

Viscosity behaviour of binary mixtures of non-polar solvents

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Abstract. The viscous nature of binary liquid solutions of non-polar solvents, viz. *n*-heptane, benzene, carbon tetrachloride and paraffin oil has been studied in terms of the deviation from the ideal law. The ideal law is supposed to take the form of (weighted) geometric mean. The viscous behaviour has been observed over a range of temperatures (298–322°K). The relative excess volume and relative excess enthalpy of activation have been evaluated to study the increase in viscosity associated with the shrinkage in mixing of its components.

Keywords. Relative excess volume; relative excess enthalpy; interspecific interaction parameter; viscosity behaviour; binary mixtures; non-polar solvents.

1. Introduction

The viscosity behaviour of binary liquid solutions has been discussed as the concept of an ideal solution with a view to consider particular systems departing more or less from the ideal law. Whether the ideal law should take the form of the (weighted) arithmetic, geometric or harmonic mean is not very clear. The viscous behaviour of various solutions of a few polar liquids has earlier been studied by Stairs (1980) in terms of their deviations from ideality. The components of the binary mixtures of two organics were also studied. The influence of variation in the viscosity of solvents (by mixing solvents of widely different viscosities in different concentrations) on the relaxation behaviour of some rigid polar liquids has been investigated by Chauhan *et al* (1981, 1982) and Saxena *et al* (1981). However, not much attention has so far been given to the investigations on the departure of this physical quantity in these binary solutions from the ideal law. Taking this in view, the present study on the viscosity behaviour of the mixtures comprising of *n*-heptane, benzene, carbon-tetrachloride and paraffin oil over the temperature range 298-322 K, has been undertaken. The quantity *H* is supposed to describe the deviation from the ideality behaviour. The relative excess volume and relative excess enthalpy of activation for viscous flow furnish information about the increase in viscosity associated with the shrinkage in mixing of its components. The results obtained have been discussed in terms of the ideal behaviour of the solutions.

2. Theory

In the case of an ideal binary solution, the absolute theory gives the excess thermo-

dynamic function, provided that the free enthalpy of activation (ΔG) should be additive on a mole fraction (x) basis,

$$\Delta G = \Delta G_1 x_1 + \Delta G_2 x_2; \quad (1)$$

subscripts 1 and 2 refer to the two components of binary mixture. This implies the geometric mean law,

$$\ln \eta_g = x_1 \ln \eta_1 + x_2 \ln \eta_2 \quad (2)$$

The free volume approach for the variation of η and with temperature suggests that the fluidity is dependent of relative free volume (V_0) as

$$\eta^{-1} = a\rho^{-1} = B(V - V_0)/V_0. \quad (3)$$

This was suggested by Hilderband (1971) for the variation of both viscosity (η) and density (ρ) as a modification of Batschinski (1973). The constant B is an insensitive function of molecular size and shape. V_0 is also known as intrinsic volume.

It is assumed that ideal solutions show no change in volume on mixing. This led to the expectation that if two kinds of molecules (of similar shape and size) are mixed, they would form an ideal solution and the fluidities should be additive. Since η_g is roughly the average value of arithmetic and harmonic mean fluidities, it may be defined as the ideal viscosity (η_i). The deviation from the ideal law is represented in terms of the quantity,

$$H = \eta/\eta_g = \eta/\eta_i \quad (4)$$

η , being the observed viscosity.

This relation suggests that the systems exhibiting large deviations may also exhibit negative deviations. If the free volume was necessary for flow, then shrinkage on mixing of components should be associated with the increase in the viscosity. This change is relative to the quantity H . V_0 may be obtained from the plot η^{-1} vs molar volume (V) Hilderband and Batschinski (relation 3) as the volume intercept. The ideal free volume $v (= V - V_0)$ exists if there had been no shrinkage and $v_i = v - V^E$. V^E , being the excess volume. It is negative because of shrinkage. In terms of volume equation (4) would become

$$H = \frac{B_i V_i / V_{oi}}{B_v / V_o}. \quad (5)$$

Assuming $B_i = B$ and $V_{oi} = V_o$, i.e. all the non ideality appears in terms of free volume, then

$$H = v_i / v = v_i / v_i + V. \quad (6)$$

Being a temperature-independent variable, the relative excess volume (as percentage) may be computed from,

$$\begin{aligned}
 V_r^E &= 100 \left(\frac{V - V_1 x_1 - V_2 x_2}{V_1 x_1 + V_2 x_2} \right), \\
 &= 100 \left(\frac{(x_2^{-1} - 1) M_1 / M_2 + 1}{\rho (x_2^{-1} - 1) M_1 / M_2 \rho_1 + 1 / \rho_2} - 1 \right), \quad (7)
 \end{aligned}$$

where V , ρ , M and x have their usual meanings.

