]<sub>ass.</sub> solvates ion pairs only. For results based on other assumptions, see Discussion below and Table VIII.

The ion pair "solvation numbers" in the last column of Table VI are maximum ones which would apply only in the absence of the solvation of other species. Since only 10-20% of the total salt is in this form, it seems more probable that the actual solvation is less, some of the MeOH solvating quadrupoles.

(32) K. H. Stern and E. A. Richardson, *J. Phys. Chem.*, **64**, 1901 (1960).

(33) Ph.D. Dissertation of J. Bufalini.

A better calculation of ion pair solvation can be made by assuming a formal equilibrium between free MeOH, free ion pairs and solvated ion pairs. For such an equilibrium we write



where

$I$  = concentration of unsolvated ion pairs

$X$  = concentration of free MeOH

$Y$  = concentration of ion pairs each solvated by  $n$  molecules MeOH

This formulation assumes that (1) some unsolvated ion pairs exist, (2) that the solvation can be described by a single (or average) solvation number.  $I$  is not known but can be replaced by  $(S - Y)$ , where  $S$  is the total ion pair concentration calculated from dielectric data and shown in Table VI. The equilibrium constant  $K$  then is given by

$$K = \frac{Y}{(S - Y)X^n} \quad (1)$$

A simple rearrangement gives

$$\frac{X^n S}{Y} - \frac{1}{K} = X^n \quad (2)$$

If the correct value of  $n$  is chosen, then  $X^n$  plotted against  $S$  yields a straight line with slope  $X^n/Y$  and intercept  $K^{-1}$ .

A plot of  $X^n$  vs.  $S$  for several, small, integral values of  $n$  was prepared.<sup>33</sup> Only for  $n = 1$  is a straight line obtained. This result is not unreasonable in view of the relatively specific nature of the hydrogen bond. The least that can be said is that the result is consistent with the original formulation of the equilibrium which admittedly rests on somewhat heuristic grounds.

Using concentrations in Table VI the thermodynamic functions in Table VII are calculated.

TABLE VII

THERMODYNAMIC FUNCTIONS FOR THE SOLVATION OF  $\text{Bu}_4\text{NBr}$  ION PAIRS BY MeOH

$t$ ( $^{\circ}\text{C}$ .)	$K$	$\Delta F$ (kcal.)	$\Delta H$ (kcal.)	$\Delta S$ (e.u.)
25	65.2	-2.47		
45	30.7	2.17	-6.65	-14.0
60	20.0	1.98		

The value of  $\Delta H$  is in good agreement with the widely accepted value of  $\sim 5$  kcal. for the formation of a hydrogen bond,<sup>21,22</sup> and  $\Delta S$  matches closely the value of  $-13.6$  e.u. obtained by Tsubomura<sup>22</sup> for the association of phenol and hexamethylene-tetramine in  $\text{CCl}_4$ .

From the values in Tables VI and VII, it now becomes possible to present a detailed picture of this system. Solutions of  $\text{Bu}_4\text{NBr}$  and MeOH in benzene according to our model contain the following species for the concentration ranges indicated:  $\text{Bu}_4\text{N}^+$  cations,  $\text{Br}^-$  anions;  $(\text{Bu}_4\text{N}^+)(\text{Br}^-)$  and  $(\text{Bu}_4\text{N}^+)(\text{Br}^-)(\text{Bu}_4\text{N}^+)$  triple ions. These charged species probably are solvated, but their concentrations are several orders of magnitude less than those of the uncharged species.  $\text{Bu}_4\text{N}^+\text{Br}^-$  ion pairs, both unsolvated and solvated by one mole MeOH, *i.e.*,  $\text{Bu}_4\text{N}^+\text{Br}^- \cdots \text{HOCH}_3$ ; non-polar (square configuration)  $\text{Bu}_4\text{NBr}$  quadrupoles, both solvated and unsolvated as shown in Table VIII, free MeOH, and MeOH associated with

the electrolyte as indicated. The concentrations of these species are shown in Table VIII. Activity coefficient effects have been neglected in these calculations. Based on the entropy data for the ion pair-quadrupole equilibrium<sup>32</sup> it is reasonable to conclude that no solvation of uncharged species by benzene occurs.

TABLE VIII

CONCENTRATIONS OF VARIOUS SPECIES IN THE  $\text{Bu}_4\text{NBr}$ -MeOH- $\text{C}_6\text{H}_6$  SYSTEM AT 25 $^{\circ}\text{C}$

$C_{\text{tot.}} \times 10^3$	$S \times 10^3$	$Y \times 10^3$	$I \times 10^3$	$Q \times 10^3$	$X \times 10^3$	$[\text{MeOH}]_s/Q$
(A) $[\text{MeOH}]_{\text{tot.}} = 20 \times 10^{-3}$						
3.00	0.661	0.333	0.328	2.34	15.52	1.77
4.00	0.783	.346	.437	3.22	14.50	1.60
6.00	1.05	.425	.625	4.95	12.75	1.38
8.00	1.23	.528	.702	6.77	11.53	1.17
10.00	1.41	.626	.784	8.59	10.40	1.02
(B) $[\text{MeOH}]_{\text{tot.}} = 10 \times 10^{-3}$						
3.00	0.561	0.187	0.374	2.44	7.69	0.87
4.00	.652	.172	.480	3.35	7.18	.84
6.00	.820	.205	.615	5.18	6.16	.70
8.00	.955	.249	.706	7.05	5.42	.61
10.00	1.07	.295	.775	8.93	4.90	.54
(C) $[\text{MeOH}]_{\text{tot.}} = 2.5 \times 10^{-3}$						
3.00	0.450	0.053	0.397	2.55	1.94	0.198
6.00	.650	.053	.597	5.35	1.60	.158
8.00	.760	.063	.697	7.24	1.38	.146
10.00	.850	.073	.777	9.15	1.21	.133

<sup>a</sup> Symbols used

$C_{\text{tot.}}$	= molar concentration of $\text{Bu}_4\text{NBr}$
$S$	= molar concentration of $\text{Bu}_4\text{NBr}$ ion pairs
$I$	= molar concentration of $\text{Bu}_4\text{NBr}$ unsolvated ion pairs
$Y$	= molar concentration of $\text{Bu}_4\text{NBr}$ solvated ion pairs
$Q$	= molar concentration of $\text{Bu}_4\text{NBr}$ quadrupoles (in moles of electrolyte)
$X$	= molar concentration of free MeOH
$[\text{MeOH}]_s/Q$	= solvation number of $\text{Bu}_4\text{NBr}$ quadrupoles per ion pair

The most striking conclusion to be drawn from the data in Table VIII is the relative preferential solvation of ion pairs over quadrupoles at the lower MeOH concentration. This general trend is not unexpected in view of the greater polarity of ion pairs, but the high quadrupole solvation at high MeOH concentration may be a consequence of the model which requires a single ion pair solvation number over the entire range of concentration.

The observations on 1-butanol and tertiary butanol are similar to those on methanol except that they exhibit dimer formation at lower concentrations and that the spectral shift from hydrogen bonding in the dimer to hydrogen-anion is more marked. The study of *N*-methylacetamide indicates that the phenomenon discussed here is a general one for hydrogen bonds and not valid only for the O-H group. This suggests that the effect of even dilute electrolyte solutions on biologically important materials which exhibit hydrogen bonding may be quite significant.

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