$$\frac{F^s}{RT} = N^s B + N^s \ln C^s + \frac{1}{V^s}\beta_{11}N^{s\,2} \qquad (A2)$$

$$F^g/RT = N^g B + N^g \ln C^g \qquad (A3)$$

where s denotes the standard, i.e., the liquid state and g the gas state.

At equilibrium, we write

$$\partial F^g/\partial N^g = \partial F^s/\partial N^s \qquad (A4)$$

Using the following relations, $C^s = N^s/V^s = 1/V_1$; $\partial C^s/\partial N^s = 0$; $C^g = N^g/V^g$; at constant volume $\partial C^g/\partial N^g = 1/V^g$; $PV^g = N^g RT$; and combining eq A2, A3, and A4, we obtain

$$\ln P = \ln\frac{RT}{V_1} + \frac{\beta_{11}}{V_1} - 1 \qquad (A5)$$

but

$$\Delta H^v = -R\,\frac{\partial \ln P}{\partial(1/T)} \qquad (A6)$$

hence

$$\Delta H^v = RT - \frac{R}{V_1}\frac{\partial\beta_{11}}{\partial(1/T)} \qquad (A7)$$

Therefore

$$\beta_{11} = -\frac{\Delta H^v - RT}{RT}V_1 + D \qquad (A8)$$

where D is a constant independent of temperature.

Using the definition of δ given above

$$\beta_{11} = -\frac{\delta_1{}^2 V_1{}^2}{RT} + D \qquad (A9)$$

The significance of D would require arguments as those given by Guggenheim, as quoted by Hildebrand and Scott,[14] but the actual effect would be to shift all δ values upward.

This alternative derivation of δ from the total free energy can explain the fact that the chemical potential $\bar{\mu} - \bar{\mu}^{ideal}$ correlates better with $\bar{F}^E$ than with $\bar{H}^E$ in regular solution theory, a point which has been emphasized by Scott.[10]

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(16) Leffler and Grunwald[8] suggested to rewrite the expansion series of Scatchard and Prentiss in terms of molar concentrations rather than molar fractions.[7] They point out that in this way we get for dilute solutions the known relation $\bar{F}_i = \bar{F}_i{}^0 + RT \ln C_i$. Using this kind of expansion we have to analyze the coefficient β_{ij} which we do in Appendix A.

The Influence of Solute Size on the Thermodynamic Parameter of Transfer of a Nonpolar Hydrophobic Solute from Gas to Water or from Light to Heavy Water

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Using the modified versions of the scaled particle theory amended by Stillinger, we have considered the influence of nonpolar solute size on its thermodynamic parameters of transfer from gas to water or from light to heavy water. In the first case it is found that the process is dominated by an entropy contribution at small solute size and an enthalpy contribution at larger size. In the second process the increase in solute size also results in a change in the sign of the free energy and enthalpy of transfer, which is supported by our experimental data on bulky solutes, such as adamantanemethanol or sodium adamantanecarboxylate.

I. Introduction

In a previous paper,[1] we have considered the influence of solvent size on transfer of nonpolar hydrophobic solutes from one solvent to another or to the gaseous state. It has been observed that the difference in solvent size is important to determine the free energy of transfer of the solute.

That the solute size may well be important in the solution processes into water appears from experimental studies of various solutes. Whereas Philip and Jolicoeur[2] have shown

that the scaled particle theory (SPT), as suggested previously,[3] gives the possibility of predicting various thermodynamic properties of transfer of solutes with linear alkyl chains from H_2O to D_2O, Jolicoeur and Lacroix[4] have shown that replacing linear chains by branched one in ketones, thus increasing the bulkiness of the solute, changes the sign of ΔG of transfer from H_2O to D_2O; the ΔH also becomes much more positive. They have ascribed these changes to the possibility that a large solute may break H bonds in water instead of fitting into the water cages as this possibility is generally ascribed to linear alkyl chains.[4] Very recently it has been found by Wilson and Wen.[5] that the bulky bicyclic quaternary ammonium halides (azoniaspirohalides) had a distinctly more positive heat of transfer from H_2O to D_2O than the tetra-n-alkylammonium halides with comparable molar volume.

