Absolute Viscosity and Density of Trisubstituted Phosphoric Esters

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This paper presents measurements on the absolute viscosity (η) and density (ρ) of trisubstituted phosphoric esters which are useful in understanding their flow mechanism necessary for accessing their role as plasticizers. The effect of chain length and branching has been examined on the η and ρ trends. From η data, by using the Vogel−Tammann−Fulchur (VTF) equation, the VTF temperature (T_o) has been obtained which also represents the ideal glass transition temperature. T_o is related to the flexibility of the molecules. It is observed that T_o initially decreases with molecular weight, reaches a minimum, and increases thereafter. The initial decrease in T_o has been attributed to the enhanced flexibility of the phosphate esters. Reversal of flexibility with relative molar mass beyond 400 is due to the gentle collision of the arms of the trisubstituted phosphoric esters. This has been further corroborated from the molar mass exponent as exhibited in the η−molar mass plot. The isomeric effect on η has also been investigated in tricresyl phosphates, hitherto for the first time. The ortho isomer has highest η among the isomers. The para isomer was found to have lowest T_o and hence highest flexibility compared to the ortho and meta isomers.

Introduction

Despite the commercial importance of phosphate esters as plasticizers and lubricants, their flow behavior has not been studied in detail. An understanding of the flow behavior would help in the elucidation of the molecular mechanism of plasticization and hence would facilititate proper selection and design of plasticizers. The flow behavior in liquids is generally described from Eyring's free volume model in terms of free energy of activation for the viscous flow ($\Delta G^{\#}_n$) which is obtained directly from absolute viscosity (η) and density (ρ) data at a given temperature. In this paper, we present an investigation on the η and ρ of a homologous series of phosphate ester, namely trialkyl phosphate esters, as a function of temperature. Tricresyl phosphate is the most widely used fire retardant plasticizer, but the isomeric effect in their plasticizing or flow properties has not been studied. We are also examining here the effect of isomers on the η and ρ values of tricresyl phosphates. These data on the above long-chain esters have not been reported hitherto.

Materials

$POCl_3$, alcohols, tertiary amines, and solvents, of analytical grade, were procured from SD Fine Chemicals, Bombay. They were purified by distillation using standard procedures (*1*). The phosphate esters, synthesized in the present investigation, are given in Tables 1 and 2.

Preparation of Esters

The pentavalent trisubstituted phosphoric esters ($PO(OR)_3$) have been synthesized and classified into aliphatic and aromatic based on the nature of the R group.

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† This article is dedicated to the memory of Prof. K. Kishore.

Table 1. Structure and Molecular Weight of Trialkyl Phosphates, $P(O)(O-(CH_2)_x-CH_3)_3$

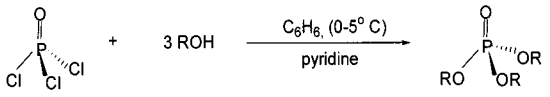
	name (triphosphate)	abbrev	molecular formula	molecular weight
1	methyl	tmp	$C_3H_9O_4P$	140
2	ethyl	tep	$C_6H_{15}O_4P$	182
3	*n*-propyl	tpp	$C_9H_{21}O_4P$	224
4	isopropyl (B)[a]	isop	$C_9H_{21}O_4P$	224
5	*n*-butyl	nbp	$C_{12}H_{27}O_4P$	266
6	isobutyl (B)	isob	$C_{12}H_{27}O_4P$	266
7	isoamyl (B)	isoam	$C_{15}H_{33}O_4P$	308
8	*n*-hexyl	thp	$C_{18}H_{34}O_4P$	350
9	*n*-decyl	tdp	$C_{30}H_{63}O_4P$	519
10	*n*-dodecyl	tdodp	$C_{36}H_{75}O_4P$	603

[a] B, Branch in alkyl arms.

Table 2. Structure and Molecular Weight of Triaromatic Phosphates, $P(O)(OR)_3$

	name (triphosphate)	abbrev	molecular formula	molecular weight
1	*o*-cresyl	*o*-tcp	$C_{21}H_{21}O_4P$	368
2	*m*-cresyl	*m*-tcp	$C_{21}H_{21}O_4P$	368
3	*p*-cresyl	*p*-tcp	$C_{21}H_{21}O_4P$	368

Aliphatic Esters. All the esters were prepared by the condensation of $POCl_3$ and alcohols, (as given below) in ice-cold conditions using pyridine as the acid quencher (*2*). The liquid esters were purified by fractional distillation, while the solid esters were purified by recrystallization.



