The insertion of silylene into silane is known to be efficient.[2a,23] In the silyl radical–silane system the two mechanisms dimerization and disproportionation cannot be distinguished unless a silylene scavenger is found which does not trap silyl radicals. No such reagent is known.

In the trimethylsilyl radical–trisilane system no such disproportionation mechanism can give rise to the observed product hexamethyltrisilane. Therefore it seems certain that dimerization is the mechanism for self-reaction of trimethylsilyl radicals. The small amount of *tert*-butoxytrimethylsilane formed in extended irradiations of *tert*-butyl peroxide–trimethylsilane mixtures (Figure 7) is evidently not a primary product. Its mode of formation is still being investigated.

While the argument is far from rigorous, one may point out that the similarity of rate constants and activation parameters for the self-reactions of silyl radicals and trimethylsilyl radicals makes it likely if not certain that both reactions are dimerizations in solution at low temperature.

Summary

Bimolecular self-reaction has been established as the dominant path for the disappearance of silyl and trimethylsilyl radicals dissolved in the corresponding silane. Rate constants were determined for trimethylsilyl radical self-reaction over the temperature range +20 to $-82°$. The activation parameters deduced from the temperature dependence of the rate constant and the rate constants themselves are typical for group IV radicals. Similar rate constants were found for the self-reaction of silyl radicals at -120 and $-150°$. Product studies indicate that dimerization is the principal self-reaction mechanism for trimethylsilyl radicals. A chain-carrying displacement of hydrogen atoms from a silane by a silyl or trimethylsilyl radical is not an important reaction under the present reaction conditions. The formation of disilane, the dimer of SiH_3, and the similarity of the self-reaction rates of silyl and trimethylsilyl radicals strongly suggests that direct dimerization is the mechanism for silyl radical self-reaction in solution.

Acknowledgment. We thank Professor S. I. Weissman for the design of the pulsed photolysis apparatus and for the many indispensable suggestions which facilitated these experiments. Dr. Haim Levanon is also thanked for his guidance in the operation of the esr apparatus. We thank the U. S. Atomic Energy Commission for financial support.

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[23] M. Bowry and J. H. Purnell, *J. Amer. Chem. Soc.*, **92**, 2594 (1970).

Solvation of Halide Ions in Water and Dipolar Aprotic Solvents Studied by Halogen Nucleus Nuclear Magnetic Resonance

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Abstract: Chemical shift measurements on $^{35}Cl^-$, $^{79}Br^-$, and $^{127}I^-$ in the solvents water, CH_3OH, CH_3CN, DMSO, and DMF show that the dependence on solvent is strong and that the dependence on the cations of this study, $(C_2H_5)_4N^+$, Li^+, Na^+, K^+, is comparatively weak. This suggests the use of nmr solvent shifts as a probe of the immediate environment of an ion. A close correlation between chemical shifts and the charge transfer to solvent (CTTS) uv absorption band energies strongly suggests that the nmr paramagnetic term is dominant in determining shifts, and that the important excited state is the CTTS state. The nmr behavior of Cl^- and I^- ions in mixtures of DMSO and CH_3CN with water indicated that there is no strong preference in either case for the aprotic solvent as a component of the immediate solvent environment. Rather, the strong preferential solvation which is observed in the CH_3CN–H_2O mixtures is in large part the result of the nonideal behavior of CH_3CN–H_2O mixtures. The relationship between spectroscopic studies of solvation and the thermodynamics of transfer of ions from one solvent to another is discussed.

An ion dissolved in a polar solvent has considerable influence on its surroundings. The environment of an ion may be conceptualized by a three region model. The regions are: the region of the ordering effect of the ion on its immediate neighborhood; the region of disordering of solvent structure; and the bulk region where solvent structure is unperturbed. Studies of solvation by thermodynamic or transport experiments include all effects. It has been the aim of spectroscopic studies of solvation to take advantage of the short-range interactions dominating spectroscopic observables to probe the ordering imposed by an ion on the solvent molecules directly in contact with it.

