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THE EFFECT OF GASEOUS CONTAMINANTS ON THE SHEAR VISCOSITY OF LIQUIDS

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Temperature dependences of shear viscosity were measured for 2,4-lutidine, 3,4-lutidine and α-picoline within their liquid range after purification and degassing, and the addition of selected gases. In each liquid, three Arrhenius temperature subregions, separated by characteristic temperatures T_{ij}, were found. The values of the activation energy and pre-exponential coefficient in the Arrhenius equation undergo a change in these subregions. The results were discussed on the basis of a quasi-crystalline close-range molecular model.

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1. Introduction

For many years now, research has been carried out into the anisotropy of molecular reorientation and effect of this anisotropy on transport processes in liquids. It is suggested in the literature that disturbance of the rotational freedom of molecules is responsible for deviations from the Arrhenius temperature dependences of such parameters as viscosity [1, 6], the translational autodiffusion coefficient [2, 3], nuclear relaxation [7–10] etc, according to the formula:

$$Q_i = Q_{0i} \exp(E/RT), \tag{1}$$

where Q_i is a given physical parameter, E is the activation energy, R is the gas constant, T is the temperature. The temperature dependences of these parameters have been variously described [4–6]. Also, a number of theoretical, semi-empirical and empirical criteria have been put forward according to which the liquid range could be divided into Arrhenius and so-called non-Arrhenius subregions [5, 7, 8].

It has been observed in some liquids [9, 10, 16, 17, 19], that the deviation from the Arrhenius dependence in low temperature regions is not of the non-Arrhenius type, but is a transition to a new Arrhenius region with a different set of the constants Q_{0i} and E.

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Such a temperature dependence of the rate of nuclear relaxation were observed for the first time in the pure, liquid, methyl derivatives of benzene and pyridine [9, 10]. In addition to the usual methods of purification prior to measuring parameters such as viscosity and diffusion rate, these liquids were degassed.

This paper presents the results of studies which aimed to establish the effect of gaseous contaminants on the temperature dependence of the shear viscosity of selected liquid methyl derivatives of pyridine.

2. *Results and discussion*

The shear viscosity η for 2,4-lutidine, 3,4-lutidine and α-picoline over the whole of their liquid range was measured using an Ostwald viscometer with a constant lower liquid level [11] (see Fig. 1). The viscometer was adapted for the vacuum (of the order of 10^{-6} mm Hg) degassing of liquids by repeatedly applying the freezing–evacuation–melting cycle [12, 13]. This cycle was repeated four or five times for the liquids studied here which, prior to degassing, had been chemically purified in accordance with accepted methods [14]. In Figs. 2, 3 and 4, the solid dots (●) indicate the temperature dependences of viscosity η for 2,4-lutidine, 3,4-lutidine and α-picoline, respectively.

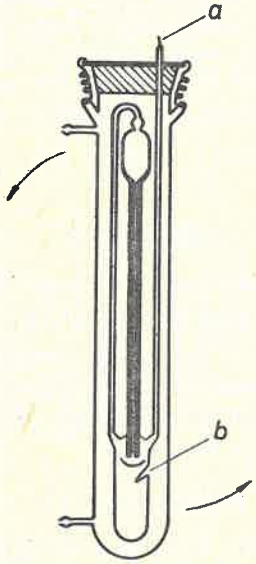

Fig. 1. Viscometer with a constant lower liquid level: a — outlet to vacuum apparaturs, b — inlet to termocouple

After making these measurements, the samples were saturated with gases. The results obtained for liquids saturated with air at normal pressures are shown by vertical crosses (+). Fig. 2 also shows the temperature dependence of viscosity for 2,4-lutidine saturated with nitrogen under reduced pressure. Fig. 5 shows the temperature dependence of viscosity η

at high temperatures for 2,4-lutidine: degassed (solid dots.). saturated with air (vertical crosses +), saturated with argon at 1 atm pressure (solid triangles ▲), after repeating the degassing cycle three times (open circles ○), and saturated with nitrogen at reduced pressure (diagonal crosses ×).

The following conclusions may be drawn from the dependences shown on the graphs:

(*i*) The temperature dependences of the shear viscosity obtained for the purified, but not degassed, liquids are similar to those usually found in the literature: Arrhenius behav-

