

NATURE OF THE KINEMATIC SHEAR VISCOSITY OF BENZENE AND ITS DERIVATIVES

N.P. MALOMUZH, A.V. OLEYNIK, A.P. RUDENKO¹, A.M. KHLOPOV¹

UDC 532.133
© 2007

Department of Theoretical Physics, Odesa National University
(2, Dvoryans'ka Str., Odesa 65026, Ukraine; e-mail: mnp@normaplus.com),

¹Department of Physics, Poltava Pedagogical University
(2, Rudenko Str., Poltava 65086, Ukraine; e-mail: amh@rudenko.com)

The paper is devoted to the detailed analysis of the kinematic shear viscosity ν of benzene as a function of the normalized temperature t and specific volume \tilde{v} ($t = T/T_c$, $\tilde{v} = v/v_c$, where T_c and v_c are the critical temperature and specific volume). Using experimental values of ν , t , and \tilde{v} for benzene and argon on their coexistence curves, it is shown that the kinematic shear viscosities of these liquids are fully similar in the manner of the principle of corresponding states. It is surprising since their equations of state are only approximately similar. It is rigorously proved that the kinematic shear viscosity of benzene has no activation character. The explicit formula for ν of argon and benzene is proposed. It is shown that the behavior of ν is mainly determined by the specific volume. Such a peculiarity is inherent to Batchinski's formula, although the character of such an influence is quite different. The manifestation of the hard-core effects is discussed.

two characteristic configurations, when benzene rings are parallel to each other or perpendicular [4,5]. In addition, if the interparticle distance between two neighbor molecules is smaller than 3\AA , their interaction energy becomes noticeably more than the energy of their thermal motion. For this reason, the association processes in liquid benzene are of interest. Namely, this circumstance was taken into account as the most characteristic of liquid benzene and its derivatives in [6]. Using the formalism of chemical reactions [7,8] and the notions of irreversible thermodynamics [9], it was shown [6] that the shear viscosity of benzene and its derivatives can be described by the formula

$$\eta(T, v) = \frac{1}{\kappa} \frac{h}{v} \exp\left(-\frac{\Delta S_1}{k_B}\right) \exp\left(\frac{\Delta H_1}{k_B T}\right), \quad (1)$$

1. Introduction

There exists the extensive literature on the nature of the shear viscosity η of liquids (see [1–3]). However, this question remains to be open up to now. This is connected with two essential circumstances: 1) absence of the quite satisfactory zero approximation and 2) effective perturbation theory for kinetic processes. The most progress in the theory of the shear viscosity and other kinetic coefficients is observed for liquids with spherical molecules, especially for inert gases. The formulas for η , proposed in [1,2] for liquid argon, give only the correct order of magnitude. They are not able to describe the main peculiarities of η in the whole range of liquid states, including the crystallization and critical points, and even on the vapor-liquid coexistence curve. The correct description of the density dependence of the shear viscosity proves to be a difficult problem. Furthermore, the situation becomes complicated for liquids with non-spherical molecules and with strongly anisotropic intermolecular potential.

Liquid benzene is one of the simplest examples of such a system. The benzene molecule has the form of a puck in ice hockey. The interaction energies of two benzene rings are essentially different for

where h and k_B are the Planck and Boltzmann constants, correspondingly, T and v are the temperature and molecular volume, κ is the so-called transmission coefficient [3], ΔS_1 and ΔH_1 are the changes of entropy and enthalpy because of the formation of the optimal molecular complex. The numerical values of ΔS_1 and ΔH_1 can be determined by using the experimental data on η . Although these data are fitted by (1) quite satisfactorily in the narrow temperature intervals, values of the "activation energy" ΔH_1 are often comparable with the energy of thermal motion $k_B T$ [6] and can be even smaller than it.

Such a temperature dependence of the shear viscosity is also characteristic of the activation mechanism of the viscosity developed by Frenkel [10] for liquids with a crystal-like character of thermal motion. Difficulties connected with little values of the activation energy remain here too. This implies that the usage of the crystal-like representations is also incorrect for the description of thermal motion in many liquids, in particular, in benzene and its derivatives.

Difficulties of both these approaches become especially considerable for large temperature intervals

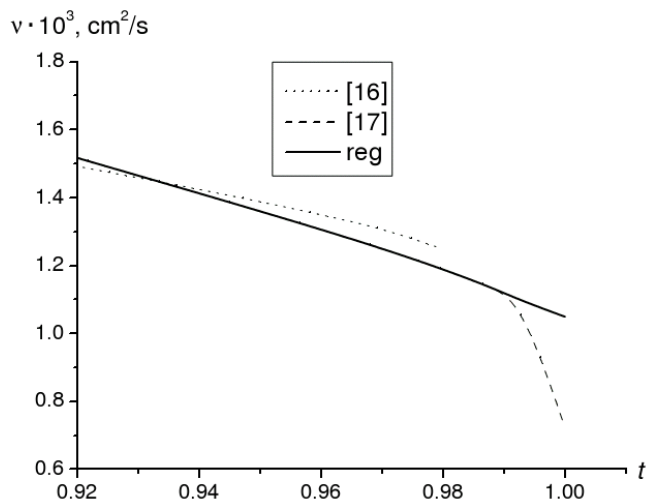


Fig. 1. Temperature dependence of the kinematic shear viscosity of benzene on its vapor-liquid coexistence curve near its critical point according to experimental data [16,17]. The solid line corresponds to the regular contribution to $\nu^{(B)}(t)$

[11]. The qualitative analysis of the situation on the whole was given in [12].