The SPT in its original version[6] does not incorporate explicitly[1] tetrahedral water coordination, but its Stillinger's amended version[7] does and therefore is more suitable to considering changes in solute thermodynamic properties when the hard sphere solute diameter is increased from zero to infinity.

In the first part of the Discussion we shall consider the thermodynamic properties of transfer of a nonpolar hard-sphere solute from the gaseous state to water and in the second part the transfer of the solute from H_2O to D_2O.

II. Discussion

(a) *Transfer of a Nonpolar Hard-Sphere Hydrophobic Solute from the Gaseous State to Water at Infinite Dilution.* A hard-sphere solute is characterized by its hard-sphere diameter a_2. The process of solution is defined by $\Delta G = RT \ln K$, where K, the Henry constant, is equal to p/x, p being the partial pressure of the solute in the gaseous state and x its mole fraction in solution. (In the following calculations p is in atmospheres.) The ΔG, ΔH, and $T\Delta S$ have been computed by the same procedure as in ref 1 from data in ref 7.

The ΔG, ΔH, and $T\Delta S$ have been computed at 4 °C. The influence of dispersion has been neglected, as it is more difficult to assess in Stillinger's than in Pierotti's analyses.

In Figure 1 we have plotted the reduced quantities $\Delta G/a_2^2$, $T\Delta S/a_2^2$, and $\Delta H/a_2^2$ computed from modified SPT (labeled STL from Stillinger) and original SPT against the solute hard-sphere diameter a_2 in angstroms as the abscissa.

These plots show some interesting features: if it is assumed that Stillinger's analysis improves upon Pierotti's, then the original SPT is excellent for $a_2 < 1.4$ Å and acceptable as an approximation for $a_2 < 4$ Å, in the sense that the G_{SPT} differs only from G_{STL} by less than 10%, and $T\Delta S$ by 25%. At higher values for a_2, the SPT gives different, and presumably much less accurate, results. (A possible exception is for the ΔG values which seem relatively insensitive to the fact that tetrahedral coordination of water has been or not built into the model. This supports the conclusions of ref 1 on the relative insensitivity of ΔG to structural features, opposed to the large influence of solvent structure on ΔH and $T\Delta S$. This implies also that there is a large compensation between enthalpy and entropy.) At higher values for a_2, the process of solution as viewed from the Stillinger model is dominated by the enthalpy rather than the entropy contribution.

From purely extrathermodynamic, intuitive grounds, these findings suggest that the possibility exists that the influence of the solute on water structure may be the opposite when the solute is small where it may not disrupt the water structure, or when it is large where the high positive enthalpy and small
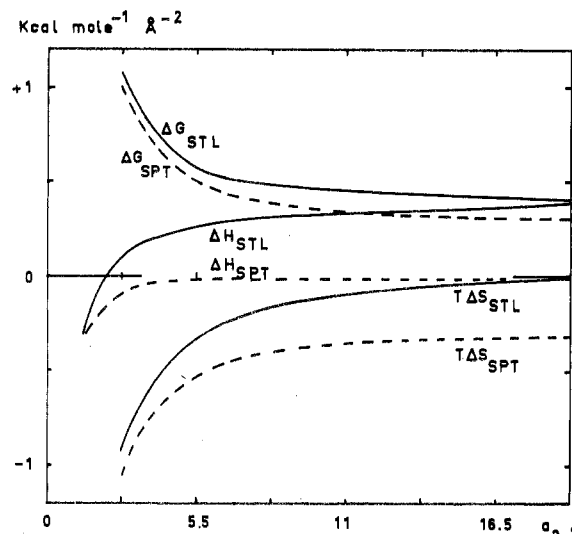

Figure 1. Plots of the reduced quantities $\Delta G/a_2^2$, $\Delta H/a_2^2$, and $T\Delta S/a_2^2$ against solute hard-sphere diameter a_2 as the abscissa: full lines, Stillinger's model; dotted line, original SPT. Temperature 4 °C.

negative entropy seem more consistent with a process of breaking H bonds.

The initial success of calculations using the SPT[2,6] can be explained because it dealt mainly with small solutes,[2] or large solutes[6] with linear alkyl chains which can fit in the water structure,[8] and therefore could perhaps be considered as cumulating the effect of methylene and methyl groups, the size of which does not exceed 3.2 Å, so that it is in the range where the SPT still does work.

