734. *Volume Changes on mixing Organic Liquids with Dinitrogen Tetroxide: Comparison with Sulphur Dioxide Systems.*

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The density of pure liquid dinitrogen tetroxide, and volume changes on mixing with eleven organic liquids, have been determined over the temperature range −20° to +20°. Non-donor compounds (*e.g.*, *cyclo*hexane) give positive values of ΔV, and their mixtures approach the behaviour of regular solutions. 'Onium donor liquids (*e.g.*, acetic anhydride) give negative values of ΔV which are not symmetrical with respect to molal composition. π-Donors (aromatic hydrocarbons) give only small volume changes. The results are correlated with data for corresponding organic liquid–sulphur dioxide systems.

As a preliminary stage in the study of various physical properties of dinitrogen tetroxide–organic liquid mixtures, it was necessary to establish accurate densities for them. It was observed that the volume changes on mixing showed some correlation with the type of organic liquid used, and with corresponding liquid sulphur dioxide systems. The results are now reported.

Density of Liquid Dinitrogen Tetroxide.—Some measurements have been reported at temperatures above 0°. The liquid readily supercools below its m. p. (−11·2°) and measurements were possible down to −20° (Table 1). The values are accurate to ±0·0001, and in the range above 0° agree well with more recently published values.[1-3] Three samples separately prepared gave d_4^{20} 1·44687, 1·44687, and 1·44703 (compared with 1·44750 by Bousfield [1] and 1·44703 by Pascal and Garnier [2]); two separate samples gave d_4^{0} 1·49268 and 1·49271, compared with 1·4925 (at 0·08°) [1] and 1·490 [2]. There is no discontinuity in the density of the supercooled liquid, and the values over the full temperature range are well represented by the equation

TABLE 1. *Density of dinitrogen tetroxide.*

Temp.	d_4^t	Temp.	d_4^t	Temp.	d_4^t	Temp.	d_4^t	Temp.	d_4^t	Temp.	d_4^t
−20·0°	1·5364	−13·0°	1·5214	−7·0°	1·5081	0·0°	1·4927	8·0°	1·4747	17·0°	1·4538
−17·0	1·5301	−10·0	1·5147	−5·0	1·5037	3·0	1·4860	11·0	1·4677	19·0	1·4493
−15·0	1·5256	−9·0	1·5125	−3·0	1·4992	6·0	1·4793	13·0	1·4632	20·0	1·4469

$$d_4^t = 1{\cdot}4927 - 2{\cdot}235 \times 10^{-3}t - 2{\cdot}75 \times 10^{-6}t^2.$$

Volume Changes on Mixing.—The molal volume V_0 of the ideal solution was obtained from the relation $V_0 = x_1V_1 + x_2V_2$, where suffixes 1 and 2 denote dinitrogen tetroxide and organic liquid respectively. The measured molal volume V of the mixture, $(x_1M_1 + x_2M_2)/d_4^t$, was plotted against mole-fraction x of the components; these units being used, the deviation ΔV $(= V - V_0)$ from the straight line joining values for pure components gives a true indication of volume changes. The variation of ΔV with composition at 20° is shown for seven liquids in Fig. 1 (for key see Table 2). The order of organic liquids so obtained agrees closely with that obtained on the basis of vapour-pressure deviations.[4] Strongest positive deviations occur with *cyclo*hexane, where molecular interaction is small. The polarity of the C–Cl bond in carbon tetrachloride results in some polar attraction, which reduces the volume expansion, and with chloroform, where there is a resultant dipole, ΔV is further reduced. The probability of molecular association between aromatic hydrocarbons and dinitrogen tetroxide by π-orbital overlap has been discussed.[5] This assists molecular orientation and association in the liquid state,

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[1] Bousfield, *J.*, 1919, **115**, 45.
[2] Pascal and Garnier, *Bull. Soc. chim. France*, 1919, **25**, 309.
[3] Mittasch, Kuss, and Schlueter, *Z. anorg. Chem.*, 1927, **159**, 1.
[4] Addison and Sheldon, *J.*, 1957, 1937.
[5] *Idem*, *J.*, 1956, 1941.