Here, we would like to mention the old work of Batchinsky [13] who paid attention to the density dependence of the shear viscosity, as the most essential.

The present paper is devoted to the careful study of the kinematic shear viscosity ν for benzene. Our analysis is based on the detailed comparison of the temperature and density dependences of ν for benzene and argon on their coexistence curves. We use the normalized variables characteristic of the principle of corresponding states [14] (see also [15], where such an approach was first successfully applied to the investigation of the kinematic shear viscosity of water). Similarly, the nature of the kinematic shear viscosity for argon is also studied.

2. Comparative Behavior of the Kinematic Shear Viscosities of Benzene and Argon

To understand the nature of the thermodynamic and kinetic properties of liquids with non-spherical molecules and anisotropic intermolecular interaction, it is necessary to compare their behavior with one of the liquids, properties of which are supposed to be known. From the geometric point of view, the benzene molecule can be considered as an ellipsoid of rotation. Therefore, it seems to be natural to compare properties of benzene with those for argon, whose atoms assume a spherical form.

From this point of view, it is necessary to compare thoroughly the temperature dependence of different quantities for benzene and argon in the manner of the principle of corresponding states [14]. More exactly, the compared quantities should be normalized with respect to their regular values at the critical point ($\tilde{\nu}(t) = \frac{\nu(t)}{\nu_R}$), and temperature should be measured in the reduced units $t = \frac{T}{T_c}$, where T_c is the critical temperature.

In this section, our attention will be focused on the nature of the kinematic shear viscosity of benzene. Note that the kinematic shear viscosity ν is one of the fundamental kinetic characteristic of liquids. The dynamic shear viscosity η close to it is a more complex characteristic, since it depends additionally on the mass density ρ : $\eta = \nu\rho$. In general, the kinematic shear viscosity is a function of the temperature t and the normalized specific volume per molecule $\tilde{v} = \frac{v}{v_c}$, where $v = \frac{m}{\rho}$, m is the mass of a molecule, and v_c is the critical value of v . The roles of both these arguments in $\nu = \nu(\tilde{v}, t)$ are not equivalent. For inert gases in their liquid states, the dependence upon \tilde{v} is stronger [16].

However, the detailed information about the dependence $\nu(\tilde{v}, t)$ on its arguments is absent for benzene. Therefore, we restrict ourselves to the comparison of the kinematic shear viscosities for benzene $\tilde{\nu}^{(B)}$ and argon $\tilde{\nu}^{(Ar)}$ on their vapor-liquid coexistence curves. In this case, \tilde{v} is a function of the temperature and, vice versa, $t = t(\tilde{v})$. The regular value ν_R is determined by the parabolic extrapolation of the kinematic shear viscosity from the range, where the fluctuation effects are inessential. In such a way, we obtain

$$\nu_R^{(Ar)} = 5.07 \times 10^{-4} \text{ cm}^2/\text{s},$$

$$\nu_R^{(B)} = 1.049 \times 10^{-3} \text{ cm}^2/\text{s}.$$

As follows from Fig. 1 and Fig. 2, the fluctuation effects noticeably influence the values of $\tilde{\nu}^{(B)}$ and $\tilde{\nu}^{(Ar)}$ only in the narrow temperature intervals near the critical point: $0.95 < t < 1$. Note that the values of the kinematic shear viscosity for benzene from different sources are close to each other near the critical point as well as far from it. Unlike this, the situation is not so good in the case of argon. Here, the noticeable divergence of experimental data from different sources is observed in the whole range of liquid states, especially in the vicinity of the critical point.

The comparative behavior of $\tilde{\nu}^{(B)}(t)$ and $\tilde{\nu}^{(Ar)}(t)$ with the obtained values of $\nu_R^{(B)}$ and $\nu_R^{(Ar)}$ are presented in Fig. 3. It is worth to note that the normalized