Aromatic Esters. These esters were synthesized by interfacial condensation using tetra-*n*-butylammonium bromide (TBAB) as the phase transfer catalyst (*3*). The chloroform solution of $POCl_3$ was added dropwise to the aqueous solution of sodium salt of aromatic alcohols in ice-cold conditions. The compounds were isolated from the

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Table 3. Viscosity Data

T/K	η/mPas	T/K	η/mPas	T/K	η/mPas	T/K	η/mPas	T/K	η/mPas
				trimethyl phosphate (tmp)					
293.0	2.257	303.0	1.823	313.0	1.526	323.0	1.340	333.0	1.217
294.0	2.215	304.0	1.787	314.0	1.503	324.0	1.326	334.0	1.207
295.0	2.170	305.0	1.752	315.0	1.482	325.0	1.312	335.0	1.198
296.0	2.124	306.0	1.718	316.0	1.461	326.0	1.298	336.0	1.189
297.0	2.077	307.0	1.687	317.0	1.441	327.0	1.285	337.0	1.180
298.0	2.032	308.0	1.656	318.0	1.423	328.0	1.273	338.0	1.171
299.0	1.987	309.0	1.628	319.0	1.405	329.0	1.261	339.0	1.162
302.0	1.862	312.0	1.549	322.0	1.355	332.0	1.228	342.0	1.139
				triethyl phosphate (tep)					
294.0	1.769	307.0	1.546	315.6	1.386	324.0	1.234	339.9	0.995
297.5	1.716	309.4	1.502	317.3	1.354	325.1	1.216	340.2	0.992
298.5	1.700	310.8	1.475	317.5	1.341	326.5	1.193	342.5	0.963
302.0	1.640	311.5	1.462	319.8	1.309	328.2	1.165	345.6	0.926
303.1	1.619	312.1	1.451	320.2	1.301	335.3	1.057	346.1	0.921
304.1	1.602	314.9	1.398	322.7	1.258	337.7	1.025	347.4	0.906
306.4	1.560	315.4	1.388	323.3	1.248	339.0	1.007	352.0	0.858
				tri-*n*-propyl phosphate (tpp)					
323.0	2.393	330.2	1.919	338.8	1.603	346.4	1.446	357.0	1.315
326.0	2.161	331.2	1.871	339.5	1.586	347.8	1.424	358.0	1.306
327.0	2.096	332.6	1.809	341.1	1.548	350.8	1.383	362.0	1.272
328.0	2.035	334.3	1.744	342.3	1.522	354.2	1.344	364.0	1.256
329.3	1.965	336.0	1.685	343.4	1.500	355.0	1.335		
				triisopropyl phosphate (isop)					
296.6	2.425	302.2	2.104	308.1	1.829	317.3	1.483	323.8	1.285
297.7	2.358	304.0	2.013	310.7	1.721	317.7	1.471	324.9	1.253
299.4	2.258	305.1	1.962	311.1	1.706	320.5	1.381	327.1	1.195
300.8	2.178	307.3	1.861	314.1	1.592	321.3	1.358	328.7	1.154
				tri-*n*-butyl phosphate (nbp)					
293.0	3.882	303.0	3.016	313.0	2.440	323.0	2.091	333.0	1.865
294.0	3.797	304.0	2.944	314.0	2.397	324.0	2.064	334.0	1.846
295.0	3.708	305.0	2.876	315.0	2.356	325.0	2.038	335.0	1.829
296.0	3.614	306.0	2.811	316.0	2.317	326.0	2.013	336.0	1.812
297.0	3.521	307.0	2.749	317.0	2.280	327.0	1.989	337.0	1.796
298.0	3.429	308.0	2.691	318.0	2.245	328.0	1.966	338.0	1.780
299.0	3.340	309.0	2.635	319.0	2.211	329.0	1.944	339.0	1.765
300.0	3.255	310.0	2.583	320.0	2.179	330.0	1.923	340.0	1.750
301.0	3.171	311.0	2.533	321.0	2.148	331.0	1.903	341.0	1.736
302.0	3.091	312.0	2.485	322.0	2.119	332.0	1.883	342.0	1.722
				triisobutyl phosphate (isob)					
296.6	4.412	303.8	3.325	309.6	2.734	319.4	2.071	331.5	1.622
297.6	4.219	304.6	3.238	311.5	2.578	320.2	2.035	332.4	1.598
299.7	3.884	306.2	3.056	313.0	2.461	323.4	1.890	335.8	1.521
301.1	3.686	307.6	2.916	315.5	2.297	327.4	1.740	336.9	1.500
302.9	3.436	308.2	2.864	316.6	2.230	328.0	1.722		
				triisoamyl phosphate (isoam)					
301.0	4.050	309.0	3.245	316.0	2.700	323.0	2.270	331.0	1.884
302.0	3.937	310.0	3.159	317.0	2.632	324.0	2.217	333.0	1.799
303.0	3.828	311.0	3.075	318.0	2.566	325.0	2.165	334.0	1.758
304.0	3.722	312.0	2.995	319.0	2.503	326.0	2.115	335.0	1.718
305.0	3.620	313.0	2.917	320.0	2.442	328.0	2.018	336.0	1.678
306.0	3.522	314.0	2.842	321.0	2.383	329.0	1.972	337.0	1.639
307.0	3.426	315.0	2.769	322.0	2.326	330.0	1.927	338.0	1.601
				tri-*n*-hexyl phosphate (thp)					
299.0	6.460	323.0	3.612	330.0	3.101	340.9	2.502	348.7	2.197
302.9	5.870	323.9	3.536	333.2	2.901	341.4	2.479	350.0	2.154
306.9	5.318	325.5	3.414	336.0	2.746	343.0	2.412	352.7	2.070
311.0	4.806	326.4	3.345	337.2	2.681	344.8	2.340	356.8	1.959
319.5	3.916	328.1	3.229	338.0	2.639	347.1	2.253	361.0	1.862
				tri-*n*-decyl phosphate (tdp)					
303.0	15.710	312.0	11.812	320.0	9.318	328.0	7.512	336.0	6.176
304.0	15.210	313.0	11.455	321.0	9.060	329.0	7.324	337.0	6.032
305.0	14.730	314.0	11.113	322.0	8.811	330.0	7.143	338.0	5.891
306.0	14.264	315.0	10.783	323.0	8.573	331.0	6.968	339.0	5.753
307.0	13.816	316.0	10.465	324.0	8.342	332.0	6.799	340.0	5.617
308.0	13.384	317.0	10.162	325.0	8.123	333.0	6.636	341.0	5.484
309.0	12.969	318.0	9.869	326.0	7.912	334.0	6.478	342.0	5.353
310.0	12.569	319.0	9.588	327.0	7.708	335.0	6.325	343.0	5.223

