INFLUENCE OF POLYVINYLPYRROLIDONE ON THE INTERACTION BETWEEN WATER AND METHANOL

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Abstract - The present work aims to determine the influence of a dissolved polymer, polyvinylpyrrolidone, on the interaction between water and methanol. First, the dynamic viscosities were measured for polymer solutions by a rotational concentric cylinder at 25 °C and for the polymer concentration range from 0.1 to 0.6 g/dl. The results show a polynomial dependence of the viscosity on polymer concentration. On the hypothesis of a quasi-binary system, a pseudo Grumberg-Nissan constant, d_p', was introduced to quantify the interaction between unlike molecules in the presence of polymer. The interaction between unlike molecules due to the presence of the polymer was quantified by the deviation of the Grumberg-Nissan constant, $\delta d_p' = d_p' - d_p$. Generally, this constant is negative which means that the interactions between water and methanol decrease in the presence of polyvinylpyrrolidone at 25 °C. The presence of the polymer induces a perturbation of the dynamic equilibrium between free and complexed molecules.
Keywords: Viscosity; Rheology; Polymer; Mixed solvents; Interaction.

INTRODUCTION

It is well established that the mixture of water and an amphiphilic molecule provides a network due to the hydrogen bonds (Laaksonen *et al.*, 1997; Wakisaka *et al.*, 1998; Guo *et al.*, 2003; Dixit *et al.*, 2002; Dougan *et al.*, 2004; Georgiev *et al.*, 2007). In fact, experimental studies supported by computational investigations have been used to study the micro-scopic structure of this type of system, where clusters are formed between like and/or unlike molecules (Mikhail and Kimel, 1961; Zhao and Malinowski, 1999; Yilmaz, 2002; Gonzalez-Salgado and Nezbeda, 2006). In this type of system, the interaction between unlike molecules can be quanti-fied from viscosity measurements and by calculating the Grumberg-Nissan constant d' (Grumberg and

Nissan, 1949). In our previous work (Guettari and Gharbi, 2011), a correspondence between the Grumberg-Nissan constant d' variation and the com-plexation in water/methanol mixtures was established. This result was extended to the mixture of water/ amphiphilic molecule.

Several studies have investigated the effect of the addition of an impurity, ionic or non-ionic, to a binary liquid mixture. These works were interested in the effect of an added impurity on the viscosity (Oleinikova *et al.*, 1997; Huque *et al.*, 2006; Zhao *et al.*, 2006; Wang *et al.*, 2004; Haldar and Das, 2008), conductivity (El. Dossoki, 2010), molar volume (Zhao *et al.*, 2006), and density (Huque *et al.*, 2006) of the binary liquid mixture. However, the effect on the microscopic structure of the binary liquid mixture was not taken into account, and only

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phenomenological interpretations were reported. In this study, we quantify the effect of the addition of a small quantity of a polymer, polyvinylpyrrolidone (PVP), on the microscopic structure of water/ methanol mixtures at 25 °C and over a large range of mixture composition. The polymer used has been the subject of our previous investigations (Guettari *et al.*, 2008; Guettari *et al.*, 2010; Guettari and Gharbi, 2010), and this work is an extension of our earlier investigation (Guettari and Gharbi, 2011) concerning the microscopic structure of water/amphiphilic molecule mixtures by studying the interaction between unlike molecules. When the polymer concentration is small, the mixture can be considered as quasi-binary; thus, the mixture composition is assumed to be unchanged after polymer addition. Taking into account the last hypothesis, the deviation of the Grumberg-Nissan constant $\delta d_p'$ due to the presence of the polymer was calculated as described in the theoretical background section.

First, the viscosities of polymer solutions were measured with a rotating co-axial cylinder. Then, the effects of the presence of the polymer on the microscopic structure of water/methanol mixtures were quantified and discussed according the deviation of the Grumberg-Nissan constant values.

THEORETICAL BACKGROUND

Competing forces include excluded-volume interactions, van der Waals interaction, and the solvent-mediated hydrodynamic interaction. According to Grumberg-Nissan (Grumberg and Nissan, 1949), the interaction between unlike molecules 1 and 2 can be quantified by calculating the constant d' at a mole fraction of liquid 1, X_1, according to the following equation:

$$\ln(\eta_m) - [X_1 \ln(\eta_1) + (1 - X_1) \ln(\eta_2)] = X_1(1 - X_1)d' \quad (1)$$

where η_1, η_2 and η_m are respectively the dynamic viscosity of liquids 1, 2 and the mixture. When a polymer is dissolved in a solvent i=(1,2) at low concentration C, the viscosity of solution η_i^* can be approximated by the following equation (Couarraze and Grossiord, 2000):

$$\eta_i^* = \eta_{i,0}(1 + a_{1,i}C + a_{2,i}C^2 + a_{3,i}C^3 + ...), \quad (2)$$

where $a_{1,i}$, $a_{2,i}$ and $a_{3,i}$ are deduced from the viscosity data adjustment. $\eta_{i,0}$ is the viscosity of liquid i at zero polymer concentration.