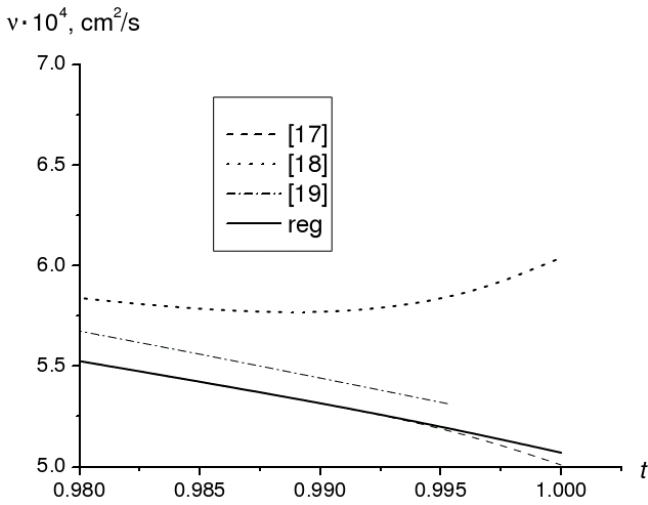


Fig. 2. Temperature dependence of the kinematic shear viscosity of argon on its vapor-liquid coexistence curve near the critical point according to experimental data [17–19]. The solid line corresponds to the regular contribution to $\nu^{(Ar)}(t)$

crystallization temperatures $t_m^{(i)} = \frac{T_m^{(i)}}{T_c^{(i)}}$ for argon and benzene are different: $t_m^{(Ar)} = 0.56$ and $t_m^{(B)} = 0.5$ (it follows from [16,17] that $T_m^{(Ar)} = 83.806$ K and $T_m^{(B)} = 278.7$ K). Therefore, at $t < t_m^{(Ar)}$, the values of $\tilde{\nu}(t)$ as well as $\tilde{\nu}^{(B)}(t)$ for benzene in the supercooled region can be obtained with the help of the parabolic extrapolations:

$$\tilde{\nu}_{ext}^{(Ar)}(t) = 32.30 - 81.17t + 55.30t^2, \quad t < 0.56, \quad (2)$$

$$\tilde{\nu}_{ext}^{(B)}(t) = 203.07 - 263.44t + 89.58t^2, \quad t < 0.5. \quad (3)$$

The numerical values of the coefficients in (2) and (3) are determined from the experimental data on the kinematic shear viscosity of argon from the intervals $0.56 \leq t \leq 0.7$ and $0.5 \leq t \leq 0.65$, respectively.

The primary impression generated by Fig. 3 is the non-equivalency of the mechanisms forming the shear viscosity in benzene and argon. However, we have noted above that the dependences of the kinematic shear viscosity of argon on t and $\tilde{\nu}$ are also non-equivalent. Supposing that an analogous peculiarity is also inherent to benzene, we compare the behavior of

$$\tilde{\nu}^{(B)}(t) = \frac{\nu^{(B)}(t)}{\nu_c^{(B)}} \quad \text{and} \quad \tilde{\nu}^{(Ar)}(t) = \frac{\nu^{(Ar)}(t)}{\nu_c^{(Ar)}},$$

on the coexistence curves of benzene and argon, where $\nu_c^{(i)}$, $i = B, Ar$, are the corresponding critical values (Fig. 4).

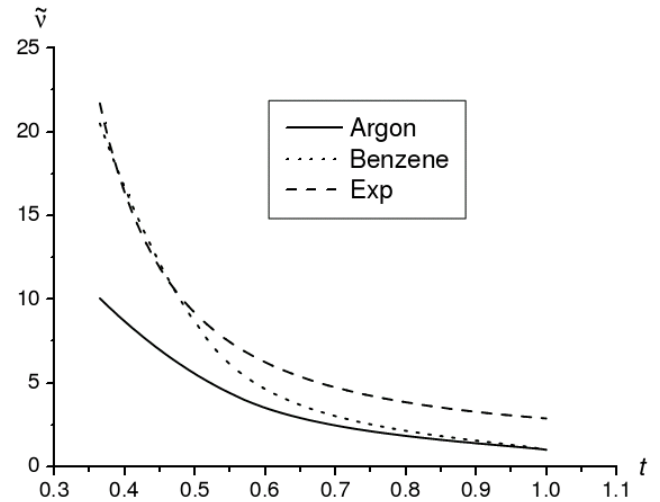


Fig. 3. Comparative behavior of the normalized kinematic shear viscosities of benzene and argon in the temperature interval (0.36, 1). The experimental data are taken from [17]. The broken curve corresponds to the exponential fitting $\tilde{\nu}^{(B)} = \tilde{\nu}_0 \exp \frac{\varepsilon}{t}$ with parameters $\tilde{\nu}_0 = 0.90$ and $\varepsilon = 1.16$

