

### 353. *The Viscosity of Dinitrogen Tetroxide and its Binary Mixtures with Organic Solvents.*

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The viscosity of pure liquid dinitrogen tetroxide and of its mixtures with six organic solvents has been determined over the temperature range  $-20^{\circ}$  to  $+20^{\circ}$ . The 'onium donors diethylnitrosamine, ethyl acetate, and acetic anhydride give viscosity-composition isotherms which show pronounced maxima. The isotherm for the donor toluene shows little deviation from linearity, while the non-donors cyclohexane and carbon tetrachloride show negative deviations. The experimental results are presented in the form of fluidity-composition isotherms; the position of the minima in these isotherms gives a more reliable indication of the mole ratios involved in molecular association in the liquid state. The influence of this association is also shown in the variation of viscosity with temperature. Non-donor solvents give straight-line plots of  $\log \eta$  against  $1/T$ , but donor solvents give curves. Fluidity deviations are correlated with volumes of mixing.

DILUTION of liquid dinitrogen tetroxide with organic solvents enhances the solution properties and the reactivity of the liquid, while retaining the essential features of the dinitrogen tetroxide solvent system. In consequence, the physical properties of these mixtures have been studied to determine the nature of the molecular interactions involved. Diethylnitrosamine forms a solid 2 : 1 compound with dinitrogen tetroxide (m. p.  $-37^{\circ}$ ), and in 1953 Addison and Conduit reported kinematic viscosity data for this system.<sup>1</sup> A series of isotherms was obtained with pronounced maxima at the 2 : 1 molar ratio, and this was regarded as evidence that the addition compound itself represented the major species in the liquid. Later, vapour pressures,<sup>2</sup> densities,<sup>3</sup> and particularly ultra-violet absorption spectra<sup>4</sup> of mixtures of dinitrogen tetroxide with many electron-donor solvents showed that, although partial electron-transfer undoubtedly occurs, there is no direct evidence for the existence of individual molecules of addition compound in the liquid state. A systematic study of the dynamic viscosities of several typical systems has therefore been undertaken.

#### EXPERIMENTAL

*Viscometer.*—An all-glass viscometer of the pattern described by Greenwood and Wade<sup>5</sup> was used. This incorporates the weir system to maintain a constant rate of flow. Times of flow were of the order of 100 sec., measurable to 0.1 sec. Being totally enclosed, the viscometer

<sup>1</sup> Addison and Conduit, *J.*, 1952, 1390.

<sup>2</sup> Addison and Sheldon, *J.*, 1957, 1937.

<sup>3</sup> Addison and Smith, *J.*, 1958, 3664.

<sup>4</sup> Addison and Sheldon, *J.*, 1958, 3142.

<sup>5</sup> Greenwood and Wade, *J. Inorg. Nuclear Chem.*, 1957, **3**, 349; *J. Sci. Instr.*, 1957, **34**, 288.

is convenient for use with volatile and readily hydrolysed liquids, and was completely submerged in a thermostat bath for measurements over a temperature range. The viscometer was calibrated by using the five liquids to be employed in the mixtures. In the equation  $\eta t/d = At^2 - B$ , where  $t$  = time of flow in sec. and  $d$  = density, values for the constants  $A$  and  $B$  of  $4.65 \times 10^{-3}$  and 4.0 centistokes  $\text{cm.}^{-1}$  respectively gave the values for the pure solvents shown in col. 3 of Table 1; these are compared with recorded values (col. 4). The viscosity of each

TABLE 1.

