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TEMPERATURE DEPENDENCE OF THE BULK ELASTICITY MODULUS OF ALIPHATIC ALCOHOLS AND THEIR FLUORINATED ANALOGS

The density of some fluorinated and non-fluorinated normal monoatomic alcohols and the sound propagation velocity in them have been studied experimentally in a temperature interval of 293–363 K. The bulk modulus of elasticity is calculated, and its relation with the intermolecular interaction energy is analyzed. The energy of intermolecular interaction in fluorinated alcohols is shown to be lower than in their non-fluorinated analogs. The substitution of hydrogen atoms by fluorine ones in the molecules of aliphatic alcohols increases the equilibrium distance between the molecules.

Keywords: fluorinated alcohols, sound velocity, elasticity modulus, intermolecular interaction.

1. Introduction

Fluorinated alcohols are widely used in industry as coolants and refrigerants, in medicine as anesthetics and blood substitutes, and in agriculture as pesticides and dyes. They also play the role of intermediate products in organic synthesis, as well as monomers for the fabrication of polymer materials [1–3].

Despite the fluorinated alcohols are widely used in various domains, their physical properties have been studied much worse than the properties of non-fluorinated alcohols [4]. However, it is of interest to trace the changes in the physical properties of alcohols, when the latter are subjected to the fluorination. The aim of this work is to study the acoustic and rheologic properties of fluorinated monoatomic alcohols and to analyze the fluorination effect on the physical properties of alcohols.

2. Experimental Part

It is known that the velocity c of sound propagation in visco-elastic media, including alcohols, is related

to the bulk elasticity modulus K by the formula

$$c = \sqrt{K/\rho}, \quad (1)$$

where ρ is the medium density. Therefore, in order to study the temperature dependence of the bulk elasticity modulus in alcohols and how fluorination affects this behavior, a number of experiments were carried out, in which the velocity of sound propagation was measured at various temperatures. Both non-fluorinated (ethanol-1, propanol-1, and heptanol-1) and fluorinated (2,2,2-trifluoroethanol-1; 2,2,3,3,3-pentafluoropropanol-1; 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptanol-1; and 1H,1H-tridecafluoroheptanol-1) aliphatic alcohols were selected for researches.

Experimental measurements were carried out in a temperature interval of 293–363 K. The density ρ was determined with an error of 0.05% within the pycnometric method. The sound propagation velocity c was measured, by using the pulsed method of varied distance at a frequency of 27.5 MHz. The total measurement error for the sound propagation velocity was equal to 1%. The methods used in the measurements for those quantities were described in work [5] in detail.

In Figs. 1 and 2, the experimental temperature dependences of the sound propagation velocity in non-fluorinated (ethanol-1, propanol-1, and heptanol-1) and fluorinated (2,2,2-trifluoroethanol-1; 2,2,3,3,3-pentafluoropropanol-1; 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptanol-1; and 1H,1H-tridecafluoroheptanol-1) alcohols, respectively, are shown. As one can see, the sound velocity in both the non-fluorinated and fluorinated alcohols almost linearly depends on the temperature in the examined temperature interval. The sound velocity in the fluorinated alcohols is much lower than in their non-fluorinated analogs. As the temperature increases, the velocity of sound propagation decreases.

The insets in Figs. 1 and 2 demonstrate the dependence of the sound propagation velocity on the molar mass of alcohols at the temperature $T = 293$ K. For the non-fluorinated alcohols, the sound propagation velocity increases with the molar mass. For the fluorinated alcohols, the situation is inverse: with increasing the molar mass, the sound propagation velocity decreases.

Using the measured values for the density of alcohols and the velocity of sound propagation in them, the value of the bulk modulus of elasticity K was calculated from formula (1). Furthermore, the temperature dependences of this parameter were analyzed for the non-fluorinated alcohols and their fluorinated analogs. Those dependences are similar to one another, and they will be analyzed below in the framework of the hole model of liquid structure.

