986.   *Temperature-dependence of the Liquid Viscosities of Some Phosphorus Compounds.*

By M. F. MOLE, W. S. HOLMES, and J. C. McCOUBREY.

Measurements of the coefficient of viscosity over a range of temperatures are reported for three inorganic and nine organic phosphorus compounds. The results demonstrate the breakdown for the organophosphorus compounds of the simple relation $\eta = A \exp E_{vis}/RT$ at temperatures approaching the melting point. These facts are used to provide comments on the simple theories of liquid viscosity.

In particular it is suggested that the experimental results can be explained qualitatively by a quasi-lattice model if we assume that to form holes in these liquids, appropriate for molecular transport, requires an energy which increases markedly at low temperatures owing to the larger steric hindrances at the higher liquid densities.

INVESTIGATIONS of the temperature-dependence of liquid viscosity coefficients η show that viscous flow can, in general, be explained [1] in terms of an activated flow process governed by rate equations which are, to a first approximation, of the form

$$\eta = A \exp E_{vis}/RT \qquad (1)$$

where η is measured at temperature T, E_{vis} is the activation energy for viscous flow, and A is a proportionality constant, the temperature-dependence of which is usually taken to be small.

A simple relation between E_{vis} and the energy of vaporisation E_{vap} was introduced by Eyring *et al.*,[1] who showed that a ratio $E_{vap}/E_{vis} > 1$ could be explained by postulating the idea of a co-operative hole formation and movement process for viscous flow which involved less energy in total than that arising in the " uncompensated " hole formation of the evaporative process, the ratio of the energies being ~4 for " normal " liquids.

The variation of the ratio E_{vap}/E_{vis} for different liquids was explored by Grunberg and Nissan,[2] who suggested its dependence upon the structural co-ordination number and molecular association, illustrating this with the typical fact that the ratio runs from 2 to 3 for water between 0 and 100°.

Ubbelohde and his co-workers [3] have demonstrated experimentally that a simple relation (1) will not suffice to interpret the temperature range just above the melting point. They have found E_{vap}/E_{vis} to vary with temperature in this region for a number of large, non-polar, bulky polyaromatic compounds, some of which can be readily supercooled and form rigid glasses. They have suggested a molecular interlocking mechanism as the cause of the anomaly and have interpreted their results to mean that an increased molecular association occurs as the temperature of the liquid is reduced.

Despite the formal possibilities of this association treatment, it gives a rather unsatisfactory physical picture of the phenomena, since a lattice model can be used to explain some of the transport properties of simple liquids. If a lattice model, in which only nearest-neighbour van der Waals interactions are important, is envisaged for the treatment of the transport properties of liquids in general (and McLaughlin [4] has shown that such a model can be used very satisfactorily for liquids such as methane or benzene), then it is difficult to visualise associations other than, say, specific chemical hydrogen-bonded associations,

[1] Eyring, *J. Chem. Phys.*, 1936, **4**, 283; Glasstone, Laidler, and Eyring, " Theory of Rate Processes," McGraw–Hill, 1941.

[2] Grunberg and Nissan, *Trans. Faraday Soc.*, 1949, **45**, 125.

[3] Andrews and Ubbelohde, *Proc. Roy. Soc.*, 1955, *A*, **228**, 435; McLaughlin and Ubbelohde, *Trans. Faraday Soc.*, 1958, **54**, 1804.

[4] McLaughlin, *Trans. Faraday Soc.*, 1959, **55**, 28.

without causing considerable artificiality in defining the monomeric and the polymeric units. It would seem logical first to examine the possibility of treating the pre-freezing anomalies in terms of a modified lattice model, rather than postulating specific associations, particulrly since no evidence of any other unusual behaviour like liquid-crystal formation has been observed for the liquids in question.

Magill and Ubbelohde [5] have shown that for liquids which readily form glasses values of the activation energies for flow at low temperatures approach quite closely to the energy necessary to form a Schottky hole. Their work was concerned with large multi-ring aromatic compounds melting near 200° and it is desirable to examine the extent of occurrence of such phenomena for simpler liquids.

