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Enthalpies and Gibbs free energies of solvation in ethylene glycol at 298 K: Influence of the solvophobic effect

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ABSTRACT

Enthalpies of solution of low-polar substances: aliphatic and aromatic hydrocarbons, including alkar cycloalkanes, alkylbenzenes, naphthalene, biphenyl, and halobenzenes in ethylene glycol were m sured at temperature T = 298.15 K using semi-adiabatic solution calorimetry. For some of these syste previously unknown values of limiting activity coefficients were also determined using GC headsp analysis. Consideration of compensation plots of the Gibbs free energy vs enthalpy of solvation sho that the behavior of solutions in ethylene glycol is different from that of solutions in non-associa aprotic solvents. The Gibbs energies of solvation are significantly increased relative to the enthalp which is the sign of the solvophobic effect. The contribution of the solvophobic effect into the Gi energies of solvation of various substances was quantified using an extrathermodynamic approach linear correlation between this quantity and a molecular volume of dissolved compound was found. T solvophobic effect in ethylene glycol is stronger than in monohydric alcohols, weaker than in formam and much weaker than in water. It is also entropy-driven and does not affect the enthalpies of solut of the studied substances in ethylene glycol.

1. Introduction

Ethylene glycol (EG) $HOCH_2CH_2OH$ is a polar protic organic solvent, which is widely used in industry. Most of it is used as a component of automotive antifreeze, engine coolants, and in synthesis of polymers (mainly polyethylene terephthalate). Besides a low price, a very important feature of EG is that it is miscible with water in any proportion and is very hygroscopic. Thus, EG also finds its application as a desiccant, particularly to prevent formation of gas hydrates in pipelines.

Strong affinity between EG and water is due to the similarity in structure of the liquid phase of these two solvents. Both molecules simultaneously have proton acceptor and donor sites. In the bulk phase, each molecule of EG in average engages in slightly lower than four hydrogen bonds [1], as well as each molecule in liquid water [2]. Molecular dynamics simulations show [3] that in liquid EG molecules form a water-like three-dimensional network of hydrogen bonds. Among other dihydric alcohols, which may exhibit similar behavior, EG is the simplest compound that has the highest concentration of hydrogen bonds in the bulk phase and should therefore be the most water-like.

A very important and interesting phenomenon observed aqueous solutions is the hydrophobic effect. It has diverse ma ifestations, most notably affecting thermodynamic properties solutions. In EG, similar (solvophobic [4]) effects take place. Apo substances have low solubilities and high values of the Gibbs ener of dissolution in both solvents, while highly polar organic solut which are capable to form hydrogen bonds, are well-soluble in bo water and EG. The hydrophobic effect is a driving force of mice formation processes in solutions of amphiphilic substances. In I formation of micelles from nonionic [4] and cationic [5] surfacta has been observed.

Some other properties of EG and solutions in it have been used show the presence of solvophobic effects [6], such as a low value isothermal compressibility, dependencies of excess heat capac and surface thermodynamic functions [7] of solutions from co centration.

However, thermodynamic properties of solutions in EG have n been studied extensively enough, despite their interesting chara teristics and industrial importance of mixtures containing ethyle glycol. The enthalpies of solution are unknown even for the si plest organic molecules. The aim of the present work is to exte our knowledge about thermodynamic properties (enthalpies a Gibbs free energies at 298.15 K) of solution of low polar compoun in EG and the solvophobic effect which takes place in them. The v ues of thermodynamic functions of solution are not only of inter in order to compare the behavior of EG and aqueous solutions, b

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