3. Discussion of Results

In work [6], on the basis on the hole model for the liquid structure and by analyzing experimental data, it was shown that the temperature dependence of the low-frequency elasticity modulus K in alcohols is described by the equation

$$K = \frac{\gamma RT}{V_\mu} \exp\left(\frac{\Delta G}{RT}\right), \quad (2)$$

where $\gamma = C_P/C_V$ is the ratio between the heat capacities at a constant pressure and a constant volume, R the universal gas constant, and V_μ the molar volume. The parameter

$$\Delta G = \Delta H - T\Delta S \quad (3)$$

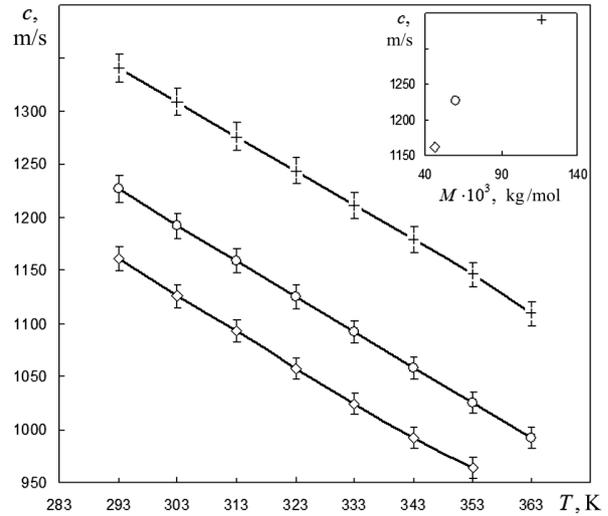


Fig. 1. Temperature dependences of the sound propagation velocity in non-fluorinated alcohols: ethanol-1 (\diamond), propanol-1 (\circ), and heptanol-1 ($+$). The dependence of the sound velocity on the molar mass in non-fluorinated alcohols at a temperature of 293 K is shown in the inset

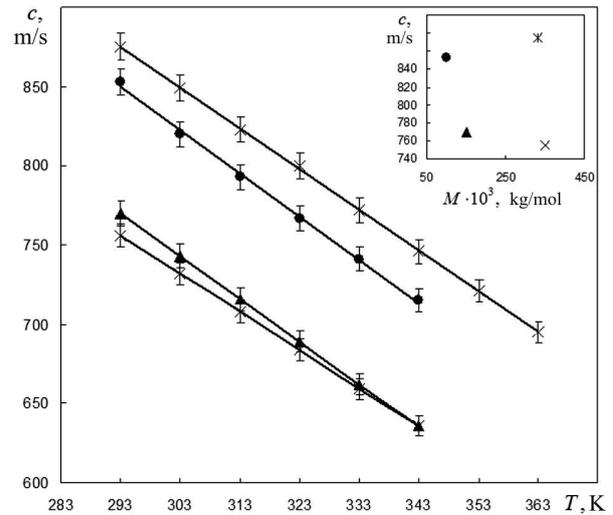


Fig. 2. Temperature dependences of the sound propagation velocity in fluorinated alcohols: 2,2,2-trifluoroethanol-1 (\bullet); 2,2,3,3,3-pentafluoropropanol-1 (\blacktriangle); 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptanol-1 ($*$), and 1H,1H-tridecafluoroheptanol-1 (\times). The dependence of the sound velocity on the molar mass in fluorinated alcohols at a temperature of 293 K is shown in the inset

is a change of the Gibbs potential per one mole at the hole formation, where ΔH and ΔS are the corresponding changes of the specific enthalpy and the specific entropy, respectively. Then Eq. (2) can be rewritten

