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INFLUENCE OF FLUORINATION ON THE PHYSICAL PROPERTIES OF NORMAL ALIPHATIC ALCOHOLS

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Rheological properties of normal aliphatic alcohols and their fluorinated analogs have been studied. The temperature dependences of the density and the kinematic viscosity of fluorinated and normal alcohols are shown to have the same character. The density growth for fluorinated alcohols is revealed, with the shear viscosity growing more pronouncedly, if more hydrogen atoms in the alcohol molecule are substituted by fluorine ones. The calculated thermodynamic properties of a viscous flow testify that fluorinated aliphatic alcohols are more structured in comparison with normal ones.

Keywords: fluorinated aliphatic alcohols, shear viscosity, thermodynamic parameters, viscous flow.

1. Introduction

Fluoroorganic compounds are widely used in industry as heat carrier or refrigerant agents, in agriculture as pesticides and dyes, in medicine as anesthetics and blood substitutes. Simultaneously, they continue to conquer new areas of application, serve as intermediate products in organic synthesis and monomers in the fabrication of polymeric materials, and are used in fourth-generation reactors [1]. Therefore, the extension of our knowledge concerning the properties of fluorine-substituted substances determines the practical value of researches dealing with their physical parameters [2, 3].

Nowadays, fluorinated alcohols are used in pharmacology and in the manufacture of pesticides, electroconducting additives at electrochemical fluorination, components of high-temperature heat carriers, lubricants, glues, and so forth [3–7]. At the same time, the physico-chemical properties of those compounds have not been studied enough till now.

Of considerable interest for condensed matter physics are the fundamental aspects in studying the halogenated compounds. Therefore, this work aimed at elucidating the influence of introducing fluorine atoms into molecules of normal aliphatic alcohols on

their physical properties, first of all, the thermodynamic parameters of a viscous flow.

2. Materials and Methods

Reagent-grade normal aliphatic alcohols and their fluorinated analogs – 1-propanol (C_3H_7OH) and 2,2,3,3-tetrafluoro-1-propanol ($HCF_2CF_2CH_2OH$, TFP), 1-pentanol ($C_5H_{11}OH$) and 2,2,3,3,4,4,5,5-octafluoro-1-pentanol ($H(CF_2)_4CH_2OH$, OFP), 1-heptanol ($C_7H_{15}OH$) and 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoro-1-heptanol ($H(CF_2)_6CH_2OH$, DFH) – are studied. The fluorinated alcohols with 99.0% purity were synthesized at the Department of Fluoroorganic Compounds of the Institute of Organic Chemistry of the NAS of Ukraine.

The rheological parameters of viscous fluids were measured in a temperature interval of 293–363 K, by using the standard techniques. The density ρ of a specific fluid was determined using the pycnometric method with an error of 0.05%. The kinematic viscosity ν was studied with the help of a capillary viscometer. The corresponding viscosity measurement error did not exceed 2%.

3. Experimental Results and Their Model Representation

The experiment was carried out to obtain data on the temperature dependences of the densities, $\rho = \rho(T)$,

and the kinematic viscosities, $\nu = \nu(T)$, of the examined alcohols. The shear viscosity was calculated from the experimental data using the known formula

$$\eta_S = \rho\nu. \quad (1)$$

To study the mechanism of a viscous flow in fluids, we use the model [8], which makes it possible to evaluate the variations of thermodynamic parameters and to draw conclusions concerning the structural features of the intermolecular interaction in the alcohols and their fluorinated analogs. According to the theory of absolute reaction rates [8] developed for nonideal systems [9], there are the activated complexes in fluids; every of them is a local nonequilibrium state of the system, i.e. a fluctuation, at which the corresponding volume element of the system transits into a thermodynamically unstable state.

The analysis of the obtained experimental data testifies that the substitution of hydrogen atoms in alcohol molecules by fluorine ones gives rise to a growth of the fluid density by a factor of almost two. In addition, the temperature dependences of the densities, $\rho = \rho(T)$, are linear in the analyzed temperature interval. The temperature dependences of the shear viscosity for fluorinated and normal alcohols found by formula (1) are depicted in Fig. 1. The corresponding analysis shows that the derivatives $d\eta/dT$ for the fluorinated alcohols are much larger than for the normal ones. Note that the kinematic viscosities of all researched alcohols almost coincide at a maximum experimental temperature of 363 K.

