

<https://doi.org/10.15407/ujpe65.5.419>

A.M. HETALO,¹ O.V. KHOROLSKYI,¹ S.A. STETSENKO,² S.O. SAMOILENKO,²
O.S. SVECHNIKOVA³

¹ Poltava V.G. Korolenko National Pedagogical University

(2, Ostrograds'kogo Str., Poltava 36000, Ukraine; e-mail: khorolskiy.alexey@gmail.com)

² Ukrainian Medical Stomatological Academy

(23, Shevchenko Str., Poltava 36011, Ukraine)

³ Taras Shevchenko National University of Kyiv

(64/13, Volodymyrs'ka Str., Kyiv 01601, Ukraine)

SIMILAR BEHAVIOR OF RHEOLOGICAL PROPERTIES AND THE EVALUATION OF THE MELTING TEMPERATURES OF FLUORINATED ALIPHATIC ALCOHOLS

On the basis of experimental data obtained for the viscosity, density, and refractive index of fluorinated alcohols and proceeding from the similarity laws, the structural features of molecules of the researched liquids are determined. A comparison of molecular refraction values determined for fluorinated and non-fluorinated alcohols made it possible to reveal a modification of the structure of fluorinated alcohol molecules. Namely, this is a probable minor change in the arrangement of fluorine atoms in the alcohol molecule, at which the structure of a molecule remains similar to the structure of molecules of aliphatic alcohols. A similarity in the behavior of the rheological properties of 2,2,3,3-tetrafluoropropan-1-ol and 1H,1H-pentafluoropropan-1-ol, on the one hand, and propan-1-ol, on the other hand, as well as 1H,1H,7H-dodecafluoroheptan-1-ol and 1H,1H-tridecafluoroheptan-1-ol, on the one hand, and heptan-1-ol, on the other hand, is found. A method for estimating the melting temperatures of halogenated molecular liquids, which is based on the similarity of the rheological properties of those liquids, is proposed. The melting temperatures for 1H,1H-pentafluoropropan-1-ol, $T_m = (244.5 \pm 1.0)$ K, and 1H,1H-tridecafluoroheptan-1-ol, $T_m = (255.0 \pm 1.0)$ K, which are not available in the literature, are evaluated.

Keywords: fluorinated alcohol, viscosity, density, similarity law, melting temperature.

1. Introduction

Fluorinated aliphatic alcohols are used as intermediates in pharmacology and organic synthesis; specific solvents; the components of high-temperature coolants, lubricants, and glues; as well as in the manufacture of pesticides and electrically conductive additives for the electrochemical fluorination. They continue to conquer new areas of application by playing the role of monomers in the production of polymeric materials [1, 2].

The research of the physical properties of normal aliphatic alcohols and their aqueous solutions

is a promising direction in the physics of liquids and liquid systems [3–5]. In particular, a number of papers published by Ukrainian scientists were devoted to the study of the structure and properties of propan-1-ol and heptan-1-ol [6–10]. At the same time, despite a wide application of fluorinated alcohols in various industries, their physical properties (even their melting and boiling temperatures) remain poorly investigated.

For the physics of liquids and liquid systems, of considerable interest are the fundamental aspects in the study of halogen derivatives. All molecular liquids obey the van der Waals equation, which leads to similarities of their physical properties. More specifically, being expressed in terms of certain variables, the behavior of the physical properties of various liq-

© A.M. HETALO, O.V. KHOROLSKYI,
S.A. STETSENKO, S.O. SAMOILENKO,
O.S. SVECHNIKOVA, 2020

uids is similar, and the corresponding deviations do not exceed 4–5% [11]. Therefore, one should expect that the fluorination in an organic liquid cannot drastically change the structure of a molecule and destroy the similarity in the behavior of physical properties. Instead, it would only lead to a modification of parameters in the intermolecular interaction potential. In other words, the reasons for a similarity to exist between the physical properties of fluorinated liquids and their non-fluorinated analogs are as follows: (i) the properties of molecular fluids are described by the van der Waals equation, which is valid for liquids with various potentials of the intermolecular interaction, and (ii) the substitution of hydrogen atoms by fluorine ones cannot radically change the behavior of the physical properties of the liquid, but only gives rise to a change in the depths of the maxima and minima in the intermolecular interaction potential.

Therefore, the aims of this work are

- to determine the effect of substitution of hydrogen atoms by fluorine ones in the molecules of normal aliphatic alcohols on the structure of alcohol molecules, and
- based on the similarity in the behavior of the rheological properties of poorly studied fluorinated alcohols, to evaluate their melting temperatures making use of similarity laws.

