

\mathbf{z} within this (closed) triangle. If \mathbf{z} is expressed as a linear combination of the nuclear charge vectors at the three vertices, then the total energy of the molecule of charges \mathbf{z} is larger than or equal to the linear combination of total energies of molecules defining the three vertices, if the same linear coefficients are taken.

It is interesting to note that similar relations may also be obtained in some more exotic applications of the above results to hypothetical "quarkonium molecules", present perhaps in the early stages of the universe, i.e., to formal molecules with fractional nuclear charges of multiples of $1/3$. However, the relations derived above are of primary interest in studying potential surface problems of real molecules of integer nuclear charges, e.g., in providing energy bounds for the fundamental group Π_1 of reaction

mechanisms of a family of reactions confined to a given potential energy hypersurface.^{13,14} These groups (one-dimensional homotopy groups, independent of molecular symmetry groups or permutation groups) depend on an upper bound for energy, as well as on the topology of the hypersurface, and may serve as aids to synthesis design.

Acknowledgment. This work has been supported by a research grant from the Natural Sciences and Engineering Research Council of Canada.

(13) P. G. Mezey, *Int. J. Quant. Chem. Symp.*, **18**, 77 (1984).

(14) P. G. Mezey, *Theor. Chim. Acta*, **67**, 43, 91(1985).

Linear Solvation Energy Relationships. 29. Solution Properties of Some Tetraalkylammonium Halide Ion Pairs and Dissociated Ions

Robert W. Taft,* Michael H. Abraham,* Ruth M. Doherty,* and Mortimer J. Kamlet*†

Contribution from the Department of Chemistry, University of California, Irvine, California 92717, Department of Chemistry, University of Surrey, Guildford, Surrey GU2 5XH, United Kingdom, and Naval Surface Weapons Center White Oak Laboratory, Silver Spring, Maryland 20910. Received February 21, 1984

Abstract: Free energies of transfer of tetramethyl- and tetraethylammonium chloride, bromide, and iodide ion pairs (IP) and dissociated ions (DI) are well correlated through equations of the form

$$\Delta G_t^\circ = (\Delta G_t^\circ)_0 + s\pi^* + a\alpha + h\delta_H^2$$

Inclusion of a $\beta\delta$ term shows only a minimal dependence on β and no improvement in the statistical goodness of fit, which indicates that there is no significant association between the solvents and the R_4N^+ ions acting as Lewis acids. The s , a , and h coefficients are significantly smaller in magnitude for IP's than for their corresponding DI's. The $-a$ values increase significantly, as expected, for both IP's and DI's in the sequence $I^- < Br^- < Cl^-$. These and other smaller structural effects are discussed.

In Part 13 of this series,¹ we reported that free energies of solution of nondipolar solutes (rare gases, alkanes, tetramethyltin) in nonpolychlorinated non-hydrogen bonding aliphatic solvents² were well correlated through equations of the form of eq 1a. The

$$\Delta G_s^\circ = (\Delta G_s^\circ)_0 + h\delta_H \quad (1a)$$

$$\delta_H = [(\Delta H_v - RT)/V]^{1/2} \quad (2)$$

δ_H term in eq 1a, the Hildebrand solubility parameter,³ is defined by eq 2 (where ΔH_v is the molar heat of vaporization to a gas at zero pressure and V is the molar volume) and is the solvent property which measures the work necessary to separate the solvent molecules (disrupt and reorganize solvent/solvent interactions) to create a suitably sized cavity for the solute. Accordingly, $h\delta_H$ has been characterized as the *cavity term*, but the results do not exclude the possibility that the term also includes contributions from solute/solvent dispersion interactions.

It has since been pointed out to us⁴ that, rather than the first power of δ_H , regular solutions theory requires that the linear regressions of ΔG_s° be with δ_H^2 as in eq 1b. However, since the correlation coefficient of δ_H with δ_H^2 is 0.992 over the 7.27–13.0 range considered, correlations by eq 1a and 1b are of comparable statistical quality.

$$\Delta G_s^\circ = (\Delta G_s^\circ)_0 + h\delta_H^2 \quad (1b)$$

In accordance with our practice of treating sequentially interactions of progressively increasing complexity, we next con-

sidered free energies of solution and of transfer of dipolar solutes under conditions where neither solutes nor solvents were hydrogen bond donors,² i.e., hydrogen-bonding effects were excluded. In Part 19 of this series,⁵ we reported that such cases are well correlated by equations of the form of eq 3a, where the π^* term is

$$\Delta G_s^\circ = (\Delta G_s^\circ)_0 + s\pi^* + h\delta_H \quad (3a)$$

the solvatochromic parameter that measures the ability of the solvent to interact with a dipolar solute by virtue of dipole/dipole or dipole/induced dipole interactions. For dipolar solutes, the solute/solvent dipolar interaction is exoergic (negative sign of s) and the cavity term is endoergic (positive sign of h). As before, for the 41 solutes considered, correlations with the square of the Hildebrand solubility parameter (eq 3b) were of similar quality to correlations by eq 3a.

$$\Delta G_s^\circ = (\Delta G_s^\circ)_0 + s\pi^* + h\delta_H^2 \quad (3b)$$

In the present paper we consider multiple solvation interactions of next greater complexity, the case of free energies of solution and of transfer of anionic hydrogen bond acceptor (HBA) solutes in both hydrogen bond donor (HBD) and non-HBD solvents. Here

(1) Kamlet, M. J.; Carr, P. W.; Taft, R. W.; Abraham, M. H. *J. Am. Chem. Soc.* **1981**, *103*, 6062.