Solvent	Temp.	$\eta$ , obs. (c.p.)	Lit. values for $\eta$ (c.p.)	Solvent	Temp.	$\eta$ , obs. (c.p.)	Lit. values for $\eta$ (c.p.)
Cyclohexane ...	25°	0.899	0.898, <sup>6</sup> 0.900 <sup>7</sup>	Toluene ...	20°	0.593	0.5866 <sup>6</sup>
" "	20	0.982	0.980 <sup>6</sup>	EtOAc ...	30	0.402	0.400 <sup>11</sup>
CCl <sub>4</sub> .....	25	0.902	0.9019, <sup>8</sup> 0.902, <sup>9</sup> 0.904 <sup>7</sup>	" "	25	0.426	0.4244, <sup>12</sup> 0.425 <sup>9</sup>
" "	20	0.976	0.968 <sup>9</sup>	" "	20	0.451	0.452 <sup>9</sup>
" "	15	1.046	1.038 <sup>10</sup>	Ac <sub>2</sub> O .....	20	0.915	0.892, <sup>11</sup> * 0.912, <sup>13</sup> * 0.9417 <sup>14</sup>

\* Interpolated values.

solvent was also determined over a temperature range down to  $-20^\circ$  (except for cyclohexane, m. p.  $6.6^\circ$ ) and each solvent gave a straight-line plot of  $\log \eta$  against  $1/T$ . The constants in the equation  $\log_{10} \eta = C/T - K$ , together with activation energies for viscous flow, are given in Table 2.

TABLE 2.

Solvent	C	K	$\Delta E^\ddagger$ (kcal. mole <sup>-1</sup> )	Solvent	C	K	$\Delta E^\ddagger$ (kcal. mole <sup>-1</sup> )
Cyclohexane ...	650	2.225	2.97	EtOAc .....	444	1.860	2.03
CCl <sub>4</sub> .....	570	1.956	2.61	Ac <sub>2</sub> O .....	565	1.966	2.58
Toluene .....	476	1.850	2.18				

*Materials.*—Dinitrogen tetroxide was prepared and purified as already described.<sup>15</sup> Organic solvents were rigorously purified by conventional methods. No chemical reaction occurred in solution during the experiments. For reproducible results with these mixtures, particular care was necessary to remove the last traces of grease from the solvents. The viscometer was cleaned at intervals with nitric acid-alcohol. Small obstructions which occasionally lodged in the capillary tube could be removed satisfactorily by using mercury.

## RESULTS AND DISCUSSION

*Viscosity of Dinitrogen Tetroxide.*—Since the liquid readily supercools, viscosity measurements below the m. p. ( $-11.2^\circ$ ) were made without difficulty. Values for the dynamic viscosity are given in Table 3. The density values used were those already determined by the authors.<sup>3</sup> The values for  $\eta$  lie on the straight line  $\log_{10} \eta = 400/T - 1.742$ , and no discontinuity is observed at the m. p. Earlier measurements<sup>13,16</sup> are restricted to the temperatures above  $0^\circ$ , but are in good agreement.

The activation energy of viscous flow for dinitrogen tetroxide is 1830 cal. per mole, and

<sup>6</sup> "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Institute of Technology, American Petroleum Institute Research Project 44, Pittsburgh, 1953.

<sup>7</sup> Hammond and Stokes, *Trans. Faraday Soc.*, 1955, **51**, 1641.

<sup>8</sup> Grunberg, *Trans. Faraday Soc.*, 1954, **50**, 1293.

<sup>9</sup> Mumford and Phillips, *J.*, 1950, 75.

<sup>10</sup> Timmermans and Martin, *J. Chim. phys.*, 1926, **23**, 747.

<sup>11</sup> Timmermans and Hennaut-Roland, *J. Chim. phys.*, 1930, **27**, 401.

<sup>12</sup> Chadwell, *J. Amer. Chem. Soc.*, 1926, **48**, 1912.

<sup>13</sup> Thorpe and Rodger, *Phil. Trans.*, 1894, **185**, A, 451.

<sup>14</sup> Lewis, *J.*, 1940, 32.

<sup>15</sup> Addison and Thompson, *J.*, 1949, S. 218.

<sup>16</sup> Richter, Reamer, and Sage, *Ind. Eng. Chem.*, 1953, **45**, 2117.

the molar heat of vaporisation is 9100 cal. at the b. p. (21.15°).<sup>17</sup> The ratio  $\Delta E^\ddagger/\Delta E^\eta = 4.66$  is therefore rather high.<sup>18,19</sup> This suggests that the unit of flow might be smaller than dinitrogen tetroxide, possibly nitrogen dioxide.