When the liquids are mixed, the viscosity of the polymer solution η_m^* can be also expressed at low concentration by the following equation:

$$\eta_m^* = \eta_{m,0}(1 + a_{1,m}C + a_{2,m}C^2 + a_{3,m}C^3 + ...), \quad (3)$$

where $a_{1,m}$, $a_{2,m}$ and $a_{3,m}$ are deduced from the viscosity data adjustment. $\eta_{m,0}$ is the viscosity of the mixed liquid at zero polymer concentration.

By assuming that the presence of polymer does not affect the composition of the binary mixture, we can define a pseudo Grumberg-Nissan constant d_p' at a mole fraction X_1 of liquid 1. This parameter quantifies the interactions between water and methanol in the presence of polymer at low concentration:

$$\ln(\eta_m^*) - [X_1 \ln(\eta_1^*) + (1 - X_1) \ln(\eta_2^*)] = X_1(1 - X_1)d_p' \quad (4)$$

where η_m^*, η_1^* and η_2^* are respectively the dynamic viscosity of the mixture, liquid 1 and 2, in the presence of polymer at low concentration.

By combining Equations (2), (3) and (4), the pseudo Grumberg-Nissan constant d_p' can be connected to the Grumberg-Nissan constant d' as in Equation (5):

$$d_p' - d' = \frac{\ln(\Gamma_p)}{X_1(1 - X_1)}, \quad (5)$$

where Γ_p is a function depending on the polymer concentration C and the mole fraction of liquid 1 in the mixture, X_1; the coefficients $a_{i,j}$ ($1 \leq i \leq 3$ and j=1,2,m) are deduced from the viscosity data adjustment as defined in Equations (2) and (3):

$$\Gamma_p(X_1, C) = \frac{1 + a_{1,m}C + a_{2,m}C^2 + a_{3,m}C^3}{\left(1 + a_{1,1}C + a_{2,1}C^2 + a_{3,1}C^3\right)^{X_1} \left(1 + a_{1,2}C + a_{2,2}C^2 + a_{3,2}C^3\right)^{1-X_1}} \quad (6)$$

Finally, the effect of the presence of a polymer on the interaction between unlike molecules in a binary liquid mixture can be expressed by the Grumberg-

Nissan constant deviation $\delta d_p'$ given by the following expression:

$$\delta d_p' = d_p' - d_p \tag{7}$$

EXPERIMENTAL

Sample Preparation

The chemical components, methanol of purum grade and PVP (M = 360,000 g/mol) of monodisperse grade, were purchased from Aldrich. Bidistilled water and alcohol were separately filtered through Millipore filters of 0.22 μm to eliminate dust. Then, water and methanol mixtures were prepared by weight. To minimize experimental error, the total mass of the prepared mixture, at a given methanol mole fraction X_1, was taken as m_T =50 g. The concentration, C, of the dissolved polymer was less than the critical concentration for overlapping, C*, estimated to be close to 0.6 g/dl (Guettari *et al.*, 2010).

Rotational Concentric Cylinder Viscometer

A Brookfield DV-II + Pro Viscometer of the rotational variety with coaxial cylinder geometry was used. The apparatus measures the torque required to rotate an immersed element, the spindle, in a solution. The spindle is driven by a motor through a calibrated spring. The cylindrical spindle, which we used, is adapted to characterize small samples of low viscosities. For this apparatus the shear rate, $\dot{\varepsilon}$, and shear stress, τ, are given by the following equations (Couarraze and Grossiord, 2000; Steffe, 1996):

$$\dot{\varepsilon} = \frac{2\omega R_c^2}{(R_c^2 - R_b^2)}\left(s^{-1}\right) \tag{8}$$

$$\tau = \frac{M}{2\pi R_b^2 L}\left(dyn/cm^2\right), \tag{9}$$

where, R_c and R_b are respectively, the container and spindle radius, ω is the angular velocity of the spindle (rad/sec), M is the torque (dyn.cm) and L is the length of the spindle. For a Newtonian fluid, the shear rate is proportional to shear stress according to the linear equation:

$$\tau = \eta \dot{\varepsilon}, \tag{10}$$

where η(cP) is the dynamic viscosity of the solution. In practice, the dynamic viscosity is the slope of the rheogram: $\tau = f(\dot{\varepsilon})$. The dynamic viscosities were measured with relative errors less than 3%.

