Heat of Mixing of Dinitrogen Tetroxide with Organic Liquids

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Heat is absorbed when dinitrogen tetroxide is mixed with non-polar non-donor liquids, and is evolved on mixing dinitrogen tetroxide with polar or donor liquids. Heats of mixing at different concentrations of 16 binary mixtures containing dinitrogen tetroxide are reported.

Dinitrogen tetroxide is an electron acceptor which forms molecular addition compounds with a range of electron donor solvents. Many addition compounds with organic liquids melt below room temperature,[1,2] and studies related to association in the liquid phase have involved measurements of u.v. spectra,[3] density,[4] viscosity,[5] and vapour pressure.[6] This paper describes a further investigation of the physical properties of binary liquid mixtures. Addison, Conduit, and Thompson [7] investigated the heat of mixing with diethylnitrosamine, and heats of mixing at different concentrations of 16 other binary mixtures containing dinitrogen tetroxide are reported here.

RESULTS AND DISCUSSION

Previous work [1-7] has supported the classification of organic solvents under three headings: (a), onium donors; these contain an atom which has one or more lone pairs of electrons in *s* and *p* orbitals, and form molecular addition compounds with dinitrogen tetroxide; (b), π-donors; these are aromatic hydrocarbons and their derivatives, having electrons available in molecular π orbitals, which interact relatively weakly with the π-system of the tetroxide molecule; (c), non-donors; typical examples are the aliphatic hydrocarbons, which show negligible interaction with the tetroxide. The heat of mixing depends upon the polar nature, and the electron donor properties, of the organic solvent used. Heat is absorbed when dinitrogen tetroxide is mixed with non-polar non-donor liquids, and is evolved on mixing dinitrogen tetroxide with polar or donor liquids. In Figures 1—3, heat of mixing ΔH^M/kJ mol^{-1}, is plotted against mole fraction of organic liquid, x_2. Results with cyclic compounds are shown in Figure 1, with non-cyclic compounds in Figure 2, and with some non-cyclic onium donors in Figure 3. Maximum values of heat of mixing and concentrations of maximum heat change are recorded in the Table. Most of the measurements were at 20 °C and reasonably reproducible values were obtained although the b.p. of dinitrogen tetroxide is 21·15 °C. Estimated experimental errors are between 20 and 40 J mol^{-1}. Measurements at -10 °C were the same as those at 20 °C within the limits of experimental error.

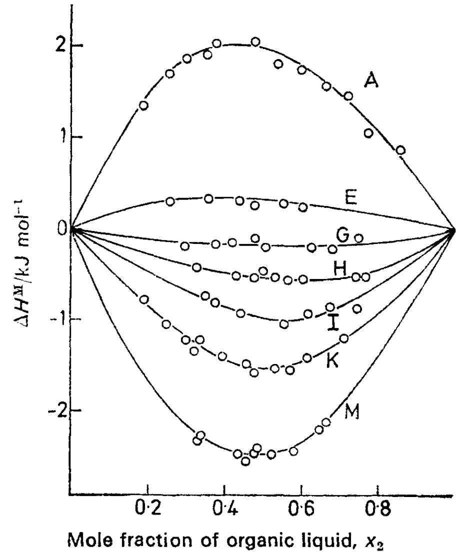

FIGURE 1 Heats of mixing of some organic liquids with dinitrogen tetroxide at 20 °C (see Table for labelling of curves)

Heat is absorbed (ΔH^M positive) when dinitrogen tetroxide is mixed with cyclohexane, n-hexane, carbon tetrachloride, chloroform, chlorobenzene, and 1,2-dichloroethane, and these solvents are typical non-donors.

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[1] C. C. Addison and J. C. Sheldon, *J. Chem. Soc.*, 1956, 1941.

[2] C. C. Addison and J. C. Sheldon, *J. Chem. Soc.*, 1956, 2709.

[3] C. C. Addison and J. C. Sheldon, *J. Chem. Soc.*, 1958, 3142.

[4] C. C. Addison and B. C. Smith, *J. Chem. Soc.*, 1958, 3664.

[5] C. C. Addison and B. C. Smith, *J. Chem. Soc.*, 1960, 1783.

[6] C. C. Addison and J. C. Sheldon, *J. Chem. Soc.*, 1957, 1937.

