Viscosity of Binary Liquid Mixtures Involving Sulfolane and Alcohols

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Increasing use of non aqueous mixed solvents as media for electrochemical studies as well as for organic and inorganic reactions has prompted us to undertake a systematic investigation[1-4] of the behaviour of binary mixtures involving sulfolane (tetrahydrothiophene 1:1 dioxide). As a part of this work, the transport properties of binary systems of sulfolane (component 1) with nine normal or branched alcohols [methanol (2), ethanol (3), propanol (4), butanol (5), pentanol (6), isopropanol (7), isobutanol (8), sec-butanol (9) and ter-butanol (10)] are reported hereafter.

The purification of the sulfolane (kindly supplied by the Italian Shell Co., Industrial Division) and of the alcohols has been already reported[2, 4]. The measured physical values of the purified chemicals strictly agreed with literature data, but for n-pentanol (see Table 1). Viscosity measurements were made with suspended Ubbelohde bulb level viscometers under a moisture free atmosphere. Apparatus

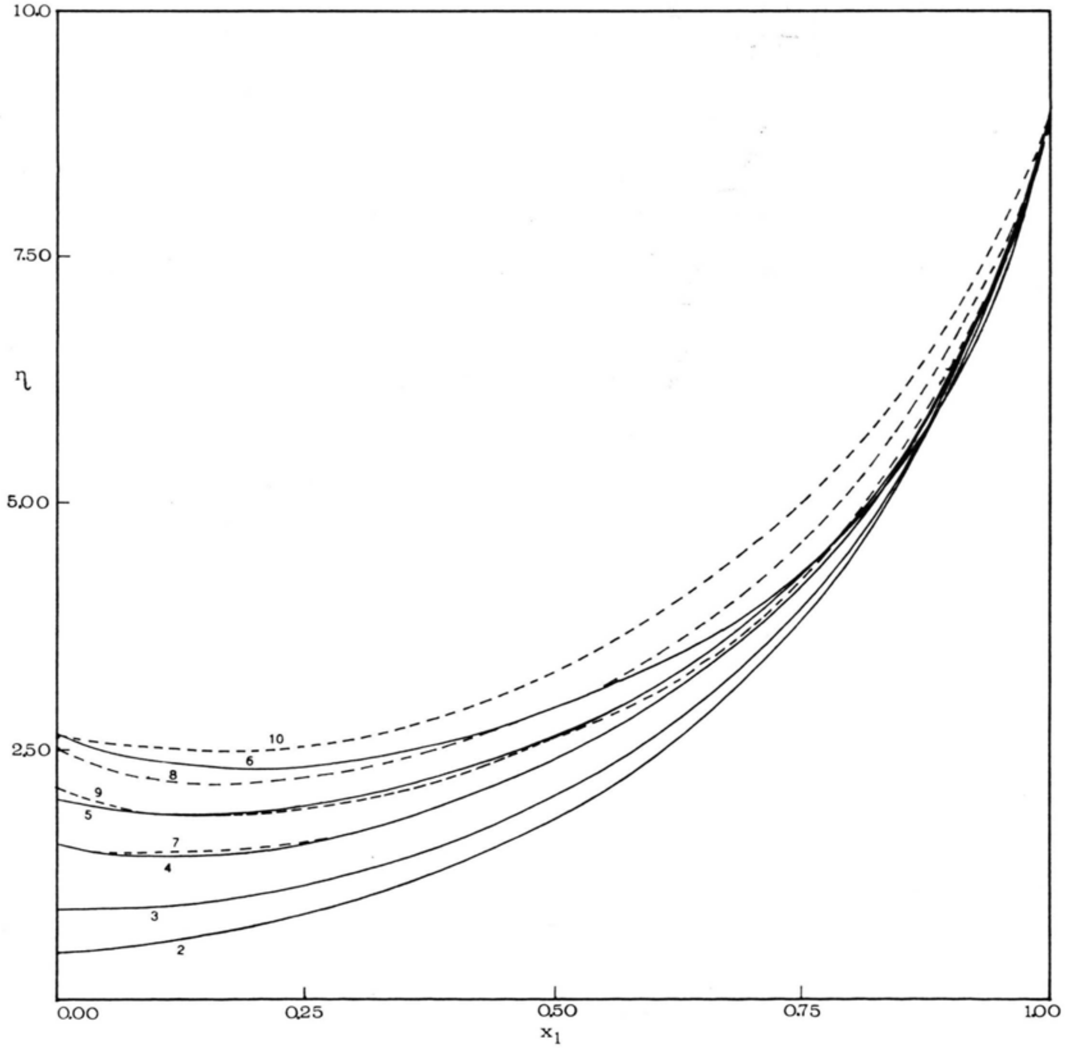

Fig. 1. Variation of viscosity (η) with mole fraction (x_1) of sulfolane at 35 °C, for the numbers of Table 2.