Table 3 (Continued)

T/K	η/mPas	T/K	η/mPas	T/K	η/mPas	T/K	η/mPas	T/K	η/mPas
				tri-*n*-dodecyl phosphate (tdodp)					
315.0	14.274	321.0	11.749	327.0	9.803	333.0	8.295	338.0	7.267
316.0	13.808	322.0	11.387	328.0	9.526	334.0	8.076	339.0	7.079
317.0	13.359	323.0	11.043	329.0	9.259	335.0	7.864	340.0	6.895
318.0	12.930	324.0	10.712	330.0	9.003	336.0	7.659	341.0	6.715
319.0	12.520	325.0	10.397	331.0	8.757	337.0	7.641	342.0	6.537
320.0	12.126	326.0	10.093	332.0	8.522				
				tri-*o*-cresyl phosphate (*o*-tcp)					
290.7	144.67	297.6	89.42	303.6	59.90	309.6	40.76	314.8	29.54
291.5	136.66	298.4	84.69	304.4	56.86	310.4	38.76	315.6	28.14
292.3	129.14	299.2	80.24	305.2	53.98	311.2	36.87	316.4	26.81
293.1	122.06	300.0	76.04	306.0	51.26	312.8	33.39	318.0	24.36
294.7	109.16	301.6	68.34	307.6	46.26	313.6	31.79	319.6	22.15
296.8	94.44	302.8	63.13	308.8	42.87				
				tri-*m*-cresyl phosphate (*m*-tcp)					
300.5	44.13	311.6	25.78	321.8	17.12	334.4	11.34	350.6	7.57
302.0	40.78	313.7	23.55	323.3	16.22	335.9	10.86	355.7	6.83
303.5	37.76	315.2	22.12	324.8	15.38	337.4	10.42	360.8	6.23
305.0	35.04	316.7	20.81	326.9	14.32	339.5	9.850	365.3	5.79
307.1	31.66	318.2	19.61	329.9	12.99	342.5	9.120	368.5	5.52
308.6	29.51	320.3	18.10	332.9	11.85	346.1	8.370	371.7	5.28
310.1	27.55								
				tri-*p*-cresyl phosphate (*p*-tcp)					
353.5	7.24	359.6	6.27	365.0	5.54	372.2	4.73	378.2	4.22
354.1	7.14	360.8	6.10	366.2	5.40	373.4	4.61	379.4	4.07
355.3	6.94	361.4	6.01	367.4	5.25	374.6	4.50	380.6	3.97
356.5	6.74	362.0	5.93	368.6	5.12	375.8	4.38	381.8	3.88
357.7	6.55	363.2	5.77	369.2	5.05	376.4	4.33	382.4	3.83
358.9	6.37	364.4	5.62	371.0	4.86	377.0	4.28	383.0	3.78

anhydrous organic layer by removing $CHCl_3$ and then purified by vacuum distillation for liquids or recrystallization for solids.