TABLE 2. *Volume changes on mixing* N_2O_4 *with organic liquids.*

Key for Figs. 1 and 3	Solvent	Type	Molal volume V (ml./mole) of solvent (20°)	Maximum volume change, ΔV, on mixing with N_2O_4 20°	5°	0°	−20°
A	*cyclo*Hexane	Non-donor	108·0	+2·25	+2·0	—	—
B	Carbon tetrachloride	,,	96·5	+0·95	—	—	+0·84
C	Chloroform	,,	80·2	+0·62	—	—	+0·55
D	Benzene	π-Donor	88·9	+0·55	—	—	—
—	*p*-Xylene	,,	123·2	+0·38	—	—	—
E	Toluene	,,	106·5	+0·28	—	—	+0·20
—	Nitrobenzene	,,	102·3	−0·60	—	—	—
F	Ethyl acetate	Oxygen 'onium donor	97·8	−0·70	—	−0·60	—
G	Acetic anhydride	,,	94·5	−1·00	—	−0·84	−0·75
H	Diethyl ether	,,	103·8	−1·10	—	—	—
I	Diethylnitrosamine	Nitrogen 'onium donor	108·4	−1·35	—	—	−1·15

TABLE 3. *Temperature coefficients of density for* N_2O_4*–organic liquid mixtures.*

Composition of mixture (by wt.)	d_4^{20}	Coeff. (g. ml.$^{-1}$ deg.$^{-1}$)	Composition of mixture (by wt.)	d_4^{20}	Coeff. (g. ml.$^{-1}$ deg.$^{-1}$)
23·80% CCl_4	1·476	0·00215	33·45% EtOAc	1·215	0·00175
23·06% $CHCl_3$	1·449	0·00227	20·31% Ac_2O	1·358	0·00190
36·00% C_6H_5Me	1·160	0·00163	24·71% $Et_2N{\cdot}NO_2$	1·280	0·00170

and volume changes on mixing are small. With 'onium donor solvents, there is pronounced contraction, and in some cases maximum contraction occurs at compositions other than the 1 : 1 molar ratio. (In the solid state acetic anhydride forms a 1 : 1 compound, whereas ethyl acetate and diethylnitrosamine form 2 : 1 compounds.) ΔV has been measured for eleven liquids altogether, in some cases over the temperature range —20° to +20°. Details are given in Table 2.

FIG. 1.

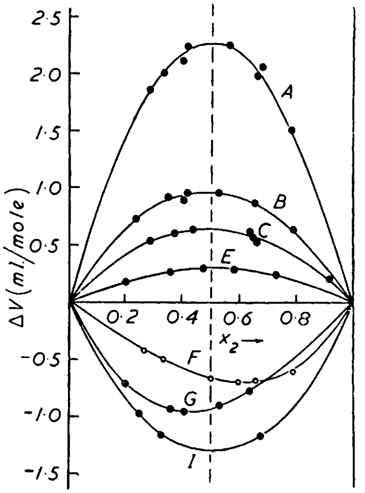
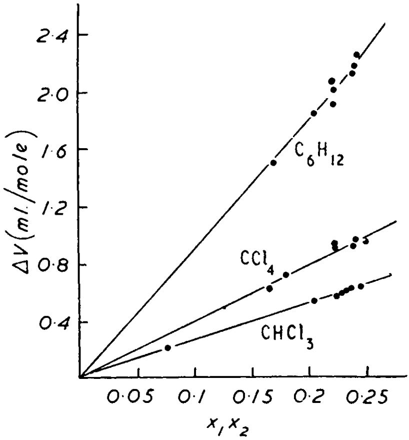


FIG. 2.



