

The Viscous Properties of Diols.

IV. 1,2- and 1,4-Butanediol in Butanols Solutions

Grzegorz Czechowski, Paweł Jarosiewicz, Arkadiusz Rabiega, and Jan Jadzyn

Institute of Molecular Physics, Polish Academy of Sciences, M. Smoluchowskiego 17, 60-179 Poznań, Poland

Reprint requests to Prof. J. J.; Fax: +4861 8684-524; E-mail: jadzyn@ifmpan.poznan.pl

Z. Naturforsch. **59a**, 119 – 123 (2004); received December 22, 2003

The paper presents the results of viscosity measurements performed on 1,2- and 1,4-butanediol in *n*-, *s*- and *t*-butanol solutions in the whole range of concentration, at different temperatures. The activation energy for viscous flow of the solutions and the viscosity excess were determined. The excess shows a peculiar behavior for 1,4-butanediol in *t*-butanol solutions.

Key words: Shear Viscosity; Butanediols; Butanols; Solutions; Viscosity Excess; Activation Energy.

1. Introduction

Peculiarities in the physical properties of hydroxylic compounds result essentially from the molecular ordering due to hydrogen bond formation. In case of diols, which are among the most self-associated liquids, the structure of the intermolecular entities depends mainly on the mutual position of OH groups within the hydrocarbon chain of the molecule.

Diols are widely used in industry, mainly because of their large temperature range of existence in the liquid state and favorable viscous properties. As highly self-associated liquids, the diols are rather viscous (especially at low temperatures), and they are used often in mixtures with water or alcohols [1, 2].

This paper presents the shear viscosity of one of the most frequently used mixtures of diols with alcohols: 1,2- and 1,4-butanediols + three isomers of butyl alcohol: *n*-, *s*- and *t*-butanol.

2. Experiment

1,2-butanediol and 1,4-butanediol (Fluka) of higher than 98% purity, and *n*-, *s*-, and *t*-butanol (2-methyl-2-propanol), (Aldrich, 99+%), were used as purchased.

The shear viscosity was measured with a Haake rotator 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 [3].

3. Results and Discussion

Figures 1 and 2 present temperature dependences of the viscosity of 1,2- and 1,4-butanediol, respectively, dissolved in butanols. The dependences can be quite well reproduced with the Arrhenius equation:

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

where the background viscosity η_o (in practice of about 1 mPas) is introduced [4]. The solid lines in Figs. 1 and 2 are the best fits of (1) to the experimental results.

Table 1. The values of the viscosity and the activation energy for pure diols and butanols studied at 30 °C.

Compound	Viscosity, mPas	Activation energy, kJ/mol
<i>n</i> -BuOH	1.916	20
<i>s</i> -BuOH	2.550	28
<i>t</i> -BuOH	3.179	49
1,2-ButD	37.230	48
1,4-ButD	48.470	35

Table 1 presents the values of the viscosity and the activation energy (at 30 °C) corresponding to the pure components of the mixtures studied, and Fig. 3 shows the activation energy of the viscosity as a function of the diols mole fraction in butanols. The results show that finding the relation between the molecular structure and the intermolecular interactions from one side, and the viscosity and its temperature dependence from the other side is not a simple task. However, the

