



MODELLING OF STRUCTURE AND CONCENTRATION CHARACTERISTICS OF WATER-ALCOHOL SOLUTIONS

M. E. Soloviev, V. V. Makaryin

Mikhail E. Soloviev, Doctor of Physics and Mathematics, Professor; Valery V. Makaryin, Candidate of Technical Sciences, Associate Professor

Yaroslavl State Technical University, Yaroslavl, Russia, soloviev56@gmail.com, vfak@yandex.ru

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Abstract. Water-alcohol solutions are widely used in pharmacy, food industry, engineering, etc. The study of their physical and chemical properties has a long history. Nevertheless, due to the complexity of these systems, there is still an interest in their research stimulated by the development of biochemistry in terms of the study and protection of the environment, global climate change, renewable energy resources and cosmochemistry. The purpose of the presented study is the quantum-chemical investigation of water clusters with methyl and ethyl alcohol molecules, as well as the modelling of concentration dependences of the excess molar volume of ethyl alcohol solution in water at different temperatures. Based on quantum-chemical calculations of paired and mixed complexes of water with methanol and ethanol, taking into account solvation effects, study reveals the formation of thermodynamically efficient complexes in liquid, in contrast to the ideal gas state, while in the mixture both individual solvated alcohol molecules and complexes will be in equilibrium. We noted a relative difference in the free energies of solvation of paired and mixed methanol and ethanol complexes. The paper proposes a technique for calculating the excess molar volume in water-alcohol mixtures by approximating the experimental dependences by Lejandre polynomials of the ninth degree. The calculation results showed high accuracy. Hence, continuous functions describe the dependences of the calculated coefficients of Lejandre polynomials on temperature.

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Introduction

According to the systematic papers of D. I. Mendeleev, the study of physicochemical properties of water-alcohol solutions has a long history (more than 150 years) [1]. Nevertheless, the interest to these objects still remains. Experimental studies of excess thermodynamic mixing functions of alcohols aqueous solutions, performed at the end of the twentieth century [2-5], showed significant anomalies in their properties due to changes in the associative structure of the solution with its concentration. It is due to the presence of strong hydrogen bonds between the components, on the one hand, and the diphilic character of alcohol molecules, on the other. As shown in [6], a simple associative equilibrium model does not allow describing



the concentration dependence of the water-alcohol solution volume contraction. Moreover, the quantitative description of this curve requires the introduction of additional corrections. On the basis of density measurements and calorimetry of concentrated aqueous solutions of different alcohols, the authors of [7] concluded as follows: in the region of high concentrations of alcohol, its molecules form clusters. And their which hydroxyl groups are oriented to the outer region where they interact with water molecules.

Thermodynamic data, however, are not sufficient to provide a more detailed assessment of the solutions structure and need to be supplemented by physicochemical methods and computer modelling. Thus, in [8], the laser interferometry method was applied to study the structure of water-alcohol clusters in near-surface layers. Possible mechanisms of transition of water fractal-cluster structures in interaction with ethanol into spatial clathrates were shown on the basis of these studies. The authors of [9] using terahertz spectroscopy and pulsed NMR with magnetic field gradient showed the presence of three different concentrations of water-alcohol solution at which the solution associative structure is critically changed.

We used the molecular dynamics method to calculate the heat capacity of water-alcohol mixtures [10-11], modelling of intermolecular interactions and associative structures [12-13] and dielectric permittivity [14]. At the same time, empirical potential force field functions, which are used in classical molecular dynamics, do not provide an adequate description of the geometrical structure and energy parameters of intermolecular complexes. Therefore, for these purposes it is necessary to use quantum chemical methods. Examples of the use of quantum-chemical calculations for these purposes are presented in [15-17].

The most common method of studying aqueous-alcohol solutions in practice is density measurement. Due to the fact that aqueous solutions of ethyl alcohol are widely used in the food industry and pharmacy, the Russian Standards Publishing House has published detailed tables of aqueous-alcohol solutions density at different temperatures and concentrations [18]. On the basis of density concentration dependences, the volume contraction dependences are calculated and used in theoretical calculations. An important anomaly of water-alcohol solutions is the presence of special points on the concentration dependences of contraction, where the curves constructed for different temperatures intersect [19-20]. On the basis of light scattering data, it was shown that the appearance of special points depends on orientation correlations in water. However, it is caused by the formation and destruction of hydrogen bonds [21].