2. Experimental Part

As objects to be studied, we selected normal aliphatic alcohols of the extra pure grade: propan-1-ol (C_3H_7OH ; hereinafter, PrOH) and heptan-1-ol ($C_7H_{15}OH$, HepOH), as well as their fluorinated analogs 2,2,3,3-tetrafluoropropan-1-ol ($HCF_2CF_2CH_2OH$, 4F-PrOH), 1H,1H-pentafluoropropan-1-ol ($CF_3CF_2CH_2OH$, 5F-PrOH), 1H,1H,7H-dodecafluoroheptan-1-ol ($H(CF_2)_6CH_2OH$, 12F-HepOH), and 1H,1H-tridecafluoroheptan-1-ol ($CF_3(CF_2)_5CH_2OH$, 13F-HepOH). The fluorinated alcohols 2,2,3,3-tetrafluoropropan-1-ol and 1H,1H,7H-dodecafluoroheptan-1-ol with a purity grade of 99.0% were synthesized at the Department of Chemistry of Organofluorine Compounds of the Institute of Organic Chemistry of the NAS of Ukraine. The alcohols 1H,1H-pentafluoropropan-1-ol (>98.0%) and 1H,1H-tridecafluoroheptan-1-ol (>95.0%) manufactured by TCI Chemicals were used as well.

The experimental measurements of rheological properties were performed in a temperature interval of 293–363 K using standard methods. The density ρ was determined with the help of the pycnometric method with an error of 0.05%. The kinematic viscosity ν was studied using the capillary viscometry method, and the corresponding measurement error did not exceed 1.0%. The refractive index n_D was measured in a temperature interval of 293–333 K with an error of 2×10^{-4} according to the procedure described in work [12].

3. Optical Properties of Fluorinated Alcohols and the Structure of Their Molecules

The optical properties of molecular liquids – in particular, the refractive index of a medium – are sensitive to the structure of the substance molecule. Therefore, a comparison between the temperature dependences of the refractive and molecular refractive indices of fluorinated alcohols, on the one hand, and the same dependences for aliphatic alcohols, on the other hand, can be used to elucidate the structural peculiarities in the molecules of fluorinated alcohols.

In order to reveal the structural peculiarities of the examined substances by analyzing their molecular refractive indices, information on the composition and molecular weight of the liquids is required. The molecular refraction is proportional to the polarization of molecules, being additive by nature. Therefore, it can be calculated by summing up a number of refractive constants for the components constituting the molecule (atoms and their groups, single and multiple bonds, rings, and so forth). The calculation of the predicted molecular refraction index is carried out on the basis of information concerning atomic refractions, group refractions, bond refractions, and structural increments available in the form of tabular data [12].

The experimental molecular refractive index was calculated using the Lorentz–Lorenz formula

$$R_D = \frac{n^2 - 1}{n^2 + 2} \frac{M}{\rho}, \quad (1)$$

where n is the refractive index, M the molecular weight, and ρ the density of the liquid. The discrepancy between the values of experimental, R_D , and additive, R_{add} , molecular refractive indices is called

Table 1. Experimental and calculated molecular refraction values for examined alcohols

Substance	$M \times 10^3$, kg/mol	ρ^{20} , kg/m ³	n_D^{20}	$R_D \times 10^6$, m ³ /mol	$R_{\text{add}}^A \times 10^6$, m ³ /mol	$R_{\text{add}}^B \times 10^6$, m ³ /mol
Propan-1-ol	60.09	803.9	1.3849	17.513	17.511	17.524
2,2,3,3-tetrafluoropropan-1-ol	132.06	1485.3	1.3214	17.708	16.643	16.580
1H,1H-pentafluoropropan-1-ol	150.05	1512.2	1.2880	17.869	16.425	16.344
Heptan-1-ol	116.20	821.9	1.4233	36.024	36.096	36.116
1H,1H,7H-dodecafluoroheptan-1-ol	332.09	1761.6	1.3183	37.215	33.487	33.284
1H,1H-tridecafluoroheptan-1-ol	350.08	1746.2	1.2850	35.757	33.269	33.048

the molecular refraction exaltation. The main origins of the exaltation, besides such factors as measurement errors and the approximate values of additive constants, are the presence of multiple bonds, backbone branching, and spatial molecular conformations. The exaltation magnitude increases rapidly with the length of molecules and the molecular weight of researched substance. According to work [12], the condition $R_D \cong R_{\text{add}}$ means that the proposed empirical formula and the substance structure are highly probable. However, if the value of R_D exceeds that of R_{add} by more than 0.4×10^{-6} m³/mol, this difference may testify either to the incorrectness of assumptions about the structure and composition of the substance or to the structural and spatial features of the substance molecules.

Note that the experimental molecular refractive indices of aliphatic and fluorinated alcohols calculated by formula (1) differ only slightly from each other, which testifies to the similarity of the structures of those alcohols. From Table 1, one can see that the values of experimental and calculated molecular refractive indices, e.g., for propyl alcohol, coincide with each other within the experimental error. At the same time, the corresponding experimental value for 2,2,3,3-tetrafluoropropan-1-ol differs substantially from the values calculated according to Vogel's tables [12] and making use of the atomic refraction (R_{add}^A) and bond refraction (R_{add}^B) methods. This fact testifies to the presence of structural features that are responsible for the molecular refraction exaltation.