In Fig. 2, the obtained data on the kinematic viscosity are plotted on the logarithmic scale as functions of the inverse temperature. One can see that the dependences $\ln \nu = f(T^{-1})$ are linear. This fact allows us to describe the temperature dependence of the shear viscosity in the framework of the Eyring theory [8, 10]. According to it,

$$\begin{aligned} \eta_S &= \frac{hN_A}{\chi V_\mu} \exp\left(\frac{\Delta G_\eta^\ddagger}{RT}\right) = \\ &= \frac{hN_A}{\chi V_\mu} \exp\left(\frac{\Delta H_\eta^\ddagger - T\Delta S_\eta^\ddagger}{RT}\right), \end{aligned} \quad (2)$$

where N_A is the Avogadro constant, h Planck's constant, χ the so-called transmission coefficient, V_μ the molar volume, R the universal gas constant, and

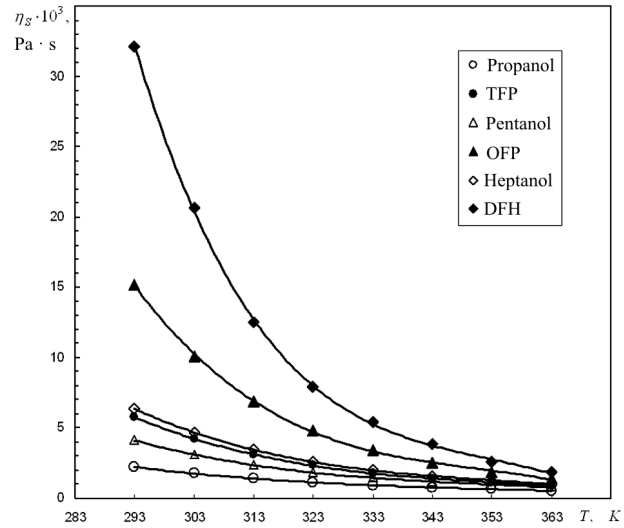


Fig. 1. Temperature dependences of the shear viscosity in the examined alcohols

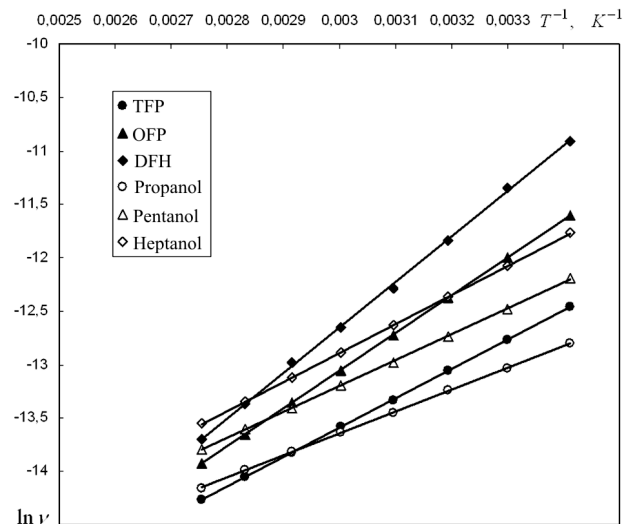


Fig. 2. Dependences of the logarithm of the kinematic viscosity on the inverse temperature for aliphatic alcohols and their fluorinated analogs

ΔG_η^\ddagger , ΔS_η^\ddagger , and ΔH_η^\ddagger are the free enthalpy, entropy, and enthalpy, respectively, of the activation of a viscous flow. Straight lines in Fig. 2 confirm that Eq. (2) adequately describes the dependences exhibited in Fig. 1 within the experimental error limits.

The data obtained for the temperature dependences of the kinematic viscosity coefficient ν in the examined objects are used to calculate the enthalpy of the activation of a viscous flow ΔH_η^\ddagger with the help

of the relation

$$\Delta H_{\eta}^{\neq} = R \frac{\partial (\ln \nu)}{\partial (T^{-1})}. \quad (3)$$

The Gibbs free energy and the entropy of activation can be calculated under the assumption that $4\pi e\chi = 1$. The corresponding values of the mentioned thermodynamic potentials are called empirical. The empirical Gibbs free energy is obtained, by using the formula

$$\Delta G_{\eta e}^{\neq} = RT \ln \left(\frac{\eta V_{\mu}}{h N_A} \right). \quad (4)$$

According to the relationship between the thermodynamic potentials $\Delta G_{\eta}^{\neq} = \Delta H_{\eta}^{\neq} - T \Delta S_{\eta}^{\neq}$, we can calculate the empirical value for the viscous flow activation entropy,

$$\Delta S_{\eta e}^{\neq} = \frac{\Delta H_{\eta}^{\neq} - \Delta G_{\eta e}^{\neq}}{T}. \quad (5)$$

