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EXTRAORDINARY PROPERTIES OF ALCOHOLS FROM THE HOMOLOGOUS SERIES OF METHANOL

Non-trivial properties of thermodynamic quantities such as the density, the critical and triple point temperatures, and their ratio, as well as the optical and dielectric properties, have been analyzed for primary alcohols from the methanol series. The aim is to reveal relationships among their values measured at the same temperatures for alcohols with different ordinal numbers m's in the methanol series. It is shown that the non-monotonic character of the temperature dependences of alcohol densities is associated with methanol rather than ethanol, as may seem at first glance. The critical temperature of methanol also deviates from the quasilinear dependence of the critical alcohol temperatures on m. With the growing m, the ratio between the critical and triple-point temperatures for alcohols is shown to tend to the corresponding value for water. Simple linear dependences of the electronic and effective static polarizabilities of alcohol molecules on m are established. The transverse and longitudinal components of the polarizability tensor for alcohol molecules are found. The dipole moments of the closest neighbor molecules in the alcohols are proved to anticorrelate, i.e. to orient in opposite directions.

Keywords: monohydric primary alcohols, density, optical and dielectric properties.

1. Introduction

In this work, we will analyze the physical properties of alcohols from the methanol series: methanol, ethanol, propanol, and so forth. Those alcohols are characterized by structural formulas of the type $CH_3(CH_2)_{m-1}OH$, where m is the ordinal number of alcohol in the methanol homologous series. Depending on the hydroxyl group location, they are classified either to primary alcohols (Fig. 1, *a*) or to their isomers (Fig. 1, *b*).

Methanol corresponds to the value $m = 1$, ethanol to the value $m = 2$, and so on. From Fig. 1, it is clear that primary alcohols are formed by replacing either of hydrogen atoms in the water molecule, $H_2O =$ $=$ HOH, with the group $CH_3(CH_2)_{m-1}$. In this case, the oxygen in primary alcohols becomes located in the line formed by the carbon atoms (see Fig. 1, *a*), and the angle between this line and the line connecting the oxygen atom with the hydrogen one is close to 104°,

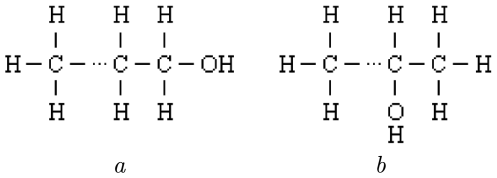


Fig. 1. Structural formulas of monohydric alcohols $CH_3(CH_2)_{m-1}OH$: primary or normal alcohols (*a*), one of possible isomers or secondary alcohols (*b*)

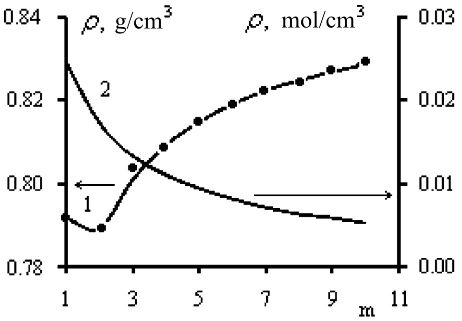


Fig. 2. Dependences of the mass (*1*) and number (*2*) densities of alcohols from the homologous series of methanol on ordinal number m of alcohol. Solid curve *1* was calculated by formula (4), circles correspond to experimental data [3]

i.e., to the valence angle in a water molecule. Similar values of the C–O–H angles are also typical of alcohol isomers.

From the facts given above, it follows that there must be a certain similarity between the properties of water and those of primary alcohols in the methanol series. However, it should be added at once that the molecules of primary alcohols can only form two hydrogen bonds with their nearest neighbors, whereas water molecules can form four such bonds. As a result, the molecules of water in the liquid state, at least near the triple point, can form a spatial network of hydrogen bonds, whereas the molecules of primary alcohols can only form linear chains. Those chains can approach one another to form loops, and those loops can cling to one another and form non-compact spatial structures [1]. It is clear that the difference in the spatial ordering of hydrogen bonds will affect, in some way, the properties of water and primary alcohols. This circumstance is particularly significant in relation to the living matter origin. It is still unclear why water considerably differs from other liquids – first of all, from the primary alcohols of the methanol series – and why it is a basis of all living things.

Taking the aforesaid into account, we will intend to analyze the following most general properties of water and primary alcohols:

- the dependences of their fractional volumes per molecule on the ordinal number m of alcohol in the methanol series;
- specific features in the dependence of the light refractive index depending on m or, in other words, the relationship between the light refractive indices of different alcohols and the electronic polarizations of their molecules;
- a specific character of the formation of the static dielectric permittivity of alcohols in the methanol series.

The research results obtained for the indicated physical properties of certain alcohols were published in a number of books (see, e.g., [2, 3]). The most attention was paid to ethanol [2–5] and methanol [3–6], which is naturally explained by their widespread applications to chemistry, pharmacology, and cosmetics. However, the dependence of the properties of indicated, as well as other, primary alcohols on their position in the homologous series remained, as a rule, beyond consideration.