As V_r^E is proportional to $x_1 x_2$, suggested by Baron (1912) and that to $\phi_1 \phi_2$ by Hilderband and Scott (1962) from (6), a linear characteristic H^{-1} vs V_r^E may be drawn which leads to the linearity of H^{-1} vs $\phi_1 \phi_2$ and H^{-1} vs $x_1 x_2$ plots.

The volume dependence of H^{-1} may be deduced by defining variables y_1 and y_2 as

$$\begin{aligned}
 y_1 &= [1 + (V_2/V_1)^K (x_2^{-1} - 1)]^{-1} \\
 y_2 &= 1 - y_1. \quad (8)
 \end{aligned}$$

Here K is an adjustable parameter y_1 and y_2 represented for K , 0 and 1 values are the mole fractions and volume fractions respectively. For $0 < K < 1$, y_1 and y_2 represent different compromises of which line fraction corresponds to $K = 1/3$ and area fraction to $K = 2/3$, since the viscosity involves the transfer of momentum across surface, within the fluid.

The dependence of H on $x_1 x_2$ has been predicted from absolute rate theory (Grunberg and Nissan 1949 and Katti and Chaudhari 1964) and is of the form

$$\ln H = - \frac{W}{RT} x_1 x_2, \quad (9)$$

where W is the interspecific interaction energy. The relative excess enthalpy G_r^E has been calculated as the uncertainty in the investigation of enthalpy of activation (ΔG) obtained from (1) and those obtained using Eyrings rate equations 1941 (from the plots of $\log \eta$ vs $1/T$). The various relations described above have been employed to study the three binary mixtures in the light of viscosity.

3. Experimental results

The three systems *viz* *n*-heptane + paraffin oil (PO), benzene + PO and *n*-heptane + carbontetrachloride (CCl₄) were investigated over the temperature range (298-322 K). These mixtures of non-polar solvents were prepared by mixing various percentages by volume (table 1).

The viscosity measurements were made by an Ostwald viscometer standardized at each temperature. The chemicals used were distilled twice before use and their boiling points were checked against their literature values.

The temperature-independent parameters, relative excess volume (V_r^E), relative excess enthalpy (G_r^E) and the observed and calculated enthalpies of activation have

Table 1. Relative excess volume and relative excess enthalpy along with enthalpy of viscous flow $y_1 y_2$ values.

Concentration		$y_1 y_2$	G (kJ mol ⁻¹)		$-V_r^R$ %	$-G_r^E$ %
1 %	2 %		Cal.	Obs.		
<i>n</i> -heptane + paraffin oil ($K = 0.82$)						
100	00	—	4.504	4.504	—	—
90	10	0.180	5.585	5.470	0.065	2.06
80	20	0.242	6.664	6.462	0.097	2.90
70	30	0.245	7.748	7.471	0.115	3.57
60	40	0.228	8.829	8.508	0.126	3.64
50	50	0.195	9.910	9.572	0.135	3.41
40	60	<u>0.156</u>	10.990	10.562	0.135	3.89
30	70	0.116	12.072	11.681	0.132	3.24
20	80	0.076	13.154	12.763	0.137	2.47
10	90	0.038	14.235	13.923	0.136	2.19
00	100	—	15.316	15.316	—	—
Benzene + paraffin oil ($K = 0.84$)						
100	00	—	10.560	10.560	—	—
80	20	0.250	11.112	10.940	0.082	1.55
60	40	0.194	11.664	11.342	0.109	2.78
40	60	<u>0.120</u>	12.216	11.781	0.113	3.57
20	80	0.051	12.768	12.258	0.127	4.06
00	100	—	13.322	13.322	—	—
<i>n</i> -heptane + CCl ₄ ($K = 0.66$)						
100	00	—	2.991	2.991	—	—
90	10	0.069	3.148	3.140	-0.144	0.06
80	20	0.130	3.304	3.251	0.078	1.60
70	30	0.181	3.461	3.306	0.082	4.48
60	40	0.291	3.618	3.472	0.061	4.04
50	50	0.244	3.775	3.751	0.032	0.64
40	60	<u>0.250</u>	3.931	4.003	-0.063	-2.36
30	70	0.234	4.088	4.240	-0.101	-3.72
20	80	0.191	4.245	4.432	-0.212	-4.41
10	90	0.115	4.401	4.586	-0.360	-3.89
00	100	—	4.558	4.558	—	—

