October, 1981] *Bull. Chem. Soc. Jpn.*, *54*, *3173—3177 (1981)* 3173

Studies in the Molten State. Viscosities of *trans*-Stilbene, *N*-Benzylideneaniline, and *N*-Benzylidene-*p*-toluidine Melts Near Their Melting Temperatures

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(Received November 21, 1980)

The viscosities and densities of *trans*-stilbene, *N*-benzylideneaniline (BA) and *N*-benzylidene-*p*-toluidene (BT) melts at various temperatures near their respective melting temperatures have been determined. In all the cases, a precursor behaviour in crystal phase at temperatures below the melting temperature has been observed. The viscosity *vs.* temperature relationships have been discussed in two parts: one in the liquid state and the other in the supercooled region. The values of energy and entropy of viscous flow are indicative of molecular association in BA and BT. The enhanced viscosity in the supercooled region has been attributed to the cluster formation. The hinderance to molecular rotation, as a factor influencing viscosity can not be ruled out.

The measurement of viscosity (η) and its temperature dependence near transitions has yielded useful information regarding liquid structure both for normal and polymeric liquids and for those which are non-Newtonian.[1–5] Rotational and ordering characteristics of molecules, intermolecular complexing tendency including hydrogen bonding, precursor behaviours of melting in crystal phase at temperatures below the melting temperature (premelting phenomenon), cluster formation prior to freezing of the liquid phase (prefreezing phenomenon) and the molecular nature of the compounds have been confirmed from the log η *versus* reciprocal of temperature plots and from the thermodynamic parameters of viscous flow.[7,8] Though viscosity behaviour of many liquids like paraffins,[9] mono- and polysubstituted benzenes;[10–14] polycyclic hydrocarbons[7] *etc.* have been investigated, molecules having flexible aromatic rings as end groups attached to a rigid central group like $\rangle C{=}C\langle$; $\rangle C{=}N{-}$, *etc.* have not received serious attention.[15,16] These type of molecules are of importance because a vast majority of compounds having such structure exhibit liquid crystallinity and constitute a potentially mesomorphic system. As a part of our investigations on such molecules,[17] we report in this paper the viscosities and densities of *trans*-stilbene, $C_6H_5CH{=}CHC_6H_5$; *N*-benzylideneaniline, $C_6H_5CH{=}NC_6H_5$ (BA); and, *N*-benzylidene-*p*-toluidine, $C_6H_5CH{=}NC_6H_4CH_3$(BT) melts at various temperatures near their respective melting region. These studies were aimed to investigate the behaviour of these compounds in molten liquid and supercooled region.

Experimental

Chemically pure sample of *trans*-stilbene (mp 124 °C) supplied by "Fluka AG" was used as such without any further purification. *N*-Benzylideneaniline (mp 51.5 °C) and *N*-benzylidene-*p*-toluidine (mp 34.2 °C) were prepared and purified following the standard established procedures.[18]

Densities of the melts were measured using a specifically designed pipette-like-pycnometer[12] of about 6 ml capacity. A fine orfice opening into the liquid prevented easy flow of the liquid after the pycnometer was filled thus reducing turbulence and crystallization in the supercooled region. The viscosities were determined with the help of an Ubbelohde suspended level viscometer. For measurements at <70 °C, a water thermostat with a temperature control of ± 0.01 °C was used for maintaining constant temperature. Distilled, deionized and degassed water was used as a reference liquid in this temperature range and the literature values of the viscosities and densities[19,20] were used to calibrate the apparatus. For higher temperatures a glycerine bath was used with an accuracy in the maintenance of temperature up to ± 0.03 °C. The calibration of pycnometer and viscometer was checked at different temperatures by measuring the density and viscosity of several known liquids in the desired temperature range. The maximum error in the density values was $\pm 2\times10^{-5}$ g cm^{-3}. The viscosities at temperatures above the melting temperature was reproducible to within 1×10^{-6} N s cm^{-2} at temperature below 70 °C and to within 2×10^{-6} N s cm^{-2} at higher temperatures. The measurements in the supercooled region was particularly tedius and reproducibility was checked by repeating the measurements four or more times. Densities and viscosities in the supercooled region could not be reproduced to better than $\pm 5\times10^{-5}$ g cm^{-3} and $\pm 5\times10^{-6}$ N s m^{-2} respectively.

