On viscosity of selected normal and associated liquids

Oleg Prezhdo a, Andrzej Drogosz b, Valentina Zubkova c, Victor Prezhdo c,⁎

a Department of Chemistry, University of Rochester, Rochester, NY 14627, USA
b Institute of Physics, Jan Kochanowski University, 15 Swietokrzyska Str., 25–406 Kielce, Poland
c Institute of Chemistry, Jan Kochanowski University, 15 Swietokrzyska Str., 25–406 Kielce, Poland

Article info
Article history:
Received 6 January 2013
Received in revised form 19 February 2013
Accepted 6 March 2013
Available online 21 March 2013

Keywords:
Viscosity
Benzene derivatives
Ordinary liquids
Associated liquids
Hydrogen bond

Abstract
The viscosity of 34 benzene derivatives was determined at 404, 445, and 457 K to establish the relationship between the macroscopic properties of ordinary liquids, in particular viscosity, and the properties of molecules these liquids consist of. The nature of changes in viscosity in homologous and isologous series of compounds along with substituted compounds was explained on the basis of this dependence. The peculiarities of viscosity of associated compounds were determined and explained by hydrogen bonding.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Formulation of a rigorous and comprehensive theory of viscosity of liquids, applicable to a wide range of substances, remains a challenging task. A number of empirical and semi-empirical formulas are used in practice, reflecting the dependence of viscosity of selected classes of liquids and solutions on temperature and chemical composition [1]. Early in the 20th century, Bachinski [2,3] suggested the following expression for the viscosity

$$\eta = \frac{C}{V_s - b_B}$$  (1)

where $V_s$ is specific volume, and C and $b_B$ are constants. The majority of organic liquids, with notable exception of alcohols and organic acids, are well described by Eq. (1). The equation is rooted in the notion that the viscosity of liquids is determined by molecular interactions.

Considering that transfer of momentum between layers of a flowing liquid occurs due to temporary association of molecules of the liquid at the interface between the layers, Andrade [4] developed the equation

$$\eta = \frac{A}{3 \pi n k T} \exp \frac{-\Delta E_p}{k T}$$  (2)

where $t_0$ is the time that the particle spends in the transition state. Typical values of $t_0$ are on the order of $10^{-13}$ s. $n$ is the number of molecules in unit volume; $E_p$ is the potential energy of intermolecular interactions; $T$ is temperature, and $k$ is the Boltzmann constant.

A number of statistical–mechanical theories of viscosity of liquids have been developed. For instance, monograph [6] discusses a practically useful, approximate approach for calculating viscosity.

In addition to the expressions derived starting from the fundamental chemical principles, a variety of empirical equations has been proposed. In 1835, Poiseuille determined experimentally an empirical equation describing the temperature dependence of the viscosity of water. The Slotte temperature–viscosity relationship is described in [7]. The expression

$$\eta = \exp \frac{C}{\frac{T}{T_0}}$$  (4)

proposed by Le Chatelier [8] forms the basis for a whole series of empirical formulas. In Eq. (4), C and $a$ are certain constants, and $T$ is

Here, the constant $A$ is proportional to the frequency of molecular vibrations, the constant $C$ is proportional to the potential energy of intermolecular interactions, and $\rho$ is the density of the liquid.

Eq. (3) shown below was obtained on the basis of the microscopic kinetic theory of Frenkel [5]. Calculations using this expression give good agreement with experimental data. The form of the expression that is commonly used in modern practice is given by
absolute temperature. An interesting variant of the Le Chatelier formula is obtained in [9]

\[ (\nu + 0.8) = \exp \frac{C}{T}, \]  

(5)

where \( \nu \) is the kinematic viscosity, and 0.8 is an empirical coefficient having the kinematic viscosity units. This equation is widely used in studies of lubrication.

Numerous publications are dedicated to investigation of the relationship between viscosity and molecular structure. A detailed account of such studies is reported by Bondi [10], who discusses several qualitative correlations. In particular, Bondi observes that increases in molecular mass, degree of branching in molecular structure and extent of intermolecular association result in viscosity growth and greater sensitivity of viscosity to changes in temperature. Introduction of double bonds into molecules of a liquid typically decreases liquid viscosity.