*Batschinski's Law.*—The specific volume  $V$  was calculated from known density values,<sup>3</sup> and values of the fluidity (reciprocal viscosity)  $\phi$  are available from Table 3. When

TABLE 3.

Temp.	20.0°	18.1°	16.8°	9.8°	1.6°	0.0°	-6.0°	-10.0°	-12.4°	-15.0°	-18.4°	-20.0°
$\eta$ (c.p.)	0.420	0.426	0.435	0.468	0.512	0.527	0.565	0.599	0.615	0.641	0.663	0.687

specific volumes over a temperature range are plotted against fluidity, a straight-line relation  $V = 0.0443\phi + 0.5855$  is obtained, and again there is no apparent discontinuity at the m. p

FIG. 1. Viscosity-composition isotherms (-20°) for mixtures of dinitrogen tetroxide with organic solvents.

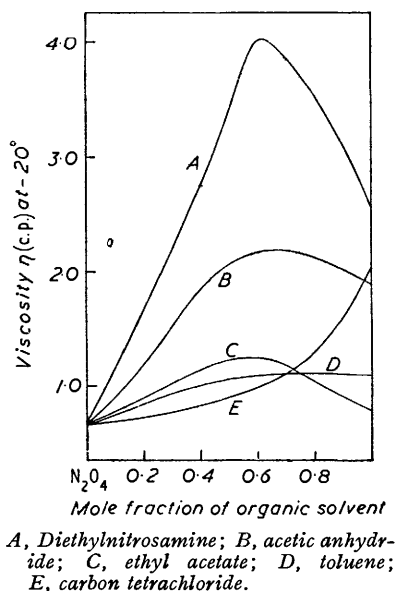
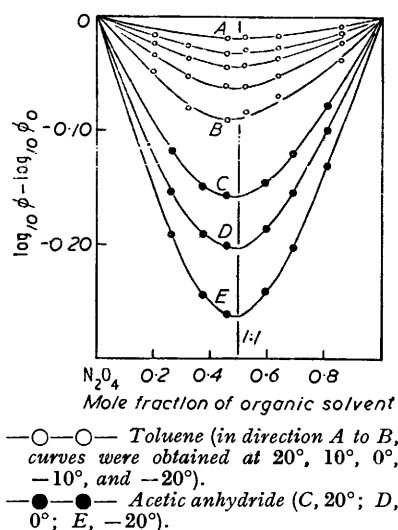


FIG. 2. Mixtures of dinitrogen tetroxide with 1:1 donor solvents.



*Viscosity of Dinitrogen Tetroxide-Organic Solvent Mixtures.*—Viscosity-molar composition isotherms for five solvents at -20° are shown in Fig. 1. Solvents may be divided into the three types: 'onium donor,  $\pi$ -donor, and inert solvents.<sup>20</sup> These three types may be clearly distinguished in the viscosity curves. The 'onium donors diethylnitrosamine, ethyl acetate, and acetic anhydride show pronounced maxima. The  $\pi$ -donor toluene shows little deviation from linearity, while the inert solvent carbon tetrachloride shows a concave isotherm. The viscosities of mixtures with cyclohexane were not measured below -10°, but isotherms for these mixtures resemble curve E.

The diethylnitrosamine curve was calculated from the kinematic viscosity.<sup>1</sup> This curve, and that for ethyl acetate, pass through maxima at 0.6 mole of solvent, and this could be correlated with the formation of 2:1 compounds which occurs in each case in the solid state. Maxima in viscosity curves have frequently been accepted as evidence for

<sup>17</sup> Giauque and Kemp, *J. Chem. Phys.*, 1938, **6**, 40.

<sup>18</sup> Ewell, *J. Appl. Phys.*, 1938, **9**, 252.

