The Viscous Properties of Diols.
II. 1,2- and 1,5-Pentanediol in Water and 1-Pentanol Solutions

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Viscosity measurements were performed for 1,2-pentanediol, $CH_3(CH_2)_2CH(OH)CH_2(OH)$, and 1,5-pentanediol, $HO(CH_2)_5OH$, dissolved in water and 1-pentanol, in the whole range of concentration (x). The viscosity excess (η^E) of the solutions studied is negative with the exception of concentrated mixtures of the diols with water, where strong anomalies in the $\eta^E(x)$ dependence are observed.

Key words: Pentanediol; Water; Pentanol; Solutions; Viscosity Excess; Activation Energy; Supramolecular Ordering.

1. Introduction

Molecular self-organization due to intermolecular hydrogen bonds is one of the most important phenomena which determine the structure and properties of numerous liquids. The entities formed can be composed of so many molecules, that the term "supramolecular polymers" is often used for describing the chains of molecules of low molecular weight linked by reversible, non-covalent interactions, such as hydrogen bonds [1 – 4]. The reversibility, which manifests itself in the supramolecular polymers molecular weight dependence on concentration, solvent polarity and temperature, is responsible for the appearance of some unusual properties, such as the gelation ability [5 – 6].

This paper presents the results of viscosity measurements performed on mixtures of hydrogen bonded liquids (diol + water or alcohol) important from both the basic research and technical point of view.

As the structure of liquid diols depends mainly on the position of hydroxyl groups, two extremely different isomers: 1,2- and 1,5-pentanediol were chosen. In the first compound two -OH groups are joined with two neighbouring carbon atoms at the end of the hydrocarbon chain, so the hydrophobic and hydrophilic parts of the 1,2-pentanediol molecule are separated. In such a situation, the intermolecular hydrogen bonds O-H. . . O lead to rather cyclic, micelle-like entities. In 1,5-pentanediol the -OH groups are located at the ends of the molecule, and self-association due to hydrogen bond formation leads rather to elongated, layer-like structures [7]. The influence of water and 1-pentanol on the viscous properties of the diols is interesting and important, as the mixtures are often used in practice.

2. Experimental

1,2-pentanediol (Fluka) and 1,5-pentanediol (Merck) 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 viscometer RV20 with the measuring system CV100. The system consists of a rotary beaker filled with the studied liquid and a cylinder sensor of Mooney-Ewart type (ME15), placed in the center of the beaker. The liquid gap was 0.5 mm. The studied liquids show Newtonian behaviour in the available range of shear rates (30 s^{-1} – 300 s^{-1}). The accuracy of the viscosity determination was 0.5%. The temperature of the sample was controlled within ±0.1 °C.

3. Results and Discussion

Figures 1 and 2 present the temperature dependences of the shear viscosity of 1,2-pentanediol and 1,5-pentanediol dissolved in water and 1-pentanol, respectively. The diol mole fraction in the solutions is the parameter of the curves. The solid lines in the fig-

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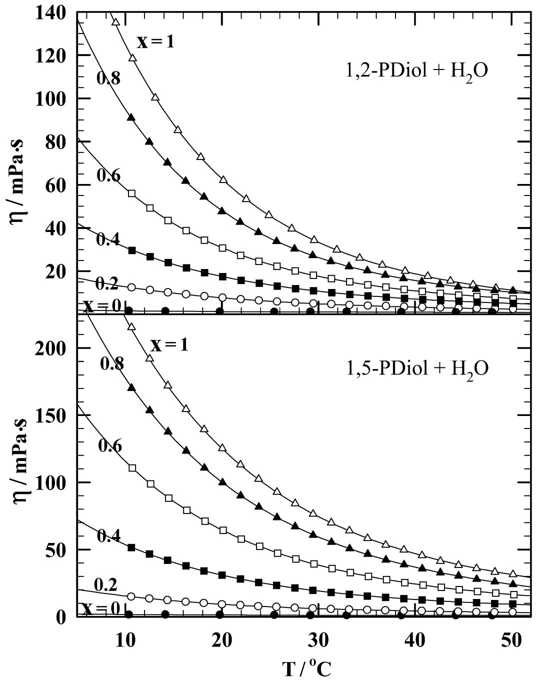

Fig. 1. Temperature dependences of the viscosity of 1,2-pentanediol (1,2-PDiol) and 1,5-pentanediol (1,5-PDiol) + water mixtures. X denotes the mole fraction of diol. The solid lines represent the best fit of (1) to the experimental data.

