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QUALITATIVE ANALYSIS OF THE CLUSTERING IN WATER SOLUTIONS OF ALCOHOLS III

Peculiarities of the clustering in aqueous solutions of monohydric alcohols have been discussed. The main attention is focused on the details of clustering in aqueous solutions of four first alcohols in the methanol homologous series, as well as butanol isomers. The volume of an elementary cluster is assumed to be smaller than the total volume of the components forming this cluster. The clustering degree is determined at a temperature of 15 °C and in the concentration interval $0 \leq x \leq x_p$, where x_p is the molar concentration of alcohol molecules at the special point. The clustering degree for the aqueous solutions of butanol isomers at 20 °C is estimated as well.

Keywords: solutions, water, monohydric alcohols, elementary clusters, special point.

1. Introduction

Aqueous alcohol solutions are complicated systems, the properties of which substantially depend on the concentrations of components. The first systematic work on the study of the bulk properties of solutions was performed by D.I. Mendeleev [1, 2]. The objects of research were aqueous solutions of ethanol and sulfuric acid, and the main attention was paid to the phenomenon of thermal solution expansion. Progress in the study of the volumetric solution properties is reflected in monographs [1, 3]. Those studies still remain challenging [4].

The deviation of solutions from ideality occurs, first of all, owing to hydrogen bonds between their molecules. Hydrogen bonds are assumed to exist between both the molecules of separate components and the molecules of different components. Such solutions include aqueous solutions of alcohols, primary and secondary amines, and solutions of two alcohols.

Every molecule of monohydric alcohol can form two hydrogen bonds, and every water molecule can form four ones. It is known that the interaction energy between the alcohol and water molecules exceeds the interaction energy in the water–water and alcohol–alcohol molecular pairs [5, 6]. For example, the hydrogen bond energy between ethanol molecules (5.66 kcal/mol) was theoretically calculated in work [7]. This value is lower than the hydrogen bond energy in the water-ethanol pair (5.85 kcal/mol).

The clustering in aqueous alcohol (methanol and ethanol) solutions in the concentration intervals $x_p \leq x \leq 1$ [8] and $0 \leq x \leq x_p$ [9], where x_p is the molar fraction of the alcohol corresponding to the special solution point [10–13], was considered in works [8, 9]. The aqueous alcohol solution is considered as a mixture of three components (substances): water, alcohol, and clusters formed by the alcohol and water molecules. The third component is formed owing to the intermolecular interaction between water and alcohol molecules. In works [8, 9], a relation was obtained for the density and the clustering degree of so-

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lutions, if some amount of alcohol is added to water [8] or some water is added to alcohol [9].

In this work, a generalization of the approach used in works [8, 9] to a wider group of the aqueous solutions of monohydric alcohols is considered.

2. Application of the Group Model to Describe the Clustering in Solutions

The main idea of the group model proposed by Langmuir [14] consists in dividing the molecules in the solution into several groups. It is assumed that all available groups make the additive contributions to the solution properties. The main results obtained in the framework of this model are described in work [15].

An important characteristic of the aqueous alcohol solutions is the degree of their clustering $Z_a(x, T)$, namely, the ratio between the number of clustered alcohol molecules, $N_a^{(c)}$, and their total number N_a ,

$$Z_a(x, T) = N_a^{(c)} / N_a.$$

In works [8, 9] in order to determine $Z_a(x, T)$, the following assumptions were made:

- 1) the solution is completely clustered at the specific point,
- 2) when adding alcohol to water [8] or water to alcohol [9], the added substance becomes clustered only partially, which is described by the degrees of clustering of alcohol, $Z_a(x, T)$, and water, $Z_w(x, T)$; both of those parameters being functions of the concentration and temperature.

In support of the indicated assumptions, we can present the conclusions from work [16], where it was claimed that, in aqueous methanol solutions with concentrations close to $x \approx 0.1669$, at least five water molecules surround one methanol molecule, which testifies [16] to the complete clustering of the solution.