The purpose of the study was quantum-chemical study of molecular complexes of water and methyl and ethyl alcohols along with an analysis of concentration dependences of the excess molar volume of aqueous ethanol solutions.

Main body

In [17], quantum-chemical modelling of geometry and energy characteristics was performed using the density functional method; the thermodynamic functions in the ideal gas state, water clusters with methanol and ethanol for different amounts of water atoms were calculated. According to the research, the cluster formation energies (binding energies) grow almost linearly with increasing amounts of water atoms in the cluster. It indicates practically independence of the amounts of atoms in the cluster on the hydrogen bonding energy per pair of atoms. Although, the formation of clusters is energetically effective (it occurs with a decrease



in electronic energy with correction for the energy of zero vibrations). Indeed, the calculation of changes in free energy shows positive changing of the Gibbs free energy in the reaction of cluster formation under standard conditions in the state of an ideal gas. Moreover, clusters should not exist in the gas phase at normal and elevated temperatures. Nevertheless, according to the article introduction, the associative structure is characteristic for water-alcohol solutions, and, therefore, clusters exist in the liquid phase. Obviously, the effects of solvation (hydration in the considered case) play an essential role in the stabilisation of clusters in the liquid phase. Therefore, the present paper deals with quantum-chemical calculations of water-alcohol clusters taking into account solvation effects.

We considered binary clusters of water, methanol, ethanol molecules, and mixed water-alcohol clusters as objects of the study. The calculation of the total electronic energies and thermodynamic functions of the compounds involved in the reactions was performed by the quantum-chemical density functional method [22, 23]. We use various hybrid functionals of the ORCA software package [24, 25]. The geometry of the initial compounds and reaction products was optimised during the calculation, and as a result, conformations with minimum potential energy were found. The presence of minima was controlled by the absence of negative eigenvalues of the Hesse matrix at critical points. We calculated the total electronic energy of the compound and the solvation energy in these conformations using the implicit C-PCM solvation model [26]. We calculated the Gibbs free energy at different temperatures on the basis of vibrational analysis [27].

Since the choice of the density functional for DFT calculations is not unambiguous [28], we performed preliminary test calculations in order to select a functional adequate to the problem. Table 1 shows an example of such calculations. However, the popular hybrid functional B3LYP/6-311G** fits better for the calculation of hydration energies in this task compared to higher-level functionals, despite the fact that it is inferior to them for the calculation of atomisation energies [28]. This functional was used in [31]. Nevertheless, for further calculations, we chose the hybrid functional TPSS/6-311G** because the average relative bias for all compounds was slightly smaller when it was used.

Table 1. Hydration free energies (in kJ/mol) calculated in the C-PCM model using different functionals for the three compounds, as well as the corresponding experimental values

Method	H ₂ O	CH ₃ OH	H ₃ O ⁺
B3LYP/6-311G**	-30.22	-21.36	-378.13
M0/62X/6-311G**	-31.39	-23.18	-379.94
wB97X-D3/6-311G**	-31.08	-22.92	-379.94
CAM-B3LYP/6-311G**	-31.08	-22.92	-379.67
TPSS/6-311G**	-29.58	-21.21	-380.16
B2PLYP/6-311G**	-30.49	-22.23	-380.54
Experiment [29, 30]	-26.36	-21.34	-432.63

Although the C-PCM method is inferior in the accuracy of the solvation energies calculation to the SMD method [32], also implemented in the ORCA package, it is more convenient in terms of this challenge. The reason is that it does not require experimentally determined physicochemical parameters of the solvent that vary with its concentration, such as



surface tension, acidity, and basicity indices. In the case of the C-PCM model, the only variable parameter is the dielectric constant, which is approximated rather well by an additive scheme when the solute concentration changes.

Tables 2 and 3 show the calculated solvation energies of methanol and ethanol individual molecules, as well as their paired complexes and complexes with water at different temperatures and two mole fractions of the solvent (water): $X_1 = 1$ (infinite dilution) and $X_1 = 0.5$ (equal mole fractions). As the mole fraction of alcohol increases, the solvation energy decreases slightly due to a decrease in the dielectric constant. An increase in temperature has a different effect on the free energy of the individual molecules and complexes solvation. It increases the absolute value of ΔG_{solv} for individual methanol molecules and mixed complexes with water, and decreases it for paired methanol complexes. For ethanol, an increase in the absolute value of ΔG_{solv} is observed only for individual molecules, while a decrease is observed for paired and mixed complexes.

