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**INVESTIGATION OF VISCOSITY AND DENSITY VERSUS
TEMPERATURE IN COMPARISON WITH ^1H NMR
RELAXATION TIME RESULTS FOR O-, M-, P- XYLEMES
AND α -, β -, γ - PICOLINES**

Key words: proton relaxation time, shear viscosity, density, temperature dependence, structure of liquids

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ABSTRACT

The paper presents the results of density and viscosity measurements in liquid derivatives of benzene and pyridine, well purified, degassed or aerated, depending on temperature, in the whole liquidity range. Gaseous admixtures were found to affect the viscosity of liquids. From one to three Arrhenius regions were observed, depending on the structure and orientational freedom of the molecules. The results are discussed on the background of ^1H NMR relaxation time studies with regard to the effect of dipole interactions on the structure of close packing.

INTRODUCTION

Translational and rotational motions have long since been investigated using different methods. It was demonstrated that many physical properties of

liquids depend on the molecular shape. In liquids, the molecules which are spherical and weakly interacting, the rotational motion can be regarded as independent of the translation. This fact, significantly facilitating theoretical considerations, leads to a good agreement with the experiment.

For liquids consisting of simple spherical and symmetrical molecules, with the Lennard-Jones interaction potential, the viscosity coefficient is described by the following equation (1)

$$\eta = \eta_o(T) \exp\{E_\eta(T) / RT\} \quad (1)$$

where both pre-exponential factor, $\eta_o(T)$, and activation energy, $E_\eta(T)$, depend on temperature.

The character of their temperature dependence can sometimes result in their mutual compensation. Then, the temperature dependence of viscosity is described by the Arrhenius equation

$$\eta = \eta_o \exp(E_\eta / RT) \quad (2)$$

Literature data on the viscosity of hydrocarbons [2] indicate that the Arrhenius relation is valid for all liquids at temperature close to the boiling point, being inadequate at low temperatures. According to [3] and considering the temperature dependence of transport coefficients, the liquidity range of substances composed of polyatomic molecules comprises the following regions: (i) high temperature Arrhenius region directly below the boiling point, (ii) two regions of non-Arrhenius behaviour of the liquid: markedly below the boiling point and close to the freezing point.

Dattagupta [13] presented a theory, consistent with generalized hydrodynamics; for phenomenological Maxwell's model [14], in which changes in viscosity are accounted for by changes in local arrangement. In addition, long-

lived local geometrical arrangement of molecules contained in cages occurs in liquids. According to his opinion, the incompatibility of orientations of two locally arranged neighbouring cages results in an internal stress and, as a consequence, in the increase in viscosity. Orientational coupling of the arranged cages causes an additional viscosity increase. This model also relates anomalous viscosity with the drops in thermal capacity. This effect was observed before experimentally [15]. Thanks to the papers of Dattagupta, the theory was linked with the model of structure dynamics [17].

Stillinger [18] introduced the concept of fluidized domains, the mobility of which differs from that of molecules of the surrounding environment. He thinks that the formation of fluidized domains should be related with temperature-dependent change in the slope of the Arrhenius plot [$\ln \eta$ upon $1/T$]. The term "fluidized domain" in this model is identical to the statistically independent "cooperatively rearranging regions" in Adam's and Gibbs' relaxation theory [19].

In the investigations of the effect of anisotropy upon transport processes, the dynamics of liquid methyl derivatives of benzene and pyridine is of particular interest. These molecules have shapes of planar symmetric tops. Molecular reorientation of benzene and pyridine was described as a rotational diffusion process [6]. According to this model, the molecular motion of benzene and pyridine derivatives can also be anisotropic. As found experimentally for some liquids [4-5], the deviation from the Arrhenius dependence may be the manifestation of the transition from one Arrhenius region to a new one with a different set of constants. Temperature, T_i , of these transitions is frequently called [6] rotational phase transition temperature.

In this paper, the results of experimental studies on the dependence of viscosity and density of liquids on temperature are reported. The application of Ertl's and Dulien's criterion [7] for the reduced boiling point value enables these liquids to be classified among non-Arrhenius liquids. The results are discussed on the background of ^1H NMR relaxation time studies.

TABLE 1

Selected Properties of Investigated Liquids: boiling (T_b) and freezing (T_m) points, molecular masses (M), dipole moments (μ), density (d) and volumetric thermal expansion coefficients (α).