In view of work [2], we may suppose that there arises a steric effect of the halogen substituent in the molecules of fluorinated alcohols, which induces the repulsion between the neighbor fluorine atoms. As a rule, the steric effect reveals itself as the changes of

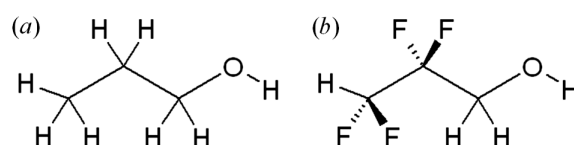


Fig. 1. Schematic structures of propan-1-ol (a) and 2,2,3,3-tetrafluoropropan-1-ol (b) molecules [13]

the bond length and the valence angle between the carbon backbone and the halogen, which results in the appearance of a tension in the intramolecular structure and a modification of the latter (Fig. 1). Namely, the zigzag structure of an aliphatic alcohol molecule changes to the helical arrangement of fluorine atoms in the corresponding fluorinated alcohol molecule [13].

Steric obstacles for the substituting atom can affect the formation of hydrogen bonds and substantially reduce the acidic properties of alcohols. This is a result of the negative inductive effect ($-I$ -effect) inherent in fluorine, which is a strong electron-acceptor substituent [13].

Hence, the fluorinated alcohols undergo a change in the arrangement of fluorine atoms in their molecules, whereas their structure remains similar to that of normal aliphatic alcohols.

4. Rheological Properties and Melting Temperatures of Fluorinated Alcohols

As was noted above, on the basis of a structural similarity between the molecules of fluorinated and normal aliphatic alcohols, one may suppose that their physical properties are also similar. In work [11], it was shown that the similarity in the behavior of the shear viscosity among low-molecular liquids is associ-

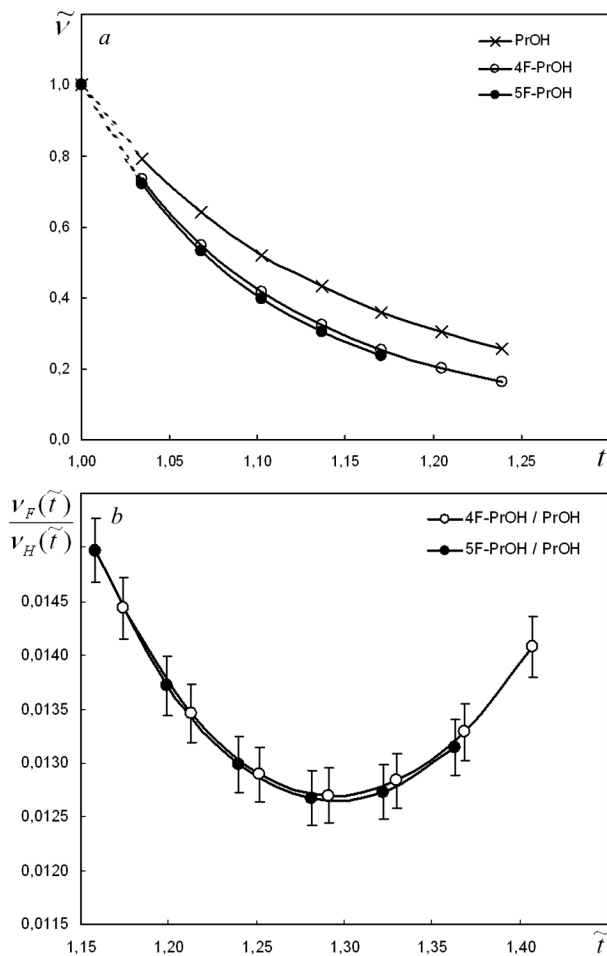


Fig. 2. Dependencies of the normalized kinematic viscosity $\tilde{\nu}$ on the normalized temperature t for heptyl alcohol (HepOH) and its fluorinated analogs (12F-HepOH and 13F-HepOH) (a) and the temperature dependences of the ratio between the kinematic viscosities of fluorinated analogs of propyl alcohol and propan-1-ol (b)

ated with the same structure of their averaged interparticle potentials, which is a consequence of the rotational motion of molecules in the liquids. The similarity of the molecular mechanisms of a viscous flow is also evidenced by the calculation of the thermodynamic properties of a viscous flow, which was performed in work [14].