To explore the possible incidence of such pre-freezing anomalies in liquids of quite different structures from those previously studied, we have examined the behaviour of some phosphorus-containing compounds. A number of organophosphorus compounds supercool. It has been demonstrated that liquid trialkyl phosphites and phosphates can exhibit different rotational isomers,[6] and this may account in part for the difficulty in crystallising them into lattices which usually consist of unique rotational isomers. A comparison of the behaviour of the viscosity coefficients of the organophosphorus compounds in the region just above the m. p. with those of the simple molecular liquids PCl_3 and $POCl_3$ has been made. This is a particularly important comparison since, apart from simple dipolar attraction, we have not been able to visualise any likely molecular association processes in the liquids of the large organophosphorus molecules, which would outweigh a regular nearest-neighbour quasi-lattice structure. Thus we might hope that a modified lattice theory could be appropriately devised to explain the transport properties of these liquids.

RESULTS

The experimental visocsity and density results are recorded in Table 1.

TABLE 1.

Densities (g./c.c.) and viscosities (centipoises) at various temperatures (°).

PCl₃			POCl₃			PSCl₃		
δ_4^t	T	η	δ_4^t	T	η	δ_4^t	T	η
1·731	−65·1	1·573	1·702	+5	1·368	1·734	−30·4	2·627
1·697	−46·0	1·146	1·684	+15	1·184	1·703	−20·4	2·102
1·664	−28·2	0·902	1·666	+25	1·018	1·687	−10·0	1·741
1·642	−16·2	0·786	1·647	+35	0·892	1·679	−5·4	1·605
1·620	−4·0	0·696	1·619	+50	0·750	1·673	0·0	1·496
1·563	+25·0	0·535	1·601	+60	0·687	1·621	+25·0	1·017
1·564	+25·6	0·519	1·583	+70	0·614	1·590	+45·0	0·806
1·546	+35·1	0·487	1·563	+80	0·564	1·559	+65·0	0·665
1·518	+50·0	0·438				1·542	+75·0	0·611
1·499	+60·1	0·411				1·531	+85·0	0·569
						1·513	+98·5	0·519

Trimethyl phosphite			Triphenyl phosphite			Monodimethylamino-phosphoryl chloride		
δ_4^t	T	η	δ_4^t	T	η	δ_4^t	T	η
1·121	−30	1·323	1·183	+25	16·05	1·425	−18	5·30
1·045	+24·7	0·547	1·175	+35	10·70	1·414	−10	3·94
1·029	+37·8	0·474	1·166	+45	7·98	1·402	0	3·16
1·012	+51·8	0·413	1·156	+55	5·90	1·380	+18	2·21
0·997	+64·4	0·369	1·148	+65	4·68	1·372	+25	1·96
0·979	+77·9	0·331	1·140	+75	3·76	1·354	+40	1·53
0·951	+98·9	0·292	1·131	+85	3·10	1·330	+60	1·22
						1·311	+75	1·02

[5] Magill and Ubbelohde, *Trans. Faraday Soc.*, 1958, **54**, 1811.
[6] Mortimer, *Spectrochim. Acta*, 1957, **9**, 270; Maiants, Popov, and Kabachnik, *Optics and Spectroscopy*, 1959, **7**, 108.

<div align="center">TABLE 1. (*Continued*.)</div>

Bisdimethylamino-phosphoryl chloride			Trisdimethylamino-phosphine oxide			Tributyl phosphate		
δ_4	T	η	$\delta_4{}'$	T	η	$\delta_4{}'$	T	η
1·228	−25	15·66	1·037	+10	4·85	1·051	−65	333
1·222	−20	12·75	1·030	+18	3·94	1·042	−55	121
1·213	−10	9·04	1·024	+25	3·34	1·033	−45	56·6
1·203	0	6·57	1·011	+40	2·52	1·024	−35	32·9
1·184	+18	4·18	0·994	+60	1·82	1·015	−25	17·7
1·176	+25	3·55	0·980	+75	1·48	1·007	−15	11·1
1·161	+40	2·64				0·998	−5	8·50
1·142	+60	1·92				0·972	+25	3·39
1·127	+75	1·54				0·963	+35	2·77
						0·954	+45	2·23
						0·937	+65	1·61

