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Solvent Isotope Effects in Chemical Potentials of Some Solutes in H_2O-D_2O Mixtures

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In theoretical treatments of acid — base reactions in $H_2O - D_2O$ mixtures,[1-3] it has been frequently assumed that the standard free energy of transfer of a solute from one water to another is linearly dependent on the change in the deuterium atom fraction of the solvent. An equivalent statement is that the "transfer activity coefficients",[2] which are incorporated in the relative equilibrium or rate coefficients in these solvents, can be represented by $(Y)^n$, where n is the deuterium atom fraction and Y is a constant charcteristic of the reaction in question.

We report here results of solubility measurements which were made to test the validity of the above hypothesis. When suitable model solutes were chosen, several points were kept in mind. The first requirement was that the solutes did not contain hydrogens exchangeable with those of the solvent, so that complications arising from isotope exchange reactions[4] could be avoided. Second, particularly in the case of electrolytes, the solubilities had to be sufficiently low to permit satisfactory estimation of the ionic activity coefficients (or, at least, the contribution of the ionic strength corrections had to be so small that any errors in them did not affect the conclusions). Third, the solutes had to have transfer free energies of widely varying magnitudes.

The results for four solutes are collected in Table 1. The measured solubilities are expressed in "aquamolal" units (mol of solute in 55.51 mol of water)[5] and are averages of at least six replicate determinations.

If the above postulate about the "transfer activity coefficients" is valid, the standard free energies of solution should be linear functions of the deuterium atom fraction n. For a sparingly soluble non-electrolyte, such as 1,3,5-trinitrobenzene, this free energy is

$$\Delta G_{soln}°(n) = -RT\ln(m)_n \qquad (1)$$

when the standard state of the solid form is the pure substance (mol fraction = 1) and the standard state of the dissolved form a hypothetical one aquamolal infinitely dilute solution. For a 1-1-electrolyte, the corresponding free energy change is

$$\Delta G_{soln}°(n) = -2RT\ln(m\gamma)_n \qquad (2)$$

where γ is the mean ionic activity coefficient at the saturation aquamolality m. For the present purpose, the activity coefficients could be satisfactorily estimated from the Debye-Hückel approximation

$$-\ln(\gamma)_n = A_n\sqrt{m}/(1 + a\beta_n\sqrt{m}) \qquad (3)$$

The parameters A_n and β_n were calculated from the densities of $H_2O - D_2O$ mixtures[6] and from the dielectric constants of light and heavy water.[7] For isotopically mixed waters, it was assumed that the dielectric constant is a linear function of n. The empirical values of Kielland[8] were used for the ion-size parameters a.

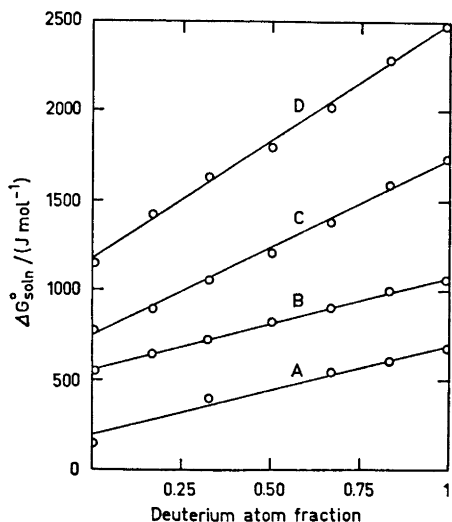The calculated values of $\Delta G_{soln}°$ are shown in Fig. 1. Although the estimated

Fig. 1. Standard free energies of solution of some substances in H_2O-D_2O mixtures at 25°C. (*A*) 1,3,5-Trinitrobenzene ($\Delta G_{soln}°$ $-14\ 700$). (*B*) Cesium perchlorate ($\Delta G_{soln}°$ $-13\ 000$). (*C*) Cesium picrate ($\Delta G_{soln}°$ $-22\ 500$). (*D*) Thallium(I) chloride ($\Delta G_{soln}°$ $-20\ 000$).

mean ionic activity coefficients may be slightly in error, this circumstance does not affect the linearity or non-linearity of the plots. In fact, quite similar plots were obtained even when the changes in the ionic activity coefficients were ignored. This was due to the circumstance that the calculated change in $-2RT \ln \gamma$ was but a small fraction of the overall change in $\Delta G_{soln}°$ (in the extreme case, with cesium perchlorate, the change in $-2RT \ln \gamma$ was about 10 % of the net change in $\Delta G_{soln}°$). Ion association, which may have a minor influence with the electrolytes studied,[9,10] would also leave the shapes of the plots of $\Delta G_{soln}°$ unaltered.

