VISCOUS FLOW AND STRUCTURAL PROPERTIES IN WATER-ETHANOL-UREA SYSTEMS

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Abstract. The structural features of water-ethanol, water-urea and water-ethanol-urea systems were studied on the basis of experimental estimates of kinematic viscosity at different temperatures and concentrations. For this purpose, the concentration dependences of the Gibbs energy of activation of the viscous flow, the enthalpy of activation of the viscous flow and the entropy of activation of the viscous flow of the studied systems were analyzed. The results show that ethanol has a structuring and then destructive effect on water up to a concentration of 0.15 molar, and urea has a destructive effect on the structure of water, starting from such small concentrations. The addition of urea to the ethanol-water system does not affect the inversion point.

Keywords: water, ethanol, urea, activation parameters of viscous flow.

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1. Introduction

Water is the most abundant substance in nature. This substance, which plays a great role in the geological history of our planet, in the formation of climatic conditions and in the formation of the living world as a source of life, has always attracted the attention of scientists due to its miraculous properties (Halonen et al., 2017; Capuci et al., 2016; Kontogeorgis et al., 2022). Although water is at first sight a simple substance, the study of its physical and chemical properties shows that it is a very complex substance. Almost all physical and chemical properties of water are anomalous. The unusual properties of water help it to perform a number of functions in a living organism. Water, like the environment, performs very important functions, such as transporting substances through osmosis and diffusion in the body, protecting cells and organs, and protecting the body from cold and heat due to its high heat capacity and evaporating temperature. Changes in the structure or thermodynamics of water for various reasons are reflected in all biochemical processes in living organisms (Gailus et al., 2018; Bercea and Wolf, 2021; Monteiro and Avelino, 2023; Aghayeva & Baghiyev, 2022).

Recent studies (Dakar & Korableva, 1998; Endo, 1973; Belousov & Panov, 1983; Nadeem, 2022) have shown that inversion of concentration-dependent isotherms of some physicochemical parameters found in practice for aqueous solutions of a number of organic substances is observed. For example, in the curves of adiabatic compression in the water-ethanol solution and the partial molar volume of ethanol in the solution, the

minimum of the molar fraction of ethanol is observed at values of \( x_{inv}^R = 0.06 \) (Endo, 1973a, 1973b) and \( x_{inv}^U = 0.07 \) (Belousov & Panov, 1983), respectively, and the first maximum of molecular light intensity at \( x_{max}^R = 0.09 \) (Vuks, 1977). Researchers claim that quasi-crystalline or clathrate-like (ice-like structures of 100-150 water molecules) structures are formed at inverted concentrations (Ignatov & Mosin, 2015). Since water, ethanol, and urea molecules are present in living organisms, especially in humans, the study of water-ethanol-urea systems is of great interest.

In the presented work kinematic viscosity of systems of 1) water-ethanol in the range of \( x_{et} \in [0 - 0.37] \) at temperature of 10-50 °C, 2) water-ethanol-urea \( (x_{ur} = 0.02) \) at temperature of 20-50°C, in the range of \( x_{et} \in [0 - 0.39] \), 3) water-ethanol-urea \( (x_{ur} = 0.12) \) at temperature of 20-50°C, in the range \( x_{et} \in [0 - 0.35] \), 4) water-urea at temperature of 20-50 °C, in the range \( x_{ur} \in [0 - 0.15] \), 5) water-urea-ethanol \( (x_{et} = 0.05) \) at temperature of 20-50 °C, in the range \( x_{ur} \in [0 - 0.098] \), was measured. Using the experimental results, the Gibbs energy \( (\Delta G_\eta^\#) \), the enthalpy of activation of the viscous flow \( (\Delta H_\eta^\#) \) and the entropy of the activation of the viscous flow \( (\Delta S_\eta^\#) \) at the considered temperatures and concentrations were calculated and the structural properties of the solution were analyzed based on changes in these parameters.

2. Method of calculation

One of the convenient ways to study the structural changes and existing interactions in solutions is the study of the activation parameters \( (\Delta G_\eta^\#, \Delta H_\eta^\#, \Delta S_\eta^\#) \) of the viscous flow of solutions (Dakar & Korableva, 1998; Saleh et al., 2006). Activation parameters characterizing the process of viscous flow in liquids are determined by the difference between the corresponding thermodynamic functions of 1mol liquid molecules in the active \( (G_a, H_a, S_a) \) and bound \( (G_b, H_b, S_b) \) states: \( \Delta G_\eta^\# = G_a - G_b, \quad \Delta H_\eta^\# = H_a - H_b, \quad \Delta S_\eta^\# = S_a - S_b \) (Masimov et al., 2013; 2020).

