TEMPERATURE DEPENDENCE OF THE VISCOSITY OF ORGANIC BINARY LIQUID MIXTURES

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THE study of viscosity behaviour of organic binary liquid mixtures attention has focussed on any departures from the ideal behaviour as depicted by the law of arithmetic, geometric or harmonic mean of the viscosities of individual components[1]. However, recently such investigations have also been extended[2] to understand the viscosity behaviour of binary mixtures in terms of the Eyring[3] or Hildebrand[4] theories of fluid viscosity. In the present paper we report our results on the viscosity behaviour of 1:9 mixtures by volume fraction of toluene and cyclohexane, and of toluene and paraffin along with that of neat toluene over a temperature range 293–353°K. These systems were chosen because they offer two extreme cases in which the individual components in the toluene-cyclohexane mixture have almost similar viscosities whereas in the case of toluene-paraffin mixture they have dissimilar viscosities[5, 6]. Analysis of our results in terms of the Eyring model conforms to the temperature (T) dependence of viscosity (η) as was described by Eyring on the basis of absolute reaction rate theory.

Eyring derived a relation describing the temperature dependence of liquid viscosity which may be expressed[3] as

$$\eta = \eta' \exp (W/\mathrm{kT}), \qquad (1)$$

where k is the Boltzmann constant, η' a constant for a given liquid system which involves Planck's constant and average molar volume of the constituent molecules in a mixture, and W the activation energy per molecule for the viscous flow. Evidently from (1) we see that a plot of ln η versus $1/T$ is linear with intercept ln η' and slope W/k. Thus from the experimental value of slope we can evaluate W, the constant k being known.

In the experiment, viscosities at different temperatures of neat toluene (TN), the toluene-cyclohexane (TC) and the toluene-paraffin (TP) mixture were determined[6, 7] by using standard Ostwald viscometers of appropriate ranges and a temperature regulated waterbath whose temperature could be controlled within an accuracy of ± 0.01°C. Further, for estimating the values of viscosity, the densities of these liquid systems were determined at different temperatures by using a density bottle. The chemicals used were of analytical grade. Our experimental values of viscosity were reproducible to within 5%. Our viscosity values for neat toluene also fairly agree with reported[8] values.

In figure 1 we plot our experimental values of ln η versus $1/T$ for dilute mixtures and for the neat toluene. The experimental points lie very close to the least square fit straight line in each case and no experimental point deviates from the respective least squares fit straight line by more than 1%, thus establishing the validity of equation (1) for application to mixtures and to neat toluene. The least square fit values of the activation energy per mole of viscous flow for neat toluene, the toluene-cyclohexane and the toluene-paraffin mixture are estimated respectively to be 2.2, 2.9 and 7.2 kcal. As the viscosity of TP system is much higher than that of TC and TN systems and the viscosity of TC system, in turn, is slightly higher than that of TN system at all the temperatures, the values of activation energy for these liquid systems are in qualitative agreement with the Eyring theory. In Eyring's formulation of viscosity a liquid is considered as more or less a regular array of molecules with occasional holes in the medium and hence if a molecule has to jump into a

