INTERMOLECULAR FORCES AND VISCOSITY OF SOME POLAR ORGANIC VAPOURS

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ABSTRACT. Viscosity of several polar organic vapours has been measured by a precision all-metal oscillating-disc viscometer, over the temperature range 30°–200°C and below a pressure of 10 cm Hg. The results have been utilised to obtain some significant information on inter-molecular forces in these substances.

INTRODUCTION

Amongst transport properties like thermal conductivity and thermal diffusion, viscosity is not significantly affected by inelastic collisions. This property, with the recent improvements in the techniques (Kestin *et al*, 1959; Flynn *et al*, 1963) can be measured very accurately. Consequently, temperature dependence of viscosity is one of the most important sources of information regarding inter-molecular forces in polyatomic gases. For polar gases a further complication in the intermolecular forces is the angle-dependent dipole-dipole interaction. In order to have precise knowledge of intermolecular forces in polar gases we have taken up a programme for the measurement of viscosity of these gases over a range of temperatures. In this paper we have reported the viscosity data for three polar organic vapours, viz. diethyl ether, ethyl acetate and ter-butyl alcohol over the temperature range 30°—200°C.

EXPERIMENTAL

The viscosity was measured by an all-metal oscillating-disc viscometer similar in design to that of Kestin and Leidenfrost (1959). The apparatus together with its accessories have been described in detail by Pal *et al* (1967). At low densities it is possible to calculate viscosity from the following simple expression, (Clifton, 1963),

$$\eta = C^{-1}[(\lambda/\tau)-(\lambda_0/\tau_0)], \qquad \ldots \text{(1)}$$

where η is the viscosity of the gas, λ, λ_0 and τ, τ_0 are the logarithmic decrements and time periods of oscillation in the gas and vacuum respectively and C is a constant of the apparatus. In order to determine the constant C, H_2 and N_2 were taken as the calibrating gases (purity better than 99.95%). The viscosity data for these gases were taken from the best available sources (Barua *et al*, 1964, Kestin

et al, 1963). Diethyl ether, ethyl acetate and ter-butyl alcohol were of analytical reagent standard and were distilled and dried by specific drying agents. The reproducibility of dampings were within 0.1% and the overall accuracy of our measurements should be well within 1%.

The viscosity values for these polar gases have been recorded in table 1. Previous viscosity data are available only for diethyl ether. For this substance the present data are 7-8% lower than those reported by Titani (1933) in the higher temperature range. In the lower temperature range as well (upto 77.8°C) our values are 4-5% lower than those reported by Craven *et al* (1951). The possible causes have been discussed in detail in a previous paper (Pal *et al*, 1967).

INTERMOLECULAR POTENTIALS

The intermolecular potential for polar gases is usually represented by the Stockmayer or 12-6-3 potential which can be written as,

$$\phi(r) = 4\epsilon[(\sigma/r)^{12}-(\sigma/r)^6+\delta(\sigma/r)^3], \tag{2}$$

$$\delta = \tfrac{1}{4}\mu^{*2}g(\theta_1, \theta_2, \varphi); \quad \mu^* = \mu/(\epsilon\sigma^3)^{\tfrac{1}{2}}, \tag{2a}$$

$$g(\theta_1, \theta_2, \varphi) = 2\cos\theta_1\cos\theta_2-\sin\theta_1\sin\theta_2\cos\varphi \quad\quad \dots \tag{2b}$$

where μ_1, μ_2 are the dipole moments of the interacting molecules, θ_1, θ_2 are angles of inclination of the dipoles to the line joining the centres of the molecules, φ is the azimuthal angle. For μ_1, or $\mu_2 \to 0$, eq. (2) reduces to the well-known Lennard-Jones (12:6) potential for non-polar molecules (Hirschfelder *et al*, 1954). Moncuick *et al* (1961) have calculated the collision integrals for the 12-6-3 potential by assuming equal probability for all the relative orientations of the interacting dipoles. In order to fit the viscosity data to the 12-6-3 potential we have followed the procedure of Monchick *et al* (1961) according to which we have the following equations :

$$\log[\eta \times 10^7/M^{\tfrac{1}{2}}T^{7/6}] = \log[T^{*2/3} <\Omega^{(2,2)*}(T^*)>]^{-1}+0.05377-\tfrac{4}{3}\log\mu$$

$$+\tfrac{2}{3}\log\delta_{max}, \tag{3}$$

$$\log T = \log T^*+\log(\epsilon/k), \tag{4}$$

where η is in $g/cm.$ sec, M the molecular weight in gm/mole, T is in °K and μ in debyes (1 debye $=10^{-18}$ esu). If the model is capable of representing the data, a plot of the experimeptal quantities $\log[10^7\eta/M^{\tfrac{1}{2}}T^{7/6}]$ vs. $\log T$ should be superposable by translation of axes on a plot of $\log[(T^*)^{2/3} < \Omega^{(2,2)*}(T^*) >]^{-1}$ vs. $\log T^*(<\Omega^{(2,2)*}>$ being the averaged collision integrals). The amount of translation

along the abscissa determines ϵ/k and that along the ordinate gives δ_{max} which is given by the relation

