

Studies in Molten State: Viscosity of Nitrophenol Melts

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The viscosity data of three nitrophenol melts (ONP, MNP, and PNP) are reported in the melt region (30.0–140°C). The results show an Arrhenius behavior in the high-temperature and supercooled regions. In the supercooled region the Arrhenius equation is obeyed with different Arrhenius parameters. The volume fraction of clusters ϕ and equilibrium constants for the equilibrium $A_g \rightleftharpoons gA$ are calculated in the supercooled region and are reported. The viscosity increase near and below the melting point may be attributed to cluster formation and to hindrance to rotation because of the low available volume.

A large amount of work has been devoted to the study of melts of nonpolar liquids (3, 10, 16) because no complicating effects due to association are present. However, less attention has been paid to the melt regions of polar liquids, such as the disubstituted benzenes where the effect of substituent positions as well as steric and volume effects on various physical properties would become significant. In continuation with our studies of nitrotoluene melts, it was considered of interest to study the viscosity of nitrophenol melts and to estimate the effect of hydrogen bonding.

Experimental

Purification of samples. Samples of *o*-, *m*-, and *p*-nitrophenols (ONP, MNP, and PNP) were purified and recrystallized several times according to methods described in the literature (17). Finally, recrystallized samples were dried under reduced pressure over P₂O₅. The melting points of the final samples were 44.9°, 96°, and 114°C, respectively, agreeing closely with literature values (6, 11).

Density and viscosity measurements. The densities of these melts were measured with the help of a specially designed pipet pycnometer described earlier (13). Viscosity was measured by an Ubbelohde suspended level viscometer. The temperature was controlled to $\pm 0.05^\circ\text{C}$ with a toluene regulator and a calibrated thermometer of sensitivity 0.1°C. The estimated relative error in density was ~ 1 in 10^4 and in viscosity ~ 2 in 10^3 . Supercooling was obtained by heating the samples in the viscometer to a temperature sufficiently above their melting point and cooling to the required temperature in a constant temperature bath without disturbing the viscometer (5).

Results

The density and viscosity data of ONP, MNP, and PNP melts are given in Tables I–III. Viscosity data were plotted according to the Arrhenius equation:

$$\log \eta = A + \frac{B}{T} \quad (1)$$

as $\log \eta$ vs. $1/T$ in Figure 1. The Arrhenius parameters A and B thus obtained for all three nitrophenols are recorded in Table IV. These viscosity data in the supercooled region were fitted with the Einstein equation (β):

$$\eta/\eta_i = 1 + 2.5\phi + 7\phi^2 \quad (2)$$

where η_i is the viscosity extrapolated from the high-temperature region, η is the actual viscosity, and ϕ is the volume fraction of clusters. Values of ϕ for all three isomers thus obtained are tabulated in Table V, and a plot of $\log \phi$ vs. $1/T$ for ONP is shown in Figure 2.

Discussion

Viscosity and its variation in the melt region can give an insight into the structural changes. Generally, at temperatures above the melting point, the Arrhenius equation is obeyed by most of the systems. In many cases near the melting point, the plot of $\log \eta$ vs. $1/T$ shows a break at temperature T_A just above the melting point. In our case, this break is at approximately 47°, 98.5°, and 117°C for ONP, MNP, and PNP, respectively. The functional dependence of η on T may change below this temperature. For the purpose of discussion, we have divided the temperature range under study into a region

Table I. Density and Viscosity of ONP Melts

Temp, °C	Density, g/ml	Viscosity, cP
30.0	1.3039	3.721
35.0	1.3024	3.285
37.0	1.3017	3.116
40.0	1.2984	2.899
42.0	1.2972	2.776
45.0	1.2941	2.586
47.0	1.2918	2.487
50.0	1.2879	2.312
52.0	1.2867	2.207
55.0	1.2829	2.072
57.0	1.2809	2.008
60.0	1.2769	1.895
62.0	1.2757	1.847
65.0	1.2723	1.724
67.0	1.2701	1.658
70.0	1.2669	1.596
72.0	1.2645	1.535
75.0	1.2615	1.456

