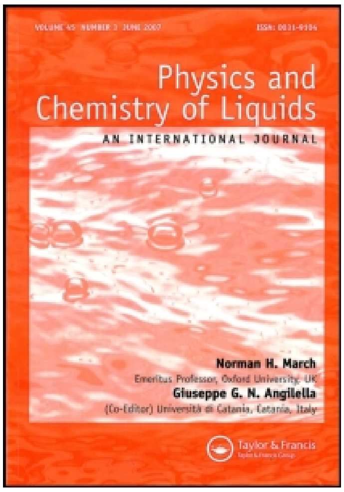

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# VISCOSITY OF SOME PROPANOLS AND AMINOPROPANOLS IN MIXTURES WITH 1,4-DIOXANE

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The results of viscosity measurements for mixtures of 1-propanol, 2-propanol, 3-amino-1-propanol and (±)1-amino-2-propanol with 1,4-dioxane at 20, 30 and 40°C are presented and comparatively discussed. From the temperature dependence of viscosity, activation energies are determined.

*Keywords*: Viscosity; hydrogen bonding

## INTRODUCTION

Studies of the transport properties of pure liquids and liquid mixtures are important from theoretical and practical viewpoints. An informative property in that regard is the viscosity, which reflects intermolecular interactions. Increasing interaction ability, *e.g.* because of the occurrence of hydrogen bonding, leads in general to increased viscosity.

Monohydric alcohols are typical hydrogen bonding substances. The hydroxy group can act as proton donor as well as acceptor, which results in the well known association in liquid alcohols via O···H—O bonds. Additional hydrogen bonding sites are offered in aminoalcohols, where also N···H—O and O···H—N bonds are feasible.

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Information on the effectiveness of the different bonding possibilities may be obtained from the comparison of aminoalcohols with analogous alcohols containing only the OH group. Previously we have studied the molar volume [1] and the dielectric relaxation behaviour [2] of a number of binary mixtures of aminoalcohols with 1,4-dioxane as mixture component. Both properties show clearly that aminoalcohols are more strongly associated than the non-substituted analogues. In continuation of that work, the present paper reports the viscosity of those mixtures, comparing some molecules of equal chain length ($C_3$), that is two non-substituted and two $NH_2$-substituted propanol isomers.

The following substances have been studied over the whole mixture range with 1,4-dioxane: 1-propanol, 2-propanol, 3-amino-2-propanol and (±)1-amino-2-propanol. Temperatures were 20, 30 and 40°C.

## EXPERIMENTAL

The alcohols were supplied by Aldrich. They were stored over activated 4 Å molecular sieve. Dioxane was double-distilled before use.

The viscosity was determined with a Haake viscometer Rotovisco RV 20 with measuring system CV 100, the shear rate being 275 $s^{-1}$. The sensor system was of Mooney-Ewart type (ME 15). The measuring system was thermostated to ±0.05 K using a Haake F3 ultrathermostat. The viscosity data were reproducible to ±0.5%.

## RESULTS

The viscosities found for the pure liquids are listed in Table I. The results for the four mixture systems are given graphically in Figure 1 as

TABLE I Viscosities of the pure substances studied

| *Substance* | $\eta$/mPa s | | |
|---|---|---|---|
| | 20°C | 30°C | 40°C |
| 1-propanol | 2.198 | 1.644 | 1.282 |
| 2-propanol | 2.381 | 1.638 | 1.278 |
| 3-amino-1-propanol | 38.68 | 23.26 | 13.71 |
| 1-amino-2-propanol | 30.94 | 17.49 | 10.70 |
| 1,4-dioxane | 1.288 | 1.084 | 0.877 |

