
PECULIARITIES OF THE TEMPERATURE DEPENDENCE OF KINEMATIC SHEAR VISCOSITY OF FLUORINE DERIVATIVES OF BENZENE

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We study the temperature dependence of the kinematic shear viscosity of ten fluorine derivatives of benzene. Experimental data are obtained in the temperature interval (293÷363) K. It is shown that the temperature dependence of the majority of investigated fluids has the same character as that of benzene and argon which are simpler by their structure. We deduce a formula adequately describing a behavior of the viscosity of fluorine derivatives of benzene. It is established that only the viscosity of 1,3-bistrifluoromethylbenzene has activation character.

1. Introduction

Fluorine derivatives of benzene play a significant role in the modern scientific practice, technique, and technologies [1–4]. They are used in medicine, paint-varnish and food industries, radioelectronics, *etc.* For this reason, their physical and chemical properties remain to be objects of studies [4–6].

Here, we investigate specific features of the temperature dependence of the kinematic shear viscosity of fluorine derivatives of benzene, whose list is given in Table 1.

We use the following notation: ρ is the density, η is the dynamical shear viscosity, c is the sound velocity, and T_i , $i = m, b$, are the temperatures of melting and boiling, respectively. Values of ρ , η , and c correspond to a temperature of 293 K. All fluids, excluding benzene and methoxybenzene, are studied for the first time. The

arrangement of fluids in Table 1 conforms to the increase in their molecular masses.

The choice of namely these objects is determined by their chemical and thermal stabilities and by a possibility to trace, in a rather simple way, the dependence of their physical properties on the type of substitution of a hydrogen atom by molecular groups containing atoms of halogens.

We note that the nontriviality of the problem studied in the present work is due to the following circumstances. It was shown in works [9, 12] that the temperature dependence of the kinematic shear viscosity of benzene in the whole region of existence of its liquid state from the crystallization point to the critical one has argon-like character and is adequately described by the formula

$$\tilde{\nu}(\tilde{v}, t) = \frac{\zeta_0}{(\tilde{v} - \tilde{v}_0)^{1/3}} (1 + \mu(t)), \quad (1)$$

where $\tilde{\nu}(t) = \frac{\nu(t)}{\nu_R}$, ν_R is the regular part of the shear viscosity at the critical point, $t = \frac{T}{T_c}$, $\tilde{v} = \frac{v}{v_c}$, $v = \frac{1}{n}$, n is the density of molecules, T_c and v_c are the critical values of temperature and volume, $\tilde{v}_0 = \frac{v_0}{v_c}$, v_0 is the intrinsic volume of a molecule, ζ_0 is a constant, and $\mu(t)$ is a function taking the weak dependence of the viscosity of benzene on the temperature into account. In agreement with (1), the shear viscosity of benzene is determined, first of all, by a change of the fractional volume

Table 1. Physico-chemical constants of fluorine derivatives of benzene

Name	Structure formula	ρ , kg/m ³	$\eta \times 10^6$, Pa·s	c , m/s	T_m , K	T_b , K
Benzene	C ₆ H ₆	878.7	652	1318	278.2	353.2
Methoxybenzene	C ₆ H ₅ OCH ₃	994.0	786	1417	235.6	428
Methoxydifluorbenzene	C ₆ H ₅ OCHF ₂	1183.2	900	1190	191.8	413
Methoxydifluorchlorobenzene	C ₆ H ₅ OCClF ₂	1202.9	1014	1170.7	160.8	403
Methoxytrifluorbenzene	C ₆ H ₅ OCF ₃	1225.8	673	952	172.2	374
Phenylmethylsulfide	C ₆ H ₅ SCH ₃	1058.1	1576	1499	258	461
Phenyldifluormethylsulfide	C ₆ H ₅ SCHF ₂	1227.1	1503	1239	272	345
Phenyltrifluormethylsulfide	C ₆ H ₅ SCF ₃	1263.2	1011.7	1030	173.9	433
Phenyldifluormethylsulfate	C ₆ H ₅ O ₂ SCHF ₂	1397.7	1562.6	1322	239.6	412
Phenyltrifluormethylsulfate	C ₆ H ₅ O ₂ SCF ₃	1415.6	3840	1098	189.4	473

