Viscosities of binary liquid mixtures of polar

and non-polar solvents at 303.15 k

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Abstract – *explain the various characteristics of liquid and liquid mixtures. In this paper viscosities for the binary liquid mixtures of methyl ethyl ketone with benzene, nitrobenzene, cblorobenzene and bromobenzene were determined at 303.15 K. The deviation in viscosity was calculated and its behaviours was studied as a function of mole fraction. The deviation in viscosity is negative in the system methyl ethyl ketone with benzene and is positive in the other systems. The results were discussed in terms of interactions.*

Key words: Viscosity, molecular interactions, excess viscosity and polarizability.

1. INTRODUCTION

Pioneering attempts have been made by several workers [1-4] to study the interactions in the binary liquid mixtures but only a few [5-7] has used the viscosity data for this purpose. In this paper we have found the viscosities of different liquids from the literatures and then calculated the viscosities of the mixtures derived in the theoretical part.

2. THEORETICAL CALCULATION :

The following relation [8] has been given for the actual value of fluidity of the mixture,

$$\phi_m(\alpha) = \frac{V_m}{hN} \exp - \left\{ \left[\left(x_1 \Delta E_1 + x_2 \Delta E_2 \right) / 2.45 \frac{-\Delta G_m}{2.45} \right] / RT \right\} \tag{1}$$

where, $\phi_m(\alpha)$ = fluidity of the mixture, V_m = molar volume of the mixture, h = Plank's constant, N = Avogadro's number, ΔE_1 and ΔE_2 = energy of vaporization of the components whose mole fractions are x_1 and x_2, respectively, ΔG_m = excess free energy of mixture, R = gas constant, and T = temperature in absolute. Rewriting the above equation in terms of viscosity of the mixture $[\eta_m(a)]$ and taking logarithm on both sides, one gets,

$$\ln \eta_m(a) = \ln \frac{V_m}{hN} = \left(\frac{x_1 \Delta E_1 + x_2 \Delta E_2}{2.45 \ RT} \right) - \frac{\alpha \ \Delta G_m}{RT} \tag{2}$$

The fraction $\dfrac{1}{2.45}$ of the excess free energy of mixing in equation (1) has been represented by a in equation (2). But remembering that $\Delta G^* = \Delta G/2.45$ (energy of activation), the viscosity of ideal mixture in the light of equation.

$$\phi_m(i) = \frac{V}{hN} \exp \left\{ -\left(x_1 \Delta G_1^* + x_2 \Delta G_2^* \right) / RT \right\} \tag{3}$$

takes the following form,

$$\ln \eta_m(i) + \ln \frac{V}{hN} = \frac{x_1 \Delta E_1 + x_2 \Delta E_2}{2.45 \ RT} \tag{4}$$

and from equations (3) and (4) we obtain,

$$\alpha \ \Delta G_m = - RT \left[\ln \eta_m(a) - \ln \eta_m(i) \right] \tag{5}$$

Katti et al [5] proposed the following equation for the theoretical evaluation of viscosity,

$$\ln \eta_m(a). \ V_m = x_1 \ln \eta_1 \ V_1 + x_2 \ln \eta_2 \ V_2 + x_1 x_2$$

$$= \frac{W_{vis}}{RT} \tag{6}$$

where, W_{vis} represents the interaction energy between the components. Hind et al. used the following expression for the viscosity of a liquid mixture,

$$\eta_{mix} = x_1^2 \ \eta_1 + 2x_1 x_2 \ \eta_{12} + x_2^2 \ \eta_2 \tag{7}$$

where, η_1 and η_2 are the viscosities of pure liquid components whose mole fractions are x_1 and x_2 and x_{12} is the viscosity at equimolar concentrations. The value of η_{12} is obtained by the relation,

$$\eta_{12} = 0.5 \ \eta_{(m)1} + 0.5 \ \eta_{m(2)}$$

This value of η_{12} is used to obtain rim at other compositions.

The viscosity of a liquid mixture according to Frenkel [9,] and Naidu [10] is obtained by the following two different equations, respectively,

$$\log \eta_m(a) = x_1 \log \eta_1 + x_2 \log \eta_2 + 2x_1 x_2 \log \eta_{12} \tag{8}$$

$$\ln \eta_m = x_1^2 \ln \eta_1 + x_2^2 \ln \eta_2 + 2x_1 x_2 \ln \eta_{12} \tag{9}$$

3. RESULTS & DISCUSSION :

We have the relation for the density as given below

$$\rho = \frac{x_1 M_1 + x_2 M_2}{x_1 V_1 + x_2 V_2 + V^E} \tag{10}$$

where, Y^E is the excess volume.

We can calculate the excess volume (V^E) from above equation. The values of density and viscosity are obtained from the standard tables. Excess viscosities are calculated using the relation.