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Table 1. Properties of n-Pentanol at 25 °C.

	Present study	Lit. values
density (g/ml)	0.81098	0.81096 [a] 0.8116 [b] 0.8083 [c]
refractive Index	1.40794	1.40796 [d]
viscosity (cP)	3.491	3.556 [b] 3.347 [c] 3.441 [e] at 24.9 °C
dielectric const	13.92	13.90 [d]

[a] J. P. Bare and J. F. Skinner, J. Phys. Chem. **76**, 434 [1972].

[b] P. Bamelis, P. Huyskens, and E. Meeussen, J. Chim. Phys. **62**, 158 [1965].

[c] W. J. Jones, S. T. Bowden, W. W. Yarnold, and W. H. Jones, J. Phys. Coll. Chem. **52**, 753 [1948].

[d] Technique of Organic Chemistry, Vol. 7, p. 98 (Second Edition), Interscience Publishers Inc., New York 1955.

[e] L. H. Thomas and R. Meatyard, J. Chem. Soc. **1963**, 1986.

and procedure were already described[3]. Solutions were prepared by weight. Density measurements were reported in an earlier paper[4].

The viscosities of the mixtures, η, vs. the mole fraction x_1 are reported in Table 2 for $t = 30°$, $35°$ and 40 °C, whereas only the data at $35°$ are plotted in Figure 1. Concerning n.alcohols, the viscosities of the $(1+2)$ and $(1+3)$ mixtures steadily increase with sulfolane content, while the $(1+4)$, $(1+5)$, $(1+6)$ mixtures exhibit at $x_1 < 0.2$ viscosity minima, increasingly shifted towards the sulfolane richer region with increasing molar weight of the alcohol. In agreement with the Eyring equation:

$$\eta = (\mathcal{N} h/V) \exp\{-\Delta S^{\ddagger}/R\} \exp\{\Delta H^{\ddagger}/R T\}$$

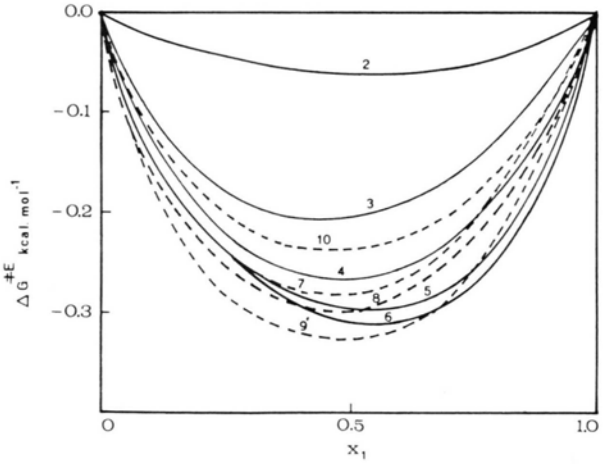

Fig. 2. Variation of the excess free energy of activation ($\Delta G^{\ddagger E}$) with the mole fraction of sulfolane (x_1) at 35 °C.

the plots $\log \eta V$ vs. $1/T$ are linear. They enable to calculate the enthalpy and entropy of activation of viscous flow, and to derive the $\Delta G^{\ddagger}$ values, at 35 °C, included in Table 2.

Assuming a linear dependence of $\Delta G^{\ddagger}$ on composition for ideal systems[5], the excess free energies of activation, $\Delta G_{35°}^{\ddagger E}$, were calculated and plotted vs. x_1 in Figure 2. They are negative over the entire composition range with minima (not far from $x_1 = 0.5$) which are the lower, the larger the carbon atom number of the alcohol (Fig. 3); only slight influences of branching are observed with the exception of the system containing ter-butanol, likely owing to the peculiar shape of the alcohol molecule.

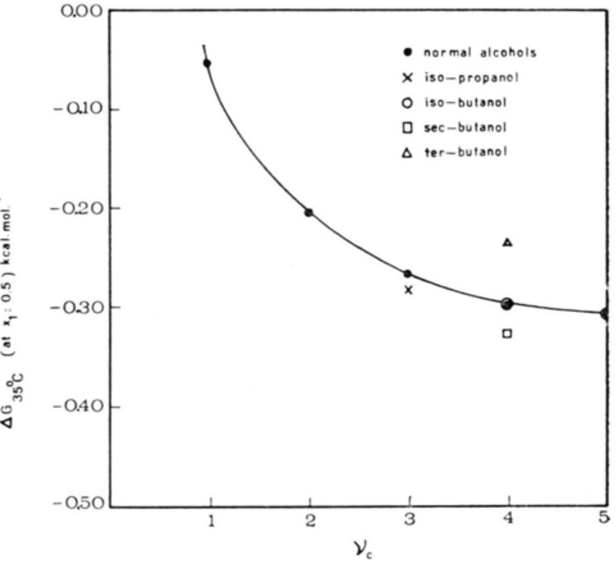

Fig. 3. Variation of the excess free energy of activation ($\Delta G^{\ddagger E}$) with the number of carbon atoms in alcohols (ν_c) at 35 °C and $x_1 = 0.5$.