In the future, we are going to study the caloric properties of alcohols. The researches will be based on experimental data, including the data obtained at Taras Shevchenko National University of Kyiv while studying the homologous series of monohydric alcohols from methanol to decanol with the use of vibrational spectroscopy methods [7, 8].

2. Densities of Primary Alcohols from the Methanol Series

The most common characteristic of alcohols, as well as all other liquids, is their mass density ρ (g/cm^3). The values of this parameter measured for the primary alcohols from the homologous series of methanol at a temperature of 20 °C are plotted by curve *1* in Fig. 2 as a function of the ordinal number m of alcohol in the homologous series. A non-monotonic character of this dependence is evident: ethanol, which corresponds to $m = 2$, deviates from the monotonic dependence formed by the densities of all other alcohols. However, whether the minimum in curve *1* is an indicator of a certain specific molecular structure of ethanol or not can be understood only after an additional analysis. First of all, it is worth changing from

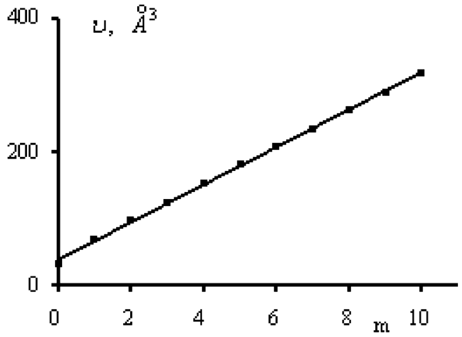


Fig. 3. Specific volume per molecule for alcohols from the homologous series of methanol at a temperature of 20 °C as a function of their ordinal number m. The value $m = 0$ corresponds to water

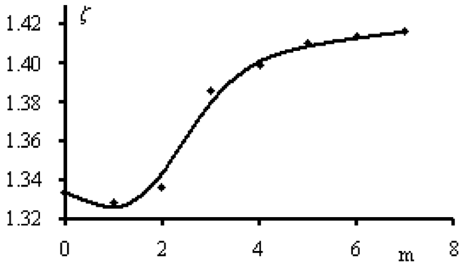


Fig. 4. Refractive indices of primary alcohols from the methanol series as a function of their ordinal number m according to experimental data [3]. The value $m = 0$ corresponds to water

the mass density of alcohols to the number density $n = \rho/M$, where M is the mass of the specific alcohol molecule (see curve *2* in Fig. 2). As one can see, the number density of primary alcohol molecules does not reveal any specific features: it decreases monotonically with the increasing number m, which is naturally explained by a decrease in the packing degree of molecules, as their length increases.

Even more illustrative is the dependence of the reciprocal number density – or the specific volume per molecule, v_m – on the number m: $v_m(m) = 1/n(m)$ (see Fig. 3). One may verify that the specific volumes of primary alcohols at a temperature of 20 °C for m-values starting from ethanol ($m = 2$) satisfy the formula

$$v_m[\text{Å}^3] \approx 97 + 27.45(m-2), \tag{1}$$

in which $v_{\text{eth}} = 97$ Å^3 corresponds to the specific volume of an ethanol molecule. The error of relationship (1) does not exceed 0.01. The application of formula (1) to the determination of the specific methanol volume ($m = 1$) gives the value $v_{\text{meth}} \approx 69.48$ Å^3, which slightly exceeds the experimental value $v_{\text{meth}} \approx 67$ Å^3. Accordingly, formula (1) can be generalized as follows:

$$v_m[\text{Å}^3] \approx 96.9 - 2.36\,\delta_{m1} + 27.45(m-2), \tag{2}$$

where δ_{m1} is the Kronecker delta.

It should be noted that the linear increase of the specific volume v_m with the ordinal number m of primary alcohols in the methanol series is naturally explained by the thermal rotation of alcohol molecules, mainly around the axis formed by the carbon atoms and the oxygen. Qualitatively, the rotation of methanol molecules around the C–O axis has the same character, but the angular rotational velocity is significantly higher due to a lower moment of inertia. Therefore, the role of hydrogen bonds in the formation of a specific volume diminishes for methanol. In works [9–11], it was shown that the account for hydrogen bonds increases the specific volume of a molecule by a few percent.

Thus, a conclusion can be drawn that the specific volume of methanol – rather than ethanol, as may seem from the behavior of alcohol densities – deviates from the mutual dependence for primary alcohols with higher ordinal numbers. The specific volume of water also demonstrates a substantial deviation from the linear dependence (1): $v_{\text{w}} \approx 30.6$ Å^3. But this effect is associated with a significant change in the rotation character of its molecules.