Results and Discussion

The densities and viscosities of the three compounds in the molten state at various temperature in the vicinity of their respective melting temperatures are recorded in Table 1.

The densities were found to vary linearly with the temperature, the deviations in most cases being within the experimental uncertainties of the data.

The results of viscosity measurements are plotted as log η *vs.* T^{-1} in Fig. 1. It is observed that the viscosities follow two different linear relationships, one above the melting point and the other in the supercooled region with a break at temperature T_t and some uncertain points around this temperature. This is an indication of premelting or prefreezing transitions taking place in these compounds. For BT the break in log η *vs.* T^{-1} plot below the melting point is not as sharp and curvature not as high as is normally expected for melts deviating from the Arrhenius equation. Nevertheless, we have satisfied ourselves that the deviations from the Arrhenius line below the melting point are significant being larger

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TABLE 1. DENSITIES AND VISCOSITIES OF COMPOUNDS IN THE MOLTEN STATE AT VARIOUS TEMPERATURES NEAR THE MELTING TEMPERATURE

Temperature K	Density g cm^{-3}	Viscosity × 10^4 N s m^{-2}	Temperature K	Density g cm^{-3}	Viscosity × 10^4 N s m^{-2}
	trans-Stilbene		329.15	1.0331	36.88
396.15	0.95932	10.595	331.15	1.0323	34.89
397.15	0.95861	10.398	333.15	1.0303	32.92
398.15	0.95789	10.296	335.15	1.0277	31.32
400.15	0.95635	10.096	337.15	1.0264	29.66
403.15	0.95421	9.756	339.15	1.0252	28.26
406.15	0.95168	9.357	341.15	1.0228	26.93
408.15	0.95029	9.112	343.15	1.0217	25.78
410.15	0.94875	8.866		*N*-Benzylidene-*p*-toluidine	
413.15	0.94652	8.545	293.15	1.0443	154.16
416.15	0.94433	8.376	296.15	1.0422	137.03
418.15	0.94282	8.245	298.15	1.0403	125.15
423.15	0.93908	7.915	300.15	1.0383	112.79
	N-Benzylideneaniline		302.15	1.0369	104.47
299, 15	1.0580	106.30	304.15	1.0357	96.49
301.15	1.0563	96.53	306.15	1.0342	93.34
303.15	1.0546	87.30	308.15	1.0325	85.00
305.15	1.0530	80.55	310.15	1.0312	77.66
307.15	1.0513	73.65	313.15	1.0293	69.79
309.15	1.0496	68.12	315.15	1.0278	64.18
311.15	1.0479	63.28	317.15	1.0258	56.78
313.15	1.0462	58.84	319.15	1.0246	55.28
315.15	1.0447	54.59	321.15	1.0227	51.74
317.15	1.0431	51.46	323.15	1.0211	48.97
319.15	1.0411	47.87	325.15	1.0195	45.43
321.15	1.0391	45.22	327.15	1.0180	42.86
323.15	1.0378	42.87	329.15	1.0163	40.37
325.15	1.0371	41.72	331.15	1.0151	38.16
327.15	1.0352	39.13			