(2) We have restricted the correlations to aliphatic nonpolychlorinated solvents to exclude variable polarizability effects.

(3) Hildebrand, J. H.; Scott, R. L. "The Solubility of Nonelectrolytes"; 3rd ed.; Dover Publications: New York, 1964. Hildebrand, J. H.; Scott, R. L. "Regular Solutions"; Prentice-Hall: Englewood Cliffs, NJ, 1952.

(4) Private communication with Prof. Peter W. Carr, University of Minnesota.

(5) Abraham, M. H.; Kamlet, M. J.; Taft, R. W. *J. Chem. Soc., Perkin Trans. 2* **1982**, 923.

* Naval Surface Weapons Center.

Table I. Solvatochromic Parameters Used in Correlations for Tetramethylammonium Chloride^a

solvent	π^*	α	β	δ_H^2	δ_C^2
hexane	-0.08	0	0	52.9	
cyclohexane	0	0	0	67.2	
diethyl ether	0.27	0	0.47	55.7	
ethyl acetate	0.55	0	0.45	79.2	
2-butanone	0.67	0.06	0.48	84.8	
acetone	0.71	0.08	0.48	92.2	
dimethylformamide	0.88	0	0.69	138.3	
<i>N</i> -methylpyrrolidone	0.92	0	0.77	127.7	
dimethyl sulfoxide	1.00	0	0.76	169.0	
nitromethane	0.85	0.22	0.20	159.0	
acetonitrile	0.75	0.19	0.31	137.8	
<i>tert</i> -butyl alcohol	0.41	0.68	1.01	112.3	84.6
isopropyl alcohol	0.48	0.76	0.95	132.3	100.0
<i>n</i> -butyl alcohol	0.47	0.79	0.88	130.0	96.0
<i>n</i> -propyl alcohol	0.52	0.78	0.87	141.6	104.0
ethanol	0.54	0.83	0.77	161.3	112.4
methanol	0.60	0.93	0.62	210.3	127.7
water	1.09	1.17	0.18	547.6	327.6

^aSolvatochromic parameters from ref 6.

in addition to the cavity and dipolarity terms, we have the effects of solvent donor/solute acceptor (type A) hydrogen bonding. According to our *solvatochromic comparison methodology*,^{1,5-7} correlations of such data should take the form of eq 4a or 4b, where α is the solvatochromic parameter that measures the ability of the solvent to act as an HBD to HBA solutes:

$$\Delta G_s^\circ = (\Delta G_s^\circ)_0 + s\pi^* + a\alpha + h\delta_H \quad (4a)$$

$$\Delta G_s^\circ = (\Delta G_s^\circ)_0 + s\pi^* + a\alpha + h\delta_H^2 \quad (4b)$$

The data to be treated are free energies of transfer of the tetramethyl- and tetraethylammonium chloride, bromide, and iodide and tetra-*n*-propylammonium iodide dissociated ions (DI) and ion pairs (IP) from methanol to up to seventeen widely varying aliphatic solvents. Abraham⁸ has reported molar solubility data for the tetraalkylammonium halides in these solvents and, using mainly literature data for ion pair association constants, has calculated free energies of solution of the dissociated species $R_4N^+ + X^-$ and the ion pairs R_4NX . These data are assembled in Table II in terms of the free energies of transfer from methanol on the mol fraction scale. The $(\Delta G_t^\circ)_0$ values and the coefficients of the independent variables in eq 4b for each correlation are also given in Table II. The solvatochromic parameters used in the correlations are assembled in Table I.

Results

Before we proceed with the main interpretations of the correlation results, four important questions need to be answered. The first of these derives from the fact that eq 1a and 1b break down badly for nondipolar non-hydrogen-bonding solutes in alcohol solvents and water. In an earlier paper,⁹ we have rationalized this as follows: Amphoteric ROH compounds are self-associated through hydrogen bonding, acting simultaneously as hydrogen bond donors (acids) and acceptors (bases). These hydrogen bonds are broken in both the process of vaporization and the process of separating the ROH molecules to form a cavity for the solute. The ROH compounds do not to any significant extent reassociate in the vapor phase. In the liquid phase, however, after the nondipolar solute has filled the cavity, a new pattern of hydrogen-bonded self-association is formed by the ROH molecules surrounding the solute. This contributes an exoergic reorganization energy to the cavity term in the scaled particle theory of solutions. On this basis, we defined and suggested for use in calculation of

solubility properties a new parameter, δ_C , which is the Hildebrand solubility parameter for self-associated solvents, back calculated from solubilities of nondipolar solutes and eq 1a.⁹ It becomes important, therefore, to ascertain whether correlations with δ_H or δ_C better accommodate the present data. In earlier correlations of solubility data for non-ionic HBA base solutes, we had found the better statistical fits to be with δ_C and our a priori expectation had been that the same would be the case with the present correlations.