[7] C. C. Addison, C. P. Conduit, and R. Thompson, *J. Chem. Soc.*, 1951, 1303.

The heat of mixing curves are not symmetrical with respect to mole fraction, and plots of ΔH^{M} against x_1x_2 are not linear. The curves are more symmetrical with respect to volume concentration, and plots of $\Delta H^{M}/V_0$ against $\phi_1\phi_2$ are linear within experimental error. V_0 is ideal molar volume, and ϕ_1 and ϕ_2 are volume fractions of dinitrogen tetroxide and organic liquid respectively.

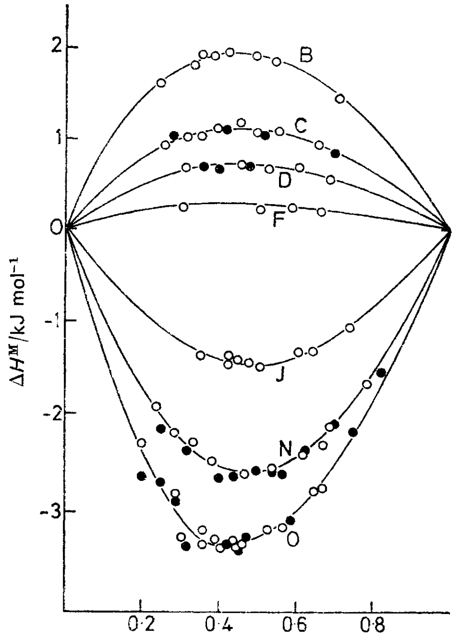

FIGURE 2 Heats of mixing (see Table for labelling of curves); measurements at 20 °C, open circles; measurements at − 10 °C, filled circles

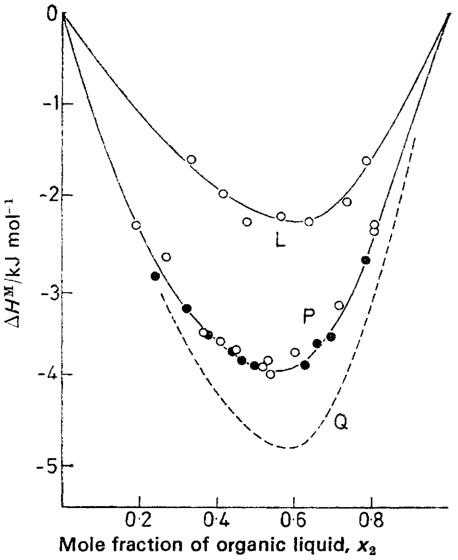

FIGURE 3 Heats of mixing (see Table for labelling of curves); measurements at 20 °C, open circles; measurements at − 10 °C, filled circles; curve Q is derived from data in ref. 7

Compound formation between the tetroxide and π-donors is a property of the solid state, and arises because both the N_2O_4 molecule and the aromatic ring are flat, and have π-systems of similar size which can lie parallel, and thus overlap, in a rigid solid. Previous studies [1-7] of the physical properties of liquid mixtures have provided no evidence that compound formation of this type can occur in the liquid state. Polar attraction is also minimal, so that benzene, toluene, and *p*-xylene (Figure 1) show only small negative heats of mixing. Consistent with this, the heats of mixing with nitromethane and nitrobenzene will be determined largely by the polar attraction between the nitro-group and the tetroxide molecule, and it is found (Figures 1 and 2) that the heats of mixing are similar in the two cases. The greatest evolution of heat occurred on mixing dinitrogen tetroxide with onium donors which are polar molecules, *viz.* acetonitrile, acetic anhydride, diethyl ether, ethyl acetate, and diethylnitrosamine, and there is some correlation between the composition at which maximum heat of mixing is found, and the molecular ratio of the solid adducts which crystallise from the mixtures. Maximum heat evolution occurred at *ca.* $x_2 = 0{\cdot}6$ with known 1 : 2 onium donors, *viz.* diethyl ether, ethyl acetate, and diethylnitrosamine, at $x_2 = 0{\cdot}40$ with acetic anhydride (a 1 : 1 onium donor) and at $x_2 = 0{\cdot}45$ with acetonitrile which forms both 1 : 1 and 1 : 2 solid addition compounds.

