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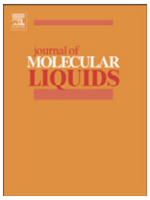

Hydrogen bonding in neat aliphatic alcohols: The Gibbs free energy of self-association and molar fraction of monomer

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ABSTRACT

The magnitudes of the Gibbs free energies of self-association for several primary aliphatic alcohols at 298 K are calculated. The fraction of monomeric molecules in bulk alcohols is determined. We started from the experimental data on the Gibbs free energies of vaporization of alcohols, and quantified the contributions from three types of solvation effects: non-specific van der Waals interactions, solvophobic effects, and hydrogen-bonding processes (self-association) using an extrathermodynamic approach. Calculated values for monomer fractions are compared and found to be in general agreement with the results obtained from various association models: CPA, NRHB, sPC-SAFT, and other data reported in literature. The influence of hydrogen bond cooperativity on the process of self-association is shown.

1. Introduction

The process of self-association of aliphatic alcohols has attracted attention of scientists for a long time [1]. Simple molecules forming intermolecular hydrogen bonds are considered as convenient models that should help us to understand noncovalent binding processes in complicated biological and supramolecular systems. The energetic and structural properties of associates, dynamics of association processes have been extensively studied in neat monohydric aliphatic alcohols and their mixtures with other organic substances using thermodynamic [2–5], spectroscopic [6–8], and theoretical [9–11] methods. A large number of semi-empirical models for the association process were suggested [3–5,12–15].

There is a huge number of possible structures of alcohol associates, but in the simplest models of association process the number of considered associates is limited (e.g. only monomeric molecules and cyclic tetrameric associates are considered [16]). Less strict limitation used in many advanced models is that there may exist associates of any size, but the thermodynamic functions of H-bond formation are the same for all H-bonds either there is only a small number of H-bond types which differ by their energies. It is well-known that real hydrogen-bonding processes are cooperative [17–19]. The enthalpy and Gibbs energy of dimerization of alcohols are significantly less negative than that of addition of the third and subsequent monomeric molecules to the associate, and the corresponding constants of association are larger in magnitude [20–23]. Thus, at least two different values of each thermodynamic function – one for dimerization and one for subsequent self-association – are required to describe the process of association in realistic models.

In a number of spectroscopic studies, a simplified classification of the types of alcohol molecules and their OH groups that does not take cooperative effects into account is used [7]. Free monomer molecules and their hydroxyls are called type α, type β is for terminal free OH groups, γ for OH groups with non-H-bonded lone pair electrons of oxygen, and δ for molecules bonded with other alcohol molecules from both sides. All the molecules or bonds of each type are assumed to have similar OH frequencies in vibrational spectra and similar values of partial molar thermodynamic functions (enthalpy, Gibbs energy, entropy). In literature, the fractions of α–γ types in neat alcohols are obtained as a result of analysis of experimental data on the basis of various model assumptions.

2. Methodology

2.1. Gibbs energy and monomer fraction

Nevertheless, it is possible to characterize the thermodynamics of association processes in neat alcohols without any arbitrary assumptions about the energies of association and the structure of associates. One may use average thermodynamic function of association $\Delta_{ass}f^{ROH}(f=G,H,S)$ which reflects the change in the Gibbs energy, enthalpy, or entropy when one mole of alcohol ROH is changing from its monomeric state in the neat phase into the equilibrium mixture of associates that forms the same neat phase. In other words, the initial state of considered process is the monomer diluted in the bulk alcohol with the certain standard concentration