The second question, already touched on above, was whether δ or δ^2 would lead to better correlations when the alcohols and water were included in the data set and the δ range was extended to 18.1 (δ_C) or 23.4 (δ_H), i.e., whether eq 4a or 4b would lead to better statistical goodness of fit for ROH solvents. Thirdly, the possibility exists that the tetraalkylammonium cations might have sufficiently strong Lewis acid character to cause complexation with HBA solvents. If such were the case, the solvatochromic equations should also include $b\beta$ terms, β being the solvatochromic parameter that measures the solvent's ability to donate an electron pair to an HBD or Lewis acid solute. The final, particularly important, question is whether the independent variables of eq 4 are in fact distinctly non-collinear, as is required for a statistically valid separation of the terms in this equation.

These four questions are readily answered by the correlations which we have carried out. First, contrary to initial expectations, significantly more precise correlations result from the use of δ_H than of δ_C . For example, for the dissociated $Me_4N^+ + Cl^-$ data ($n = 13$), the standard deviation for eq 4a is 1.5 kcal/mol, whereas it increased to 2.3 kcal/mol with the use of δ_C rather than δ_H . Secondly, eq 4b is found to be more precise than eq 4a. For the dissociated $Me_4N^+ + Cl^-$ data, for example, the $sd = 0.75$ kcal/mol ($sd = 1.4$ kcal/mol using δ_C^2). For the Me_4NCl ion pair data ($n = 17$), as a further example, $sd = 0.5$ kcal/mol for eq 4b compared with 0.7 kcal/mol for eq 4a (for eq 4b using δ_C^2 , $sd = 0.8$ kcal/mol). Thirdly, the inclusion of a $b\beta$ term in eq 4b for both the Me_4NCl ion pair data and the $Me_4N^+ + Cl^-$ dissociated ion data does not significantly change the overall correlation coefficient, the standard deviation, the $(\Delta G_s^\circ)_0$ term, or values of the s , a , and h coefficients, and the b values are not statistically significant. Fourthly, using the favored eq 4b to correlate all of the data of Table II gives the results shown in both Table II and Table III. The latter table shows that for each correlation the squares of the coefficients of correlation between the (assumed) independent variables of eq 4b, i.e., π^* vs. α , α vs. δ_H^2 and π^* vs. δ_H^2 , are insignificant compared to the overall r^2 (that is, the variables are independent ones for most intents and purposes).

An additional critical test has been made of the latter (fourth) question, and the results are also recorded in Table III. All of the tetramethyl- and tetraethylammonium salt data have been correlated also by eq 4b, omitting the points for both water and methanol, and the results of these correlations are compared with those for the full data sets. The purpose of omitting the water and methanol data points was to ascertain whether the statistical measures of goodness of fit of eq 4b are significantly influenced by the resulting alterations in the correlation coefficients between the independent variables or by the significantly shortened ranges of the α and δ_H^2 values in the data sets. The results given in Table III show that there are, indeed, no significant changes in either the squares of the overall correlation coefficients, the standard deviations, or the $(\Delta G_t^\circ)_0$, s , a , and h values. As expected for the reduced ranges of the α and δ_H^2 values upon omission of the methanol and water points, the error limits in the latter coefficients are all significantly increased.

Finally, it is important to note that the intercept term, $(\Delta G_t^\circ)_0$ in eq 4b does not act as an adjustable parameter. This term is a consequence of our choice (for convenience) to use free energies of transfer based on methanol as the standard solvent, whereas the solvent parameters, π^* , α , and δ_H have different standards ($\pi^* = \alpha = 0$ for cyclohexane, and $\delta_H = 0$ for the gas phase). Thus, $(\Delta G_t^\circ)_0$ corresponds to the free energy of transfer from methanol to a hypothetical solvent having $\delta_H = \pi^* = \alpha = 0$. This term can be eliminated by replacing π^* in eq 4b by $\pi^*(\text{solv}) - \pi^*(\text{MeOH})$,

(6) Kamlet, M. J.; Abboud, J.-L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877.

(7) Kamlet, M. J.; Abboud, J.-L. M.; Taft, R. W. *Prog. Phys. Org. Chem.* **1981**, *13*, 485.

(8) Abraham, M. H. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1343.

(9) Kamlet, M. J.; Doherty, R. M.; Taft, R. W.; Abraham, M. H. *J. Am. Chem. Soc.* **1983**, *105*, 6741.