Activation of viscous flow Gibbs energy \( (\Delta G_\eta^\#) \) according to Eyring’s theory (Belousov and Panov, 1983) has been defined as (dos Santos et al., 2020):

\[
\Delta G_\eta^\# = RT\ln(Mv/N_A h)
\]

Here \( v \) is the kinematic viscosity of the solution corresponding to the absolute temperature \( T, R = 8.31 \text{ J/(K \cdot mol)} \) - universal gas constant, \( N_A = 6.02 \cdot 10^{23} \text{ mol}^{-1} \) - Avogadro's number, \( h = 6.63 \cdot 10^{-34} \text{ J \cdot s} \) - Planck constant, \( M = x_1 M_1 + x_2 M_2 + \cdots + x_N M_N \) which is the molar mass of the solution. Viscous flow activation enthalpy \( (\Delta H_\eta^\#) \) has been defined as (Kancharla et al., 2020):

\[
\Delta H_\eta^\# = R \frac{\partial (M v / N_A h)}{\partial (1/T)}
\]

Viscous flow activation entropy \( (S_\eta^\#) \) has been defined as (Cao et al., 2019; Kaneko et al., 2023):

\[
\Delta G_\eta^\# = \Delta H_\eta^\# - T \Delta S_\eta^\#.
\]

3. Experimental

Aqueous solutions of different concentrations, consisting of water-ethanol-urea systems, were taken as research objects. Used ethanol (C₂H₅OH) and urea (NH₂CONH₂) are chemically pure substances and were purchased from Sigma-Aldrich. Measurements
were made at normal atmospheric pressure. The solutions were prepared by gravimetric method. Bidistilled water was used to prepare the solutions. During the preparation of the samples, an analytical scale manufactured by "KERN 770" was used and the measurements were taken with an accuracy of 0.0001 g. In the study, the viscosity was measured with a 0.34 mm diameter CLV-2 capillary viscometer. The flow time of the liquid was determined with an accuracy of ± 0.01 s. on the viscometer. All measurements were made three times and their average values were taken as a result of the experiment. The temperature was measured with an accuracy of ± 0.05 K.

4. Results and discussions

The dependence of the activation parameters of the viscous flow of water-ethanol, water-urea and water-ethanol-urea systems (\(\Delta G_\eta^e\), \(\Delta H_\eta^e\), \(\Delta G_\eta^e\)) on the concentration (x) at a temperature of 20\(^0\)C is shown in Figures 1-6.

Fig.1. Dependence of Gibbs energy of activation of viscous flow of water-ethanol systems on molar part of ethanol (t = 20\(^0\)C).
1 - \(x_{et}=0\), 2 - \(x_{et}=0.02\), 3 - \(x_{et}=0.12\)

Fig.2. Dependence of Gibbs energy of activation of viscous flow of water-urea-ethanol systems on the molar fraction of urea (t=20\(^0\)C).
1 - \(x_{ur}=0\), 2 - \(x_{ur}=0.05\)

Fig.3. Dependence of the enthalpy of activation of the viscous flow of water-ethanol-urea systems on the molar part of ethanol (t = 20\(^0\)C).
1 - \(x_{et}=0\), 2 - \(x_{et}=0.02\), 3 - \(x_{et}=0.12\)

Fig.4. Dependence of the enthalpy of activation of the viscous flow of water-urea-ethanol systems on the molar part of urea (t=20\(^0\)C).
1 - \(x_{ur}=0\), 2 - \(x_{ur}=0.05\)
As a result of our research, it was determined that the concentration dependence of all three parameters at other temperatures studied varies with the same regularity at a temperature of 20°C. Therefore, only graphs of results corresponding to a temperature of 20°C are given in the study.

As can be seen from Figure 1 and 2, the temperature and concentration in the considered range $\Delta G_{\eta}$ increase with increasing concentration for the aqueous solutions studied, as well as for a given temperature and concentration $\Delta G_{\eta}$ (water-ethanol) > $\Delta G_{\eta}$ (water-ethanol-urea ($x_{ur}=0.02$)) > $\Delta G_{\eta}$ (water-urea) < $\Delta G_{\eta}$ (water-urea-ethanol ($x_{et}=0.05$)). According to Eyring's theory, $\Delta G_{\eta}$ is the energy expended to cross the potential wall of a molecule. It is clear that in the solutions we studied, along with water molecules, ethanol, urea, or ethanol and urea molecules, respectively, will become active. This will lead to an increase in $\Delta G_{\eta}$ with the increase in the concentration of both ethanol and urea.

As can be seen from Figure 3, in the water and ethanol and water-ethanol-urea systems in the considered temperature and concentration range, first $\Delta H_{\eta}$ increases as the ethanol concentration increases, exceeds the maximum and then decreases, as well as for a given temperature and concentration $\Delta H_{\eta}$ (water-ethanol) > $\Delta H_{\eta}$ (water -ethanol-urea ($x_{ur}=0.02$)) > $\Delta H_{\eta}$ (water-ethanol-urea ($x_{ur}=0.12$)). Figure 4 shows that in the considered temperature and concentration range, water-urea and water-urea-ethanol systems $\Delta H_{\eta}$ only decrease with increasing urea concentration, but also $\Delta H_{\eta}$ (water-urea) < $\Delta H_{\eta}$ (water-urea-ethanol ($x_{et}=0.05$)). Note that the changes in the solution $\Delta H_{\eta}$ are characterized in terms of energy. Thus, as the concentration increases, the increase in $\Delta H_{\eta}$ indicates that the system in question has become relatively more structurally structured, and vice versa (Masimov et al., 2015; 2017).

