

Viscosities of binary liquid mixtures of polar-apolar and polar-polar systems at 303.15 K

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Abstract. Viscosities for the binary liquid mixtures of methylethylketone with benzene, toluene, chlorobenzene, bromobenzene and nitrobenzene were determined at 303.15 K. The deviation in viscosity was calculated and its behaviour was studied as a function of mole fraction. The deviation in viscosity is negative in the system methylethylketone with benzene and is positive in the other systems. The results are discussed in terms of dipole-induced dipole and dipole-dipole interactions.

Keywords. Excess viscosity; molecular interactions; polarizability.

1. Introduction

As part of a study of viscosities of liquid mixtures (Reddy and Naidu 1979, 1981) we have measured the viscosities for methylethylketone with benzene, toluene, chlorobenzene, bromobenzene and nitrobenzene to investigate the molecular interactions. These systems have been selected for studying the effect of molecular interactions due to substitution of different groups on benzene ring, along with benzene in presence of a polar component. A literature survey has shown that the viscosity data for these systems have not been reported except for methylethylketone with benzene system at 308.15 K (Yadava and Yadava 1981).

2. Experimental

Viscosities of pure liquids and mixtures were measured at 303.15 K using an Ostwald viscometer and were accurate to 0.5 per cent. Densities for the pure components were measured using a bicapillary pycnometer and in case of mixtures densities were obtained from excess volume, V^E , data (Jayalakshmi and Reddy 1983) using the relation

$$\rho = \frac{x_1 M_1 + x_2 M_2}{x_1 V_1 + x_2 V_2 + V^E} \quad (1)$$

Density values in both the cases were accurate to $\pm 5 \times 10^{-5} \text{ g cm}^{-3}$.

Methylethylketone, benzene and toluene (all ВДН) were purified by methods described earlier (Reddy and Naidu 1977, 1978). Chlorobenzene (ВДН), bromobenzene

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(E Merck) and nitrobenzene (BDH) were dried over calcium chloride and fractionally distilled. The purity of the samples was ascertained by comparing the values of density, boiling point and refractive index with the literature values (Timmermans 1950, 1965).

3. Results and discussion

The values of density and viscosity are given in table 1. Excess viscosities are calculated using the relation

$$\Delta \ln \eta = \ln \eta - (x_1 \ln \eta_1 - x_2 \ln \eta_2). \quad (2)$$

The values of $\Delta \ln \eta$ are accurate to ± 0.005 and are included in table 1. Excess viscosities are represented by an empirical equation of the form

$$\Delta \ln \eta = x_1 x_2 [A_0 + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2]. \quad (3)$$

The values of the constants A_0 , A_1 and A_2 are obtained by the method of least squares and are given in table 2 along with the standard deviation $\sigma(\Delta \ln \eta)$.

The data included in table 1 show that the excess viscosity is negative in the system methylethylketone with benzene and the values are positive in the remaining systems. The observed data may be explained on the basis of the following factors, mutual loss of dipolar association due to addition of second component and difference in polarizabilities, size and shape of the components (Yadava and Yadava 1981). In the system methylethylketone with benzene, the dipolar association of ketone breaks when benzene is added, further a weak dipole-induced dipole interaction may arise between unlike components. As a result the mixture becomes more fluid (less viscous) than the pure components and the deviation in excess viscosity becomes negative. The positive deviation in excess viscosity observed in the system methylethylketone with toluene may be ascribed to the presence of a methyl group in toluene which increases the π -electron density in the aromatic ring due to the hyperconjugation effect. Consequently, molecular interactions may be enhanced in mixtures and become less fluid than the pure components. In the systems methylethylketone with chlorobenzene, bromobenzene and nitrobenzene a strong dipole-dipole interaction may be present between unlike molecules. Thus the flow may be further decreased and excess viscosity becomes more positive. The algebraic values of $\Delta \ln \eta$ fall in the order shown for the five systems:

$$\text{benzene} < \text{toluene} < \text{nitrobenzene} < \text{chlorobenzene} < \text{bromobenzene}.$$

This order is not in parallel with the order in polarizabilities of the noncommon components. On the basis of polarizabilities $\Delta \ln \eta$ values are expected to be more positive in the system methylethylketone with nitrobenzene than in the systems methylethylketone with chlorobenzene and bromobenzene. This discrepancy in the order may be attributed to the difference in size and shape of the substituted groups.