Multiple scientists proposed empirical rules relating structural characteristics of molecules to viscosity [11–17]. At the same time, it remains challenging to relate molecular structure to viscosity in a direct way, for instance, to predict viscosity values based on the substituents present in the molecule. Therefore, the approach advocated in the current work relies on comparison of compounds that differ from each other in only one structural or any other integral feature [18–20]. The general idea is justified and widely used for determination of macroscopic physical properties. The macroscopic properties are ultimately determined, under the same thermodynamic conditions (\( p \) and \( T \)), by the characteristics of microscopic particles constituting the substance, in particular, particle size (\( V_0 \)), shape (\( \psi \)), mass (\( m \)), polarizability (\( \alpha \)), dipole moment (\( \mu \)), etc. Taking this into account, one can obtain useful insights into the macroscopic properties by considering a series of compounds that are similar in most respects and differ only in one or few characteristics [21–23]. Simultaneous variations in many microscopic properties make such analysis more difficult and applicable to a relatively narrow range of compounds, without showing clear physical reasons for the changes in the macroscopic properties. The current work presents an analysis of viscosity of a series of benzene derivatives on the basis of the microscopic properties of the molecules constituting the liquid.

2. Experimental section

2.1. Materials

The nitrobenzene, 2-nitrophenol, 3-nitrophenol, 4-nitrophenol, 2-nitroanisole, 3-nitroanisole, 4-nitroanisole, 2-hydroxybenzaldehyde, 3-hydroxybenzaldehyde, 4-hydroxy-benzaldehyde, acetophenone, 2-hydroxycacetophenone, 3-hydroxyacetophenone, 4-hydroxyacetophenone, 2-methoxyaceto-phenone, 3-methoxyacetophenone, 4-methoxyacetophenone, ethyl benzoxide, 2-methylphenol, 3-methylphenol, 4-methylphenol, 2-methoxytoluen, 3-methoxytoluen, 4-methoxy-toluen, phenol, and anisole were of high purity grade reagents produced by Merck. Phenol, 2-methoxytoluene, 3-methoxytoluene, 4-methoxy-toluene, phenone, ethyl benzoate, 2-methylphenol, 3-methylphenol, 4-methylphenol, 2-methoxytoluene, 3-methoxytoluene, 4-methoxy-toluene, phenol, and anisole were of high purity grade reagents produced by Merck. Eight other compounds: 2-methoxy-benzaldehyde, 3-methoxybenzaldehyde, 4-methoxybenzaldehyde, 2-hydroxyethyl benzoate, 3-hydroxyethyl benzoate, 2-hydroxyethyl benzoate, 2-methoxyethyl benzoate, and 4-methoxyethyl benzoate (Table 1) were synthesized and purified according to the techniques described in literature [24]. The composition formulas of the associated liquids under study are presented in Table 2. The identification of the synthesized compounds was carried out with the IR and NMR spectroscopy [25]. All samples were degassed by heating and cooling just before use. The purity grade and viscosities of pure components are given in Table 1, showing good agreement with the literature data [26,27]. The densities of compounds under study are given in Ref. [28].

2.2. Measurement

Both literature data on viscosity of liquids and the results of own measurements are presented in Table 1. The viscosity measurements of the compounds under study were made using a U-tube Ostwald viscometer. The viscometer was connected with a glass stopper with two openings for thermometer and pycnometer. A plug was inserted in the thin section of the thermostat. The laboratory thermostat had control unit MPC-E and heat capacity of 473 K was used to maintain the constant temperature [29]. All measurements were carried out using the same viscometer with the water efflux time equal to 131 s. In the vast majority of cases, \( t_0 \), \( d_0 \) were determined for two or more samples of the same substance. The divergence between single measurements of \( t_0 \) was ± 0.5 s at most. The \( d_0 \) values were determined at the same time [28]. In most cases, the obtained values of \( \eta_k \) are in good agreement with the literature data (Table 1). The efflux time \( t \) was measured at 404, 445, and 457 K for 34 compounds (Table 1). The viscosity was determined according to Eq. (6):

\[ \eta = \frac{d_0 t_0}{d_0 t_k}, \]

(6)

where \( \eta \) is the viscosity coefficient for water at 20 °C, \( d_0 \) is density and \( t_0 \) is the efflux time for water at 20 °C; \( \eta_k, d_0 \) and \( t_k \) are the values for the compound under study, correspondingly.