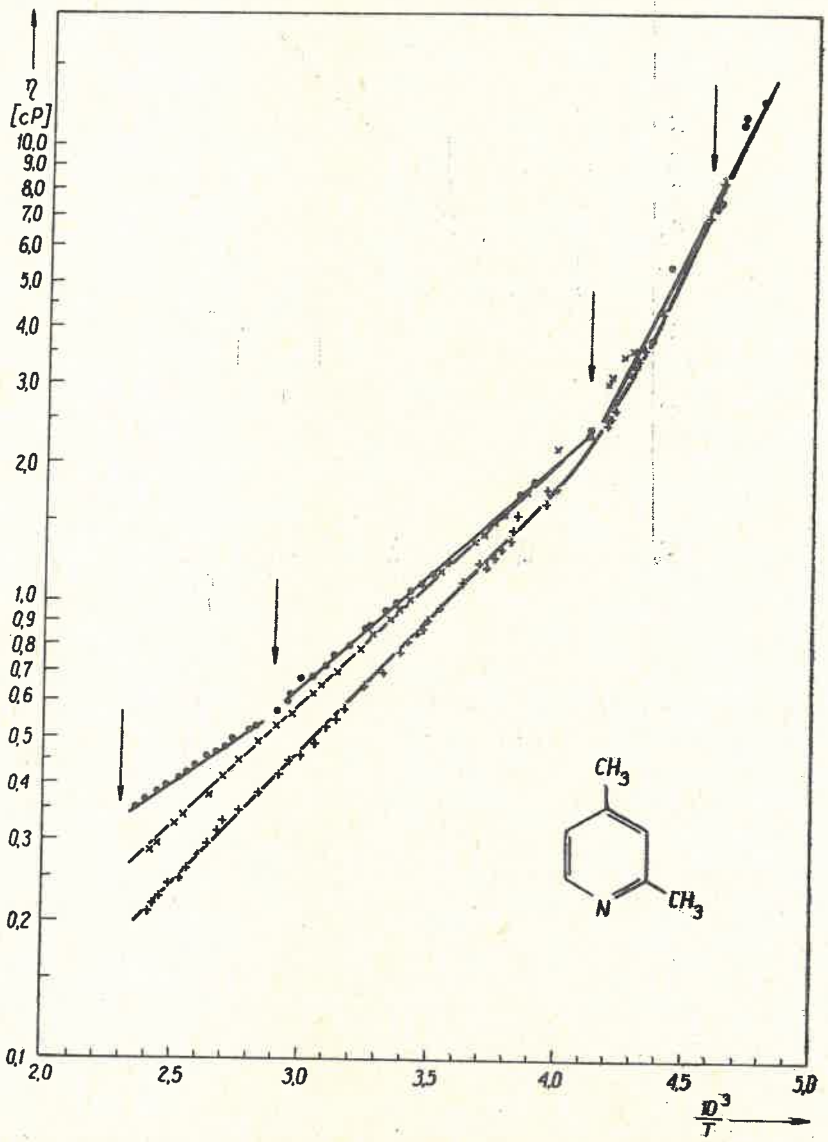

Fig. 2. Temperature dependence of viscosity for 2,4-lutidine degassed (solid dots ●), saturated with air (vertical crosses +), saturated with nitrogen under reduced pressure (diagonal crosses ×)

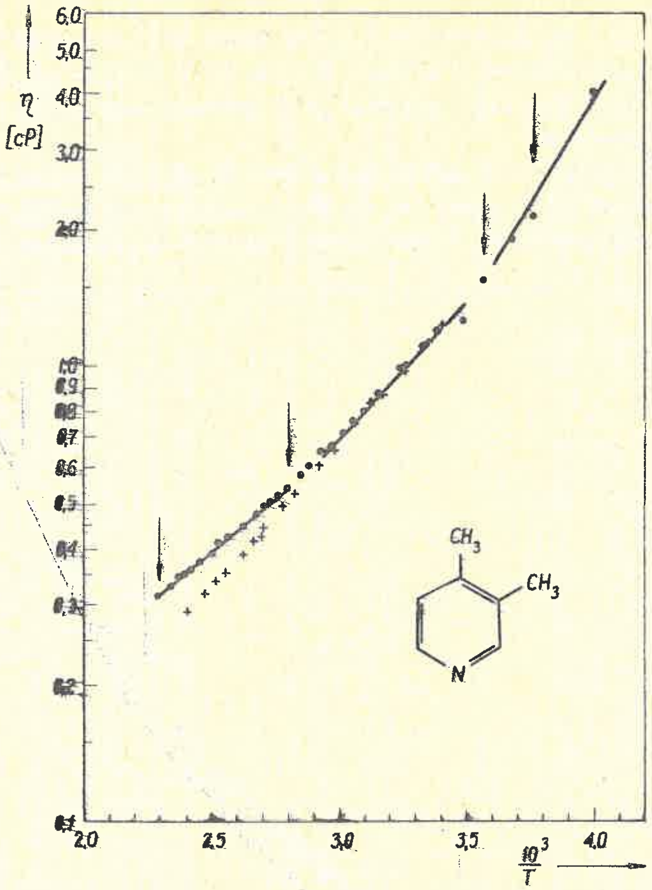

Fig. 3. Temperature dependence of viscosity for 3,4-lutidine degassed (solid dots ●) and satureted with air (vertical crosses +)

iour in high temperature ranges (below boiling point). non-Arrhenius behaviours over low temperature ranges (above melting point).