The minimum in the density of primary alcohols is described by the following formulas. By definition, the density of the m-th primary alcohol equals $\rho = M_m/v_m$. With regard for formula (2), as well as

$$M_m = M_{\text{meth}} + (m-1)M(\text{CH}_2),$$

where $M(\text{CH}_2)$ is the mass of the CH$_2$ group, the molecular mass of alcohol with the number m looks like

$$M_m = [32 + 14(m-1)] \times 1.66 \times 10^{-24}.$$

As a result,

$$\rho_m = \frac{[32 + 14(m-1)] \times 1.66}{96.9 - 2.36\delta_{m1} + 27.45(m-2)}. \tag{3}$$

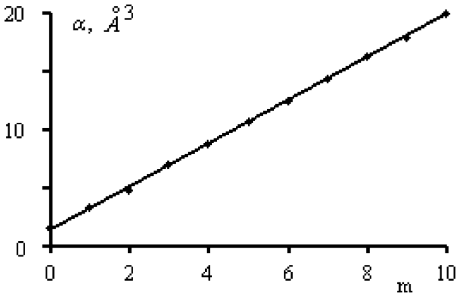


Fig. 5. Molecular polarizability of primary alcohols from the methanol series as a function of their ordinal number m [4]. The value $m = 0$ corresponds to water

An agreement between the alcohol densities calculated by formula (3) and experimental data is illustrated in Fig. 2. As one can see, the density ρ_m is minimum at $m = 2$.

3. Refractive Indices of Primary Alcohols from the Methanol Series

The refractive index ζ of a system is its simplest polarization characteristic. It is determined by the properties of electron shells in the molecules. The dependence of the parameter ζ for primary alcohols on their ordinal number in the methanol series (see Fig. 4) is rather complicated and does not allow the regularities of its formation to be understood. The deviations of the refractive indices for methanol and ethanol from the mutual dependence are especially noticeable.

The complicated character of the refractive index behavior arises due to the fact that it is formed (see work [12]) by both the electronic polarizability of alcohol molecules α and their concentration $n = \rho/M$:

$$\frac{\zeta^2 - 1}{\zeta^2 + 2} = \frac{4\pi}{3}\frac{\rho}{M}\alpha.$$

From whence, it follows that the molecular polarizability α of alcohol molecules may have a much simpler dependence on m. This expectation is completely confirmed by Fig. 5.

The polarizability values of alcohol molecules can be approximated by the formula

$$\alpha(m) = 1.53 + 1.845m \tag{4}$$

with an acceptable accuracy. To interpret the coefficient values in Eq. (4), it is pertinent to use the additive model [12–15] for the molecular polarizability. According to this model, the polarizability of a molecule can be calculated as the sum of polarizabilities of its fragments,

$$\alpha(m) = \alpha(\mathrm{H_2O}) + m \times \alpha(\mathrm{CH_2}), \tag{5}$$

where $\alpha(\mathrm{H_2O})$ and $\alpha(\mathrm{CH_2})$ are the polarizabilities of the water molecule and the $\mathrm{CH_2}$ group, respectively. The comparison of Eqs. (4) and (5) makes it possible to assert that

$$\alpha(\mathrm{H_2O}) \approx 1.35\ \text{Å}^3, \quad \alpha(\mathrm{CH_2}) \approx 1.845\ \text{Å}^3.$$

However, the polarizability of an isolated water molecule is somewhat higher [16],

$$\alpha(\mathrm{H_2O}) \approx 1.41\ \text{Å}^3,$$

whereas the polarizability of an alkyl group is somewhat lower [4]:

$$\alpha(\mathrm{CH_2}) \approx 1.77\ \text{Å}^3.$$

As was shown in work [15], those discrepancies in the polarizability values can be eliminated, if two-particle effects are taken into account.

Note that the polarizability of elongated molecules of primary alcohols has a tensor character. In a rather satisfactory approximation, the polarization tensor of primary alcohol molecules can be represented in the form

$$\alpha_{ik} = \alpha_i\delta_{ik} + (\alpha_l - \alpha_t)\mathbf{e}_i\mathbf{e}_k,$$

where α_t and α_l are the transverse and longitudinal, respectively, components of the polarization tensor, and $\mathbf{e}$ is the unit vector directed along the symmetry axis formed by the carbon and oxygen atoms. It is clear that it is the longitudinal component of the polarizability that is a function of m: $\alpha_l = \chi m$. The refractive index α of the system is determined by the polarization tensor averaged over the molecular orientations: $\langle\alpha_{ik}\rangle = \alpha\delta_{ik}$. Therefore, we obtain

$$\alpha = \frac{1}{3}(\alpha_l + 2\alpha_t) \Rightarrow \frac{1}{3}(2\alpha_t + \chi m).$$

By comparing this expression with Eq. (4), we find that

$$\alpha_t = 2.025\ \text{Å}^3, \quad \chi = 5.535\ \text{Å}^3.$$

4. Static Dielectric Permittivities of Alcohols from the Methanol Series

As was done in the previous section, our main attention will be focused on the behavior of the effective polarizability of alcohol molecules (see Fig. 6),

$$\alpha_{\rm eff} = \frac{3}{4\pi n}\frac{\varepsilon - 1}{\varepsilon + 2},$$

where ε is the low-frequency (static) limit of the dielectric permittivity of the system. Let us analyze the dependence of $\alpha_{\rm eff}$ on the temperature T and the ordinal number m of alcohol in the methanol series. The temperature dependence of $\alpha_{\rm eff}$ is an important characteristic, because it allows us to understand the mechanism of formation of system's static dielectric permittivity.

