

The Viscous Properties of Diols.

III. 1,2- and 1,4-Butanediol in Water and 1-Pentanol

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Z. Naturforsch. **58a**, 569 – 572 (2003); received July 23, 2003

Viscosity measurements were performed for solutions of $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2(\text{OH})$ and $\text{HO}(\text{CH}_2)_4\text{OH}$, in water and 1-pentanol, at 10–50 °C. The activation energy and viscosity excess were derived from the data. A peculiarity in the concentration dependence of the viscosity excess was observed for both diols dissolved in water.

Key words: Shear Viscosity; Butanediol; Water; Pentanol; Solutions; Viscosity Excess; Activation Energy.

1. Introduction

The structure and properties of hydroxylic compounds are of interest for scientists and technicians because molecular self-organization, due to directional intermolecular hydrogen bonds $\text{O}-\text{H} \cdots \text{O}$, is so efficient that their physical properties differ essentially from those of the non-associated liquids. Of course, the most self-associated compound is water. By introducing the hydrocarbon chain between two $\text{O}-\text{H}$ groups one obtains a new class of compounds – the diols, the physical properties of which depend mainly on the mutual position of the $\text{O}-\text{H}$ groups within the chain. The simplest diol, methanediol, is extremely unstable. Indeed, our studies of the viscosity of the homologous series of $1,n$ -diols did show an anomalously low viscosity expected for methanediol [1].

Some diols are widely employed because of their large temperature range of their existence in the liquid state. Due to the high degree of molecular self-association by hydrogen bonds, the diols are rather viscous liquids (especially at low temperatures) and they are often used in mixtures with water or alcohols.

This paper concerns the shear viscosity of one of the most frequently used diols – butanediol, pure and in mixtures with water and 1-propanol. Two isomers: 1,2- and 1,4-butanediol were chosen because of their extreme difference in the distribution of the hydrophobic and hydrophylic parts within the diol molecule [2].

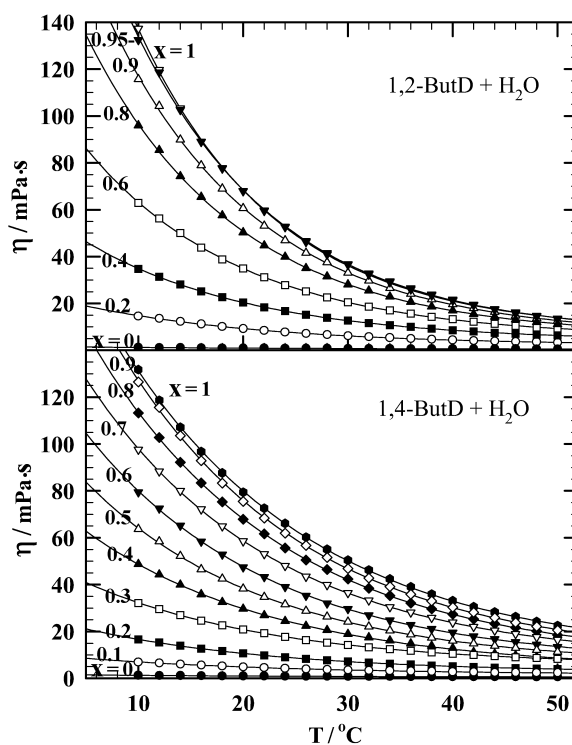


Fig. 1. Temperature dependences of the viscosity of 1,2-butanediol (1,2-ButD) and 1,4-butanediol (1,4-ButD) + water mixtures. x denotes the mole fraction of diol. The solid lines represent the best fit of (1) to the experimental data.

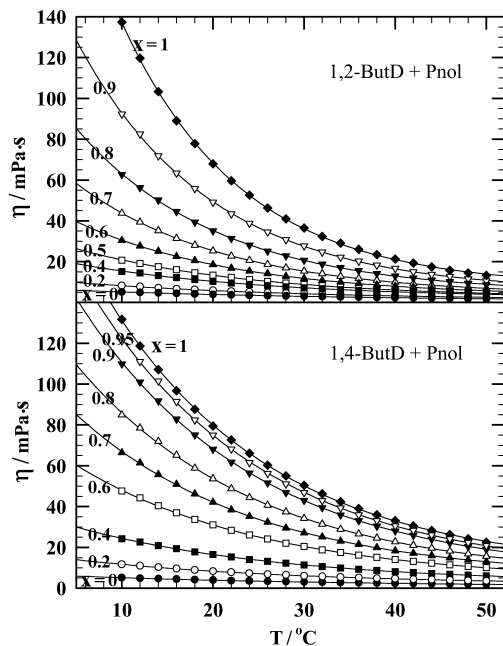


Fig. 2. Temperature dependences of the viscosity of 1,2-butanediol and 1,4-butanediol + 1-pentanol (Pnol) mixtures. The solid lines represent the best fit of (1) to the experimental data.

