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Thermodynamics of Transfer of Nonelectrolytes from Light to Heavy Water. II. Evaluation of Solvation Energy of Transfer Applying the Internal Charge Distribution of Solute Molecule Estimated by CNDO Calculations

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A part of the transfer energy of solvation was estimated on the basis of the internal charge distribution of the solute molecule calculated by the CNDO molecular orbital method for some aromatic hydrocarbons, aromatic ethers, and nitrobenzenes. The magnitude of this energy was about 30 % of the transfer free energy from H_2O to D_2O for nitrobenzenes. Nonelectrolytes like nitrobenzenes are so called "structure breakers" which closely resemble electrolytes.

Many theories have been created to clarify the conceptions that deal with the structure of aqueous nonelectrolyte solutions, but the problem is not easily solved. The common laws and rules that hold in liquids are not valid in water and aqueous solutions. There is a unanimous agreement about the fact that a nonreacting solute increases the waterlike structure in its immediate neighborhood.[1] In this respect, the aliphatic hydrocarbons are ideal compounds.

The water layer just around the solute is of greatest importance and most of the attention must be paid to it. The usual concept of the constitution of the energy that is needed when a solute is transferred from the gas phase to solution can be applied to this case. First of all, there is an energy component which a solute needs to create a proper hole or cavity into the solvent. Secondly, the solute brings about a certain arrangement of solvent molecules around the solute. If this occurs in a waterlike manner in water, the solute is known as "structure maker". The effects of another kind are regarded as "structure breaking". Thirdly, there is an energy component which is associated with interactions between the solute molecule and water. There are three kinds of interactions, namely, isotropic, anisotropic, such as caused by hydrogen bonds, and those caused by dispersion forces.

The most proper quantities to illustrate the energy effects mentioned above would, no doubt, be the changes in enthalpy and entropy when the solute is transferred from the gas phase to solution. It is to be expected that the respective quantities of transfer for the solute from H_2O to D_2O would reflect this phenomenon still more profoundly. The values of enthalpy and entropy of transfer determined with the aid of the van't Hoff method have generally a very low accuracy for drawing further conclusions. It is, however, to be anticipated that some of the effects mentioned above will appear when they are studied by the aid of the values of transfer free energies.

CALCULATIONS

The isotropic component can be described in the following way. The change in the isotropic energy component when the solute is transferred from vacuum into water can be estimated by eqn. (1) of Born[2] and Hoijtink *et al.*[3] This equa-

$$\Delta E = -\sum \frac{Q_i Q_j}{2r_{ij}}\left(1 - \frac{1}{D_{H_2O}}\right) \tag{1}$$

tion has later been widely applied by Daudel.[4] In the equation Q_i and Q_j are the apparent charges of atoms i and j, r_{ij} is the distance between them except in the case when i and j are identical. In this latter case r_i represents the estimated covalent radius according to Pauling.[5] Furthermore, D_{H_2O} is an effective dielectric constant of water.

When a solute is transferred from light to heavy water, the corresponding form for eqn. (1) is expressed by equation (2). When the values of D_{H_2O} and D_{D_2O} are 78.39 and 78.06,

$$\Delta E_t = -\sum \frac{Q_i Q_j}{2r_{ij}} \left(\frac{1}{D_{H_2O}} - \frac{1}{D_{D_2O}} \right) \qquad (2)$$

respectively,[6] and joule/mol is chosen as the energy unit, eqn. (3) is obtained. This equation gives information of the isotropic interaction energy for the transfer of a solute from H_2O

$$\Delta E_t = 75 \sum \frac{Q_i Q_j}{2\,r_{ij}} \qquad (3)$$

to D_2O. However, this energy represents only a part of the whole transfer energy.