Table II. Free Energy of Transfer Data and Correlation Equations for Tetraalkylammonium Halide Ion Pairs and Free Ions^a

solvent	ΔG_t° (ion pairs), kcal/mol							ΔG_t° (dissociated ions), kcal/mol					
	Me ₄ NI	Me ₄ NBr	Me ₄ NCl	Et ₄ NI	Et ₄ NBr	Et ₄ NCl	Pr ₄ NI	Me ₄ N ⁺	Me ₄ N ⁺	Me ₄ N ⁺	Et ₄ N ⁺	Et ₄ N ⁺	Et ₄ N ⁺
								+ I ⁻	+ Br ⁻	+ Cl ⁻	+ I ⁻	+ Br ⁻	+ Cl ⁻
hexane	13.3	18.3	21.3	13.3	18.3	21.3							
cyclohexane	12.4	17.4	20.4	12.5	17.4	20.4							
diethyl ether	8.0	12.5	15.1	8.3	12.7	15.1	7.3	19.7	24.7	27.7	19.0	24.0	27.0
ethyl acetate	4.1	6.7	9.0	4.8			4.4	12.0			11.8		
2-butanone	2.1	4.7		2.7	5.5		1.6	4.1	7.7	11.0	4.2	7.8	11.2
acetone	1.6	4.3	6.6	1.9	4.3	6.6	1.2	2.9	6.0	8.9	2.8	5.9	8.8
dimethylformamide	-0.5	1.9	3.5	0.5	3.1	4.6	0.6	-1.0	2.1	4.3	-0.1	3.0	5.2
N-methylpyrrolidone	-0.1	2.8	4.7	0.5	3.3	5.4							
dimethyl sulfoxide	-0.8	1.4	3.0	0.2				-2.4	0.4	2.6	-0.5	2.3	4.5
nitromethane	-0.2	1.6	3.1	1.0	3.3	5.0	1.5	-0.6	2.0	4.1	-0.4	2.2	4.3
acetonitrile	0.4	2.2	4.5	1.2	2.9	5.1	1.0	0.3	2.8	5.6	0.3	2.8	5.6
tert-butyl alcohol	3.1	3.7	3.9	3.3	3.6	3.9							
isopropyl alcohol	1.6	2.1	2.3	2.0	2.3	2.6		4.0	4.6	5.2	4.2	4.8	5.4
n-butyl alcohol	1.5	2.0	2.2	1.6	1.8	2.1	0.6	3.9	4.5	5.1	3.7	4.3	4.9
n-propyl alcohol	1.1	1.6	1.9	1.4	1.6	1.9		3.1	3.6	4.1	3.0	3.5	4.0
ethanol	0.8	1.3	1.5	1.1	1.4	1.6	0.2	2.0	2.5	3.0	2.1	2.6	3.1
methanol	0	0	0	0	0	0	0	0	0	0	0	0	0
water	-1.3	-2.0	-3.0	0.1	-0.7	-1.8	2.2	-2.3	-3.0	-3.7	-0.9	-1.6	-2.3
Correlation Equations: $\Delta G_t^\circ = (\Delta G_t^\circ)_0 + s\pi^* + a\alpha + h\delta_H^2$													
$(\Delta G_t^\circ)_0$	10.9 ± 0.2	15.1 ± 0.3	18.3 ± 0.3	10.9 ± 0.2	15.4 ± 0.3	18.2 ± 0.3	9.5 ± 0.7	28.2 ± 1.3	32.8 ± 1.2	36.2 ± 1.2	26.6 ± 1.5	31.2 ± 1.5	34.7 ± 1.3
<i>s</i>	-15.6 ± 0.4	-18.8 ± 0.6	-20.0 ± 0.6	-14.9 ± 0.4	-18.0 ± 0.6	-18.9 ± 0.6	-14.8 ± 1.3	-42.0 ± 2.4	-44.5 ± 2.2	-45.5 ± 2.2	-39.3 ± 2.8	-41.9 ± 2.6	-42.8 ± 2.4
<i>a</i>	-6.2 ± 0.3	-10.4 ± 0.4	-13.3 ± 0.5	-6.8 ± 0.3	-11.4 ± 0.4	-14.2 ± 0.5	-8.0 ± 0.7	-16.4 ± 1.3	-20.7 ± 1.2	-23.9 ± 1.2	-16.3 ± 1.5	-20.6 ± 1.4	-23.7 ± 1.3
<i>h</i> × 100	2.2 ± 0.1	2.8 ± 0.1	2.9 ± 0.2	2.4 ± 0.1	3.1 ± 0.2	3.1 ± 0.2	3.3 ± 0.3	6.3 ± 0.6	6.7 ± 0.5	6.8 ± 0.5	6.3 ± 0.7	6.7 ± 0.6	6.8 ± 0.6
<i>n</i>	18	18	17	18	16	15	11	14	13	13	14	13	13
<i>r</i> ²	0.994	0.992	0.994	0.994	0.994	0.994	0.980	0.976	0.986	0.989	0.962	0.977	0.985
<i>sd</i> , kcal/mol	0.3	0.5	0.6	0.4	0.5	0.6	0.5	1.1	0.9	0.9	1.2	1.1	1.0

^aFree energy data from ref 8, on the mol fraction scale.