Water-methanol solutions were also studied in work [17]. The distances between the molecules were used as a clustering criterion. For water, this criterion was proposed in work [18]. Two water molecules are considered to be bound through a hydrogen bond, if the distance between their oxygen atoms is shorter than 3.2 \AA [18]. In work [19], the clustering criterion is the distance between carbon molecules. The cited authors showed that, at the concentration $x = 0.1$, the clustering degree reaches a value of 74.9%; the

concentration at the special point is $x_p = 0.165$. The same result was obtained in work [20].

In aqueous solutions of methanol, a maximum in the viscosity isotherm is observed at a water-alcohol molecular ratio of 7 : 2 [20]. The presence of the maximum is explained by the fact that the hydrogen bonds of water molecules become saturated with alcohol molecules at this temperature, and the total clustering of the solution takes place. In work [21], on the basis of the idea about the maximum stabilization of a water structure by non-electrolyte molecules, it was shown that this phenomenon is observed in aqueous methanol solutions at the concentrations $x \approx 0.17$.

Let the solution consist of N solvent and solute molecules, $N = N_w + N_a$, where, N_w and N_a are the numbers of water and alcohol molecules, respectively. The water molecules, N_w , are divided into the molecules that are in clusters, $N_w^{(c)}$, and the "free" molecules, $N_w^{(nc)}$. Similarly, for the alcohol molecules, we have $N_a^{(c)}$ and $N_a^{(nc)}$.

According to the group model, the volume of the mixture is equal to

$$V_s = v_w N_w^{(nc)} + v_a N_a^{(nc)} + v_c (N_w^{(c)} + N_a^{(c)}),$$

where v_w , v_a , and v_c are the molar volumes of water, alcohol, and the clustered component, respectively. After simple transformations, we obtain

$$V_s = v_w N_w + v_a N_a + N_a^{(c)} (v_c - v_a) + N_w^{(c)} (v_c - v_w).$$

Taking into account that $N_a = xN$ and $N_w = (1 - x)N$, where x is the molar fraction of alcohol in the solution, we have

$$V_s = v_w (1 - x)N + v_a xN + N_a^{(c)} (v_c - v_a) + N_w^{(c)} (v_c - v_w).$$

The parameter $Z_a = N_a^{(c)} / N_a$ describes the fraction of clustered alcohol molecules and determines the solution volume V_s ,

$$V_s = v_w (1 - x)N + v_a xN + Z_a xN (v_c - v_a) + N_w^{(c)} (v_c - v_w).$$

As was done earlier in works [8, 9], the cluster composition will be determined using the parameter $k = N_w^{(c)} / N_a^{(c)}$, i.e. the ratio between the numbers of water and alcohol molecules in the clusters. Then, for

the number of water molecules that compose the clustered component, we have $N_w^{(c)} = kN_a^{(c)} = kZ_a x N$, and, for the molar volume of the solution,

$$V_\mu = v_w(1 - x - kZ_a x) + v_a(1 - Z_a)x + v_c(1 + k)Z_a x. \quad (1)$$

Accordingly, for the solution density, we obtain

$$\rho_s = \frac{m_w(1 - x) + m_a x}{V_\mu}.$$

From whence, it follows that the clustering degree of alcohol molecules satisfies the equation

$$Z_a = \frac{1}{x} \frac{m_w(1-x) + m_a x}{\rho_s} - v_a x - v_w(1 - x) / (v_c(1 + k) - v_a - v_w k). \quad (2)$$

Note that the clustering degrees of alcohol, Z_a , and water, $Z_w(x, T) = N_w^{(c)}/N_w$, molecules are connected by the relation

$$Z_w(1 - x) = Z_a x k.$$

At the special solution point, according to Eq. (2), $Z_a = 1$, which confirms our basic assumption [8, 9] that the solution is completely clustered at the special point, and the parameter k equals

$$k = \frac{1 - x_p}{x_p}. \quad (3)$$

The clustering degree of all solution molecules equals

$$Z_s = \frac{N_w^{(c)} + N_a^{(c)}}{N_w + N_a} = \frac{Z_a N_a + Z_a N_a k}{N_w + N_a} = Z_a(1 + k) \frac{N_a}{N_w + N_a} = Z_a(1 + k)x. \quad (4)$$

At the special point, Eq. (4) acquires the form $Z_s = Z_a(1 + k)x_p = Z_a$, which is identical to that obtained in works [8, 9].