Solvent dependent nmr shifts of the nuclei ^{59}Co, ^{23}Na, and ^{35}Cl have been proposed as measures of the composition of the immediate solvation shell[2-4] with the suggestion that shifts should vary approximately

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[1] Author to whom correspondence should be addressed.

[2] L. S. Frankel, C. H. Langford, and T. R. Stengle, *J. Phys. Chem.*, **74**, 1376 (1970).

[3] E. G. Bloor and R. G, Kidd, *Can. J. Chem.*, **46**, 3425 (1968).

[4] C. H. Langford and T. R. Stengle, *J. Amer. Chem. Soc.*, **91**, 4014 (1969).

linearly with solvent shell composition in mixed solvents. (The suggestion of linear dependence on solvation shell composition received independent conformation in the case of the ^{59}Co study.) The preliminary study of ^{35}Cl included the observation that Cl^- was not strongly preferentially solvated by water in dimethyl sulfoxide (DMSO)-water mixtures[4] despite the large change of chloride activity on transfer from water to DMSO.[5]

An analysis of the solvation of iodide ion parallel to the nmr solvent shift analysis for chloride has been based on the energy of the uv absorption band assigned as a charge transfer to solvent (CTTS) transition.[6,7] In this paper, we consider the relationship of halide nmr solvent shifts to CTTS spectra and the preferential solvation behavior of I^- and Cl^- in mixtures of DMSO and CH_3CN with water.

Experimental Section

All salts were anhydrous and of the highest purity commercially available. Sources were Eastman Organic Chemicals, Ventron Corp., and Fisher Scientific Co. Organic solvents were dried spectrograde. Solution preparation was carried out in a glove bag under an atmosphere of dry nitrogen.

The nmr spectra were recorded on a Varian DP instrument operating at 4.3 MHz for chloride and 8.1 MHz for bromide and iodide. The absorption signal was recorded for chloride, while bromide and iodide spectra were recorded as the first derivative of the absorption. Spectra were calibrated by the usual sideband technique. The reported chemical shifts are referred to an aqueous solution of the appropriate halide as an external standard. The nmr sample tubes were 14 mm in diameter, and spectra could be recorded with meaningful precision at salt concentrations of 0.2 *M* in most cases. The reported chemical shifts are the average of at least 3 determinations.

The uv spectra were recorded between 190 and 340 nm on a Cary Model 14 spectrophotometer using 1-cm quartz absorptionc ells. The salt concentrations were approximately 1×10^{-4} *M*. All spectral measurements were made at room temperature, *ca.* 23°.

Results

Table I contains a summary of the chemical shift of $^{35}Cl^-$ as a function of solvent, counterion, and salt concentration. The reference is 1 *M* aqueous NaCl, and chemical shifts are reported to a precision of ±2 ppm. Energies of the two measureable CTTS bands (in CH_3CN and H_2O) are quoted from ref 8. Some of the data in Table I were published in a preliminary communication.[4] Table II contains chemical shift data from solutions of $^{79}Br^-$ together with CTTS data from ref 8. The shift reference is 0.20 *M* NaBr, and shifts are precise to ±5 ppm. Table III summarizes $^{127}I^-$ data with chemical shifts referred to the 0.20 *M* aqueous NaI solution. Chemical shift precision is ±10 ppm. Iodide CTTS data have been collected and reviewed elsewhere.[9] It can be seen from the tables that the solvent is the most important variable, but there are secondary effects due to counterion and concentration.

Table I. ^{35}Cl Chemical Shift of Cl^- (ppm) from 1.0 *M* Aqueous NaCl[a]

Solute	Solvent	Concn, *M*	Shift, ppm	CTTS E_{max}, kcal
NaCl	$(CH_3)_2SO$	0.1	−69	
LiCl	H_2O	0.25	0	
	$(CH_3)_2SO$	0.12–0.25	−66	
$(C_2H_5)_4NCl$	H_2O	0.12	0	
		0.17	0	
		0.22	−2	
		0.25	−2	
		0.42	−4	
		1.63	−7	
	CH_3NO_2	0.25	−14	
	CH_3CN	0.11–0.25	−33	
		1.35	−38	
	$(CH_3)_2NCHO$	0.25	−42	
	$(CH_3)_2SO$	0.25	−65	
	H_2O			155.8
	CH_3CN			144.8

[a] The available CTTS maxima are presented for comparison. CTTS maxima are measured at a concentration several orders of magnitude lower than that used for chemical shift measurements.