$\tilde{\nu}$ per molecule of a fluid. Hence, formula (1) reminds the Batchinski formula [6, 12] in some aspects and, like the latter, has no activation character. However, the situation changes at the transition to fluids with a more complicated structure of molecules and a more involved character of intermolecular interaction. As the simplest example, we mention the temperature dependence of the shear viscosity of nitrobenzene [7, 8]. It is different from both the dependence given by formula (1) and the dependence

$$\nu = \frac{hN_A}{34,15 \chi \rho V_M} \exp\left(-\frac{\Delta S_\eta^\ddagger}{R}\right) \exp\left(\frac{\Delta H_\eta^\ddagger}{RT}\right) \quad (2)$$

following from the activation theory of viscosity [10, 11]. Here, h and N_A are the constants of Planck and Avogadro, χ is the transmission coefficient, V_M is the molecular volume, and ΔS_η^\ddagger and ΔH_η^\ddagger are the entropy and enthalpy of activation, respectively.

In this connection, it is quite natural to raise the question about a character of the temperature dependence of the kinematic shear viscosity of fluorine derivatives of benzene. The answer to it will allow one to obtain a reliable information about a character of the thermal motion of molecules in the indicated class of fluids.

2. Peculiarities of a Temperature Dependence of Kinematic Shear Viscosity

The experimental measurements of the kinematic shear viscosity of fluorine derivatives of benzene were carried out in the interval of temperatures (293 ÷ 363) K. It is easy to verify that the temperature dependence of ν in a sufficiently narrow temperature interval can be quite successfully approximated by the exponential formula of the activation theory

$$\nu(T) = \nu_0 \exp\left(3 \frac{T_m}{T} \varepsilon\right), \quad (3)$$

Table 2. Normalized values of activation energy per molecule for the studied fluorine derivatives

Fluid	ε
C ₆ H ₆	1.46
C ₆ H ₅ OCH ₃	2.19
C ₆ H ₅ OCHF ₂	1.98
C ₆ H ₅ OCF ₃	1.92
C ₆ H ₅ SCH ₃	1.86
C ₆ H ₅ SCHF ₂	1.79
C ₆ H ₅ SCF ₃	1.72
C ₆ H ₅ O ₂ SCHF ₂	4.52
C ₆ H ₅ O ₂ SCF ₃	3.35
C ₆ H ₅ OCClF ₂	1.88
C ₆ H ₄ (CF ₃) ₂	1.05

where ε is the activation energy per molecule measured in units of the mean kinetic energy of a molecule $3k_B T_m$ at the melting temperature T_m (with regard for the fact that a molecule of benzene has three longitudinal and three rotational degrees of freedom). Thus, ε shows how much the activation energy exceeds the energy of thermal noise. Numerical values of ε for the studied fluorine derivatives are collected in Table 2.

The necessary condition for the application of the activation theory of viscosity is a substantial excess of the activation energy over the energy of thermal noise (i.e., over the kinetic energy of a molecule). In other words, the following inequality must be satisfied:

$$\varepsilon \gg 1. \quad (4)$$

As seen from Table 1, this condition is valid at a certain stretch only for phenyldifluormethylsulfate. This fluid is obtained from benzene by the substitution of a hydrogen atom by two oxygen atoms and a difluoromethyl group. The difference in the kinematic shear viscosities of phenyldifluormethylsulfate and other fluorine derivatives is more well pronounced in Fig. 1. It seems probable that this effect appears due to a stronger dipole