From the basic relations, it is easy to obtain a relation for Z_a , Z_w , and Z_s :

$$Z_s = Z_w(1 - x)Z_a x.$$

It should be emphasized that Z_a and Z_w also depend on the concentration and the temperature.

Let us consider Eq. (2) more carefully. Taken Eq. (3) into account, this formula reads

$$Z_a = \frac{x_p}{x} \frac{V^E(x)}{V^E(x_p)} = \frac{V^E(x)/x}{V^E(x_p)/x_p}, \quad (5)$$

$$V^E(x) = V - V_{id},$$

where $V^E(x)$, V_{id} , and V_s are the excess, ideal, and real volumes of the solution, respectively. It should be noted that Eq. (5) was obtained provided that the parameter k is constant and determined by formula (3).

Note that the concentration dependence of the excess volume is most often approximated by the Redlich–Kister formula [22, 23]

$$V^E = x(1 - x) \sum_{i=1}^n A_i(T, P)(1 - 2x)^i,$$

where $A_i(T, P)$ are functions of the temperature and pressure. As a result, at $x \rightarrow 0$, the ratio $V^E(x)/x$ has a finite value.

At the special point, the clustering degree of alcohol achieves the maximum value: $(\partial Z_a / \partial x)_{PT} = 0$. Since

$$\frac{\partial Z_a}{\partial x} = \frac{x_p}{V^E(x_p)} [v_w - \bar{v}_w] \quad (6)$$

the extremum in the concentration dependence of Z_a is reached provided

$$(v_w - \bar{v}_w)|_{x=x_p} = 0,$$

where $\bar{v}_w = V - x(\partial V / \partial x)_{PT}$.

The calculation by formula (6) for aqueous methanol solutions demonstrates a very satisfactory agreement with the results obtained by a digital processing of the derivative of expression (2). As was expected, the concentration dependence of the clustering degree becomes maximum at the special point.

Those facts confirm our assumption about the formation of elementary clusters in methanol solutions [6, 24] with the ratio $k = N_w^{(c)}/N_a^{(c)} \approx 5.06$. But, for the solutions of other alcohols, if the parameter k is independent of the solution concentration, the results of calculations by Eqs. (6) and (2), as was done in works [8, 9], give incorrect values for $x \leq x_p$.

In works [8, 9], it was shown that $Z_a \leq 1$ for methanol solutions in the whole range of their concentrations. But for ethanol, there is a section in the

concentration dependences of Z_a , where $Z_a > 1$. This problem was overcome in works [8, 9] by introducing the dependence of k on the solution concentration,

$$k(x) = \begin{cases} (1 - x_p)/x_p, & x \leq x_p, \\ (1 - x)/x, & x > x_p. \end{cases} \quad (7)$$

Such a definition of the parameter k can be explained by the fact that, in the concentration interval $x > x_p$, clusters more complicated than elementary ones are formed in the solution [6, 24]. In this case, only elementary clusters are formed in the aqueous solutions of alcohols from methanol to butanol to the left of the special point ($x \leq x_p$) [6, 24]. This conclusion agrees with the results of works [25–28].

In work [29], on the basis of purely geometric considerations, a model was proposed for calculating the molar volumes of non-electrolyte solutions, and some other properties of those solutions were explained. In particular, the value of the molar volume of the solution, V_μ , was found to equal

$$V_\mu = v_w + (\zeta - 1)v_w x, \quad (8)$$

where ζ is the number of water molecules displaced by one non-electrolyte molecule from the framework of hydrogen bonds without destroying its structure. In particular, $\zeta = 2$ for methanol and $\zeta = 3$ for ethanol (at a temperature of 15 °C).