An interpretation may be attempted in terms of alcohols self-association and of interactions between the binary components. As generally accepted[6], alcohols are self-associated by hydrogen bonds, though not strongly enough to form distinguishable dimers, etc. It results a continuous network structure of hydrogen bonded alcohol chains with hindered rotation around the hydrogen bonds and presumably with aligned dipoles[7]. The flow of such structured systems implies the passage of $-$OH groups past each other, resulting in higher values of viscosity with respect to less structured similar substances (homomorph hydrocarbons[8]).

Owing to its higher viscosity (the sulfolane is ~20 times more viscous than methanol and ~3 times more viscous than ter-butanol), the addition

Table 2. Viscosity and calculated thermodynamic parameters.

x_1	η in cP.			$\Delta G^{\ddagger}_{35\,^\circ\mathrm{C}}$ (kcal $\cdot$ mol^{-1})
	$t=30$ °C	$t=35$ °C	$t=40$ °C	
Sulfolane (1) + Methanol (2)				
0.0	0.507_5	0.474_5	0.444_5	2.38
0.0680	0.585_6	0.547_4	0.513_3	2.51
0.1103	0.651_2	0.608_1	0.568_6	2.60
0.1658	0.756_0	0.704_2	0.657_4	2.73
0.2274	0.899_9	0.834_4	0.778_7	2.87
0.3087	1.13_0	1.04_7	0.975_3	3.06
0.4056	1.49_5	1.37_8	1.27_9	3.28
0.5284	2.14_2	1.96_0	1.80_3	3.56
0.6422	3.02_5	2.75_3	2.51_5	3.82
0.7703	4.55_1	4.10_0	3.72_2	4.11
1.0	10.29_5	9.03_3	8.00_7	4.70
Sulfolane (1) + Propanol (4)				
0.0	1.73_9	1.54_9	1.38_4	3.47
0.0761	1.64_8	1.47_7	1.32_9	3.45
0.1702	1.73_1	1.55_1	1.39_9	3.49
0.2436	1.86_3	1.67_1	1.50_6	3.55
0.3357	2.09_3	1.87_6	1.69_1	3.63
0.4393	2.44_3	2.19_1	1.97_6	3.74
0.5374	2.89_4	2.59_5	2.34_2	3.87
0.6403	3.56_7	3.19_8	2.88_4	4.01
0.7554	4.71_4	4.21_4	3.78_8	4.19
0.8835	6.85_5	6.07_0	5.42_4	4.43
Sulfolane (1) + Pentanol (6)				
0.0	3.03_4	2.64_8	2.32_0	4.02
0.1119	2.68_6	2.36_6	2.09_6	3.94
0.2324	2.74_9	2.41_6	2.14_0	3.95
0.3323	2.95_1	2.57_8	2.27_8	3.98
0.4328	3.21_8	2.80_7	2.47_9	4.02
0.5236	3.48_9	3.08_2	2.72_9	4.07
0.6267	3.95_6	3.49_1	3.11_1	4.14
0.7208	4.59_4	4.07_7	3.64_1	4.23
0.8145	5.61_8	4.98_6	4.45_4	4.33
0.9043	7.27_3	6.44_1	5.73_5	4.48
Sulfolane (1) + Isobutanol (8)				
0.0	2.94_2	2.52_0	2.17_0	3.90
0.0598	2.60_6	2.26_1	1.97_1	3.83
0.1852	2.54_1	2.22_2	1.95_4	3.82
0.2590	2.64_8	2.31_9	2.04_5	3.84
0.3891	2.97_1	2.61_1	2.30_9	3.92
0.5066	3.41_6	3.01_7	2.68_1	4.01
0.5903	3.85_3	3.41_4	3.04_3	4.08
0.7089	4.76_3	4.22_9	3.77_8	4.22
0.7888	5.67_7	5.03_7	4.49_3	4.33
0.9464	6.70_8	7.66_7	6.78_6	4.58
Sulfolane (1) + Ter-butanol (10)				
0.0	3.40_2	2.65_8	2.09_6	3.95
0.1916	2.99_5	2.51_3	2.12_1	3.92
0.2786	3.12_0	2.64_4	2.26_6	3.95
0.3584	3.32_5	2.84_4	2.46_7	3.99
0.4717	3.71_2	3.21_3	2.80_6	4.05
0.5569	4.13_5	3.60_2	3.16_9	4.12
0.6312	4.59_5	4.02_2	3.55_3	4.19
0.7320	5.49_5	4.83_2	4.28_5	4.31
0.8339	6.74_7	5.93_8	5.26_4	4.43
0.9188	8.27_7	7.27_6	6.42_4	4.56
Sulfolane (1) + Ethanol (3)				
0.0	0.991_9	0.905_2	0.827_6	3.00
0.0680	1.00_8	0.924_7	0.848_2	3.03
0.1147	1.06_3	0.976_0	0.894_5	3.08
0.2119	1.24_1	1.13_5	1.03_9	3.20
0.2710	1.38_0	1.26_4	1.15_5	3.29
0.3740	1.69_6	1.54_6	1.41_7	3.43
0.4742	2.11_6	1.92_2	1.75_5	3.60
0.5738	2.69_1	2.43_6	2.21_6	3.77
0.7403	4.23_9	3.82_0	3.44_6	4.10
0.8574	6.14_1	5.47_0	4.89_9	4.35
Sulfolane (1) + Butanol (5)				
0.0	2.28_2	2.01_5	1.78_5	3.75
0.1066	2.08_4	1.85_5	1.65_9	3.70
0.1910	2.14_8	1.91_2	1.71_1	3.72
0.2871	2.32_0	2.06_0	1.84_2	3.77
0.3889	2.58_2	2.29_1	2.04_8	3.83
0.4851	2.91_4	2.59_0	2.31_6	3.91
0.5891	3.39_5	3.02_8	2.71_5	4.01
0.6937	4.11_7	3.67_6	3.30_0	4.13
0.7935	5.21_8	4.65_0	4.16_7	4.28
0.9023	7.19_2	6.36_9	5.66_9	4.47
Sulfolane (1) + Isopropanol (7)				
0.0	1.79_7	1.55_7	1.35_8	3.49
0.0756	1.63_4	1.43_8	1.27_1	3.45
0.1606	1.70_5	1.48_9	1.32_4	3.49
0.2446	1.82_3	1.61_6	1.44_2	3.54
0.3418	2.06_7	1.83_7	1.64_4	3.63
0.4362	2.38_6	2.12_8	1.90_8	3.73
0.5514	2.94_0	2.62_6	2.35_6	3.87
0.6552	3.66_2	3.27_4	2.94_5	4.02
0.7540	4.70_1	4.19_0	3.75_4	4.19
0.8754	6.71_3	5.99_2	5.33_2	4.42
Sulfolane (1) + Sec-butanol (9)				
0.0	2.54_5	2.13_3	1.80_0	3.79
0.0998	2.15_1	1.85_8	1.61_5	3.71
0.1988	2.16_1	1.88_4	1.65_5	3.72
0.2898	2.29_9	2.01_5	1.78_1	3.76
0.3908	2.55_0	2.24_6	1.99_3	3.83
0.4973	2.93_3	2.59_7	2.31_6	3.92
0.5943	3.42_8	3.04_9	2.72_8	4.03
0.7033	4.26_6	3.79_9	3.40_1	4.10
0.7800	5.13_8	4.57_6	4.09_7	4.26
0.9045	7.38_3	6.52_9	5.80_6	4.49