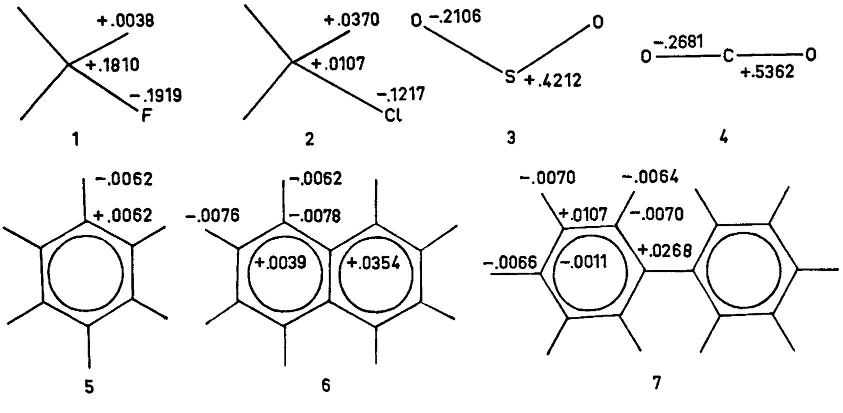
The changes in free energy of transfer from H_2O to D_2O for the solutes have been reported earlier.[7]

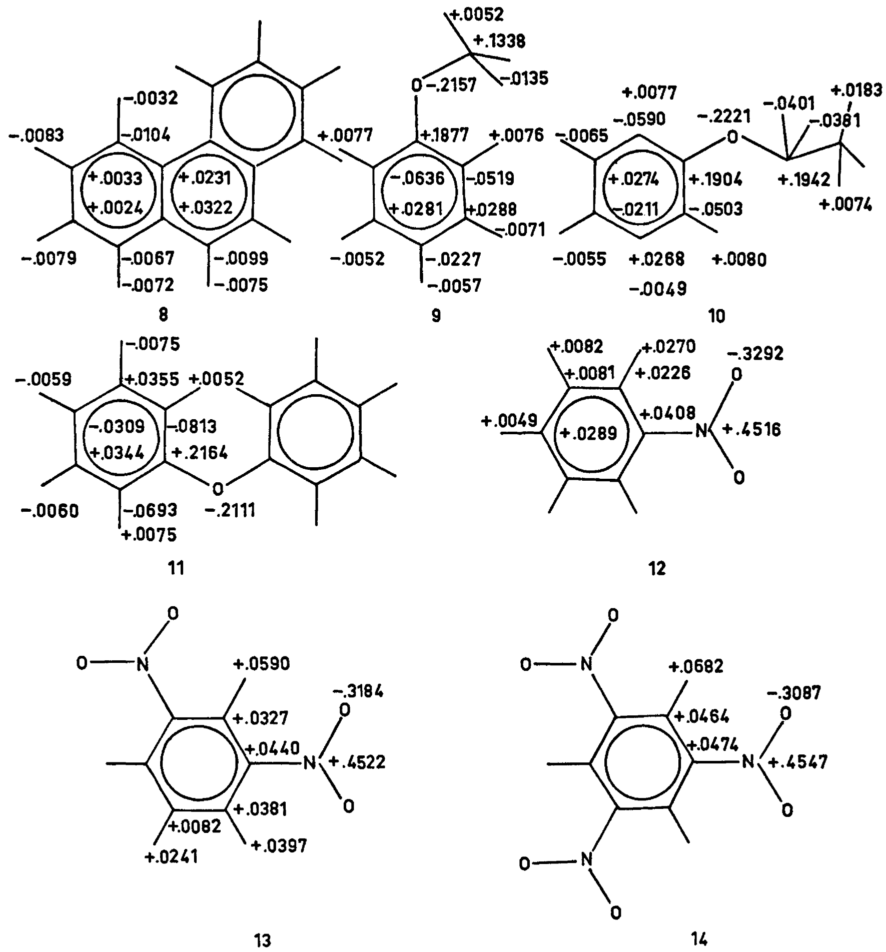
Atomic populations of the solutes were calculated applying the CNDO treatment formulated by Pople and Segal.[8a,b,c] The calculations were carried out on a Univac 1108 computer, with the aid of the program described by Pople and Beveridge.[9] The data needed for the computer consisted of the cartesian coordinates and atomic numbers of each atom in the solute molecule. This program yields atomic populations from which the apparent charges of atoms could be calculated. Only atoms with an atom number below 18 could be treated in this way.