ures represent the best fit of the Arrhenius-like equation [8,9]

$$\eta(T) = \eta_{\mathrm{A}} \exp\left(\frac{E_{\mathrm{A}}}{RT}\right) + \eta_0 \qquad (1)$$

to the experimental data. In the equation a constant background η_0 is introduced as a modification of the Arrhenius equation. As shown in [8,9], the relatively small viscosity background (of the order of 1 mPa·s) in (1) allows one to obtain a very good empirical description of the experimental data, with the conservation of a useful meaning of the activation energy (E_{A}). Equation (1) contains three fitting parameters: η_{A}, η_0, and E_{A}.

Figure 3 presents the activation energy obtained from the fitting procedure as a function of diol mole fraction in water and 1-pentanol solutions. In both solvents with increasing molar fraction of diol, the activation energy changes monotonously. For concentrated solutions in water the change is not too pronounced, especially in case of 1,5-pentanediol.

The most striking differences in the viscosities of 1,2- and 1,5-pentanediol dissolved in water and 1-pentanol can be seen in Figs. 4 and 5, where, at constant temperature, the viscosity is plotted against the mole fraction of the diols. A common feature of the solutions is a negative deviation of the measured viscosity from additivity. Figures 6 and 7 present the viscosity excess

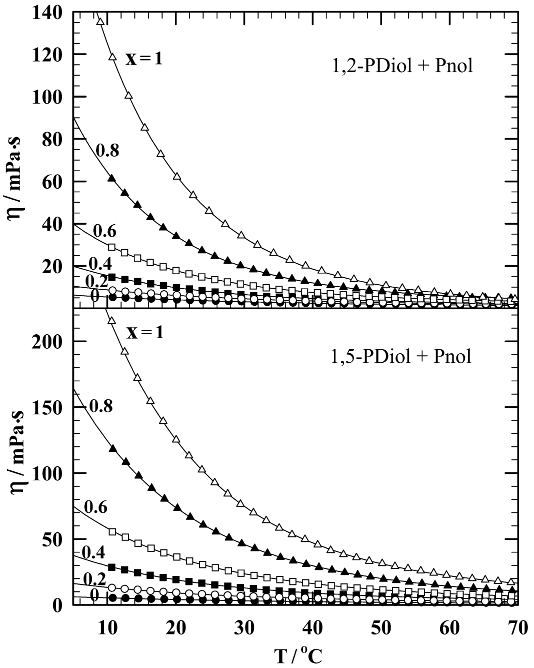

Fig. 2. Temperature dependences of the viscosity of 1,2-pentanediol and 1,5-pentanediol + 1-pentanol (Pnol) mixtures. The solid lines represent the best fit of (1) to the experimental data.

$$\eta^{\mathrm{E}} = \eta^{\mathrm{meas}} - \left[\eta_{\mathrm{diol}} \cdot x + \eta_{\mathrm{solv}} \cdot (1-x)\right], \qquad (2)$$

as a function of the mole fraction x of the diols, at different temperatures. In (2) η_{diol} and η_{solv} stand for the viscosity of the pure components of the mixtures.

The results show an exceptional influence of water on the viscous properties of the diols. The viscosities of the mixtures of both 1,2- and 1,5-pentanediol with x_{water} up to about 0.5 show strong anomalies if compared to the diol mixtures with 1-pentanol. In the latter case the viscosity excess as a function of diol concentration can be represented by a quite smooth curve, however, the maximum of η^{E} is about two times greater than that of the mixtures with water (see Fig. 8).

The viscosity of mixtures of 1,5-pentanediol with water, up to about 20% (in mole fraction) content of water, is quite perfectly additive in the whole temper-