The viscometer was calibrated with spectroscopic grade 1-butanol and doubly distilled water at the experimental temperature. An electronic digital stopwatch with accuracy of ± 0.01 s was used for the efflux time measurements. The temperature of the samples was controlled with an external thermostat. The uncertainty in dynamic viscosities was about \( ± 3 \times 10^{-3} \) mPa·s. The kinematic viscosity can be obtained from the ratio of the dynamic viscosity and the density of a substance.

3. Results and discussion

3.1. Viscosity of ordinary liquids

The dependence of viscosity (\( \eta \)) on molecular mass follows from the data for \( \eta \) of isotopic compounds, which differ from each other mainly in the mass of molecules. As additional measurements showed [29], the viscosity of such compounds, e.g. methane and deuterated methane at 90.1 K, increases proportionally to \( \sqrt{m} \). The dependence

\[ \eta = \eta_0 \frac{m}{M}, \]

(7)

where \( \eta_0 \) are all other properties of molecules except for \( m \), is in good agreement with many viscosity formulas derived from kinetic or statistical theories by Fischer [30], G.M. Panchenkov [31], O.V. Frenkel [5], etc. For instance, in the Panchenkov theory, \( \eta = \eta_0 \frac{m}{M} \), where \( \rho \) is the density equal to \( N^* \) and \( M = N \) or \( M = N \); \( N^* \) is the number of molecules per unit volume, and \( N \) is Avogadro’s number. In the Frenkel theory the oscillation frequency is proportional to the inverse square root of mass, \( \nu \sim \frac{1}{\sqrt{M}} \).

The value of the reduced property \( \eta/\sqrt{M} \) in homo-isologous ranks of the first type does not change with variation in \( \nu \) i.e.

\[ \left( \frac{\eta}{\nu \sqrt{M}} \right) = \text{const} \]

(8)

where \( \nu \) are all of the other properties of molecules except for mass and size. It follows from the formula that viscosity does not depend on the size of the molecules. In most empirical and theoretically derived formulas of viscosity, the specific or molar volume along with the length of molecules is taken into consideration, what should
show the contrary. However, the formulas, in which the length of molecules can be found (for example, in polymer homology), do not consider changes in length along with changes in mass and polarizability of the molecules [32] for the compounds under study. On the other hand, the molar volume (or specific volume \( V_m \)) is equal to \( V = N V_0 + V_e \), i.e. it is equal to the sum of molecular volumes (\( NV_0 \)) and the free volume of a liquid (\( V_e \)), which is determined by distance between the molecules. The analysis of the derivations on the basis of formulas with \( V \) or \( V_e \) [33] shows that these values appear, when the mechanism of viscous flow is considered, as the result of taking into account the distances between the molecules and their changes with the temperature, i.e. \( V_l \) not \( V_m \). In other words, these formulas testify to the fact proved by Bachinski that viscosity depends on free volume of a liquid [34,35], or else the accessible volume [36]. However, the dependence (8) does not mean that the size of molecules does not influence viscosity at all. The change in molecular size can show some opposite influences that mutually compensate each other. For example, if we believe that \( \eta \) depends, on the one hand, on the number of molecules in contact layers, proportional to \( m \), and, on the other hand, on the number of collisions between molecules, proportional to \( V_e^{3/2} \), the viscosity ceteris paribus may not depend on the size of molecules.