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

Table 1. Mole fraction of methyl ethyl ketone x_i, densities ρ, viscosities η, and excess viscosities at 303.15 k.

x_1	$\dfrac{\rho}{gcm^{-1}}$	$\dfrac{\eta}{CP}$	$\ln\eta$	$\Delta \ln\eta$
Methyl ethyl ketone + Benzene M				
0.0000	0.86730	0.584	-0.558	–
0.1023	0.86011	0.549	-0.621	-0.031
0.2042	0.85294	0.520	-0.676	-0.043
0.3950	0.83934	0.478	-0.663	-0.051
0.5129	0.83068	0.455	-0.612	-0.047
0.6822	0.81794	0.431	-0.927	-0.047
0.8530	0.80476	0.407	-0.974	-0.024
1.0000	0.79332	0.389	–	–
Methyl ethyl ketone + Nitrobenzene				
0.0000	1.19219	1.624	0.479	–
0.1487	1.14217	1.331	0.279	0.026
0.3244	1.07892	1.050	0.040	0.042
0.4126	1.04570	0.936	-0.079	0.053
0.4992	1.01198	0.831	-0.199	0.058
0.7145	0.92350	0.618	-0.502	0.069
0.7800	0.89503	0.561	-0.599	0.066
1.0000	0.79332	0.389	-0.974	–
Methyl ethyl ketone + Chlorobenzene				
0.0000	1.09549	0.732	-0.328	–
0.0982	1.07007	0.697	-0.378	0.023
0.2470	1.02991	0.647	-0.453	0.044
0.3771	0.99322	0.604	-0.524	0.057
0.5481	0.94159	0.552	-0.615	0.077
0.6776	0.90239	0.510	-0.696	0.079
0.8508	0.84562	0.493	-0.731	0.056
1.0000	0.79332	0.389	-0.974	–
Methyl ethyl ketone + Bromobenzene				
0.0000	1.48329	1.018	0.008	–
0.1487	1.39554	0.910	0.107	0.042
0.2073	1.35970	0.969	0.154	0.052
0.3888	1.24418	0.751	0.302	0.082
0.5263	1.15130	0.667	0.423	0.096
0.7046	1.02362	0.567	0.588	0.106
0.8307	0.92803	0.497	0.721	0.097
1.0000	0.79332	0.389	0.974	–

$$\Delta \ln \eta = \ln \eta - (x_1 \ln \eta_1 - x_2 \ln \eta_2) \tag{11}$$

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

$$\Delta \ln \eta = x_1 x_2 \left[A_0 + A_1 (x_1 - x_2) + A_2 (x_1 - x_2)^2\right]$$

(12)

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 $\sigma (\Delta \ln \eta)$.

Table 2. The constant 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
Nitrobenzene	0.197	0.172	0.102	0.001
Chlorobenzene	0.250	0.151	0.024	0.002
Bromobenzene	0.335	0.265	0.222	0.003

+ Signifies the representation of mixture, for example, methyl-ethylketone benzene etc.

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 [11]. 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 derivation in excess viscosity becomes negative. The positive deviation in excess viscosity observed in the system methylethylketone with chlorobenzene may be ascribed to the presence of a methyl group in chloro benzene 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 nitrobenzene, chlorobenzene, and bromobenzene 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 :

benzene < nitrobenzene < chlorobenzene < bromobenzene.

This order is not in parallel with the order in polarizabilities of the noncommon components. On the basis of polarizabilities A hi fl 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 contributions of A_1 increases from benzene to nitrobenzene. This shows that the molecular interactions become more unsymmetric in polar-polar systems than in polar–polar 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. Obtained from the standard tables. Excess viscosities are calculated using the relation

REFERENCES

1. Gugganheim, E.A., "Mixtures", Oxford University Press, Oxford (1952).
2. Reddy, K.C., Subrahthanyan, S.V. and Bhimsenachar, J.C., J. Physics, Soc., Jpn., 19, 539 (1964). 21
3. Zabransky, M., Ruzicka, V., Domalski, E.S., J. Phys. Chem. Ref. Data, 30, 1199 (1964).
4. Medeiros, M.J., Phys. Chem. B, 108, 2676 (2004).
5. Katti, P.K. and Chaudhuri, M.M., J. Chem. Eng., Data, 9, 1442 (1944).
6. Ram Moorthy, K., Indian J. Pure Appl. Phys., 11, 554 (1973).
7. Liovell, F. Peters, C.J., Vega, L.F., Fluid Phase Equilib., 248, 115 (2006).
8. Glasstone, S., Laidler, K.J. aad Eyring H., "The Theory of Rate Process", McGraw-Hill, New York 01941).
9. Frenkel, Petroleum (London), 9, 27 (1946).
10. Naidu, P.K., Aust. J. Chem., 23, 967 (1970).
11. Yadava, R.R. and Yadava, S.S., Indian J Chem., 20, 221 (1981).
12. Maxsudov, D. (2019). THE DEVELOPMENT OF TRANSMITTED AND RATIONAL TAFSIRS. *The Light of Islam*, *2019*(1), 9.
13. Махсудов, Д. (2020). Развитие исламоведения (корановедения) в Узбекистане: история и современность. *Вестник КазНУ. Серия религиоведение*, *21*(1), 60-67