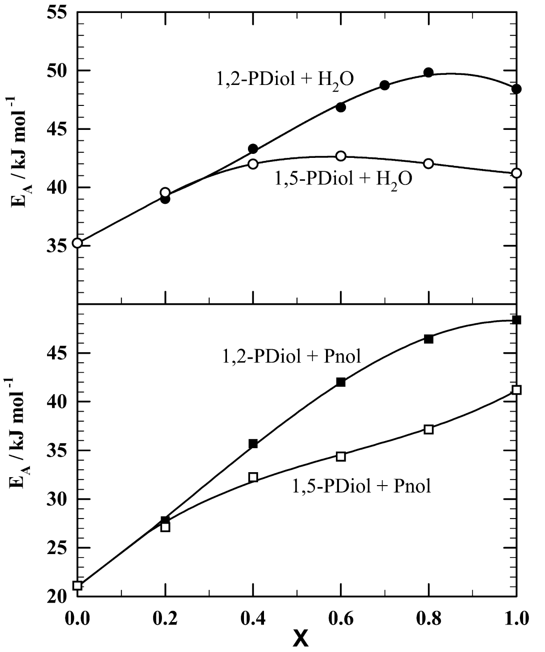

Fig. 3. The activation energy of the viscosity as a function of the mole fraction of 1,2- and 1,5-pentanediol dissolved in water and 1-pentanol.

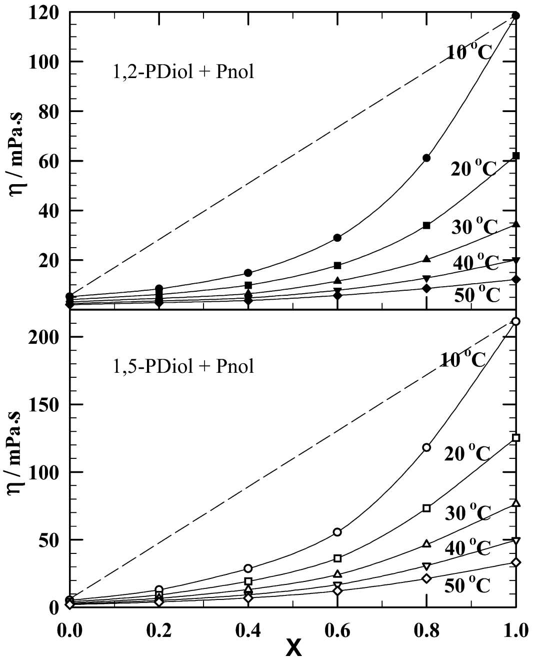

Fig. 5. The dependence of the isothermal viscosity of 1,2- and 1,5-pentanediol on it mole fraction in 1-pentanol. The dashed line corresponds to additive behaviour of the viscosity of the mixture.

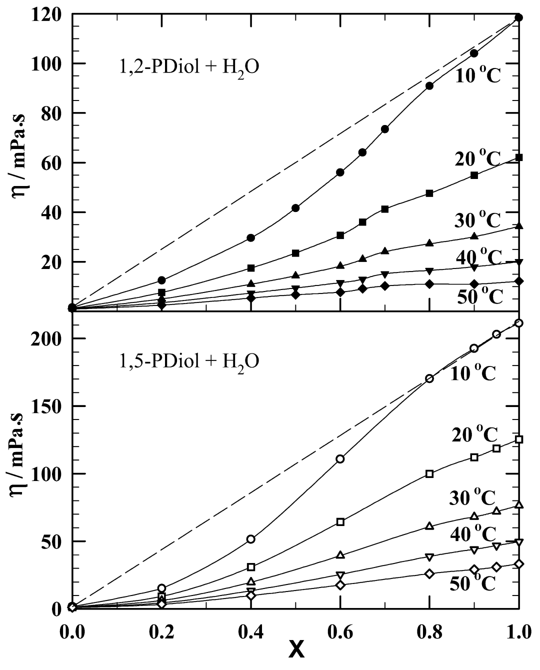

Fig. 4. Isothermal viscosity dependences on 1,2- and 1,5-pentanediol mole fraction in water. The dashed line corresponds to additive behaviour of the viscosity of mixture.

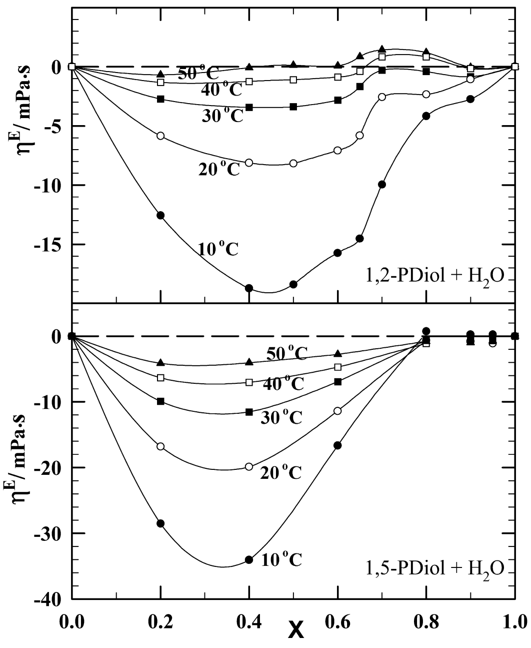

Fig. 6. Viscosity excess as a function of the mole fraction of 1,2- and 1,5-pentanediol in water.