Taking into consideration the independence of \( \eta \) from \( V_m \), the viscosity value in homo-isologous series of the second type should regularly vary with polarizability of molecules (\( \alpha \)). If we take into account the influence of small differences in molecular mass and consider the change in volume for \( \eta_l \sqrt{m} \) rather than \( \eta_l \), we will see that \( \eta \) increases in these series proportionally to \( \alpha^{2.4} \) (Fig. 1) i.e.

\[
\left( \frac{\eta}{\sqrt{m}} \right)_{p,T,\Phi,D} = \text{const} \ (MR_0)^{1.2},
\]

where \( MR_0 \) is a molecular refraction. Characteristically, the slope of the line is the same for all series of the halogen derivatives. The dependence (9) should reflect the influence of dispersion forces on viscosity, which are proportional to \( e^2 \) (according to London) or \( \alpha^{3/2} \) (according to Slater and Kirkwood) [37].

### Table 2

<table>
<thead>
<tr>
<th>Associated compound</th>
<th>Metameric ether (ester)</th>
<th>Temperature, K</th>
<th>( \frac{\text{sum}}{\text{mass}} )</th>
<th>( z ) by Eq. (15)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n-C_2H_5COOH )</td>
<td>( C_2H_5COOC_2H_5 )</td>
<td>293</td>
<td>3.80</td>
<td>1.95</td>
</tr>
<tr>
<td>( n-C_4H_9COOH )</td>
<td>( C_4H_{10}COOC_2H_5 )</td>
<td>323</td>
<td>4.23</td>
<td>2.05</td>
</tr>
<tr>
<td>( n-C_6H_{13}COOH )</td>
<td>( n-C_6H_{13}COOC_2H_5 )</td>
<td>323</td>
<td>4.79</td>
<td>2.18</td>
</tr>
<tr>
<td>( n-C_8H_{17}COOH )</td>
<td>( n-C_8H_{17}COOC_2H_5 )</td>
<td>323</td>
<td>3.68</td>
<td>1.92</td>
</tr>
<tr>
<td>( n-C_6H_{13}COOCH_3 )</td>
<td>( n-C_6H_{13}COOC_2H_5 )</td>
<td>323</td>
<td>3.76</td>
<td>1.92</td>
</tr>
<tr>
<td>( n-C_8H_{17}COOCH_3 )</td>
<td>( n-C_8H_{17}COOC_2H_5 )</td>
<td>323</td>
<td>4.01</td>
<td>2.00</td>
</tr>
<tr>
<td>( n-C_6H_{13}COCH_3 )</td>
<td>( n-C_6H_{13}COOC_2H_5 )</td>
<td>293</td>
<td>12.78</td>
<td>3.57</td>
</tr>
<tr>
<td>( n-C_8H_{17}COCH_3 )</td>
<td>( n-C_8H_{17}COOC_2H_5 )</td>
<td>293</td>
<td>11.64</td>
<td>3.41</td>
</tr>
</tbody>
</table>
The typing compounds are isoperiodic compounds.

It follows from Fig. 2 that the viscosity in isoperiodic series changes regularly with changes in the dipole moment of the molecules and increases in a linear way according to:

\[ \eta_{\text{p,T, o,m,a}} = A + \text{const} \mu. \]  

In this case, the value of constant A almost coincides with the value of \( \eta \) for the appropriate member of the series with \( \mu = 0 \), e.g. a hydrocarbon. The value of the constant decreases with rising temperature (Fig. 2) due to decrease of the role of orientation forces. We do not expect a strictly linear relationship in the compounds under study because their molecules show some variations in mass, polarizability, and shape. Only the members of the series containing OH- and COOH- (except for compounds with intramolecular hydrogen bonding) deviate from the dependence (10). The influence of dipole orientation on \( \eta \) of liquids has been mentioned widely [27,38]. The orientation is expected to influence the value of the constant \( B \) in the formula for changes of viscosity with temperature [27]: \( \eta = A \mu^B/T \). The constant can be considered as the activation energy of viscous flow [39]. However, if the value of \( B \) were equal to the energy of interaction of a pair of molecules in the equilibrium position, a more substantial increase in \( \eta \) would be expected with rise in \( \mu \).