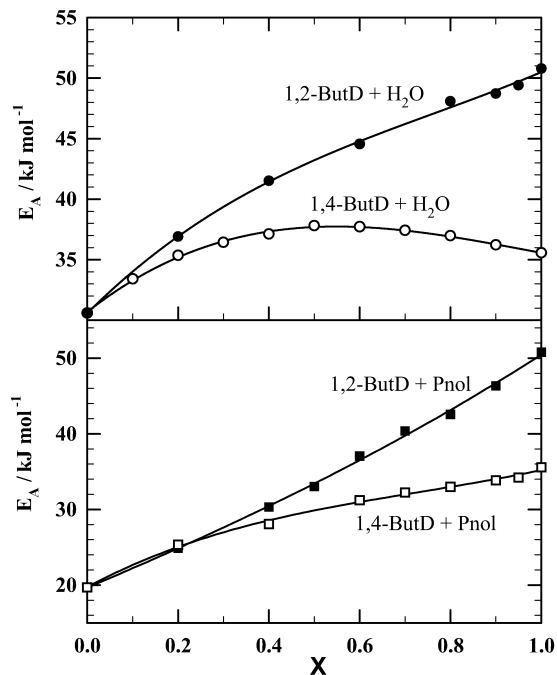


Fig. 3. The viscosity activation energy as a function of the mole fraction of 1,2- and 1,4-butanediol dissolved in water and 1-pentanol.

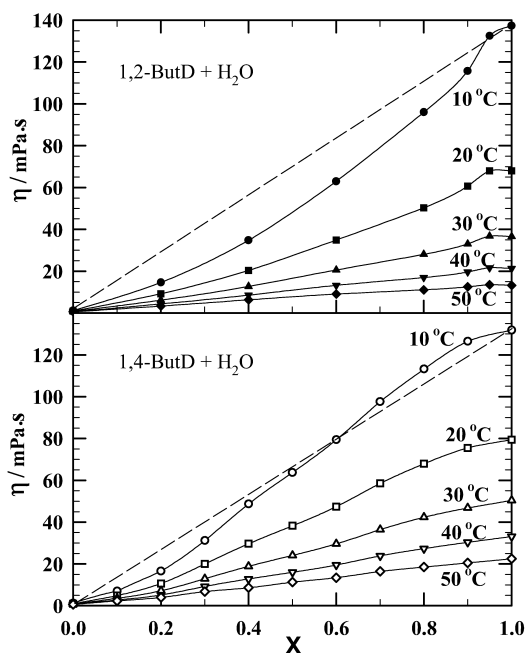


Fig. 4. Isothermal viscosity dependences on the mole fraction of 1,2- and 1,4-butanediol in water. The dashed line corresponds to additive behavior.

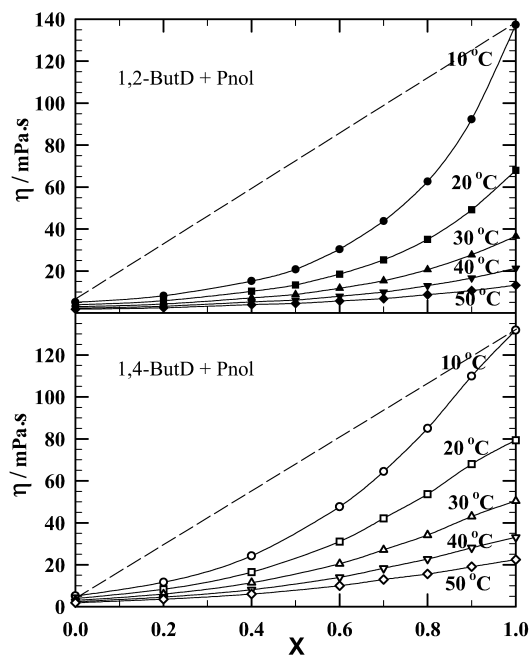


Fig. 5. Isothermal viscosity dependences on the mole fraction of 1,2- and 1,4-butanediol in 1-pentanol. The dashed line corresponds to additive behavior.