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and the final state is just the bulk alcohol. If we assume that for monomer diluted in the neat phase the change of the chemical potential with concentration can be described by Flory–Huggins expression, then the Gibbs energy of self-association of alcohol $\Delta_{ass}G^{ROH}$ is related to the volume fraction of monomeric alcohol among all associates $\varphi_1 = V_m(ROH)[ROH]/\sum\limits_{n=1} V_m((ROH)_n)\left[(ROH)_n\right]$ through $\Delta_{ass}G^{ROH} = RT\ln\varphi_1$. Here and below all possible isomers of associates (e.g. linear and cyclic) with the same n are supposed to be included in the sums as separate terms, i.e. $\sum\limits_{n=1}$ means not only summation over n, but also over all possible isomers with the same n. The magnitude of φ_1 is almost equal to the fraction x_1 of free monomer among all molecules of alcohol engaging in different types of associates:

$$\begin{aligned}&V_m(ROH)[ROH]\Big/\sum_{n=1} V_m((ROH)_n)\left[(ROH)_n\right]\\&\qquad\approx V_m(ROH)[ROH]\Big/\sum_{n=1} nV_m(ROH)\left[(ROH)_n\right] =\\&= [ROH]\Big/\sum_{n=1} n\left[(ROH)_n\right] = x_1, \text{and therefore } \Delta_{ass}G^{ROH} = RT\ln x_1.\end{aligned} \tag{1}$$

In contrast, the enthalpy of self-association $\Delta_{ass}H^{ROH}$ relating to the same process is described by a more complicated formula: it is the weighted average enthalpy of association over all possible associates:

$$\Delta_{ass}H^{ROH} = \sum_n x_n \Delta_{ass}H_n \Big/ \sum_n nx_n \tag{2}$$

where $\Delta_{ass}H_n$ is the enthalpy of formation of the associate from n monomeric molecules, $x_n = \left[(ROH)_n\right]/\sum\limits_{n=1} n\left[(ROH)_n\right]$. The entropy of self-association is given by

$$\Delta_{ass}S^{ROH} = \left(\Delta_{ass}H^{ROH} - \Delta_{ass}G^{ROH}\right)\Big/T. \tag{3}$$

It is important that the fraction of free monomer molecules x_1 keeps the same physical meaning in most of the association models, even if the energy of associates is dependent on their size and structure. The values of x_1 and $\Delta_{ass}G^{ROH}$ obtained from different models and experiments can be used to compare and justify them. One possible method is the analysis of intensities of OH vibrations in IR-spectrum of the neat alcohol and its solutions in inert solvents. Such study has been done by Luck [24]. Another way to estimate x_1 and $\Delta_{ass}G^{ROH}$ is comparing the vapor pressures of alcohol and its non-associated homomorph [2,25]. The data on free monomer fraction have also been obtained from various association models [26].

2.2. Intermolecular interactions in associated solvents and their contributions to the Gibbs energy

In our present work, we use an extrathermodynamic approach to determine the values of x_1 and $\Delta_{ass}G^{ROH}$ for a number of neat saturated alcohols from C_1 to C_8 on the basis of their experimental Gibbs free energies of vaporization $\Delta_{vap}G^{ROH}$.

All considered systems are at $T = 298$ K, $p = 1$ bar. We use the molar fractions-based standard state for the solutions.

In our recent work [27], we have shown that the Gibbs energy of solvation in self-associated solvents, e.g. aliphatic alcohols, can be represented as a sum of three contributions: due to nonspecific (van der Waals) solvation effects $\Delta_{solv(nonsp)}G^{A/ROH}$, due to the solvophobic effect $\Delta_{s.e.}G^{A/ROH}$, and the contribution of hydrogen bonding processes (specific interactions) $\Delta_{int(sp)}G^{A/ROH}$:

$$\Delta_{solv}G^{A/ROH} = \Delta_{solv(nonsp)}G^{A/ROH} + \Delta_{s.e.}G^{A/ROH} + \Delta_{int(sp)}G^{A/ROH}. \tag{4}$$