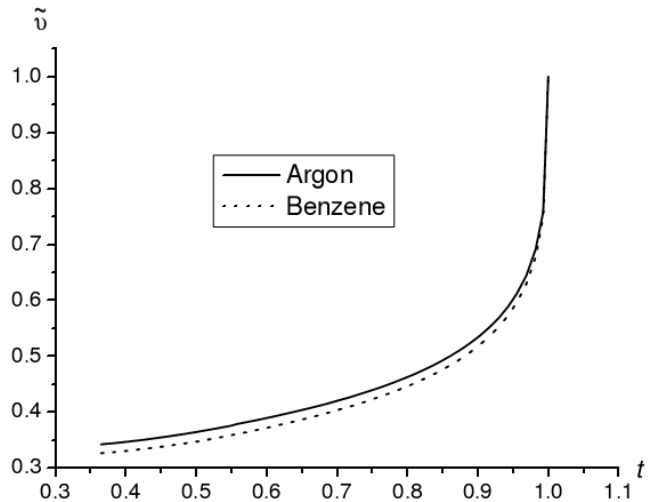


Fig. 4. Temperature dependence of the normalized specific volume for benzene and argon. The experimental data are taken from [17]

As seen, the values of $\tilde{\nu}^{(B)}(t)$ and $\tilde{\nu}^{(Ar)}(t)$ are noticeably different in the wide temperature range, which can essentially influence the kinematic shear viscosity. Only at $t \rightarrow 1$, the asymptotic rapprochement of $\tilde{\nu}^{(B)}(t)$ and $\tilde{\nu}^{(Ar)}(t)$ is observed. In accordance with Fig. 3, it is accompanied by the respective rapprochement of $\tilde{\nu}^{(B)}(t)$ and $\tilde{\nu}^{(Ar)}(t)$.

The comparable behavior of the kinematic shear viscosities of benzene and argon versus $\tilde{\nu}$ on their

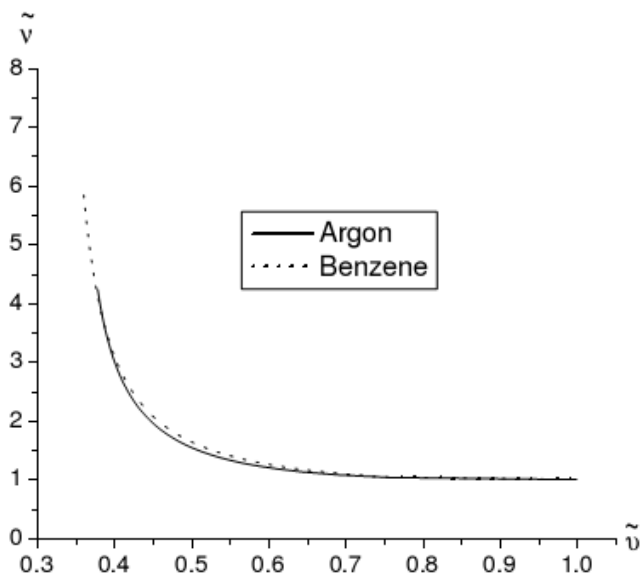


Fig. 5. Dependences of the normalized kinematic shear viscosities of benzene and argon on the normalized specific volume

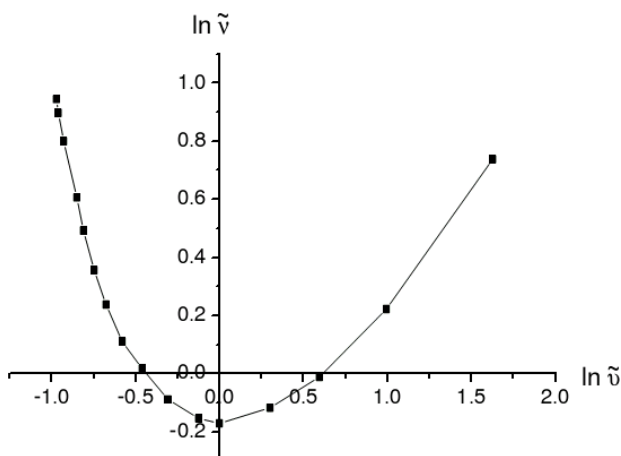


Fig. 6. Kinematic shear viscosity of argon versus the normalized specific volume on the critical isotherm

coexistence curves is presented in Fig. 5. The identity of their dependences for the whole ranges of their liquid states, from the melting point up to the critical one is very surprising. This means that the kinematic shear viscosity for benzene, similar to that for argon, has no activation character. More exactly, one can suppose that, inside the temperature and pressure ranges restricted by the inequalities $t_m < t < 1$ and $p_m < p < 1$, where $p = P/P_c$ is the dimensionless pressure, the kinematic shear viscosity of benzene has the argon-like character. Probably, such a conclusion can be made for many benzene derivatives as well.