Triphenyl phosphate			Tris-(2-ethylhexyl) phosphate			Trioctyl phosphine oxide		
$\delta_4{}'$	T	η	$\delta_4{}'$	T	η	$\delta_4{}'$	T	η
1·205	+50	10·04	0·985	−60	8080	0·844	+65	10·05
1·200	+55	8·62	0·977	−50	2560	0·838	+75	7·11
1·196	+60	7·34	0·969	−38·5		0·831	+85	5·48
1·191	+65	6·56	0·963	−30	260	0·821	+98·5	4·02
1·188	+70	5·77	0·955	−20·5	133			
1·183	+75	5·17	0·947	−10				
1·180	+80	4·61	0·941	0				
1·176	+85	4·19	0·924	+25·5	11·4			
1·172	+90	3·86	0·916	+35	8·21			
			0·908	+45·5	6·07			
			0·893	+65	3·76			
			0·886	+75·5	3·12			

<div align="center">DISCUSSION</div>

The viscosities of $POCl_3$ determined here disagree with those of Luchinskiĭ and Gut-mann,[7] but are in good agreement with values reported by Bowden and Morgan.[8] For PCl_3 the data are in some disagreement with those of the Russian workers, but agree moderately well with the work of Bowden and Morgan.[8] In both cases our evidence is that the viscous behaviour of the liquids is normal, *i.e.*, the plot of log η against $1/T$ is linear over the whole range of temperatures. We do not feel that the anomalous viscosity behaviour previously reported for PCl_3 in this temperature range is correct. Plots (not shown) of $1/\eta$ against density for these two compounds based on previous results are linear over the range 208—333°K for PCl_3, or 278—353°K for $POCl_3$.

Table 2 shows the values of the activation energies for flow derived from eqn. (1) at temperatures both near to and well removed from the freezing points. In view of the simple behaviour demonstrated for PCl_3 and $POCl_3$, the more complex behaviour observed for the approximately spherical $PSCl_3$ molecule near the melting point is somewhat surprising, but the large value of E_{vap}/E_{vis} at higher temperatures is also strange, and suggests a peculiarly easy flow process for this liquid in the " normal " region.

The viscosities of all the organophosphorus compounds cannot be fitted to a simple equation (1) over the whole of the temperature range.

The lattice and hole model of liquid transport properties most fully explored is that due to McLaughlin, whose analytical expression for viscosity contains a product of exponential terms involving the probability of a nearest neighbouring hole being available for transport, together with the energy of activation required for an appropriate migration against the repulsion envelopes of nearest neighbours. This theory is suitable for simple

[7] Luchinskiĭ, *J. Gen. Chem. U.S.S.R.*, 1937, **7**, 2116; Gutmann, *Monatsh.*, 1952, **83**, 164.
[8] Bowden and Morgan, *Phil. Mag.*, 1940, **29**, 367.

TABLE 2.

Formula	M. p. (°K)	Expt. at $T°$K	E_{vis} (kcal./mole)	$\dfrac{E_{vap}}{E_{vis}}$	Formula	M. p. (°K)	Expt. at $T°$K	E_{vis} (kcal./mole)	$\dfrac{E_{vap}}{E_{vis}}$
PCl_3	161	208	1·5	4·5	$(Me_2N)_2POCl$	246	247	5·4	2·4
		333	1·5	4·5			281	3·9	3·2
$POCl_3$	274·5	278	2·3	3·8			328	3·3	3·8
		353	2·3	3·8	$(Me_2N)_3PO$	280	286	4·5	2·9
$PSCl_3$	238	244	2·8	3·2			341	3·2	4·0
		370	1·6	5·5	$(Bu^nO)_3PO$	~193	222	7·2	2·0
$(MeO)_3P$	183·5	254	2·5	3·6			303	4·2	3·4
		323	1·9	4·4			350	3·1	4·5
$(PhO)_3P$	298	316	5·8	3·1	$(PhO)_3PO$	323	328	6·4	3·0
		333	5·2	3·5			348	5·1	3·7
		343	5·0	3·6			363	5·0	3·8
Me_2NPOCl_2	253	260	4·8	2·3	$(iso\text{-}C_8H_{17}O)_3PO$ *	~200	223	11·7	2·2
		282	2·8	3·9			263	8·1	3·2
		323	2·7	4·0			303	6·5	4·0
					$(n\text{-}C_8H_{17})_3PO$	325	339	8·2	
							364	5·8	

* 2-Ethylhexyl.

spherically symmetrical molecules, the intermolecular forces between which are approximately given by the Lennard–Jones 12 : 6 potential [9]

$$\phi(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right]$$

where $\phi(r)$ is the intermolecular potential at a molecular separation r, ε is the depth of the potential well and σ is the collision diameter.