From Eqs. (1) and (8), it follows that

$$\zeta = \left[\frac{v_c}{v_w} \frac{1}{x_p} - k - \frac{v_a}{v_w} \right] Z_a + \frac{v_a}{v_w}, \quad (9)$$

ζ depends on the ratios between the molar volumes of non-electrolyte and the clustered component, on the one hand, and water, on the other hand. Furthermore, like Z_a , the parameter ζ depends on the concentration and the temperature.

Table 1. ζ -values for aqueous alcohol solutions at a temperature of 15 °C in the concentration interval $0 \leq x \leq x_p$

Alcohol	ζ
Methanol	$2.06 \leq \zeta \leq 2.10$
Ethanol	$2.94 \leq \zeta \leq 3.22$
1-propanol	$3.81 \leq \zeta \leq 3.99$
1-butanol	$4.70 \leq \zeta \leq 4.77$

In the case where all ethanol molecules become clustered, i.e. $Z_a = 1$, we find for the molar volume:

$$V_\mu = v_w + [(v_c/v_w)/x_p - k - 1]v_w x.$$

From a comparison of this expression with the Malenkov formula (see work [29]), it follows that

$$\zeta = \frac{1}{x_p} \frac{v_c}{v_w} - k.$$

Taking the temperature dependence of the ratio v_c/v_w into account, we obtain that the parameter ζ increases linearly from 3.28 at 0 °C to 3.49 at 40 °C, which agrees satisfactorily with the results of work [29], where this parameter took the value $\zeta = 3$ for the aqueous ethanol solution. Our calculations showed that $\zeta = 3.43$ at a temperature of 15 °C.

Another condition, $Z_a = 0$, is associated with the value of ζ from 3.17 to 3.28 in the temperature interval from 0 to 40 °C. At 15 °C, $\zeta \approx 3.22$.

A similar calculation can also be done for water-methanol solutions. In the temperature interval from 0 to 20 °C, ζ changes from 2.02 to 2.07, which practically coincides with $\zeta = 2$ obtained in work [29]. In the cited work, it was marked that the value of the parameter ζ has a value that is smaller than the expected one. The cited authors explained this by that not all voids in the structure are occupied by water molecules.

The calculation of the concentration dependence of the parameter ζ in the interval $0 \leq x \leq x_p$ using formula (9) led to the ζ -values quoted in Table 1. From the presented data, it follows that, at low concentrations, there is a very satisfactory agreement of the calculated ζ -values with the results of work [29].

In work [30], the average molar volume of the solution was determined using the formula

$$V_s = \frac{1}{n_w + n_a} \left[n_w^{(nc)} v_w + n_a^{(nc)} v_a + \sum_i n_i V_i \right], \quad (10)$$

where n_{and} is the number of molecular complexes, and V_{and} their molar volumes. This result is consistent with ours (see Eq. (1)), if only the first contribution is taken into account in the third term of expression (10).

3. Clustering Degrees in Aqueous Solutions of Primary Alcohols Belonging to the Homologous Series of Methanol

In what follows, we confine the consideration to the primary alcohols from the homologous series of methanol with concentrations in the interval to the left from the special point x_p . We emphasize that the important place in our approach belongs to the following assumptions:

1) the solution is completely clustered at the special point;

2) in the indicated interval, the solution consists of water, alcohol, and elementary clusters.

In order to compare the concentration dependences of the clustering degrees in the aqueous solutions of various alcohols, let us introduce the normalized concentration x' according to the formula

$$x' = \frac{x}{x_p}, \quad (11)$$

where x_p is the concentration of the aqueous solution at the special point of the corresponding alcohol. The further analysis of the concentration behavior of the clustering degree of alcohols is performed according to the density of their aqueous solutions: methanol [31], ethanol [32], 1-propanol [33], and 1-butanol [34], depending on the normalized concentration (see Fig. 1).

From Fig. 1, one can see that as the order number of alcohol in the homologous series (from methanol to 1-propanol) grows, the clustering degree of alcohol molecules decreases toward 1-butanol, for which the Z_a -curve (4) is located above curve 1.