Table II. Density and Viscosity of MNP Melts

Temp, °C	Density, g/ml	Viscosity, cP
90.0	1.2933	4.139
92.0	1.2912	3.988
94.0	1.2892	3.730
96.0	1.2872	3.581
98.0	1.2851	3.423
100.0	1.2831	3.261
102.0	1.2811	3.137
104.0	1.2790	3.006
106.0	1.2770	2.872
108.0	1.2750	2.761
110.0	1.2729	2.663
115.0	1.2679	2.428
120.0	1.2628	2.206
125.0	1.2577	2.017

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above T_A labeled as the high-temperature region, and that below T_A as the low-temperature region. The latter includes the supercooled region.

High-temperature region. In this temperature region, all three nitrophenol melts obey the Arrhenius equation (1). ONP has a slightly lower viscosity. When there is a possibility of intramolecular H-bonding, the *o*-isomers have a lower melting point compared to the other two. Similar effects may be responsible for the slightly lower viscosity of ONP. The same was found to be true in the case of cresols (12). However, available literature data are at present insufficient for drawing general conclusions. E_{vap} of ONP and PNP was calculated from vapor-pressure data (11) at 20–30°C above the melting point. For MNP no such data were available. The E_{vap} of ONP is of the order of E_{vap} of nitrotoluenes (12), showing an absence of strong intermolecular interactions probably because of intermolecular hydrogen bonding. In the case of PNP, strong association (due to the intermolecular hydrogen bonding) is reflected in its high E_{vap} values. The ratios $E_{vap}/E_{vis} = 3.06$ and 3.34 for ONP and PNP and fall in the region 3.4 for normal liquids (4); that is, the E_{vis} is also high due to association in the liquid state and compensates for the high value of E_{vap} .

Table III. Density and Viscosity of PNP Melts

Temp, °C	Density, g/ml	Viscosity, cP
106.0	1.2926	4.633
108.0	1.2910	4.408
110.0	1.2890	4.236
111.0	1.2880	4.106
112.0	1.2872	4.036
113.0	1.2860	3.902
114.0	1.2854	3.814
115.0	1.2844	3.755
117.0	1.2828	3.630
120.0	1.2803	3.410
122.0	1.2781	3.281
125.0	1.2758	3.099
127.0	1.2726	2.999
130.0	1.2721	2.816
132.0	1.2700	2.762
135.0	1.2669	2.605
140.0	1.2626	2.385

The free energy of activation for flow (ΔG^*) as shown in Table IV was calculated as described earlier (13) at the break point T_A . The ratio $E_{vap}/\Delta G^*$ varies less as compared to E_{vap}/E_{vis} . This ratio is ≈ 2.87 for ONP in agreement with the reported ratio (15), but for PNP it is equal to 3.5. The entropies of activation (ΔS^*) are calculated from the Arrhenius parameter according to the Eyring equation and are recorded in Table IV. The values are in the order of $m- > p- > o-$, i.e., 1.73, 0.71, and -0.60 eu. Assuming that the entropies in the activated states are similar, increasing association in the liquid state would increase the entropy of activation by decreasing the entropy of the initial state. Thus, the above data show that association in the liquid state decreases in the order $m- > p- > o-$.

Low-temperature region. Several relationships, empirical, semiempirical, and theoretical, have been proposed (1) for the low-temperature region. In particular, many liquids seem to fit into a free volume equation proposed by Doolittle. Evidence of the applicability of the Doolittle equation for nitrophenol melts is not conclusive. Rather, we find that the Arrhenius equation is obeyed with a new set of parameters A and B . In the supercooled region, however, E_{vis} values for nitrophenol melts are high, except for ONP, and indicate either a hindrance to the translational jumps of the molecules or strong intermolecular association. In this region for all three isomers, there is a trend toward more positive values in ΔS^* , i.e., 2.70, 4.04, and 3.98 eu for ONP, MNP, and PNP, respectively. These values of ΔS^* are much higher than the values quoted by Tyuzyo (15) for all molecules, irrespective of polar or nonpolar nature, except for spherical molecules. This trend in ΔS^* again indicates an increase in association between molecules.

