

Short Communications

Properties of Binary Alcohol–Octane Solutions. Temperature Dependence of the Viscosities

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During the last few years, much effort has been focused on investigations on so-called microemulsions, which are defined as thermodynamically stable solutions of water, oil and surfactant and, frequently, an additional amphiphilic compound (“co-surfactant”). The solutions are transparent and homogeneous and the aggregates are reversibly formed. It has been clarified that the aggregates in these solutions vary in shape and structure as the polarity of the association medium undergoes changes. For the same surfactant a higher polarity in the medium brings about more open aggregates where aggregate geometries and strictly defined hydrophilic and hydrophobic domains have minor significance.

In previous papers we have viewed the behaviour of aqueous alcohol solutions.^{1–3} These investigations were undertaken since it has been stressed how important the interaction between water and the polar alcohol molecules are when reversed micelles or so-called w/o microemulsions are formed in hydroxylic environments. When w/o microemulsion formation and stability is studied in quaternary systems with a non-polar solvent (“oil”) as fourth component, we require information on the nature of the interaction between the oil and the alcohols. As a step in this direction we here present the temperature dependence of the viscosities together with activa-

tion energies of some binary alcohol-*n*-octane solutions. Octane has been used in many microemulsion investigations as a model hydrocarbon.

Experimental. Chemicals and preparation of samples. All chemicals together with the preparation of solutions have been described earlier.⁴

Apparatus. The viscosities were measured with capillary viscosimeters as described earlier.⁴

The calibration constants were determined separately at 298, 303 and 313 K.

Results. The effect of a dilution with octane at different temperatures on the viscosity of the alcohols (decanol, pentanol and ethanol) is shown in Fig. 1. For ethanol with or without octane we observe only a minor decrease in η as temperature is increased. Pentanol shows a reduction of 1.5 cP as T increases 15 K, while the value of pure decanol is almost halved for the same temperature change. Fig. 1 also illustrates the pronounced dilution effect on the alcohol with the longest hydrocarbon chain.

Assuming that the temperature dependence of viscosity follows the Arrhenius' equation⁵

$$\eta = A \exp(E^+/RT) \quad (1)$$

where η is the viscosity, A a constant, and E^+ the activation energy, a linear behaviour of $\ln(\eta)$

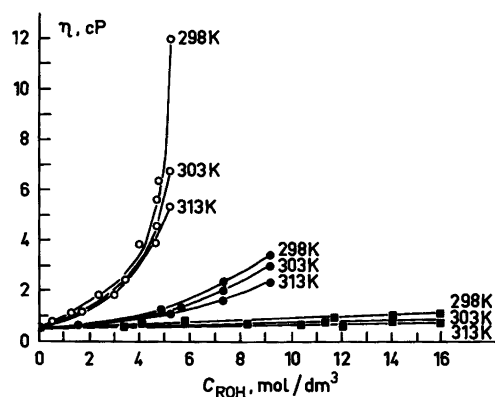


Fig. 1. The viscosities of alcohol–octane solutions at different temperatures. ○ decanol, ● pentanol, ■ ethanol.

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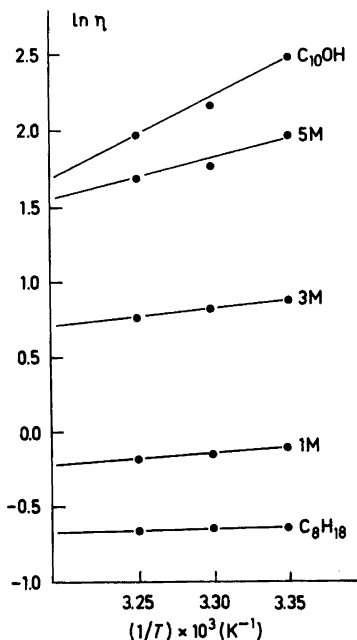


Fig. 2. A typical plot of $\ln(\eta)$ given in arbitrary units versus the inverse temperature T^{-1} . The molarity refers to the alcohol.

when plotted versus $1/T$, is predicted. This analysis is undertaken in Fig. 2. The prediction is fulfilled in all cases except for the highest contents of decanol.

The activation energies have been evaluated

Table 1. Activation energies as calculated from eqn. (1).

$C_n\text{OH} + C_8\text{H}_{18}$	C_{ROH} mol dm ⁻³	E^+ kJ mol ⁻¹
$n=2$	16 ^a	10
	8	6
	4	3
$n=5$	9.1 ^a	19
	8	18
	4	3
$n=10$	5.4 ^a	39
	5	21
	3	3

^a This concentration refers to the pure alcohol.

from Fig. 2 and are summarized in Table 1. The highest values are those of decanol. The values obtained for pure pentanol are in agreement with those given by D'Aprano *et al.*⁶

Discussion. In previous papers we have investigated the effect of an addition of water to different alcohols. Especially for long-chain alcohols we have observed a pronounced decrease of the alcohol self-association. In this study we have changed the polar additive to a completely nonpolar, *i.e.* octane. It is our intention to illustrate how changes in the hydrophobic interaction influence the self-association level of the alcohol. Although octane is a good representative for this purpose, a choice of just one solute can naturally not give a complete picture. The alcohols have been chosen to represent different self-association levels according to our previous data. A dilution with octane gives quite different results depending on the length of the hydrocarbon chain of the alcohol. Comparison of results at constant temperature (for instance 298 K) reveals that the reduction in viscosity is most pronounced for decanol and almost negligible for ethanol. A possible explanation is that the incorporation of octane into the hydrocarbon moiety of the alcohol does not leave the original self-association pattern invariant as long as the alcohol is hydrophobic enough. In the case of ethanol the viscosities could be explained by a "dilution" of the polymeric alcohol species with octane. Dielectric measurements have, however, shown that diluting ethanol with octane is accompanied by a large decrease in the dielectric constant indicating considerable reorientations in the OH-moments.³ In the case of decanol the alkane does not obviously cause large deviations in the direction of the hydroxylic OH-moments.

Fig. 1 shows that the solutions poorest in octane are most sensitive to change in temperature. The magnitude of the reduction in viscosity decreases when proceeding from decanol to ethanol. In this respect a parallel can be drawn to the dilution with the alkane. An increase in temperature should be accompanied by a breaking of hydrogen bonds and an enhanced flexibility of the hydrocarbon chains. Both these effects should lower the extent of self-association in the alcohol. Therefore it is not so surprising that the value of E^+ for the long-chain alcohol in Table 1 exceeds 20 kJ/mol, which is usually needed for a rupture of hydrogen bonds. The activation energies of the pure compounds reveal that the associated species become much more bulky and flow less easily when one proceeds from ethanol to decanol. One cannot, however, conclude from the increased viscosity whether the reduced fluidity is due to a higher monomeric association

or to the increase in hydrocarbon chain length.

This study together with our earlier ones indicates that long-chain alcohols, like decanol, certainly retain traces of the strict molecular arrangements characterizing the solid lipid alkanols.⁷ At the actual temperature a formation of linear complexes, probably even with a feature of a double-layer structure, seems to predominate in the solution. For short-chain alcohols, like ethanol, the solution structures seem to be more closed and compact, perhaps even with a cyclic character. A natural expansion of this picture would be the formation of clusters or clathrates in the shortest alcohol, *i.e.* water.

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