of sulfolane itself would result in an enhanced viscosity, if some additional effects did not overlap in determining the dependence of the viscosity on composition.

The presence of sulfolane, in fact, owing to the steric hindrance of its globular molecule, breaks the continuity of the network structure of alcohols, whence a decrease of viscosity would be expected. On the other hand, alcohol chain fragments may form clusters or rings and may interact, though weakly, with sulfolane itself. Also volume contractions on mixing[9] are to be taken into account. All these effects indeed reflect on viscosity (Fig. 1), resulting in a steady increase of viscosity on addition of sulfolane, for lower alcohols, where reasonably more remarkable interactions between unlike molecules are present; curves with minima are observed for higher alcohols where the structure breaking effect of sulfolane predominates at least at lower mole fractions. In other words, (sulfolane + alcohol)-systems may be thought of, at molecular level, as microregions of alcohol chain fragments and sulfoelane globular molecules, which more and more weakly interact with each other when the molar weigth of the alcohol increases, culminating in phase separation in the case of alcohols with more than seven carbon atoms. This is in agreement with the observed $\Delta G^{\neq E}_{35^\circ}$ behaviour. In fact, as stated elsewhere[5, 10], $\Delta G^{\neq E}$ values are negative in the case of solutions of not associated and self-associated substances, becoming the less negative and the more positive, the more noticeable are the interactions between unlike molecules.

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