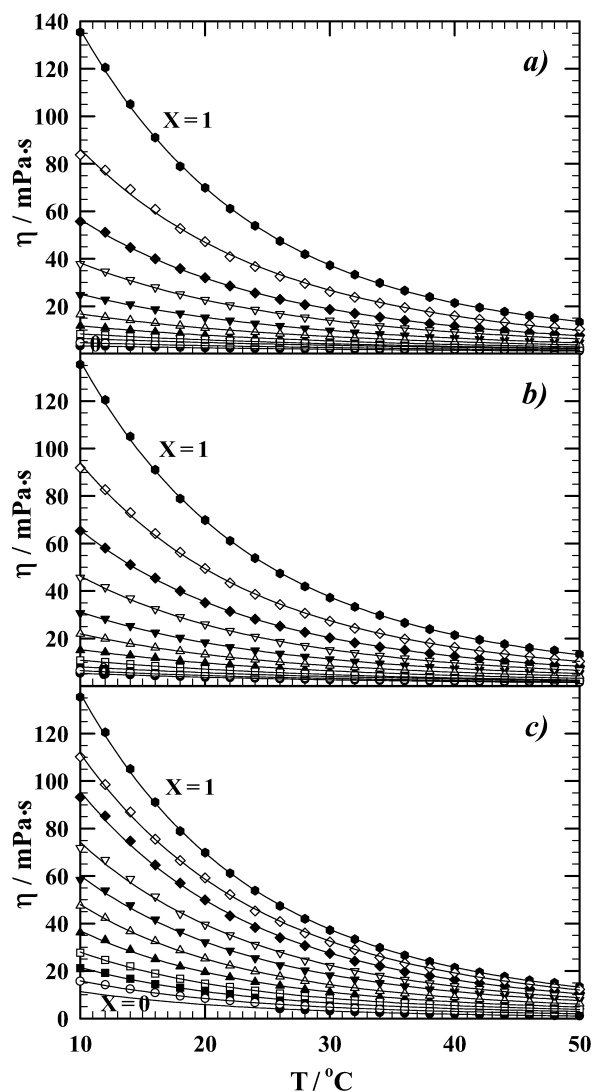


Fig. 1 (top, left). Temperature dependences of the viscosity of 1,2-butanediol in *n*-butanol (a), *s*-butanol (b) and *t*-butanol (c) solutions. *X* denotes the mole fraction of diol. The solid lines represent the best fit of (1) to the experimental data.

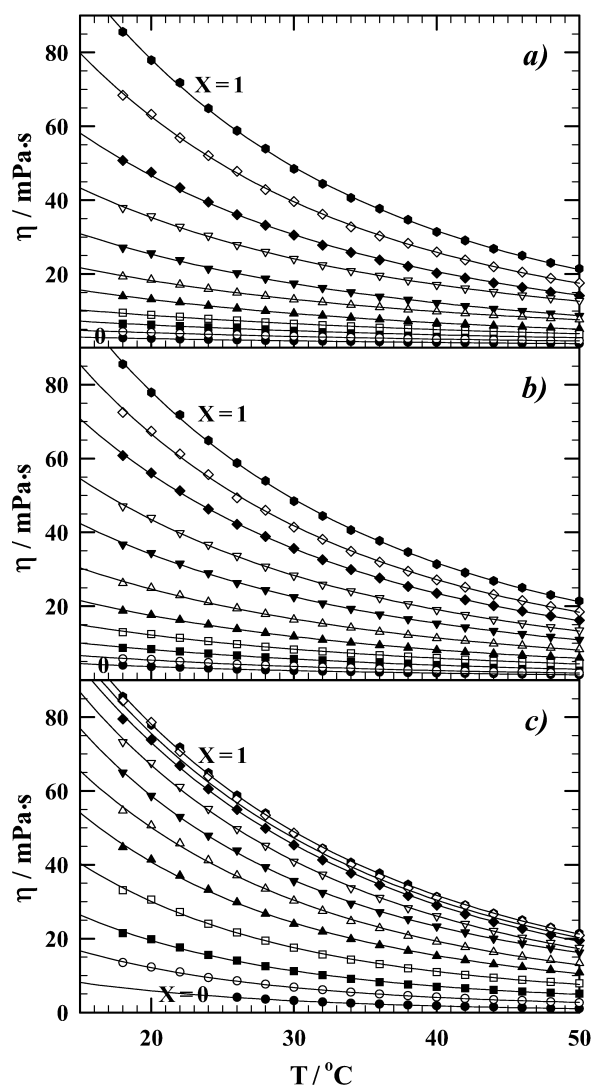


Fig. 2 (top, right). Temperature dependences of the viscosity of 1,4-butanediol in *n*-butanol (a), *s*-butanol (b) and *t*-butanol (c) solutions. *X* denotes the mole fraction of diol. The solid lines represent the best fit of (1) to the experimental data.