	T_b [K]	T_m [K]	M	μ [D]	d_{290K} [kg/m ³]	$10^3\alpha$ [K ⁻¹]
<i>o</i> -xylene	417.6	248.1	106.17	0.39	887.0	1.0558
<i>m</i> -xylene	412.3	225.3	106.17	0.35	872.5	1.0544
<i>p</i> -xylene	411.7	286.4	106.17	0	868.3	1.0822
α picoline	402.9	206.7	93.14	1.72	947.8	1.2258
β picoline	417.7	255.0	93.14	2.30	957.8	1.1355
γ picoline	418.6	276.8	93.14	2.57	962.4	1.1316

EXPERIMENTAL RESULTS

Viscosity of *o*-, *m*-, *p*-xylenes and α -, β -, and γ -picolines was measured with an accuracy of ± 0.5 % by means of a modified Ostwald's viscosimeter described previously [4]. The liquids were dried and purified according to conventional methods described by Vogel [12].

Shear viscosity coefficient was measured in degassed samples (freeze - pump - thaw cycles) in the whole liquidity range. Next, some of the samples were next aerated under normal pressure, and the measurement was repeated. Temperature was stabilized with an accuracy of ± 0.05 K using a glycol-water mixture (for $T > 290$ K) or nitrogen vapour (for $T < 290$ K) as heat-transfer fluids, and measured by means of a thermocouple. Density was measured by the method of hydrostatic lift. Weighting was performed on an analytical balance with an accuracy of 10^{-4} g. The liquids were thermostatted similarly as in the viscosimeter.

Table I summarizes selected properties of the liquids examined [20]: boiling

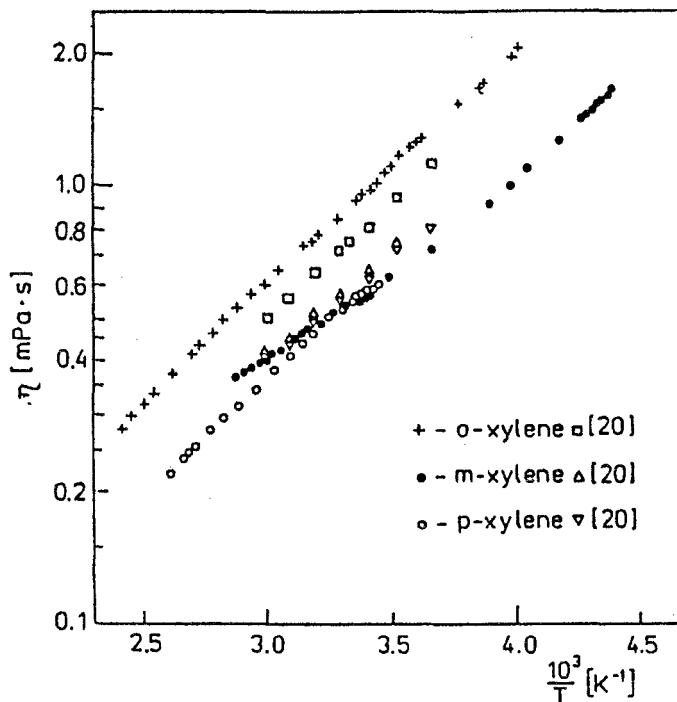


FIG.1 Temperature dependence of the viscosity coefficient of degassed o-, m- and p-xylanes (triangles and squares - literature data[20] for comparison).

(T_b) and freezing (T_m) points, molecular mass (M), dipole moments (μ), density (d), relating to 290 K, and thermal expansion coefficients (α).

The results of viscosity measurements versus temperature are shown in Figures 1-4 for: 1) degassed o-, m-, and p-xylanes; 2) aerated m-xylene; 3) degassed α -, β - and γ -picoline and 4) aerated α -picoline, respectively. For comparison, Figures 1-3 also contain some literature data [8,9].

The following conclusions can be drawn based on the plots presented:

- Temperature dependence of shear viscosity obtained for purified but not degassed liquids is similar to that commonly presented in the literature, i.e.