The temperature dependences of $\alpha_{\rm eff}$ for methanol, ethanol, and water at their coexistence curves are shown in Fig. 6. To a certain extent, they resemble the behavior of the effective polarizability for a gas, whose molecules possess own dipole moments $\mathbf{d}$,

$$\alpha_{\rm eff} = \alpha_{\rm el}\left(1 + \frac{t_d}{t}\right). \tag{6}$$

Here, $\alpha_{\rm el} = \alpha_{\rm el}(m)$ is the contribution made by the electron shells of alcohol molecules (see Eq. (4)) to the polarizability, $t = T/T_{\rm c}$ is the dimensionless temperature, $T_{\rm c}$ is the critical temperature of the systems, and $t_d = |\mathbf{d}|/(3k_{\rm B}T_{\rm c}\alpha_{\rm el})$. Note that the curves in Fig. 6 are cut off at the left side, because there are no reliable experimental values for the dielectric permittivities of alcohols at the temperatures $T < 1.5T_{\rm c}$.

For alcohols in the liquid state, owing to strong electrostatic interaction between their molecules, the values of the parameters a and b in the formula

$$\alpha_{\rm eff} = \alpha_{\rm el}\left(a + \frac{b}{t}\right) \tag{7}$$

should be significantly different from the corresponding values 1 and t_d in formula (6). By expressing the parameter b in the form

$$b = \gamma(t)t_d,$$

where

$$\gamma(t) = \gamma_0\left(1 + \frac{c}{t} + ...\right),$$

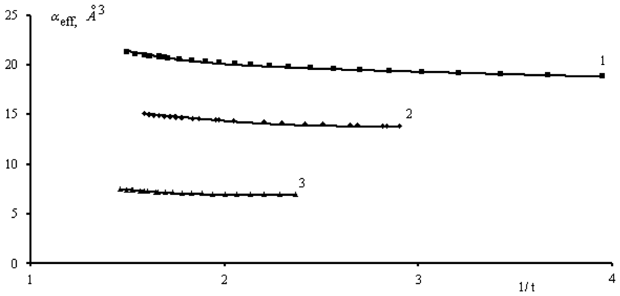


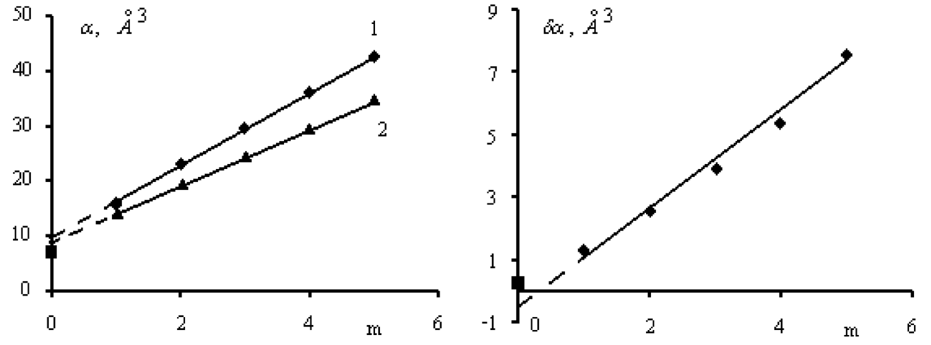
Fig. 6. Effective polarizabilities of ethanol (*1*), methanol (*2*) and water (*3*) molecules at a temperature of 20 °C. Experimental values for the dielectric permittivity were taken from works [17–22] for methanol and works [23, 24] for ethanol

we obtain the values of the coefficients t_d, a, γ_0, and c for methanol, ethanol, and water that are quoted in Table. The closeness of the coefficient values obtained for alcohols supports our expectation concerning the similarity among the temperature dependences of the effective static polarizability for the primary alcohols from the methanol series.

As one can see, the most non-trivial facts are as follows: (i) the values of the coefficient a in formula (7) are much larger than unity for both methanol and ethanol; and (ii) the values of the coefficient b in Eq. (7) for both methanol and ethanol are appreciably smaller as compared with the corresponding values of the coefficients a in the liquid state of alcohols (note that the situation for their vapors is opposite). But a more significant fact is that they have a negative sign. This circumstance radically distinguishes their origin from that of their vapors at the coexistence curves. It is important to note that the effective polarization of water demonstrates the same features in its behavior [25, 26]. In the case of water, such a behavior is associated with the thermal excitation of clusters formed in water and with strong orientational correlations that only result in the appearance of fluctuation dipole moments in clusters.

Parameters t_d, a, γ_0, and c for primary alcohols and water

Substance	t_d	a	γ_0	c
Water	8.86	7.82	−0.320	−0.230
Methanol	4.075	5.82	−0.258	−0.165
Ethanol	2.834	7.64	−0.345	−0.144



a *b*

Fig. 7. Dependences of (*1*) α_{eff} and (*2*) α_{eff} (panel *a*) and $\delta\alpha_{\text{eff}}$ (panel *b*) on m. The squares at $m = 0$ correspond to water: $\alpha_{\text{eff}} = 7.156$ Å^3, $\alpha_{\text{eff}} = 6.897$ Å^3, and $\delta\alpha_{\text{eff}} = 0.259$ Å^3

The anticorrelation of dipole moments in neighbor alcohol molecules is also supported by the Kirkwood theory of dielectric permittivity [27]. As follows from this theory,

$$\gamma = 1 + z\,\overline{\cos\Theta},$$

where z is the number of the nearest neighbors, and $\overline{\cos\Theta}$ is the average cosine of the angle between the dipole moments in the neighbor molecules. It is clear that the parameter γ becomes negative only provided that

$$\overline{\cos\Theta} < -\frac{1}{z},$$

which corresponds to almost opposite directions of the dipole moments in the nearest neighbor molecules. This circumstance was also marked in work [28], and it is in accordance with the requirement that the average energy of the electrostatic field in the system should be minimum.