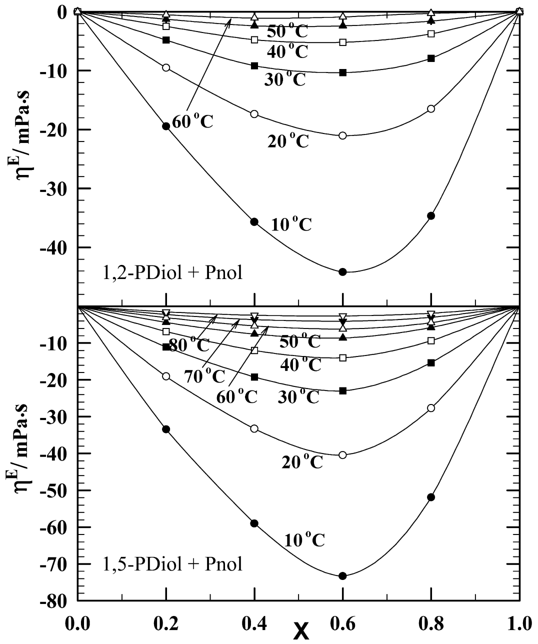

Fig. 7. Viscosity excess as a function of the mole fraction of 1,2- and 1,5-pentanediol in 1-pentanol.

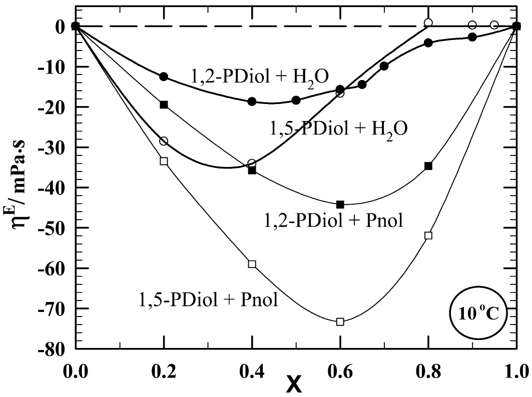

Fig. 8. Comparison of the viscosity excess dependences on the 1,2- and 1,5-pentanediol mole fraction in water and 1-pentanol, at 10 °C.

ature range studied. This shows that a relatively small amount of water added to the diol, remains built in the hydrophilic area formed by the OH end groups of the diol, without changing the general structure of the liquid.

The situation is somewhat different in case 1,2−pentanediol, where even a small amount of water molecules makes the viscosity non additive, and the effect is strongly temperature dependent up to an appearance of a positive viscosity excess at higher temperatures.

[1] V. A. Durov, J. Molec. Liq. **103 – 104**, 41 (2003).

[2] R. P. Sijbesma, F. H. Beijer, L. Brunsveld, B. J. B. Folmer, J. H. K. Ky Hirschberg, R. F. M. Lange, J. K. L. Lowe, and E. W. Meijer, Science **278**, 1601 (1997).

[3] S. Boileau, L. Bouteiller, F. Lauprêtre, and F. Lortie, New J. Chem. **24**, 845 (2000).

[4] J. Jadżyn, M. Stockhausen, and B. Żywucki, J. Phys. Chem. **91**, 754 (1987).

[5] F. Lortie, S. Boileau, L. Bouteiller, C. Chassenieux, B. Demé, G. Ducouret, M. Jalabert, F. Lauprêtre, and P. Terech, Langmuir **18**, 7218 (2002).

[6] K. Hanabusa, K. Shimura, K. Hirose, M. Kimura, and H. Shirai, Chem. Lett. **1996**, 885.

[7] A. G. Petrov, The Lyotropic State of Matter, Gordon and Breach Sci. Publ., Amsterdam 1999.

[8] J. Jadżyn, G. Czechowski, and T. Lech, Acta Phys. Polon. **101**, 495 (2002).

[9] G. Czechowski and J. Jadżyn, Z. Naturforsch. **58a**, 317 (2003).