The Gibbs energy of vaporization can be considered as the Gibbs energy of solvation of compound in itself with the opposite sign: $\Delta_{vap}G^{ROH} = -\Delta_{solv}G^{ROH/ROH}$. Thus, for solvation of alcohol ROH in itself:

$$\begin{aligned}\Delta_{ass}G^{ROH} &= \Delta_{int(sp)}G^{ROH/ROH}\\&= -\Delta_{vap}G^{ROH} - \Delta_{solv(nonsp)}G^{ROH/ROH} - \Delta_{s.e.}G^{ROH/ROH}.\end{aligned} \tag{5}$$

The contributions of nonspecific solvation to the Gibbs energy of solvation for various solutes A in various solvents S have been shown [28] to follow an empiric equation:

$$\begin{aligned}&\Delta_{solv(nonsp)}G^{A/S} = \Delta_{solv}G^{A/S_0} + \left(\delta g^S - \delta g^{S_0}\right)\cdot {V_x}^A +\\&+\left[a + b\sqrt{\delta g^S}\right]\cdot\left[\left(\Delta_{solv}G^{A/S_R} - \Delta_{solv}G^{A/S_0}\right) - \left(\delta g^{S_R} - \delta g^{S_0}\right)\cdot {V_x}^A\right];\\&a = -\sqrt{\delta g^{S_0}}\Big/\left(\sqrt{\delta g^{S_R}} - \sqrt{\delta g^{S_0}}\right);\\&b = 1\Big/\left(\sqrt{\delta g^{S_R}} - \sqrt{\delta g^{S_0}}\right).\end{aligned} \tag{6}$$

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, V_x^A is McGowan characteristic volume [29] of solute A calculated by an atom-additivity scheme, δg^S, δg^{S_R}, δg^{S_0} are the relative cavity formation Gibbs energies for each solvent. δg^S is given by the following equation:

$$\delta g^S = \left(\Delta_{solv}G^{C_8H_{18}/S} - \Delta_{solv}G^{C_8H_{18}/C_{16}H_{34}}\right)\Big/{V_x}^{C_8H_{18}}, \tag{7}$$

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

The standard solvents S_0 and S_R can be chosen arbitrarily, but they cannot form hydrogen bonds with solute A and should have different values of the δg^S parameter. If it is so, Eq. (6) allows to calculate the Gibbs energy of nonspecific solvation using one solute size parameter — V_x^A, and two experimental Gibbs solvation energies of A in the standard solvents that are required to know how the Gibbs energy of nonspecific interactions is changing with the growth of solvent propensity to intermolecular interactions described by δg^S parameter. We always used n-hexadecane as the standard solvent S_0 since it is inert, has $\delta g^S = 0$, and hundreds of values of the solvation Gibbs energies for various solutes in n-hexadecane are available. DMSO and benzene showed good performance as the standard solvents S_R.

δg^S is the only solvent parameter in Eq. (6). It is important to note that in the case of associated solvents such as aliphatic alcohols, it is necessary to take the solvophobic effects into account. For example, if we try to calculate the Gibbs energies of hydrogen bonding processes of various solutes with alcohols using Eq. (4) assuming $\Delta_{s.e.}G^{A/ROH} = 0$, we will obtain positive values for some solutes, which is an unphysical result that breaks the second law of thermodynamics. Moreover, in associated solvents the value of $\Delta_{solv}G^{C_8H_{18}/S}$ in Eq. (7) is influenced by the solvophobic effect. We have made a correction for the solvophobic effect of octane in order to calculate the values of δg^S for alcohols, what has been described in details in our previous paper [27].

2.3. Empiric parameters for description of solvation properties of aliphatic alcohols

In one of our previous works [30], we have discussed the difficulties of choice of the standard solvents in Eq. (6) for aliphatic alcohols. Good accuracy of Eq. (6) is achieved when two standard solvents have greatly different values of the δg^S parameter. However, the choice of standard solvents is reduced to alkanes and some of their halogenated derivatives, since alcohols form hydrogen bonds even with such solvent as benzene. Thus, we would obtain more accurate results if we will write Eq. (6) in an equivalent form with empiric