Table II. ^{79}Br Chemical Shift of Br^- (ppm) from 0.2 *M* Aqueous NaBr[a]

Solute	Solvent	Concn, *M*	Shift, ppm	CTTS E_{max}, kcal
NaBr	$(CH_3)_2NCHO$	0.2	−110	
	$(CH_3)_2SO$	0.2	−167	
LiBr	H_2O	0.2	0	
	CH_3CN	0.4	+41	
	$(CH_3)_2NCHO$	0.2	−110	
	$(CH_3)_2SO$	0.2	−179	
KBr	H_2O	0.2	0	
	$(CH_3)_2NCHO$	0.2	−110	
	$(CH_3)_2SO$	0.2	−154	
$(CH_3)_4NBr$	H_2O	0.2	0	
	$(CH_3)_2SO$	0.2	−154	
$(C_2H_5)_4NBr$	H_2O	0.2	−22	135.4
	CH_3CN	0.2	−79	125.2
	$(CH_3)_2NCHO$	0.2	−110	
	$(CH_3)_2SO$	0.2	−159	
	CH_3OH			139.2

[a] The available CTTS maxima are presented for comparison. CTTS maxima are measured at a concentration several orders of magnitude less than that used for chemical shift measurements.

Table III. ^{127}I Chemical Shift of 0.20 *M* I^- Solutions in Several Solvents[a]

	Solvent				
Solute	H_2O	CH_3CN	$(CH_3)_2$-NCHO	$(CH_3)_2SO$	CH_3OH
LiI	0	−115	−118	−266	
NaI	0	−70	−167	−266	+35
KI	0	−105	−167	−261	
$(C_2H_5)_4NI$	−19	−100	−161	−252	
CTTS E_{max}, kcal	126.3	115.8	106.8		129.8

[a] The available CTTS maxima are presented for comparison. CTTS maxima are measured at a concentration several orders of magnitude less than that used for chemical shift measurements.

Armed with the results in pure solvents, we proceed to the consideration of solvation in mixed solvents, restricting attention to low salt concentrations to minimize the counterion effects. The results will be presented in a unified fashion employing the assumption

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(5) A. J. Parker, *Advan. Phys. Org. Chem.*, **5**, 173 (1967).

(6) M. Smith and M. C. R. Symons, *Trans. Faraday Soc.*, **54**, 338 (1958).

(7) M. J. Blandamer, T. E. Gough, and M. C. R. Symons, *ibid.*, **60**, 488 (1964).

(8) M. J. Blandamer, T. R. Griffiths, L. Shields, and M. C. R. Symons, *ibid.*, **60**, 1524 (1964).

(9) M. J. Blandamer and M. F. Fox, *Chem. Rev.*, **70**, 59 (1970).