The underlined $y_1 y_2$ values are those at which maximum values of $H = \eta/\eta_1^{x_1} \eta_2^{x_2}$ were attained.

been reported in table 1, along with the product $y_1 y_2$, calculated from (8). The variation of non-ideality H at 306 K and that of V_r^E and G_r^E with the change in the mole fraction of component 2 (x_2) has been exhibited in figures 1, 2 and 3 respectively. In table 2, the maximum values of deviation from ideality, H_{\max} and the relative excess volume, V_r^E , have been given along with interspecific interaction parameter (W) at each temperature investigated.

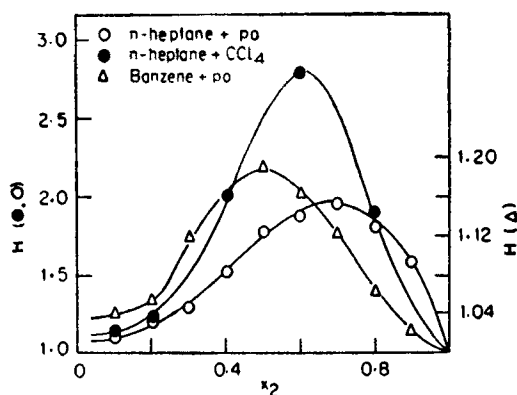


Figure 1. Variation of deviation from ideality (H) with mole fraction x_2 .

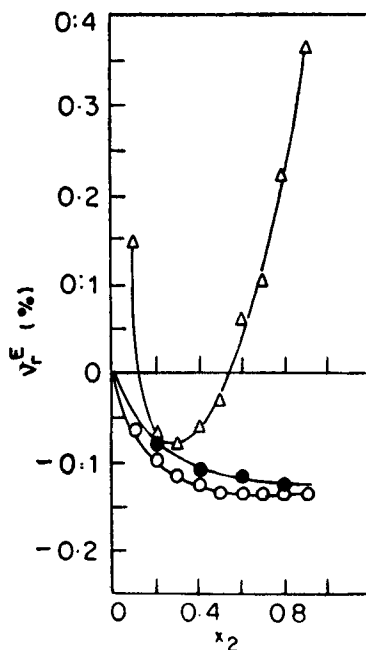


Figure 2. Variation of relative excess volume (V_r^E) with mole fraction x_2 .

4. Discussion

Since the two systems of the three investigated *i.e.*, *n*-heptane + PO and benzene + PO have components of widely different viscosities they exhibit only the shrinkage in molar volume on the mixing of its components. The third system, *n*-heptane + carbon tetrachloride exhibits both the positive and negative values of V_r^E and G_r^E parameters suggesting both decrease and increase in viscosity on the mixing of its components *i.e.* both the expansion and shrinkage of molar volume.

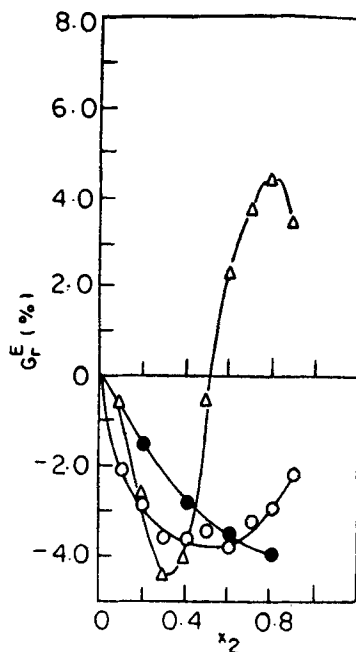


Figure 3. Variation of relative excess enthalpy (G_r^E) with mole fraction x_2 .

Table 2. Maximum values of deviation from ideality $H = \eta/\eta_1^{x_1}\eta_2^{x_2}$ and relative excess volume along with interspecific interaction parameter.