The data for heteromorphous compounds (Fig. 2) show a regular change in \( \eta \) with the shape of molecules. Thus, the tertiary compounds, independently of the functional group, possess a greater value of \( \eta \) than the corresponding linear compounds. At 293–298 K the differences are 10–20%. It may be suggested that other factors, such as mass, polarizability and dipole moment, are also different for primary, secondary, and tertiary amines, pointing to a sharp decrease in viscosity during transition to tertiary, more symmetrical compounds [34,40]. The cyclic shape facilitates a sharp rise in viscosity in comparison to the linear shape. The differences are by a factor of 2–4 at 298 K [34]. The ratio of \( \eta_{\text{cyclic}}/\eta_{\text{linear}} \) grows with increase in the number of carbon atoms in the ring and chain. A similar effect is seen with surface tension.

The aforementioned dependences allow us to explain the nature of changes of \( \eta \) in series of compounds that differ in several molecular constants. Molecules of the members of homologous series, beginning from the third or fourth member, differ only in mass, polarizability, and size. According to Eqs. (7), (8), and (9), in different homologous series (see, for example Figs. 1, 3) \( \eta/\bar{m} \) increases proportionally to \( \alpha^{2+} \) or \( (MR^2)^{3/2} \). In this case, Eq. (9) holds at different temperatures, and the slope of the line decreases with increasing temperature. At the same temperature, the value of the constant may vary a little with change in functional groups. At low temperatures in some homologous series [41] (Fig. 4), \( \eta/\bar{m} \) increases proportionally to \( \alpha^2 \). A careful examination of the \( \eta \) data for these compounds reveals some additional factors. Comparison of several dependences (9) explains the changes in nature of \( \eta \) with variation in the number \( n \) of carbon atoms in the hydrocarbon chain. For two neighboring members of the homologous series the dependence is:

\[ \frac{\eta_{\text{p(n+1)}}}{\eta_n} = \left( \frac{M_{\text{p(n+1)}}}{M_n} \right)^{1/2} \left( \frac{MR_{\text{p(n+1)}}}{MR_{\text{p(n)}}} \right)^{3/2}. \]  

The aforementioned dependences allow us to explain the nature of changes of \( \eta \) in series of compounds that differ in several molecular constants. Molecules of the members of homologous series, beginning from the third or fourth member, differ only in mass, polarizability, and size. According to Eqs. (7), (8), and (9), in different homologous series (see, for example Figs. 1, 3) \( \eta/\bar{m} \) increases proportionally to \( \alpha^{2+} \) or \( (MR^2)^{3/2} \). In this case, Eq. (9) holds at different temperatures, and the slope of the line decreases with increasing temperature. At the same temperature, the value of the constant may vary a little with change in functional groups. At low temperatures in some homologous series [41] (Fig. 4), \( \eta/\bar{m} \) increases proportionally to \( \alpha^2 \). A careful examination of the \( \eta \) data for these compounds reveals some additional factors. Comparison of several dependences (9) explains the changes in nature of \( \eta \) with variation in the number \( n \) of carbon atoms in the hydrocarbon chain. For two neighboring members of the homologous series the dependence is:

\[ \frac{\eta_{\text{p(n+1)}}}{\eta_n} = \left( \frac{M_{\text{p(n+1)}}}{M_n} \right)^{1/2} \left( \frac{MR_{\text{p(n+1)}}}{MR_{\text{p(n)}}} \right)^{3/2}. \]  

Fig. 1. The dependence of \( \eta/\sqrt{MR} \) on the molecular refraction \( MR^{1/2} \) at 298 K for C6H4J (○), n-C6H5Br (×), n-C6H5Cl (□), n-C6H5OH (●), n-C6H5OOH (★), n-C6H5OCH3 (☆), n-C6H5OC2H5 (●), n-C6H5OH (◦), and n-C6H5Br (●). The typing compounds are homo-isologous of second type.

Fig. 2. The dependence of \( \eta \times 10^7 \text{mPa s} \) on the dipole moment \( \mu \times 10^{20} \text{C/m} \) at 298 K (unbroken line) and 404 K (broken line) for C6H5OH (●), C6H6(OC2H5)2 (●), C6H5(CH2)3-CH=CH2 (○), C6H4(OCH3)2CH=CH2-CH2-(×) , C6H2(OH)CH=CH2 (□), CH2=CHCOOH (●), CH2=CHCOOH (★), CH2=CHCOOH (□), CH2=CHCOOH (○), C6H6(OC2H5)2 (●), C6H6(OC2H5) (●), C6H6(OC2H5) (◆), and C6H5-CH2=CH2OH (●). The typing compounds are isoperiodic compounds.

