



Solvation of hydrocarbons in aqueous-organic mixtures



I.A. Sedov^{*}, T.I. Magsumov, B.N. Solomonov

Chemical Institute, Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

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ABSTRACT

We study the solvation of two hydrocarbons, n-octane and toluene, in binary mixtures of water with organic cosolvents. Two polar aprotic cosolvents that are miscible with water in any proportions, acetonitrile and acetone, were considered. We determine the magnitudes of thermodynamic functions of dissolution and solvation at $T = 298.15$ K in the mixtures with various compositions. Solution calorimetry was used to measure the enthalpies of solution, and GC headspace analysis was applied to obtain limiting activity coefficients of solutes in the studied systems. For the first time, the enthalpies of solution of alkane in the mixtures with high water content were measured directly. We observed well-pronounced maxima of the dependencies of enthalpies of solvation from the composition of solvent and no maxima for the Gibbs free energies of solvation. Two factors are concluded to be important to explain the observed tendencies: high energy cost of reorganization of binary solvent upon insertion of solute molecules and preferential surrounding of hydrocarbons with the molecules of organic cosolvent. Enthalpy-entropy compensation leads to a steady growth of the Gibbs free energies with increasing water content. On the other hand, consideration of the plots of the Gibbs free energy against enthalpy of solvation clearly shows that the solvation properties are changed dramatically after addition of a rather small amount of organic cosolvents. It is shown that they suppress the hydrophobic effect very effectively even at low concentration, and acetonitrile suppresses the hydrophobic effect less than acetone.

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1. Introduction

The interest to binary and especially to mixed aqueous-organic solvents is due to a number of reasons. First, the physico-chemical properties of these solvents can be controlled by variation of their composition. In addition, binary solvents may have such properties that no one individual solvent has. For example, in an aqueous-organic media, both slightly polar organic molecules and inorganic salts can be soluble, which makes them suitable for homogeneous chemical syntheses. Unusual regioselectivity and reactivity were observed in such solvents [1]. Aqueous-organic mixtures are used for synthesis of peptides [2] and preparation of nanomaterials [3]. They are also widely used in industrial and laboratory separation processes. In particular, HPLC, one of the most general and widely applied methods of qualitative analysis and separation of substances, is impossible to imagine without using binary solvent systems. They are also interesting for pharmaceutical chemistry in order to solubilize drugs that are poorly soluble in water [4,5]. Many interesting phenomena have been found in the studies of proteins and enzymes in aqueous-organic solvents. Addition of

organic solvents to aqueous solutions of proteins usually leads to their destabilization, denaturation and decrease of enzymatic activity, but there are some evidences of enhancing the rate and selectivity of enzyme-catalyzed reactions [6,7].

The solvent effect on reactivity of dissolved molecules, their solubility and ADME (Absorption, Distribution, Metabolism, and Excretion in living organisms) properties is determined by the value of the chemical potential (partial molar Gibbs free energy) change upon dissolution of a substance. In turn, the Gibbs free energy consists of the enthalpy and entropy components. We can determine the thermodynamic functions of dissolution and solvation in binary solvents from the experimental studies or using predictive thermodynamic models, if the last ones are enough precise. This knowledge can help us to adjust the reactivity and solubility of substances in various applications and to optimize separation processes.

Despite their importance, thermodynamic properties of dilute solutions in mixed solvents are way much less studied experimentally than in individual solvents. There are relatively more data for solvation in (water + alcohol) mixtures [8] and less for other organic solvents that are infinitely miscible with water. This is in part because of a large number of compositions for each mixture that should be considered. Thermochemical studies of dissolution in binary solvents reveal interesting features [9].

^{*} Corresponding author. Tel.: +7 9600503916.

E-mail address: igor_sedov@inbox.ru (I.A. Sedov).

Many thermodynamic models that can be used to describe the properties of multi-component systems have been developed, but none of them is focused on description of aqueous-organic mixtures. Moreover, modeling of any system with cross-association between the components is a difficult task [10]. One of the features of binary solvents that attracts attention of researchers is the so-called preferential solvation [11]. This term stands for the fact that a composition of the solvation shell immediately surrounding a solute molecule is different from a composition of the bulk solvent. It is challenging to account the preferential solvation correctly in the models of solutions, except for the explicit solvent simulations. However, even such simulations are facing their own problems [12]. One needs to tune the force field parameters of organic molecule to reproduce the thermodynamic properties of aqueous-organic mixtures accurately. In literature, there are very few simulation studies of the structure of solvation shells and/or thermodynamic properties of solutions in binary solvents [13,14]. There is still a need in obtaining robust experimental data for a variety of systems as well as in accurate models. These data can help to improve the existing models for use in industrial applications.

2. Methodology

In the present work, we consider the solvation of an alkane and an aromatic hydrocarbon – n-octane and toluene. We determine the magnitudes of thermodynamic functions of dissolution and solvation in the aqueous-organic mixtures with various compositions. Alkanes are very simple compounds in the sense of intermolecular interactions. They participate only in dispersion interactions with other molecules. This makes them a cornerstone for development of solvation models. Arenes are slightly more polar and polarizable. Octane and toluene are convenient solutes from experimental point of view (not too volatile), and their solvation properties are known in a huge number of different solvents [15,16].

