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ВЯЗКОСТЬ ВОДНЫХ РАСТВОРОВ МОНО-, ДИ- И ТРИЭТИЛЕНГЛИКОЛЕЙ ПРИ ТЕМПЕРАТУРЕ 298,15 K

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Целью данного исследования является анализ изменения структуры комплексов в водных растворах низкомолекулярных гликолей в зависимости от состава смеси. Были проведены измерения динамической вязкости водных растворов низкомолекулярных гликолей (моно-, ди- и триэтиленгликоля) во всем концентрационном диапазоне при температуре 25 °С и атмосферном давлении. Предложена новая концентрационная шкала для общего описания концентрационных зависимостей вязкости. На основе экспериментальных данных рассчитана избыточная вязкость. Для водного раствора моноэтиленгликоля избыточная вязкость отрицательна во всем концентрационном диапазоне. Показано, что для водного раствора диэтиленгликоля избыточная вязкость отрицательна в диапазоне от 0 до 20 мол.% и становится положительной в области, богатой диэтиленгликолем. В случае раствора триэтиленгликоль-вода избыточная вязкость отрицательна в интервале от 0 до 10 мол.%. Был рассчитан параметр Грюнберга-Ниссана. Было установлено соответствие между характером изменения параметра Грюнберга-Ниссана и динамикой комплексообразования в зависимости от концентрации раствора на основании опубликованных в литературе параметров водородных связей. Показано, что из концентрационной зависимости параметра Грюнберга-Ниссана можно выделить области концентрации, на границе которых происходит изменение характера взаимодействия между водой и молекулами гликоля.

Ключевые слова: вязкость, водный раствор гликоля, избыточная вязкость, параметр Грюнберга-Ниссана

VISCOSITY OF MONO-, DI- AND TRIETHYLENE GLYCOL AQUEOUS SOLUTIONS AT 298.15 K

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The aim of this study was to analyze the change in the complex structure formed in water-glycols mixture under mixture composition. The dynamic viscosity for various glycol (mono-, di- and triethylene glycol) aqueous solutions have been measured over wide range of concentration at temperature 25 °C and atmospheric pressure. The new scale of viscosity concentration dependences of various glycols for common description in range of low glycol composition was suggested. From experimental data, the excess viscosity (deviation in viscosity) was calculated. Excess viscosity was negative for monoethylene glycol – water mixture over the entire range of composition. In the case diethylene glycol –water mixture excess viscosity values were found to be negative between 0 and 20 mol %, then became positive in the diethylene glycol rich region. In the case triethylene glycol – water mixture excess viscosity values were negative between 0 and 10 mol %. The Grunberg-Nissan parameter was calculated. By comparing the monoethylene glycol – water hydrogen bonding, reported in literature and Grunberg-Nissan parameter variation versus glycol molar fraction, a correspondence between Grunberg-Nissan parameter and the complex varieties was established.

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It was shown, that concentration dependence of the Grunberg-Nissan parameter separates the different concentration regions. The variation of the Grunberg-Nissan parameter with glycol molar fraction deals with the interaction variation between water and glycol molecules, the Grunberg-Nissan parameter slop varies.

Key words: viscosity, glycol aqueous solution, excess viscosity, Grunberg-Nissan parameter

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INTRODUCTION

Glycols or diols are chemical compounds containing two hydroxyl groups. They described with the general formula $HO\text{-}CH_2\text{-}CH_2\text{-}(O\text{-}CH_2\text{-}CH_2)_n\text{-}OH$, where *n* defines various glycols. For *n* = 0 it is monoethylene glycol (MEG) or simply ethylene glycol; for *n* = 1 it is diethylene glycol (DEG) and for *n* = 2 it is triethylene glycol and so on.

Glycols are very important chemicals widely used in various industrial fields, such as aviation, explosives, food, pharmaceuticals, cosmetics, house hold etc. They are completely soluble in liquid water, alcohols and ethers due to hydrogen-oxygen bonds. The volumetric properties of the aqueous mixtures are scientifically important because their link with the size and shape of the molecules, the intermolecular forces, geometrical packing, free volume and their associations [1].