If a linear dependence takes place between the entropy and the empirical entropy, the so-called kinetic compensation effect is observed in this fluid system [9]. Its presence testifies to the similarity of molecular processes running at viscous flows of the examined fluids. Mathematically, it can be express in the form

$$\Delta H_{\eta}^{\neq} = A + T^* \Delta S_{\eta e}^{\neq}, \quad (6)$$

where T^* is the isokinetic temperature of the active complex, at which the mechanism of the process drastically changes. By plotting the dependences $\Delta H_{\eta}^{\neq} = f(\Delta S_{\eta e}^{\neq})$ and using the intersections of the obtained curves with the coordinate axes, we can determine the coefficient A in Eq. (6) and the quantity $R \ln(4\pi e\chi)$ [9]. Then, in the framework of the used model, the true values of ΔS_{η}^{\neq} and ΔG_{η}^{\neq} can be calculated by the formulas [9]

$$\begin{aligned} \Delta S_{\eta}^{\neq} &= \Delta S_{\eta e}^{\neq} - R \ln 4\pi e\chi, \\ \Delta G_{\eta}^{\neq} &= \Delta G_{\eta e}^{\neq} + RT \ln 4\pi e\chi. \end{aligned} \quad (7)$$

The transmission coefficient χ , which determines the probability of a transition of the system into an unstable state, can be determined as the tangent of the slope of the dependence $\Delta H_{\eta}^{\neq} = f(\Delta S_{\eta e}^{\neq})$. It is associated with the fluctuation in the oscillation energy of the active complex, ΔE^+ , required for the complex

to transit into an unstable state, which gives rise to a break of molecular bonds,

$$\chi = \frac{1}{2} \exp \left[- \left(\frac{\Delta E^+}{RT^*} \right)^2 \right]. \quad (8)$$

In the framework of the applied model, RT^* is a standard energy fluctuation of the active complex characterized by the isokinetic temperature T^* . In the framework of the model concerned, the processes that run under shear deformations are conventionally regarded as monomolecular reactions giving rise to the break or formation of intermolecular bonds between associates in the dynamical system, e.g., in the volume of any fluid. Suppose that active complexes emerge as a product of the normal reactions that are linear combinations of plenty of elementary reactions giving rise to the break of intermolecular bonds between associates and complexes in the researched fluids [9].

The relaxation time for the shear viscosity is calculated by the formula

$$\tau_{\eta} = \frac{1}{4\pi e\chi} \frac{h}{kT} \exp \left(\frac{\Delta G_{\eta}^{\neq}}{RT} \right), \quad (9)$$

where k is the Boltzmann constant. The thermodynamic parameters of a viscous flow relevant to our model and the relaxation times of the shear viscosity are quoted in Table.

4. Discussion of Results

Among all halogens, fluorine has the smallest van der Waals atomic radius (0.135 nm), close to the radius of a hydrogen atom (0.12 nm) [11]. Therefore, when hydrogen atoms are substituted by fluorine ones, the size of an alcohol molecule changes insignificantly. For example, as was shown in work [12], the introduction of a fluorine atom into a benzene molecule results in the growth of the fluid molar volume by 6%, which is associated just with the increase in the effective volume of fluid molecules. At the same time, the molecular mass becomes more than twice as large. The parameters of the intermolecular interaction are changed considerably in this case: intermolecular bonds of the type C-H...H in alcohols transform into bonds of the type C-F...H in their fluorinated analogs [13]. The substitution of hydrogen atoms by halogen ones results in the increase of

Thermodynamic parameters of a viscous flow in the objects under study

Substance	$\Delta H_{\eta}^{\ddagger}$, kJ/mole	$\Delta S_{\eta e}^{\ddagger}$, kJ/(mole K)	$\Delta G_{\eta e}^{\ddagger}$, kJ/mole	$\Delta S_{\eta}^{\ddagger}$, kJ/(mole K)	$\Delta G_{\eta}^{\ddagger}$, kJ/mole	$\tau_{\eta} \times 10^{11}$, s
Propanol	17.2	8.5	14.4	14.1	12.8	6.8
TFP	22.9	18.6	16.9	44.5	9.3	21.1
Pentanol	20.1	10.4	16.8	15.9	15.1	18.3
OFP	29.3	28.9	20.0	54.8	12.4	87.0
Heptanol	22.5	12.8	18.4	18.3	16.8	28.1
DFH	35.3	42.1	22.3	68.1	14.7	173.8

the adiabatic and isothermal compressibilities of the fluid, with the effect depending on the halogen number in the Periodic table, whereas the character of their temperature dependences remains invariable in whole [12]. According to the researches [14], the values of the free enthalpy of the activation of a viscous flow in one-atomic alcohols coincide with the experimental values of free enthalpy of the activation of the acoustic relaxation to within the accuracy of experimental errors.