Table III. Effect on Correlation Parameters of Omission of Water and Methanol Data Points^a

a. Ion Pairs												
	Me ₄ NI		Me ₄ NBr		Me ₄ NCl		Et ₄ NI		Et ₄ NBr		Et ₄ NCl	
(ΔG_i°) _o	10.9 ± 0.2	11.2 ± 0.3	15.4 ± 0.3	15.8 ± 0.5	18.3 ± 0.3	18.8 ± 0.6	10.9 ± 0.2	11.0 ± 0.3	15.4 ± 0.3	15.5 ± 0.6	18.2 ± 0.3	18.1 ± 0.8
<i>s</i>	-15.6 ± 0.4	-15.1 ± 0.5	-18.8 ± 0.6	-18.2 ± 0.9	-20.0 ± 0.6	-19.2 ± 1.1	-14.9 ± 0.4	-14.7 ± 0.5	-18.0 ± 0.6	-17.7 ± 1.0	-18.9 ± 0.6	-19.1 ± 1.3
<i>a</i>	-6.2 ± 0.3	-5.8 ± 0.4	-10.4 ± 0.4	-10.0 ± 0.6	-13.3 ± 0.5	-12.8 ± 0.7	-6.8 ± 0.3	-6.4 ± 0.4	-11.4 ± 0.4	-11.1 ± 0.7	-14.2 ± 0.5	-14.2 ± 0.9
<i>h</i> × 100	2.2 ± 0.1	1.6 ± 0.5	2.8 ± 0.2	2.1 ± 0.8	2.9 ± 0.2	2.0 ± 1.0	2.4 ± 0.1	2.1 ± 0.5	3.1 ± 0.2	2.8 ± 1.0	3.1 ± 0.2	3.4 ± 1.3
<i>n</i>	18	16	18	16	17	15	18	16	16	14	15	13
<i>sd</i>	0.34	0.33	0.54	0.56	0.60	0.63	0.36	0.31	0.52	0.55	0.59	0.64
<i>r</i> ²	0.994	0.996	0.992	0.992	0.994	0.992	0.994	0.996	0.994	0.994	0.994	0.994
<i>r</i> ² (π^* vs. α)	0.017	0.009	0.017	0.009	0.021	0.007	0.017	0.009	0.049	0.000	0.062	0.000
<i>r</i> ² (δ_H^2 vs. α)	0.413	0.211	0.413	0.211	0.402	0.194	0.413	0.211	0.440	0.325	0.428	0.301
<i>r</i> ² (δ_H^2 vs. π^*)	0.343	0.508	0.343	0.508	0.361	0.569	0.343	0.508	0.366	0.477	0.392	0.558
b. Dissociated Ions												
	Me ₄ N ⁺ + I ⁻		Me ₄ N ⁺ + Br ⁻		Me ₄ N ⁺ + Cl ⁻		Et ₄ N ⁺ + I ⁻		Et ₄ N ⁺ + Br ⁻		Et ₄ N ⁺ + Cl ⁻	
(ΔG_i°) _o	28.2 ± 1.3	28.1 ± 1.4	32.8 ± 1.2	32.7 ± 1.3	36.2 ± 1.2	36.2 ± 1.2	26.6 ± 1.5	26.5 ± 1.6	31.2 ± 1.5	36.1 ± 1.5	34.7 ± 1.3	34.6 ± 1.3
<i>s</i>	-42.0 ± 2.4	-40.7 ± 4.6	-44.5 ± 2.2	-43.9 ± 3.9	-45.5 ± 2.2	-42.7 ± 3.6	-39.3 ± 2.8	-39.5 ± 5.3	-41.9 ± 2.6	-42.8 ± 4.7	-42.8 ± 2.4	-41.4 ± 4.1
<i>a</i>	-16.4 ± 1.3	-15.4 ± 2.4	-20.7 ± 1.2	-20.1 ± 2.0	-23.9 ± 1.2	-22.1 ± 1.9	-16.3 ± 1.5	-16.0 ± 2.8	-20.6 ± 1.4	-20.7 ± 2.5	-23.7 ± 1.3	-22.6 ± 2.2
<i>h</i> × 100	6.3 ± 0.6	5.4 ± 2.6	6.7 ± 0.5	6.4 ± 2.2	6.8 ± 0.5	5.0 ± 2.0	6.3 ± 0.7	6.4 ± 3.0	6.7 ± 0.6	7.4 ± 2.7	6.8 ± 0.6	5.9 ± 2.3
<i>n</i>	14	12	13	11	13	11	14	12	13	11	13	11
<i>sd</i>	1.1	1.1	0.9	0.9	0.9	0.9	1.2	1.3	1.1	1.1	1.0	1.0
<i>r</i> ²	0.976	0.976	0.986	0.986	0.989	0.990	0.962	0.963	0.977	0.977	0.985	0.985
<i>r</i> ² (π^* vs. α)	0.001	0.191	0.006	0.246	0.006	0.246	0.001	0.191	0.006	0.246	0.006	0.246
<i>r</i> ² (δ_H^2 vs. α)	0.413	0.188	0.391	0.139	0.391	0.139	0.413	0.188	0.391	0.139	0.391	0.139
<i>r</i> ² (δ_H^2 vs. π^*)	0.391	0.308	0.377	0.301	0.377	0.301	0.391	0.308	0.377	0.301	0.377	0.301

^aThe second column of correlation parameters obtained from eq 4b for each compound is for the total data set minus the water and methanol data points.