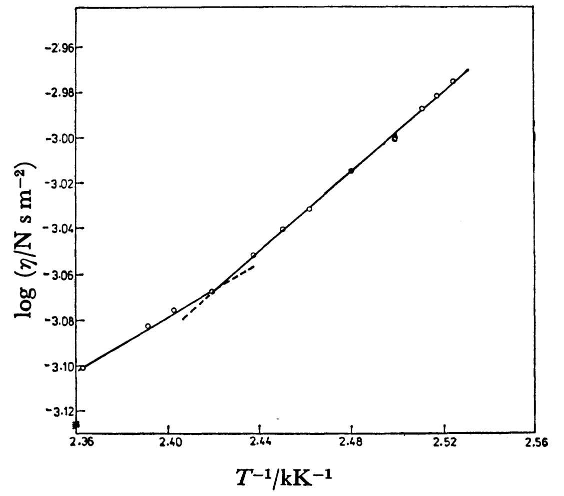

Fig. 1(a). The variation of viscosity (η) with temperature (T) for *trans*-stilbene.

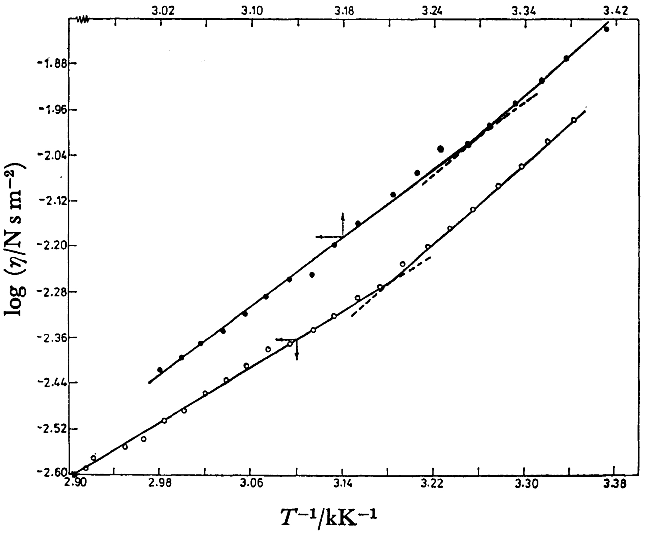

Fig. 1(b). The variation of viscosity (η) with temperature (T) for *N*-benzylideneaniline (○) and *N*-benzylidene-*p*-toluidine (●).

than the order of magnitude of the experimental error involved. It is observed that at any temperature, the liquid densities of the three compounds increases in the order *trans*-stilbene<BT<BA whereas the viscosities follow the order *trans*-stilbene<BA<BT. The viscosity of BT is higher than that of BA and reveals that the substitution of methyl group by hydrogen in BT facilitates its flow.

The Arrhenius parameters for the melts have been calculated for the two regions and recorded in Table 2.

TABLEE 2. ARRHENIUS PARAMETERS FOR THE MELTS

	Temperature range / K	Slope × 10^2	Intercept.	E_{vis} / kcal mol^{-1}	ΔG^* at T_t / kcal mol^{-1}	ΔS^* / cal K^{-1} mol^{-1}
trans-Stilbene	396.1—412.3	8.85	−5.209	4.05	4.92	−2.14
	412.3—423.1	5.85	−4.484	2.68		−5.46
N-Benzylidene aniline	299.1—314.2	17.17	−7.719	7.86	4.85	9.52
	314.2—343.1	12.58	−6.256	5.75		2.82
N-Benzylidene-*p*-toluidine	293.1—302.1	16.95	−7.592	7.76		8.78
	302.1—331.1	15.18	−7.008	6.95	5.12	6.11