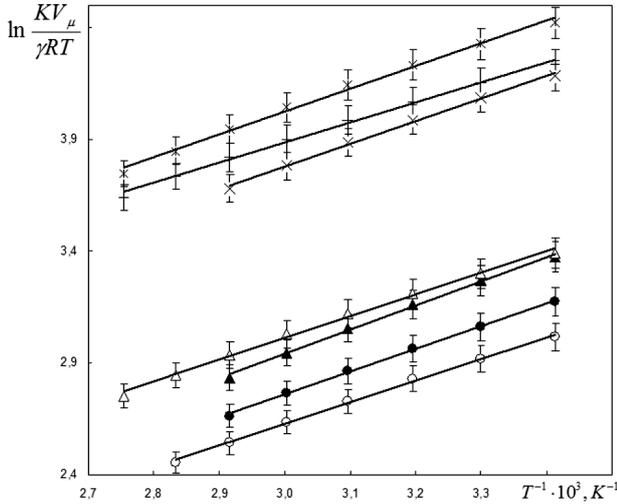


Fig. 3. Dependences of the quantity $\ln \frac{KV_\mu}{\gamma RT}$ on the inverse temperature for ethanol-1 (\diamond), trifluoroethanol-1 (\bullet), propanol-1 (\circ), pentafluoropropanol-1 (\blacktriangle), heptanol-1 ($+$), dodecafluoroheptanol-1 ($*$), and tridecafluoroheptanol-1 (\times)

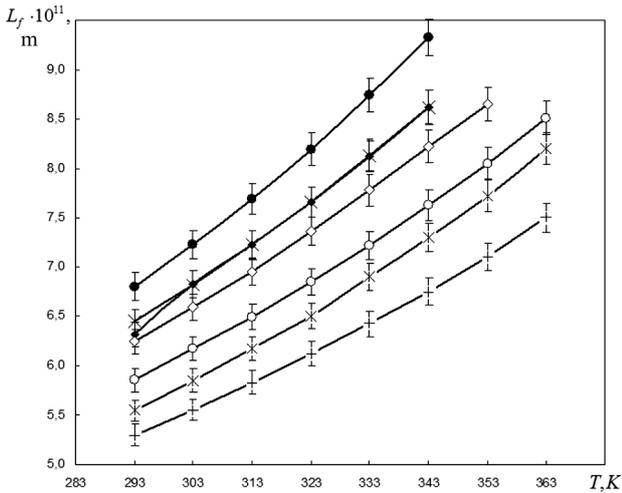


Fig. 4. Temperature dependences of the intermolecular distance L_f for ethanol-1 (\diamond), trifluoroethanol-1 (\bullet), propanol-1 (\circ), pentafluoropropanol-1 (\blacktriangle), heptanol-1 ($+$), dodecafluoroheptanol-1 ($*$), and tridecafluoroheptanol-1 (\times)

ten in the form

$$K = \frac{\gamma RT}{V_\mu} \exp\left(\frac{\Delta H}{RT} - \frac{\Delta S}{R}\right). \quad (4)$$

From whence, it follows that

$$\ln \frac{KV_\mu}{\gamma RT} = \frac{\Delta H}{RT} - \frac{\Delta S}{R}. \quad (5)$$

Hence, the quantity on the left-hand side of Eq. (5) has to be a linear function of the inverse temperature within the experimental error limits. In Fig. 3, this dependence is shown for the examined alcohols. The results obtained allowed us to determine the specific enthalpy ΔH for the researched non-fluorinated alcohols and their fluorinated analogs. The corresponding data are quoted in the second column of Table.

The analysis of those data testifies that the fluorination increases the specific enthalpy of hole formation. In work [7], it was shown that, in the framework of the hole model, the ratio between the hole, V_0 , and molecule, V_M , volumes equals

$$\frac{V_0}{V_M} = \frac{\Delta H}{\Delta H_V}, \quad (6)$$

where ΔH_V is the specific enthalpy of vaporization. The entropy of vaporization is known to be directly related to the potential of intermolecular interaction [8]: the larger the magnitude of intermolecular interaction, the larger the enthalpy of vaporization.