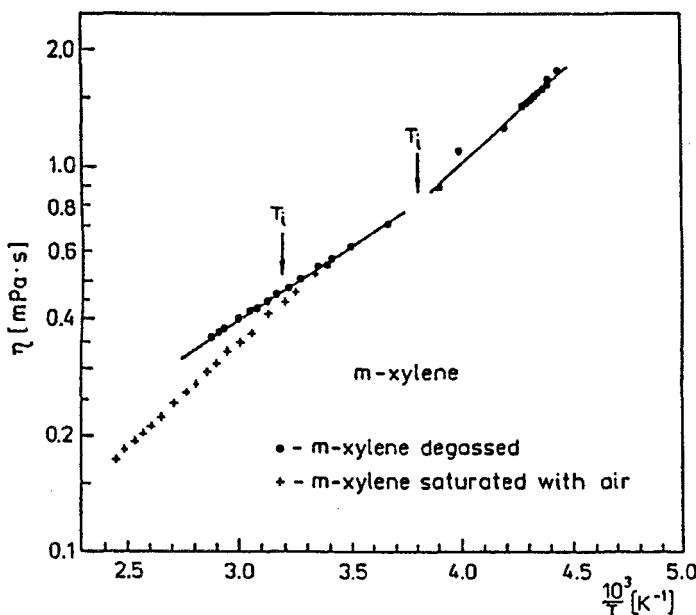


FIG.2 Temperature dependence of the viscosity coefficient of aerated and degassed m-xylene.

Arrhenius-type behaviour at high temperatures, and non-Arrhenius behaviour of some liquids at lower temperatures.

- b) The degassing leads to qualitative changes in the temperature dependence of shear viscosity, i.e. one, two or three well distinguished Arrhenius subregions are present for each liquid.
- c) Temperatures, T_i , of transitions between these regions are shown in Table 2. The values of respective activation energies and pre-exponential factors are given in Table 3.
- d) Aeration: (i) reduces the liquid viscosity at high temperatures, (ii) results in the increase in the activation energy of high temperature subregion, and (iii) results

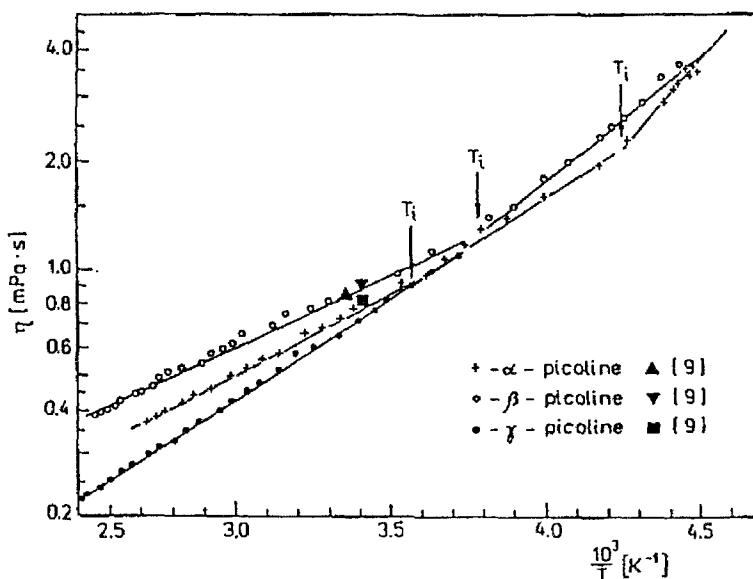


FIG.3 Temperature dependence of the viscosity coefficient of degassed α -, β - and γ -picolines (triangles and squares - literature data[9] for comparison).

in a mild viscosity change on the border between the subregions (T_i) of the plot $\ln \eta = f(1/T)$.

DISCUSSION AND CONCLUSIONS

Table 4 summarizes the values of selected properties of the liquids under examination: the reduced freezing temperature, T_r ($\equiv T_m/T_c$, where T_c is the critical temperature), mean volume per molecule (calculated based on density when assuming close hexagonal packing [19]) at 290 K, at melting and boiling points, and at rotational phase transitions temperatures, T_i , as well as volumes “swept” upon rotation about the molecular axes.