		ΔH^{M}/ kJ mol^{-1}	x_2	δ_2	V_0	ΔE^{M} (calc.)
A	Cyclohexane	2·05	0·37	8·2	80·1	0·950
B	n-Hexane	1·97	0·33	7·3	85·7	1·636
C	Carbon tetrachloride	1·13	0·40	8·6	76·8	0·724
D	Chloroform	0·732	0·44	9·3	71·0	0·385
E	Chlorobenzene	0·335	0·38	9·5	78·4	0·351
F	1,2-Dichloroethane	0·250	0·45	9·8	70·5	0·243
G	Benzene	−0·208	0·50	9·2	74·2	0·460
H	Toluene	−0·586	0·60	8·9	79·6	0·590
I	*p*-Xylene	−1·025	0·55	8·8	84·0	0·703
J	Nitromethane	−1·45	0·50	12·6	58·2	0·063
K	Nitrobenzene	−1·57	0·50	10·0	78·6	0·213
L	Diethyl ether	−2·30	0·60	7·4	79·0	1·456
M	Benzonitrile	−2·51	0·50	10·0	78·8	0·213
N	Acetonitrile	−2·62	0·45	11·2	57·6	0·013
O	Acetic anhydride	−3·43	0·40	10·4	76·0	0·113
P	Ethyl acetate	−3·77	0·60	8·6	77·6	0·732
Q	Diethylnitrosamine	−4·81	0·60			

The list given in the Table arranges the organic liquids in increasing order of their total interaction with dinitrogen tetroxide, as indicated by heats of mixing. This order is very similar to that derived from other physical properties;[1-6] the variations which do occur indicate that all properties are not similarly influenced by the two main factors, *i.e.* polar attractions (orientation forces) and compound formation. There is a particularly close relation between heats of mixing and the deviations of vapour pressure from ideal (Raoult's Law) behaviour.[6] The correlation is shown in Figure 4; vapour pressure deviations are expressed as percentage deviation of the observed pressure (P) from ideality (P_0), *i.e.* $100\ (P - P_0)/P_0$, and all points lie close to one straight line, which does not pass through the origin.

In contrast, we may relate heats of mixing to other properties (*e.g.* energies of mixing, and dipole moment of the solvent) which take no account of donor–acceptor interactions, and the different classes of solvents are then clearly distinguished. Ideal solutions are formed with zero heat of mixing. Frequently, non-polar liquids have positive heats of mixing and theories of regular solutions[8,9] relate energy of mixing, E^{M}, to solubility parameters, δ, where solubility parameter is the square root of energy of vaporisation per ml.

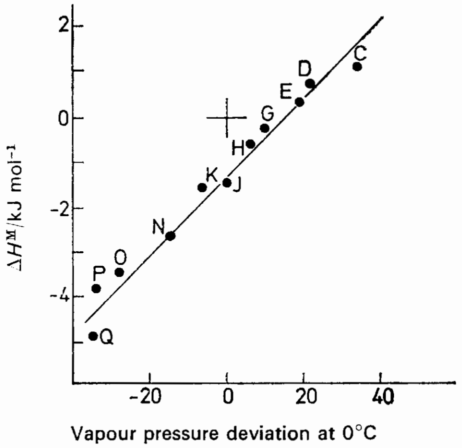

FIGURE 4 Correlation between heats of mixing and deviations from ideal vapour pressure of mixtures

$$\Delta E^{M} = (x_1V_1 + x_2V_2)(\delta_1 - \delta_2)^2\phi_1\phi_2$$

The heat of vaporisation of dinitrogen tetroxide at its b.p. is 9110 cal mol^{-1},[10] and the calculated solubility parameter, $\delta_1 = 11{\cdot}57$. A positive heat of mixing is accompanied normally by an increase in volume, and the heat of mixing of a regular solution is greater than energy of mixing[11,12] by a factor $(1 + \alpha T)$. For dinitrogen tetroxide solutions the coefficient of expansion, α, is *ca.* $1{\cdot}7 \times 10^{-3}$, whence $\Delta H^{M} = ca.\ 1{\cdot}5\Delta E^{M}$.