Let us plot the temperature dependences of the normalized kinematic viscosity of the studied liquids calculated by the formula

$$\tilde{\nu} = \frac{\nu_i(T)}{\nu_i(T_0)}, \quad (2)$$

where $i = \text{PrOH}, 4\text{F-PrOH}, 5\text{F-PrOH}, \text{HepOH}, 12\text{F-HepOH},$ or 13F-HepOH ; $\nu_i(T)$ is the kinematic viscosity of the i -th alcohol at the temperature T ($T = 293 \div 363$ K); and $\nu_i(T_0)$ the kinematic viscosity of the i -th alcohol at the temperature $T_0 = 293$ K. In the framework of the rigorous approach, the kinematic viscosity should be normalized by its value at the corresponding critical or triple-point temperature [15]. However, owing to the lack of experimental data, we selected room temperature $T_0 = 293$ K as the normalization one for all alcohols.

From Figs. 2, a and 3, a, one can observe the partial similarity of the plots for the dependences of the normalized kinematic viscosity $\tilde{\nu}$ on the normalized temperature $t = T/T_0$ obtained for alcohols forming the group “aliphatic alcohol–fluorinated alcohol–perfluorinated alcohol”. The similarity of curves is not obvious in the temperature interval $t = 1.00 \div 1.05$. But, at higher temperatures, the curves are almost identical (they coincide within the experimental error limits). In our opinion, the shift of the curves with respect to one another is a result of the improper choice of a normalization temperature.

It seems clear that the normalized kinematic viscosity versus the normalized temperature plots should exhibit a similar behavior for the group “aliphatic alcohol–fluorinated alcohol–perfluorinated alcohol”, so that the corresponding curves could be superimposed on one another to within the experimental error under certain conditions. We may assume that the latter include the temperature normalization by the reference temperature value inherent in every particular molecular liquid, e.g., the critical, triple-point, and boiling or melting temperatures. Because of a considerable lack of information on the thermodynamic properties of fluorinated alcohols, we chose the melting temperature T_m to play this role. The specific values of this parameter were taken from the literature: $T_m = 146.95$ K for propan-1-ol [16], $T_m = 258$ K for 2,2,3,3-tetrafluoropropan-1-ol [17], $T_m = 242$ K for heptan-1-ol [18], $T_m = 242$ K for 1H,1H,7H-dodecafluoroheptan-1-ol [17]. We have not found any information in the literature concerning the melting temperatures of 1H,1H-pentafluoropropan-1-ol and 1H,1H-tridecafluoroheptan-1-ol.

In order to avoid the influence of the reference point selection on the similarity degree, we will not carry out the normalization by the rheological property taken at a certain temperature for one substance. In-

stead, we will analyze the ratio between the rheological property of fluorinated alcohol and the rheological property of aliphatic alcohol at the same temperature within the group “aliphatic alcohol–fluorinated alcohol–perfluorinated alcohol”. Let us formulate the similarity condition for the temperature dependences of the kinematic viscosities of aliphatic and fluorinated alcohols as the ratio

$$\frac{\nu_F(\tilde{t})}{\nu_H(\tilde{t})} = f(\tilde{t}), \quad (3)$$

where $\nu_F(\tilde{t})$ is the kinematic viscosity of fluorinated alcohol (4F-PrOH, 5F-PrOH, 12F-HepOH, 13F-HepOH) at the reduced temperature $\tilde{t} = T/T_m$, $\nu_H(\tilde{t})$ is the kinematic viscosity of normal aliphatic alcohol (PrOH, HepOH) at the same reduced temperature \tilde{t} , and T_m is the melting temperature of alcohol. The temperature dependences of the ratio of the kinematic viscosities between the corresponding pairs “fluorinated alcohol–aliphatic alcohol” are shown in Figs. 2, *b* and 3, *b* together with relative errors of 2%. Note that, owing to the absence of melting temperatures for 1H,1H-pentafluoropropan-1-ol and 1H,1H-tridecafluoroheptan-1-ol in the literature, the relevant dependences were superposed by varying the corresponding melting temperatures.

Among all halogens, the fluorine atom has the smallest van der Waals radius (0.135 nm), which is close to the radius of a hydrogen atom (0.12 nm) [19]. Therefore, when four hydrogen atoms are substituted by four fluorine atoms, the size of the molecule changes only slightly, whereas its mass increases more than twice. The parameters of the interaction between the molecules change significantly: the intermolecular bonds of the C–H...H type in the aliphatic alcohols transform into the C–F...H bonds in the fluorinated alcohols. As we showed in work [20], the process of alcohol fluorination results in the growth of the average intermolecular distances in the liquids. The substantial changes of the molecular mass and the character of intermolecular bonds give rise to an increase of the kinematic viscosities of fluorinated alcohols and a significant increase of their densities [14]. Therefore, a similarity of the temperature dependences of both the kinematic viscosities and the densities of the aliphatic and fluorinated alcohols should be expected, which follows from the similarity of the molecular structures.