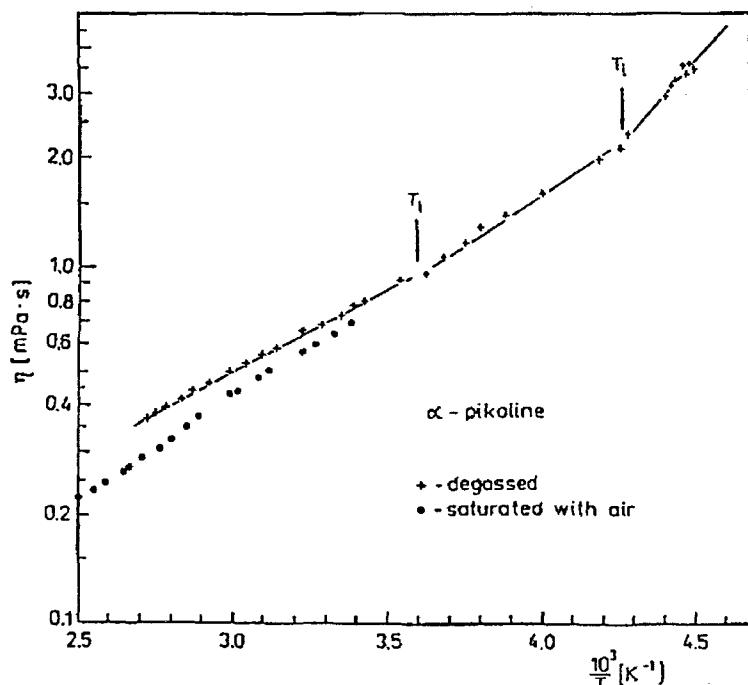


FIG.4 Temperature dependence of the viscosity coefficient of aerated and degassed α -picoline.

TABLE 2

Temperature of $T_i(\eta)$, determined by the viscosity method and by nuclear magnetic resonance $T_i(\text{NMR})$ -spin-lattice relaxation time [8,9,10, *) mean values from 8,9]

	o-xylene	m-xylene	p-xyl.	α -picoline	β -picoline	γ -picoline
$T_{iI}(\eta)$	-	-	-	281	-	-
$T_{iII}(\eta)$	277	263	-	235	265	-
$T_{iI}(\text{NMR})$	343	350	-	300	305*	348*
$T_{iII}(\text{NMR})$	273	271	-	-	265	-

TABLE 3

Values of activation energies, E_{an} , and pre-exponential factors, η_0 . Subscripts I, II, and III denote: high temperature subregion, medium temperature subregion, low temperature subregion, respectively.

	o-xylene	m-xylene	p-xylene	α -picoline	β -picoline	γ -picoline
Ea_I [kJ/mol]	9.24	8.56		9.98	7.01	9.79
Ea_{II} [kJ/mol]	9.88	10.4	8.48	10.71	12.89	11.06
Ea_{III} [kJ/mol]				15.58		
$\eta_0 I$ [μPa^*s]	17.9	19.1		13.2	49.7	13.1
$\eta_0 II$ [μPa^*s]	13.8	7.57	19.8	9.2	3.63	7.74
$\eta_0 III$ [μPa^*s]				0.778		
Ea_I [kJ/mol]ae		9.97		10.75		
$\eta_0 I$ [μPa^*s]ae		9.62		8.94	-	
r						

Based on the values of T_f given in the table, the liquids investigated can be classified in accordance with the criterion of Ertl et al. [7] among the non-Arrhenius group of liquids. The results of measurements carried out by the viscosity method, as well as by nuclear magnetic resonance, confirm the validity of this criterion, i.e. liquids displaying reduced freezing temperature lower than 0.46, belong to the non-Arrhenius group.

TABLE 4

Selected properties of investigated liquids: reduced freezing point, T_r ($\equiv T_m/T_c$), mean volumes per molecule, V (calculated from density assuming close hexagonal packing), at: 290 K V_{290} , melting, boiling, and T_i points, V_m , V_b , and V_i , respectively, and volumes "swept" upon rotation about the principal molecular axes R .

	o-xylene	m-xylene	p-xylene	o-picoline	β -picoline	γ -picoline
T_r	0.3922	0.3639	0.4633	0.3320	0.3953	0.4286
V_{290} [10^{24}cm^3]	198.7	202.0	203.0	163.1	161.4	160.7
V_m [10^{24}cm^3]	189.1	187.3	202.1	143.9	161.6	158.1
V_b [10^{24}cm^3]	234.6	237.5	239.5	189.4	198.5	188.8
V_I [10^{24}cm^3]	196.9	218.7	-	163.6	163.8	-
V_{II} [10^{24}cm^3]	-	200.3	-	150.6	155.9	-
R_x [10^{24}cm^3]	202	252	182	148	146	145
R_y [10^{24}cm^3]	225	215	265	206	208	209
R_z [10^{24}cm^3]	178	201	203	166	167	168

According to suggestions of Pajak et al. [4,8], the change in the slope of the temperature dependence of shear viscosity is due to the liberation of rotational degrees of freedom of the liquid molecules. This leads to the change in the activation energy of molecular translation.