Components	1	2	$W = 4RT \ln H_{\max}$		$-V_r^E(\max)$ %	W kJ mol^{-1}
			Temperature K	H_{\max}		
<i>n</i> -heptane		PO	298	1.95	1.37	6.38
			306	1.96		6.60
			314	1.93		6.62
			322	1.89		6.57
benzene		PO	306	2.79	1.27	10.06
			314	2.77		10.25
			322	2.72		10.32
<i>n</i> -heptane		PO	298	1.17	0.32	1.50
			306	1.19		1.71
			314	1.19		1.75
			322	1.16		1.62

4.1 *n*-heptane + paraffin oil

In this binary system, the viscosity of individual components is 4.8 mp and 43.4 mp, at 298 K, of *n*-heptane and PO respectively. The maximum deviation from ideality H_{\max} (1.95) (figure 1) occurs at the concentration 40% *n*-heptane + 60% PO respec-

tively. The occurrence of maximum deviation to more viscous component may be due to its non-associative nature *i.e.* absence of H-bonding constituents. Stairs (1980), observed that in acetone + water mixture, the maxima occur at the large percentage of water component, exhibiting the presence of large extent of hydrogen bonds. Hence it may be suggested that in the binary mixtures of non-hydrogen bonding components the factor responsible for maximum non-ideality is viscosity of the more viscous component.

The negative V_r^E (relative excess volume) values indicate the shrinkage in volume for all concentrations investigated. This may be considered to have resulted from the widely different viscosities of the components. The negative relative excess enthalpy of activation (G_r^E) also supports the concept of shrinkage of volume resulting in decrease in the internal energy of the viscous flow. The interspecific interaction parameter W varies from 6.38 to 6.62 kJ mol⁻¹ over the temperature range 298-322 K.

4.2 Benzene + paraffin oil

This system being similar to the system discussed earlier in viscosities of individual parameters give position of maxima of non-ideality (H) at similar concentration (40% benzene + 60% PO). The variation of V_r^E and G_r^E parameters with mole fraction x_2 (component 2) is similar to that of *n*-heptane + PO mixture (figures 2 and 3). All the relative excess parameters are of negative values. The interspecific interaction parameter W for this system ranges from 10.06 to 10.32 kJ mol⁻¹ over the temperature range 306-322 K. The H_{\max} values (table 2) are highest in all the three systems investigated. This may be attributed to the ring structure of benzene as compared to the straight chain of *n*-heptane molecule, causing hindrance in the viscous flow of the binary mixture.

4.3 *n*-heptane + carbon tetrachloride

In this system the two components investigated are of approximately equal individual viscosities *i.e.* *n*-heptane (4.8 mp) and CCl₄ (10.7 mp). The occurrence of H_{\max} value is at 50% *n*-heptane + 50% CCl₄ concentration. The H_{\max} at this concentration supports that the only governing factor of the deviation from ideality is the viscosity of individual components in the case of the non-hydrogen bonding solvents. The H_{\max} varies from 1.19 to 1.17 over the temperature range (298-322 K), whereas the interaction parameter W varies from 1.76 to 1.50 kJ mol⁻¹.

The excess relative parameters V_r^E and G_r^E (table 1) for this system exhibit both the positive and negative values. The V_r^E and G_r^E values for mixtures of varying concentrations, 80% *n*-heptane + 20% CCl₄ to 50% *n*-heptane + 50% CCl₄ are negative. The minima of G_r^E and V_r^E parameters occur at the 70% *n*-heptane + 30% CCl₄ concentration. With increasing percentage of CCl₄, the two parameters exhibit sharp rise and attain positive values at and beyond 40% *n*-heptane + 60% CCl₄. This increase may be due to the large number of CCl₄ molecules of smaller size. These values of V_r^E and G_r^E parameters exhibit expansion in the volume and the

increase in the enthalpy of viscous flow in the mixing of its component compromises as observed by Stairs (1980) and Hilderband (1971) in the case of two alcohols and two acids.

5. Conclusion

Neither mole fraction nor volume fraction, nor any single compromise best describe the data for all types of systems. Further, when a similar fit of excess volume data to an analogous expression was tried for a few systems, it was found that the required K values differed for the best value for viscosity to the maxima in H and V_r^E occur at different compositions.

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