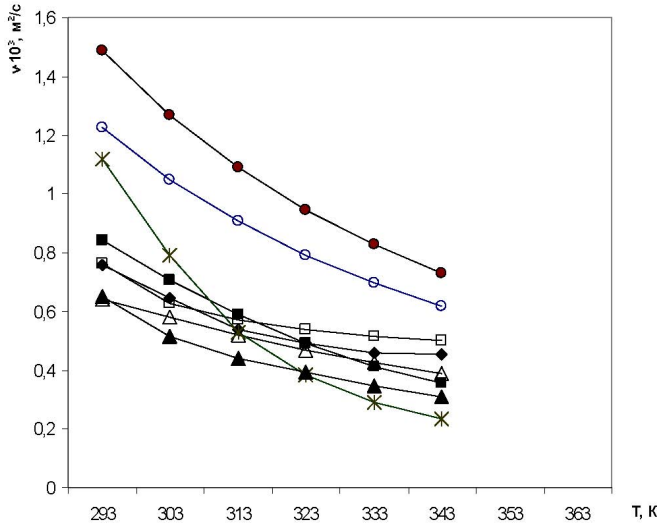


Fig. 1. Dependence of kinematic viscosity on the number of fluorine atoms: \blacktriangle – benzene, \diamond – methoxybenzene, \square – methoxydifluorbenzene, \blacksquare – methoxydifluorchlorobenzene, \triangle – 1,3-bistrifluormethylbenzene, \bullet – phenylmethylsulfide, \times – phenyldifluormethylsulfate, \circ – phenyldifluormethylsulfide

interaction between molecules which favors a local ordering of the axes of molecules.

This mechanism is absent for benzene, and, as was mentioned in Introduction, the behavior of its shear viscosity has argon-like character and is determined by formula (1). We note that condition (4) is not satisfied, and the thermal motion of molecules in fluorine derivatives is close to that in benzene. Therefore, we may conclude that the temperature dependence of their kinematic shear viscosity can be described on the basis of formula (1).

3. Description of the Kinematic Shear Viscosity of Fluorine Derivatives in a Narrow Temperature Interval

We now adjust formula (1) for the description of our experimental data on the kinematic shear viscosity of fluorine derivatives. Substituting $\nu \rightarrow \frac{m}{\rho}$, where m is the molecule mass, and ρ is the density, we present (1) in the form

$$\tilde{\nu}(\rho, t) = \frac{\zeta_0 \left(\frac{\rho(t)\rho_0}{\rho_c} \right)^{1/3}}{(\rho_0 - \rho(t))^{1/3}} [1 + \mu(t)], \quad (5)$$

where $\rho_0 = m/\nu_0$ is the liquid density maximally possible without any loss of its properties.

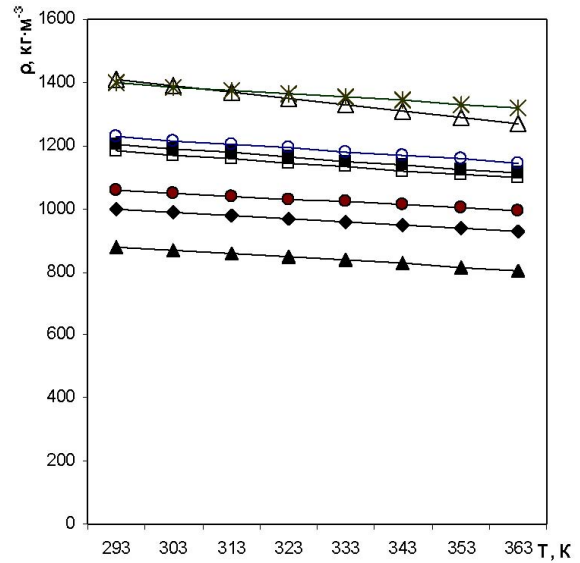


Fig. 2. Temperature dependence of densities of fluorine derivatives: \blacktriangle – benzene, \diamond – methoxybenzene, \square – methoxydifluorbenzene, \blacksquare – methoxydifluorchlorobenzene, \triangle – 1,3-bistrifluormethylbenzene, \bullet – phenylmethylsulfide, \times – phenyldifluormethylsulfate, \circ – phenyldifluormethylsulfide