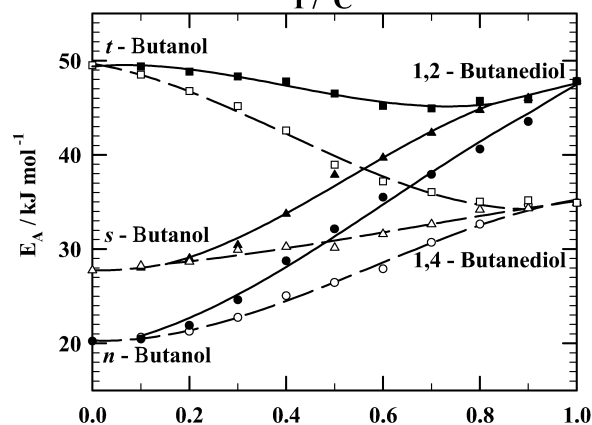


Fig. 3 (right). Activation energy of the viscosity as a function of the mole fraction of 1,2- and 1,4-butanediol dissolved in butanols.

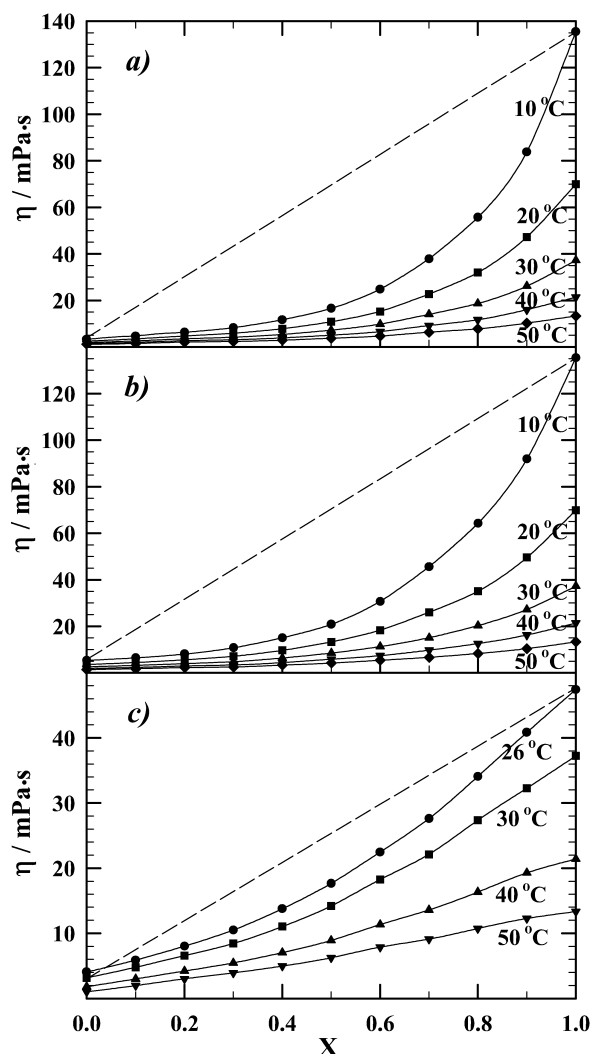


Fig. 4. Dependences of the isothermal viscosity on the 1,2-butanediol mole fraction in *n*-butanol (a), *s*-butanol (b) and *t*-butanol (c) solutions. The dashed line corresponds to additive behavior of the viscosity of mixtures.

problem is quite important as a great effort is constantly undertaken for finding liquids of an appropriate viscosity and an as weak as possible temperature dependence. The latter requirement means an as low as possible activation energy of the viscosity. As results from Table 1, the change in the shape of the alcohol molecule from elongated (*n*-butanol) to close to spherical (*t*-butanol) manifests itself as an increase of both the viscosity and its activation energy. Most significant is the change in the activation energy, which for *t*-butanol even somewhat exceeds that of 1,2-butanediol.