The transition to higher-order members in the homologous series of monohydric alcohols is accompanied by an increase in the interaction energy between the alcohol molecules. Starting from a certain alcohol, the energy of the intermolecular alcohol-alcohol interaction becomes comparable by magnitude with the energy of the water-water and water-alcohol intermolecular interactions, which leads to the limited solubility of alcohols in water. For instance, in works [35, 36], it was shown that the solubility of the first three alcohols (methanol, ethanol, and 1-propanol) is unlimited. But starting from 1-butanol, all subsequent alcohols have a limited solubility [37] (see Table 2). Tertiary butanol, which has an unlimited solubility in water at room temperature, is an exception [38].

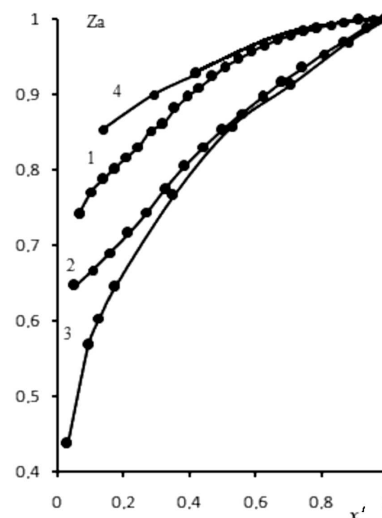


Fig. 1. Concentration dependences of the clustering degree of alcohol molecules in aqueous solutions of primary alcohols at a temperature of 15 °C: (1) methanol, (2) ethanol, (3) 1-propanol, and (4) 1-butanol. The solution densities were taken from [31] for methanol, [32] for ethanol, [33] for 1-propanol, and [34] for 1-butanol. The concentration is determined by formula (11)

The exclusive position of 1-butanol solutions (see Fig. 1), in our opinion, takes place due to the limited solubility of this alcohol in water.

4. Clustering Degrees in Aqueous Solutions of 1-Butanol and its Two Isomers

By the example of butanol, let us consider the manifestation of isometry in the concentration dependences of the clustering degree in the corresponding aqueous solutions. According to experimental data

Table 2. Positions of the special points in aqueous alcohol solutions, x_p , and the solubility of alcohols in water, x_s

Alcohol	x_p	x_s
Methanol	0.1650 [10–13]	Unlimited [35]
Ethanol	0.0742 [10–13]	"
1-propanol	0.0368 *	"
2-propanol	0.05 *	"
1-butanol	0.0140 *	0.023 [35], 0.0191 [38]
2-butanol	0.0263 *	0.051 [38]
tert-butanol	0.0365 *	Unlimited [35]

* Obtained in this work.

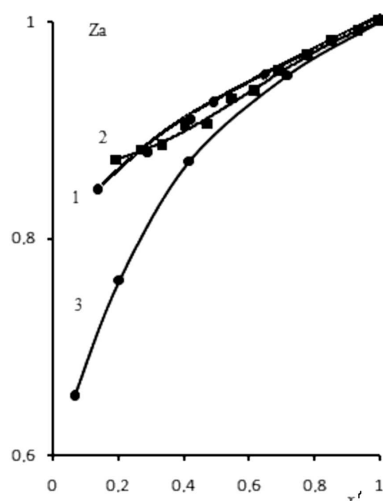


Fig. 2. Dependences of the clustering degree of the molecules of butanol isomers on the normalized concentration (see Eq. (11)) in aqueous solutions at a temperature of 20 °C: (1) 1-butanol, (2) 2-butanol, and (3) tert-butanol. The experimental density data were taken from works [27, 34, 39–42]

