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Solvation of Alcohols in *n*-Heptane and *n*-Propanol from the Acoustic Passynski Method

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The method of Passynski of calculating the solvation numbers from compressibility was applied to solutions of short-chained normal alcohols in *n*-heptane and *n*-propanol. The dependences of solvation numbers on length of the solute molecules are surprisingly similar for both solvents. Applicability of the acoustic method for determining the solvation numbers in nonaquous systems, as well as for investigation of intermolecular interactions in them was proved. Some structural similarity of associated alcohol and hydrocarbon in liquid state is suggested.

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1. Introduction

Determination of solvation numbers in aqueous [1, 2] or non-aqueous solution [3] has been of interest in physics, chemistry and, particularly, in biological sciences. In the case of electrolytic solutes, the effect of solute on solvent structure is relatively simple for description: here the electrostatic interactions dominate. However, the effect of a non-electrolyte molecule on the solvent molecules (and vice versa) is less obvious. On the other hand, short-chained alcohols as solvents seem to be excellent model systems with relatively simple structure, at least when compared to water. On the other pole there are apolar liquids, like hydrocarbons, almost unstructured where specific solute–solute interactions are dominant.

The speed of ultrasound and density measurements are very well suited for the above tasks. Their product, i.e. the adiabatic compressibility coefficient, can be determined with a very high accuracy. From compressibility, the solvation numbers can be easily calculated applying the concept of Passynski.

In this work we will show that the acoustical Passynski method of calculating the solvation numbers can be applied successfully also for non-aqueous solutions of non-electrolytes. Moreover, the results obtained suggest some structural similarity of *n*-propanol and *n*-heptane in liquid state. The reasons of this are discussed.

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2. Experimental

Solutions were prepared by weighing before measurements using commercially available compounds. All the chemicals were of very high quality (methanol — J.T. Baker, Holland, >99.8%; ethanol — POCh Gliwice, Poland, 99.8%; *n*-propanol — Chempur, Poland, 99%; *n*-butanol — Acros Organics, Belgium, 99%; *n*-pentanol — Fluka AG, Buchs SG Switzerland, puriss.; *n*-hexanol — Aldrich, Germany, 98%; *n*-heptanol — Ferak Berlin, Germany, 98%; *n*-octanol — Riedel-de Haen, 99.5%; *n*-undecanol — Merck-Schuchardt, Germany, >98%; *n*-heptadecanol — Fluka AG, Buchs SG Switzerland, pure; and *n*-heptane — Acros Organics, Belgium, 99.86%) and used without additional purification.

The maximum solute concentrations were very low, not exceeding the mole fraction of 0.025 in *n*-heptane and 0.016 in *n*-propanol solutions.

Sound speed was determined using a computer-steered OPKUD 01/100 (Optel, Poland) device, with the absolute accuracy better than ±0.2 m/s and the precision of similar order. Measurements are based on the determination of the time an acoustic signal needs to pass through the sample of known length.

Density was measured using a vibrating tube Ecolab MG-2 (Kraków, Poland) apparatus with an accuracy *ca.* ± 0.1 kg m^{-3}.

Temperature of the measurements was 25°C±0.05, stabilized by a precision MLW UH (Germany) thermostat. Its stability was controlled by digital thermometer built in the density apparatus, and the absolute value by a precision mercury thermometer.

From the sound velocity and density data the adiabatic compressibility coefficients can be calculated, using the Laplace equation

$$\kappa_{\mathrm{S}} = d^{-1}c^{-2} \tag{1}$$

(where d — density, c — velocity of sound). The relative change of compressibility was assumed by Passynski as caused by engaging some fraction of water molecules in hydration spheres, where they become incompressible. This leads to the well-known formula for the hydration number, n_{h}, known as the Passynski equation [4]:

$$n_{\mathrm{h}} \cong \frac{n_1}{n_2}\left(1 - \frac{\kappa}{\kappa_1^0}\right), \tag{2}$$

where n_1 and n_2 are the number of moles of water and solute in solution, respectively, κ is compressibility of the solution and κ_1^0 is that of pure water.

3. Results and discussion

The Passynski formula (Eq. (1)) is based on the assumption that molecules of solvent undergo electrostrictive compression in electrostatic field of ions, leading to the effect which is identical to a very high static pressure. As a result, the solvated molecules become less compressible.

The general observation (at least valid for most organic non-electrolytes in aqueous solutions) is that the hydration number is roughly proportional to the molecular mass of the solute [5–8]. This allows to suppose that the solvation numbers could be additive with individual parts of the solute molecule [9].

The two systems investigated in this paper are very different. The compressibility dependences on composition for diluted alcohols in n-propanol are linear. However, they are not linear for solutions in n-heptane, as already reported by Kiyohara and Benson [10]. This behavior has not been deeply investigated nor satisfactorily explained yet.