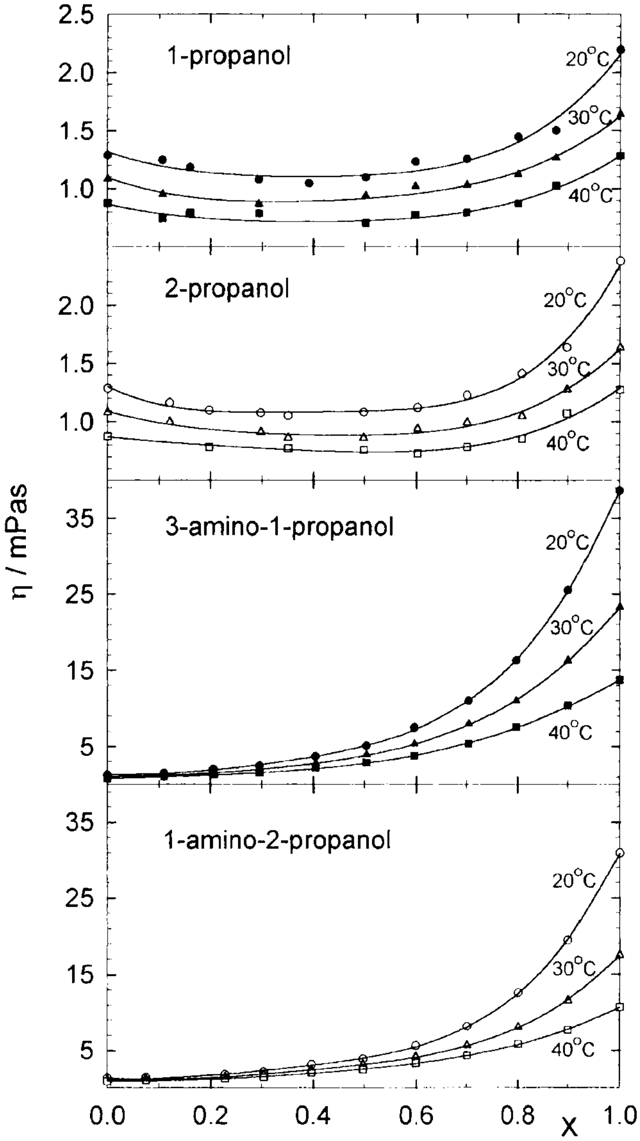

FIGURE 1 Viscosity $\eta$ vs. mole fraction $x$ of the alcoholic mixture component in 1,4-dioxane for all systems and temperatures studied.

a function of mixture composition (alcohol mole fraction $x$). For better comparability, the 20°C viscosities are gathered in one plot, Figure 2. The curvature of the $\eta - x$ plots may easier be evaluated from the excess viscosity $\eta^E$ defined by

$$\eta^E = \eta - \exp[x \ln \eta^*_{Al} + (1 - x) \ln \eta^*_{Dx}],$$

where the subscripts stand for the two mixture components and the asterisk denotes the pure substances. That quantity is shown in Figure 3.

The dependence of $\eta$ on temperature $T$ follows, within the temperature range studied, an Arrhenius relation

$$\ln \eta = A + \frac{E_a}{RT}$$

as shown in Figure 4 for one typical example. Figure 5 represents the activation energies $E_a$ for the four systems studied as dependent on the mixture composition.

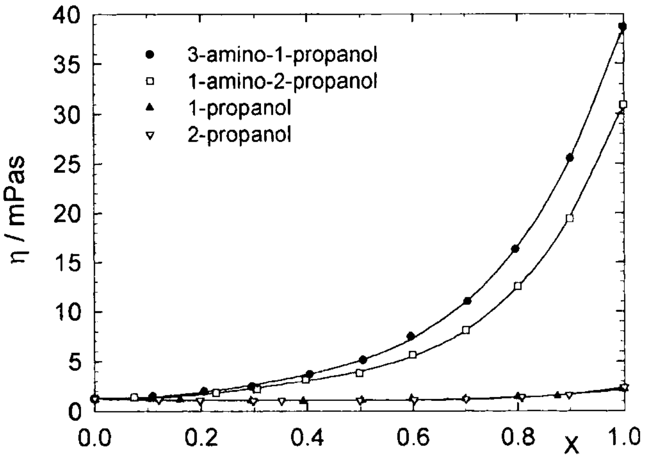

FIGURE 2 Comparison of viscosities $\eta$ vs. mole fraction $x$ at one temperature, 20°C.

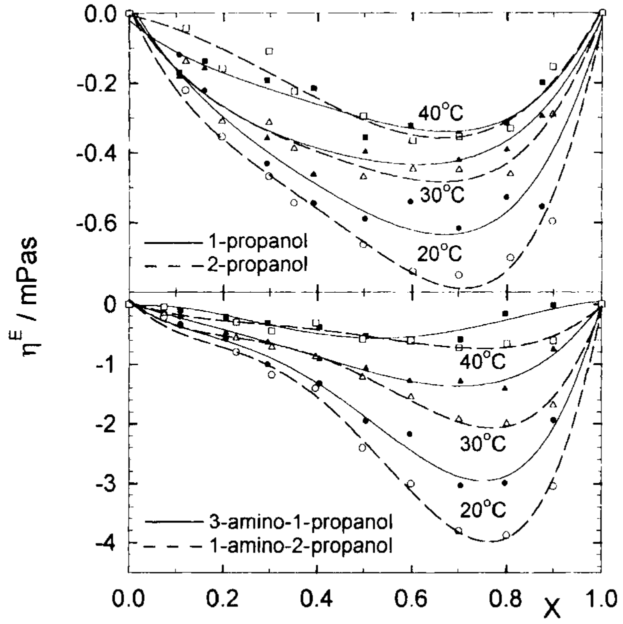

FIGURE 3 Excess viscosities $\eta^E$ vs. mole fraction $x$.