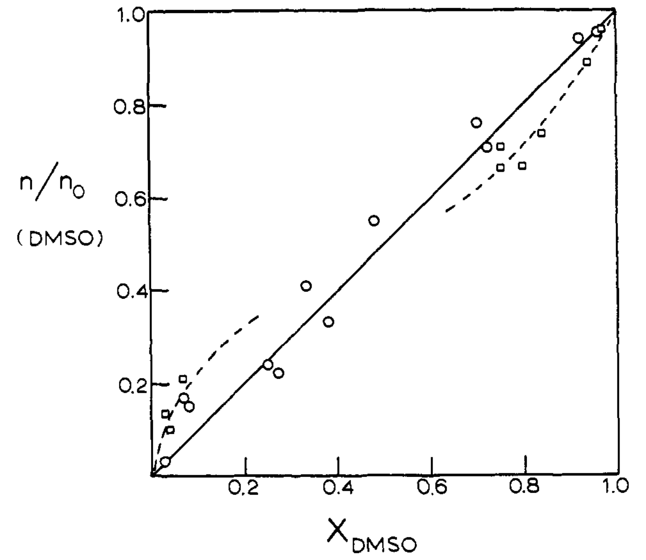

Figure 1. Nmr n/n_0 data for DMSO solvating Cl^- (○) and I^- (□) in DMSO–H_2O mixtures. The Cl^- data are from 0.25 *M* LiCl and 0.25 *M* $(C_2H_5)_4NCl$ solutions, and the I^- data are from 0.20 *M* NaI solutions. The dashed line indicates the I^- trend, and the solid line indicates the Cl^- trend.

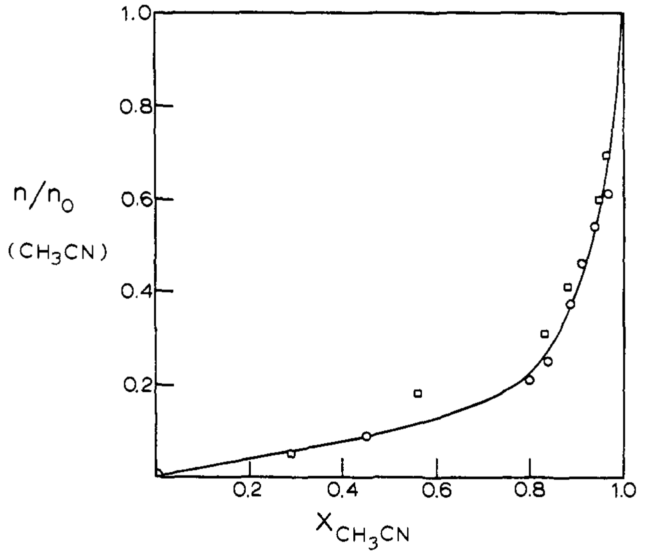

Figure 2. Nmr n/n_0 data for CH_3CN solvating Cl^- in CH_3CN–H_2O mixtures. The data are from 0.225 *M* $(C_2H_5)_4NCl$ (○) and 0.42 *M* $(C_2H_5)_4NCl$ (□) solutions.

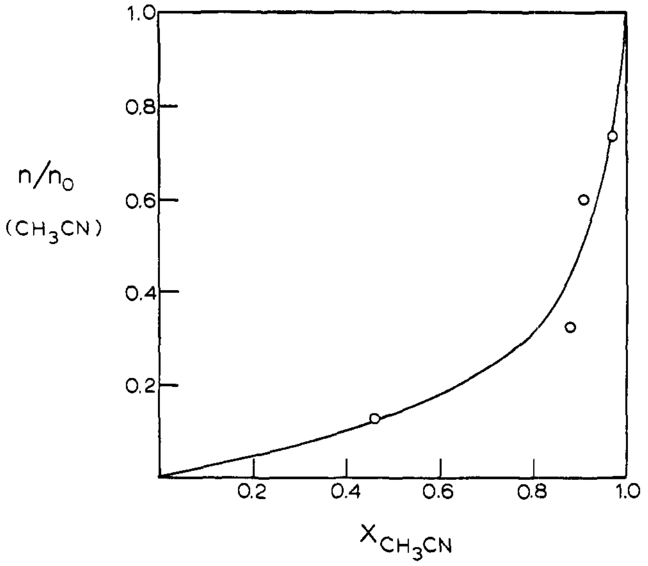

Figure 3. CTTS n/n_0 data for CH_3CN solvating Br^- in CH_3CN–H_2O mixtures. The data are from ref 8.