Study of physical properties and thermodynamics excess properties of glycols-water binary mixtures is extremely important for experimental and theoretical research [2, 3] and in industrial process for process design and optimization [4]. For example, viscosities of binary mixtures are important for processes, such as mass transfers, fluid flow etc. These properties include interactions of ethylene oxide chains in aqueous solutions, the ability to absorb on surface and interfaces and proton conductivity in polymer electrolytes [5-7].

The prediction of the viscosity of liquid mixtures is a goal of long standing with both theoretical and practical importance. A truly fundamental theory would predict the viscosity, along with other thermodynamics and transport properties from knowledge of the intermolecular forces and radial distribution function alone. Such a program has appreciable success in application to pure, simple liquids such as the liquefied rare gases. For solutions, however, although the general theory has been formulated, it has not yet been reduced successfully to numerical results.

One is thus forced to approximate approaches, of which two general types may be distinguished. The first is that of continuum hydrodynamics, whose application to molecular problems is identified with the names of Einstein and Stokes. This approach, in which the discrete molecular structure of the solvent is neglected, has been remarkably successful in explaining the viscosity of dilute solution of high polymers. Its application to solution in which both components are comparable size is less appropriate.

The second general approach is to correlate the viscosity of mixture with the properties of the pure components and with thermodynamics characteristics of the interaction between components. Properties like density, viscosity and conductivity of solutions provide great information about various molecular interactions in solution and this study enable to understand the structural fitting of one solvent into the other. Many researchers [8-13] have studied different binary liquid systems of unlike solvents to understand molecular interaction and structural fitting.

Molecular interactions in solution are our area of interest. Present work is about understanding molecular interactions and structural fitting in three binary liquid systems viz. ethylene glycol - water (EGW), diethylene glycol - water (DGW) and triethylene glycol - water (TGW) of different compositions through measurements of viscosity at 298.15 K.

EXPERIMENTAL

Reagent grade ethylene glycol, diethylene glycol and triethylene glycol purchased from ZAO “AKOS-1” were used in the experiments without further purification.

Binary mixtures of EGW, DGW and TGW of different compositions were prepared by mass using electronic balance (precision ±0.0001 g) in stoppered bottles. Bidistilled water was used for preparation of binary mixtures. The uncertainty in experimental mole fractions of each solvent is not greater than ±0.0001.

Viscosities of pure solvents and different binary systems were determined using vibro-viscousimeter SV-10 (AND, Japan). The sine-wave vibro-viscometer SV-10 has a unit to detect the viscosity of a sample, which is composed of two thin sensor plates. It drives the sensor plates to vibrate at a uniform sine-wave vibration rate in a reverse phase like a tuning fork. The sensor plates are driven with the electromagnetic force of the same frequency as resonance, which is the characteristic of each structure, in order to resonate the measuring system. When the detection unit vibrates, it produces a sizable magnitude of reaction force on the supporting unit of the sensor plates via the spring plates. However, since each sensor plate is driven in reverse phase against each other at the same vibration frequency/amplitude in order to cancel the reaction force, it enables the user to obtain stable sine-wave vibration. The electromagnetic drive unit controls the vibration of the sensor plates in a sample at uniform amplitude, utilizing the resonance of the detection unit. The driving electric current as an exciting force will be detected as the magnitude of the viscidity, which is present between the sensor plates and the sample.

RESULTS AND DISCUSSION

Experimental viscosities of pure solvents and binary systems of different compositions (mole fraction of solvents) are shown in Fig. 1.

Viscosities of EGW, DGW and TGW binary mixtures increased with increase in the mole fraction of glycols. This can be assigned to the dipole-dipole attractive interactions between unlike solvents. As mole fraction of glycols increases, solution becomes more viscous.