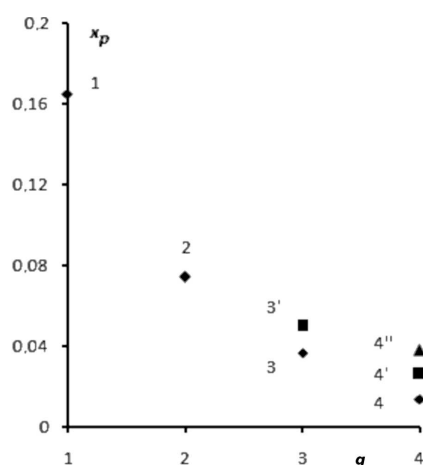


Fig. 3. Concentration dependences of monohydric alcohols at their special points on the order number g in the homologous series: (1) methanol, (2) ethanol, (3') 1-propane, (3'') 2-propanol, (4) 1-butanol, (4') 2-butanol, and (4'') tert-butanol. The solution densities were taken from [31] for methanol ($g = 1$), [32] for ethanol, [33, 43] for 1-propane and 2-propanol, [34] for 1-butanol, [39, 40, 44] for 2-butanol, and [41, 42] for tert-butanol

for the density of the solutions, the clustering degrees of alcohol molecules were calculated for 1-butanol, 2-butanol, and tert-butanol. The corresponding concentration dependences of the clustering degree Z_a of

alcohol molecules in their aqueous solutions are exhibited in Fig. 2.

From the data shown in Fig. 2, it follows that the transition from normal alcohol to the first and second isomers leads to a reduction in the degree of alcohol clustering in the corresponding solution. In addition, one can see that the degree of clustering in tert-butanol solutions is the lowest. The close values of Z_a for 1-butanol and 2-butanol are explained by the structural similarity of the molecules of those isomers.

5. Position of Special Points for Aqueous Solutions of Monohydric Alcohols

Figure 3 illustrates the concentrations at the special points of aqueous solutions of the first four alcohols in the homologous series of monohydric alcohols. From Fig. 3, it follows that, for the alcohols with larger order numbers in the homologous series, the concentration at the special point x_p decreases. Of particular interest are the results for the propanol and butanol solutions, which are characterized by the isometry.

Let $x_p^{g(j)}$ denote the concentration at the special point of the g -th alcohol and the j -th isomer in the solution. From the data presented above, it follows that the concentration differences for the isomers are equidistant,

$$x_p^{3(1)} - x_p^{3(2)} \approx x_p^{4(1)} - x_p^{4(2)} \approx x_p^{4(2)} - x_p^{4(3)} \approx 0.01 \div 0.013.$$

Note that we confined the analysis to the aqueous solutions of four alcohols because of the lack of sufficiently detailed experimental data (see, e.g., works [45, 46]).

6. Conclusions

1. The thermodynamic properties of aqueous alcohol solutions are a result of the formation of a three-component solution consisting of water and alcohol molecules, as well as clusters of the same type composed of water and alcohol molecules. The most stable are clusters with the composition $C_2H_5OH-12H_2O$ and a formation enthalpy of $3.57k_B T$.

2. The clustering degree of the solution decreases with the increasing order number of alcohol in the homologous series of monohydric alcohols (the methanol series), which are infinitely soluble in water. However, the clustering degree increases significantly for

1-butanol (from the same methanol series), which is partially soluble in water.

3. By the example of butanol, the clustering degree is found to decrease, when transiting to higher-order isomers.

4. The special points of the alcohol isomers are equidistant regardless of the order number of alcohol in the homologous series of monohydric alcohols and the number of the isomer.

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ЯКІСНИЙ АНАЛІЗ КЛАСТЕРИЗАЦІЇ
В СПИРТОВО-ВОДНИХ РОЗЧИНАХ III

У роботі обговорюються особливості кластеризації у водних розчинах одноатомних спиртів. Основна увага фокусується на деталях кластеризації у водних розчинах перших чотирьох спиртів гомологічного ряду метанолу та ізомерів бутанолу. Приймається, що об'єм елементарного кластера, виявляється меншим за сумарний молекулярних об'ємів компонент, що утворюють цей кластер. Визначено ступінь кластеризації водних розчинів за температури 15 °C у концентраційних інтервалах від 0 до концентрації, що відповідає особливій точці розчину конкретного спирту. Отримано концентраційну залежність ступеня кластеризації водних розчинів ізомерів бутанолу за температури 20 °C.

Ключові слова: розчини, вода, одноатомні спирти, елементарні кластери, особлива точка.