VISCOSIMETRIC BEHAVIOR OF WATER-n-PROPANOL SOLUTIONS

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The goal of the paper is the determination of the dynamic viscosity (η) for water-n-propanol solutions, for various concentrations and temperatures. On the basis of the experimental data, the applicability of the Guzman-Andrade and Walther-Ubbelhode equations, regarding the dependence of the dynamic viscosity on the temperature has been tested.

Also, starting from the primary experimental data, the activation parameters of viscous flow: variation enthalpy ($\Delta H_m^{\#}$), variation entropy ($\Delta S_m^{\#}$) and free Gibbs' energy ($\Delta G_m^{\#}$) using the Eyring equation have been calculated.

The characterization of the viscous flow involves also the determination of the dependence of dynamic viscosity versus the concentrations of the solutions. For the studied solutions, the excess viscosities have been calculated and it was established the type of deviation from the ideal behavior.

This study and the involved parameters are used in projection but also for the complex description of the phenomenon.

Keywords: *dynamic viscosity, activation parameters of viscous flow, excess viscosity, intrinsic parameters.*

INTRODUCTION

The intrinsic parameters of viscous flow are very important for the physical-chemical study of solutions. The primary experimental data are the densities and the viscosities for the water-n-propanol solutions at various concentrations and temperatures. The applicability of the Guzman-Andrade [1, 2], Walther-Ubbelhode [3] and Eyring [4, 5] equations has been verified through the complex processing of the primary experimental data. The calculation of the equations parameters, in linear coordinates, has allowed the numerical determination of the characteristic parameters of viscous flow: the barrier of potential energy of flow (E_{vis}), dynamic viscosity at T→∞ (B), variation enthalpy ($\Delta H_m^{\#}$), variation entropy ($\Delta S_m^{\#}$) and Gibbs`s activation energy ($\Delta G_m^{\#}$).

According to Partington [6], the conclusion may be drawn that no unique equation exists for rendering the dependence of viscosity concentration. The known equations are based, principally, on experimental data, having several restrictions, either on the nature of the solution's components or on the concentration domain or number of terms necessary in the equation.

The identical aspect of the seven isotherms studied, having their maximum placed at the same concentration values, led us to the conclusion that, independently of temperature, the functional equation will maintain its form and number of terms. The influence of temperature will be exercised exclusively on the values of some constants introduced into the equation.

The experimentally determined viscosities have also allowed to establish the dependence of the excess viscosities (η_{excess}) on the concentrations for the water-n-propanol solutions.

EXPERIMENTAL

The liquids involved in the experiments, water and n-propanol, were of analytical purity and all the solutions prepared with bi-distilled water. Ubbelohde viscosimeters with capillaries and a pycnometer equipped with internal thermometer, thermostated with a precision of 0.1 °C, were used. Preparation of the solutions was performed through weighting. This operation employed for solutions synthesizing and for density determining was performed with accuracy of 0.0001 g.

The reference liquid was n-propanol because its viscosity is closer as value with the studied solutions. The dependence of η value versus temperature T for n-propanol was calculated, using data from the literature [7], according to the following equation:

$$\ln \eta_{n-prop} = -13.52463 + 2.17307 \cdot \left(\frac{10^3}{T} \right); \; (\eta_{\text{n-prop}} \text{ in (Pa·s))} \tag{1}$$

The dependence of densities for water and n-propanol versus temperature were obtained from the equations:

$$\rho_{water} = 1085.5 - 2.9786 \cdot 10^{-1} \cdot T \tag{2}$$

$$\rho_{n-prop} = 1034.32 - 7.8666 \cdot 10^{-1} \cdot T \tag{3}$$

where the density ρ is expressed in (kg/m^3) and the temperature T in (K).

For the diminution of the number of experimental data, the determination of the densities for the water-n-propanol solutions has requested the dependence of the pycnometer`s volume on the temperature, using water, for which the variation of the density with this parameter is reproduced with precise data [8] by equation (4):

$$V = 1.9484 \cdot 10^{-5} - 2.1758 \cdot 10^{-9} \cdot T \tag{4},$$

where the volume V is expressed in (m^3) and the temperature T in (K).

Table 1 presents the density values for water and n-propanol as well as those for the water-n-propanol solutions for the used molar fractions (X_{n-prop}) and temperatures (T).