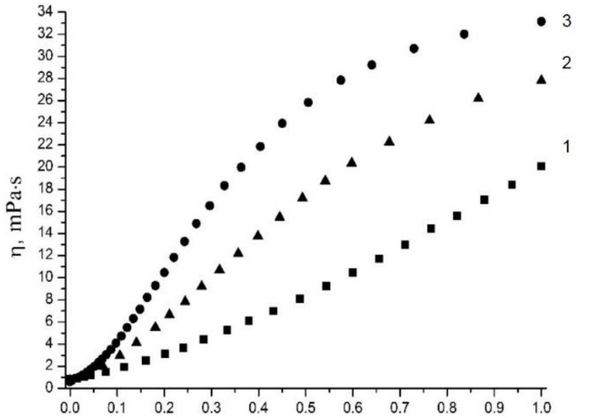

Fig. 1. Viscosity η versus glycol mole fraction for various glycol aqueous solutions at 298.15 K: monoethylene glycol - filled square, diethylene glycol – filled triangle, triethylene glycol – filled circle

Рис. 1. Вязкость η как функция мольной доли гликоля versus для водных растворов различных гликолей при температуре 298,15 К: моноэтиленгликоль - квадраты, диэтиленгликоль – треугольники, триэтиленгликоль – круги

In the framework of preliminary analysis we defined a new scale of concentration dependence for normalized viscosity, which is the viscosity concentration dependence of the solution normalized to the viscosity of the corresponding pure glycol. The normalized viscosity

$$\eta^* = \frac{\eta^{EG} - x_W \eta_0^W}{\eta_0^{EG}}$$

of various glycols as function on normalized molar ratio $\alpha\nu_W/\nu_{EG}$ are presented in Fig. 2. Here η^{EG} is the experimental viscosity, η_0^{EG} and η_0^W are viscosities of pure glycol and water (*EG* = *MEG*, *DEG*, *TEG*), x_W is the water molar fraction

$$x_W = \frac{\nu_W}{\nu_W + \nu_{EG}}$$

of the solution containing ν_W moles of water and ν_{EG} moles of glycol, that is

$$\eta^* \ versus \ \alpha \frac{\nu_W}{\nu_{EG}},$$

where α is the some coefficient.

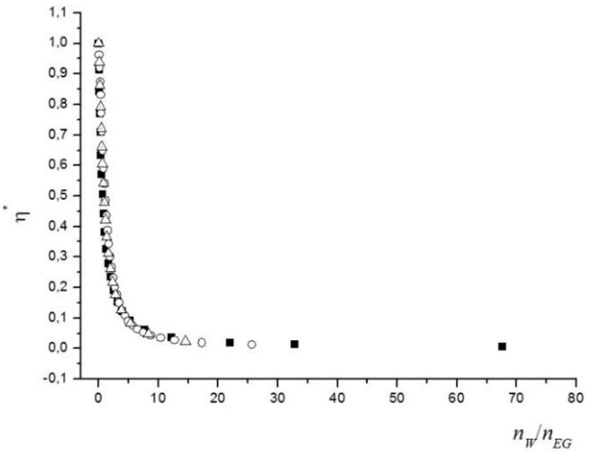

Fig. 2. Normalized concentration dependence of glycol-water mixtures viscosity: EGW – filled square, DGW – triangle, TGW – circle

Рис. 2. Нормированная концентрационная зависимость вязкости водных растворов гликолей: ЭГВ – квадраты, ДГВ – треугольники, ТГВ – круги

In fact, it is clearly shown in Fig. 2, all concentrations can be describe by general dependence at least in the water-rich region. Moreover, the values of coefficient α correspond to the ratio of glycol molar masses, as it shown in Table.

Table

Correspondence between the normalizing coefficient α and the molar mass ratio

***Таблица.* Соответствие между нормировочных коэффициентом α и отношением молярных масс**

	MEG	DEG	TEG
Molar mass, μ_{EG}	62.07	106.12	150.17
μ_{MEG}/μ_{EG}	1	1.7	2.4
α	1	1.7	2.3

However, we note that for glycol-rich region the concentration dependences deviate from general description. On our opinion, this fact requires additional consideration of interactions between molecules of glycols.