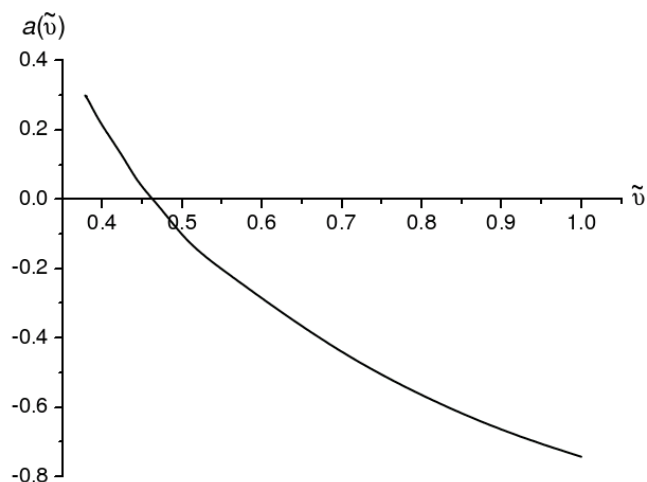


Fig. 7. Numerical values of $a(\tilde{v})$ on the critical isotherm obtained by the fitting of the experimental data [16] with the help of (4)

3. Kinematic Shear Viscosity of Argon Versus \tilde{v} and t

A circumstantial investigation of the dynamical shear viscosity η of argon and other inert gases was carried out in [16]. It was shown that $\ln \eta$ as a function of $1/t$ has practically the straight-line behavior on isochors. Therefore, $\ln \eta$ can be approximated by the formula

$$\ln \eta(\tilde{v}, t) \approx \ln \eta(\tilde{v}, 1) + a(\tilde{v}) \left(\frac{1}{t} - 1 \right), \quad (4)$$

where $\ln \eta(\tilde{v}, 1)$ is the value of $\ln \eta$ on the critical isotherm. The numerical values of $a(\tilde{v})$ and the kinematic shear viscosity $\zeta(\tilde{v}) = \frac{\eta(\tilde{v}, 1)\tilde{v}}{m}$ on the critical isotherm, obtained by the fitting of the experimental data [18] with the help of (4), are presented in Figs. 6 and 7. In the coordinates $(\ln \zeta(\tilde{v}), \ln(\tilde{v} - \tilde{v}_0))$, the relation $\zeta(\tilde{v})$ becomes especially simple. As seen from Fig. 8, it is practically linear:

$$\ln \zeta(\tilde{v}) = c \ln(\tilde{v} - \tilde{v}_0) + \zeta_0. \quad (5)$$

The optimal values of c and \tilde{v}_0 are equal to: $c = -0.34$, $\tilde{v}_0 = 0.36$, and $\ln \zeta_0 = -0.39$. Thus, with good accuracy, we have

$$\zeta(\tilde{v}) \approx \frac{\zeta_0}{(\tilde{v} - 0.36)^{1/3}}, \quad \tilde{v} < 1. \quad (6)$$

In accordance with (4) and (6), the formula for the kinematic shear viscosity reads

$$\tilde{\nu}(\tilde{v}, t) \approx \frac{\zeta_0}{(\tilde{v} - 0.36)^{1/3}} \exp \left[a(\tilde{v}) \left(\frac{1}{t} - 1 \right) \right]. \quad (7)$$

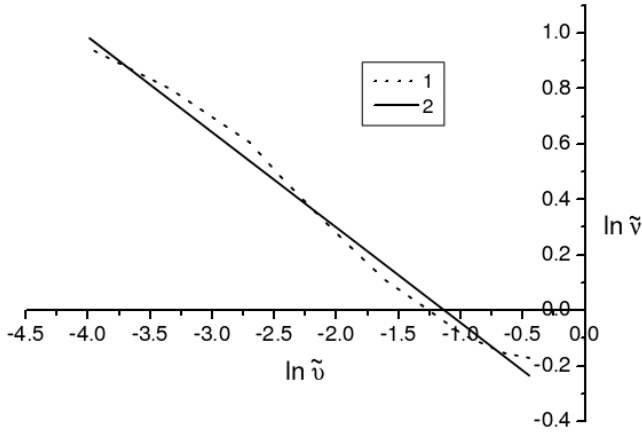


Fig. 8. Kinematic shear viscosity of liquid argon ($\tilde{v} < 1$) versus the normalized specific volume on the critical isotherm. The solid line corresponds to the relation $\ln \tilde{\nu} = -0.34 \ln(\tilde{v} - \tilde{v}_0) - 0.39$, the dotted line – to the experimental data [18]

We emphasize that the value $\tilde{v}_0 = 0.36$ determined by the kinematic shear viscosity on the critical isotherm is quite consistent with the behavior of $\nu(\tilde{v}, t)$ on the coexistence curve (see Fig. 5). Namely, near $\tilde{v}_0 = (0.35 \div 0.36)$, the kinematic shear viscosity of argon sharply increases. This is very important argument in the favor of our construction.

The exponential dependence in (7) is fictitious, since the combination $a(\tilde{v}) (\frac{1}{t} - 1)$ is of the order of unity or less. With a quite suitable accuracy, we can write

$$\tilde{\nu}(\tilde{v}, t) \approx \frac{\zeta_0}{(\tilde{v} - 0.36)^{1/3}} \mu(\tau, \tilde{v}), \quad (8)$$

where

$$\mu(\tau, \tilde{v}) = 1 + \kappa_1(\tilde{v})\tau + \kappa_2(\tilde{v})\tau^2 + \kappa_3(\tilde{v})\tau^3 + \dots$$

The coefficients in (8) takes the values given in Fig. 9.