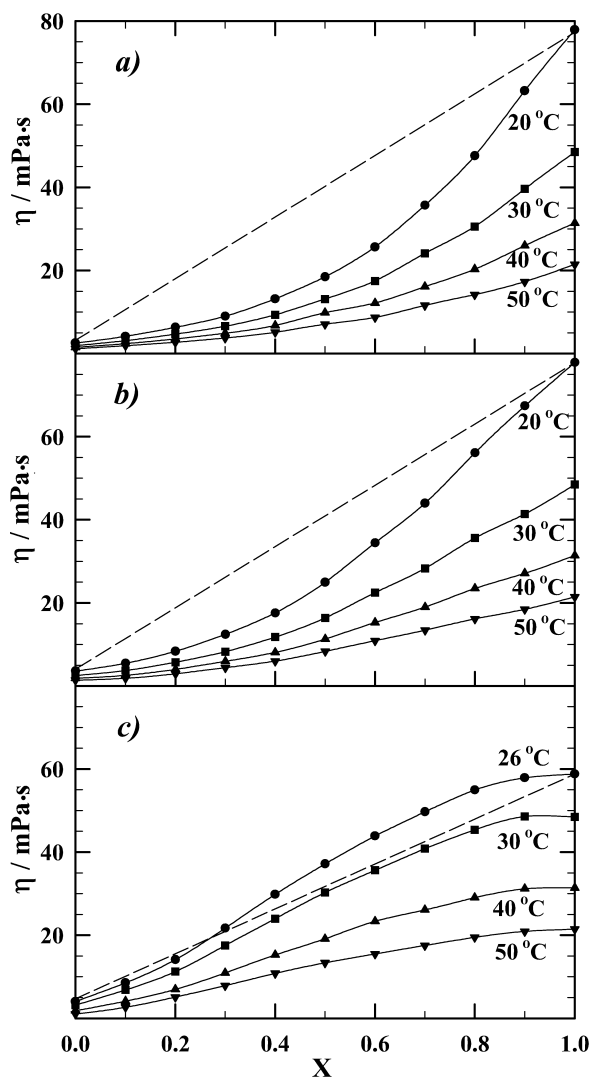


Fig. 5. Dependences of the isothermal viscosity on the 1,4-butanediol mole fraction in *n*-butanol (a), *s*-butanol (b) and *t*-butanol (c) solutions. The dashed line corresponds to additive behavior of the viscosity of mixtures.

The data obtained for the diols point out that the separation of the hydrophobic and hydrophylic parts within the diol molecule leads to a lower activation energy of the viscous flow.

As shows Fig. 3, the activation energy as a function of the diols concentration in butanols shows only a small deviation from additive behavior.

Figures 4 and 5 present the viscosity dependence on the 1,2- and 1,4-butanediol concentration in butanols, at constant temperature. For both diols one observes a regular decrease of the deviation from the additive vis-

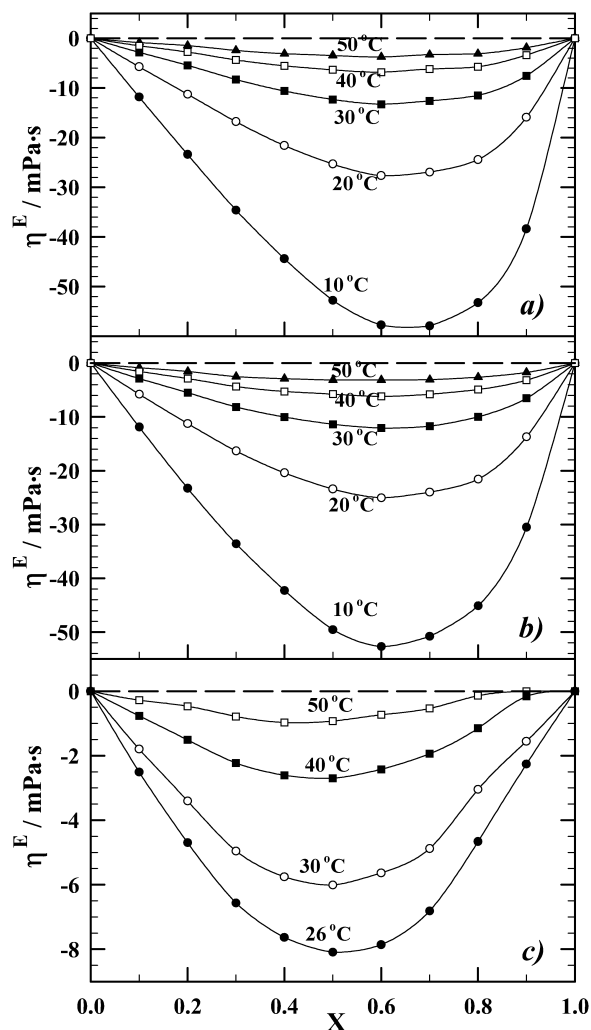


Fig. 6. Viscosity excess as functions of the mole fraction of 1,2-butanediol in *n*-butanol (a), *s*-butanol (b) and *t*-butanol (c) solutions.

cosity behavior when the admixture is changing from *n*-butanol to *t*-butanol. The effect is clearly seen in Figs. 6 and 7, 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.