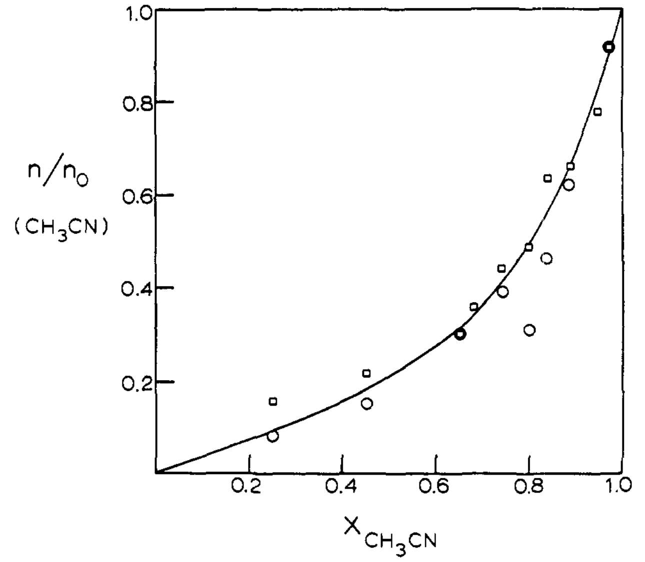

Figure 4. CTTS and nmr n/n_0 data for CH_3CN solvating I^- in CH_3CN–H_2O mixtures. The nmr data are from 0.172 *M* NaI solutions (○) and the CTTS data are from 10^{-4} *M* NaI solutions (□).

that the chemical shift[2-4] (or CTTS wavelength[10]) varies linearly with the composition of the immediate solvation shell.[11] In mixed solvents we define a parameter called n/n_0 as the ratio of the number (n) of one type of solvent molecules solvating the ion in the mixture to the number (n_0) of that type of solvent molecules solvating the ion in the pure solvent. For example, n/n_0 (CH_3CN) for chloride dissolved in a CH_3CN–H_2O mixture is the number of CH_3CN molecules solvating Cl^- in that mixture compared to the number of CH_3CN molecules solvating Cl^- in pure CH_3CN. From the linearity relationship it follows that

$$n/n_{0(\mathrm{CH_3CN})} = \frac{\sigma_{\mathrm{M}} - \sigma_{\mathrm{CH_3CN}}}{\sigma_{\mathrm{H_2O}} - \sigma_{\mathrm{CH_3CN}}} \qquad (1)$$

where σ designates the chemical shift, M designates the mixed solvent, and CH_3CN and H_2O designate the pure solvents. For a CTTS band with a maximum at the wavelength λ, a corresponding equation is

$$n/n_{0(\mathrm{CH_3CN})} = \frac{\lambda_{\mathrm{M}} - \lambda_{\mathrm{CH_3CN}}}{\lambda_{\mathrm{H_2O}} - \lambda_{\mathrm{CH_3CN}}} \qquad (2)$$

Two solvent systems will be considered. In Figure 1 preferential solvation data obtained from nmr chemical shifts are given for Cl^- and I^- in the DMSO–H_2O system. In the CH_3CN–H_2O system, Cl^- data from nmr are given in Figure 2, Br^- data from CTTS spectra in

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(10) T. R. Griffiths and M. C. R. Symons, *Trans. Faraday Soc.*, **56**, 1125 (1960).

(11) The validity of this assumption is demonstrated by studies at high temperature where solvation is not preferential. When the distribution of solvent molecules in the first shell equals that in the bulk solvent, a plot of spectroscopic parameters *vs.* bulk composition will be linear. Such behavior was observed for the CTTS transition of I^- in several systems by M. Smith and M. C. R. Symons, *Discuss. Faraday Soc.*, **24**, 206 (1957).

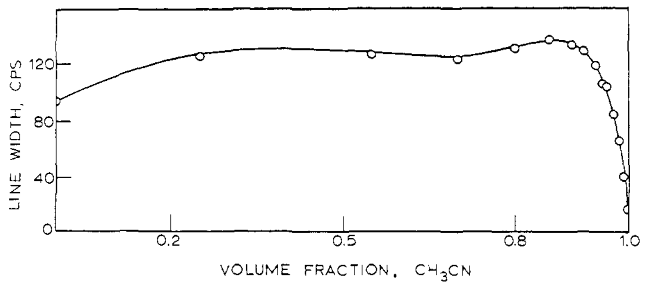

Figure 5. Line width of the ^{35}Cl nmr signal as a function of solvent composition in the CH_3CN-H_2O system. The data are from 1.03 *M* $(C_2H_5)_4NCl$ solutions.