Bond lengths and angles were taken from literature.[10a,b] All aromatic compounds were assumed to be planar, with the exception of diphenyl, in which the plane of the second ring was assumed to be twisted by an angle of 45° with respect to the first ring. This evidently had no effect on the calculated charges. The methyl group was supposed to have its normal tetrahedral structure. The ethyl group in ethoxybenzene was assumed to have a staggered conformation. The difference in ΔE_t values between staggered and eclipsed conformations is negligible in this case. The calculated apparent charges on various atoms of the solutes are presented in Scheme 1 (only the mean values of the charges have been reported for symmetrical molecules).

RESULTS AND DISCUSSION

This kind of investigation has, of course, a semiquantitative character. When the same molecular orbital method is applied to compounds having nearly similar structures, the possible correlations are reliable. Using the CNDO method it was possible to calculate the apparent charges for all the atoms in the solute molecule. Therefore, the summation could also be made over all the atoms in the solute compound. The dipole moments obtained in




-.0032
-.0083
-.0104
+.0077
+.0033
+.0024
+.0231
+.0322
-.0079
-.0067
-.0072
-.0099
-.0075
8
+.0052
+.1338
O
-.2157
-.0135
+.1877
+.0076
-.0636
+.0281
-.0519
+.0288
-.0071
-.0052
-.0227
-.0057
9
+.0077
-.0590
-.0065
-.2221
O
-.0401
+.0183
-.0381
+.0274
-.0211
+.1904
-.0503
+.1942
+.0074
-.0055
+.0268
+.0080
-.0049
10
-.0075
-.0059
+.0355
+.0052
-.0309
+.0344
-.0813
+.2164
O
-.0060
-.0693
-.2111
+.0075
11
+.0082
+.0081
+.0270
+.0226
-.3292
O
+.0049
+.0289
+.0408
N
+.4516
O
12
O
O
N
+.0590
-.3184
+.0327
O
+.0440
N
+.4522
+.0381
O
+.0082
+.0241
+.0397
13
O
O
N
+.0682
-.3087
+.0464
O
+.0474
N
+.4547
O
O
N
O
14

Scheme 1.

connection with the calculations of the internal charge distribution agree satisfactorily with those reported in literature.[11] For instance, for methoxybenzene the values were 1.47 D and 1.38 D, respectively (1 D = 3.33 10^{-30} A s m). Nitrobenzene had the largest deviation when compared with the literature value, namely, 5.08 D and 4.22 D, respectively. For the compounds which by symmetry should have the zero dipole moment this method gave values from 0.00009 D (naphthalene) to 0.0398 D (1,3,5-trinitrobenzene).

The plot of the transfer free energy, ΔG°_t, *versus* ΔE_t is presented in Fig. 1. In the first place, it can be noticed that normal aromatic hydrocarbons like benzene, naphthalene, di-

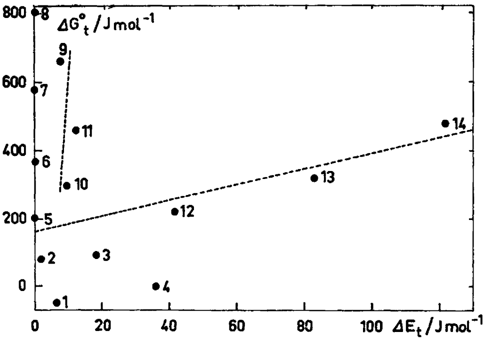


Fig. 1. Plot of the transfer free energy from H_2O to D_2O (ΔG°_t) *versus* the solvation energy (ΔE_t) for some nonelectrolyte solutes (For numbers, see Scheme 1).

phenyl, and phenanthrene show no sign of isotropic interactions. Aromatic ethers seem to have a nearly similar behavior. On the basis of the plot ΔE_t would contribute at the most only a few percentages of $\Delta G°_t$. On the other hand, when nitrobenzenes are examined, there is found an evident linear correlation, the contribution of ΔE_t to $\Delta G°_t$ being about 30 %. It seems quite obvious that there does not exist any overall correlation between $\Delta G°_t$ and ΔE_t. This can especially be seen by studying the points for methyl halides (*1,2*) sulfur dioxide (*3*), carbon dioxide (*4*), and aromatic ethers (*9,10,11*).