In the framework of the considered Eyring model theory, it follows that, within a group of fluids with a similar molecular structure, the shear viscosity is larger for fluids with a higher energy of the collective interaction between particles and with a higher activation energy for a viscous flow. The critical temperature and the latent evaporation heat of a fluid also increase at that [15]. Formulas (3)–(9) are used to calculate the thermodynamic parameters of a viscous flow in the examined fluids. The kinetic compensation effect is detected, which allowed the thermodynamic parameters of a viscous flow to be analyzed and their true values to be found (Table). The empirical coefficient A is determined from Fig. 3 and equals $A_S = 6.87$ kJ/mole for aliphatic alcohols and $A_{FS} = 13.57$ kJ/mole for their fluorinated analogs. The isokinetic temperature T^* was found to be lower for fluorinated alcohols ($T_{FS}^* = 421$ K) than for aliphatic ones ($T^* = 542$ K). The values obtained for the isokinetic temperatures are in good agreement with the data obtained for aqueous electrolyte solutions (see work [16]), which testifies to the correspondence of the vibration frequencies for those bonds of the center of an activated complex that become broken in a viscous flow. The analysis of Fig. 3 allowed us to calculate the value of transmission coefficient for a number of non-fluorinated alcohols ($\chi_S = 1.5 \times 10^{-2}$) and for a number of their

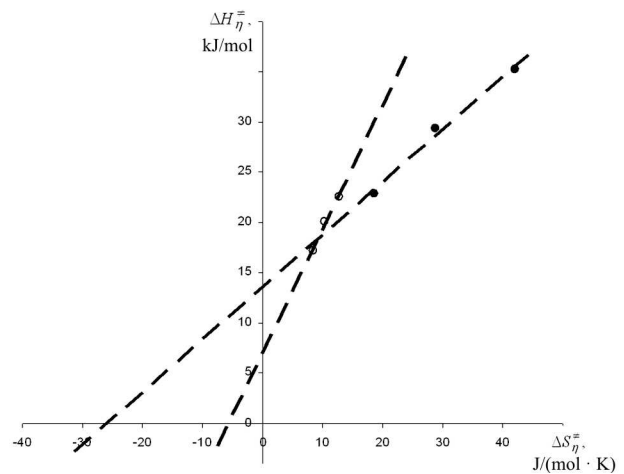


Fig. 3. Dependences of the viscous flow activation enthalpy $\Delta H_{\eta}^{\ddagger}$ on the entropy $\Delta S_{\eta e}^{\ddagger}$ for the studied normal aliphatic alcohols (—○—) and fluorinated alcohols (—●—)

fluorinated analogs ($\chi_{FS} = 1.3 \times 10^{-3}$). In the framework of the selected model, all the aforesaid testifies that the probability for a transition state to emerge in the active complex is lower for fluorinated alcohols in comparison with non-fluorinated ones. Therefore, the fluorinated aliphatic alcohols are more structured than non-fluorinated ones [6].

It is found that if the lateral hydrogen atoms are substituted by fluorine ones, the enthalpy of the activation of a viscous flow increases. This fact can be explained, if we assume that a larger number of bonds have to be broken in order to maintain the excitation energy in the active complex at a required level: the fluctuation of the active complex energy ΔE^+ increases in fluorinated alcohols.

The growth of the shear viscosity relaxation time in the normal alcohol–its fluorinated analog pairs is more considerable if more hydrogen atoms were substituted, which can be associated with the increase

in the volume and, especially, the mass of associates participating in a viscous flow.

5. Conclusions

Our experimental researches have shown that if hydrogen atoms in normal aliphatic alcohols are substituted by fluorine ones, the shear viscosity and the density of fluorinated alcohols increase: the larger the number of substituted atoms in the alcohol molecule, the larger is the growth.

The analysis of the thermodynamic parameters of a viscous flow at the substitution of hydrogen atoms in the molecule of a normal aliphatic alcohol by fluorine atoms testifies to the molecular processes of the same type in the series of both non-fluorinated and fluorinated aliphatic alcohols. In the thermodynamic parameters of a viscous flow in fluorinated alcohols, the entropic factor plays a more considerable role against the expected growth of the enthalpic factor.

The calculated thermodynamic parameters agree well with the values obtained for other fluid systems. They testify that fluorinated aliphatic alcohols are more structured in comparison with normal ones.

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ВПЛИВ ФТОРУВАННЯ НОРМАЛЬНИХ АЛІФАТИЧНИХ СПИРТІВ НА ЇХ ФІЗИЧНІ ВЛАСТИВОСТІ

Резюме

Досліджено реологічні властивості нормальних аліфатичних спиртів та їх фторзаміщених аналогів. Показано, що температурні залежності густини та кінематичної в'язкості фторзаміщених та нормальних спиртів мають подібний характер. Встановлено зростання густини фторзаміщених спиртів. При цьому їх зсувна в'язкість зростає тим відчутніше, чим більше атомів водню замінено атомами фтору в молекулі спирту. Розраховані термодинамічні величини в'язкої течії, які вказують на те, що фторзаміщені аліфатичні спирти є більш структурованими у порівнянні з нормальними спиртами.