α by $\alpha(\text{solv}) - \alpha(\text{MeOH})$, and δ_H^2 by $\delta_H^2(\text{solv}) - \delta_H^2(\text{MeOH})$. We have confirmed that, when this is done, the resulting $(\Delta G_i^\circ)_0$ values are zero within two standard deviations for all of the correlations in Table II.

Discussion

It is seen in Table II that for dissociated ions (DI) the s , a , and h values are much greater than corresponding values for the ion pairs (IP). For s and h values, the average factor is 2.5 ± 0.2 times greater for DI than for IP; for a values the average factor is 2.0 ± 0.2 . Thus, the result of the stronger cation-anion attraction in IP's is to significantly reduce the magnitudes of the endoergic solvent cavity terms, as well as the exoergic anion-solvent attractive terms. Fuller interpretations of these results will be presented in the following discussions.

Considering first the results for the two exoergic anion-solvent interaction terms, the results of Table II show that for both DI's and IP's $s > a$. That is, for transfer from a hydrocarbon solvent like cyclohexane ($\pi^* = \alpha = 0.00$) to a relatively strongly solvating solvent like water, with $\pi^* \cong \alpha \cong 1.1$, the dominant solvation term is that of solvent dipolarity/polarizability. However, the s/a ratio is strongly variable, increasing from a value of 1.3 for Et_4NCl to 2.6 for $\text{Me}_4\text{N}^+ + \text{I}^-$. This is, indeed, the result expected for increased charge localization in the anion (i.e., $\text{I}^- < \text{Br}^- < \text{Cl}^-$) having a greater effect on the shorter range hydrogen bonding interactions ($X^-_{\text{HBA}}/\text{solvent}_{\text{HBD}}$) compared to the larger but long range Coulombic ion-dipole/polarizability interactions. Thus, for DI's (independent of the Me_4N^+ or Et_4N^+ cations), the anionic charge localization increases the magnitudes of $-a$ values in the ratio 1.00/1.26/1.45 ($\text{I}^-/\text{Br}^-/\text{Cl}^-$), whereas the magnitudes of $-s$ values increase by the factors 1.00/1.06/1.08.

The reduction in the magnitudes of both the corresponding $-s$ and $-a$ values (by factors of 1.7 to 2.7) for IP's compared to DI's is, of course, expected from Coulombic electrostatics because of weaker solvent dipolarity/polarizability interactions with dipolar (IP) relative to polar (DI) solutes. However, there is greater discrimination in IP's than for DI's as the anionic size is decreased. Thus, compared to the above ratios for DI's, the magnitudes of $-a$ values for IP's increase by the factors (also independent of counterion) 1.00/1.68/2.12 and for $-s$ values by 1.00/1.21/1.28 ($\text{I}^-/\text{Br}^-/\text{Cl}^-$). This greater discrimination evidently results from greater relative reduction in charge localization caused by the counterion interaction as the anion size increases. The increase in size of the tetraalkylammonium ion in IP's also increases charge localization, as shown by increasing $-a$ values for Me_4NI (6.2) $< \text{Et}_4\text{NI}$ (6.8) $< \text{Pr}_4\text{NI}$ (8.0), as well as for Me_4NBr (10.4) $< \text{Et}_4\text{NBr}$ (11.4), and Me_4Cl (13.3) $< \text{Et}_4\text{NCl}$ (14.2). By way of contrast, the a values for the DI's are, as expected, independent of the nature of the counterions.

It is of interest to compare the hydrogen-bonding and dipolarity/polarizability contributions calculated from the $-a$ and $-s$ values of Table II for transfer of $\text{Et}_4\text{N}^+ + \text{I}^-$ from cyclohexane to water and to dimethyl sulfoxide (for which $\alpha\alpha = 0$).

halide ion	$(\text{CH}_3)_2\text{SO}$		H_2O	
	$-s\pi^*a$	$-s\pi^*a$	$-a\alpha^a$	$-(s\pi^* + a\alpha)^a$
I^-	39	43	19	62
Br^-	42	46	24	70
Cl^-	43	47	28	75

^a In kcal/mol.