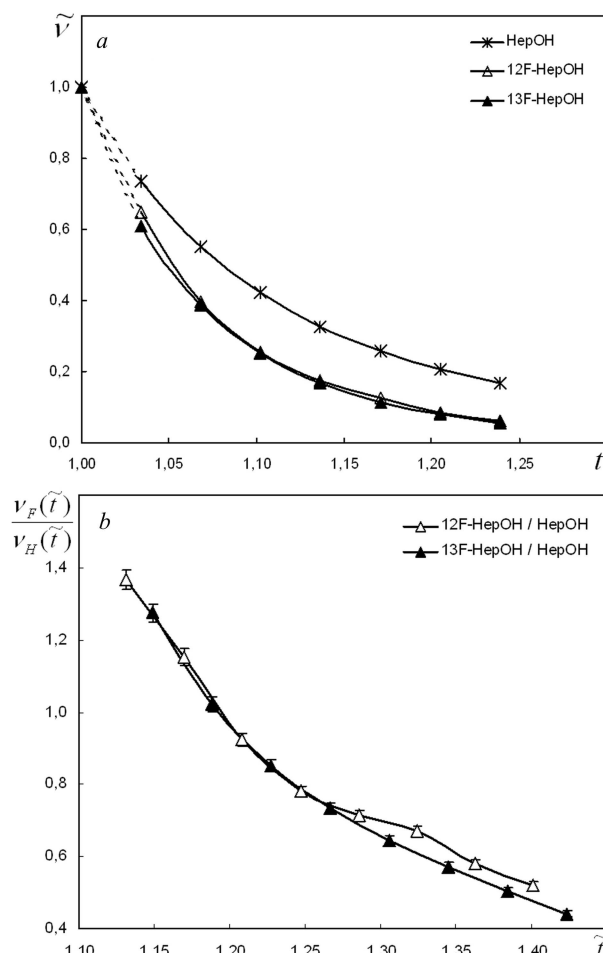


Fig. 3. Dependences of the normalized kinematic viscosity $\tilde{\nu}$ on the normalized temperature \tilde{t} for propyl alcohol (PrOH) and its fluorinated analogs (4F-PrOH and 5F-PrOH) (a) and the temperature dependences of the ratio between the kinematic viscosities of fluorinated analogs of heptyl alcohol and heptan-1-ol (b)

The similarity condition for the temperature dependences of the densities of the aliphatic and fluorinated alcohols is formulated as the ratio

$$\frac{\rho_F(\tilde{t})}{\rho_H(\tilde{t})} = \psi(\tilde{t}), \quad (4)$$

where $\rho_F(\tilde{t})$ is the density of fluorinated alcohol (4F-PrOH, 5F-PrOH, 12F-HepOH, 13F-HepOH) at the reduced temperature \tilde{t} , and $\rho_H(\tilde{t})$ is the density of normal aliphatic alcohol (PrOH, HepOH) at the same reduced temperature \tilde{t} . Figure 4 demonstrates the temperature dependences of the density ratio for the

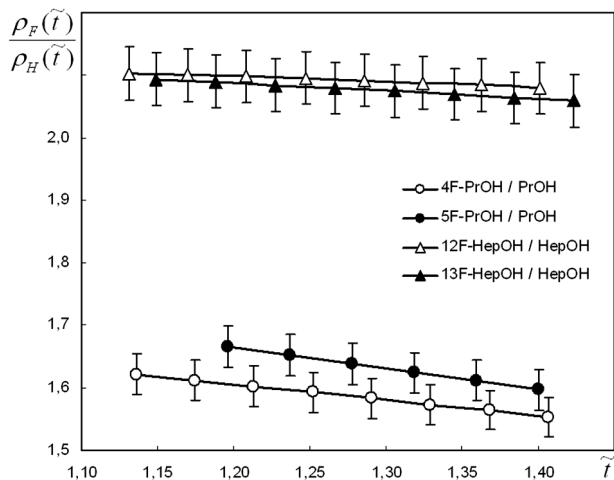


Fig. 4. Temperature dependences of the ratio between the densities of fluorinated analogs of propyl alcohol and the kinematic viscosity of propan-1-ol (lower lines) and the ratio between the densities of fluorinated analogs of heptyl alcohol and the kinematic viscosity of heptan-1-ol (upper lines)

corresponding pairs “fluorinated alcohol–aliphatic alcohol”. For all plots, the vertical bars corresponding to a relative error of 2% are indicated. Note that the temperature dependences of the density ratio between the fluorinated and aliphatic alcohols are similar. They are not superposed because of the improper choice of normalization temperatures. This means that we expect the curves to completely coincide in the case of normalization by the density taken at the critical or triple-point temperature of the corresponding liquid.

Analogously to what was done in the case of the kinematic viscosity ratio dependences, the superposition of the density ratio dependences for 1H,1H-pentafluoropropan-1-ol and 1H,1H-tridecafluoroheptan-1-ol was carried out by varying the corresponding melting temperatures. In such a way, using the similarity ratios (3) and (4) and applying the graphical method, we evaluated the melting temperatures of 1H,1H-pentafluoropropan-1-ol ($T_m = 244.5 \pm 1.0$ K) and 1H,1H-tridecafluoroheptan-1-ol ($T_m = 255.0 \pm 1.0$ K).