There have been two approaches for explaining the anomalous increase in viscosity in the supercooled region. McLaughlin and Ubbelohde (8) and Kigoshi (7) postulated formation of clusters as the temperature decreases. Due to the cluster formation, viscosity may be raised either because an additional energy will be required for depolymerization if a single molecule remains as the unit of flow, or alternatively because the bulkier clusters may themselves be the unit of flow. We have calculated and tabulated from Equation 2, ϕ , the volume fraction of clusters at various temperatures in the supercooled region and found it to be $\sim 5 \times 10^{-3}$ at the melting point. The magnitude of ϕ is not very much different from that

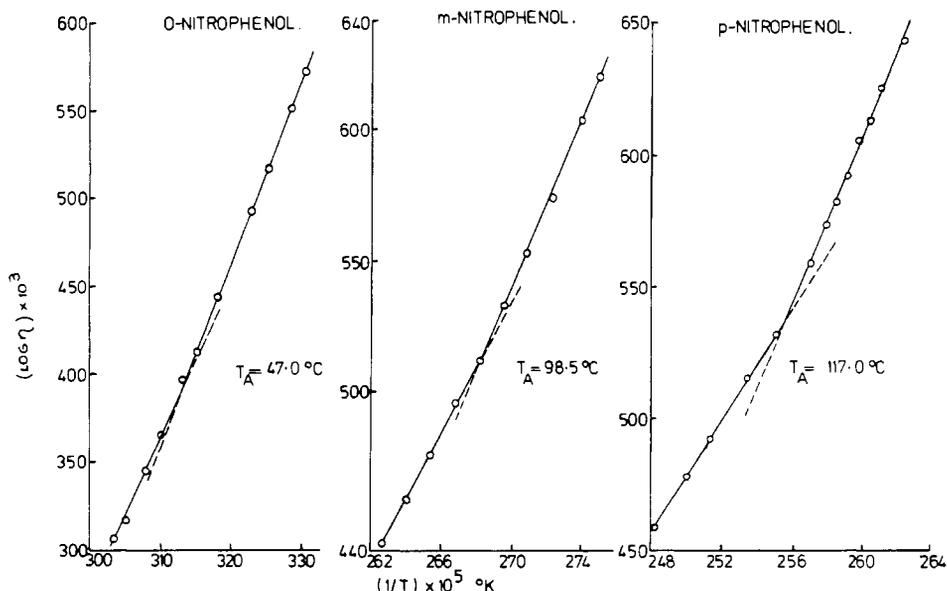


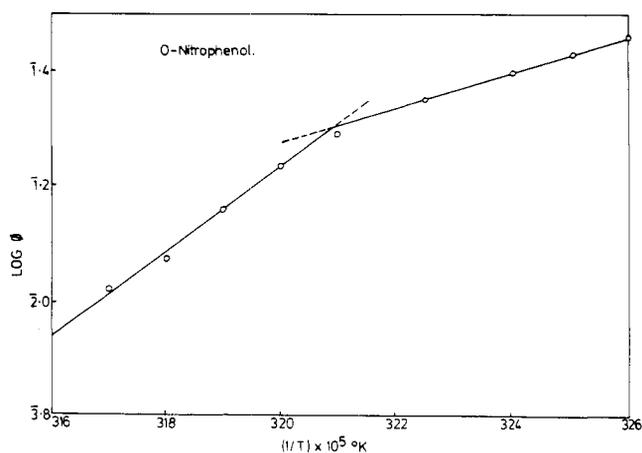
Figure 1. Viscosity of nitrophenol melts at various temperatures