Characterization. The purified esters were characterized by FT-NMR and FT-IR spectroscopic techniques. ^1H NMR spectra were recorded at 298 K on a Bruker AMX-200 spectrometer using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. The FT-IR spectra were recorded using a Bio-Rad FTS-7 spectrometer, as neat for the liquid samples and as KBr pellets for the solid samples.

Experimental Techniques

Absolute Viscosity Measurement. The atmospheric pressure absolute viscosity measurements were carried out for tmp, tep, tpp, isop, nbp, and thp (see Table 1) by Brookfield viscometer and for the rest by Ubbelohde viscometer.

Brookfield Viscometer. The Brookfield viscometer employs the principle of rotational viscometry (*4*). The viscometer was calibrated using the NBS viscosity standards available from Brookfield Engineering Laboratories (*4*). The reading obtained from the display on the digital viscometer was multiplied by a factor (obtained from the "factor finder" supplied with the instrument) to calculate the absolute viscosity in mPas. The error in the viscocity data was ±2.5%.

Ubbelohde Viscometer. The kinematic viscosity (υ) was determined as a function of temperature by a calibrated Ubbelohde viscometer. The measurement is based on the American Society for Testing Materials (ASTM) method (*5*) D445. The temperature of the bath was maintained constant up to ±0.1 °C. The viscometer was calibrated using tri-*n*-butyl phosphate standard. The absolute viscosity was determined by the following equation

$$\eta = \upsilon\rho \qquad (1)$$

where ρ is the density. Since the flow was considered as Newtonian under the experimental conditions, no correction was made for the shear viscosity. By keeping high efflux times (above 200 s), the error due to kinetic energy was minimized. The error in the viscosity data was found to be ±3.5%. The error in the Ubbelohde viscometric measurements was higher than that for the Brookfield viscometer as the absolute viscosity was derived from two measured quantities the ν and ρ whose errors get added up. The viscosity data are given in Table 3.

Density Measurements. The atmospheric pressure liquid densities were determined as a function of temperature by a dilatometric method following ASTM procedure (*6*) D 1480. The thermostat medium and the temperature range of measurements were made identical to those used for viscosity determinations. The dilatometer was calibrated by using mercury. The error involved in the measurements was less than ±0.1%. The density data are given in Table 4.

Results and Discussion

The density data reflect the packing of the molecules and would reveal the free volume that may be available in the system. Among trialkyl phosphates, trimethyl phosphate possesses the highest density (see Table 4). The network of dipole − dipole forces ($P^{\delta+} = 0^{\delta-}$) binds the molecules together promoting close packing in trimethyl phosphate. With an increase in molecular weight, the dipolar forces are gradually diluted by increasing the presence of alkyl groups; as a result, the molecules are loosened progressively and hence the density decreases with molar mass (Figure 1). To understand the effect of branching, two systems, namely, butyl (*n*- and iso) and propyl (*n* and iso) phosphate esters, were analyzed. Among butyl phosphate esters, the density of *n*-butyl is higher than the iso isomer at lower temperature but reversal takes place at higher temperature (above 40 °C) (Figure 2). As the temperature increases (Table 4), the free volume increases and the