(b) *Thermodynamic Properties of Transfer from H_2O or D_2O for Nonpolar Hard-Sphere Solutes.* They can be computed by applying the preceding procedure to D_2O and subtracting the related quantities obtained with H_2O as a solvent. However as the radial distribution function for D_2O is not known except at 4 °C,[9] we have to make some assumptions about the value of the function $G(\lambda)$ which is used[7] in the calculation of ΔG. First we assume that D_2O has more structure than H_2O so that it behaves as H_2O colder by a few degrees. That assumption, usual in that type of studies, is now questioned.[10] However, Narten states[9] that "the distribution of O- - -H(D)-O angles about a mean value is sharper in D_2O than in H_2O" at 4 °C. This may be interpreted as showing that D_2O is really more structured than H_2O,[5] so that D_2O has the same $G(\lambda)$ as H_2O at a lower temperature. We have now to decide to what extent D_2O is "colder" than H_2O. A first estimate can be made considering the fact that D_2O melts 4 °C higher than H_2O. Another different estimate can be made, since the isothermal expansion coefficient, which is probably an index of the structure in the liquid, is equal to zero, 7 °C higher for D_2O than for H_2O. Therefore we have carried out the calculation of the G of transfer in two cases, assuming first that D_2O at 25 °C has the same $G(\lambda)$ as H_2O at 19 °C, or the same as H_2O at 22 °C in the second case. Then from data in ref 7, it is possible to compute $G(\lambda)$ for D_2O in the two cases. In the calculations the same value a for the diameter of H_2O and D_2O has been taken.

Now if we want to compute ΔH and $T\Delta S$ as well, it is necessary to make some assumptions about the variation of $G(\lambda)$ with the temperature for D_2O. As D_2O's boiling point is 1.5 °C higher than that of H_2O, from melting and boiling point we may assume that the structure of D_2O changes in a temperature range of 97.5 °C to the same extent as that of H_2O in a
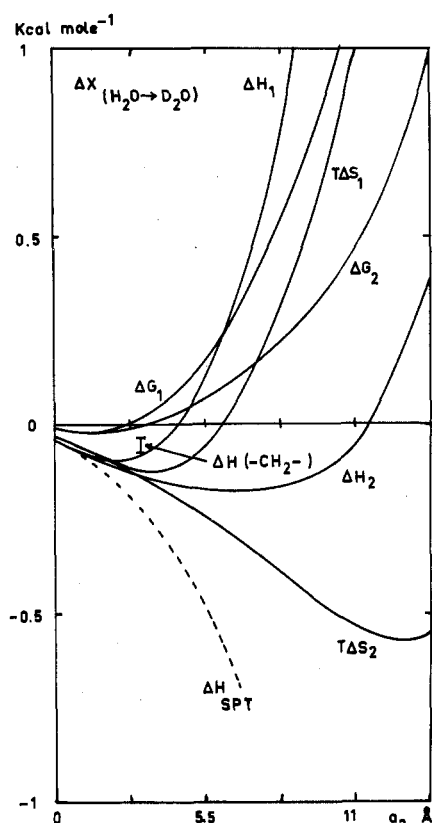
Figure 2. Plots of the ΔG, ΔH, and $T\Delta S$ of transfer of a nonpolar hard-sphere solute from H_2O to D_2O against solute hard sphere diameter a_2 as the abscissa: full lines, Stillinger's model with assumptions 1 (curves labeled 1) or assumptions 2 (curves labeled 2); dotted line, original SPT. Temperature 25 °C.

range of 100 °C, or from the temperature at which the two liquids have their expansion coefficient equal to zero and their boiling points, the structure of D_2O changes in a temperature range of 90 °C as that of H_2O in a range of 96 °C. In the first case $dG(\lambda)/dT$ is assumed to decrease 1.025 time faster for D_2O than for H_2O, and 1.06 time faster in the second case. In fact in the calculations we have used the slightly smaller values of 1.02 and 1.05. Then the calculations have been carried out with the following assumptions. In the first case $G(\lambda)$ for D_2O at 25 °C is the same as for H_2O at 19 °C and $dG(\lambda)/dT$ for D_2O is 1.05 time that for H_2O. In the second case $G(\lambda)$ for D_2O at 25 °C is the same as for H_2O at 22 °C and $dG(\lambda)/dT$ for D_2O is 1.02 time that for H_2O. In Figure 2 we have plotted the ΔG, ΔH, and $T\Delta S$ of transfer for a nonpolar solute from H_2O to D_2O, against solute hard-sphere diameter a_2 (in angstroms) as the abscissa. Curves 1 refer to parameters computed with the first assumption. Curves 2 refer to the second assumption. Dotted curves are calculated from the original SPT.