Table IV. Arrhenius Parameters of Nitrophenol Melts

Isomer	Temp range, °C	$A \times 10^5$	$B \times 10^{-2}$	$E_{vis},$ K-cal/mol	$\Delta S^*,$ eu	ΔG^* at $T_A,$ K-cal/mol
o-Nitrophenol	30.0–47.0	5.23	10.89	4.98	2.70	
	47.0–75.0	1.99	8.53	3.90	-0.60	4.14
m-Nitrophenol	90.0–98.5	0.48	14.27	6.53	4.04	
	98.5–125.0	1.54	12.40	5.67	1.73	5.03
p-Nitrophenol	106.0–117.4	2.57	15.04	6.88	3.98	
	117.0–140.0	0.49	12.26	5.61	0.71	5.31

Table V. Volume Fraction of Clusters (ϕ) and Equilibrium Constant (K) of Nitrophenol Melts in Supercooled Region

Isomers	Temp (1/T) $\times 10^5,$ K	$\phi \times 10^3$	K values		$\Delta H_g,$ K-cal/mol	
			$g = 2$	$g = 3$	$g = 2$	$g = 3$
o-Nitrophenol	315.0	7.2	270.9	388.1		
	316.0	9.1	218.5	324.8		
	317.0	10.9	180.0	288.6		
	318.0	11.8	165.0	247.8		
	319.0	14.3	136.3	204.1		
	320.0	17.0	114.2	170.7		
	321.0	18.8	163.0	153.9		
	322.5	22.2	86.6	130.5		
	324.0	24.9	77.2	115.3		
	325.0	28.6	72.2	107.6		
	326.0	29.2	63.7	97.5		
	327.6	31.7	60.1	89.5		
	329.0	34.2	55.3	82.8	31.16	35.05
					14.21	14.89
m-Nitrophenol	271.0	5.6	351.6	526.4		
	272.0	8.1	242.6	363.7		
	273.0	9.9	198.5	297.3		
	273.5	11.7	166.0	249.6		
	274.0	13.5	144.4	216.0		
	275.0	16.0	121.4	181.7		
	275.5	17.0	114.7	171.6	44.62	60.22
p-Nitrophenol	258.0	5.4	365.2	546.9		
	259.0	7.1	277.1	415.2		
	260.0	9.9	198.5	297.3		
	261.0	12.7	153.4	229.9		
	262.0	15.3	127.2	190.4		
	263.0	15.7	123.6	185.0	57.78	56.10


Figure 2. Volume fraction of clusters of o-nitrophenol in supercooled region

of nitrotoluenes (14). The plots of $\log \phi$ vs. $1/T$ are straight lines. As in the case of o-nitrotoluene, this plot for ONP also shows a break at 39.5°C (Figure 2). But in the literature no data are available for the existence of any transition in ONP corresponding to this temperature. Taking the number, g , of molecules in a cluster to be 2 or 3 and following McLaughlin and Ubbelohde (8), the equilibrium constant K for the equilibrium



have been calculated and are reported in Table V. The plots of $\log K$ vs. $1/T$ would yield ΔH_g , the heat of depolymerization, which should be commensurable with $g \times \Delta H_m$. The plots of $\log K$ vs. $1/T$ form one straight line for MNP and PNP, whereas for ONP these are two intersecting lines as shown in Figure 3. The point of intersection is at the same temperature as for the case $\log \phi$ vs. $1/T$ plots. The ΔH_g values are commensurable with $g \times \Delta H_m$.