(*ii*) The removal of gaseous contaminants leads to qualitative changes in the temperature dependences of the shear viscosity η: each liquid exhibited three Arrhenius temperature subregions with different sets of the constants η_0 and E, separated by transition temperatures T_{ij} characteristic of each liquid.

The values of the pre-exponential coefficients η_0, the activation energy E for high temperature (I), medium temperature (II) and low temperature (III) regions, and the transition temperatures $T_{\mathrm{I,II}}$, $T_{\mathrm{II,III}}$ are set out in Table I.

(*iii*) The changes in the behaviour of the temperature dependences of viscosity of the liquids, which are brought about by additions of gases, are independent of the kind of gas. Addition of gases:

— reduces the viscosity of the liquids in regions I and II;

— increases the activition energy E_{I} and equalises the values of the activation energies E_{II} and E_{III};

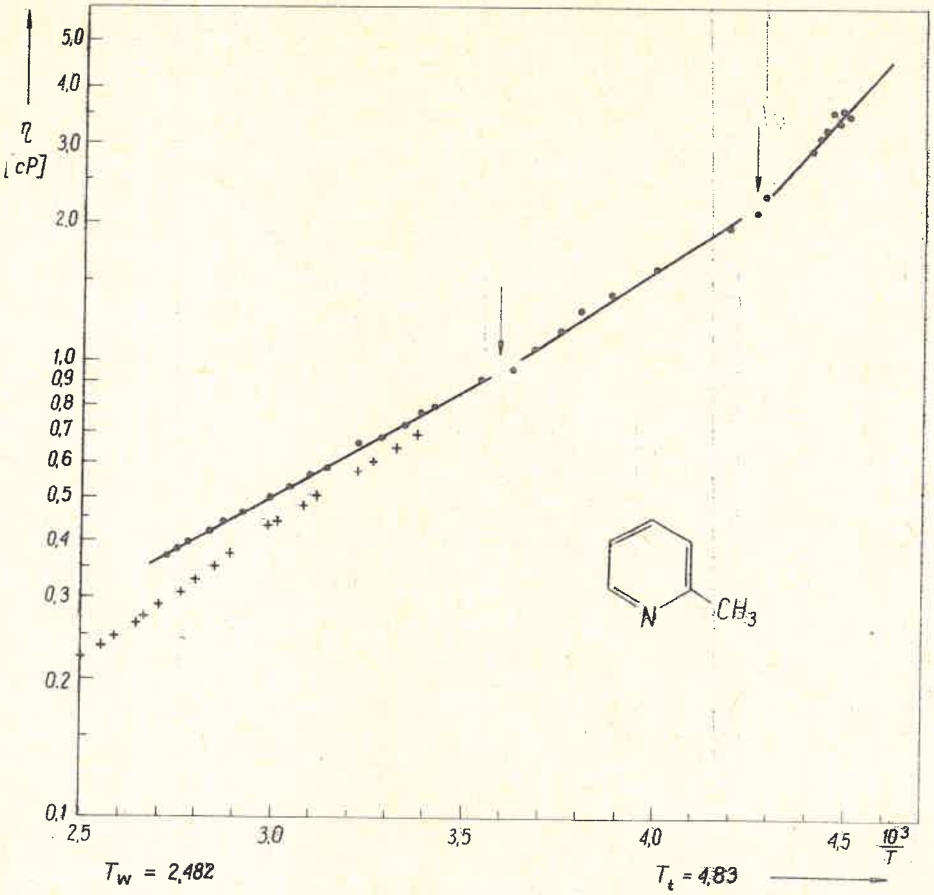

Fig. 4. Temperature dependence of viscosity for α-pikoline degassed (solid dots ●) and saturated with air (vertical crosses +)

— smoothes out the sharp boundary between Arrhenius subregions on the log $\eta = f1/T$ plot at temperatures $T_{\mathrm{II,III}}$.

Table II gives the values of the pre-exponential coefficients and the activation energy in the Arrhenius region for liquids saturated with gases.

Measured at the same time were the temperature dependences of PMR chemical shifts of protons in the aromatic ring of molecules in the liquids [16, 17, 19]. The dependences obtained confirm the existence of characteristic temperatures for the liquids studied, but do not reveal any observable effect due to the addition of gases on their nature. The values of temperatures $T_{\mathrm{I,II}}$ and $T_{\mathrm{II,III}}$ determined by PMR are compared in Table I with temperatures defined from η.

