Thermodynamic functions of solvation of benzene in various binary aqueous-organic solvents

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ABSTRACT

Composition dependences of the thermodynamic functions of solvation in various aqueous-organic mixtures are studied. Limiting activity coefficients and solvation Gibbs free energies of benzene in the mixtures of water with acetone, 1,4-dioxane, dimethyl sulfoxide, and *tert*-butanol with different compositions at 298 K were determined. The results were combined with literature data for the enthalpies of solution in these mixtures and known values of thermodynamic functions of solvation of benzene in several other aqueous-organic solvents. We observed general tendencies of nonlinear enthalpy-entropy compensation, preferential solvation, and existence of a critical composition of the mixtures when the maximum of $\Delta_{solv}H$ and the bend in $\Delta_{solv}G$ vs $\Delta_{solv}H$ plot are observed. The nature of both organic cosolvent and solute influences the concentration of water corresponding to this critical composition. For benzene, it lies between 0.75 and 0.95 mole percent of water in all considered systems. In the same range of compositions, extrema of many other properties of aqueous-organic mixtures were observed. It is concluded that at these compositions, solvation in the mixture is characterized with the highest enthalpy cost of reorganization of binary solvent upon insertion of solute molecules and diminishment of the hydrophobic effect.

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1. Introduction

Many lower members of organic homologous series with polar functional groups are liquids miscible with water in any proportions. Binary aqueous-organic mixtures are used as reaction media [1], eluents in chromatography [2], solvents for pharmaceuticals [3]. In these applications, solvation properties of mixtures play a crucial role. A remarkable feature of binary solvents containing water is a non-linear change of the excess thermodynamic functions (primarily Gibbs free energies, enthalpies, and entropies) of solutes at infinite dilution with the change of solvent composition expressed in mole fractions as well as in volume fractions [4–8]. One of the reasons of such behavior is that low polar molecules or parts of molecules are preferentially solvated with organic cosolvent. Another important factor is significant energetic costs of reorganization of solvent structure and change of its local composition around a solute. These costs are responsible for prominent maxima in the dependencies of the excess enthalpies of dissolved hydrocarbons from the fraction of water observed in water-rich regions [9].

It is clear that the shape of the mentioned dependences is linked with the balance between the abilities of solute, water, and organic cosolvent to donate and accept hydrogen bonds. Analysis of the experimental data on thermodynamics of solvation of various compounds

in different binary mixtures is necessary to understand the role of hydrogen bonds in solubilization, solvophobicity, and cononsolvency phenomena. A particular attention should be paid to the solutes that form no or weak hydrogen bonds with water, primarily hydrocarbons. For these compounds, interactions between the molecules of cosolvents (water–water, water–organic component and organic component–organic component) become the most important factor. Unfortunately, the excess enthalpies and Gibbs free energies together are known only for a relatively small number of systems, which urges us for further experimental studies of solvation properties of hydrocarbons in aqueous-organic mixtures.

2. Methodology

There are indeed not so many works reporting the experimental quantities that enable us to calculate both the enthalpy and entropy of solvation of low polar molecules at 298 K over a broad range of aqueous-organic solvent compositions. The examples are the studies of argon [10] and methane [11] in *tert*-butanol + water mixtures, naphthalene in ethanol + water [12,13] and ethylene glycol + water mixtures [14], anthracene in ethanol + water and *tert*-butanol + water [15]. Moreover, the enthalpies of solution/solvation in all those studies were calculated from the temperature dependence of solubility, which gives much less precision than direct calorimetric studies. In our recent

works, we obtained the data for solvation of octane and toluene in tetrahydrofuran + water [16], acetone + water and acetonitrile + water [9], and benzene in N-methylformamide + water mixture [17] by means of calorimetry (enthalpies) and gas chromatography (Gibbs free energies). In addition, calorimetric studies of dissolution of benzene in aqueous-organic solvents were conducted by Korolev et al. in the mixtures of water with methanol [18], dimethyl sulfoxide, 1,4-dioxane, and acetone [6], by Desnoyers et al. in the mixtures of water with 2-propanol [19] and by Kustov et al. in the mixtures of water with *tert*-butanol [20]. In the present work, we combine their data with the Gibbs free energies of solvation calculated from the values of activity coefficients. These values were previously reported for benzene in the mixtures of water with methanol [21,22] and 2-propanol [21] and are measured in the present work in the mixtures of water with dimethyl sulfoxide, 1,4-dioxane, acetone, and *tert*-butanol.

In literature, thermodynamics of solvation can be characterized with a number of interrelated quantities. Besides standard thermodynamic functions of solvation from the gas phase $\Delta_{solv}f^\circ$ ($f = G,H,S$), thermodynamic functions of solution $\Delta_{soln}f^\circ$ from the standard (liquid or solid) state are commonly used, as well as thermodynamic functions of transfer from one solvent to another $\Delta_{transfer}f^\circ$. Limiting activity coefficients γ^∞ are often reported instead of the Gibbs free energies of solution/solvation. The following formulas were used to convert these quantities into the standard thermodynamic functions of solvation:

$$\Delta_{solv}f^\circ = \Delta_{soln}f^\circ - \Delta_{vap}f^\circ \qquad (1)$$

$$\Delta_{soln}G^\circ = RT \ln\gamma^\infty \qquad (2)$$

$$\Delta_{soln}G^\circ = \Delta_{soln}H^\circ - T\Delta_{soln}S^\circ \qquad (3)$$

$$\Delta_{solv}f^\circ(\text{in solvent } S_1) = \Delta_{solv}f^\circ(\text{in solvent } S_2) \\ + \Delta_{transfer}f^\circ(\text{from } S_2 \text{ into } S_1) \qquad (4)$$

Here, $\Delta_{vap}f$ is the standard thermodynamic function of vaporization. All the magnitudes in the present work are at 298.15 K. The standard state for solutions is mole fraction-based, the standard pressure is 1 bar. The values of $\Delta_{vap}G^\circ = 5.1$ kJ mol^{-1} [23] and $\Delta_{vap}H^\circ = 33.8$ kJ mol^{-1} [24] for benzene were used in calculations.