The enthalpy of vaporization at the normal boiling temperature can be calculated, by using the Kistiakowsky method [9]. The corresponding values for the researched alcohols are shown in the third column of Table. The analysis of the presented data testifies

Influence of the fluorination on the specific enthalpy of hole formation ΔH , the specific enthalpy of vaporization ΔH_V , and the average intermolecular distance L_f

Substance	ΔH , kJ/mol	ΔH_V , kJ/mol	$\frac{V_0}{V_M}$	$L_f \times 10^{11}$, m
Ethanol-1 C_2H_5OH	7.6	39.4	0.19	6.25
Propanol-1 C_3H_7OH	8.6	41.7	0.21	5.86
Heptanol-1 $C_7H_{15}OH$	6.6	51.7	0.13	5.30
Trifluoroethanol-1 CF_3CH_2OH	8.2	38.7	0.21	6.32
Pentafluoropropanol-1 $CF_3CF_2CH_2OH$	9.1	39.6	0.23	6.80
Dodecafluoroheptanol-1 $H(CF_2)_6CH_2OH$	7.7	50.8	0.15	5.55
Tridecafluoroheptanol-1 $F(CF_2)_6CH_2OH$	8.4	47.9	0.18	6.45

that the fluorination reduces the specific enthalpy of vaporization in alcohols and, accordingly, reduces the intermolecular interaction. Going further and using formula (6) in the framework of the hole model for liquids, we can find the ratio between the volumes of a hole and an alcohol molecule. The results of corresponding calculations are given in the fourth column of Table. As one can see, the substitution of hydrogen atoms in the alcohol molecules by fluorine ones increases the hole volume with respect to the molecule volume.

In the framework of the hole model and using the data of the acoustic experiment, the average intermolecular distance L_f can be estimated [10]:

$$L_f = \frac{K_J}{\sqrt{K}}. \quad (7)$$

Here, K_J is the Jacobson constant, which is a dimensional quantity and depends on the temperature [10]. The temperature dependences of the intermolecular distance L_f , which were calculated for the examined alcohols on the basis of the corresponding temperature dependences of the bulk elasticity modulus, are depicted in Fig. 4. The analysis of the plots shows that the fluorination of alcohols increases the average intermolecular distances in them. Those results obtained in the framework of the hole model correlate with the results of X-ray diffraction experiments [11] and molecular dynamics simulation [12]. In particular, in the cited works, it was shown that the substitution of a hydrogen atom in the molecules of organic compounds by a fluorine atom increases the average distance between the molecules.

4. Conclusions

To summarize, the researches of the temperature dependences of the sound propagation velocity in ethanol-1; propanol-1; heptanol-1; 2,2,2-trifluoroethanol-1; 2,2,3,3,3-pentafluoropropanol-1; 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptanol-1; and 1H,1H-tridecafluoroheptanol-1, as well as the densities of those liquids are carried out. The temperature dependences of the bulk elasticity modulus for the indicated alcohols are calculated. The enthalpies of formation of one mole of holes in the mentioned alcohols are found in the framework of the hole model. In the non-fluorinated alcohols, the energy of intermolecular interaction is shown to be higher, and the average distance between the molecules shorter than in their fluorinated analogs.

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ТЕМПЕРАТУРНА ЗАЛЕЖНІСТЬ ОБ'ЄМНОГО
МОДУЛЯ ПРУЖНОСТІ АЛІФАТИЧНИХ СПИРТІВ
ТА ФТОРОВАНІХ ЇХ АНАЛОГІВ

Р е з ю м е

Експериментально досліджені швидкість поширення звуку та густина низки фторованих та нефторованих нормальних одноатомних спиртів в температурному інтервалі 293–363 К. Розраховано об'ємний модуль пружності, проаналізовано його зв'язок з енергією міжмолекулярної взаємодії. Показано, що у фторованих спиртах енергія міжмолекулярної взаємодії менша, ніж у їх нефторованих аналогах. Заміщення атомів водню на атоми фтору в молекулах аліфатичних спиртів призводить до збільшення рівноважної відстані між молекулами.