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Physico-Chemical Properties and Components Interaction in the Solutions of *para*-Substituted Benzoic Acids in Aqueous Ethanol[1]

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Abstract—The intermolecular interaction and the structural fitting has been studied in the case of solutions of 4-aminobenzoic and 4-hydroxybenzoic acids in the ethanol–water mixture (70 : 30 by volume) by analysis of the density, viscosity, and refractice index data at 303.15 K. Viscometry data has been fitted to the Jones–Dole equation, and the respective parameters have been determined. It has been demonstrated that the introduction of benzoic acids leads to structuring of the aqueous ethanol mixed solvent. Concentration dependences of viscosity and density have revealed the strong interactions between molecules of the solvent and the solute, enhancing with increasing concentration of the acid.

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Intermolecular interactions in the solutions of 4-aminobenzoic (**I**) and 4-hydroxybenzoic (**II**) acids, suitable model organic compounds, are of great theoretical interest. The components of water–ethanol mixtures efficiently interact, forming the intermolecular hydrogen bonds. The introduction of benzoic acid, also capable of the hydrogen bonds formation, to these mixtures changes the solution structure substantially. Important conclusions on the solutions structure can be driven by analysis of such physico-chemical properties as density, viscosity, refractive index, sound velocity, apparent molar volume, partial molar volume, etc. The solute–solvent interactions have been studied in a number of works [1–6].

In continuation of the previously started studies of the intermolecular interactions in solutions [7–9], here we present the analysis of physico-chemical properties of the solutions of 4-aminobenzoic and 4-hydroxybenzoic acids in the ethanol–water mixture (70 vol % of ethanol) at 303.15 K.

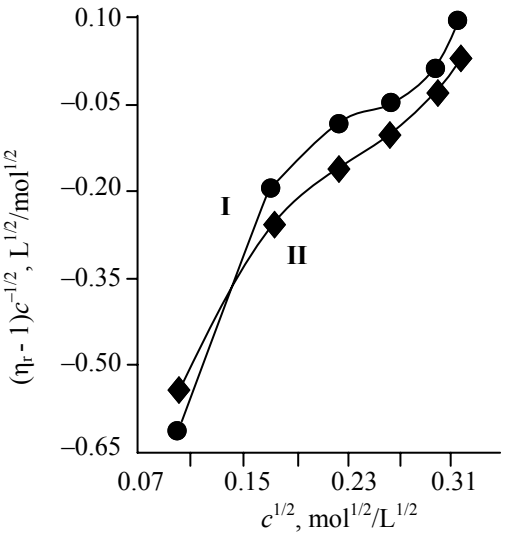
Table 1 shows the measured density, viscosity, and the refractive index of the solutions of **I** and **II**. Both the density and the refractive index increased with the benzoic acids concentration, thus evidencing about solution contraction due to enhanced intermolecular interactions.

The specific refraction R_D of the solutions was calculated using Eq. (1) [10].

$$R_D = \frac{(n_D^2 - 1)}{(n_D^2 + 2)} \cdot \frac{1}{\rho}. \quad (1)$$

The specific refraction values are given in Table 1 as well; R_D increased with the solute concentration.

The concentration dependence of viscosity is utilitarian in many practical applications. The relative



Concentration dependences of the studied solutions viscosity in the Jones–Dole equation coordinates.

[1] The text was submitted by the authors in English.

Table 1. Density (ρ), absolute viscosity (η), refractive index (n_D), and specific refraction (R_D) of the solutions of **I** and **II** in aqueous ethanol (70 vol % EtOH) at 303.15 K

c, mol/L	ρ, g/cm^3	n_D	η, mPa s	R_D, cm^3/g	ρ, g/cm^3	n_D	η, mPa s	R_D, cm^3/g
	I				**II**			
0.01	0.8842	1.3560	1.68	0.247	0.8842	1.3541	1.69	0.430
0.03	0.8860	1.3570	1.72	0.247	0.8869	1.3580	1.70	0.438
0.05	0.8869	1.3575	1.75	0.247	0.8878	1.3601	1.72	0.445
0.07	0.8887	1.3595	1.76	0.248	0.8896	1.3625	1.74	0.451
0.09	0.8896	1.3600	1.79	0.248	0.8923	1.3641	1.77	0.465
0.10	0.8923	1.3605	1.83	0.248	0.8941	1.3660	1.80	0.478