Deviation in physical properties of all mixtures from the ideal system can be estimate in terms of excess properties. The molecular interactions present in binary mixtures can be interpreted from excess properties of solutions [14, 15]. The sign and magnitude of excess functions depends on strength of molecular interactions between solvent molecules in binary mixtures [16]. Deviations (negative or positive) of physical properties from ideal values are a result of molecular interactions between unlike components of mixture and these deviations reflect extend of molecular interactions [3]. Excess viscosity $\Delta\eta$ of presented binary systems were calculated using equation [13]

$$\Delta\eta = \eta - \left(x_{EG}\eta_0^{EG} - x_W\eta_0^W \right),$$

where x_{EG} and x_W are mole fractions of glycols and water.

The calculated values of $\Delta\eta$ for different mole fractions of glycols in binary mixtures are presented in Fig. 3.

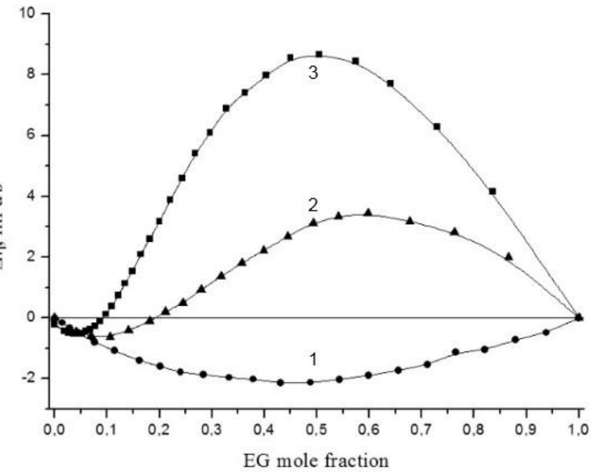

Fig. 3. Excess viscosity Δη versus glycol mole fraction for various glycol aqueous solutions at 298.15 K: monoethylene glycol - filled circle, diethylene glycol – filled triangle, triethylene glycol – filled square. The solid line shown only for the best view

Рис. 3. Избыточная вязкость Δη водных растворов различных гликолей как функция мольной доли гликоля при температуре 298,15 K: моноэтиленгликоль - круги, диэтиленгликоль – треугольники, триэтиленгликоль – квадраты. Линия показана только для удобства представления данных

Excess viscosity of EGW mixture is negative over entire range of composition. According to [17], analysis of O-H and O-O distances of two participating hydroxyl groups indicates, that at $X_{MEG} = 0.4$ MEG (acceptor) – MEG (donor) H-bonds are strongest and H_2O (acceptor) – H_2O (donor) bonds are weakest. That is, the minimum of excess viscosity divides the concentration range on two parts: for $x_{MEG} > 0.46$ water mixed bonds (MEG – Water) dominate over like bonds (H_2O-H_2O), for $x_{MEG} < 0.46$ MEG mixed bonds dominate over like bonds.

In fact, the excess viscosity is the signature of the non-ideality of glycol-water mixtures. This non-ideality due to complex formation between molecules of water and glycols caused by hydrogen bonding. Several authors confirm the presence of clusters in water-glycol mixture by different experimental techniques, usually supported by computational investigations [12, 18-21]. So, for mole fraction of MEG mixture with $X_{MEG} = 0.46$ at t = 25 °C the complex formula take the form $(H_2O)_m(H_2C_2O_2)_n$ with $m/n = 4/3$.

But for DGW and TGW mixtures excess viscosity has negative values in composition range $0 < x_{DEG} < 0.19$ and $0 < x_{TEG} < 0.09$, respectively, that corresponds to molar ratio $\nu_W/\nu_{DEG} = 4$ and $\nu_W/\nu_{TEG} = 9$, and complex formulas $(H_2O)_m(DEG)_n$ with $m/n = 4:1$ for DGW and $(H_2O)_m(TEG)_n$ $m/n = 9:1$ for TGW. However, the excess viscosity behavior and influence of oxygen atoms on complex formation requires additional theoretical analysis and additional experiments.