Let us discuss the obtained results using the dimensionality reasons. The kinematic shear viscosity has the dimensionality $[\nu] = L^2/T$. The simplest combination of the relevant molecular parameters with such a dimensionality is l^2/τ_s , where $l \sim n^{-1/3}$ is the interparticle spacing, n is the numerical density, $\tau_s \sim l/v_T$ is the characteristic time of soft collisions, and v_T is the thermal velocity of a molecule. As seen, the value $l^2/\tau_s \sim v_T/n^{1/3}$ decreases as the density grows, which is characteristic of the self-diffusion coefficient, having the same dimensionality. Unlike this, the kinematic shear viscosity should increase with density.

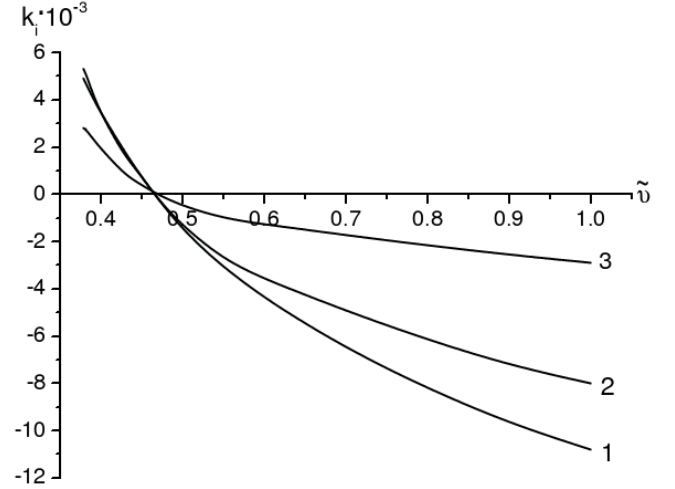


Fig. 9. Numerical values of the coefficients κ_i , $i = 1, 2, 3$, considered as a function of the normalized specific volume

Another combination of parameters having the suitable dimensionality and the correct dependence on temperature and density is $v_T^2 \sigma \tau_v / l$, where σ is the molecular diameter, τ_v is the characteristic vibration time, $\tau_v \sim \sigma(m/\varepsilon)^{1/2}$, and ε is the interaction energy parameter of intermolecular potential. Note that we write σ and τ_v instead of l and τ_s to avoid the objectionable dependences on density and temperature. We expect that

$$\nu(v, t) \sim \frac{T_c \sigma^2}{(m\varepsilon)^{1/2} v_c^{1/3}} \frac{t}{\tilde{v}^{1/3}}. \quad (9)$$

As seen, the dependence of (9) on specific volume v and temperature is similar to that in (8). Putting $\varepsilon \sim T_c$ and $v_c \sim \frac{2\pi}{3} \sigma^3$, as it is supposed in the theory of the van der Waals equation of state, we get the following order of magnitude for the dimensional combination in (9):

$$\frac{T_c \sigma^2}{(m\varepsilon)^{1/2} v_c^{1/3}} \sim \sigma v_T(T_c) \sim 10^{-3} \text{ cm}^2/\text{s}, \quad (10)$$

which exactly corresponds to the experimental value of the kinematic shear viscosity near the critical point.

We note that combination (10) is the simplest from those having the necessary dimensionality.

Using the same reasons as in the derivation of the van der Waals equation of state, Eq. (9) can be generalized in the following way:

$$\nu(v, t) \approx \frac{T_c \sigma^2}{(m\varepsilon)^{1/2} v_c^{1/3}} \frac{t}{(\tilde{v} - \tilde{v}_0)^{1/3}}. \quad (11)$$

Here, $\tilde{v}_0 = v_m/v_c$, and $v_m = \frac{\pi}{6} \sigma^3$ is the molecular volume. In accordance with the van der Waals theory,

$v_c = 4v_m$, so \tilde{v}_0 is expected to be 0.25. This value is rather smaller than that in (8), where $\tilde{v}_0 \approx 0.36$. This means that the effect of own molecular volume in kinetic and thermodynamic properties is manifested in different ways. Such a conclusion is quite allowable.

The behavior of the kinematic shear viscosity of argon in its gas-like region ($\tilde{v} > 1$) will be discussed in a separate paper.