Further conclusions about the values and the character of the effective polarizability of primary alcohol molecules can be drawn from the following consideration. Since the dielectric permittivities of primary alcohols, as well as that of water, satisfy the inequality $\varepsilon \gg 1$, we have

$$\alpha_{\text{eff}} = \frac{3}{4\pi}v\left(1 - \frac{3}{\varepsilon} + ...\right).$$

From whence, it follows that α_{eff} looks like

$$\alpha_{\text{eff}} = \alpha_{\text{eff}} + \delta\alpha_{\text{eff}},$$

where the major contribution to the polarizability equals

$$\alpha_{\text{eff}}(m) = \frac{3}{4\pi}v_m \Rightarrow \frac{3}{4\pi}[v_{\text{meth}} + 27.6(m-1)],$$

and the small correction $\delta\alpha_{\text{eff}}$ is the very component that is responsible for the dielectric permittivity value,

$$\varepsilon_m \approx \frac{9}{4\pi}\frac{v_m}{\delta\alpha_{\text{eff}}(m)}. \tag{8}$$

Relation (8) for primary alcohols is somewhat enigmatic today, although it is consistent with dimensionality considerations. Analogously, the meaning of the equation

$$a_m + \frac{b_m}{t} \approx \frac{3}{4\pi}\frac{v_m}{\alpha_{\text{el}}(m)} \tag{9}$$

at every temperature still remains obscured, although it may point at a certain relation with the second virial coefficient. This relation will be discussed in a separate paper in more details.

The deviations of α_{eff}-values from α_{eff}-ones are shown in Fig. 7. The linear character of the dependences of the quantitiesα_{eff}, α_{eff}, and $\delta\alpha_{\text{eff}}$ on the ordinal number m of primary alcohols is described by the formulas

$$\begin{aligned} &\alpha_{\text{eff}}(m) = 9.99 + 5.14m, \\ &\alpha_{\text{eff}}(m) = 9.53 + 6.69m, \\ &\delta\alpha_{\text{eff}}(m) = -0.46 + 1.55m. \end{aligned} \tag{10}$$

As a result, the dielectric permittivity of primary alcohols from the methanol series is determined by the relation

$$\varepsilon_m \approx -\frac{9}{4\pi}\frac{v_{\text{meth}} + 27.54(m-1)}{1.09 + 1.55(m-1)}.$$

The closeness of the corresponding polarizability values for water to the linear formulas (10) extrapolated to $m = 0$ is an extremely interesting fact, although not entirely clear.

Finally, let us briefly consider the dependence of the intrinsic dipole moments of alcohol molecules on their ordinal number m in the methanol series. The values of dipole momentscorresponding to the gaseous state of alcohols are depicted in Fig. 8. As one can see, those values vary within a very narrow interval. This is so, because the dipole moments $\mathbf{d}(m)$ of primary alcohol molecules are determined by the sum of dipole moments of the hydroxyl group and the molecular skeleton S formed by the carbon and hydrogen atoms,

$$\mathbf{d}(m) \approx \mathbf{d}(\mathrm{OH}) + \mathbf{d}_s(m).$$

The dipole moment of a hydroxyl group is approximately equal to $|\mathbf{d}(\mathrm{OH})|\approx 1.51$ D, and the dipole moment of the skeleton is $|\mathbf{d}_s(m)|\approx 0.9$ D. The angle between those two vectors is 76° (for more details, see work [30]). Here, as was done earlier, we neglected, in the zeroth approximation, the mutual interaction of the OH group and S, as well as the weak dependence of the dipole moment of the skeleton on the number m. It is the latter dependence that leads to weak deviations of $\mathbf{d}(m)$ from the ordinal alcohol number.

5. Discussion of the Results

In this work, main attention was focused on the properties that have the simplest dependence on the ordinal number m of primary alcohol in the methanol series. In particular, it was shown that (i) it is expedient to characterize the spatial distribution of molecules within the system by the fraction volume per molecule, which linearly depends on m; (ii) the electronic polarizability of alcohol molecules, which characterizes system's response to the electromagnetic radiation in the optical range, also varies linearly with m; (iii) the major contribution of alcohol molecules to the effective static polarization is proportional to their fractional volume, i.e. it increases linearly with m. All those facts testify to a similarity of the mechanisms governing the formation of static dielectric permittivities ε in water and alcohols, although they are not identical, because the exact values of ε in alcohols are determined by small deviations from the main contribution.