Let us discuss the method of evaluating the melting temperatures of halogenated molecular liquids, which is based on the similar behavior of their rheological properties, in more details. First of all, it is important to correctly select the reference temperatures in order to obtain the maximum similarity of rheolog-

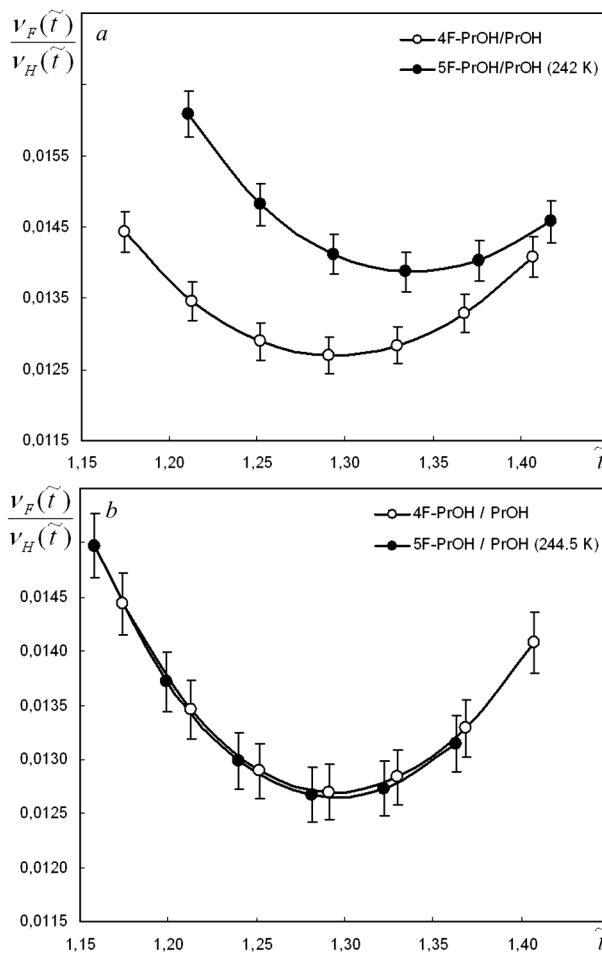


Fig. 5. Temperature dependences of the kinematic viscosity ratio between the fluorinated analog of propyl alcohol (5F-PrOH) and the kinematic viscosity of propan-1-ol for an improper (a) and a proper (b) choice of the melting temperature for 5F-PrOH

ical curves. Figures 2, a and 3, a are examples of the incorrect choice of the temperature normalization, which is testified by the absence of a superposition of the curves describing the temperature dependence of the normalized kinematic viscosity, although a certain similarity of their behavior can be observed. Second, the variation of the melting temperature should lead to the evident similarity of the temperature behavior of the rheological curves. In other words, as the temperature approaches the sought melting temperature of the fluorinated alcohol, the temperature dependences of the rheological properties of the fluorinated and aliphatic alcohols should coincide within the ex-

Table 2. Comparison of experimental melting temperatures T_m^{exp} with the values obtained using the Joback–Reid, T_m^{JR} , Gold–Ogle, T_m^{GO} , and Lorenz–Gerz, T_m^{LG} , methods, as well as the estimates of this work

Compound	CAS no.	T_m^{exp} , K	T_m^{JR} , K	T_m^{GO} , K	T_m^{LG} , K	This work
Propan-1-ol	71-23-8	146.95	184.4	212.0	216.0	–
2,2,3,3-tetrafluoropropan-1-ol	76-37-9	258	174.2	194.4	223.3	–
1H,1H-pentafluoropropan-1-ol	422-05-9	–	192.2	189.9	207.3	244.5
Heptan-1-ol	111-70-6	242	229.5	264.8	262.4	–
1H,1H,7H-dodecafluoroheptan-1-ol	335-99-9	259	233.6	236.6	258.1	–
1H,1H-tridecafluoroheptan-1-ol	375-82-6	–	251.7	237.6	245.2	255

perimental error (see Fig. 5, *b*). Therefore, the melting temperature of fluorinated alcohol F_2 , $T_m(F_2)$, was determined under the condition that it had to satisfy the relation

$$T_m(F_2) = T_m(F_1) \frac{T_{\min}(F_2)}{T_{\min}(F_1)}, \quad (5)$$

where $T_m(F_1)$ is the known melting temperature of fluorinated alcohol F_1 , $T_{\min}(F_1)$ the temperature of the minimum in the temperature dependence of the rheological property of fluorinated alcohol F_1 , and $T_{\min}(F_2)$ is its counterpart for the fluorinated alcohol F_2 . As one can see from Fig. 5, *a*, an insignificant variation in the melting temperature of fluorinated alcohol can result in the absence of a similarity for the temperature dependences of the kinematic viscosity ratios. This fact may testify to a potential accuracy of the method proposed for the determination of the melting temperatures of halogenated compounds.