4. Kinematic Shear Viscosity of Liquid Benzene

As shown in Section 1, the normalized kinematic shear viscosity of benzene in suitable variables is similar to that for argon. Here, it is appropriate to note that the values of $\tilde{\nu}^{(B)}(\tilde{v}^{(B)}, t)$ and $\tilde{\nu}^{(Ar)}(\tilde{v}^{(Ar)}, t)$ on their coexistence curves are mainly determined by hard-core effects. Therefore, we conclude that the behavior of $\nu^{(B)}(\tilde{v}, t)$ in the range of liquid states ($t_m^{(B)} < t < 1$ and $p_m^{(B)} < p < 1$) can be described by the formula

$$\nu^{(B)}(\tilde{v}, t) \approx \frac{\zeta_0}{(\tilde{v} - 0.36)^{1/3}} \nu_R^{(B)} \mu^{(B)}(\tau, \tilde{v}), \quad (12)$$

where

$$\mu^{(B)}(\tau, \tilde{v}) = 1 + \kappa_1^{(B)}(\tilde{v})\tau + \kappa_2^{(B)}(\tilde{v})\tau^2 + \kappa_3^{(B)}(\tilde{v})\tau^3 + \dots$$

with the coefficients $\kappa_i^{(B)}$ close to those for argon. Some difference between them should be caused by the rotational degrees of freedom inherent to the benzene molecules. Since $\tilde{v}^{(B)}(t)$ and $\tilde{v}^{(Ar)}(t)$ are different on their coexistence curves, the values of $\tilde{\nu}^{(B)}(\tilde{v}^{(B)}, t)$ and $\tilde{\nu}^{(Ar)}(\tilde{v}^{(Ar)}, t)$ should also be distinct from each other. It is naturally consistent with Fig. 3.

Unfortunately, the absence of the corresponding experimental data does not allow us to verify immediately the applicability of this formula in a wide range of benzene states, in particular, on isochores.

The possibility of using (8) for the description of the kinematic shear viscosity for argon and benzene means that they obey the principle of corresponding states. Usually, the last [14] is formulated for the equations of state for liquids with close molecular parameters. Since the shapes of argon and benzene molecules, as well as their intermolecular potentials, are not similar, the thermodynamic similarity in them (see (Fig. 4) can only be an approximation. It is surprising that the similarity in the behavior of their kinematic shear viscosities is expressed with greater accuracy. At any case, they are practically identical on the coexistence curves.

The leading role of the specific volume dependence in the formation of the dynamic shear viscosity was taken into account by Batchinski [13]:

$$\eta = \frac{b(T)}{v - v_B}, \quad (13)$$

where v_B is attributed to the own molecular volume. Although the specific volume dependences in (12) and (13) are different, this is not manifested if variations of v are not considerable. Namely, this circumstance was inherent to experimental data used in [13].

Analogously, the exponential behavior

$$\tilde{\nu}^{(B)}(t) = \tilde{v}_0 \exp\left(\frac{\varepsilon}{t}\right) \quad (14)$$

is indistinguishable in narrow temperature intervals from the polynomial one and others. The non-applicability of (14) to the description of $\tilde{\nu}^{(B)}(t)$ is seen from Fig. 3. At best, one can speak about the correspondence of (14) to experimental data only in the temperature interval, the size of which does not exceed (50 ÷ 70) K. But even in this case, it is impossible to give a suitable physical meaning to (14), since $\frac{\varepsilon}{t} \sim 1$. Moreover, the usage of more complicated expressions of the type

$$\tilde{\nu}^{(B)}(t) = \tilde{v}_1 \exp\left(\frac{\varepsilon_1}{t}\right) + \tilde{v}_2 \exp\left(\frac{\varepsilon_2}{t}\right) + \dots \quad (15)$$

is also meaningless.

5. Conclusion

The similarity of the kinematic shear viscosities of benzene and argon is the main result of this paper. Such a behavior of $\nu^{(B)}(\tilde{v}^{(B)}, t)$ and $\nu^{(Ar)}(\tilde{v}^{(Ar)}, t)$ is naturally explained if we take into account that, in both these cases, the hard-core effects play the main role. Indeed, in accordance with (8), (11), and (12), $\nu(\tilde{v}, t) \sim (\tilde{v} - \tilde{v}_0)^{-1/3}$, where \tilde{v}_0 is the relative value of the molecular volume manifested in viscous processes. As we have seen, the numerical value of $\tilde{v}_0 \approx 0.36$ is noticeably more than that given by the van der Waals theory [14]: $\tilde{v}_0^{(W)} = 0.25$. The augmentation of \tilde{v}_0 in the comparison with $\tilde{v}_0^{(W)}$ is accompanied by the suppression of details of intermolecular interactions. Probably, due to this, the principle of corresponding states works better for the kinematic shear viscosity than for the equation of state. The construction of the theoretical estimates for \tilde{v}_0 remains to be an important problem.

The similarity in the behavior of $\nu^{(B)}(\tilde{v}^{(B)}, t)$ and $\nu^{(Ar)}(\tilde{v}^{(Ar)}, t)$ implies that the character of thermal motion in argon and benzene is close in many relations.

In particular, the clusterization or association process in benzene in the whole temperature interval from the melting point up to the critical one is impossible. Therefore, the exponential formulas for $\bar{\nu}^{(B)}(t)$ of type (14) and (15) have only meaning as fitting ones.