Both of these exponential terms have been approximated by McLaughlin. The leading term in this exponent is the repulsion barrier term, which reduces to $\frac{1}{3}E_{vap}$. His calculations suggest, however, that the energy of forming a hole suitable for transport to ensue is small for idealised fluids at the hole temperatures in question, and it is this condition which leads to a ready simplification of his transport equations. The temperature-dependence of the small energy term associated with hole formation is compensated by a small temperature dependence of the pre-exponential terms for these fluids and eqn. (1) then becomes an approximately suitable relation.

It is only one step from this to the situation which obtains with complex molecules of anistropic geometry at low temperatures. Since we know that the influence of temperatures and density upon E_{vap} for a normal liquid is small, it seems clear that the change in the barrier term $\frac{1}{3}E_{vap}$ for viscous flow is also probably small. However, the energy required to *form* a hole in the liquid suitable for transport will depend quite markedly upon the proximity of large sterically hindered molecular groups, and for large polyatomic molecules at temperatures near melting might be expected greatly to exceed the value ascribed to it by McLaughlin for his quasi spherical molecules, *viz.*, $\varepsilon(V_0/V)^4$ where ε is the equilibrium attraction potential of the 12 : 6 potential, V is the molar volume and V_0 the normalising volume $N\sigma^3$ of the same potential. If the energy term associated with hole formation, though only a small fraction of E_{vap} for the liquid at moderate temperatures can, at sufficiently low temperatures and for sufficiently bulky molecules, become equivalent to the energy of formation of a Schottky defect, then this could explain anomalous viscosity behaviour near the melting point. Thus, though the value of E_{vap} is not appreciably changed by temperature, the quantity E_{vap}/E_{vis} might only be expected to be constant in that temperature range where the molecular packing is not too tight, and the energy of forming a hole is small, so that the energy required to pass over the barrier of neighbouring repulsions to the available hole is the dominant term. If this is so then the difference E_{vis} (low

[9] Hirschfelder, Curtiss, and Bird, " Molecular Theory of Gases and Liquids," Chapman and Hall, London, 1954.

temperature) — E_{vap} (limiting high temperature) approximately represents the additional energy required to form a suitably sized hole against the steric repulsions of the inter-molecular interactions at the high packing densities.

A search for a correlation between anomalous liquid behaviour and structure in these phosphorus compounds reveals little beyond the broad picture that in general, molecules containing bulky groups might be expected to give rise to pre-freezing anomalies in their liquid viscosity behaviour. Tests (not shown) for a correlation between molecular dipole moment and anomaly, or between plots of " reduced " density $(\delta_T - \delta_{m.p.})/\delta_{m.p.}$ against " reduced " temperature $T/T_{m.p.}$ and anomaly, apparently show no direct connections.

Not all bulky organic molecules give viscosity anomalies (McLaughlin and Ubbelohde found the molecule triphenylene to give normal behaviour, but not the molecule *o*-terphenyl). In this connection, is the probable importance of the melting temperature $T_m = \Delta H_{fusion}/\Delta S_{fusion}$. If the crystal can, without melting, permit some molecular libration, then (*a*) the m. p. will be high and (*b*) the liquid produced on melting will form a less crowded molecular lattice, showing transport properties which can be explained adequately by eqn. (1).