Table 4. Density Data

T/K	ρ/g cm^{-3}	T/K	ρ/g cm^{-3}	T/K	ρ/g cm^{-3}	T/K	ρ/g cm^{-3}	T/K	ρ/g cm^{-3}
trimethyl phosphate (tmp)									
298.0	1.205	307.0	1.194	317.0	1.182	326.0	1.171	335.0	1.160
299.0	1.204	308.0	1.193	318.0	1.181	327.0	1.170	336.0	1.159
300.0	1.202	310.0	1.190	319.0	1.180	328.0	1.169	337.0	1.158
301.0	1.201	311.0	1.189	320.0	1.178	329.0	1.168	338.0	1.157
302.0	1.200	312.0	1.188	321.0	1.177	330.0	1.166	339.0	1.156
303.0	1.199	313.0	1.187	322.0	1.76	331.0	1.165	340.0	1.154
306.0	1.195	316.0	1.183	325.0	1.172	334.0	1.162		
triethyl phosphate (tep)									
298.0	1.109	308.0	1.107	319.0	1.105	328.0	1.103	337.0	1.1017
299.0	1.109	309.0	1.107	320.0	1.105	329.0	1.103	338.0	1.1016
300.0	1.109	312.0	1.106	321.0	1.105	330.0	1.103	339.0	1.1013
301.0	1.109	313.0	1.106	322.0	1.104	331.0	1.102	340.0	1.1011
302.0	1.108	314.0	1.106	323.0	1.104	332.0	1.102	341.0	1.1009
303.0	1.108	315.0	1.106	324.0	1.104	333.0	1.102	342.0	1.1007
304.0	1.108	316.0	1.106	325.0	1.104	334.0	1.102	343.0	1.1005
305.0	1.108	317.0	1.105	326.0	1.104	335.0	1.102	344.0	1.1003
306.0	1.108	318.0	1.105	327.0	1.103	336.0	1.101	345.0	1.1001
307.0	1.107								
tri-*n*-propyl phosphate (tpp)									
323.0	1.006	330.0	1.005	337.0	1.004	343.0	1.002	349.0	1.0018
324.0	1.006	331.0	1.005	338.0	1.003	344.0	1.002	350.0	1.0016
325.0	1.006	332.0	1.004	339.0	1.003	345.0	1.002	351.0	1.0014
326.0	1.006	333.0	1.004	340.0	1.003	346.0	1.002	352.0	1.0012
327.0	1.005	334.0	1.004	341.0	1.003	347.0	1.002	353.0	1.0010
328.0	1.005	335.0	1.004	342.0	1.003	348.0	1.001	354.0	1.0008
329.0	1.005	336.0	1.004						
triisopropyl phosphate (isop)									
298.0	0.984	308.0	0.982	318.0	0.980	327.0	0.978	336.0	0.9772
299.0	0.984	309.0	0.982	319.0	0.980	328.0	0.978	337.0	0.977
300.0	0.983	310.0	0.982	320.0	0.980	329.0	0.978	338.0	0.976
301.0	0.983	311.0	0.981	321.0	0.980	330.0	0.978	339.0	0.976
302.0	0.983	312.0	0.981	322.0	0.979	331.0	0.978	340.0	0.976
303.0	0.983	313.0	0.981	323.0	0.979	332.0	0.977	341.0	0.976
304.0	0.983	314.0	0.981	324.0	0.979	333.0	0.977	342.0	0.976
305.0	0.982	315.0	0.981	325.0	0.979	334.0	0.977	343.0	0.975
306.0	0.982	316.0	0.980	326.0	0.979	335.0	0.977	344.0	0.975
307.0	0.982	317.0	0.980						
tri-*n*-butyl phosphate (nbp)									
298.0	0.972	306.0	0.965	316.0	0.957	326.0	0.948	336.0	0.939
299.0	0.971	307.0	0.964	317.0	0.956	327.0	0.947	337.0	0.938
300.0	0.971	310.0	0.962	318.0	0.955	328.0	0.946	338.0	0.937
301.0	0.970	311.0	0.961	319.0	0.954	329.0	0.945	339.0	0.936
302.0	0.969	312.0	0.960	322.0	0.951	330.0	0.944	340.0	0.936
303.0	0.968	313.0	0.959	323.0	0.950	331.0	0.943	341.0	0.935
304.0	0.967	314.0	0.958	324.0	0.950	334.0	0.941	342.0	0.934
305.0	0.966	315.0	0.957	325.0	0.949	335.0	0.940		
triisobutyl phosphate (isob)									
300.0	0.961	311.0	0.959	322.0	0.957	332.0	0.955	342.0	0.954
301.0	0.961	312.0	0.959	323.0	0.957	333.0	0.955	343.0	0.953
302.0	0.961	313.0	0.959	324.0	0.957	334.0	0.955	344.0	0.953
303.0	0.960	314.0	0.959	325.0	0.957	335.0	0.955	345.0	0.953
304.0	0.960	315.0	0.958	326.0	0.956	336.0	0.955	346.0	0.953
305.0	0.960	316.0	0.958	327.0	0.956	337.0	0.954	347.0	0.953
306.0	0.960	317.0	0.958	328.0	0.956	338.0	0.954	348.0	0.952
307.0	0.960	318.0	0.958	329.0	0.956	339.0	0.954	349.0	0.952
308.0	0.960	319.0	0.958	330.0	0.956	340.0	0.954	350.0	0.952
309.0	0.959	320.0	0.957	331.0	0.955	341.0	0.954	351.0	0.952
310.0	0.959	321.0	0.957						
triisoamyl phosphate (isoam)									
298.0	0.957	307.0	0.956	315.0	0.954	323.0	0.953	331.0	0.952
299.0	0.957	308.0	0.956	316.0	0.954	324.0	0.953	332.0	0.951
300.0	0.957	309.0	0.955	317.0	0.954	325.0	0.953	333.0	0.951
301.0	0.957	310.0	0.955	318.0	0.954	326.0	0.952	334.0	0.951
302.0	0.957	311.0	0.955	319.0	0.954	327.0	0.952	335.0	0.951
303.0	0.957	312.0	0.955	320.0	0.953	328.0	0.952	336.0	0.951
304.0	0.956	313.0	0.955	321.0	0.953	329.0	0.952	337.0	0.950
305.0	0.956	314.0	0.955	322.0	0.953	330.0	0.952	338.0	0.950