It is apparent that for solutes with a moderate size (<4.8 Å) the sign of ΔH and $T\Delta S$ is the same in the three cases considered (original SPT, first, and second assumptions). In contrast the ΔG_{tr}, always negative when computed from the original SPT, is positive for $a_2 > \sim 3.0$ Å. This is consistent with the trend observed by Jolicoeur[4] for branched aliphatic ketones. Data for hydrocarbons are very scarce and not consistent: ΔG_{tr} for butane is either slightly negative[11] (-17 cal mol^{-1}) or positive[12] ($+8$ cal mol^{-1}) at 25 °C; ΔG_{tr} for cyclohexane at 25 °C is slightly positive.[13] The more accurate ΔG_{tr} measured for a series of sodium n-alkyl carboxylate[14] shows an increase of ca. 2 cal mol^{-1} by addition of a methylene group

TABLE I: Molal Heat of Solution (kcal mol^{-1}) of Various Solutes from the Solid State to Dilute Solution in Water^{a,b,d}

	D$_2$O	H$_2$O	ΔH_{tr}(H$_2$O–D$_2$O)
Methanol			$(-0.18)^c$
tert-Butyl alcohol	-4.45	-4.00 ($-4.14)^e$	-0.45 ($-0.51)^c$
1-Adamantanol	$+0.45$	-0.70	$+1.15$
Sodium acetate	-3.49	-3.54	$+0.05$ ($+0.07)^c$
Sodium trimethylacetate	-6.68	-6.33	-0.35
Sodium adamantylcar-boxylate	-3.30	-4.40	$+1.10$

^{a} For the sodium salts, the transfer is measured from a 0.02 m NaOH solution in H$_2$O to a 0.02 m NaOH solution in D$_2$O in order to prevent hydrolysis. The added salt final molality is about 3×10^{-3} M. A correction for the Debye–Hückel limiting law should be applied to the heat solutions ($-0.9c^{1/2}$ in kcal mol^{-1}), but in the transfer this correction nearly cancels, due to similar dielectric constant of H$_2$O and D$_2$O. ^{b} Reproducibility better than ±0.05 kcal mol^{-1}. ^{c} Literature values (ref 15). ^{d} Improved adiabatic calorimeter as in J. Jordan, *J. Chem. Educ.*, **40**, A5 (1963). ^{e} D. J. T. Hill, Ph.D. Thesis, University of Queensland, Queensland, Australia, 1965. For the alcohols no correction has been done for the OH isotopic exchange.

neglecting the first terms in the series. On the other hand, there are many calorimetric data available for the ΔH of transfer of various classes of solutes with linear alkyl chains.[15] The ΔH_{tr} corresponding to the addition of a methylene group is between -30 and -60 cal mol^{-1} depending upon the class investigated: if the size of such a group is about 3.4 Å, this is smaller than the -80 cal mol^{-1} predicted in the present calculations (with ΔH_1), but this last value is nevertheless a marked improvement upon the -220 cal mol^{-1} predicted by the original SPT. When more bulky solutes as 6-azoniaspiroalkane bromide are considered,[5] the ΔH_{tr} is found to be 0.24 kcal mol^{-1} more positive than for the corresponding tetra-n-alkylammonium bromide with the same molar volume, in agreement with the trend exhibited by curve 1 for ΔH_{tr} in Figure 2.

In order to examine which approximate choice for the parameters is the best for the ΔH_{tr}, we have measured the heat of solution of some solutes of increasing bulkiness: sodium acetate, sodium trimethylacetate, sodium adamantanecarboxylate, *tert*-butyl alcohol, and 1-adamantanol in order to examine the influence of the solute bulkiness.

Due to the poor solubility of the corresponding hydrocarbons more soluble compounds as alcohols or acid sodium salts have to be used.

The enthalpy of solution and enthalpy of transfer, with some experimental details, are given in Table I.