Due to the interactions between water molecules and molecules of solute in aqueous solutions, the structure of such solutions differs significantly from the structure of water (Dakar, 2001). Structural changes in the solution are characterized by the parameter $\Delta S_{\eta}$. Thus, as the concentration increases, the increase in $\Delta S_{\eta}$ indicates that the system becomes more structured, and the decrease becomes relatively structured (Dakar & Korableva, 1998; Pashayev & Rajabov, 2022). As can be seen from Figure 5, the temperature
and concentration in the considered range $\Delta S^*_\eta$ first increase with increasing ethanol concentration in water-ethanol and water-ethanol-urea systems, exceeding the maximum at $x_{et} \approx 0.15$ and then decreasing, as well as for a given temperature and concentration $\Delta S^*_\eta$ (water-ethanol) > $\Delta S^*_\eta$ (water-ethanol-urea($x_{ur} = 0.02$)) > $\Delta S^*_\eta$ (water-ethanol-urea ($x_{ur} = 0.12$)). Figure 6 shows that in the considered temperature and concentration range, the increase in concentration of urea in water-urea and water-urea-ethanol systems only decreases $\Delta S^*_\eta$, but also $\Delta S^*_\eta$ (water-urea) < $\Delta S^*_\eta$ (water-ethanol-urea ($x_{et} = 0.05$)). The increase in $\Delta S^*_\eta$ with the increase in the concentration of ethanol is primarily due to the structuring effect of ethanol on water at low concentrations, and the decrease in $\Delta S^*_\eta$ is due to the structural destructive effect of ethanol at high concentrations. $x_{et}, \Delta S^*_\eta$ is maximum at point $x_{et} \approx 0.15$ can be explained by the formation of more stable quasicrystalline structures in solution. At this point, the solution appears to be in its most structured state. The increase in the concentration of urea and the decrease in $\Delta S^*_\eta$ are due to the destructive effect of urea on the structure of water. The structural destructive effect of urea and the structuring effect of ethanol in small concentrations is also manifested in three-component water-ethanol-urea systems. Thus, the addition of urea to the water-ethanol system ($x_{ur} = 0.02$ and $x_{ur} = 0.12$) leads to a certain decrease in $\Delta S^*_\eta$, and the addition of ethanol to the water-urea system at low concentrations ($x_{et} = 0.05$) leads to a certain increase in $\Delta S^*_\eta$.

The interaction of water with alcohol can be explained as follows: at small concentrations of alcohol, its molecules enter the cage without destroying the water cage, and there is a structural effect, mainly by hydrogen bonding with free water molecules. Of course, the entry of alcohol molecules into the cage without destroying the structure of water can only continue to a certain concentration. Most likely, starting from a certain value of this concentration (in this case, it corresponds to the value of $x_{et} \approx 0.15$), alcohol molecules gradually form hydrogen bonds with bound water molecules, which form a quasi-crystalline structure, which leads to the collapse of the resulting structure. Urea can be considered as a typical representative of organic substances that have a strong effect on the structure of water (Barone et al, 1970; Rezus & Bakker, 2006). It should be noted that urea increases the solubility of many compounds in water and weakens hydrophobic interactions. Urea also has strong protein denaturing properties. Analysis of the results of ultrasound and thermal measurements shows that urea destroys the structure of water (Arakawa & Takenaka, 1967; Kancharla et al., 2019). It seems that urea has a destructive effect on the structure of water, starting from such small concentrations, interacting with the bound water molecules that create the quasicrystalline structure of water.

The figures show that the addition of urea to the water-ethanol system and the addition of ethanol to the water-urea system do not change the nature of the dependencies $\Delta G^*_\eta = f(x), \Delta H^*_\eta = f(x)$ and $\Delta S^*_\eta = f(x)$. In addition, urea do not affect the inversion point observed in $\Delta H^*_\eta = f(x)$ and $\Delta S^*_\eta = f(x)$ dependencies. Therefore, the above considerations for the water-ethanol and water-urea system can also be applied to the three-component water-ethanol-urea system.

5. Conclusion

Analysis of the viscous flow properties of water-ethanol, water-urea and water-ethanol-urea systems shows that ethanol initially has a structuring effect on the structure
of water and water-urea systems with increasing concentration, and destructive effect after value $x_{et} \approx 0.15$ of concentration. Urea has only a destructive effect on the structure of both water and the water-ethanol system. The addition of urea to the water-ethanol system does not affect the inversion point ($x_{et} \approx 0.15$) observed in the dependence $\Delta S^n_\eta = f(x)$.

References