RESULTS AND DISCUSSION

The shear stress-shear rate rheograms were established for solutions of PVP at 25 °C. All the rheograms obtained showed a linear variation of the shear stress versus the shear rate, as shown by the examples of Figure 1. These rheograms reveal the Newtonian behaviour of the studied solutions and their slopes give us the dynamic viscosities of these solutions.
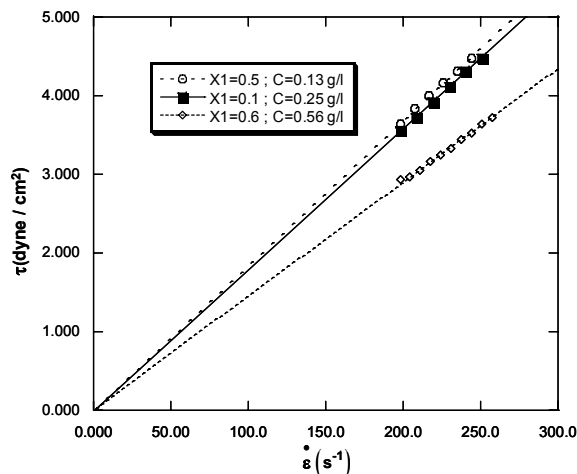

Figure 1: Rheograms of polymer solution for different methanol compositions and polymer concentrations at 25 °C.

We report in Figure 2 the dynamic viscosities of the studied polymer solutions versus the concentration, for different composition of the binary mixture. These curves show a polynomial dependence according to Equation (2). For polymer in pure solvents, the fit of the experimental curves shows that the solution viscosities depend on the polymer concentration at 25 °C according to the following equations:

In methanol:

$$\eta_1^*(C) = 0.541(1 + 1.227C + 3.096C^2 - 1.994C^3 + ...) \tag{11}$$

In water:

$$\eta_2^*(C) = 0.984(1 + 1.634C$$

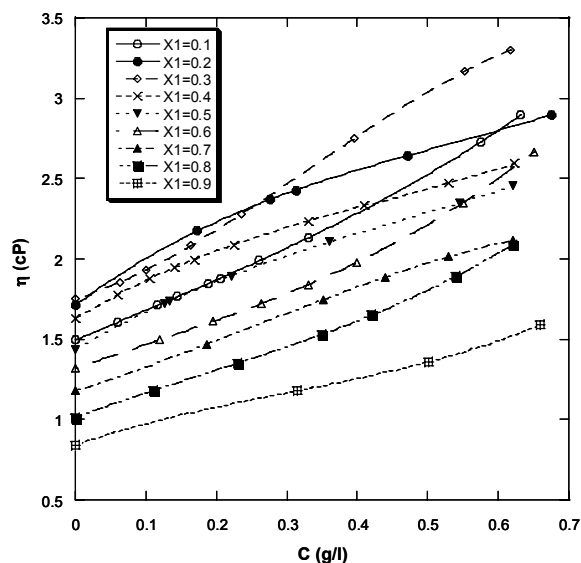$$- 1.346C^2 + 1.375C^3 + ...)$$

(12)

Figure 2: Dynamic viscosity η(cP) of polymer solutions vs. polymer concentration for different mixture compositions at 25 °C.

For polymer in mixed solvents, the fit of the experimental curves shows that the solution viscosities follow a polynomial dependence. Table 1 reports the coefficients deduced from the viscosity data adjustment as defined in Equation (3).

Table 1: The fitted dynamic viscosity coefficient $a_{i,m}$ (i=1-3) and the viscosity at zero polymer concentration $\eta_{m,0}$ for the polymer solutions at different composition of the mixture

X_1	$\eta_{m,0}$	$a_{1,m}$	$a_{2,m}$	$a_{3,m}$
0.1	1.495	1.253	-0.157	0.821
0.2	1.712	1.921	-2.317	1.468
0.3	1.753	0.773	2.790	-2.796
0.4	1.629	1.652	-2.114	1.583
0.5	1.439	1.780	-1.833	1.281
0.6	1.32	1.148	-0.378	1.582
0.7	1.178	1.182	1.062	-1.445
0.8	1.014	1.596	-1.146	2.146
0.9	0.841	1.715	-2.210	2.516

According to Equations (5) and (6), we have calculated the deviation of the Grumberg-Nissan constant, $\delta d_p'$, which is due to the presence of the polymer in the binary liquid, for different compositions X_1 and polymer concentrations C. The variation of the deviation of the Grumberg-Nissan constant versus methanol mole fraction X_1 were plotted in