We chose two polar aprotic solvents that are miscible with water in any proportions: acetonitrile and acetone. Such organic solvents are often contrasted to water. The term “hydrophobic effect” is used to describe the difference in behavior of aqueous solutions from that of non-aqueous solutions, e.g. a poor solubility of apolar molecules in water. An interesting question is how the addition of an organic solvent affects the hydrophobic effect. It is known that the hydrophobic effect is a driving force for micelle aggregation and protein folding. It is also known that addition of an organic cosolvent leads to disruption of micelles and denaturation of proteins at certain point. This is another point for studying the thermodynamic functions of solvation of low polar substances in aqueous-organic mixtures with various compositions.

In our experiments, the aqueous-organic mixtures have different compositions, and the concentration of a solute is very low and it can be considered as being at infinite dilution. The temperature is $T = 298.15$ K and the standard pressure is $p = 1$ bar. The organic component of the binary solvent is denoted in indices as 1, and water as 2. For example, x_2 is the molar fraction of water in the solvent. The thermodynamic functions of solvation $\Delta_{solv}f$ ($f = G, H, S$) are related to the transfer of a solute from the gas phase into the solvent. The thermodynamic functions of solution $\Delta_{soln}f$ are related to the transfer of liquid octane or toluene into the solvent. We use the molar fractions-based standard state for the solutions.

We determine the enthalpies, Gibbs free energies and entropies of solvation in pure organic solvents and then in the aqueous-organic mixtures with molar fraction of water increasing by step 0.1 (10%), or 0.05 at high water content. For octane, we were able to go up to 80% of water, when the solubility becomes too low to obtain accurate data. For toluene, it was possible to study the mixtures with 90 and sometimes even 95 molar percent of water.

3. Experimental

3.1. Chemicals

The source and purity of the chemicals we used are given in table 1. No additional purification was conducted, the absence of significant amounts of impurities in these chemicals has been confirmed by gas chromatography. Deionized water (Millipore) was used to prepare the binary solvents.

3.2. Measurement of limiting activity coefficients

Limiting activity coefficients of n-octane and toluene in aqueous-organic solutions were determined by GC headspace analysis using PerkinElmer Clarus 580 chromatograph with a headspace autosampler. The samples of equilibrium vapor phase were taken from thermostated 22 ml vials containing 5 ml of a solution. The area S of the chromatographic peak of a solute is proportional to its vapor pressure p over a solution. The area S_0 of the chromatographic peak of n-octane or toluene over the sample of a pure compound at the same conditions is proportional to its saturated vapor pressure p_{sat} . Thus, the activity coefficient of a solute γ given by

$$\gamma = p / (p_{sat} \cdot x), \quad (1)$$

can be determined from the chromatographic data using a formula

$$\gamma = S / (S_0 \cdot x). \quad (2)$$

To determine the limiting activity coefficient γ_∞ , we carried out the measurements at 3 to 4 different concentrations of a solute in the range 0.1 to 1.5 volume % and repeated 2 times for each concentration. No significant difference between the values of the activity coefficients at different concentrations in this range was observed, which allows us to conclude that infinite dilution is achieved. In all experiments, we made a correction of initial molar fraction of solute x_0 for the quantity of evaporated solute:

$$x = x_0 - \frac{Sp_{sat}V_{free}}{S_0RTv}, \quad (3)$$

where $V_{free} = 17$ ml – headspace volume of a vial, v is the total number of moles of components of the binary solvent mixture in a vial. An average value of the Gibbs free energy of solution

$$\Delta_{soln}G = RT \ln \gamma_\infty, \quad (4)$$

from all measurements for the same system was taken. The Gibbs free energy of solvation can be calculated using a formula

$$\Delta_{solv}G = \Delta_{soln}G - \Delta_{vap}G, \quad (5)$$

where the Gibbs free energy of vaporization $\Delta_{vap}G$ equals $9.9 \text{ kJ} \cdot \text{mol}^{-1}$ for octane and $8.1 \text{ kJ} \cdot \text{mol}^{-1}$ for toluene (calculated from vapor pressures given in [17]). Results are presented in tables 2 and 3. For solvation in pure organic solvents, our results are in agreement with the values calculated from the vapor-liquid distribution coefficients measured by Park *et al.* [16] ($\Delta_{solv}G = 0.1, -4.1, -4.5, -6.5 \text{ kJ} \cdot \text{mol}^{-1}$ for n-octane dissolved in acetonitrile,

TABLE 1
Source and purity of the chemicals as stated by the supplier.

Chemical name	CAS number	MW	Source	Mass fraction purity
n-Octane	111-65-9	114.23	Acros Organics	0.99
Toluene	108-88-3	92.14	Acros Organics	0.998
Acetone	67-64-1	58.08	Acros Organics	0.999
Acetonitrile	75-05-8	41.05	JT Baker	0.998
Water	7732-18-5	18.02	Deionized, Millipore	

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