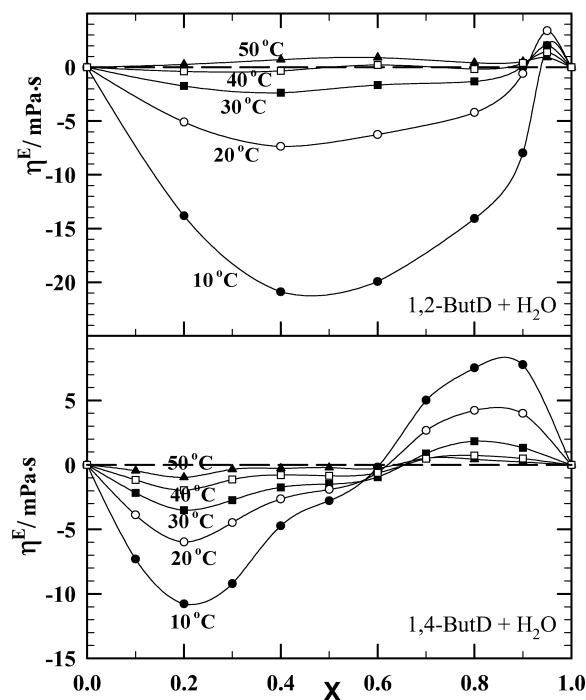


Fig. 6. The viscosity excess as a function of the mole fraction of 1,2- and 1,4-butanediol in water.

2. Experiment

1,2-butanediol and 1,4-butanediol (Fluka) of purity higher than 98%, and 1-pentanol (Aldrich, 99+%) were used as purchased. Water was twice distilled and deionised.

The shear viscosity was measured with a Haake rotatory viscometer RV20 with an accuracy of 0.5%. The temperature of the sample was controlled within ± 0.1 °C. The experimental details are described in [1].

3. Results and Discussion

The temperature dependences of the shear viscosity of 1,2-butanediol and 1,4-butanediol, dissolved with the mole fraction χ in water and in pentanol, are depicted in Figs. 1 and 2. The temperature dependences of the viscosity fulfill quite well the Arrhenius equation, when one introduces a relatively small (of the order of 1 mPa·s) viscosity background η_0 [3]:

$$\eta(T) = \eta_A \exp\left(\frac{E_A}{RT}\right) + \eta_0. \quad (1)$$

η_A , E_A and η_0 are the fitting parameters.

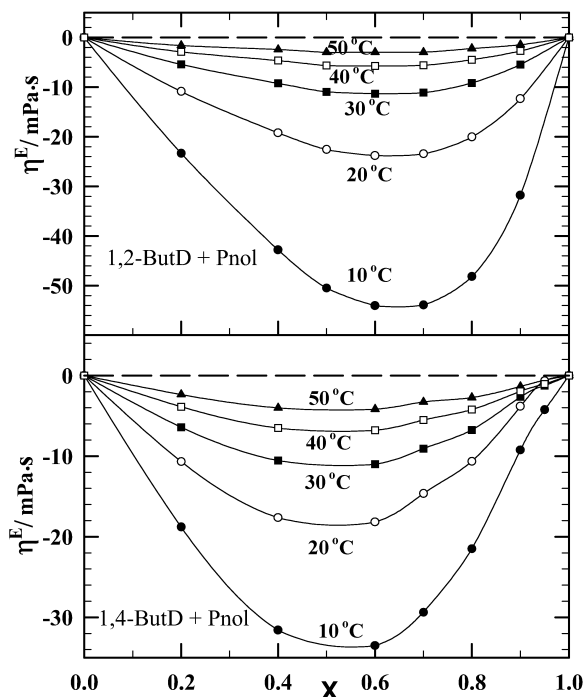


Fig. 7. The viscosity excess as a function of the mole fraction of 1,2- and 1,4-butanediol in 1-pentanol.