A significant peculiarity of the temperature dependence of the density of fluorine derivatives in rather wide temperature intervals is its almost linear character (see Fig. 2). Therefore, we will approximate the liquid density and $\mu(T)$ in a vicinity of the melting temperature by relations linear in the temperature:

$$\rho(T) = \rho_m + \lambda(T - T_m) + \dots \quad (6)$$

$$\mu(T) = \mu_m + \mu_1(T - T_m) + \dots$$

As follows from Fig. 2, the coefficient λ for almost all fluids is close to $-10^{-3} \text{ g/cm}^3 \text{ degr}$.

Using (6), we can rewrite formula (5) in a simpler form:

$$\nu(\rho, T) = \nu_R \zeta_0 \left(\frac{[\rho_m + \lambda(T - T_m) + \dots]\rho_0}{\rho_c(\rho_0 - [\rho_m + \lambda(T - T_m) + \dots])} \right)^{1/3} \times [1 + \mu_m + \mu_1(T - T_m) + \dots]. \quad (7)$$

The smallness of variations of the density in the temperature interval (293 ÷ 363) K under study and a weak temperature dependence of $\mu(T)$ are the basis for the further simplification of (7):

$$\nu(\rho, T) \approx \frac{\nu_m}{\left[1 - \frac{\rho_m}{\rho_0} - \frac{\lambda}{\rho_0}(T - T_m) \right]^{1/3}}. \quad (8)$$

Table 3. Values of parameters in formula (8)

Fluid	T_m, K	$\nu_m, \text{cm}^2/\text{s}$	$\rho_m, \text{g}/\text{cm}^3$	$-\lambda \times 10^3, \text{g}/\text{cm}^3\text{degr}$	$\rho_0, \text{g}/\text{cm}^3$
Phenylmethylsulfide	258	0.222×10^{-2}	1.091	0.94	1.09
Phenyldifluoromethylsulfide	272	0.154×10^{-2}	1.252	1.19	1.27
Methoxydifluorbenzene	191.8	0.127×10^{-2}	1.250	1.23	1.26
Methoxybenzene	235.6	0.162×10^{-2}	1.048	0.96	1.05
1,3-bistrifluoromethylbenzene	189.5	0.736×10^{-2}	1.444	2.01	1.67
Benzene	278.2	0.735×10^{-2}	0.890	1.06	0.98

Here, $\nu_m = \nu_R \zeta_0 \left(\frac{\rho_m}{\rho_c} \right)^{1/3}$ is the shear kinematic viscosity at the point of melting. As seen, the temperature dependence of the kinematic shear viscosity depends critically on the ratio of components $1 - \frac{\rho_m}{\rho_0}$ and $\frac{\lambda}{\rho_0} (T - T_m)$ in the denominator of (8). In Table 3, we collected the values of all parameters ensuring the optimum fit of the experimental values of kinematic shear viscosity of the studied fluorine derivatives with the use of (8).

The accuracy of the fitting of experimental values with the help of formula (8) is not less than that of experimental data.

It is worth noting that the maximum densities ρ_0 for benzene and 1,3-bistrifluoromethylbenzene, whose molecules have a relatively simple structure and do not form specific intermolecular bonds, are considerably higher than the densities ρ_m at their points of melting. In all other cases, the values of ρ_0 and ρ_m do not differ from one another within experimental errors. Thus, we must conserve all terms in formula (8) near the points of melting of all studied fluorine derivatives.