$$4\epsilon\sigma_0\delta_{max} = 2\mu^2 \qquad \ldots \ (5)$$

It has, however, been observed that the viscosity data cannot be fitted satisfactorily to the 12-6-3 potential by the method described above. The discrepancy is more pronounced in the lower temperature region. As a typical example, the experimental and the theoretical plots from eqs. (3) and (4) are shown in figs. 1 and 2 for diethyl ether. It is clear from a look at figs. 1 and 2 that the two curves are not at all superposable at lower temperatures. At higher temperatures the
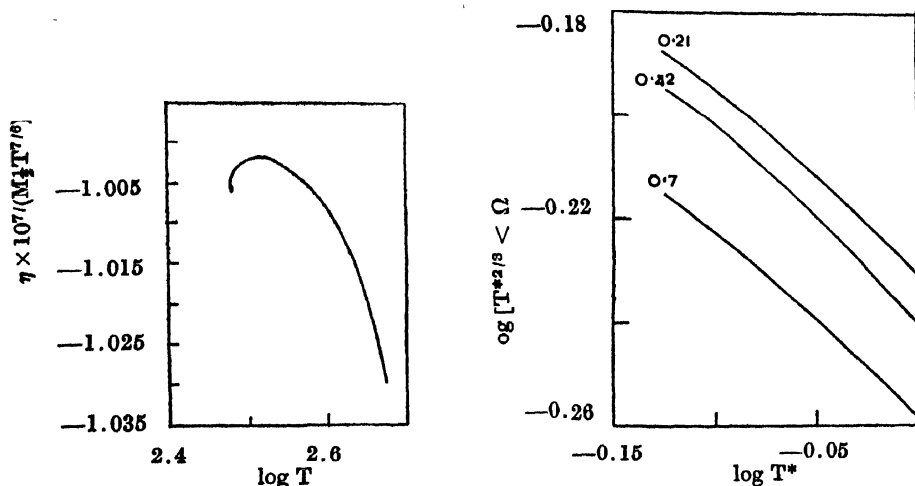

Figure 1. Plot of log $[\eta 10^7/M^{1/2}T^{7/6}]$ vs. log T. Figure 2. Plot of log $[T^{*2/3} < \Omega^{(2,2)*}T^*]$ vs. log T^*.

plots are almost straight lines and are superposable. This feature is quite understandable from physical considerations. The assumption of equal probability for all the relative orientations of the interacting dipoles will hold when the time of interaction is large compared to the time between collisions. This condition is likely to be satisfied better at higher temperatures. It also appears that particularly at lower temperatures viscosity is affected significantly by the dipole-dipole forces. Thus the suggestion of Monchick *et al* (1961) that the viscosity is insensitive to the dipole-dipole forces probably holds only at high temperatures.

At lower temperatures when the collision time increases, the dipoles may get a chance to reorient during an encounter. Different pairs of molecules will thus interact with different relative orientations and it is possible to assume an 'effective' relative orientation for all the molecules which will be a function of temperature. This idea can easily be tested by taking δ to be an independent parameter (Itean *et al* 1961). Under this condition we have the following equations

$$\log [\eta \times 10^7/(MT)^{\frac{1}{2}}] = \log [\Omega^{(2,2)*}(T^*, \delta)]^{-1} + \log 266.93 - 2\log \sigma \qquad \ldots \ (6)$$

$$\log T = \log T^* + \log (\epsilon/k) \qquad \ldots \ (7)$$

where $\Omega^{(2,2)*}$ (δ, T^*) is the unaveraged collision integrals which have been eva-luated by Itean *et al* (1961) and also by Monchick *et al* (1961).

Table 1

Viscosity of diethyl ether, ethyl acetate and ter-butyl alcohol at different temperatures and force constants for the 12-6-3 model by assuming an effective relative orientation of the dipole

Substance	T°C	$\eta \times 10^6$ (g.cm^{-1}.sec.$^{-1}$)	Potential parameters		
			σ(Å)	ϵ/k(°K)	δ
Diethyl ether	30.0	66.56			
	55.2	73.87			
	100.0	85.20	5.684	476.4	0.63
	150.5	96.96			
	200.0	106.50			
Ethyl acetate	30.5	68.12			
	54.5	75.29			
	99.2	86.56	5.711	475.8	0.64
	150.2	98.78			
	200.1	109.50			
ter-Butyl alcohol	30.0	67.41			
	55.6	74.34			
	100.0	85.10	5.699	457.1	0.63
	149.7	95.73			
	200.0	105.25			

A series of plots of $\log [\Omega^{(2,2)*}(T^*)]^{-1}$ vs. $\log T^*$ for different δ values were made. On these plots another plot of $\log \left[\dfrac{\eta \times 10^7}{M^{\frac{1}{2}} T^{\frac{1}{2}}}\right]$ vs $\log T$ was superposed by the translation of axes. The value of δ was determined from the curve which gave the best fit and ϵ/k were obtained from the amount of translations along the ordinate and abscissa respectively. The effective value of g was obtained from the relation

$$g_{eff} = \frac{\sigma_0^3 . \delta . (\epsilon/k)}{1811\mu^2} \qquad \dots (8)$$

where σ is in Å, ϵ/k is in °K and μ is expressed in debye However, it may be seen that δ as obtained by us are positive which correspond

to repulsive orientation of the dipole and are physically less probable. This may be due to the offcentre nature of the dipoles. Some progress in this direction has been made for equilibrium properties by Lawley *et al* (1963).

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