<sup>19</sup> Glasstone, Laidler, and Eyring, "The Theory of Rate Processes," Chap. 9, International Chemical Series, McGraw-Hill Co., 1941.

<sup>20</sup> Addison and Sheldon, *J.*, 1956, 1941.

the stoichiometry of complexes formed in solution, but the danger of attaching too great significance to the position of these maxima has been stressed by Ewell.<sup>21</sup> This view is supported by the curve for acetic anhydride (Fig. 1). This compound gives a solid 1:1 complex with dinitrogen tetroxide, yet the maximum in the dynamic viscosity isotherm occurs at 0.62 mole fraction of solvent. (The kinetic viscosity shows a maximum at 0.8 mole of acetic anhydride.) Nevertheless, the shape of the viscosity isotherms gives clear evidence for donor-acceptor behaviour, and the positive deviation is a sensitive measure of the extent of association.

FIG. 3. Mixtures of dinitrogen tetroxide with 2:1 donor solvents.

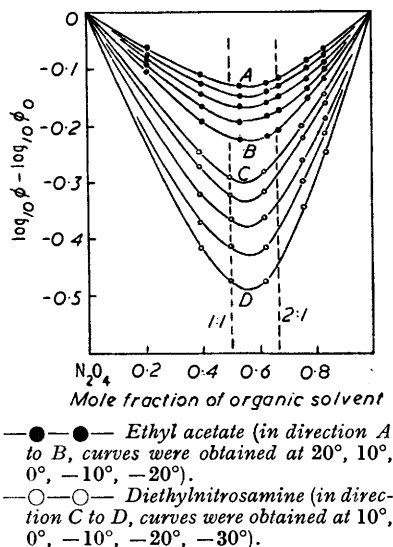
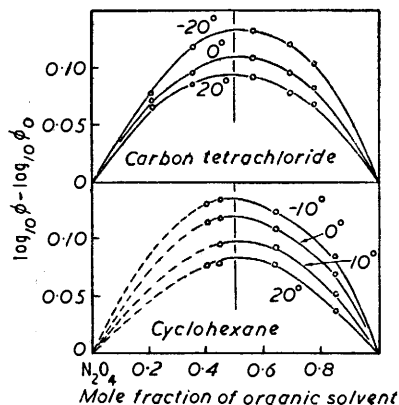


FIG. 4. Mixtures of dinitrogen tetroxide with non-donor solvents.



*Fluidity Relationship.*—Ideal fluidity relations may be applied to binary mixtures in which the components have similar activation energies.<sup>19</sup> The fluidities of ideal solutions are related by the equation

$$\log \phi_0 = x_1 \log \phi_1 + x_2 \log \phi_2$$

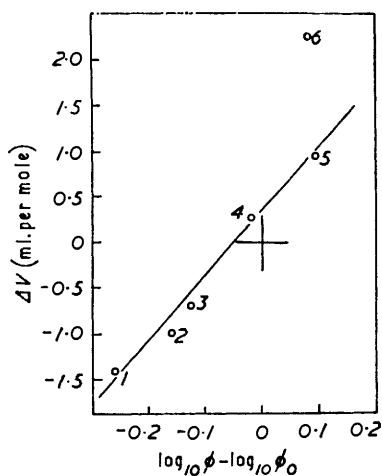
where concentrations are expressed in terms of the molar fraction  $x$ , and subscripts 0, 1, 2 refer to ideal solution, dinitrogen tetroxide, and organic solvent respectively. Although maxima in actual viscosity curves for dinitrogen tetroxide solutions are not related to the stoichiometry of molecular association in solution, yet the deviation of fluidity from ideal behaviour should have more significance. The results obtained in this work are therefore presented in this way. The function  $\log_{10} \phi - \log_{10} \phi_0$  (where  $\phi$  is the measured fluidity) is plotted against molar fraction of solvent (Figs. 2—4) for the six systems investigated. Molecular association in solution gives rise to negative deviations (Figs. 2, 3), while the non-donors carbon tetrachloride and cyclohexane give positive deviations (Fig. 4). Where no association occurs, or when such association involves a 1:1 molar ratio, deviations would be expected to be approximately parabolic and symmetrical with respect to 1:1 molar composition. This is the case for carbon tetrachloride and cyclohexane, and also for toluene. Acetic anhydride has particular interest; in terms of fluidity deviation (Fig. 2) the curves show a clear maximum at 1:1 ratio. This is now consistent with the known 1:1 compound formed with dinitrogen tetroxide in the solid, and in contrast to the maximum at higher solvent concentrations observed for the viscosity curve (Fig. 1). This supports the view that fluidity deviations give real evidence for the ratios involved