By moving away from the point of melting, we observe that the temperature dependence of kinematic shear viscosity becomes essentially smoother and can be generally approximated by the dependence linear in the temperature:

$$\nu(\rho, T) = \nu_* + \gamma_*(T - T_*) + \dots \quad (9)$$

Here, T_* is some temperature far from the point of melting,

$$\nu_* = \frac{\zeta_0 \left(\frac{\rho_* \rho_0}{\rho_c} \right)^{1/3}}{(\rho_0 - \rho_*)^{1/3}}$$

is the kinematic viscosity at the point T_* , and

$$\gamma_* = \frac{1}{3} \lambda \nu_* \frac{\rho_0}{\rho_*(\rho_0 - \rho_*)} + \mu_1 \nu_* \quad (10)$$

The width ΔT of a temperature interval, in which formula (8) can be used, is determined by the inequality

$$\Delta T < (\ll) \frac{1}{\lambda} (\rho_0 - \rho_*) \quad (11)$$

As the temperature interval is widened, the accuracy of the approximate formulas (8) or (9) and (7) decreases. In this case, it is necessary to return to the most exact input formula (5) or (1).

Discussion of Results

We present the results of experimental and theoretical studies of the kinematic shear viscosity of a number of fluorine derivatives of benzene. We focus namely on the behavior of the kinematic shear viscosity, rather than on that of the dynamical shear viscosity, because the temperature dependence of the latter depends in a certain way on a change of the density. In other words, the kinematic shear viscosity of a system is a more fundamental characteristic.

It is shown that the temperature dependence of the kinematic shear viscosity of the studied fluorine derivatives is described, except for one case, by formula (8) which has nothing in common with the exponential formulas of the activation theory of viscosity. It is very important that the structure of formula (5) underlying formula (8) used by us is the same like that for liquid benzene and argon (see [8]). This means that the static values of kinematic viscosity of the studied fluorine derivatives are mainly formed by the longitudinal degrees of freedom like the case of benzene and argon. Moreover, we must state that the character of thermal motion of molecules of all studied fluids, except for phenyldifluoromethylsulfate, is similar to that of argon.

The effective potential of interparticle interaction determining a behavior of the main thermodynamic and kinetic quantities is formed by the averaging of the input intermolecular potential over the coordinates describing a spatial orientation of asymmetric molecules. Such coordinates vary essentially more faster than those related to the longitudinal degrees of freedom. As a result of the averaging over rotational motions, an asymmetric molecule acquires effectively a spherical shape. This is associated with the conclusion that the temperature dependence of the density of fluorine derivatives must be expected to be similar to that of simple fluids. In par-

ticular, the maximum value ρ_0 of the density of fluorine derivatives should be observed at the melting temperature, which agrees completely with experimental data. We note that the transfer to the spherical shape of a molecular volume must be manifested in the equation of state and, as was shown in [9], in the temperature dependence of the kinematic shear viscosity.

Only in a single case for liquid phenyldifluormethylsulfate, condition (4) for the application of the activation theory of viscosity [10,11] is satisfied. It is probable that a molecular fragment joining a benzene ring induces strong orientation correlations. As a result, a change in local molecular orientation configurations can occur only by the activation mechanism, by a jump-like change of one local configuration for the other one.

An important additional information about the character of the intermolecular interaction can be obtained from the comparative analysis of temperatures and densities of fluids at the points of melting, the compressibility of fluids, or the static velocities of sound. We intend to consider these questions elsewhere.

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ОСОБЛИВОСТІ ТЕМПЕРАТУРНОЇ ЗАЛЕЖНОСТІ КІНЕМАТИЧНОЇ ЗСУВНОЇ В'ЯЗКОСТІ ФТОРПОХІДНИХ БЕНЗОЛІУ

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Резюме

В роботі досліджено температурну залежність кінематичної зсувної в'язкості десяти фторпохідних бензолу. Експериментальні значення отримано в температурному інтервалі (293–363) К. Показано, що температурна залежність більшості з досліджених рідин має той самий характер, що у більш простих за структурою бензолі та аргоні. Отримано формулу, яка адекватно описує поведінку в'язкості фторпохідних бензолу. Встановлено, що лише в'язкість 1,3-бістрифторметилбензолу має активаційний характер.