In the Table, energies of mixing per mole for mixtures of dinitrogen tetroxide with organic liquids have been calculated at concentrations $\phi_1 = \phi_2 = 0{\cdot}5$, and in Figure 5 the maximum observed heat of mixing is plotted against energy of mixing. The straight line $\Delta H^{E} = 1{\cdot}5\Delta E^{M}$ falls near points corresponding to mixtures of dinitrogen tetroxide with non-donors of low dipole moment. All other mixtures fall well below this line, and distance from the line provides a measure of the sum of donor–acceptor interactions and orientation forces.

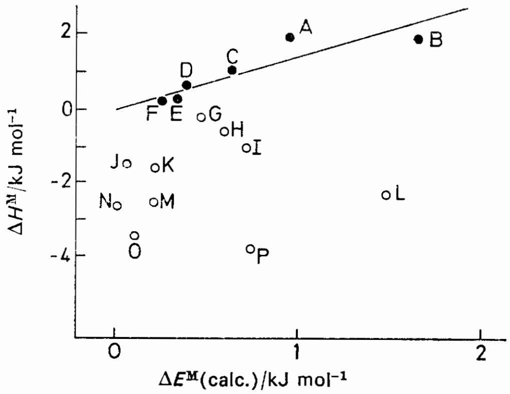

FIGURE 5 Heats and energies of mixing

A somewhat different picture emerges when the heat of mixing is graphed against dipole moment of the organic liquid, since the orientation forces between permanent dipoles are then taken account of in the variation of dipole moment. In Figure 6, a straight line can be drawn through most of the known non-donor solvents. The aromatic hydrocarbons have zero dipole moments and fall below the line because, of all solvents studied, they approach most closely to ideal behaviour when mixed with dinitrogen tetroxide. Because their shape, and the size of the molecules and π-systems, resemble those of the tetroxide molecule, they mix readily in the liquid state, and do not set up the type of interaction which in other cases gives rise to large positive heats of mixing. They are therefore exceptional so far as the treatment in Figure 6 is concerned. The only solvents possessing appreciable dipole moments which fall well below the line are those known to possess strong electron donor properties. Nitromethane, which fell below the line in Figure 5 because of its dipole, now falls on the line in Figure 6, in agreement with its non-donor character.

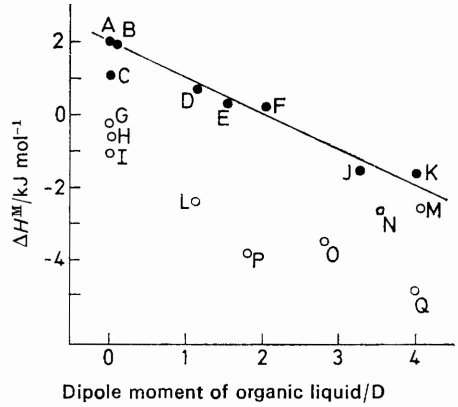

FIGURE 6 Correlation between dipole moment of organic liquid and heat of mixing with dinitrogen tetroxide

Although the correlation with dipole moment in Figure 6 is satisfactory for most solvents, dipole moment itself does not completely reflect the dipolar character of a solvent so far as mixtures with dinitrogen tetroxide are concerned. Thus, carbon tetrachloride falls below the line in Figure 6. Though the CCl_4 molecule possesses no dipole moment, the C–Cl bond is itself polar, and cancellation of identical opposed dipoles is not completely effective at distances of the order of molecular dimensions.

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EXPERIMENTAL

Dinitrogen tetroxide was prepared from lead nitrate.[13] Organic solvents were purified carefully by conventional methods.

Two different calorimeters were used. The first, a simplified version of the calorimeter designed by Brown, Mathieson, and Thynne,[14] was used with cyclohexane, acetonitrile, acetic anhydride, and ethyl acetate. The mixing vessel was of mild steel, and temperature changes were measured with a Beckmann thermometer. Heats of mixing with other liquids were measured in a calorimeter similar to that used by Addison, Conduit, and Thompson.[7] This calorimeter had a low thermal capacity and small heats of mixing gave comparatively large temperature changes. Both calorimeters were calibrated electrically. Agreement within experimental error was obtained on mixing dinitrogen tetroxide with ethyl acetate in either calorimeter.

We thank Dr. D. Feakins and Dr. J. C. J. Thynne for helpful discussions.

[3/2334 *Received*, 13*th November*, **1973**]

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