In summarising the observed temperature dependences of the viscosity of chemically purified and degassed liquids, the effect of additions of gas on these dependences and the temperature dependences of the PMR chemical shift found experimentally can be initially interpreted thus [18, 19]:

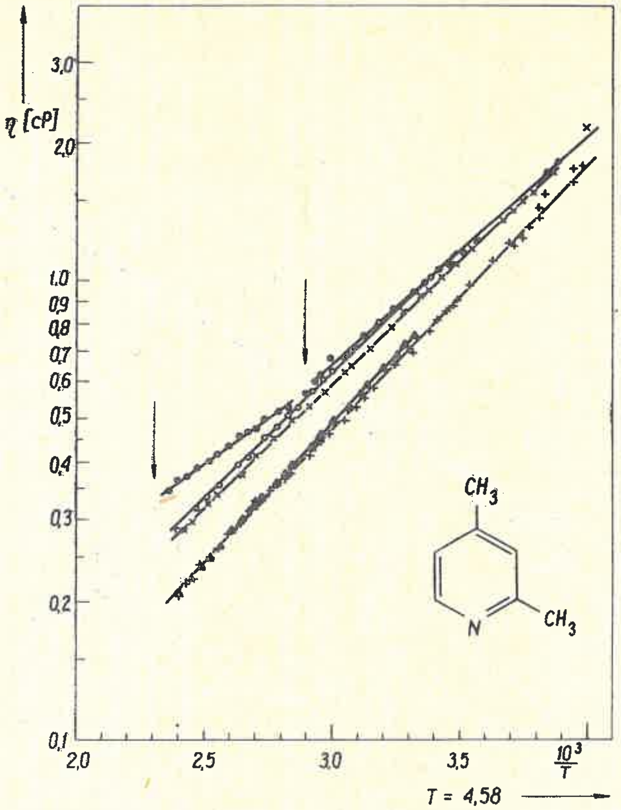

Fig. 5. Temperature dependence of viscosity at high temperatures for 2,4-lutidine degassed (solid dots ●), saturated with air (vertical crosses +), saturated with argon at 1 atm pressure (solid triangles ▲), after repeating the degassing cycle three times (open circules ○) and saturated with nitrogen at reduced pressure (diagonal crosses ×)

TABLE I

Comparison of activation energy E_{ai}, pre-exponential coefficient η_0 and characteristic temperatures T_{ij} for degassed liquids

Parameter	2,4-lutidine	3,4-lutidine	α-picoline
E_{aI}[kJ/mol]	7.8	9.2	8.4
E_{aII}[kJ/mol]	9.5	11.0	11.4
E_{aIII}[kJ/mol]	21.5	19.3	18.0
η_{0I}[P]	1.577×10^{-3}	1.74×10^{-3}	3.4×10^{-3}
η_{0II}[P]	1.92×10^{-3}	2.07×10^{-3}	4.39×10^{-3}
η_{0III}[P]	2.54×10^{-2}	1.29×10^{-2}	1.93×10^{-2}
$T_{I,II}$[K]η	243	279	235
PMR	243	291	—
$T_{II,III}$[K]η	345	367	281
PMR	345	360	300

— gaseous additions to liquids cause defects or a fluctuation of the quasi-crystalline composition in the coordination sphere of the given molecule. This increases the translational mobility of the liquid molecules.

— the characteristic temperatures T_{ij} correspond to the temperatures at which the successive rotational degrees of freedom of the molecules are "frozen out"; the disappearance or decrease of the sharpness of transition between Arrhenius subregions in a liquid has occurred when the close-range ordering is disturbed i.a. by the introduction of other molecules, e.g. of gases, into the liquid.

TABLE II

Comparison of activation energy E_a, pre-exponential coefficients η_0 in the Arrhenius subregion for liquids containing additions of gas

Gas added	2,4-lutidine		3,4-lutidine		α-picoline	
	E_a[kJ/mol]	η_0[P]	E_a[kJ/mol]	η_0[P]	E_a[kJ/mol]	η_0[P]
air ($p = 1$ atm)	10.8	2.8×10^{-3}	12.1	3.3×10^{-3}	11.0	2.8×10^{-3}
air ($p < 1$ atm)	10.6	3.4×10^{-3}	—		—	
argon ($p = 1$ atm)	11.6	2.4×10^{-3}	—		—	
nitrogen ($p < 1$ atm)	10.3	3.0×10^{-3}	—		—	

In conclusion, it can be stated that the results presented here indicate the significant influence of the additions of gas on momentum transfer processes in liquids. This applies in particular to liquids capable of dissolving large volumes of gases and the molecules of gases differ from those of the studied liquids in shape and in the nature of their molecular interactions.

Only when liquids would be free of all contaminating gases, including dissolved air it would be possible to obtain data on the structure and dynamics of the molecular movement characteristics of a given liquid.

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