We would like to emphasize an important circumstance that the change from the normalization by the rheological property at a definite temperature for one substance to the ratio between the rheological property values of the fluorinated and aliphatic alcohols at the same temperature brought about a transition from monotonically descending curves to nonmonotonic ones (Fig. 5, *b*).

Let us compare the results of our estimates of melting temperatures with those obtained in the framework of the most widespread approximate methods used for calculating this parameter (Table 2): according to group contributions to the molecular structure (the Joback–Reid method, T_m^{JR} [21]), according to the boiling temperature (the Lorenz–Hertz method, T_m^{LG} [22]), and according to both the boiling tempera-

ture and group contributions (the Gold–Ogle method, T_m^{GO} [23]). Attention has to be paid that those methods are statistical and based on a generalization of experimental data obtained for various classes of compounds, so that the average relative error of calculations can reach 35% [22].

As can be observed from Table 2, the higher the molecular weight of the test liquid, the better the results of the selected methods correlate with the experimental data. Significant deviations of the experimental melting temperature values from those calculated with the use of the statistical methods may arise owing to the underestimation of the role of hydrogen bonds in the examined alcohols and the fluorination of the latter.

Thus, the method proposed for evaluating the characteristic temperatures from the rheological data of liquids possessing similar structures of molecules – in particular, organic compounds and their halogenated derivatives – needs a further substantiation and experimental verification for several classes of compounds, which will be dealt with in future publications.

5. Conclusions

On the basis of experimental data for the refractive index of normal aliphatic alcohols and their fluorinated analogs, the experimental molecular refraction index is calculated and compared with the corresponding theoretical value. The difference between the experimental and calculated values may testify to modifications in the structure of molecules in fluorinated alcohols. A conclusion is drawn that the structure of fluorine alcohols becomes slightly altered. Namely, the zigzag structure of aliphatic al-

cohol molecules transforms into the helical arrangement of fluorine atoms in the molecules of fluorinated alcohols.

On the basis of similarity laws, the temperature dependences of the kinematic viscosity and the density of aliphatic alcohols and their fluorinated analogs have been analyzed. A similarity in the behavior of the rheological properties of 2,2,3,3-tetrafluoropropan-1-ol, 1H,1H-pentafluoropropan-1-ol, 1H,1H,7H-dodecafluoroheptan-1-ol, and 1H,1H-tridecafluoroheptan-1-ol in comparison with those of propan-1-ol and heptan-1-ol within the fluorination series and the error limits is revealed.

A method is proposed for evaluating the melting temperatures of halogenated molecular liquids, which is based on the similarity in the behavior of their rheological properties. From the similarity of the temperature dependences of the kinematic viscosity and density, the melting temperatures of 1H,1H-pentafluoropropan-1-ol and 1H,1H-tridecafluoroheptan-1-ol, which are absent from the literature, are determined: $T_m = 244.5 \pm 1.0$ K and 255.0 ± 1.0 K, respectively.

The authors are grateful to Academician L.A. Bulavin for his permanent attention to and comprehensive support of our research of fluorinated molecular fluids. The authors are also deeply thankful to Professor M.P. Malomuzh for a thorough discussion of the results obtained.

1. L.M. Yagupolskii. *Aromatic and Heterocyclic Compounds with Fluorine-Containing Substituents* (Naukova Dumka, 1988) (in Russian).
2. P. Kirsch. *Modern Fluoroorganic Chemistry: Synthesis, Reactivity, Applications* (Wiley-VCH, 2013).
3. A. Oleinikova, L. Bulavin, V. Pipich. Critical anomaly of shear viscosity in a mixture with an ionic impurity. *Chem. Phys. Lett.* **278**, 121 (1997).
4. L.A. Bulavin, O.I. Belous, O.S. Svechnikova. Anomalous ultrasound attenuation near the critical point of n-pentanol–nitromethane solution stratification. *Ukr. J. Phys.* **61**, 375 (2016).
5. L.A. Bulavin, O.I. Belous, O.S. Svechnikova. Relaxation time of concentration fluctuations in a vicinity of the critical stratification point of the binary mixture n-pentanol–nitromethane. *Ukr. J. Phys.* **61**, 879 (2016).
6. V. Pogorelov, L. Bulavin, I. Doroshenko, O. Fesjun, O. Veretennikov. The structure of liquid alcohols and the temperature dependence of vibrational bandwidth. *J. Mol. Struct.* **708**, 61 (2004).