Moreover, in the case of both methanol and ethanol, the free energy of solvation is larger in absolute value for complexes (especially for mixed ones) compared to its value for individual molecules. Therefore, in liquids, in contrast to the ideal gas state, the formation of complexes will be thermodynamically effective, while in a mixture both individual solvated alcohol molecules and complexes will be in equilibrium. The relative difference in the solvation free energies of the paired and mixed complexes of methanol and ethanol can also be noted. In the case of methanol, there should be fewer paired complexes in solution than mixed and individual molecules. However, for ethanol there should be more paired complexes than individual molecules. It indicates that ethanol should be a more associated liquid than methanol, which seems quite obvious.

Table 2. Free energies of solvation of methanol and methanol-water molecules and complexes at different temperatures and solvent mole fractions

Molecule/associate	T, K	ΔG_{solv} , kJ/mol	
		$X_1 = 1$	$X_1 = 0.5$
CH ₃ OH	273.15	-21.59	-21.48
CH ₃ OH	283.15	-21.59	-21.48
CH ₃ OH	293.15	-21.60	-21.49
CH ₃ OH	303.15	-21.61	-21.50
CH ₃ OH	313.15	-21.62	-21.51
CH ₃ OH_H ₂ O	273.15	-44.13	-43.96
CH ₃ OH_H ₂ O	283.15	-44.13	-43.97
CH ₃ OH_H ₂ O	293.15	-44.13	-43.97
CH ₃ OH_H ₂ O	303.15	-44.14	-43.98
CH ₃ OH_H ₂ O	313.15	-44.14	-43.99
CH ₃ OH_CH ₃ OH	273.15	-17.88	-20.23
CH ₃ OH_CH ₃ OH	283.15	-17.75	-20.20
CH ₃ OH_CH ₃ OH	293.15	-17.62	-20.16
CH ₃ OH_CH ₃ OH	303.15	-17.49	-20.13
CH ₃ OH_CH ₃ OH	313.15	-17.36	-20.10

**Table 3.** Free energies of solvation of ethanol and ethanol-water molecules and complexes at different temperatures and solvent mole fractions

Molecule/associate	T, K	ΔG_{soln} , kJ/mol	
		$X_1 = 1$	$X_1 = 0.5$
C ₂ H ₅ OH	273.15	-21.77	-21.57
C ₂ H ₅ OH	283.15	-21.78	-21.58
C ₂ H ₅ OH	293.15	-21.80	-21.59
C ₂ H ₅ OH	303.15	-21.81	-21.60
C ₂ H ₅ OH	313.15	-21.82	-21.62
C ₂ H ₅ OH_H ₂ O	273.15	-41.22	-40.81
C ₂ H ₅ OH_H ₂ O	283.15	-41.21	-40.79
C ₂ H ₅ OH_H ₂ O	293.15	-41.19	-40.78
C ₂ H ₅ OH_H ₂ O	303.15	-41.18	-40.76
C ₂ H ₅ OH_H ₂ O	313.15	-41.16	-40.74
C ₂ H ₅ OH_C ₂ H ₅ OH	273.15	-31.13	-32.17
C ₂ H ₅ OH_C ₂ H ₅ OH	283.15	-31.08	-32.13
C ₂ H ₅ OH_C ₂ H ₅ OH	293.15	-31.02	-32.10
C ₂ H ₅ OH_C ₂ H ₅ OH	303.15	-30.95	-32.06
C ₂ H ₅ OH_C ₂ H ₅ OH	313.15	-30.89	-32.02

The geometrical structure of the complexes of methanol and ethanol with water in calculations taking into account solvation similar to the one obtained in [17]. The calculations in the ideal gas state indicates insignificant change of the nature of hydrogen bonds.

Thus, quantum-chemical calculation provides the existence of clusters formed by alcohol and water molecules in water-alcohol solutions and allows their structure describing. At the same time, such calculations do not allow us to obtain quantitative dependences of thermodynamic functions on the solution composition due to limitations on the model size due to the lack of computational resources.