Fig. 3. The dependence of \( \eta/\sqrt{MR} \) on the molecular refraction \( MR^{1/2} \) at 323 K (unbroken line) and 343 K (broken line) for n-C6H4Cl + xCOOH, where n = 3 (●), n = 4 (×), n = 5 (□), n = 6 (○), n = 7 (●), n = 8 (★), n = 9 (●), n = 11 (●), n = 15 (●), and n = 17 (∴).

Fig. 4. The dependence of \( \eta/\sqrt{MR} \) on the molecular refraction \( MR^{1/2} \) at 293 K (unbroken line) and 353 K (broken line) for n-C6H4Br, where n = 9 (●), n = 10 (×), n = 11 (○), n = 12 (□), n = 13 (●), n = 15 (★), and n = 17 (∴).
Since $M_{n+1}/M_n$ and $MR_{D(n+1)}/MR_{D(n)}$ are always greater than one, $\eta$ should always increase along the series, unlike, for instance, the change in density in these series. Herewith, a relative increase of $\eta$ decreases with rise in $n$. For example, for normal hydrocarbons the ratios are $\eta_{(n-6)}/\eta_{(n-5)} = 1.35$ and $\eta_{(n-11)}/\eta_{(n-10)} = 1.28$. Both $M_{n+1}/M_n$ and $MR_{D(n+1)}/MR_{D(n)}$ approach one when $n$ approaches infinity.

The change of $\eta$ in homologous series has been explained, as a rule, by variations in the mass of molecules. For instance, the Gartenmeister formula gives $\eta = \text{const} M^2$, and the Dunstan and Thole equations are $\ln \eta = AM + B$ or $\ln \eta = A \ln M + B$ [27]. However, these formulas do not fully account for the dependence on mass, because $\alpha$ also grows with $\tau$ in these series. Hence, the equations for $\eta$ implicitly capture the changes of polarizability with mass. Since the mass of molecules is additive, the aforementioned formulas were used for construction of different additive schemes for viscosity. Taking the additivity of $MR_D$, and putting the values $M = A + 14n$ and $MR_D = A^* + 4.6n$ into Eq. (11) leads to

$$\frac{\eta_{n+1}}{\eta} = \left[\frac{A + 14(n+1)}{A + 14n}\right]^{1/2}\left[\frac{A + 4.6(n+1)}{A + 4.6n}\right]^{3/2}.\,$$

This relation shows that it is fundamentally impossible to construct a proper and widely applicable additive model, because the difference in $\eta$ and $\ln \eta$ for neighboring members of the homologous series cannot remain constant with $n$ and $A$ in the nature of the functional group ($A + n^* A'$).

With alkyl group substituted to sulfur, oxygen, selenium, or nitrogen, the properties of the molecules in the series change in the same way, except for minor variations in the dipole moment. Hence, the change of $\eta$ during formation of ethers can be compared with the corresponding change during appropriate lengthening of the hydrocarbon chain, namely:

$$\frac{\eta_{C_4H_9SH}}{\eta_{C_4H_9}} \approx 1.\,$$

This relationship holds, for example, with thiols:

$$\frac{\eta_{C_4H_9SH}}{\eta_{C_4H_9}} = \frac{551}{596} = 0.92.\,$$

In isologous series, the members differ from each other substantially in mass, and a little in polarizability and molecular size. The aforementioned dependences show that the influence of $\alpha$ on $\eta$ cannot be compensated by the influence of $v_M$. That is why the approximate proportionality of viscosity to the mass of molecules in isologous series does not reflect its real dependence on the latter. As in homologous series, in isologous series

$$\frac{\eta}{\sqrt{m}} = \text{const} (MR_D)^{3/2}.\,$$

(Figs. 1, 5). As before, fluorine derivatives of the lipid series and OH- and COOH-containing compounds do not obey this dependence: they exhibit slightly decreased and highly increased values of $\eta/\sqrt{m}$, for appropriate members of the series, e.g. hydrocarbon, with $\mu$ equal to zero. Sharp divergence skewed to higher values of $\eta/\sqrt{m}$ is shown only by OH-, COOH- and NH$_2$ (aromatic) containing compounds. Small deviations from the linear dependence for other members of the series can be caused mainly by difference in molecular shape.