Note that any characteristic of all primary alcohols from the methanol series has to be compared at the temperatures of corresponding states [13, 14, 31],

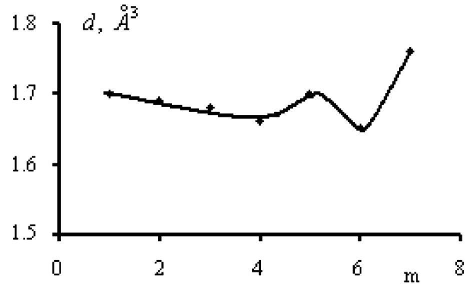


Fig. 8. Molecular dipole moments of alcohols from the homologous series of methanol in the gaseous state as a function of their ordinal number m. Symbols correspond to experimental data from work [29]

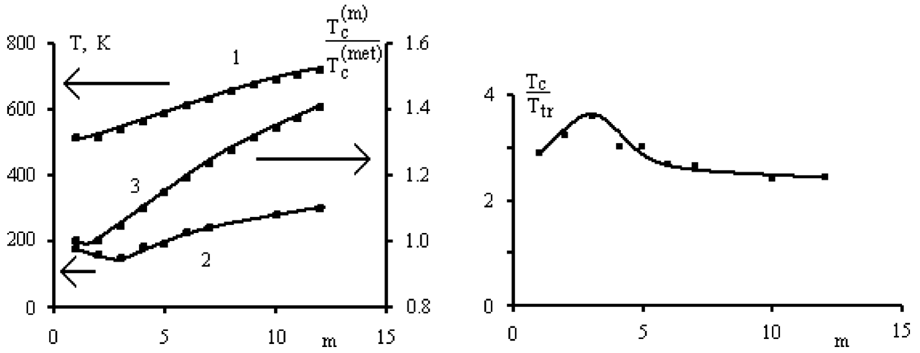
$$\frac{T_m}{T_\mathrm{c}^{(\mathrm{m})}} = \frac{T_\mathrm{meth}}{T_\mathrm{c}^{(\mathrm{meth})}},$$

or at the same dimensionless temperature $t = T/T_\mathrm{c}$. The effective polarizabilities of the methanol and ethanol molecules, which are compared in Fig. 5, were calculated just at such temperatures.

The values of the critical, T_c, and triple-point, T_tr, temperatures for primary alcohols, as well as the ratio $T_\mathrm{c}^{(\mathrm{m})}/T_\mathrm{c}^{(\mathrm{meth})}$, are plotted in Fig. 9. As one can see, the ratio $T_\mathrm{c}^{(\mathrm{m})}/T_\mathrm{c}^{(\mathrm{meth})}$ smoothly increases within the interval $1 \leq T_\mathrm{c}^{(\mathrm{m})}/T_\mathrm{c}^{(\mathrm{meth})} \leq 1.4$.

Furthermore, the values of T_c and T_tr for primary alcohols with $m \geq 8$ become close to the corresponding characteristic temperatures for water: $T_\mathrm{tr}^{(\mathrm{w})} = 273.15$ K and $T_\mathrm{c}^{(\mathrm{w})} = 648.5$ K. These are the m-values at which the energy of the van der Waals interaction between the skeletons of neighbor molecules becomes comparable with the hydrogen bond energy. Here, a non-trivial circumstance consists in that the numerical value of the ratio $T_\mathrm{c}^{(\mathrm{m})}/T_\mathrm{c}^{(\mathrm{meth})}$ for methanol (see Fig. 9, curve *3*) also deviates from the quasilinear dependence describing alcohols with higher ordinal numbers.

Another non-trivial fact consists in that the ratio $T_\mathrm{c}^{(\mathrm{m})}/T_\mathrm{tr}^{(\mathrm{m})} \to T_\mathrm{c}^{(\mathrm{w})}/T_\mathrm{tr}^{(\mathrm{w})}$ with the growth of the ordinal number m at $m > 10$. In other words, the relative width $T_\mathrm{c}^{(\mathrm{m})}/T_\mathrm{tr}^{(\mathrm{m})} - 1$ of the temperature intervals in which the primary alcohols exist in the liquid state tends (at $m > 10$) to a value that is characteristic of water, $(T_\mathrm{c}^{(\mathrm{m})}/T_\mathrm{tr}^{(\mathrm{m})}) - 1 \to 1.37$. On the other hand, if the ordinal number of alcohols decreases, the width



a *b*

Fig. 9. Dependences of the critical T_c (*1*) and triple-point T_tr (*2*) temperatures, the ratio $T_\text{c}^\text{(m)}/T_\text{c}^\text{(meth)}$ (*3*) (panel *a*) and the ratio $T_\text{c}^\text{(m)}/T_\text{tr}^\text{(m)}$ (panel *b*) on m for primary alcohols. The T_c-values were taken from work [32]. The T_tr- were taken from work [33] for methanol, ethanol, and 1-propanol; from work [34] for 1-butanol; from work [35] for 1-pentanol; from work [36] for 1-hexanol; from work [37] for 1-heptanol; and from work [38] for 1-decanol and 1-udecanol

of the temperature interval of their liquid state existence increases and reaches a maximum value for 1-propanol. Now, not only methanol but also ethanol, which have the lowest molecular weights, violate the tendency typical of senior alcohols.