Table 4 (Continued)

T/K	ρ/g cm^{-3}	T/K	ρ/g cm^{-3}	T/K	ρ/g cm^{-3}	T/K	ρ/g cm^{-3}	T/K	ρ/g cm^{-3}
tri-*n*-hexyl phosphate (thp)									
303.0	0.949	313.0	0.947	323.0	0.945	333.0	0.944	342.0	0.942
304.0	0.949	314.0	0.947	324.0	0.945	334.0	0.943	343.0	0.942
305.0	0.949	315.0	0.947	325.0	0.945	335.0	0.943	344.0	0.942
306.0	0.948	316.0	0.947	326.0	0.945	336.0	0.943	345.0	0.942
307.0	0.948	317.0	0.947	327.0	0.945	337.0	0.943	346.0	0.941
308.0	0.948	318.0	0.946	328.0	0.945	338.0	0.943	347.0	0.941
309.0	0.948	319.0	0.946	329.0	0.944	339.0	0.943	348.0	0.941
310.0	0.948	320.0	0.946	330.0	0.944	340.0	0.942	349.0	0.941
311.0	0.948	321.0	0.946	331.0	0.944	341.0	0.942	350.0	0.941
312.0	0.947	322.0	0.946	332.0	0.944				
tri-*n*-decyl phosphate (tdp)									
303.0	0.907	313.0	0.905	323.0	0.903	332.0	0.902	341.0	0.900
304.0	0.907	314.0	0.905	324.0	0.903	333.0	0.902	342.0	0.900
305.0	0.906	315.0	0.905	325.0	0.903	334.0	0.902	343.0	0.900
306.0	0.906	316.0	0.905	326.0	0.903	335.0	0.901	344.0	0.900
307.0	0.906	317.0	0.904	327.0	0.903	336.0	0.901	345.0	0.900
308.0	0.906	318.0	0.904	328.0	0.903	337.0	0.901	346.0	0.900
309.0	0.906	319.0	0.904	329.0	0.902	338.0	0.901	347.0	0.899
310.0	0.906	320.0	0.904	330.0	0.902	339.0	0.901	348.0	0.899
311.0	0.905	321.0	0.904	331.0	0.902	340.0	0.901	349.0	0.899
312.0	0.905	322.0	0.904						
tri-*n*-dodecyl phosphate (tdodp)									
315.0	0.892	321.0	0.891	327.0	0.890	333.0	0.889	338.0	0.888
316.0	0.892	322.0	0.891	328.0	0.890	334.0	0.889	339.0	0.888
317.0	0.892	323.0	0.891	329.0	0.890	335.0	0.889	340.0	0.888
318.0	0.892	324.0	0.891	330.0	0.890	336.0	0.889	341.0	0.888
319.0	0.891	325.0	0.890	331.0	0.889	337.0	0.888	342.0	0.888
320.0	0.891	326.0	0.890	332.0	0.889				

T/K	ρ/g cc^{-1}	T/K	ρ/g cc^{-1}	T/K	ρ/g cc^{-1}	T/K	ρ/g cc^{-1}	T/K	ρ/g cc^{-1}
tri-*o*-cresyl phosphate (*o*-tcp)									
299.7	1.180	312.9	1.177	326.1	1.174	336.6	1.172	346.6	1.170
301.5	1.180	314.7	1.177	327.9	1.174	338.4	1.172	348.4	1.169
303.3	1.179	316.5	1.176	329.7	1.174	340.2	1.171	350.2	1.169
306.3	1.179	319.5	1.176	331.5	1.173	341.6	1.171	351.6	1.169
308.1	1.178	321.3	1.175	333.3	1.173	343.4	1.171	353.4	1.168
309.9	1.178	323.1	1.175	335.1	1.172	345.2	1.170	355.2	1.168
tri-*m*-cresyl phosphate (*m*-tcp)									
314.1	1.179	321.9	1.177	329.7	1.176	337.5	1.174	344.1	1.173
315.3	1.179	323.1	1.177	330.9	1.175	338.7	1.174	345.3	1.172
316.5	1.179	324.3	1.177	332.1	1.175	340.5	1.173	346.5	1.172
317.7	1.178	325.5	1.177	333.9	1.175	341.7	1.173	348.0	1.172
318.9	1.178	327.3	1.176	335.1	1.175	342.9	1.173	352.2	1.171
320.7	1.178	328.5	1.176	336.3	1.174				
tri-*p*-cresyl phosphate (*p*-tcp)									
344.9	1.171	350.7	1.170	356.5	1.169	362.3	1.168	368.1	1.166
345.9	1.171	351.7	1.170	357.5	1.169	363.3	1.167	369.1	1.166
346.9	1.171	352.7	1.170	358.5	1.169	364.3	1.167	370.1	1.166
347.9	1.171	353.7	1.170	359.5	1.168	365.3	1.167	371.1	1.166
348.9	1.171	354.7	1.169	360.5	1.168	366.3	1.167	372.1	1.166