Table 2. Relative viscosity (η_r) and $(\eta_r - 1)c^{-1/2}$ of the solutions of **I** and **II** in aqueous ethanol (70 vol % EtOH) at 303.15 K

c, mol/L	$c^{1/2}$, mol$^{1/2}$/L$^{1/2}$	η_r	$(\eta_r - 1)c^{-1/2}$, L$^{1/2}$/mol$^{1/2}$	η_r	$(\eta_r - 1)c^{-1/2}$, L$^{1/2}$/mol$^{1/2}$
		I		**II**	
0.01	0.1000	0.94	–0.615	0.95	–0.542
0.03	0.1732	0.97	–0.195	0.96	–0.253
0.05	0.2236	0.98	–0.081	0.96	–0.159
0.07	0.2646	0.99	–0.047	0.97	–0.099
0.09	0.3000	1.00	0.011	0.99	–0.028
0.10	0.3162	1.03	0.091	1.01	0.027

viscosities of the solutions of **I** and **II** are shown in Table 2, as calculated using Eq. (2). Noteworthily, at fairly low concentration of the both studied acids, the solution viscosity was somewhat decreased. That could be due to structural rearrangements due to the organic molecules solvation.

$$\eta_r = \frac{\eta}{\eta_0} = \frac{\rho t}{\rho_0 t_0} . \quad (2)$$

In Eq. (2): η, solution viscosity, ρ, solution density, t, flow time of the solution; the respective parameters with 0 subscript refer to the pure solvent properties.

The relative viscosity was analyzed in the frame of the Jones–Dole equation (3) [11]. The parameters A and B of that equation were determined via graphical extrapolation of the $(\eta_r - 1)c^{-1/2}$ as function of $c^{-1/2}$ (see figure); their values are given in Table 3.

$$\frac{\eta_r - 1}{\sqrt{c}} = A + B\sqrt{c} . \quad (3)$$

It is generally assumed that the A coefficient characterizes the interactions between the solute molecules [12]; the B coefficient accounts for the solute–solvent interactions [13].

It should be noted that the data points corresponding to the most dilute solutions of benzoic acids were worst fitted to the theoretical linear dependence. That could be due to the highest error of the relative viscosity determination (subtraction of the very close values of the flow time for the solvent and the solution, divided then by a small value of concentration) as well as by the peculiarities of the acids solvation leading to the differences in the behavior of the most diluted and more concentrated solution (electrolyte effect). The experimental data fitting with excluded points corresponding to the most dilute solutions gave slightly different valued of A and B; however, that did not influence the general conclusions made below.

In the cases of the both benzoic acids solutions, A was negative, meaning that the solute molecules

Table 3. The Jones–Dole equation parameters of the solutions of **I** and **II** in aqueous ethanol (70 vol % EtOH) at 303.15 K

Coefficient	**I**	**II**
A (L$^{1/2}$ mol$^{-1/2}$)	–0.81	–0.74
B (L mol$^{-1/2}$)	2.91	2.45

interactions were very weak or even not reflected in the flow properties. The *B* parameter was shown to reflect the solvation of the solute molecules and its ability to disrupt or strengthen the solvent intermolecular interactions [14], or, in other words, indicated the solution structure change upon addition of the solute [15]. In the cases of both benzoic acids studied, *B* was positive and quite high, confirming the strong solvent–solute interactions [16, 17]. *B* was somewhat higher in the case of **I** solutions, seemingly due to stronger solvation of **I** as compared with **II**. From the large positive values of *B* we conclude that the studied 4-aminobenzoic and 4-hydroxybenzoic acids interact efficiently with the mixed solvent components, inducing the structuring effect.

EXPERIMENTAL

Aqueous ethanol (70 vol % EtOH), used as a mixed solvent throughout the work, was prepared in glass volumetric flask. The benzoic acids solutions were prepared by dissolving of the weighed acid sample in the aqueous ethanol. The solutions density was measured with a single-capillary glass pycnometer (10 mL) calibrated with distilled water at 303.15 K. Electronic balance Vibra $T_2$996 was used for weighing. The solutions viscosity was determined with the thermostatted suspended level viscometer.

Refractive index was determined using Abbes refractometer (Rico Sci. Ind., RSR-F1; measuring range of 1.3000–1.7000; ±0.001). At least three refract-tometer readings were averaged for each of the solutions. The refractometer was calibrated with distilled water at 298 K. In the course of measurement, the sample temperature was maintained constant. Temperature of solution was maintained constant by circulation of water from water bath through the refracttometer water jacket.

Density, viscosity, and refractive index were measured immediately after the solvents preparation.

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