According to Mclaughlin,[1] E_{vis} is made up of two terms namely the energy required to overcome the barrier for transport E_1; and the energy required for forming a hole, E_2. The former is related to the energy of vaporization, $E_{\mathrm{vap}}(\simeq 3E_1)$. The magnitude of E_2 is normally small in comparison to E_{vap} for liquids at moderate temperatures. In fact, for most of the normal liquids, the ratio $E_{\mathrm{vaq}} : E_{\mathrm{vis}}$ is something between 3 and 4. At sufficiently low temperatures, and, for sufficiently bulky molecules, E_2 become predominant[2] and hence the ratio tend to a value lower than 3. Grumberg and Nissan[3] pointed out that the ratio for polar associated liquids would depend upon the extent of association both in the liquid and vapours state and the geometry of packing in the liquid state. The ratio of $E_{\mathrm{vap}} : E_{\mathrm{vis}}$ for *trans*-stilbene, BA and BT is ≈5.2, 1.9, and 1.2 respectively. Further, the ratio $E_{\mathrm{vap}}/\Delta G^*$ for *trans*-stilbene is ≈2.8 in agreement with the reported ratio of 2.45. For BA and BT, the value is far less. These observations are clear indicative of intramolecular association in BA and BT. The entropy of activation values recorded in Table 2 support this surmise. Tyuzyo[4] reported a value of $\Delta S^* = -2.9$ cal deg^{-1} mol^{-1} for a large number of compounds including polar ones. For *trans*-stilbene, ΔS^* is more negative in the liquid region indicating less ordering in it. Higher values of ΔS^* for BA and BT suggest that the ordering in these compounds exists to a much larger extent especially in supercooled region as compared to many organic liquids. This is also confirmed by Batschinski's plot of the viscosity data.[5,6] According to Batschinski:

$$\frac{1}{\eta} = \frac{v}{c} - \frac{v_0}{c}, \qquad (1)$$

where, v=specific volume; v_0=limiting value of specific volume at infinite viscosity and c is a constant. The plots of η^{-1} *versus* v yielded straight line plots with break at T_t and uncertain region around this temperature. The value of v_0 for the three compounds obtained from these plots are recorded in Table 3. These values, though different from those reported for many other organic liquids,[5] are close to the one reported for Cresols[14] where strong hydrogen bonding and structuring exist in the liquid state.

Several functional relationships, emperical, semi-emperical and theoretical have been proposed[6] for the viscosity in the low temperature region. For many compounds the viscosity data in this region fit into the Doolittle equation.[21]

$$\log \eta = A' + B'/(T - T_0), \qquad (2)$$

where T_0 is evisaged as a second order transition temperature. The evidence of applicability of Doolittle equation for our systems was not conclusive because the region of supercooling is rather short. A rough numerical fit yielded T_0 values of <10 K for the three compounds. These values are unexpectedly low considering that normally T_0 is about 20—100 K less than the melting temperature.[22] We consider it reasonable therefore, to assume that even below the melting temperature, the supercooled liquid follow an Arrhenius equation with different values of the constants.

It is observed that the E_{vis} and ΔS^* values are more positive in the supercooled region as compared to the high temperature region indicating an increase in association between molecules and a non-cooperative mechanism of flow. Two approaches based on the hinderance to rotation at or below T_t and on the cluster formation may be proposed to explain the enhanced viscosity in the supercooled region. The most commonly used procedure to establish the existence of hinderance to rotation is to compare the volume swept by rotation of the molecule, V_r, about a suitable axis with the actual volume available to it on the basis of experimental density data. Following Ubbelohde's procedure,[7] V_r for the molecules around the longer axis have been calculated and compared with the molar volumes in Table 3. The V_r is far in excess of the available volume, indicating that the enhanced viscosity of melts may result from hinderance to rotation.

In the alternate approach in terms of cluster formation it is assumed that the increase in viscosity and hence E_{vis} is due to the formation of clusters, the volume fraction ϕ of clusters have been calculated from the

TABLE 3. SOME CALCULATED PARAMETERS OF THE COMPOUNDS

	v_0 at temperatures		V_r / cm^3 mol^{-1}	Molar volume range[a)] / cm^3 mol^{-1}	E_{vap} / kcal mol^{-1}
	$<T_t$	$<T_t$			
trans-Stilbene	0.968	0.985	368	187—192	14.0
N-Benzylideneaniline	0.942	0.933	435	170.5—178	11.1[b)]
N-Benzylidine-*p*-toluidine	0.952	0.947	500	185.5—191	8.0[b)]

a) From liquid density data at temperatures around T_t. b) Extrapolated using Trouton's rule.