There are several correlation equations for liquid mixtures viscosity [22-25]. A simple one is the Grunberg-Nissan model, which for a binary mixtures is given by

$$\ln\eta = x_1\ln\eta_1 + x_2\ln\eta_2 + x_1x_2G,$$

where G is an interaction parameter depend on the components and temperature and x is mole fraction, subscripts 1 and 2 denote the mixture components. We report in Fig.4 the variation of the Grunberg-Nissan constant G versus glycol molar fraction on 25 °C according to equation

$$G = \frac{\ln\eta - x_{EG}\ln\eta_0^{EG} - x_W\ln\eta_0^W}{x_{EG}x_W}.$$

We distinct three different regions, where Grunberg-Nissan parameter G varies linearly with different slopes. The MEG molar fraction separating the different regions with $X_{MEG1} = 0.46$ and $X_{MEG2} = 0.11$ are very close to those reported by [17] (0.4 and 0.1, the x resolution is limited by the small number of data points), these molar fraction delimit the composition range of MGW mixture where complexes have different formula.

As mentioned in [17], for low MEG concentrations, unexpectedly large value n_{HB} intermolecular H-bonds per MEG molecule were obtained in the $X_{MEG} = 0.1$ mixture. Then, we can conclude, that a correspondence between complex varieties and the variation of the Grunberg-Nissan parameter is evident. Moreover, we must note, that specific conductivity measurements of EGW binary mixture shown maximum at concentration $X_{MEG2} = 0.11$.

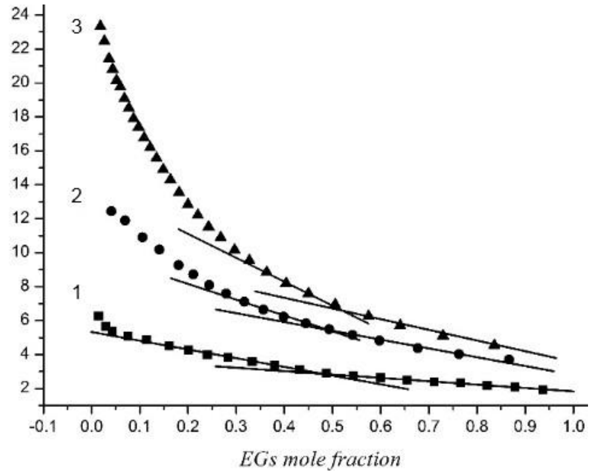

Fig. 4. Variation of the Grunberg-Nissan parameter G for the system of EG-water mixtures versus mole fraction in glycol: EGW - filled square, DGW – filled circle, TGW – filled triangle
Рис. 4. Зависимость параметра Грюнберга-Ниссана G от мольной доли гликоля для водных растворов гликолей: ЭГВ квадраты, ДГВ – круги, ТГВ – треугольники

The variation of the Grunberg-Nissan parameter *G* with glycol molar fraction deals with the interaction variation between water and glycol molecules. Since the glycol molar fraction changes, the complex formula changes and so Grunberg-Nissan constant *G* slope varies.

CONCLUTION

Viscosimetry is a powerful technique to study liquid mixture. This technique permit is one part to determine the rheological nature of mixture. The dynamic viscosity variation versus glycol molar fraction shows a non ideality of the solutions and suggests the formation of complexes between water and glycol molecules. The complex is in dynamical equilibrium with free water and glycol molecules. A correspondence between complex varieties in MEG-water mixture and the Grunberg-Nissan parameter detected at 25 °C. According to this hypothesis, there are concentration ranges of water-glycol solutions, where the form of the complex has a different structure. In particular, in MEG-water mixture existence of three concentration ranges separated by concentration values $X_{MEG} = 0.1$ and 0.4 determined. Although some of our findings are obviously of qualitative nature, the results provide a useful insight into the complex dynamics of glycol-water mixtures.

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