In methanol + water and 2-propanol + water mixtures, only one thermodynamic function is usually known at certain solvent composition. To calculate the entropy of solvation or plot $\Delta_{solv}G^\circ$ against $\Delta_{solv}H^\circ$, the Gibbs free energies were determined using polynomial interpolation at the compositions when the enthalpy of solution is known. In the rest of the solvents, we measured the activity coefficients at exactly the same compositions as the enthalpies of solution were previously obtained (see Supplementary material for all the values of thermodynamic functions taken or calculated from the literature data).

The composition dependences of thermodynamic functions of solvation and the plots of $\Delta_{solv}G^\circ$ or $\Delta_{solv}S^\circ$ against $\Delta_{solv}H^\circ$ are valuable to study preferential solvation and nonlinear enthalpy-entropy compensation phenomena [7,9,25]. A linear correlation between these quantities (described by equation $\Delta_{solv}G^\circ = 0.627\Delta_{solv}H^\circ + 16.3$ (5)) [26] exists for many different compounds dissolved in aprotic solvents, while solutions in water and other individual self-associated solvents show deviations from this correlation due to the hydrophobic and solvophobic effects [27]. It was shown [9,16] that a curvilinear shape of the ΔG vs ΔH plot for low polar solutes dissolved in aqueous-organic mixtures with different composition is a result of both preferential solvation and the enthalpic cost of the process of reorganization of the mixture, which is required to make a solute preferentially solvated. It is interesting that for the mixtures of acetone or tetrahydrofuran with water, the data points in the plot mentioned above lie rather close to the "apolar solvents line" even at high water contents [9,16]. This is linked with the ability of these organic solvents to suppress the hydrophobic effect very effectively even at low concentrations.

3. Experimental

Source and purity of the chemicals used in experiments are given in Table 1. Dimethyl sulfoxide and *tert*-butanol were dried with 4 Å molecular sieves. No additional purification of other compounds was done. The content of water in these chemicals was measured by Karl Fisher titration. The absence of significant amounts of organic impurities was confirmed by gas chromatography. Binary solvents were prepared by weighing precalculated amounts of each pure component and mixing them.

Measurements of limiting activity coefficients in aqueous-organic mixtures were conducted by GC headspace analysis technique as described in details in our previous works [9,28]. Results are presented in Table 2 together with the values of $\Delta_{soln}G^\circ$ and $\Delta_{solv}G^\circ$ calculated by Eqs. (1) and (2). For solvation in pure organic solvents, our results are in good agreement with the previously reported values.

4. Discussion

In Fig. 1a–c, the Gibbs free energies, enthalpies, and entropies of solvation of benzene in different mixtures are plotted against their composition. In Fig. 1 and all the subsequent figures, lines are connecting the nearest data points and cannot be used to estimate the experimental values in the regions where they have not been measured.

The Gibbs free energy of solvation steadily grows up with increasing water content in all the mixtures. In an ideal case when the distribution of two solvents around a solute is random and their molecular size is the same, the Gibbs free energy should be linear from x_2. The dependence is close to linear for the mixtures of water with methanol, which is "more similar" to water than other solvents due to its small molecular size and the presence of OH-group. The shape of the curves for all the mixtures is consistent with the concept of preferential solvation of benzene with an organic component.

The most prominent feature of the enthalpy vs fraction of water curves is a maximum in water-rich region, which was attributed [16] to reorganization of mixture around a solute molecule. Position of this maximum depends on the nature of cosolvent. The entropies of solvation show little variation over a wide range of water concentrations. At mole fractions of water >0.8, they start to decrease, reaching a minimum for solvation in pure water, at the same time the hydrophobic effect quickly strengthens over this range of compositions. This conclusion can be also supported by the disposition of the data points in $\Delta_{solv}G^\circ$ vs $\Delta_{solv}H^\circ$ plot that can be used to test for the presence of the hydrophobic and solvophobic effects [26] (Fig. 2).

The curves in this plot look similar to those previously obtained for solvation of octane and toluene in aqueous-organic mixtures [9]. The $\Delta_{solv}G^\circ$ vs $\Delta_{solv}H^\circ$ plot for toluene in the mixtures of water with acetone, tetrahydrofuran, and acetonitrile is shown in Fig. 3. With increasing water content, the curves follow a direction almost parallel to line (5), and make a turn towards the data point for pure water only when x_2 reaches 0.75–0.95. In a wide range of compositions, the enthalpy–entropy compensation properties for solutions in aqueous-organic mixtures

Table 1
Source and purity of the chemicals.

Chemical name	CAS number	MW	Source	Mass fraction purity	Measured mass fraction of water
Benzene	71-43-2	78.11	Sigma-Aldrich	0.99	0.00048
Acetone	67-64-1	58.08	Acros Organics	0.999	0.00051
Dimethyl sulfoxide	67-68-5	78.13	Component-Reaktiv	0.998	0.00007
1,4-dioxane	123-91-1	88.11	Component-Reaktiv	0.995	0.00009
tert-Butanol	75-65-0	74.12	Component-Reaktiv	0.998	0.00005
Water	7732-18-5	18.02	Deionized, millipore	–	–