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A method to determine the Gibbs energy of specific interactions in solutions. Hydrogen bonding of proton donating solutes in basic solvents

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ABSTRACT

One of two fundamental types of solute–solvent intermolecular interactions are the specific interactions, such as hydrogen bonding complexation between solute and solvent. The Gibbs energy of specific interactions is an important quantity that determines rate and equilibrium constants in solutions, but it is difficult to obtain by direct measurement. We proposed equations allowing to determine the contribution of specific interactions to the Gibbs energy of solvation in nonelectrolyte solutions. Applying it for the case of proton donating solutes with one acidic hydrogen atom dissolved in basic solvents, we obtained the values of the Gibbs energies of 1:1 complexation in pure base. These values have been compared with the Gibbs energies of 1:1 complexation in tetrachloromethane. Most of the hydrogen bonds are found to have the same energy in pure base and in CCl_4, however, some weakly bound complexes seem to become even more weakened in pure base medium. Suggested method is applicable in a general situation when multiple associates of different stoichiometry and structure are formed.

1. Introduction

Solute–solvent specific interactions, which are defined as donor–acceptor interactions between Lewis acidic and basic centers of solute and solvent molecules, play an important role in various physico-chemical phenomena. They can be contrasted with the nonspecific interactions—London dispersion forces and polarity/polarizability interactions. Solute–solvent specific interactions strongly influence thermodynamic functions of solution and solvation as well as all other properties of dissolved species. The most common example of specific interactions are hydrogen bonds [1,2]. Hydrogen bonds in solutions are especially significant because of their decisive meaning for chemical processes in live organisms [3].

There were several works aimed to quantify the specific interaction enthalpy between solute and solvent in infinitely diluted solutions of nonelectrolytes from calorimetric data [4–9]. It was found that the specific interaction enthalpies of H-donors in basic solvents are close to the enthalpies of 1:1 hydrogen bonding complexation in tetrachloromethane even for most polar bases [4]. Recently, Solomonov et al. [10] suggested a novel general method to separate the specific interactions contribution from the enthalpy of solution/solvation. It allowed to calculate the enthalpy of specific interactions between solute and solvent for a wide range of systems, including a particularly interesting case of the enthalpy of self-association of aliphatic alcohols. However, there were no methods allowing to calculate the Gibbs energy of solute–solvent specific interactions. There are several models (UNIFAC [11], LSER [12,13], CODESSA [14], COSMO-RS [15], SPACE [16], SMx [17]) that can successfully predict the Gibbs energies of solvation and limiting activity coefficients for large sets of various solutes and solvents, including those with solute–solvent specific interactions. However, these models do not focus on separation of the hydrogen bonding interaction contribution. For example, though LSER and CODESSA models contain acidity/basicity parameters and parameters of other types of interactions (electrostatic, polarization, and dispersion) of a solute, there are also a number of adjustable parameters of solvent, which are optimized in order to fit solvation energy the best. As a result, hydrogen bonding energy can be partially redistributed between other terms in equations. The hydrogen bonding terms present in such models are not considered separately from other terms neither compared with experimental Gibbs energies of hydrogen bonding.

Experimental studies of complexation equilibria between noncharged molecules are usually carried in inert solvents by spectroscopic means. The techniques for determining association constants developed along with the development of spectroscopic methods [18,19]. IR-spectroscopy is the oldest and the most widely used experimental method. One should measure the intensities of bound and unbound bands at different concentrations of one or both of the complexing agents. In some cases, if measurements are carried for a series of structurally close compounds with the

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same acid or base, it is also possible to estimate the Gibbs energy from the linear correlation with the stretching vibration frequency shifts ($\Delta\nu$) of O–H or other bonds involved in complexation [19]. In NMR spectra, the chemical shifts of atoms involved in complex formation depend on the degree of complexation, so high-resolution NMR-spectroscopy is another tool that allows measuring the Gibbs energies of association. UV-spectroscopy is also applicable to determine the concentrations of bonded and unbonded forms. It should be noted that each method introduces its own systematic errors, so that the results obtained for the same system using different techniques may differ significantly (see experimental data [18] for numerous examples).

The Gibbs energy of complexation for the appropriate standard states is related to the complexation constant through equation $\Delta G = -RT \ln K$. Most of the experimental data are obtained in tetrachloromethane, and, for some systems, in liquid hydrocarbons, mainly hexane and cyclohexane. Relatively few data are available for other media. However, spectroscopic methods are inapplicable to determine the complexation constant of a solute with pure solvent, because we cannot change the degree of complexation of a solute in such case.

In the present work, we propose a method to determine the Gibbs energy of solute–solvent specific interactions using the experimental value of the Gibbs energy of solvation. Specific interactions between solutes and solvents with multiple donor and acceptor centers can lead not only to 1:1 complexes, but to a large number of complexes with different compositions and structures, and also to the shift of solvent associates equilibrium in the case of associated solvents. The set of systems considered in present work is limited to proton donors with 1 acidic hydrogen atom dissolved in basic solvents, so that only 1:1 hydrogen bonded complexes are likely to form. Our results are compared with the Gibbs energies of complexation in tetrachloromethane medium.

The method developed in this work is applicable, as already noted above, to any complexation equilibria in infinitely diluted solutions. The processes of HB-association engaging more than two molecules are known to have cooperative energetics [20], i.e. the energy of bonding differs from the sum of energies of single bonds. Widely recognized importance of this phenomenon for biochemical systems determines the necessity to have a method allowing to determine the energy of cooperative hydrogen bonding from experimental data. In a work [21], such method [10] was successfully applied for the enthalpies of cooperative hydrogen bonding. Now we are going to quantify the Gibbs energy of hydrogen bonding in solutions.