Table 1. Experimental data for density values ρ [kg·m^{-3}]

X_{n-prop}	T [K]				
	292.15	299.15	305.15	311.15	317.15
0	998.480	996.395	994.608	992.820	991.033
0.1239	944.162	940.300	936.991	933.681	930.371
0.2505	900.625	896.277	892.551	888.824	885.098
0.3779	863.741	860.478	857.682	854.885	852.090
0.4996	852.733	848.068	844.069	840.070	836.071
0.6293	835.117	830.278	826.131	821.984	817.837
0.7534	824.160	818.633	813.895	809.158	804.421
0.8791	812.308	807.044	802.532	798.020	793.509
1	801.878	797.381	793.526	789.672	785.818

The dynamic viscosity η for the water-n-propanol solutions was calculated with the equation for the relative method of determination, namely:

$$\eta = \eta_0 \frac{\rho \cdot \tau}{\rho_0 \cdot \tau_0} \tag{5}$$

the „0" index refers to the reference liquid; where η and η_0 are the dynamic viscosity of the solution and n-propanol, respectively; ρ and ρ_0 – density of the solution and of n-propanol, respectively; τ and τ_0 – flow times for the solution and for n-propanol, respectively. The accuracy of viscosity measurements was $\pm 10^{-4}$ cP.

Table 2 presents the dynamic viscosity values η, calculated using the primary experimental data, ρ, τ, τ_0.

Table 2. Experimental data for dynamic viscosity $\eta \cdot 10^3$ [Pa·s]

X_{n-prop}	T [K]				
	292.15	299.15	305.15	311.15	317.15
0	1.0293	0.8794	0.7729	0.6826	0.6058
0.1239	2.6069	2.2196	1.8877	1.5557	1.2238
0.2505	3.0553	2.5987	2.2074	1.8160	1.4247
0.3779	2.9924	2.5506	2.1719	1.7933	1.4146
0.4996	2.8196	2.4275	2.0915	1.7554	1.4194
0.6293	2.5736	2.2350	1.9447	1.6545	1.3643
0.7534	2.3870	2.0866	1.8291	1.5716	1.3141
0.8791	2.2614	1.9836	1.7454	1.5072	1.2690
1	2.2735	1.9103	1.6560	1.4435	1.2649

RESULTS AND DISCUSSION

Generally, for the dependence of liquids viscosity versus temperature are known the Guzman-Andrade and Walther-Ubbelohde equations. These equations need to be verified for each category of pure liquids, with similar molecular structure, and even more for solutions.

Due to the fact that aqueous solutions are generally met in the process of liquid-liquid extraction, for industrial and pilot level, the physical parameters: density (ρ), dynamic viscosity (η) and kinematic viscosity (ν) are necessary for the improvement of the process. As a result, a study of these parameters, for the pure components (water, n-propanol) and for their solutions, was carried out.

The experimental data for these solutions may offer, next to the intrinsic parameters of viscous flow for pure liquids and solutions, thermodynamic parameters offering information about the intermolecular forces.

1. Influence of Temperature

1.1. Verification of the Guzman-Andrade Equation and the Determination of the E_{vis} and B Parameters

For the electrolytic not dissociable liquids and their solutions, the dependence of viscosity versus temperature is expressed by the semiempirical equation proposed by Guzman and Andrade:

$$\log_e \eta = \log_e B + \frac{E_{vis}}{RT} \tag{6}$$

where B is the dynamic viscosity at T→∞, E_{vis} the barrier of potential energy of flow, denominated as activation energy of viscous flow and R is the universal gas constant.

The confirmation of the equation (6) was made using the Mathcad program [9]. From the slope of the lines the activation energy of viscous flow was determined and from the intercept, the dynamic viscosity at T→∞. The values are presented in table 3.

For the studied solutions, in the proposed domains of concentration and temperature, the obtained results (the equations of the regression lines have the correlation coefficients >0,95) confirm the validity of the Guzman-Andrade equation.

Table 3. Values of the barrier of potential energy of flow (E_{vis}) and the dynamic viscosity at T→∞ (B) parameters from Equation (6)

X_{n-prop}	$10^{-4} \cdot E_{vis}$ [J·mol^{-1}]	$10^{8} \cdot B$ [Pa·s]	The correlation coefficient (R^2)
0	1.6332	123.678	0.9999
0.1239	2.3063	20.3984	0.9905
0.2505	2.3265	22.0176	0.9904
0.3779	2.2853	25.5203	0.9906
0.4996	2.0963	52.0682	0.9919
0.6293	1.9404	89.9041	0.9928
0.7534	1.8261	133.133	0.9935
0.8791	1.7681	159.868	0.9938
1	1.8066	133.763	0.9999

1.2. Verification of the Walther-Ubbelohde Equation

Using the experimental data from tables 1 and 2, there have been calculated the linear coordinates of the Walther-Ubbelohde equation, $\log_{10}(\log_{10}(v+0.6))$ and $\log_{10}(T)$. The results, obtained using the Mathcad program, confirm, with the experimental errors limit, the validity of this equation, proposed and verified for viscous organic liquids, oils etc [10 - 14]. The equation is:

$$\log_{10}[\log_{10}(v + 0.6)] = m \log_{10} T + n \tag{7}$$

where m, n, 0.6 are experimental constants, presented in table 4.