<sup>21</sup> Ewell, *J. Chem. Phys.*, 1937, 5, 967.

in molecular association in the liquid state, and it is in this light that the curves for ethyl acetate and diethylnitrosamine (Fig. 3) should be considered. The positions of maximum fluidity deviation are displaced from the 1 : 1 towards the 2 : 1 mole ratio characteristic of the solid addition compounds. Although electron-transfer to the tetroxide by these weak donors occurs only partially under these physical conditions, it seems clear that more than one solvent molecule takes part in electron-donation to each tetroxide molecule.

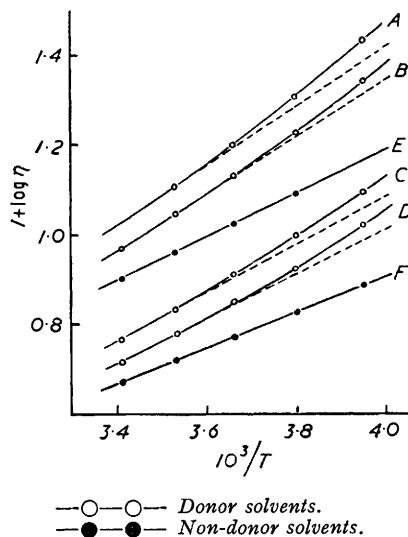
*Correlation with Volumes of Mixing.*—In Fig. 5 the maximum fluidity deviations at 20° are plotted against the observed volume changes on mixing.<sup>3</sup> Points for the five polar solvents lie close to a straight line which passes near the origin. (Carbon tetrachloride

FIG. 5. Correlation of volume changes on mixing with excess fluidity function for binary mixtures of liquid dinitrogen tetroxide and organic solvents at 20°.



- 1, Diethylnitrosamine;
- 2, acetic anhydride;
- 3, ethyl acetate;
- 4, toluene;
- 5, carbon tetrachloride;
- 6, cyclohexane.

FIG. 6. Influence of temperature on viscosity of dinitrogen tetroxide-organic solvent mixtures.



—○—○— Donor solvents.  
—●—●— Non-donor solvents.

Solvents	Molar fraction of solvent
A Diethylnitrosamine	0.390
B Acetic anhydride	0.594
C Ethyl acetate	0.627
D Toluene	0.454
E Cyclohexane	0.852
F Carbon tetrachloride	0.351

is included here since the C-Cl bond is polar though the dipole moment is zero.) Positive fluidity deviations correspond to increases in volume, and negative deviations accompany contraction on mixing. Values for the non-polar cyclohexane do not correspond with those for the polar solvents. This exceptional behaviour of the hydrocarbons was observed also in the correlation of dipole moment of solvent with the partial pressure of the tetroxide over the mixtures.<sup>2</sup>

*Variation of Viscosity with Temperature.*—This variation is shown in Fig. 6, where donor and non-donor solvents are readily distinguished. The slopes of the  $\log \eta - 1/T$  lines, and thus the activation energy for viscous flow, of solutions of dinitrogen tetroxide in non-donors carbon tetrachloride and cyclohexane are independent of temperature. In this respect these solutions resemble pure liquids. Where molecular association occurs, the degree of association increases with decreasing temperature (curves A to D, Fig. 6). This

results in a progressive increase in activation energy since the energy required to create a hole in the liquid is augmented by the energy of association.

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