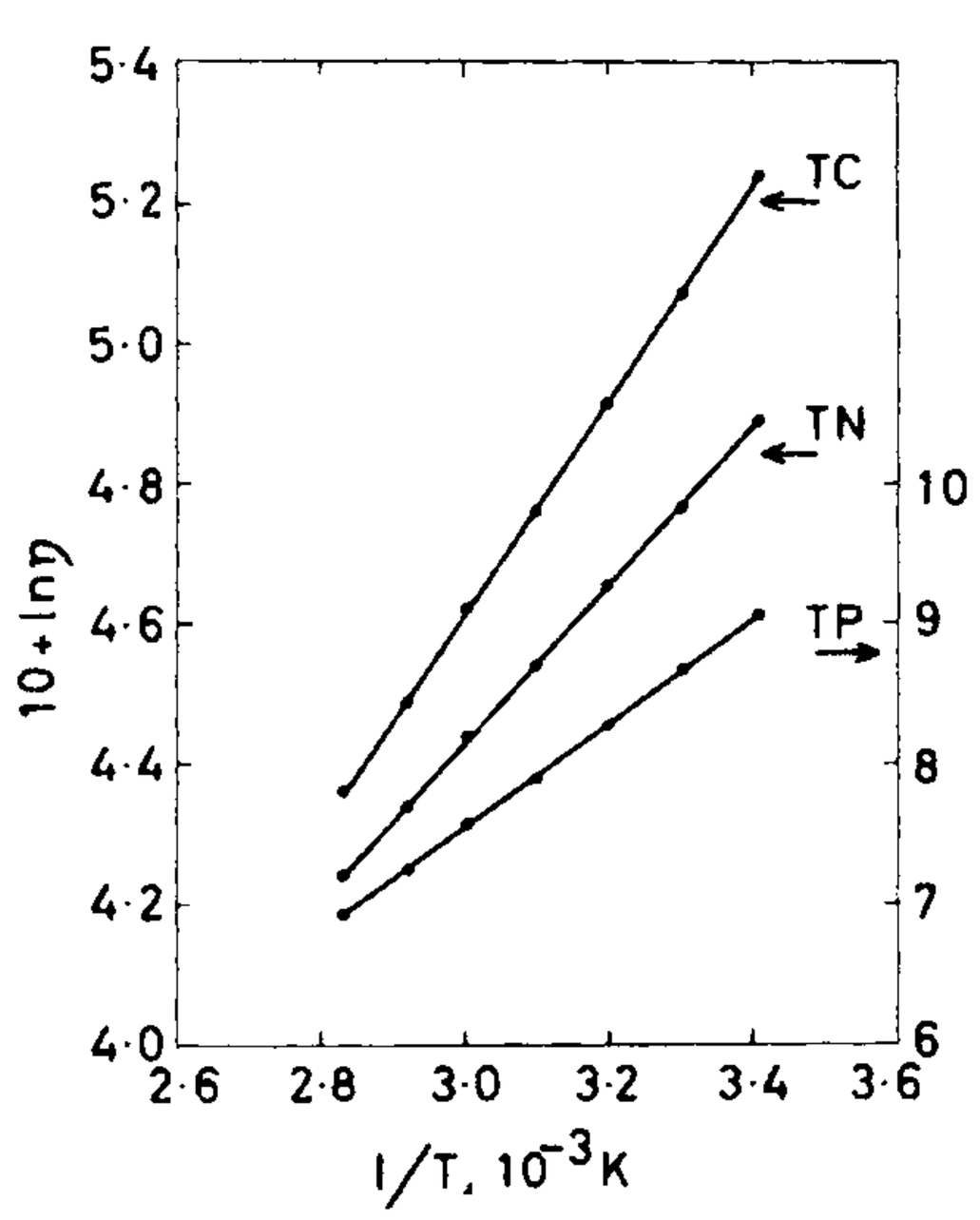

Figure 1. Eyring plot of temperature dependence of viscosity for the neat toluene (TN), the toluene-cyclohexane (TC), and the toluene-paraffin (TP) systems.

hole and thus move from one equilibrium position to another it certainly requires greater energy in a viscous system comprising larger molecules than in a relatively less viscous system comprising smaller molecules. Thus because of the larger size of paraffin molecules and stronger intermolecular forces the activation energy per mole for viscous flow in TP system is greater compared to that in TC and TN systems and evidently slightly greater in TC system compared to that in TN system. However, for a more quantitative understanding of the viscosity behaviour of binary mixtures in terms of their constituent parts, a study over a wide range of temperature comprising mixtures of precise molecular constituents is essential.

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1. Stairs, R. A., *Can. J. Chem.*, 1980, **58**, 296.
2. Chauhan, M., Rajni Mishra, Amarsingh, Shukla, J. P. and Saxena, M. C., *Pramana*, 1983, **20**, 77.
3. Glasstone, S., Laidler, K. J. and Eyring, H. E., *The theory of rate processes*, McGraw-Hill, London, 1941, p. 477.
4. Hildebrand, J. H., *Viscosity and diffusivity*, Wiley-Inter Science, New York, 1977, p. 1.
5. Mathad, R. D., *Pramāna*, 1985, **25** (in press).
6. Mathad, R. D., Doctoral thesis, Karnatak University, Dharwad, 1983.
7. Glasstone, S., *Textbook of physical chemistry*, Macmillan, London, 1968, p. 497.
8. Kaye, G. W. C. and Laby, T. H., *The tables of physical and chemical constants*, Longmans, London, 1962, p. 36.

ON THE NATURE OF LOCAL STRAINS DURING SELF-DIFFUSION IN CUBIC METALS

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ATOMIC diffusion in solids involves local strains in the lattice but their nature is not clear at the moment. We suppose that the activation energy for diffusion may be related to the elastically stored energy. Since any strain can be resolved into dilational and shear components, the activation energy may be directly related to the products of shear and dilational strains with Shear and Bulk Modulii. This communication presents an empirical analysis of the data available for a wide range of metals to indicate the nature of strain involved in diffusion.

We find that activation energy for self-diffusion can be described by the following relation:

$$Q = (AK + BG)\,\Omega\,N/J$$

where, Q is activation energy for self-diffusion in Kcal/mol; K is bulk modulus in Pascals; G is shear modulus in Pascals; Ω is atomic volume in meter^3; N is Avogadro's number, (6.023×10^{23} atoms/mol); J is heat equivalent in Kcal/Joule, (4.17×10^{-3} Kcal/Joule). A and B are coefficients which depend upon the crystal structure.

Values of A and B for B.C.C. structure are 0.172 and 0.058 respectively while the corresponding values for F.C.C. structure are 0.002 and 0.587.

Table 1 presents the data and the calculated activation energies for B.C.C. metals. It may be seen that the fit is extremely good for some elements such as Fe, Nb,

Table 1 *Experimental data and calculated values of Q for B.C.C. metals*

Metal	K (GPa) (1, 2)	G (GPa) (1, 2)	$\Omega \times 10^{30}$, (m^3) (3)	Q observed, (Kcal/mol) (l)	Q calculated, (Kcal/mol)
V	158.00	46.69	13.8	73.65	59.98
Cr	160.00	115.30	12.0	73.70	59.94
Fe	169.79	81.60	11.7	61.30	57.73
Nb	170.29	37.50	17.9	96.00	81.83
Mo	261.20	125.60	15.5	92.20	117.57
Ta	196.29	69.19	18.0	98.70	98.37
W	311.00	160.60	15.8	140.30	143.87
Li	11.80	4.24	21.6	12.67	7.10
Na	8.30	2.53	39.4	10.09	8.99
K	3.30	1.30	76.3	9.75	7.09
Rb	2.30	00.91	89.2	9.40	5.78