Figure 3, and I^- data from both nmr and CTTS data in Figure 4. The width of the halide ion nmr signal is often much greater in mixed solvents than in pure solvents. Figure 5 shows the variation of the line width of the ^{35}Cl resonance in CH_3CN-H_2O mixtures. This line broadening effect is responsible for the absence of potentially interesting points in the mid-concentration range of DMSO-H_2O mixtures, and also for the lack of nmr data on ^{79}Br in mixed solvents. In these cases the nmr signal is too wide to permit accurate chemical shift measurements. It should be added that the strong absorption of DMSO in the ultraviolet precludes measurement of CTTS bands in that solvent.

Discussion

(1) Origin of Solvent Shifts. In a recent review of halogen nmr, Hall[12] has suggested several factors which might be expected to influence solvent shifts: (i) molecular volume and packing geometry; (ii) hydrogen bonding interactions; (iii) charge transfer to solvent interactions; (iv) orbital overlap with large atoms in the solvent; and (v) charge distributions in solvent molecules. A review of the data collected in Tables I-III provides no clear cut affirmative evidence for any of these except (iii), and the evidence for the role of (iii) is quite specific. Figure 6 shows the solvent shifts plotted *vs.* the wavelength maxima of the CTTS bands. This corresponds to a plot of the chemical shift against the reciprocal of the excitation energy, and the plots are satisfactorily linear.

Shielding constants are commonly divided into a diamagnetic and a paramagnetic term.[13] In a free gaseous halide ion where the electron distribution has spherical symmetry, only the diamagnetic term contributes to the shielding. In solution the ion is perturbed by the solvent molecules, and the ground state is no longer purely ^1S. Here the paramagnetic term becomes important. It arises from the lack of spherical symmetry of the electric potential, and it operates to reduce the shielding. The magnitude of the paramagnetic term depends upon the amount by which excited electronic states mix with the ground state under the perturbation of the magnetic field. This varies with the reciprocal of the "average excitation energy" of the ion. Such an approach was used by Deverell and Richards[14] in their treatment of halide ion chemical shifts in aqueous solution. Since the CTTS represents the lowest lying excited state of the halide ion, the "average excitation energy" is dominated by it! That this is indeed the case is shown by Figure 6.

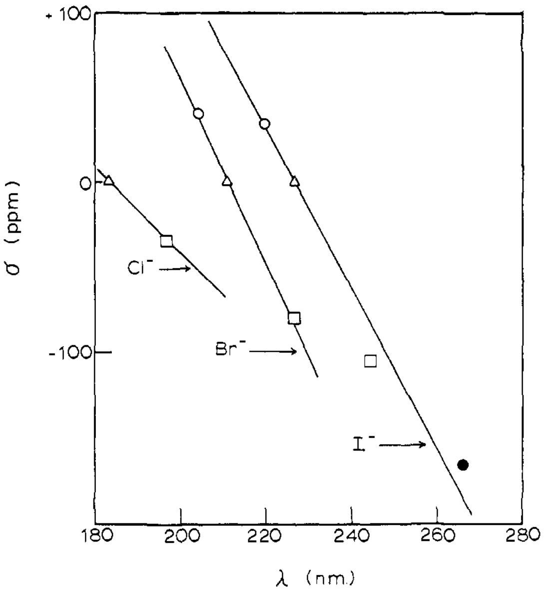

Figure 6. The variation of the halide ion chemical shift with the wavelength of the CTTS band in several solvents. The shift reference is the aqueous solution, and the solvents are CH_3OH (○), H_2O (△), CH_3CN (□), and $(CH_3)_2NCHO$ (●).