Using the experimental values of κ_S, the average solvation numbers of alcohols were calculated from Eq. (2), valid in the region of very low solute contents, where specific or non-specific solute–solute interactions can be neglected [11]. The final results are collected in Table and illustrated in Fig. 1. Let us note that in the case of solutions in n-propanol water is included as a solute, too. The reason is that water can be treated as the first homologue in the series of alcohols.

TABLE

The solvation numbers calculated from acoustic data.

Solute	Solvent	
	n-heptane	n-propanol
water	–	0.51
methanol	–0.33	–0.14
ethanol	–0.26	–0.20
n-propanol	–0.16	0.00
n-butanol	–0.12	0.08
n-pentanol	0.01	0.19
n-hexanol	0.11	0.28
n-heptanol	0.23	0.35
n-octanol	0.29	0.42
n-undecanol	–	0.73
n-heptadecanol	–	1.35

The thermodynamics of liquid solutions of alcohol + alkane has been of vivid interest for many years, mainly due to their applications as fuels or as binary azeotropes in rectification processes. From the cognitive point of view they are particularly interesting because of very weak intermolecular interactions in pure hydrocarbons compared to stronger, specific ones in alcohols. Typically, the results are presented in the form of excess values (in the sense of deviations from additivity of different physical parameters).

Both the dependences of solvation numbers on the chain length of the solute shown in Fig. 1 are almost perfectly linear except the first two or three members of the family of alcohols (including water) in n-propanolic solutions. It should be

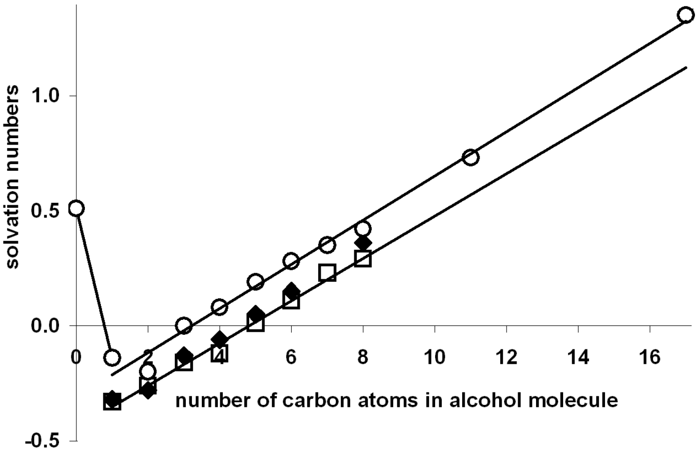

Fig. 1. Solvation numbers of normal alcohols in two solvents under investigation vs. the length of solute molecule; ○ — in n-propanol, □ — in n-heptane, ◆ — in n-heptane calculated from the data of Kiyohara and Benson [10] for comparison. The lines are only for guiding eyes.

mentioned that the negative values of the solvation numbers can be understood in terms of weakening of the local solvent structure in close neighborhood of the solute molecules, a similar phenomenon was already proposed by Chong and Hirata for aqueous solutions [12]. In general, negative solvation would mean the weakening of intermolecular interactions with addition of solute.

Water behaves a little different than other members of the family of alcohols: it affects the structure of n-propanol much stronger than expected from its location in the series. The reason is the unique character of this compound. Last but not least, molecules of water are able to form simultaneusly four hydrogen bonds, while these of alcohols one or two, depending on the steric hindrance of the hydrocarbon chain. Therefore, the solvation number of water in n-propanol ($n_\mathrm{S} = 0.51$) is even lower than expected.

For both solvents, the increment of solvation resulting from successive addition of $-\mathrm{CH_2}-$ group to the chain is the same, equal to 0.094 [molecule of solvent per $-\mathrm{CH_2}-$ group]. This is much less than that in water (*ca.* 0.999 [13]). Therefore, the fact that alcohols affect the local compressibility of such different liquids like n-propanol and n-heptane needs deeper explanation.

Aprotic solvents like heptane are characterized by very weak intermolecular interactions. In n-propanol strong hydrogen bonds are formed in the liquid state, leading to association. However, comparison with water can be risky. Association of water molecules led to formation of three-dimensional network of H-bonds, while in alcohols the associates are much smaller [14].

The dimer of n-propanol is (roughly) linear quasimolecule with hydrocarbon tails on its two sides, very similar in size and ability to bend to a n-heptane molecule. Concluding, we suppose that similarity in solvation in these two solvents under consideration arises from dimerization of *n*-propanol which leads to associates very similar to *n*-heptane structurally and in size. It seems meaningful that boiling temperatures of *n*-propanol and *n*-heptane are so close (97.4 and 98.4°C for *n*-propanol and *n*-heptane, respectively [15]).

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