Table 4. The values of the m and n parameters from equation (7)

X_{n-prop}	$10^8 \cdot m$	n	The correlation coefficient (R^2)
0	2.3705	-0.65395	0.9946
0.1239	8.1939	-0.65397	0.9999
0.2505	10.1044	-0.65398	0.9999
0.3779	10.2261	-0.65398	0.9999
0.4996	9.1182	-0.65397	0.9999
0.6293	8.0117	-0.65397	0.9999
0.7534	7.15627	-0.65397	0.9999
0.8791	6.7144	-0.65397	0.9999
1	6.9218	-0.65397	0.9939

1.3. Calculation of the parameters of viscous flow according to Eyring

The viscous flow is considered to be similar to the phenomenon of passing of the molecules from an equilibrium state to another similar state, over a barrier of potential energy. This mechanism was discussed by Eyring, through similitude with the theory of absolutes rates of reactions [15]. The proposed equation has the following form:

$$\eta = \frac{h \cdot N_m}{V_m} \cdot \exp \frac{\Delta G_m^{\#}}{RT} \tag{8}$$

where $\Delta G_m^{\#}$ is Gibbs`s activation energy of viscous flow, for 1 mol; $N_m$ – Avogadro`s number, V_m- molar volume of the liquid and h – Planck`s constant.
As, $\Delta G_m^{\#} = \Delta H_m^{\#} - T \cdot \Delta S_m^{\#}$, equation (8) takes the following form:

$$R \log_e \frac{\eta \cdot V_m}{h \cdot N_m} = \frac{\Delta H_m^{\#}}{T} - \Delta S_m^{\#} \tag{9}$$

For the confirmation of the equation, linear coordinates $R \log_e \frac{\eta \cdot V_m}{h \cdot N_m}$ and $10^3/T$ were

used, where the molar volume has been calculated with the relation:

$$V_m = \rho^{-1} \cdot \left[M_{water} + x_{n-prop} \cdot \left(M_{n-prop} - M_{water} \right) \right] \tag{10}$$

M is the molar weight; η and ρ represent the experimental data for the studied liquids, from tables 1 and 2.

The calculation of the parameters of the lines in linear coordinates has allowed the numerical determination of the activation parameters, $\Delta H_m^{\#}$ and $\Delta S_m^{\#}$, and then, for exemplification, $\Delta G_m^{\#}$ at T = 305.15 K have been calculated (Table 5).

Table 5. Values of the Eyring activation parameters variation enthalpy ($\Delta H_m^{\#}$), variation entropy ($\Delta S_m^{\#}$) and Gibbs`s activation energy ($\Delta G_m^{\#}$)

$X_{n\text{-prop}}$	$\Delta H_m^{\#}$ [kJ·mol^{-1}]	$\Delta S_m^{\#}$ [J·mol^{-1}·K^{-1}]	$\Delta G_m^{\#}$ [kJ·mol^{-1}]
0	16.102	23.186	9.026
0.1239	22.610	34.831	11.981
0.2505	22.729	31.805	13.024
0.3779	22.437	29.201	13.524
0.4996	20.355	21.349	13.840
0.6293	18.760	15.423	14.054
0.7534	17.514	10.776	14.226
0.8791	16.960	8.380	14.403
1	17.443	9.355	14.589

2. Influence of Concentration

Many empirically equations for the correlation between the solutions viscosity and the pure components viscosity are proposed in the literature. For the ideal behavior of the solutions, the most adequate equation is the one proposed by Arrhenius [16] and modified by Kendall and Monroe [17]:

$$\log_e \eta_{id} = X_{n-prop} \log_e \eta_{n-prop} + (1 - X_{n-prop}) \log_e \eta_{watet} \tag{11}$$