7. V. Balevicius, V. Sablinskas, I. Doroshenko, V. Pogorelov. Propanol clustering in argon matrix: 2D FTIR correlation spectroscopy. *Ukr. J. Phys.* **56**, 855 (2011).
8. P. Golub, V. Pogorelov, I. Doroshenko. Quantum-chemical simulation of the cluster structure of liquid n-heptanol. *Ukr. J. Phys.* **57**, 166 (2012).
9. V.E. Chechko, V.Ya. Gotsulsky, N.P. Malomuzh. Surprising thermodynamic properties of alcohols and water on their coexistence curves. *J. Mol. Liq.* **272**, 590 (2018).
10. V.Ya. Gotsulsky, N.P. Malomuzh, V.E. Chechko. Extraordinary properties of alcohols from the homologous series of methanol. *Ukr. J. Phys.* **65**, 31 (2020).
11. P.V. Makhlaichuk, V.N. Makhlaichuk, N.P. Malomuzh. Nature of the kinematic shear viscosity of low-molecular liquids with averaged potential of Lennard-Jones type. *J. Mol. Liq.* **225**, 577 (2017).
12. B.V. Ioffe. *Refractometric Methods of Chemistry* (Khimiya, 1983) (in Russian).
13. O.P. Rudenko, O.V. Khorolskyi, A.M. Hetalo, O.V. Saienko. Rheological and optical properties of 2,2,3,3-tetrafluoropropan-1-ol. *Visn. Kyiv. Univ. Ser. Fiz. Mat. Nauky* No. 1, 223 (2010) (in Ukrainian).
14. L.A. Bulavin, A.M. Getalo, O.P. Rudenko, O.V. Khorolskyi. Influence of fluorination on the physical properties of normal aliphatic alcohols. *Ukr. J. Phys.* **60**, 428 (2015).
15. N.P. Malomuzh, V.N. Makhlaichuk. On the similarity of the self-diffusion and shear viscosity coefficients in low-molecular liquids. *J. Mol. Liq.* **295**, 111729 (2019).
16. N.B. Vargaftik, *Handbook of Physical Properties of Liquids and Gases: Pure Substances and Mixtures* (Hemisphere, 1983).
17. B.N. Maximov. *Organofluorine Industrial Products: A Handbook* (Khimiya, 1990) (in Russian).
18. *CRC Handbook of Chemistry and Physics*, edited by J. Rumble (Taylor and Francis, 2019).
19. *Fluorine Compounds, Modern Technology, and Applications*, edited by N. Ishikawa (Russian translation) (Mir, 1984).
20. A.M. Hetalo, O.P. Rudenko, O.V. Khorolskyi, S.O. Samoilenko, L.A. Bulavin. Temperature dependence of the bulk elasticity modulus of aliphatic alcohols and their fluorinated analogs. *Ukr. J. Phys.* **63**, 134 (2018).
21. K.G. Joback, R.C. Reid. Estimation of pure component properties from group contributions. *Chem. Eng. Commun.* **57**, 233 (1987).
22. E.A. Stolyarov, N.G. Orlova. *Calculation of Physicochemical Properties of Liquids. A Handbook* (Khimiya, 1976) (in Russian).
23. P.I. Gold, G.J. Ogle. Estimating thermophysical properties of liquids. Part 4. Boiling, freezing and triple-point temperatures. *Chem. Eng.* **76**, 119 (1969).

Received 17.11.19.

Translated from Ukrainian by O.I. Voitenko

А.М. Гетало, О.В. Хорольський,
С.А. Стеценко, С.О. Самоїленко, О.С. Свечнікова

ПОДІБНІСТЬ ПОВЕДІНКИ
РЕОЛОГІЧНИХ ВЛАСТИВОСТЕЙ
ТА ОЦІНКА ТЕМПЕРАТУР ПЛАВЛЕННЯ
ФТОРЗАМІЩЕНИХ АЛІФАТИЧНИХ СПИРТІВ

Резюме

На основі експериментальних даних про температурні залежності в'язкості, густини і показника заломлення та спираючись на закони подібності виявлено особливості структури молекул фторзаміщених спиртів. Порівняння молекулярних рефракцій фторзаміщених та незаміщених спир-

тів дозволило виявити незначну зміну структури молекул фторзаміщених спиртів: ймовірна зміна розташування атомів фтору в молекулі спирту при збереженні подібності структури до будови аліфатичних спиртів. Виявлено подібність поведінки реологічних властивостей 2,2,3,3-тетрафторпропанолу-1 і 1Н,1Н-пентафторпропанолу-1 у порівнянні з пропанолом-1 та 1Н,1Н,7Н-додекафторгептанолу-1 і 1Н,1Н-тридекафторгептанолу-1 у порівнянні з гептанолом-1. Запропоновано метод оцінки температур плавлення галогензаміщених молекулярних рідин, який ґрунтується на подібності поведінки їх реологічних властивостей. Отримано оцінки температур плавлення 1Н,1Н-пентафторпропанолу-1 $T_m = (244,5 \pm 1,0)$ К та 1Н,1Н-тридекафторгептанолу-1 $T_m = (255,0 \pm 1,0)$ К, які відсутні у літературних джерелах.