(2) Preferential Solvation. Examination of Figures 1 to 4 suggests that we have two quite different cases. There is little evidence of preferential solvation of either Cl^- or I^- in the DMSO-H_2O system. The composition of the solvation shell probed spectroscopically remains close to the bulk composition of the solvent mixture. In contrast, water seems to be distinctly preferred over acetonitrile by all three halides in CH_3CN-H_2O mixtures. The order of water preference is not unexpected, $Cl^- > Br^- > I^-$. The difference between DMSO and CH_3CN is puzzling when these results are compared to data on the free energies of transfer of the ions from water to the dipolar aprotic solvents. According to the extra thermodynamic analysis of Alexander and Parker,[15] transfer from H_2O to DMSO is accompanied by a free energy change of +10.1, +6.9, and +2.9 kcal/g-ion for Cl^-, Br^-, and I^-, respectively, and transfer from H_2O to CH_3CN is accompanied by free energy changes of +11.6, +8.1, and +4.8 kcal/g-ion for Cl^-, Br^-, and I^-, respectively. There is a much larger difference among the halides than between DMSO and CH_3CN.

Part of the puzzle is resolved by specifying exactly what process is under observation. In preferential solvation studies, the idealized process is conceived of as the removal of a solvent molecule of one type (*e.g.*, H_2O) from the bulk liquid mixture and its transfer to the solvation shell with corresponding removal of a solvent molecule of the other type (*e.g.*, CH_3CN) from the solvation shell and its transfer to the bulk mixture as shown in eq 3.

$$H_2O(\text{bulk}) + CH_3CN(\text{s}) = CH_3CN(\text{bulk}) + H_2O(\text{s}) \qquad (3)$$

This process may be favored by either a low activity of H_2O in the solvation shell *or a high activity of H_2O in the bulk mixture*. In the latter case a small preference

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[12] C. Hall, *Quart. Rev., Chem. Soc.*, **25**, 87 (1971).

[13] A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967, Chapter 5.

[14] C. Deverell and R. E. Richards, *Mol. Phys.*, **16**, 421 (1969).

[15] R. Alexander and A. J. Parker, *J. Amer. Chem. Soc.*, **89**, 5549 (1967).

in the solvation shell is adequate to produce strong preferential solvation. Mixtures of CH_3CN–H_2O show large positive deviations from Raoult's law,[16,17] and the activity of water in such mixtures is nearly the same as that of pure water above a water mole fraction of 0.2. Figure 7 shows a plot of $n/n_0(H_2O)$ values *vs.* the relative water activity instead of the mole fraction. In this figure, where the effects of nonideality in the bulk solvent mixture are partially corrected, the behavior is much closer to that observed for DMSO. Preference for water in the solvation shell is small at most. Vapor pressure data taken at 70° on the DMSO–H_2O system show no large deviations from Raoult's law.[18] Data for lower temperatures have not been reported.

These results illustrate a point of general importance in dealing with the behavior of solutes in mixed solvents. *Small preferences in the solvation shell are magnified by nonideality of the bulk liquid mixture.* Recent reports[17,19] have illustrated the reverse of the halide case. The large complex anions $Cr(NCS)_6^{3-}$ and $Cr(NH_3)_2(NCS)_4^-$ show a preference for CH_3CN over water which is magnified by the nonideality of CH_3CN–H_2O mixtures to become the major factor in the solvolytic kinetics of the ions. In addition, it is interesting to speculate that the detailed attention given to solvent drying in electrochemical studies in CH_3CN compared to the much more casual attitude that has proved successful with respect to DMSO solutions is a further illustration of the disadvantages associated with a mixed solvent system which shows large deviations from ideality.

The final issue is the nature of the relationship between the small preference for water observed in the immediate solvation shell of halide ions in DMSO and CH_3CN mixtures and the rather large free energies of transfer of halide ions from water to the dipolar aprotic solvents. Again it is useful to specify the details of the processes compared. The process envisioned in the free energy of transfer involves stripping an ion of its solvation shell, returning those molecules to the bulk solvent, and constructing the solvation shell in the new solvent. Here the solvation shell includes both the immediate solvation shell and those molecules outside of the immediate solvation shell which are perturbed by the ion. Spectroscopic preferential solvation data reveal *only* the composition of the intimate solvation shell of the ion, and the bulk solvent activity parameters we have used in interpreting preferential solvation deal only with the unperturbed bulk liquid mixture. The data are mute as to effects in the secondary solvation region where the ion and its first solvation shell perturb normal solvent structure.