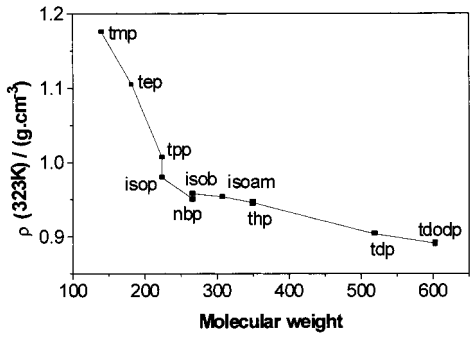

Figure 1. Variation of ρ with molecular weight in trialkyl phosphates.

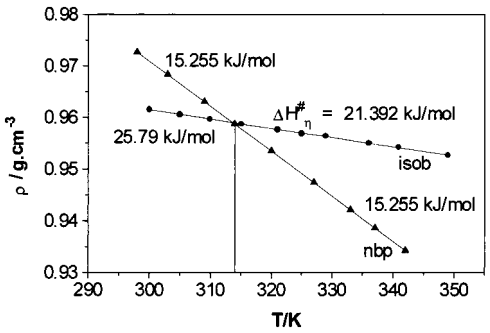

Figure 2. Dependence of ρ on temperature in butyl phosphates.

molecules accquire higher energy, these effects reduce the difference in viscosity at higher temperatures.

In *n*- and isopropyl phosphates, the *n*-propyl has higher density than isopropyl (Figure 3). Unlike in butyl phosphates, these two propyl isomers have wide difference in their density; the free volume in iso is much higher than that its linear counterpart. This is clearly reflected in their viscosity data; the viscosity of *n*-propyl is higher than that of isopropyl phosphate (Table 3).

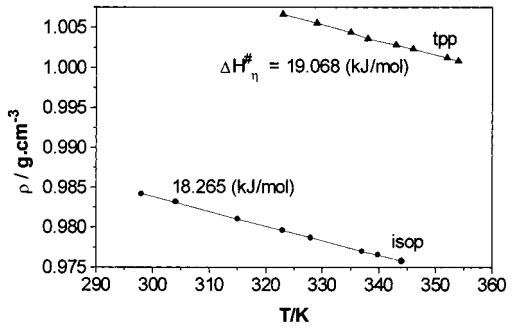

Figure 3. Dependence of ρ on temperature in propyl phosphates.

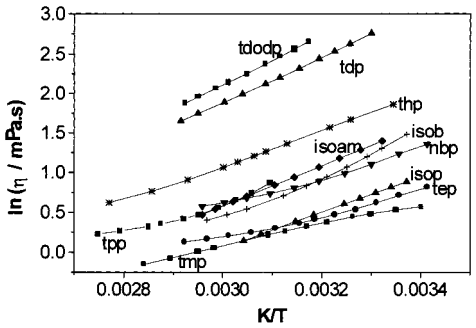

Figure 4. Variation of ln η as a function of $1/T$ in trialkyl phosphates.

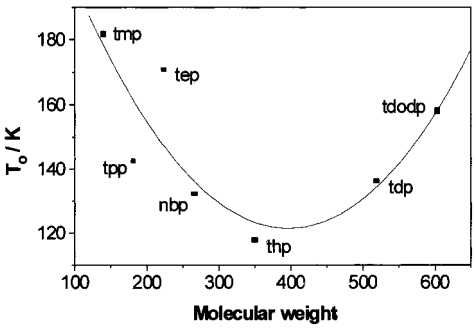

Figure 5. Variation of T_o on molecular weight in trialkyl phosphates.