It can be seen from the figure that the plots of $\Delta G_{soln}°$ against the deuterium atom fraction n are linear within the error limits of the solubility measurements. This provides some support for the formulation of the "transfer activity coefficients" presented by Gold.[2] Considering that the dissolution of a solute in liquid water alters the proportions of the different water species and creates new types of water species,

he derived for the transfer activity coefficient the expression

$$(y)_n = \prod_{i=1}^{i}(1 - n + n\phi_i)^{-\Delta_i} \quad (4)$$

Here ϕ_i is the isotopic fractionation factor for water hydrogens at site i, and Δ_i is the number of hydrogens present at this site. Taking logarithms, one obtains for the standard free energy of transfer of a solute from H_2O to a water of deuterium atom fraction n:

$$\Delta G_{tr}°(n) = -RT \sum_{i=1}^{i} \Delta_i \ln(1 - n + n\phi_i) \quad (5)$$

As the hydrogens in the perturbed or newly created water species cannot ordinarily behave very differently in isotope exchange processes from those in the bulk water, their fractionation factors ϕ_i are expected to be close to unity. Exceptions may be encountered, particularly with solutes having very strong electric force fields or hydrogen bonding ability. If the values of ϕ_i really are close to unity, eqn. (5) takes the form

$$\Delta G_{tr}°(n) = nRT \sum_{i=1}^{i} \Delta_i(1 - \phi_i) \quad (6)$$

which predicts a linear dependence of the transfer free energy on the deuterium atom fraction.

Although the present results thus seem to support the validity of the simple transfer free energy relationship in H_2O-D_2O mixtures, it is evident that additional information, in particular on electrolytes of different valence types, is needed before further generalizations can be made.

The experimental details will be described in a forthcoming publication dealing with the solubilities of numerous 1-1-electrolytes in light and heavy water.

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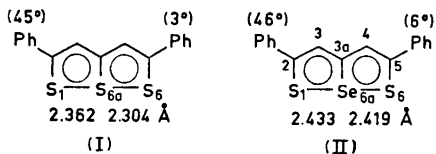10. D'Aprano, A. *J. Phys. Chem.* 75 (1971) 3290.

The Structure of 2,5-Diphenyl-6a-selenathiophthene

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The structure study of 2,5-diphenyl-6a-thiathiophthene (I) showed that although the molecule is symmetrically substituted, the S−S bonds there are

(I)

(II)

unequal,[1] *i.e.* S(1) − S(6a) = 2.362(3) Å and S(6a) − S(6) = 2.304(3) Å. The difference in S−S bond lengths in I may, according

to the results from *CNDO/2* calculations on phenyl substituted 6a-thiathiophthenes,[2] be due to the different twist of the phenyl-groups.

A structure investigation of crystals of 2,5-diphenyl-6a-selenathiophthene (II) isomorphous with those of I, have been carried out in order to find to which extent the phenyl substituents affect the sulphur-selenium bonding in II. Preliminary results are given here.

Due to the isomorphism the twist of the phenyl groups is almost the same in II as in I, and the sulphur-selenium distances in II are S(1) − Se(6a) = 2.433(3) Å and Se(6a) − S(6) = 2.419(3) Å. Thus, the sulphur-selenium bonding in II is less affected by the phenyl substituents than is the S − S bonding in I.

Other bond lengths in the 6a-selenathiophthene system of II are: S(1) − C(2) = 1.71(1) Å, Se(6a) − C(3a) = 1.87(1) Å, S(6) − C(5) = 1.72(1) Å, C(2) − C(3) = 1.38(2) Å, C(3) − C(3a) = 1.41(2) Å, C(3a) − C(4) = 1.36(2) Å, and C(4) − C(5) = 1.43(2) Å.

A sample of 2,5-diphenyl-6a-selenathiophthene was generously supplied by Reid.[3] The crystals are red and belong to the orthorhombic space group $P2_12_12_1$. The cell dimensions are $a = 12.040(4)$ Å, $b = 15.195(5)$ Å, and $c = 8.086(3)$ Å. There are four molecules per unit cell; $D_c = 1.613$ g cm^{-3}, $D_m = 1.61$ g cm^{-3}.

The structure analysis is based on X-ray data collected on a paper-tape controlled Siemens AED diffractometer using MoKα radiation. 1262 reflections were observed within $\theta = 27°$.

The structure was solved by the heavy atom method and refined by full matrix least squares. The present R factor is 0.05.

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