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Hydrogen-bonded aggregates in the mixtures of piperidine with water: Thermodynamic, SANS and theoretical studies

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ABSTRACT

Structures resembling semiclathrates probably arise in liquid aqueous solutions of piperidine at the amine mole fraction below 0.03. With the increasing concentration, the structures gradually decay, but the complexes of piperidine with water remain linked one to another through the O–H···O bonds between the hydration water molecules. A periodic order of the bicontinuous microemulsion type occurs in a range of the mole fractions from 0.08 to 0.5. In the piperidine-rich mixtures, the 1:1 complexes are dispersed uniformly in the amine. Relatively low stabilization energy of these complexes probably causes that piperidine is totally miscible with water.

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1. Introduction

Unambiguous determination of the liquid structure, similar to that achieved by the X-ray crystallographic methods for solids, is impossible at the present state of knowledge. However, intuitive molecular models of liquids often refer to ordered solid phases. Recently, piperidine and *N*-methylpiperidine were reported as promoters of the methane clathrate hydrate formation. Piperidine with methane forms sII clathrate hydrate in aqueous solutions at elevated pressures [1]. Slightly larger molecules of methylpiperidines cause the formation of sH clathrates in similar conditions [2]. Permanent interest in different clathrate hydrates is justified by their potential application as the gas-storage media [1,3–5]. Although piperidine does not form solid clathrate hydrate without a help gas [1], it seems probable that water polyhedra similar to those in the solid clathrate hydrates may occur in its liquid aqueous solutions. Obviously, the clathrate-like structures in liquids would be dynamic molecular aggregates rather than the stable ones in the solid state [6–8].

Our previous studies pointed to different modes of hydration and association in the liquid system *N*-methylpiperidine–water [9].

At low amine concentrations, semiclathrate-like structures probably arise around the *N*-methylpiperidine molecules. Along with increased amine concentration, the clathrate polyhedra gradually decay, while the amine molecules remain O–H···N bonded to water. The RN···H–OH hydrates aggregate due to the O–H···O bonds between the hydrate water molecules. Thus, the hydrophobic interactions prevail in the amine-rich mixtures. The aggregation of the RN···H–OH hydrates is probably the reason of the phase splitting of the system above the lower critical solution temperature 316.7 K at the amine mole fraction $x_1 = 0.06 \pm 0.01$ [9] (LCST 315 K at $x_1 = 0.07$ [10]). Contrary to *N*-methylpiperidine, piperidine is totally miscible with water at atmospheric pressure in the temperature range 273.15–368.15 K [11].

In the present letter, we report results of the small-angle neutron scattering (SANS) and thermodynamic studies of binary liquid system piperidine–water, supplemented by the H-bond energy and geometries of the molecular complexes calculated theoretically. We compared the present results with those obtained earlier for *N*-methylpiperidine + water [9]. Considering the molecular interactions, an important difference between *N*-methylpiperidine and piperidine is the ability of the latter to self-association due to the N–H···N bonds. The goal was to find how is that manifested in the studied thermodynamic and structural properties of the two aqueous systems. Although the density of aqueous solutions of piperidine and the speeds of sound have been reported

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