The other approach (2) in explaining the anomalous increase in viscosity has been in terms of existence of a barrier to external rotation. At low temperatures, due to the reduction in available volume, two or more rotational degrees of freedom in the molecule can become hindered. The molecule is unable to rotate between translational jumps and cannot orient itself suitably, thus increasing the viscosity. To see exactly when the rotational degree of freedom is lost, several workers (2, 10) calculated the volume swept by rotation and compared it with the actual volume available for a molecule on the basis of experimental density data. From our earlier calculation, the minimum volume will be required around the three axes R_A , R_B , and R_C , perpendicular to each other and passing through the center of the benzene ring as the center of rotation. The actual rotation would, of course, be around the center of gravity of the molecule, but the volumes swept

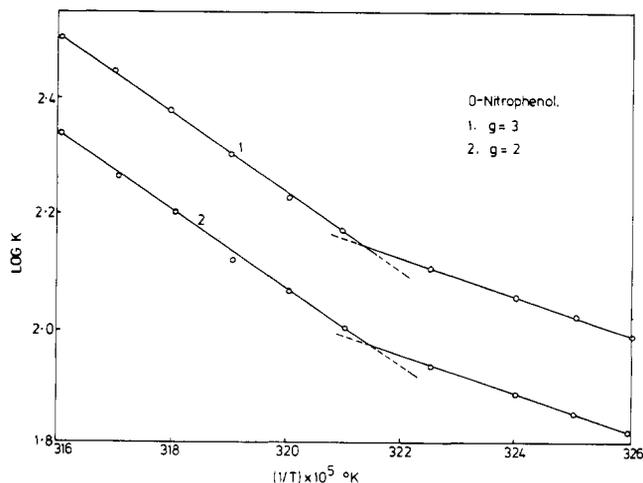

Figure 3. Equilibrium constant K of o-nitrophenol in supercooled region

Table VI. Volume (\AA^3) Swept in Rotation by Nitrophenol Molecules Around Center of Benzene Ring About Axes R_A , R_B , and R_C

Isomers	Volume of Rotation (\AA^3)		
	V_A	V_B	V_C
<i>o</i> -Nitrophenol	216.3	260.2	149.3
<i>m</i> -Nitrophenol	216.3	260.2	149.3
<i>p</i> -Nitrophenol	136.3	55.4	154.1

would be higher than those swept by rotation around the center of the benzene ring. We have computed volumes of rotation for *o*-, *m*-, and *p*-nitrophenols from the available bond lengths and bond angles (θ) as cylinders of rotation as suggested by Moore et al. (10). The results are recorded in Table VI. Compared with the volume available for one molecule, the two degrees of freedom may be restricted for ONP and MNP, whereas for PNP none is restricted. Thus, besides cluster formation, hindrance to rotation may have a role in enhancing the viscosity, and hence E_{vis} , at least for ONP and MNP.

McLaughlin and Ubbelohde (8) modified the Eyring theory for spherical and quasospherical molecules by taking into consideration the energy of forming a hole and derived the equation:

$$\eta = \frac{(2 \pi m k T)^{1/2}}{2 \pi \sigma \phi a^2} \cdot v_f^{1/3} \cdot \exp \frac{-\epsilon(V_0/V)^4}{kT} \cdot \exp \frac{\theta_0}{RT} \quad (4)$$

Here, besides θ_0 which represents the energy barrier for transport roughly of the order of $\frac{1}{3} E_{vap}$, there is an additional exponential term $\epsilon(V_0/V)^4$ which stands for the energy required for forming a hole. In fact, on this basis both the exponential and pre-exponential terms are temperature dependent.

The experimental data normally indicate these two terms to be temperature independent, probably due to the mutually compensatory temperature effects on them. Mole et al. (9) point out that the energy required to form a hole, though normally small as compared to E_{vap} for the liquids at moderate temperatures, at sufficiently low temperatures and for sufficiently bulky molecules, exceeds the value ascribed by Equation 4 and becomes predominant. This explains the increase in E_{vis} .

Thus, our studies indicate that the viscosity increase in the supercooled regions of the nitrophenols may be attributed to cluster formation. In the case of ONP and MNP, there may be an additional increase in E_{vis} due to hindrance to rotation because of the low available volume.

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Received for review July 30, 1974. Accepted June 27, 1975.