When the changes in free energy of transfer of nitrobenzenes from H_2O to D_2O are calculated by adding the $\Delta G°_t$ value of benzene and the corresponding ΔE_t values of nitrobenzenes, and the resulting values are compared with the experimental $\Delta G°_t$ values, then it is seen if the difference between benzene and its nitro derivatives could be wholly assigned to these interactions. The results of these calculations are shown in Table 1. As it is seen the agreement of the two values, namely, the calculated and the experimental ones for nitrobenzenes is rather rough but relevant. The great deviation in trinitrobenzene gives rise to the assumption that besides ΔE_t there are evidently other factors which contribute to the growth of the $\Delta G°_t$ value. Because the molecule of 1,3,5-trinitrobenzene is very symmetric, the main factor for the deviation may be the entropy effect. Of course, the assumption which is made here that the $\Delta S°_t$ values are similar for all nitrobenzenes is very rough.

It is to be expected that there will be an overall correlation between $\Delta G°_t$ and ΔE_t for solutes whose internal molecular polarizability is relatively high if the changes in transfer entropy are assumed to be equal. The behavior of this kind of solutes in water resembles closely that of electrolytes. It is fully believable that also in these compounds the structure breaking effects dominate when the compounds are dissolved in water.

Table 1. The $\Delta G°_t$ values for nitrobenzenes calculated by adding up the $\Delta G°_t$ values for benzene ($\Delta G°_{t,B}$) and the ΔE_t values.

Solute	Calculated ($\Delta G°_{t,B}+\Delta E_t$) /J mol^{-1}	Experimental $\Delta G°_t$/J mol^{-1}
Benzene	195	195
Nitrobenzene	237	218
1,3-Dinitrobenzene	278	314
1,3,5-Trinitrobenzene	317	481

Very accurate measurements of $\Delta H°_t$ would evidently cast more light on the dissolution phenomenon and on the role of ΔE_t in it. The experimental difficulties could be overcome by carrying out calorimetric measurements on compounds that have a relatively high solubility in water. On the other hand, very careful measurements applying the van't Hoff method might give more information on the problem on solutes employed in this work. This investigation is in progress in our laboratory.

REFERENCES

1. Frank, H. S. and Evans, M. W. *J. Chem. Phys. 13* (1945) 507.
2. Born, M. *Z. Phys. 1* (1920) 45.
3. Hoijtink, G. J., DeBoer, E., Van der Meij, P. M. and Weijland, W. P. *Rec. Trav. Chim. Pays-Bas 75* (1956) 487.
4. Daudel, R. In Löwdin, P.-O. *Advan. Quantum Chem. 3* (1967) 186.
5. Pauling, L. *The Nature of the Chemical Bond*, 3rd Ed., Cornell University Press, New York 1960, pp. 257 – 264.
6. Vidulich, G. A., Evans, D. F. and Kay, R. L. *J. Phys. Chem. 71* (1967) 656.
7. Vesala, A. *Acta Chem. Scand. A 28* (1974) 839.
8. a. Pople, J. A., Santry, D. P. and Segal, G. A. *J. Chem. Phys. 43* (1965) 5129; b. Pople, J. A. and Segal, G. A. *Ibid. 43* (1965) 5236; c. *Ibid. 44* (1966) 3289.
9. Pople, J. A. and Beveridge, D. L. *Approximate Molecular Orbital Theory*, McGraw, New York 1970.
10. a. *Tables of Interatomic Distances and Configuration in Molecules and Ions*, The Chemical Society, London 1958; b. Supplement, London 1965.
11. Weast, R. C., Ed., *Handbook of Chemistry and Physics*, 50th Ed., The Chemical Rubber Company, Ohio 1969, p. E-69.

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