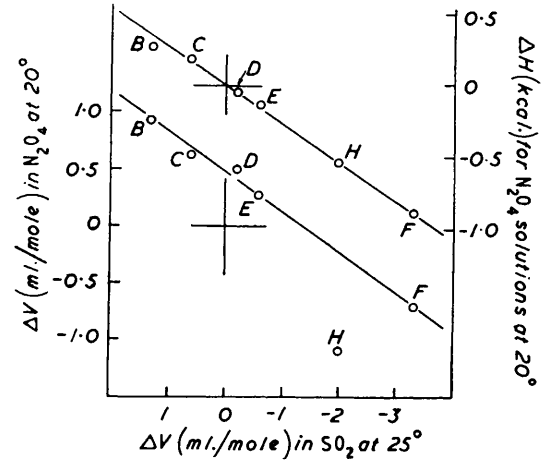
The extent to which mixtures with *cyclo*hexane, carbon tetrachloride, and chloroform approach regular behaviour has been tested by application of Biron's relationship $\Delta V = kx_1x_2$. Fig. 2 shows that this holds within experimental error; a wide scatter occurs if volumes rather than mole-fractions are used.

Temperature Coefficients.—The chemical reactivity of mixtures with donor solvents differs from that of mixtures with non-donors, but is also strongly temperature-dependent. This has been attributed primarily to equilibrium (2):

$$(\mathrm{Don})_n,\mathrm{N_2O_4} \overset{(1)}{\rightleftharpoons} n\mathrm{Don} + \mathrm{N_2O_4} \overset{(2)}{\rightleftharpoons} (\mathrm{Don})_n,\mathrm{NO^+} + \mathrm{NO_3^-}$$

where the proportion of donor liquid (Don) present in ionic species is very small. Molecular association is clearly reflected in density changes (Fig. 1), and if equilibrium (1) varies appreciably with temperature it should be reflected in variations of the temperature coefficient of density. This has therefore been examined closely by obtaining a number of values in the range —20° to +20° for the mixtures with donors and non-donors listed in Table 3. In each case the temperature coefficient was virtually constant, the curvature of the density–temperature graph being no greater than that observed for the pure components. However, donor liquids give slightly lower coefficients, which may be significant.

FIG. 3.



Comparison with Liquid Sulphur Dioxide.—Molal volumes of mixtures of liquid sulphur dioxide with carbon tetrachloride, chloroform, benzene, toluene, and ether were calculated from densities at 25° by Lewis [6] and Adams and Rogers.[7] A single measurement by Locket [8] indicates a maximum contraction of 3·3 ml./mole for mixtures with ethyl acetate. Maximum ΔV values for these six liquids in sulphur dioxide and in dinitrogen tetroxide are plotted in Fig. 3 (for key see Table 2). A linear correlation (lower line) exists for five of the liquids, sulphur dioxide showing a greater tendency towards volume contraction than does dinitrogen tetroxide. Diethyl ether is exceptional; density measurements on the tetroxide–ether mixtures were less reproducible than in other cases, and a similar observation was made during measurement of vapour pressures. A small amount of chemical reaction probably occurs which influences some, but not all, of the physical properties of the mixture. It is of interest that if ΔV in sulphur dioxide is plotted against the heat, rather than the volume, of mixing in dinitrogen tetroxide (upper line, Fig. 3) all points lie on or near a straight line passing through the origin.

EXPERIMENTAL

Density.—This was measured by using a single-stem Pyrex-glass dilatometer fitted with a B7 ground-glass cap. The volume of the bulb was about 5 ml. The dimensions of the standard-bore capillary stem were measured by using mercury, and allowed observation of meniscus

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[6] Lewis, *J. Amer. Chem. Soc.*, 1925, **47**, 626.
[7] Adams and Rogers, *ibid.*, 1939, **61**, 112.
[8] Locket, *J.*, 1932, 1501.

movement throughout the 40° cooling range. The usual corrections for vapour pressure of liquid and contraction of glass were made. Calibrated weights were corrected to vacuum, and a second identical dilatometer was used to compensate for buoyancy. For volume measurements, the dilatometer was immersed in a thermostat controlled at ±0·005°, and meniscus movements were observed with a cathetometer.

Materials.—Liquid dinitrogen tetroxide was prepared and purified as already described;[9] organic liquids were carefully purified immediately before use by accepted methods, particular care being taken to remove traces of moisture.

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[9] Addison, Allen, Bolton, and Lewis, *J.*, 1951, 1289.