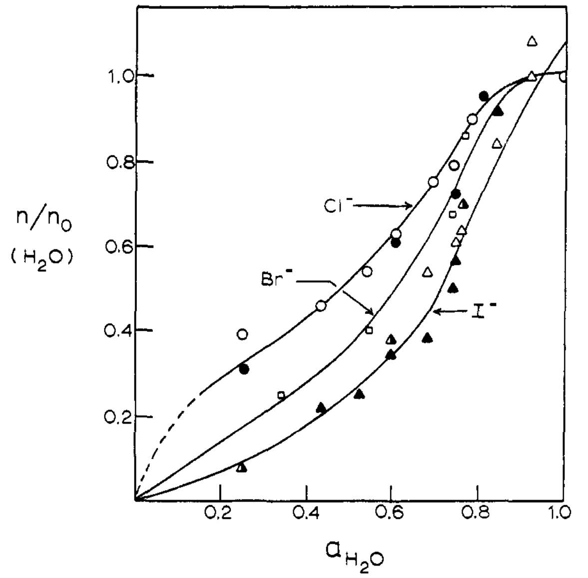

Figure 7. The variation of n/n_0 with water activity in CH_3CN–H_2O mixtures. The data for Cl^- are based on nmr measurements on 0.225 *M* $(C_2H_5)_4NCl$ solutions (○) and 0.42 *M* $(C_2H_5)_4NCl$ solutions (●). The data for Br^- are based on CTTS measurements from ref 8 (□). The data for I^- are based on nmr measurements on 0.172 *M* NaI solutions (△) and on CTTS measurements on 10^{-4} *M* NaI solutions (▲).

It is generally accepted that water solvates halide ions more strongly than DMSO or CH_3CN. Yet our results show that water is not strongly preferred in contact with halide ions in mixed solvents. A plausible explanation of this fact would focus on the interaction between the contact solvation shell and the next layers. The water molecule in contact with a halide ion must be significantly polarized. It could be thought of as presenting a "lyate ion" like aspect to its surroundings, so that it interacts favorably with water but not DMSO. When a DMSO molecule replaces a water in contact with a halide, there is a loss associated with breaking a water–halide interaction. This loss is compensated for in the next layer by elimination of unfavorable water–DMSO interactions.

The idea that the intermediate region between contact solvation and the bulk liquid is especially significant in halide solvation is important to more than the interpretation of our preferential solvation results. In electrochemical studies, halides are recognized as "net structure breakers" in water and are sometimes spoken of as "weakly hydrated."[20] Yet comparison of halide reactivity in water and dipolar aprotic solvents emphasize that there is a "strong" hydration in water.[15] The reconciliation of these two points of view requires consideration of the interaction between the contact solvation layer and immediately surrounding shells.

Acknowledgments. The authors are grateful for the helpful advice of Dr. T. R. Griffiths in the formulation of this project. This work was supported by the Air Force Office of Scientific Research under Grant AF-OSR-71-1977.

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(16) V. de Landesbug, *Bull. Soc. Chim. Belg.*, **49**, 59 (1940).

(17) V. S. Sastri, R. W. Henwood, S. Behrendt, and C. H. Langford, *J. Amer. Chem. Soc.*, **94**, 753 (1972).

(18) J. Kenttämaa and J. J. Lindbergh, *Suom. Kemistilehti B*, **33**, 98 (1960).

(19) S. Behrendt, C. H. Langford, and L. S. Frankel, *J. Amer. Chem. Soc.*, **91**, 2236 (1969).

(20) J. E. Desnoyers and C. Jolicoeur in "Modern Aspects of Electrochemistry," No. 5, J. O'M. Bockris and B. E. Conway, Ed., Plenum Press, New York, N. Y., 1969, Chapter 1.