A plot of ln η vs $1/T$ (Figure 4) shows a significant deviation from Arrhenius behavior. Continuous lowering of the activation energy of the viscous flow with lowering of temperature is an indication of non-Arrhenius behavior. Such non-Arrhenius behavior is observed in complex liquids for which the Vogel−Tamman−Fulcher equation (VTF equation) (*7*) describes the temperature dependence of the viscosity much better.

$$\ln \eta = \ln A + \frac{B}{T - T_o}(\text{VTF equation}) \qquad (2)$$

Where A, B, and T_o (VTF temperature) are constants. T_o is also called the ideal glass transition temperature. T_o was obtained for all the esters. T_o gives an idea about the relative flexibility of molecules. An increase in flexibility is indicated by the corresponding decrease in T_o. The T_o values in phosphate esters were found to initially decrease with molecular weight, reach a minimum, and thereafter start increasing again (Figure 5). The initial decrease in T_o is due to the enhanced flexibility of chains with the addition of CH_2 groups. But increase in T_o beyond a critical molar mass of ~400 the arms of the phosphoric esters may hit each other during the motion. This would reduce the flexibility of the molecules. Hence, T_o starts increasing beyond a molar mass of ~400.

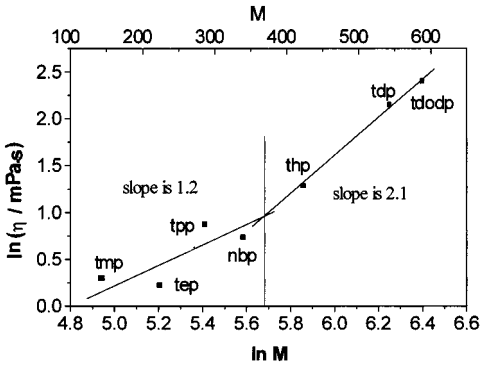

Figure 6. Variation of ln η vs ln M in trialkyl phosphates at 323 K.

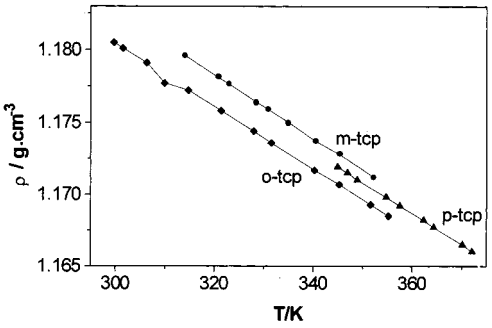

Figure 7. Variation of ρ with temperature in triaromatic phosphates.

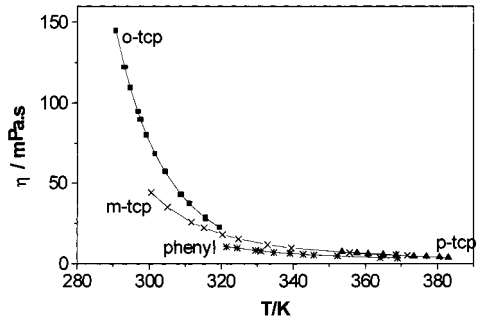

Figure 8. Variation of viscosity with temperature in triaromatic phosphates.

Variation of viscosity (at 323 K) as a function of molar mass is shown in Figure 6. It shows a nonlinear dependence on the molar mass. Up to ~400, the plot could be considered close to linear and thereafter the dependence of viscosity on molar mass increases. The molar mass dependence of viscosity could be represented by the following emperical relationship.

$$\eta = KM^{\alpha} \qquad (3)$$

Where K and α are constants. For low molar mass esters (M < 400), α is close to unity, but for higher molar mass (M > 400), α is around 2.0 which is less than 3.4 which indicates the onset of entanglement in high molecular weight polymers. In high molecular weight phosphate esters, the α value is 2.0 which indicates that there is some kind of loose entanglement or gentle collision of the arms during motion which eventually enhances the dependence of viscosity on molecular weight.

Tricresyl phosphate is one of the most widely used commercial phosphorus plasticizers for imparting fire retardancy in polymers. Here we have studied the effect of isomers (ortho, para, and meta) on their viscosity,

density, and T_o behavior. From density data (Figure 7) it is clear that the ortho isomer has lowest density and hence it has more free volume. This is adequately reflected in the viscosity data also (Figure 8), the ortho isomer has the highest viscosity among the isomers. With an increase in temperature the molecules accquire more energy and the free volume also increases so the difference in viscosity of isomers reduces as the temperature increases (see Figure 8). T_o values of these isomers were obtained from the VTF equation. The ortho and meta isomers have almost same T_o, while that of the para isomer was found to be more than 100 °C lower. The anomalous behavior of the para isomer is not clear at present.

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