In accordance with the principle of similarity, the temperature dependences of the specific volumes of various primary alcohols have to satisfy the relation

$$v_m(T) = \frac{v_\text{meth}(\lambda_m T)}{v_\text{meth}(293\lambda_m)}\big[v_\text{meth}(293\lambda_m) + 27.52(m-1)\big], \tag{11}$$

where $\lambda_m = T_\text{c}^\text{(m)}/T_\text{c}^\text{(meth)}$. Unfortunately, its careful verification is impossible, since there are no detailed experimental data for primary alcohols with sufficiently high ordinal numbers.

Nevertheless, it should be noted that, as was shown in work [13], the temperature dependences of the ratio between the fractional volumes of methanol and ethanol, on the one hand, and the fractional volume of argon, on the other hand, $R_v^\text{(m)}(t) = v_m(t)/v_\text{Ar}(t)$, are similar at their coexistence curves. Additionally, in agreement with Eq. (11), the $R_v^\text{(m)}(t)$-values are related to the $R_v^\text{(meth)}(t)$-ones by the relation

$$R_v^\text{(m)}(t) = R_v^\text{(meth)}(t)]\left[1 + \frac{27.6(m-1)}{v_\text{meth}}\right] \Rightarrow$$
$$\Rightarrow R_v^\text{(meth)}(t)[1 + 0.43(m-1)].$$

In particular, we obtain: for ethanol,

$R_v^\text{(et)}(t)/R_v^\text{(meth)}(t) \approx 1.43.$

For propanol,

$R_v^\text{(pr)}(t)/R_v^\text{(meth)}(t) \approx 1.86,$

which is in good agreement with experimental data.

To summarize, in this work, we only have considered the role of hydrogen bonds in alcohols in connection with the behavior of the alcohol density. According to the results of works [13,14], their contribution does not exceed 4% for both methanol and ethanol and should decrease with the growth of the ordinal number of alcohol in the methanol series. We intend to consider this issue elsewhere.

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1. P. Golub, I. Doroshenko, V. Pogorelov. Quantum-chemical modeling of energy parameters and vibrational spectra of chain and cyclic clusters of monohydric alcohols. *Phys. Lett. A* **378**, 1937 (2014).
2. V.N. Stabnikov, I.M. Roiter, T.B. Protsyuk. *Ethyl Alcohol* (Pishchevaya Promyshlennost, 1976) (in Russian).
3. *A Brief Handbook of Physicochemical Values.* Edited by A.A. Ravdel', A.M. Ponomareva (Spetsialnaya Literatura, 1998) (in Russian).