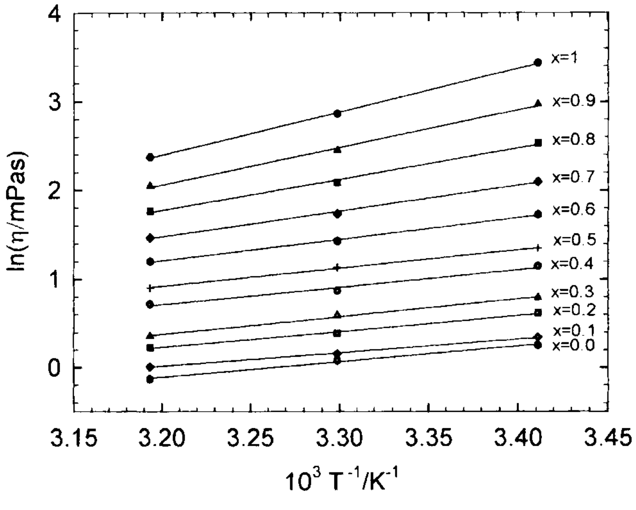

FIGURE 4 Arrhenius plot for 1-amino-2-propanol mixtures with dioxane, for different mole fractions $x$ of the alcoholic component.

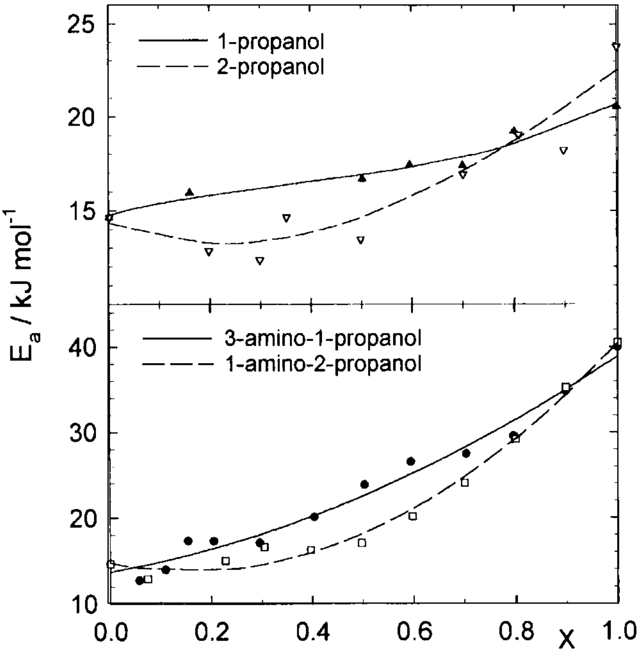

FIGURE 5 Arrhenius activation energy $E_a$ vs. mole fraction $x$ of the alcoholic mixture component in 1,4-dioxane for all systems studied.

## DISCUSSION

It is obvious from the data presented above that the mixture series with amino-propanols, on the one hand, and those with the non-substituted propanols, on the other hand, behave similar; the differences between isomers are much less striking than those between the two classes of compounds. This corresponds to the results of comparative dielectric relaxation studies which have shown that monohydric and dihydric alcohols can be arranged in two clearly distinguishable 'families' [3] and that aminoalcohols appear to belong to the diol 'family' [2]. The differences between both classes may thus be regarded in the first instance.

The viscosity of pure aminopropanols exceeds that of the pure propanols by an order of magnitude. The respective activation energies differ by a factor of roughly two. This is indicative of the formation of two hydrogen bonds in aminopropanols, in accordance with the assignment of aminoalcohols to the diol 'family'.

Turning to the mixture series, the lower concentration range (very roughly, alcohol mole fractions $x \leq 0.4$) and the higher one may be regarded separately. In the lower concentration range the viscosity $\eta$ stays relatively constant on increasing $x$ (Figs. 1, 2; a slight decrease as found for the propanols may be considered a dilution effect). Accordingly, the excess viscosities $\eta^E$ (Fig. 3) of both classes differ no more than by a factor of two. In that concentration range, the mixture behaviour is qualitatively still of the character as with non-associating mixture components. However, in the higher concentration range, where $\eta$ increases notably with $x$, the curvature of $\eta - x$ is especially pronounced in the case of aminopropanols, and this causes the minimum in $\eta^E$ to be much deeper for the aminopropanols than for the non-substituted propanols. The properties in that region are likely to be increasingly dominated by association effects. This inference is supported by the dielectric relaxation parameters [2] which show that now the contribution of associated aminopropanol exceeds that of non-associated.

Finally the differences between isomers shall briefly be considered. From Figures 1, 2 as well as Figure 5 one may conclude that, in comparison to 3-amino-1-propanol, the onset of association of 1-amino-2-propanol is shifted to higher concentrations. A corresponding observation is made for the non-substituted compounds, where the 2-propanol curves are shifted towards higher concentrations in comparison to 1-propanol. This finding is a hint at the important role of steric conditions for the association effectiveness via the hydroxy group, which is less easily accessible in 2-position than in the terminal 1-position.

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