Since the fine details of intermolecular interactions are inessential, we hope that the kinematic shear viscosities of the simplest benzene derivatives will also be satisfactory approximated by formula (12).

We cordially thank Professor Leonid Bulavin, Professor Mani Rappon, and Dr. Vladimir Kulinskii for their amicable support of this work and for the fruitful discussion of the results obtained.

1. P. Resibois and M. De Leener, *Classical Kinetic Theory of Fluids* (Wiley, New York, 1978).
2. *Physics of Simple Liquids*, Ed. by H.N.V. Temperley, J.S. Rowlinson, and G.S. Rushbrooke (North-Holland, Amsterdam, 1968).
3. I.G. Mikhailov, V.A. Solov'ev, and Yu.P. Syrnikov, *Basic Principles of Molecular Acoustics* (Nauka, Moscow, 1964) (in Russian).
4. C. Chipot, R. Jaffe, B. Maigret, D. Pearlman, and P.A. Kollman, *J. Am. Chem. Soc.* **118**, 217 (1996).
5. O. Engkvist, P. Hobza, H.L. Selzle, E.W. Schlag, *J. Chem. Phys.* **110**, 5758 (1999).
6. V.S. Sperkach, *Molecular Mechanisms of Acoustic Relaxation in Liquids* (Author's Abstract of Dr. Sci. Thesis, Kyiv, 1990); O.P. Rudenko, *Molecular Mechanisms of Nonequilibrium Processes in Some Homogeneous and Heterogeneous Liquid Systems*, Author's Abstract of Dr. Sci. Thesis (Kyiv, 1993).
7. M.M. Shakhparonov, *Mechanisms of Fast Processes in Liquids* (Vyshaya Shkola, Moscow, 1960) (in Russian).
8. H. Eyring, *J. Chem. Phys.* **4**, 283 (1936).
9. S.R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics* (North-Holland, Amsterdam, 1962).
10. J. Frenkel, *Kinetic Theory of Liquids* (Dover, New York, 1955).
11. A.L. Zvyagintsev, *Author's Abstract of PhD Thesis* (Kyiv University, Kyiv, 1971).
12. N.P. Malomuzh and I.Z. Fisher, *Fiz. Zhidk. Sost.* **1**, 34 (1973).
13. A. Batchiski, *Z. Phys. Chem.* **84**, 643 (1913).
14. L.D. Landau and E.M. Lifshitz, *Statistical Physics* (Pergamon Press, Oxford, 1980).
15. L.A. Bulavin, N.P. Malomuzh, and K.S. Shakun, *Ukr. Phys. Zh.* **50**, 653 (2005).
16. N.B. Vargaftik, *Handbook of Thermo-Physical Properties of Liquids and Gases* (Nauka, Moscow, 1972) (in Russian); N.B. Vargaftik, *Handbook of Thermo-Conductivity of Liquids and Gases* (Nauka, Moscow, 1990) (in Russian).
17. Data from NIST Standard Reference Database 69, June 2005 Release: NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry/fluid/>).
18. V.P. Slyusar', N.S. Rudenko, and V.M. Tret'yakov, *Ukr. Fiz. Zh.* **17**, 1257 (1972).
19. Younglove and H.J.M. Hanley, *J. Phys. Chem. Ref. Data*, **15**, 1323 (1986).
20. A. Rahman, *Phys. Rev. A* **136**, 405 (1964); *J. Chem. Phys.* **45**, 2585 (1966).
21. M.A. van der Hoef and D. Frenkel, *Phys. Rev. Lett.* **66**, 1591 (1991).

Received 18.04.07

ПРИРОДА КІНЕМАТИЧНОЇ ЗСУВНОЇ В'ЯЗКОСТІ БЕНЗОЛУ ТА ЙОГО ПОХІДНИХ

М.П. Маломуз, А.В. Олейнік, О.П. Руденко, А.М. Хлопов

Резюме

Детально досліджуються властивості кінематичної зсувної в'язкості ν бензолу, в першу чергу, її залежність від нормованих температури t та питомого об'єму \bar{v} ($t = T/T_c$, $\bar{v} = v/v_c$, де T_c та v_c – критичні значення температури та питомого об'єму). Спираючись на експериментальні значення ν , t та \bar{v} для бензолу та аргону на їх кривих співвідношення, показано, що поведінка кінематичних зсувних в'язкостей цих рідин є цілком подібною і свідчить про можливість застосування до них динамічного варіанта принципу відповідних станів. Цей висновок є несподіваним, оскільки їх рівняння стану задовольняють принцип відповідних станів тільки наближено. Строго доведено, що кінематична зсувна в'язкість бензолу не має активаційного характеру. Запропоновано явний вигляд формули, яка описує поведінку ν в аргоні та бензолі. Показано, що значення ν визначаються, в першу чергу, питомим об'ємом молекул у рідинах. Така ж сама особливість зсувної в'язкості властива і формулі Бачинського, хоча конкретний прояв ефектів власного об'єму молекул є суттєво різним.