4. *Chemist's Handbook, Vol. 1* (Khimiya, 1982) (in Russian).
5. *Tables of Physical Quantities.* Edited by I.K. Kikoin. (Atomizdat, 1976) (in Russian).
6. M.M. Karavaev, V.E. Leonov, I.G. Popov, E.T. Shepelev. *Technology of Synthetic Methanol* (Khimiya, 1984) (in Russian).
7. 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).
8. V. Pogorelov, A. Yevglevsky, I. Doroshenko, L. Berezovchuk, Yu. Zhovtobryuch. Nanoscale molecular clusters and vibrational relaxation in simple alcohols. *Superlat. Microstruct.* **44**, 571 (2008).
9. T.V. Lokotosh, N.P. Malomuzh, V.L. Zakharchenko. Anomalous density and permittivity effects on the structure of water. *J. Struct. Chem.* **44**, 1001 (2003).
10. N.P. Malomuzh, A.V. Oleinik. Nature of the kinematic shear viscosity of water. *J. Struct. Chem.* **49**, 1055 (2008).
11. A.I. Fisenko, N.P. Malomuzh, A.V. Oleynik. To what extent are thermodynamic properties of water argon-like? *Chem. Phys. Lett.* **450**, 297 (2008).
12. M. Born, E. Wolf. *Principles of Optics* (Cambridge Univ. Press, 1999).
13. V.Ya. Gotsul'skii, N.P. Malomuzh, V.E. Chechko. Properties of hydrogen bonds in water and monohydric alcohols. *Russ. J. Phys. Chem. A* **92**, 1516 (2018).
14. 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).
15. V.Ya. Gotsul'skii, N.P. Malomuzh, V.E. Chechko. The role of two-particle effects in the behavior of refraction of single-component liquids and two-component solutions. *Opt. Spectrosc.* **120**, 615 (2016).
16. D.S. Eisenberg, W. Kauzmann. *The Structure and Properties of Water* (Oxford Univ. Press, 2005) (ISBN: 0198570260, 9780198570264).
17. http://ddbonline.ddbst.de/DIPPR105DensityCalculation/DIPPR105CalculationCGI.exe?component=Methanol.
18. D.W. Davidson. The dielectric properties of methanol and methanol-d. *Can. J. Chem.* **35**, 458 (1957).
19. R.M. Shirke, A. Chaudhari, N.M. More, P.B. Patil. Dielectric measurements on methyl acetate + alcohol mixtures at (288, 298, 308, and 318) K using the time domain technique. *J. Chem. Eng. Data* **45**, 917 (2000).
20. R.M. Shirke, A. Chaudhari, N.M. More, P.B. Patil. Temperature dependent dielectric relaxation study of ethyl acetate – alcohol mixtures using time domain technique. *J. Mol. Liq.* **94**, 27 (2001).
21. M.T. Khimenko, V.V. Aleksandrov, N.N. Gritsenko. Polarizability and radii of molecules of some pure liquids. *Zh. Fiz. Khim.* **47**, 2914 (1973) (in Russian).
22. V.A. Granzhan, O.G. Kirillova. Physico-chemical study of N-methyl-2-pyrrolidone-methanol system. *Zh. Prikl. Khim.* **43**, 1875 (1970) (in Russian).
23. http://ddbonline.ddbst.de/DIPPR105DensityCalculation/DIPPR105CalculationCGI.exe?component=Ethanol.
24. F.X. Hasslon, R.H. Cole. Dielectric properties of liquid ethanol and 2-propanol. *J. Chem. Phys.* **23**, 1756 (1955).
25. V.N. Makhlaichuk, N.P. Malomuzh. Manifestation of cluster excitations in dielectric properties of water vapor and liquid water as well as their heat capacity. *J. Mol. Liq.* **253**, 83 (2018).
26. N.P. Malomuzh, V.M. Makhlaichuk. Dimerization degree of water molecules, their effective polarizability, and heat capacity of saturated water vapor. *Ukr. J. Phys.* **63**, 121 (2018).
27. J.G. Kirkwood. Theory of solutions of molecules containing widely separated charges with special application to zwitterions. *J. Chem. Phys.* **2**, 351 (1934).
28. I.E. Tamm. *Fundamentals of the Theory of Electricity* (Mir, 1979).
29. O.A. Osipov, V.I. Minkin, A.D. Garnovskii. *Handbook on Dipole Moments* (Vysshaya Shkola, 1971) (in Russian).
30. P. Venkateswarlu, W. Gordy. Methyl alcohol II. Molecular structure. *J. Chem. Phys.* **23**, 1200 (1955).
31. L.D. Landau, E.M. Lifshitz. *Statistical Physics* (Butterworth-Heinemann, 1980) [ISBN: 978-0-7506-3372-7].
32. M. Gude, A.S. Teja. Vapor-liquid critical properties of elements and compounds. 4. Aliphatic alkanols. *J. Chem. Eng. Data* **40**, 1025 (1995).
33. R.C. Wilhoit, J.Chao, K.R. Hall. Thermodynamic properties of key organic compounds in the carbon range C1 to C4. Part 1. Properties of condensed phases. *J. Phys. Chem. Ref. Data* **14**, 1 (1985).
34. J.F. Counsell, J.L. Hales, J.F. Martin. Thermodynamic properties of organic oxygen compounds. Part 16. Butyl alcohol. *Trans. Faraday Soc.* **61**, 1869 (1965).
35. G.S. Parks, H.M. Huffman, M. Barmore. Thermal data on organic compounds. XI. The heat capacities, entropies and free energies of ten compounds containing oxygen or nitrogen. *J. Am. Chem. Soc.* **55**, 7, 2733 (1933).
36. K.K. Kelley. The heat capacities of ethyl and hexyl alcohols from 16 to 298 K and the corresponding entropies and free energies. *J. Am. Chem. Soc.* **51**, 779 (1929).
37. G.S. Parks, W.D. Kennedy, R.R. Gates, J.R. Mosley, G.E. Moore, M.L. Renquist. Thermal data on organic compounds XXVI. Some heat capacity, entropy and free energy data for seven compounds containing oxygen. *J. Am. Chem. Soc.* **78**, 56 (1956).
38. C. Spizzichino. Contribution a l'etude des tensions de vapeur et des chaleurs de vaporisation des acides gras, esters methyliques et alcools gras a des pressions inferieures a 1 mm de mercure. *J. Recherch. CNRS* **34**, 1 (1956).

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НАДЗВИЧАЙНІ ВЛАСТИВОСТІ СПИРТІВ МЕТАНОЛОВОГО РЯДУ

Резюме

Аналізуються нетривіальні характеристики термодинамічних величин первинних спиртів метанолового гомологічного ряду, в першу чергу, їх густин, температур критичної та потрійної точок, а також їх відношення та оптичні і діелектричні поляризовності. Досліджується характер взаємного зв'язку між ними за однакових температур для спиртів з різними порядковими номерами m в ряду метанолу. Показано, що немонотонний характер температурної залежності густини спиртів обумовлений не етанолом, як здається на перший погляд, а метанолом. Критична температура останнього випадає з квазілінійної залежності значень критичних температур спиртів від m. Показано, що відношення критичної температури спиртів до температури їх потрійної точки зі зростанням m асимптотично прямує до відповідного відношення для води. Встановлено прості лінійні залежності від m електронної та ефективної статичної поляризовностей спиртів. Знайдено поперечну та поздовжню складові тензора поляризовності молекул спиртів. Доведено, що дипольні моменти найближчих сусідів в спиртах антикорелюють, тобто намагаються встановлюватись у протилежних напрямках.