It may be significant that the m. p. of triphenylene is much higher than that of *o*-terphenyl. Again, triphenyl phosphite and phosphate have melting temperatures considerably higher than their trialkyl counterparts and give liquids with more normal viscosity characteristics. This effect is not unequivocal, because the trisoctyl phosphine oxide (which, however, has a high molecular dipole moment and is a partly flexible molecule), has a m. p. much higher than that of the trisdimethylaminophosphine oxide, but still gives viscosity behaviour which is quite "anomalous." In view of the above demonstration of the generality of departures from eqn. (1), it does seem possible that such " anomalous " viscosity behaviour just above the freezing point is not inconsistent with a quasi-lattice picture of liquids and probably does not need special association explanations, but that in many cases an extension of Lennard–Jones and Devonshire's theory of liquids to non-spherical molecules might provide a qualitatively satisfactory picture of the phenomena.

EXPERIMENTAL

Materials.—Phosphorus trichloride. A sample at least 99% pure (element analysis, density, and refractive index), was obtained by fractionally distilling over anhydrous aluminium chloride a good commercial sample in nitrogen. A middle cut, b. p. 74·5°/760 mm., was used.

Phosphorus oxychloride. A good sample of commercial material was fractionally distilled in nitrogen and the middle cut, b. p. 107·5°/760 mm., was taken. Purity exceeded 99% (f. p., density, and refractive index).

Thiophosphoryl chloride. A sample of approximately 98% PSCl$_3$, obtained *via* the reaction of PCl$_3$ and S with AlCl$_3$ as catalyst, was dried (CaCl$_2$) and fractionally distilled twice. The middle fraction boiled at 124—124·4°/746 mm. The purity was approximately 99% (vapour phase chromatography and element analysis).

Trimethyl phosphite. A highly purified pilot plant product was twice fractionally distilled and a middle cut, b. p. 55·1°/100 mm., taken. Purity exceeded 99% (infrared analysis).

Triphenyl phosphite. A good commercial sample was recrystallised, m. p. 25°.

Tributyl phosphate. The commercial sample was distilled, b. p. 150°/10 mm.

Triphenyl phosphate. The commercial sample, recrystallised from ethyl alcohol, had m. p. 50°.

Tris-2-ethylhexyl phosphate. A sample obtained by distillation of commercial sample had b. p. 196—200°/1 mm.

Trisdimethylaminophosphine oxide. A purified specimen was prepared from commercial material by double recrystallisation to remove any traces of (Me$_2$N)$_2$POCl. The vapour pressure of the liquid is given by

$$\log P_{mm} = -2955 \cdot 0/T + 8 \cdot 739$$

Bisdimethylaminophosphoryl chloride. A purified specimen was prepared free from Me$_2$N·POCl$_2$ by distillation and was then freed from (Me$_2$N)$_3$PO by crystallisation. The vapour pressure of the liquid is given by: $\log P_{mm} = -2885 \cdot 2/T + 8 \cdot 544$.

Monodimethylaminophosphoryl dichloride. A specimen was obtained from a fractional distillation of a good commercial sample. The vapour pressure of the liquid is given by:

$$\log P_{mm} = -2527 \cdot 0/T + 8 \cdot 2916$$

Trioctylphosphine oxide. A laboratory sample, twice recrystallised from light petroleum, and then vacuum sublimed, had m. p. 52°.

Apparatus.—Viscometers of the standard Ostwald pattern were calibrated with oils and other standard liquids. The limbs were provided with glass connectors, containing dry $CaCl_2$ or silica gel, which excluded moisture. Calibrated short range thermometers reading to $0 \cdot 1°$ were used throughout, and the thermostat baths were controlled to better than $\pm 0 \cdot 1°$ over the whole temperature range. The density determinations were made at each operating temperature by means of accurately calibrated dilatometers, the usual correction for the expasion of the glass being made. A stopwatch reading to $0 \cdot 1$ sec. was used.

The viscosities as calculated are quoted in Table 1 to the precision obtainable, and are in general reproducible to $0 \cdot 25\%$. The absolute accuracy is probably less than this since (*a*) use was made of standard liquids of known viscosity to correct for any temperature variations in viscometer constants, and (*b*) the flow times were such that the greatest kinetic energy correction to the constants was calculated to be $<1\%$. A calculation of the possible variations in these constants suggests that they would not exceed 1% over the whole temperature range.

ALBIGHT AND WILSON, OLDBURY, BIRMINGHAM.