The total $\text{Et}_4\text{N}^+ + \text{Cl}^-$ stabilization by bulk water solvation, $-(s\pi^* + a\alpha)$, is 75 kcal/mol, whereas the corresponding quantity for $(\text{CH}_3)_2\text{SO}$ solvation, $-s\pi^*a$, is 43 kcal/mol. These results appear to be in conflict with the gas-phase binding energies, which are for Cl^- , for example, 18.6 kcal/mol for a single $(\text{CH}_3)_2\text{SO}$ molecule and 14.0 kcal/mol for a single water molecule.¹⁰ That is, the single molecule solvation energy is significantly larger for

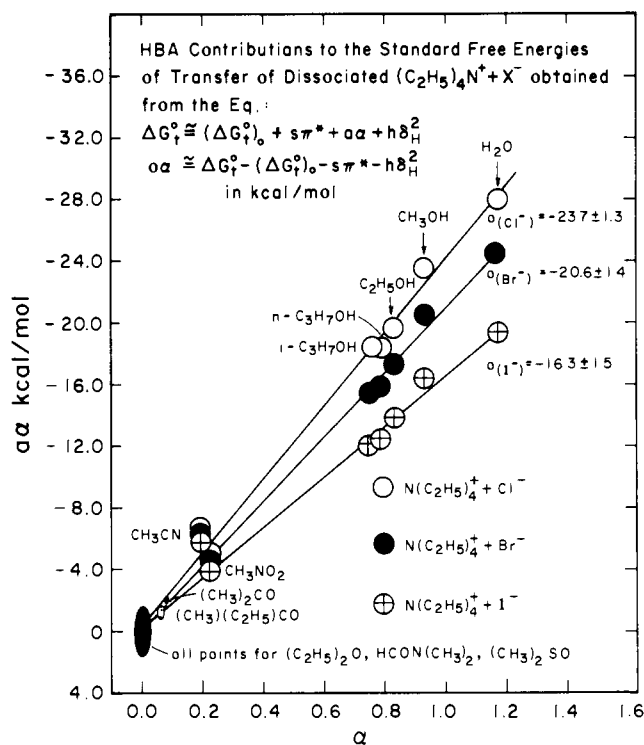


Figure 1. HBA contributions $\alpha\alpha$ to the standard free energies of transfer of dissociated $(\text{C}_2\text{H}_5)_4\text{N}^+ + \text{X}^-$ as obtained from eq 4b: $\alpha\alpha = \Delta G_i^\circ - (\Delta G_i^\circ)_0 - s\pi^* - h\delta_H^2$.

$(\text{CH}_3)_2\text{SO}$ than for H_2O , whereas in the bulk medium the reverse order of Cl^- stabilization is indicated.

However, this apparent discrepancy is readily explained in terms of effects due to solvent self-association.^{10,11} Both the π^* and α values of water are markedly enhanced by the self-association in bulk compared with monomeric water, whereas the π^* value of dimethyl sulfoxide is indicated to be little changed. (Thus, for example, the same π^* value which we use here to rationalize solvent properties of Me_2SO solvent has also been used to correlate and predict the solubility in water¹² and the octanol/water partition coefficient¹³ of Me_2SO solute.) It follows that, if the s/a ratio remains comparable for single molecule solvation and bulk solvation, the above reversal is as expected. When the same s and a values as above are used, but $\alpha_m = 0.30$ and $\pi_m^* = 0.39$ for monomeric water,¹¹ the $-(s\pi^* + a\alpha)$ term becomes $(17 + 7) = 24$ for single water solvation, which is significantly less than the $-s\pi^*$ term of 43 kcal/mol for solvation by a single $(\text{CH}_3)_2\text{SO}$ molecule.

In the gas phase, Kebarle has found that the energy of attachment of four water molecules to the halide ions appear to account for a high percentage of the heats of transfer of the bare ions to bulk water.¹⁰ We note that it is probably significant that the heats of attachment of single water molecules and of four water molecules to the halide ions are respectively for $\text{I}^-/\text{Br}^-/\text{Cl}^-$ 10.1/12.6/14.0 = 1.00/1.25/1.38 and 38.5/47.3/49.0 = 1.00/1.23/1.27, which correspond reasonably well to the ratios of $-(s\pi^* + a\alpha)$ shown above for $\text{Et}_4\text{N}^+ + \text{X}^-$ in bulk water, i.e., 62/70/75 = 1.00/1.13/1.21.

Furthermore, for attachment of a single dimethyl sulfoxide molecule in the gas phase,¹⁰ there is the same relatively smaller discrimination between the halide ions as is expected for a longer range dipolarity/polarizability interaction, i.e., $\text{I}^-/\text{Br}^-/\text{Cl}^- = 15.7/17.3/18.6 = 1.00/1.10/1.18$ (to be compared with the ratio of $-s\pi^*$ values for $\text{Et}_4\text{N}^+ + \text{X}^-$, 1.00/1.08/1.10). Finally, the

(11) Cf.: Taft, R. W.; Abboud, J.-L. M.; Kamlet, M. J.; Abraham, M. H. *J. Soln. Chem.*, in press.

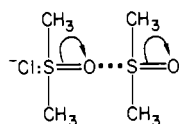
(12) Taft, R. W.; Abraham, M. H.; Doherty, R. M.; Kamlet, M. J. *Nature (London)* 1985, 313, 384.

(13) Taft, R. W.; Abraham, M. H.; Famini, G. R.; Doherty, R. M.; Kamlet, M. J. *J. Pharm. Sci.*, in press.