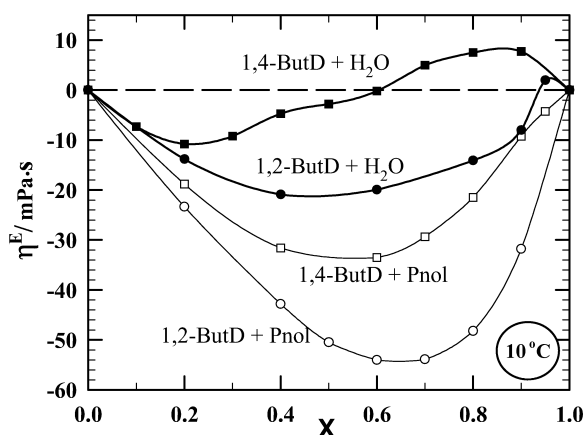


Fig. 8. Comparison of the viscosity excess dependences on 1,2- and 1,4-butanediol mole fraction in water and 1-pentanol, at 10 °C.

Figure 3 shows the activation energy of the viscosity as a function of the diols mole fraction in water and 1-pentanol. The distinctly higher values of E_A observed for 1,2-butanediol solutions than for 1,4-butanediol solutions coincide with those obtained for the previously studied 1,2-pentanediol solutions [4].

Evidently the separation of the hydrophobic and hydrophylic parts within the diol molecule leads to a stronger temperature dependence of the viscosity for the pure diols and for the mixtures. This can be important for technical reasons.

Figures 4 and 5 show the dependence of the viscosity on the concentration of the diols in water and alcohol, respectively, at constant temperature. The viscosity of these two groups of solutions shows a markedly different deviation from additivity. This effect is clearly seen in Figs. 6–8, where the viscosity excess

$$\eta^E = \eta_{\text{meas}} - [\eta_{\text{diol}} \cdot x + \eta_{\text{solv}} \cdot (1 - x)], \quad (2)$$

as a function of the diols mole fraction is drawn. In (2) η_{meas} is the measured viscosity of the solution and η_{diol} and η_{solv} are the viscosities of the pure components.

As Figs. 6–8 show, the excess of the viscosity as a function of the diol concentration behaves quite differently for the different admixtures. The solutions of both 1,2- and 1,4-butanediol in pentanol (Fig. 7) show a negative value of η^E in the whole range of the diols concentration. For 1,2-butanediol the $\eta^E(X)$ dependence is somewhat asymmetric – the minimum is shifted towards higher diol concentration if compared to the 1,4-butanediol + pentanol solutions. A negative excess of the viscosity corresponds to the situation when the mixing process of two liquids leads to destruction of the intermolecular structures existing in the pure components. Less structurized entities created in the solution, make the flowing of 1,2- and 1,4-butanediol + alcohol mixtures easier than that of the pure diols.

The picture is quite different in aqueous solutions of the diols studied. For a not too high content of water: up to about 10% (in mole fraction) in case of 1,2-butanediol, and 40% in case of 1,4-butanediol, the viscosity of the solutions is higher than that resulting from the additivity, *i. e.* the viscosity excess is positive.

The results presented in Fig. 6 show an essential difference in the role of water molecules in the reinforcement and next – in the destruction of the intermolecular entities formed by the diols of different molecular structure. The micelle-like entities created in liquid 1,2-butanediol due to the distinct separation of the hydrophobic and hydrophylic parts of the molecules can accept but an inconspicuous number of water molecules with maintaining the same structure. Our viscosity data show that, when adding water molecules, the micelle-like entities become, at first, more and more rigid up to a water concentration of about 0.05 mole fraction; for that concentration $\eta^E(x)$ shows a maximum. Next, with increasing the ratio of water to diol molecules, η^E decreases, and for the ratio 1:10 the viscosity excess is zero. The quite strong decrease of the viscosity of the mixtures observed for a further increase of water concentration is undoubtedly due to a gradual destruction of the well-organized micelle-like entities.

The intermolecular layer-like structures formed by 1,4-butanediol molecules (in which two O–H groups are located at their ends) can take in much more water molecules without changing structure. Our data suggest that the layer-like entities disappear when the water to 1,4-butanediol molecules ratio exceed about 2:5. For about 1:5, the layer-like entities exhibit the highest rigidity, which manifests itself by the highest resistance to the flow.

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