2. Theory

2.1. An equation for the nonspecific solvation Gibbs energy

Recently we suggested [22] an equation that allows calculating nonspecific solvation Gibbs energies. The process of solvation can be split into several steps: formation of a cavity in solvent, transfer of a solute from vapor into this cavity, turning on solute–solvent polarity/polarizability and dispersion interaction forces, and then turning on solute–solvent specific (donor–acceptor) interactions, including hydrogen bonds. This process without the last step is called nonspecific solvation. If there are specific interactions between solute (A) and solvent (S), the Gibbs energy of specific interactions $\Delta_{int(sp)}G^{A/S}$ is the difference between the total Gibbs energy of solvation $\Delta_{solv}G^{A/S}$ and the Gibbs energy of nonspecific solvation $\Delta_{solv(nonsp)}G^{A/S}$:

$$\Delta_{int(sp)}G^{A/S} = \Delta_{solv}G^{A/S} - \Delta_{solv(nonsp)}G^{A/S}. \qquad (1)$$

$\Delta_{solv(nonsp)}G^{A/S}$ can be viewed as the Gibbs energy of solvation of unbonded form of A, and $\Delta_{int(sp)}G^{A/S}$ is the bonding energy of unbonded solute molecules with solvent molecules. If we know how to calculate $\Delta_{solv(nonsp)}G^{A/S}$, it is possible to find $\Delta_{int(sp)}G^{A/S}$ from the experimental value of $\Delta_{solv}G^{A/S}$. We checked our equation given below (2) on those systems where no solute–solvent specific interactions occur ($\Delta_{int(sp)}G^{A/S} = 0$; $\Delta_{solv}G^{A/S} = \Delta_{solv(nonsp)}G^{A/S}$). About 800 literary values of the Gibbs energies of solvation for a large variety of solutes and solvents had been successfully predicted [23]. In a previous paper [22], mentioned equation was applied to aqueous solutions of apolar compounds to calculate the hydrophobic effect Gibbs energies. Now we will use it to quantify the most common type of specific interactions in solutions—hydrogen bonding interactions.

The nonspecific solvation Gibbs energy $\Delta_{solv(nonsp)}G^{A/S}$ was found [22] to be given by:

$$\begin{aligned}\Delta_{solv(nonsp)}G^{A/S} = {} & \Delta_{solv}G^{A/S_0} + (\delta_{cav}g^{S} - \delta_{cav}g^{S_0}) \cdot V_x^A \\ & + \left[a + b\sqrt{\delta_{cav}g^{S}}\right] \cdot \Big[(\Delta_{solv}G^{A/S_R} - \Delta_{solv}G^{A/S_0}) \\ & -(\delta_{cav}g^{S_R} - \delta_{cav}g^{S_0}) \cdot V_x^A\Big]\,;\end{aligned}$$

$$a = -\frac{\sqrt{\delta_{cav}g^{S_0}}}{\left(\sqrt{\delta_{cav}g^{S_R}} - \sqrt{\delta_{cav}g^{S_0}}\right)}; \quad b = \frac{1}{\left(\sqrt{\delta_{cav}g^{S_R}} - \sqrt{\delta_{cav}g^{S_0}}\right)}. \qquad (2)$$

Here $\Delta_{solv}G^{A/S_0}$, $\Delta_{solv}G^{A/S_R}$ are the Gibbs energies of solvation of solute A in the standard solvents S_0 and S_R, $\delta_{cav}g^{S}$, $\delta_{cav}g^{S_R}$, $\delta_{cav}g^{S_0}$ are the relative cavity formation Gibbs energies for each solvent, V_x^A is McGowan characteristic volume [24] of solute A. The standard states used in this equation and everywhere in present work are: 298.15 K temperature, 1 bar fugacity of gaseous A and the hypothetical ideal unit molar fraction solution.

In Eq. (2), four parameters of solute and solvent are used to describe cavity formation, dipolarity–polarizability interactions, and dispersion interactions energies. However, we do not calculate contributions of each type of interactions separately. Two solute parameters – Gibbs energies of solvation – are determined by direct experimental measurements, V_x^A can be calculated by a simple additive scheme, and parameter $\delta_{cav}g^{S}$ is given by the following equation:

$$\delta_{cav}g^{S} = \frac{(\Delta_{solv}G^{C_8H_{18}/S} - \Delta_{solv}G^{C_8H_{18}/C_{16}H_{34}})}{V_x^{C_8H_{18}}}, \qquad (3)$$

C_8H_{18} = n-octane, $C_{16}H_{34}$ = n-hexadecane. This parameter is supposed to reflect the nonspecific interactions of solvent molecules with both other solvent molecules and solute molecules.

The choice of standard solvents S_0 and S_R is rather free. The main restriction is that they should not interact specifically with solute A. In the above mentioned work [22], we always used hexadecane as S_0, and considered dimethyl sulfoxide, benzene, nitrobenzene and carbon tetrachloride as possible S_R's. It was found that dimethyl sulfoxide gives the best results for the whole set of considered systems, benzene and nitrobenzene give slightly worse results, and the usage of carbon tetrachloride as S_R leads to large errors in some cases. This possibility to vary the standard solvent can be very useful. If some solute A forms hydrogen bonds with some S_R or there is no data on the Gibbs energy of solvation $\Delta_{solv}G^{A/S_R}$, then we can choose another standard solvent for calculations.