The values of the coefficients A_0 , A_1 and A_2 given in table 2, indicate the nature of molecular interactions with respect to mole fraction (Prausnitz 1969). The values of A_0 and A_2 may contribute to the understanding of the extent of symmetric interactions whereas the values of A_1 suggest the extent of unsymmetric interactions. The percentage contribution of A_1 increases from benzene to nitrobenzene. This shows that the molecular interactions become more unsymmetric in polar-polar systems than in

Table 1. Mole fraction of methylethylketone x_1 , densities ρ , viscosities η , and excess viscosities at 303.15 K.

x_1	$\frac{\rho}{\text{g cm}^{-3}}$	$\frac{\eta}{\text{CP}}$	$\ln \eta$	$\Delta \ln \eta$
<i>Methylethylketone + benzene</i>				
0.0000	0.86841	0.573	-0.557	—
0.1023	0.86122	0.538	-0.620	-0.021
0.2042	0.85405	0.509	-0.675	-0.033
0.3950	0.84045	0.467	-0.762	-0.041
0.5129	0.83179	0.444	-0.811	-0.037
0.6822	0.81905	0.420	-0.868	-0.027
0.8530	0.80587	0.396	-0.926	-0.014
1.0000	0.79443	0.378	-0.973	—
<i>Methylethylketone + toluene</i>				
0.0000	0.85922	0.531	-0.634	—
0.1009	0.85426	0.516	-0.661	0.006
0.2412	0.84681	0.496	-0.701	0.014
0.3948	0.83807	0.475	-0.744	0.023
0.5240	0.83010	0.458	-0.781	0.030
0.7006	0.81815	0.431	-0.842	0.029
0.8899	0.80368	0.397	-0.942	0.012
1.0000	0.79443	0.378	-0.973	—
<i>Methylethylketone + chlorobenzene</i>				
0.0000	1.09660	0.721	-0.327	—
0.0982	1.07118	0.686	-0.377	0.013
0.2470	1.03102	0.636	-0.452	0.034
0.3771	0.99433	0.593	-0.523	0.047
0.5481	0.94370	0.541	-0.614	0.067
0.6776	0.90350	0.499	-0.695	0.069
0.8508	0.84673	0.482	-0.730	0.046
1.0000	0.79443	0.378	-0.973	—
<i>Methylethylketone + bromobenzene</i>				
0.0000	1.48440	1.007	0.007	—
0.1487	1.39665	0.899	-0.106	0.032
0.2073	1.36081	0.858	-0.153	0.042
0.3888	1.24529	0.740	-0.301	0.072
0.5263	1.15241	0.656	-0.422	0.086
0.7046	1.02473	0.556	-0.587	0.096
0.8307	0.92914	0.486	-0.720	0.087
1.0000	0.79443	0.378	-0.973	—
<i>Methylethylketone + nitrobenzene</i>				
0.0000	1.19330	1.613	0.478	—
0.1487	1.14328	1.320	0.278	0.016
0.3244	1.08003	1.039	0.039	0.032
0.4126	1.04681	0.925	-0.078	0.043
0.4992	1.01309	0.820	-0.198	0.048
0.7145	0.92461	0.607	-0.501	0.059
0.7800	0.89614	0.550	-0.598	0.056
1.0000	0.79443	0.378	-0.973	—

Table 2. The constants of (3) and the standard deviation.

Methylethylketone+	A_0	A_1	A_2	$\sigma(\Delta \ln \eta)$
Benzene	-0.151	0.076	-0.027	0.001
Toluene	0.115	0.043	-0.033	0.002
Chlorobenzene	0.250	0.151	0.024	0.002
Bromobenzene	0.335	0.265	0.222	0.003
Nitrobenzene	0.197	0.172	0.102	0.001

+ Signifies the representation of mixture, for example, methylethylketone benzene, etc.

polar-apolar systems. This behaviour is also evident from excess viscosity versus mole fraction data in which the maximum values of $\Delta \ln \eta$ are shifting towards higher mole fractions of ketone in the series from benzene to nitrobenzene.

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