In Table 2, the values of temperature T_i of the activation energy changes, determined from viscosity, were compared with the respective T_i values found by the nuclear magnetic resonance [8,9,10]. An agreement between values determined by different methods is readily seen. Temperature T_i could not be obtained by the viscosity method in the case of liquids composed of molecules with higher degrees of symmetry. For these liquids, the deviation from the Arrhenius viscosity is probably comparable to the accuracy of the method employed. The existence of

several temperature subregions with different activation energies for most liquids examined indicates the occurrence of changes in the short-range molecular structure and dynamics on the border between these subregions (i.e. close to temperature T_i). Structural changes result in the limitation of the rotational freedom with respect to the axes of symmetry of the molecule upon lowering the temperature of the liquid. According to Martinez [19], the deviations from the linearity of viscosity can be accounted for by the ability of liquid molecules to form clusters.

Pajak [8] and Jurga [9] related the observed temperature translations between the Arrhenius subregions with temperature-dependent spin - lattice relaxation time T_I to the electric dipole interaction of molecules and proposed the following expression:

$$T_I(T_i)/\mu = A_3 T + B_3 \quad (3)$$

The effect of the permanent charge distribution asymmetry upon the number of rotation degrees of freedom has already been known. Bearing the above in mind, an attempt was undertaken to formulate a possibly general description of density and viscosity. The following relations between the observed properties of liquids for all T_i were chosen as most adequate in this work:

$$\rho(T_i) = A_1 T_i + B \quad (4) \quad \text{and}$$

$$\eta(T_i)/\mu = A_2 \exp(B_2 / T_i) \quad (5)$$

where A and B are constants characteristic of each group of liquids.

The values obtained from density and viscosity measurements for well purified and degassed satisfy relations (4) and (5) for constants shown in Table 5. Separate curves were obtained for each group of compounds.

TABLE 5
Constants in equations (3),(4) and(5) for examined liquids

	A_1 [kg/m ³ K]	B_1 [kg/m ³]	A_2 [mPa*s/D]	B_2 [K ⁻¹]	A_3 [K ⁻¹]	B_3 [s/D]
Xylenes	-1,0645*10 ⁻³	0.652	1.8009*10 ⁻⁵	3027.44	~0	~3.009
Picolines	-1,1610*10 ⁻³	0.673	0.1704	490.93	~0	~3.009

Relation (3) is satisfied within the limits of the measurement accuracy for proton spin-lattice relaxation times, $T_1(T)$. Relations (4) and (5) hold true only in rame homologous series.

Different values of constants in equations (4) and (5) occurring in spite of great similarity of some properties of the liquids investigated, show that the dipole interaction is not the only factor determining, unequivocally, the close packing of the structure. Another factor affecting the microstructure, as well as the capability of molecular reorientation, is the shape of molecules which determine the free volume, v_f . If v_f reaches the critical value below which there is not enough space for free rotations of molecules about (all) symmetry axes of the molecule, the character of the temperature dependence of the viscosity of the liquid changes. Also, the data for other methyl derivatives of benzene and pyridine confirm the above conclusions. This is consistent with Dattagupta's opinion [13] about the existence of local geometrical arrangement of molecules contained in cages, and Stillinger's views [18] on the formation of fluidized domains in the liquid. It seems interesting to confirm the existence of cages by the employment of other methods for a wide variety of liquids, including non-dipolar ones, such as depolarization of scattered light, and to analyze the result with regard to the presence of Markovian processes [16].

This observation, verified for two groups of liquids, agrees with the opinion that macroscopic properties of liquids are composite functions of properties of the constituent molecules: their size, shape, mass, polarizability, dipole moment, local ordering, etc.

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