In contrast to other substituted members of the series, all molecular properties of the members of the series of metamer compounds are very similar. That is why metameric ethers and esters only slightly differ in viscosity. The difference in the values of $\eta$ for metamers can be caused by screening of the polar group: metamers with a less screened polar group have a greater value of $\eta$. Only OH- and COOH-containing metamers, in contrast to those containing SH- and COSH-groups, have a sharply increased viscosity in comparison to their metamer ethers.

**Fig. 5.** The dependence of $\eta/\sqrt{M}$ on the molecular refraction $MR_D^2$ at 293 K (unbroken line), at 353 K (broken line), and at 393 K (dotted line) for C$_n$H$_n$X, where X = F ($\circ$), Cl ($\times$), Br ($\bigcirc$), and J ($\bullet$).

**Fig. 6.** The dependence of $\eta/10^{13}$ on the dipole moment $\mu \times 10^{10}$C m at 298 K for C$_n$H$_n$X, where X = CH$_3$ ($\bullet$), OCH$_3$ ($\circ$), F ($\circ$), Br ($\bigcirc$), Cl ($\bigcirc$), J ($\bullet$), N(CH$_3$)$_2$ ($\star$), COOC$_2$H$_5$ ($\bigcirc$), COCH$_3$ ($\circ$), CN ($\bigcirc$), NC ($\bigcirc$), NO$_2$ ($\bullet$), NH$_2$ ($\bigcirc$), and OH ($\circ$).
3.2. Viscosity of associated liquids

As mentioned previously, OH- and COOH-containing members of a series show deviations from the regularity in the change of \( \eta \) determined for this series. In isoperiodic series of such type, the compounds have a value of \( \eta \) 5–8 times higher than that calculated from the dipole moment of their molecules. In case of cyclic oxides and normal alcohols, \( \eta_{\text{cyclic}}/\eta_{\text{linear}} \) is much less than one, instead of being greater than one. Thus, \( \eta \) of ethylene oxide at 235 K is almost 10 times less than that of ethanol. The formation of ethers, especially methyl ethers, leads to a sharp decrease in \( \eta \), explaining deviations from the regularity \( \eta \). For alcohols and acids at 293 K the decrease is by a factor of 3–8, for phenols at 404 and 457 K the decrease is by a factor of 2–6. In isologous series, alcohols have a greater value of \( \eta/\sqrt{m} \) MRD than their isomers. The substituted compounds also show increased values of \( \eta/\sqrt{m} \) MRD in comparison to those calculated on the basis of the molecular dipole moment. The difference is by factor of 5–10. The viscosity of alcohols and acids exceeds the viscosity of their metamer ethers by a factor of 11–17 and 4–5, respectively. The same effect is observed with substituted phenols. Thus, \( \eta \) of meta- and para-hydroxyacetophenone at 404 K is 3–5 times higher than \( \eta \) of the metamer meta- and para-methoxybenzaldehydes (Table 1).

The anomalous behavior of OH- and COOH-containing compounds is explained by the fact that they are associated and consist of complex structures formed due to hydrogen bonding [42], rather than single molecules. The effect of dimerization and higher order association of OH- and COOH-containing molecules on viscosity is confirmed by the behavior of compounds with intramolecular hydrogen bond, such as ortho-nitrophenol, ortho-hydroxybenzaldehyde, ortho-hydroxyacetophenone, and ethyl salicylate. These OH-containing compounds behave in the ordinary way, since they are devoid of the tendency to form intermolecular complexes due to formation of intramolecular hydrogen bond. Thus, the aforementioned ortho-hydroxy-compounds (Fig. 2) in isoperiodic series have the value of \( \eta \) appropriate to their dipole moment. Their methyl ethers (Table 1), as a rule, have a higher value of \( \eta \) than the initial phenol. They obey the dependence \( \eta \) on the basis of their molecules. Neglecting the difference in the dipole moments of the molecules in the complex and in metamer non-associated compounds, the value of \( \eta \) can be approximately calculated from the relation:

\[
\eta_{\text{assoc}} = \eta_{\text{metem.}}^{1/2} \text{const} \frac{\eta}{\mu_{\text{molec}}} \approx z^2.
\]