(10) Kebarle, P. *Annu. Rev. Phys. Chem.* 1977, 28, 445. Magnera, T. F.; Caldwell, G.; Sunner, J.; Ikuta, S.; Kebarle, P. *J. Am. Chem. Soc.* 1984, 106, 6140.

reduction of a and s values for IP's by factors of ca. 2 compared to DI's is reasonable on the basis of the heats of attachment of two or three solvent molecules being of primary importance in the solvation of IP's, compared with four solvent molecules for DI's. All of these considerations provide good evidence that eq 4b has made proper separations of the contributing exoergic terms. An indication of the precision of these separations is shown in Figure 1, which shows plots of the $a\alpha$ terms for $\text{Et}_4\text{N}^+ + \text{X}^-$ in each solvent, calculated from the correlation equations in Table II, vs. the solvent α values. Despite the fact that all the deviations from the equations have been placed in the calculated $a\alpha$ terms, the linear regressions are seen to be quite good.

The magnitudes of the above interaction energies strongly suggest that the formation of discrete ion-molecule complexes is involved, as well as weaker nonspecific many-molecule interactions, and that this applies for halide ion/dipole (DI's) and dipole/dipole complexes (IP's) as well as for hydrogen-bonded complexes. For the charge-localized halide ions and ion pairs, discrete ion/molecule complexes appear to be important, whereas for generally much less charge localized neutral HBA solutes, solvation of this kind is probably largely nonspecific. Nevertheless, for the dipolar non-HBD solvents included in this study, it appears that both specific and nonspecific ion/dipole and dipole/dipole interactions are adequately described by the $s\pi^*$ term. Furthermore, when multiple dipolar solvent molecules, like dimethyl sulfoxide, solvate strongly charge localized anions, it is probably unnecessary for each molecule in the cluster to be directly bonded to a different electron pair of the ion. This is because the following type of anion/dipole clusters may be sufficiently stabilized by a small extent of ion-pair transfer in solvent/solvent "head to tail" dipolar interactions:



The cavity term of eq 4b for the tetraalkylammonium halides appears to be more complex than the product of an inherent solute volume and the solvent δ_{H}^2 value. In addition to the intrinsic volumes of the bare ions, contributions to the effective volumes (\bar{V}) by solvent electrostriction¹⁴ and reorganization of hydrogen bonds¹⁵ (in self-associated solvents) have been considered to be

important. Further, for highly ordered solvents with relatively large δ_{H} values, particularly water, increasing the solvent cavity volume further increases the order of the system. That is, the cavity terms involve endoergic free energies which result from increasing loss in entropy with increasing \bar{V} . This contribution, we believe, is responsible for the larger δ_{H}^2 values being superior to δ_{C}^2 values in the correlations by eq 4b and may also play a significant role in the smaller h values for IP's than for corresponding DI's.

The h values in Table II for DI's are the same for all three halide ions within their combined uncertainties. For IP's, h values are the same for Cl^- and Br^- but are apparently slightly smaller for I^- . The nearly identical h values, rather than ones that increase in the intrinsic order $\text{Cl}^- < \text{Br}^- < \text{I}^-$, can be rationalized by solvent electrostriction contributions¹⁴ to \bar{V} , which increase in the reverse order, and probably also entropy loss contributions which increase as δ_{H}^2 increases and as the halide decreases in size.

Comparison with Findings of Glikberg and Marcus. Glikberg and Marcus¹⁶ have recently correlated $\Delta G_{\text{t}}^\circ$ values for ions, using a multiple parameter equation that includes the four solvent properties, E_{T} , DN , $1/\epsilon$, and δ_{H}^2 , as well as three ionic properties, molar refraction, radius, and an adjustable correction, Δ , to the ionic radius. There are two main reasons why no real comparison can be made between our procedure and theirs, however. Firstly, Glikberg and Marcus correlate $\Delta G_{\text{t}}^\circ$ values for single ions, so that their results depend on the assumption that $\Delta G_{\text{t}}^\circ(\text{Ph}_4\text{As}^+) = \Delta G_{\text{t}}^\circ(\text{Ph}_4\text{B}^-)$. Secondly, Glikberg and Marcus do not attribute any physical meaning to the parameters in their regression equation, whereas we have chosen the parameters π^* , α , and δ_{H}^2 specifically in order to deduce physical meaning from the coefficients of the independent variables. Thus, for the parameter δ_{H}^2 , the only one common to both methods, we find the coefficient always positive as required by a physical picture of an endoergic cavity term (corresponding to the free energy required to disrupt solvent/solvent interactions), whereas in the treatment of Glikberg and Marcus, the sign of the δ_{H}^2 term may be positive (Ph_4As^+) or negative (Me_4N^+).

Acknowledgment. The work by M.J.K. was done under N. S. W. C. Independent Research Task IR-210.

Registry No. Me_4NI , 75-58-1; Me_4NBr , 64-20-0; Me_4NCl , 75-57-0; Et_4NI , 68-05-3; Et_4NBr , 71-91-0; Et_4NCl , 56-34-8.

(14) Matteoli, E. *Z. Phys. Chem. (Wiesbaden)* **1980**, *123* (1), 141.

(15) Leyendekkers, J. V. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 357.

(16) Glikberg, S.; Marcus, Y. *J. Soln. Chem.* **1982**, *12*, 255.