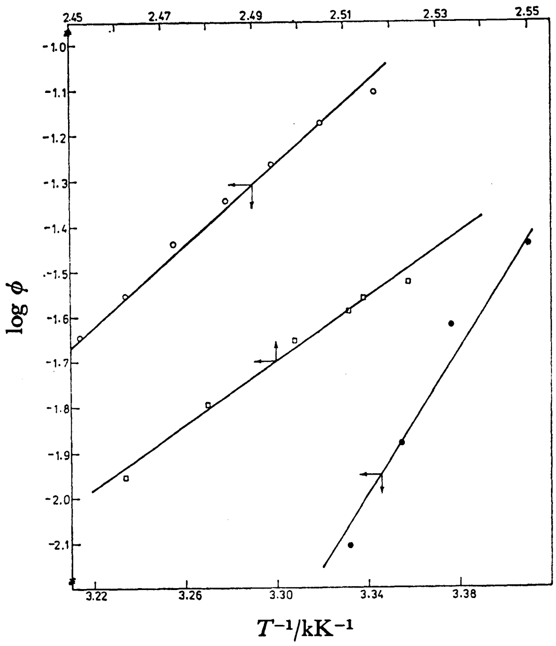

Fig. 2. The variation of Volumes fraction of Clusters (ϕ) with temperature (T) for *trans*-stilbene (□); *N*-benzylideneaniline (○); and *N*-benzylidene-*p*-toluidine (●).

Einstein equation.[23]

$$\eta/\eta_{\text{ext.}} = 1 + 2.5\phi + 7\phi^2, \qquad (3)$$

where η_{ext} is the viscosity extrapolated from high temperature region and η is the actual viscosity. The plots of log ϕ *versus* T^{-1} are shown in Fig. 2. These are similar to the one obtained by Ubbelohde for dimeric, trimeric and even polymeric clusters of organic molecules. Following Ubbelohde,[23] the equilibrium constant K for the equilibrium

$$A_n \rightleftharpoons nA, \qquad (4)$$

where n are the number of molecules in the cluster. We have calculated K at different temperatures for various values of n between 2 and 6, and also the heat of depolymerization of clusters, ΔH_d. It was found to be same for different values of n. The ΔH_d values have been compared with ΔH_f values for the compounds in Table 4. The ratio $\Delta H_d/\Delta H_f$, which is considered as the number of molecules in the cluster, n, is 2 for *trans*-stilbene, 3 for BA and 4 for BT. It is possible that these clusters also consitute the unit of flow thus raising the E_{vis} in the supercooled region. At the same time the volumetric effects due to the cluster formation seems to be too small to bring about any sharp change in density at T_t is passed.

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TABLE 4. VOLUME FRACTION OF CLUSTERS AND THEIR EQUILIBRIUM CONSTANT IN MELTS IN THE SUPERCOOLE D REGION

	Temp (T^{-1}/kK^{-1})$\times 10^{-2}$	$\phi \times 10^3$	K	ΔH_f kcal mol^{-1}	ΔH_d kcal mol^{-1}
trans-Stilbene	252.4	29.7	64.3		
	251.8	27.5	69.8		
	251.2	25.5	75.5		
	249.9	22.0	87.7		
	248.0	16.0	122.1	7.1	15.0
	246.2	11.1	177.9		n=2
N-Benzylideneaniline	334.3	78.0	33.6		
	332.1	66.8	39.9		
	329.9	54.2	50.4		
	327.7	45.2	61.4		
	325.6	36.1	78.1		
	323.5	27.7	103.3	5.6	16.7
	321.4	22.5	128.1		n=3
N-Benzylidene-*p*-toluidine	341.1	36.0	104.2		
	337.7	23.9	160.4		
	335.4	13.1	298.4		
	333.2	7.8	505.8	6.7	25.8
					n=4

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