The compounds under study behave in a normal way even in comparison to metamer ethers: ortho-hydroxyacetophenone possesses the same viscosity as metamer ortho-methoxybenzaldehyde (Table 1). The lack of intermolecular association for the ortho-hydroxycompounds and its existence for meta- and para-isomers explain the sharp decrease of \( \eta \) for the former in comparison to the latter. The decrease is by a factor of 2.5–5 at 404 and 457 K. The ortho-isomers usually have a greater value of \( \eta \) than their isomers. Cresols constitute an exception, because intramolecular hydrogen bond cannot form in the ortho-isomer.

The anomalously high value of \( \eta \) for the associated compounds, causes the aforementioned deviations, is explained by the breaking of hydrogen bonds in viscous flow and hence by an increased value of work needed for cavity formation due to “structural energy of activation” \( \eta \). However, a noticeable resistance of hydrogen bonds even at high temperatures raises doubts about the viewpoint that a single molecule is a structural unit of the viscous flow for the associated compounds. In acids the complexes are resistant even in pairs, in phenols and alcohols they are resistant in liquid state in a wide temperature range \( \eta \). The anomalously high value of \( \eta \) for the associated compounds can be explained on the basis of their macro-properties, which are determined not by the properties of their molecules but by the properties of molecular complexes being a unit of their viscous flow. Taking into consideration the fact that the mass of the complex is equal to \( z^2 \) (\( z \) is the number of molecules in the complex), and the polarizability of the complex approximately matches \( z \alpha \) or \( \alpha \) MRD, then for the associated compound

\[
\eta_{\text{assoc}}(\eta) = \frac{(zm)^{1/2}(z \alpha)^{3/2}}{(A + \text{const} \mu_{\text{molec}})} \eta_{\text{metem.}}^{1/2}
\]

Since \( z \geq 2 \) and the dipole moment of molecules in a complex either increases (for alcohols and phenols \( O-H \) type) or decreases (for acids due to formation of cyclic dimers \( R \rightarrow C \; O \cdots C \; H \; O \rightarrow R \)), it follows from Eq. (14) that the value of \( \eta \) for the associated compounds should sharply increase in comparison with that calculated on the basis of properties of single molecules. Neglecting the difference in the dipole moments of the molecules in the complex and in metamer non-associated compounds, the value of \( \eta \) can be approximately calculated from the relation:

\[
\eta_{\text{assoc}} = \eta_{\text{metem.}}^{1/2} \text{const} \frac{\eta}{\mu_{\text{molec}}} \approx z^2.
\]

In accordance with the X-ray, electronographic, and other data \[45,46\], the value of \( \eta \) nears 2 for acids and 3–4 for alcohols (Table 2). It also follows from Eq. (14) that the associated compounds obey the same dependences as ordinary liquids when the value of \( z \) remains unchanged. Since the viscosity varies in homologous series of alcohols and acids (Fig. 3) in the same way as in the series of their ethers, the lengthening of the hydrocarbon chain, at least from the fifth member, should not change the value of \( z \). The value of \( z \) does not change either during transition from an acyclic alcohol to the corresponding cyclic one.

4. Conclusions

The determined dependences between the viscosity of ordinary liquids and the properties of the molecules they consist of (polarizability, dipole moment, shape) allowed us to analyze and predict the viscosity values in series of compounds. The nature of changes in viscosity in homologous and isologous series along with those for the series of substituted hydrocarbons was explained on the basis of the established dependences. The peculiarities of viscosity were clarified for the compounds, which were associated inter- and intramolecularly through the formation of hydrogen bonds. The intermolecular hydrogen bond in associated liquids leads to increase in viscosity in comparison with ordinary liquids.

Acknowledgments

OVP acknowledges financial support of the USA Department of Energy, grant no. DE-SC0006527.

References