The deviations from the ideal behavior, explained through the variation of volume, which take place during the mixing, are demonstrated by the lake of the equality (11). The confirmation of these deviations is made by introducing the excess viscosity (η_{excess}), expressed with the equation (12):

$$\eta_{excess} = \eta - \eta_{id} \tag{12}$$

where η is the dynamic viscosity for real solutions, experimentally determined.
The processing of the experimental data using specialized programs (Mathcad and Table Curve [18]), has allowed the establishment of the following dependence of the excess viscosity (η_{excess}, (Pa·s)) versus the concentration of the water-n-propanol solutions, at constant temperature:

$$\eta_{excess} = a + b \cdot X_{n-prop} \cdot \log_e X_{n-prop} + c \cdot (X_{n-prop})^2 \log_e X_{n-prop} \tag{13}$$

The coefficients a, b and c (equation (13)) are presented in Table 6, for the five values of the temperature used in the experiment:

Table 6. The parameters a, b and c from the equation (13)

	t [^{o}C]				
	19	**26**	**32**	**38**	**44**
a	3.53012·10^{-7}	1.37939·10^{-5}	1.63882.10^{-5}	1.24319·10^{-5}	3.16084·10^{-6}
b	-0,006436	-0,005284	-0,004299	-0,003316	-0,002333
c	0,005396	0,004029	0,003064	0,002250	0,001558
(R^2)	0,9994	0,9986	0,9977	0,9974	0,9976

The validity of the empirically proposed model is shown up in Fig.1, where are presented both the experimental values of the excess viscosity and the ones calculated with the equation (12).

The empirically determined model using the experimental data is simple, as compared to others [14, 19]; it depends only on three coefficients and offers a good accordance with the experimental data. Also, this model is valid for the following systems: water-iso-propanol and water-propanoic acid.
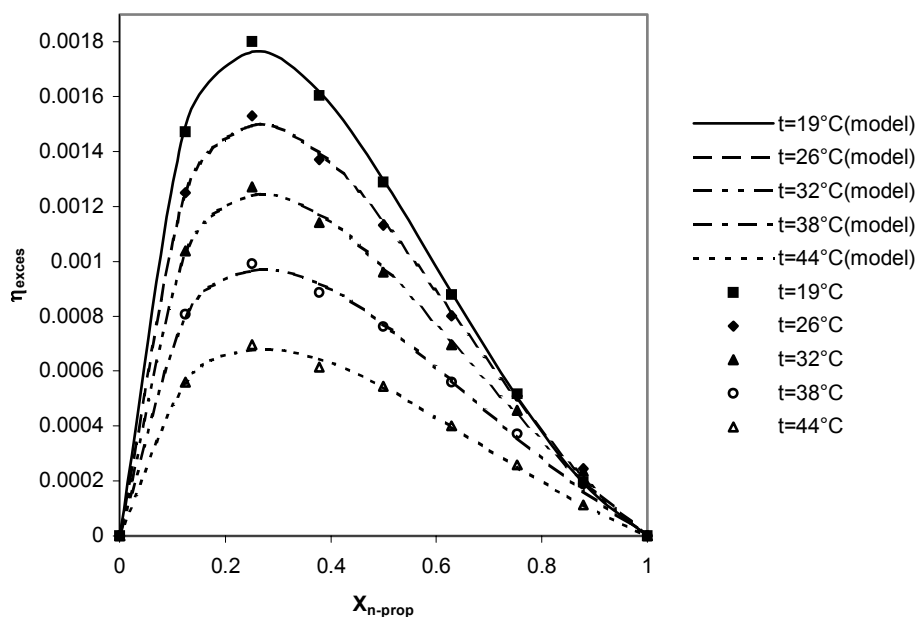

Figure 1. Influence of concentration versus the excess viscosity for water-n-propanol solutions.

CONCLUSIONS

1. There has been established the applicability of the Guzman-Andrade, Walther-Ubbelohde and Eyring equations and from these equations there have been calculated the main intrinsic parameters of the viscous flow.

2. The dynamic viscosity, η, and the molar energy, E_{vis} decrease with the increase of the n-propanol concentration, for the molar fractions $X_{n-prop}>0.25$. For the molar fractions $0<X_{n-prop}<0.25$, the dynamic viscosity increases with the increase of the concentration because, in this case, prevail the hydrogen bounds formed between the water molecules, which are stronger than the ones from the n-propyl alcohol. For all the used temperatures, the maximum of the variation curves of excess viscosities is approximately at the same concentration, $X_{n-prop} = 0.25$.

3. $\Delta G_m^{\#}$ and $\Delta H_m^{\#}$ are positive, because the passing of the molecules in an activate state requires the breaking of the hydrogen bonds.

4. For the dependence of the excess viscosity versus concentration it was established an experimental equation, with the coordinates η_{excess} and X_{n-prop},

having a very good correlation coefficient for the whole domain of the used temperatures.

5. The studied binary system presents positive deviations from the ideality.

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