The solutions studied show a negative excess of the viscosity in the whole range of diol-concentrations with the exception of 1,4-butanediol dissolved in *t*-butanol, where a negative η^E is observed only in the solutions of a relatively low concentration of the diol

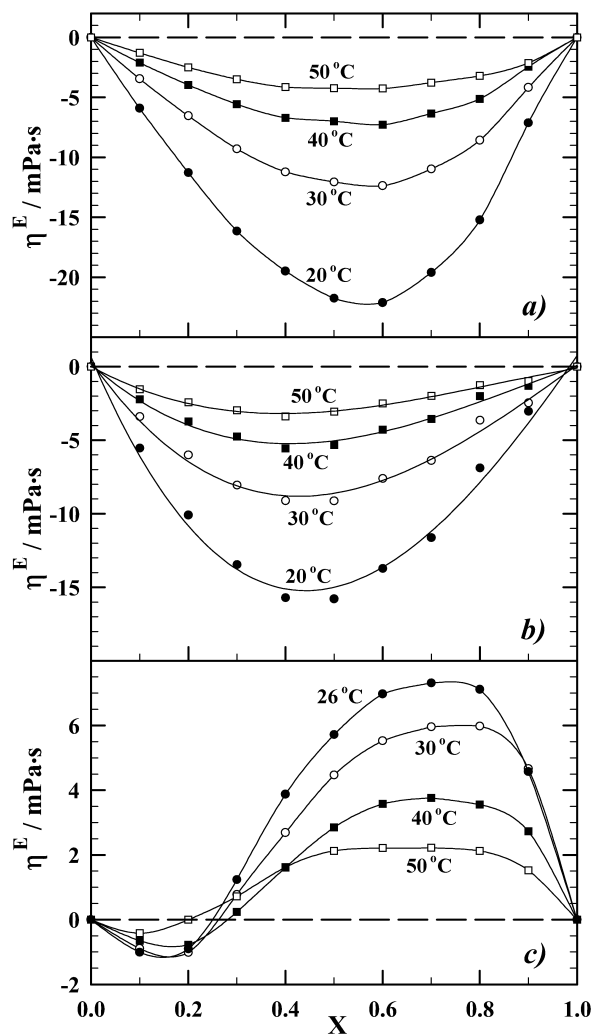


Fig. 7. Viscosity excess as functions of the mole fraction of 1,4-butanediol in *n*-butanol (a), *s*-butanol (b) and *t*-butanol (c) solutions.

(up to about 25% mol. fr.). A negative excess of the viscosity of a mixture means that its resistance to the flow is smaller than that of the pure components. The intermolecular structures existing in pure liquids are partially destroyed by a mixing process, which makes the flow easier than that of the pure liquids. This effect is often used for preparing a fluid of an appropriate viscosity at given temperature. Our results show that a surprise can be found in that field. The molecules of *t*-butanol, which as a pure liquid are hydrogen bonded in their own network, added to the much stronger self-associated 1,4-butanediol, make the hydrogen bonded entities in the mixture much more resistant to the flow

than those in pure *t*-butanol. The effect is much more pronounced than in previously studied mixtures of 1,4-butanediol with water [5].

- [1] T. Sun, R. M. Diguilio, and A. S. Teja, J. Chem. Engn. Data, **37**, 246 (1992).
- [2] C. Yang, P. Ma, F. Jing, and D. Tang, J. Chem. Engn. Data, **48**, 836 (2003).
- [3] G. Czechowski and J. Jadżyn, Z. Naturforsch. **58a**, 317 (2003).
- [4] J. Jadżyn, G. Czechowski, and T. Lech, Acta Phys. Polon. **101**, 495 (2002).
- [5] G. Czechowski, A. Rabiega, and J. Jadżyn, Z. Naturforsch. **58a**, 569 (2003).