The considered complexes with hydrogen bonds are the cause of non-ideal behaviour of the solution in terms of deviation from the additivity of thermodynamic functions. The solvation free energy given in the tables above may be an example of such deviation. Mathematically, deviation from additive behaviour in the dependences of thermodynamic functions on the mole fraction of components can be represented as an absolute deviation (excess thermodynamic functions) or a relative deviation. An example is volume contraction [19-21]. This paper contains the calculations on the dependences of the excess molar volume of the components on the mixture composition and proposes approximating functions for these dependences [18]. The excess molar volume of the mixture of two components characterises the deviation of the solution from the ideal one and is calculated by the formula



$$V_E = (V - V_1^0 n_1 - V_2^0 n_2)/(n_1 + n_2), \quad (1)$$

where V - experimentally measured volume of the mixture containing n_1 moles of water and n_2 moles of alcohol; and $V_1^0 - V_2^0$ molar volumes of alcohol and water, respectively.

The dependence of the excess molar volume of a mixture on thermodynamic parameters (temperature and pressure) can be calculated from the mixture volume on the basis of the virial expansion for the state equation. However, the virial expansion polynomial is not a set of orthogonal functions. Therefore, the coefficients of the virial expansion calculated by the least squares method on the basis of experimental data appear to be correlated and cannot be approximated by continuous functions of the mixture composition. This can be seen from the analysis of the virial expansion coefficients of the equation of state of water-alcohol mixtures given in [33]. It is more rational to approximate the dependence of the excess molar volume on the mole fractions of the components using orthogonal polynomials. For example, in [34], the dependence of the excess Gibbs free energy on the composition of ethanol-water mixtures was approximated by sixth-order Legendre polynomials. Our calculations showed that the sixth-order polynomials are not sufficient for qualitative approximation of the dependence of the excess molar volume on the composition of ethanol-water mixtures. Therefore, in the present study, we used the ninth-order Legendre polynomial to describe this dependence.

Defining the mole fraction of alcohol by x , the dependence $V_E(x)$ can be represented as follows

$$V_E(x) = \sum_{i=0}^9 a_i(T) L_i(x), \quad (2)$$

where $L_i(x)$ - are Legendre polynomials (3); $a_i(T)$ - are temperature dependences of the polynomial coefficients, which in the present paper were also approximated by Legendre polynomials of the fourth order. Thus, 50 coefficients (5 coefficients for each dependence $a_i(T)$, $i = 0, \dots, 9$) were calculated to approximate the dependences of excess molar volume on the mixture composition and temperature.

$$\begin{aligned} L_0 &= 1; \\ L_1 &= x; \\ L_2 &= (3x^2 - 1)/2; \\ L_3 &= (5x^3 - 3x)/2; \\ L_4 &= (35x^4 - 30x^2 + 3)/8; \\ L_5 &= (63x^5 - 70x^3 + 15x)/8; \\ L_6 &= 231/16 x^6 - 315/16 x^4 + 105/16 x^2 - 5/16; \\ L_7 &= 429/16 x^7 - 693/16 x^5 + 315/16 x^3 - 35/16 x; \\ L_8 &= 6435/128 x^8 - 3003/32 x^6 + 3465/64 x^4 - 315/32 x^2 + 35/128; \\ L_9 &= 12155/128 x^9 - 6435/32 x^7 + 9009/64 x^5 - 1155/32 x^3 + 315/128 x. \end{aligned} \quad (3)$$

Figure 1 shows that function (2) approximates the experimental data very well. It includes the special point (Fig. 2), where the temperature dependences have an inversion. The maximum absolute deviation of calculated and experimental values did not exceed 0.006 cm³/mol at all studied temperatures.

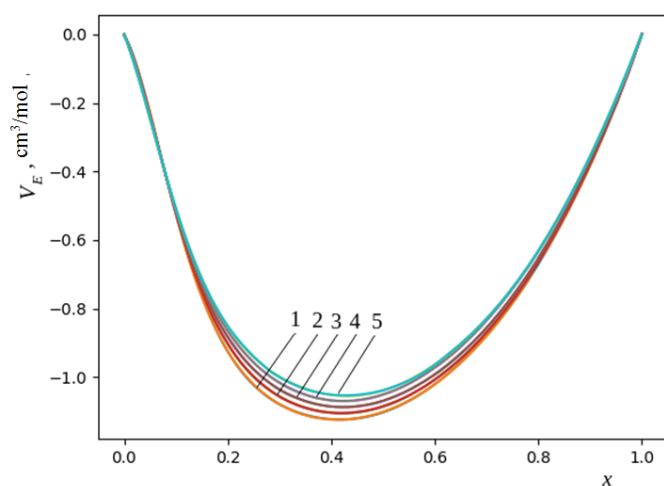


Fig. 1. Dependences of excess molar volume in water-ethanol mixture (experimental and calculated curves are indistinguishable), temperature, °C: 1 - 15; 2 - 20; 3 - 25; 4 - 30; 5 - 35