It is apparent from the data in this table that there is an increase in the ΔH_{tr} when the *tert*-butyl group is replaced by the more compact adamantyl group. This increase is very important, about 1.60 kcal mol^{-1} in the alcohol series and $+1.45$ kcal mol^{-1} in the sodium carboxylate series. These values are very similar in view of the experimental error ($+0.05$) and the fact that eight different experimental heats of transfer are involved in this type of comparison.

The increase in the enthalpy of transfer for the methyl and adamantyl group is $+1.3$ in the alcohol series and $+1.05$ in the sodium acid salt series. When the size of the alkyl group is

increased from methyl (ca. 3.4 Å in diameter) to adamantyl (ca. 7 Å), the increase in the enthalpy of transfer is about +1 kcal mol^{-1}. This shows that the approximate choice for the parameters which gives the curve labeled ΔH_1 is much better than that which gives the curve labeled ΔH_2. More experimental data are needed to further determine the parameters that give the best fit. In any case the experimental findings appear to give some support to the theory used in this paper.

Finally one may comment on the physical interpretation of the calculated thermodynamic quantities of transfer. It has been observed previously[1] that when one solute is transferred from one solvent to another with a sufficiently different molecular diameter, the ΔG_{tr} is mainly a function of the different solvent size (for a given solute hard-sphere diameter), and is relatively independent on the structural features that can be built into the model. On the contrary when two solvents are considered, with the same hard-sphere diameter and very similar molar volumes, as D_2O and H_2O, the difference in the structure of the two solvents is likely to play an important role in determining the sign of the ΔG_{tr}. Here the interpretation for the $\Delta G_{tr} > 0$ for solutes with large size is possibly that proposed by Jolicoeur,[4] that is that the large solute which cannot fit into the solvent cages is more difficult to insert in the more structured D_2O than in H_2O.

The interpretation of the sign of the ΔH_{tr} is much more difficult since it is related to the relative decrease in structure with increasing temperature of H_2O and D_2O through their $G(\lambda)$. In the present calculation, the sign of ΔH_{tr} changes with solute size because we have assumed that $G(\lambda)$ decreases sufficiently faster for D_2O than for H_2O when the temperature is increased.

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Viscosities and Conductivities of the Liquid Salt Triethyl-*n*-hexylammonium Triethyl-*n*-hexylboride and Its Benzene Solutions[1]

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The viscosity of neat liquid triethyl-*n*-hexylammonium triethyl-*n*-hexylboride ($N_{2226}B_{2226}$) decreases nonexponentially with $1/T$ by a factor of 15 in the range 20–80 °C while its equivalent conductance increases similarly by a factor of 13. Dilution of liquid $N_{2226}B_{2226}$ with an equal volume of benzene increases the specific conductance at 25 °C by a factor of 10.5.

Introduction

Triethyl-*n*-hexylammonium   triethyl-*n*-hexylboride ($N_{2226}B_{2226}$) is a liquid salt at room temperature.[2] It resembles a charged alkane: the cation and anion are nearly equal in size, and both are isoelectronic with 3,3-diethylnonane. $N_{2226}B_{2226}$ is miscible in all proportions with most organic solvents, but immiscible with hexane, which it resembles structurally, and immiscible with water, nature's ubiquitous solvent for ions.

We now have studied transport properties of $N_{2226}B_{2226}$ with two aims. First, we wanted to determine whether $N_{2226}B_{2226}$ could be a suitable conductor for electrochemical applications. Second, we wanted to compare tempera-

ture effects on its transport properties, which depend on translational diffusion, to the temperature effects on its carbon-13 spin–lattice relaxation times, which depend on rotational diffusion.

The compatibility of $N_{2226}B_{2226}$ with a wide variety of organic materials makes it intriguing for possible electrochemical uses, either as a supporting electrolyte in high concentration in nonaqueous solvents or as both solvent and supporting electrolyte in neat liquid form. Preliminary conductivity and cyclic voltammetry experiments indicated that neat $N_{2226}B_{2226}$ may be suitable for cathodic electrochemistry.[3]

Earlier information on viscosities and conductivities of molten salts at low temperature is limited to tetra-*n*-butylammonium picrate at 91 °C[4] and tetra-*n*-amylammonium thiocyanate at 52–110 °C[5]. The specific resistance of tetra-

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