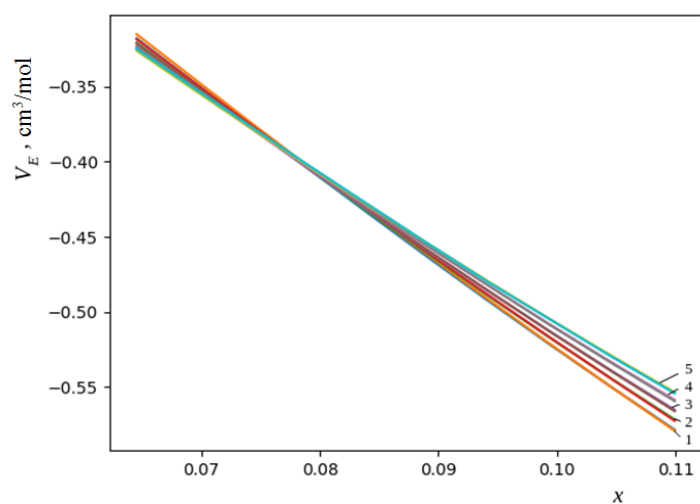


Fig. 2. Dependences of excess molar volume in the water-ethanol mixture near the special point. The curves are marked as on Fig. 1

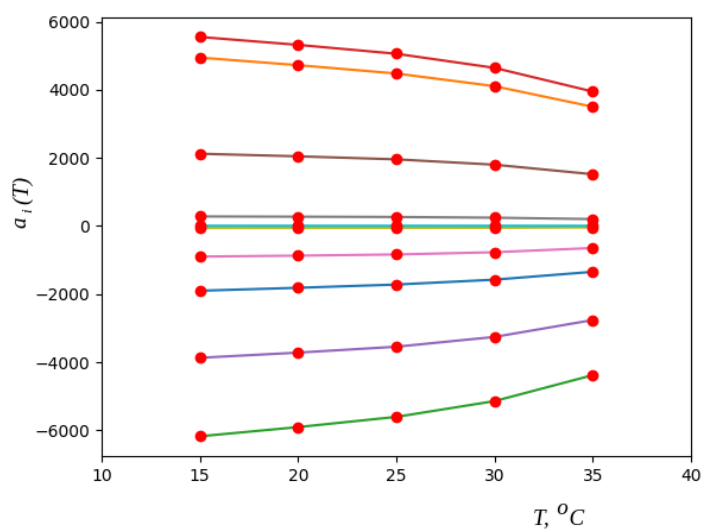


Fig. 3. Dependences of Legendre's coefficients of functions $a_i(T)$ on temperature



The temperature dependences of the Lejandre coefficients are well described by monotonic functions. By Fig. 3, the temperature dependences of the Lejandre coefficients are well described by monotonic functions. This allows us to implement model (2) to calculate the molar volume of water-ethanol mixtures at various concentrations and temperatures.

Conclusions and recommendations

Quantum-chemical calculations of paired and mixed complexes of water with methanol and ethanol taking into account solvation effects reveals that liquids, opposite to an ideal gas, form thermodynamically effective complexes. Meanwhile, in mixtures both individual solvated alcohol molecules and complexes will be in equilibrium. On the basis of the calculated values of the Gibbs free energy, the equilibrium constants for various complexes can be calculated and their relative concentrations determined.

We noted a relative difference in the solvation free energies of the paired and mixed complexes of methanol and ethanol. In the case of methanol, there should be less paired complexes in solution than mixed and individual molecules. However, ethanol should have more paired complexes.

The proposed method of calculating the excess molar volume in water-alcohol mixtures by approximating the experimental dependences by Lejandre polynomials of the ninth degree shows high accuracy. Therefore, the dependences of the calculated polynomial coefficients on temperature can be described by continuous functions. This allows us to recommend the proposed mathematical model for practical calculations of molar volume and density of alcohol solutions for different concentrations and temperatures.

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