Figures 3 and 4, respectively, for polymer concentrations of C= 0.1-0.3 g/dl and C= 0.4-0.6 g/dl. The analysis of the obtained curves show the existence of three different values of the deviation of the Grumberg-Nissan constant, i.e., negative, positive and zero.
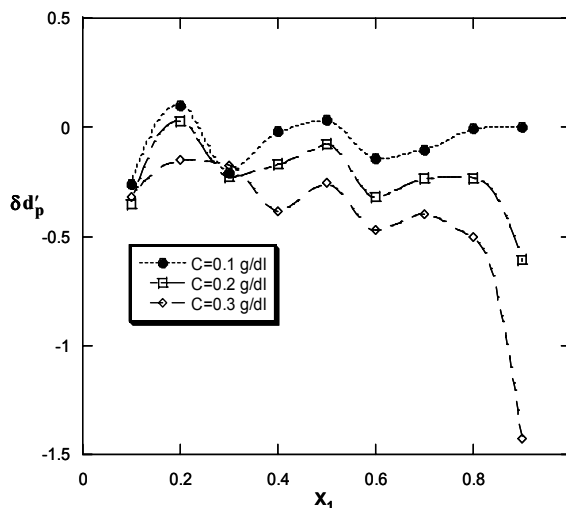

Figure 3: Deviation of the Grumberg-Nissan constant, $\delta d_p'$, vs. methanol molar fraction X_1 for the polymer concentration C=0.1-0.3 g/dl.
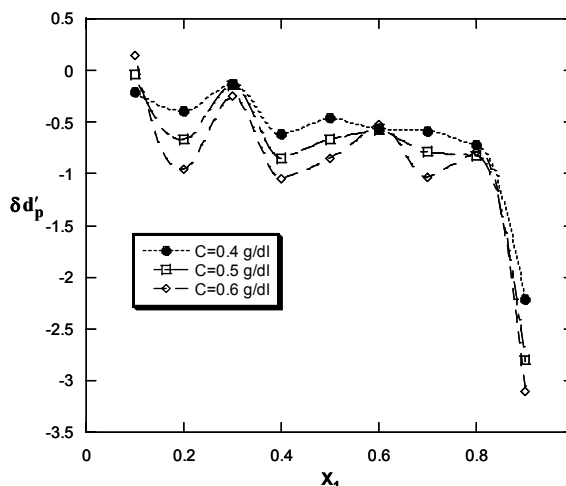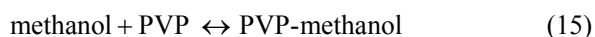

Figure 4: Deviation of the Grumberg-Nissan constant, $\delta d_p'$, vs. methanol mole fraction X_1 for the polymer concentrations C=0.4-0.6 g/dl.

Generally, the sign of the deviation of the Grumberg-Nissan constant, $\delta d_p'$, is negative, which means that the interactions between water and methanol molecules decrease in the presence of polymer. In fact, due to the hydrogen bonds, a complex can be formed between free water and

methanol molecules according to the following dynamic equilibrium (Zhao *et al.*, 1999):

$$\text{Water} + \text{methanol} \leftrightarrow \text{Water-methanol} \qquad (13)$$

The addition of PVP to the binary mixture permits the establishment of hydrogen bonds between polymer and free and/or bonded molecules in the mixture:

$$\text{Water} + \text{PVP} \leftrightarrow \text{PVP-water} \qquad (14)$$

$$\text{methanol} + \text{PVP} \leftrightarrow \text{PVP-methanol} \qquad (15)$$

In fact, this type of polymer provides a preferential interaction with one component of the mixture, depending on methanol mole fraction X_1 (Guettari and Gharbi, 2011).

Thus, the presence of the polymer induces a perturbation of the dynamic equilibrium between free and complexed molecules at fixed temperature. According to Le Chatelier's principle, the adsorption of a molecule (water or methanol) on PVP should displace the equilibrium between free molecules and the water/methanol complex. This displacement in the complex dissociation induces a reduction of the interaction between unlike molecules and thus a decrease of the Grumberg-Nissan constant, which explains the negative value of the change of the Grumberg-Nissan constant due to the presence of polymer. For the methanol mole fraction of $X_1=0.3$, the deviation of the Grumberg-Nissan constant seems to be independent of the polymer concentration.

However, in a few cases, the deviation of the Grumberg-Nissan constant vanishes. This means that the presence of polymer does not affect the interaction between unlike molecules. This situation was observed especially for the lowest polymer concentration, C=0.1 g/dl (Fig. 3), which corresponds to very little perturbation of the complex formed between water and methanol due to hydrogen bonds. As the polymer concentration increases, the deviation of the Grumberg-Nissan, $\delta d_p'$, decreases.

This means that the interactions between unlike molecules decrease upon increasing the number of polymer molecules in the mixture. On the other hand, $\delta d_p'$ decreases spectacularly in the alcohol-rich region, $X_1=0.9$, which means that the interactions between water and methanol become much lower and the dissociation of the water/methanol complex is possible.

CONCLUSION

The quantification of the interaction between unlike molecules is usually described by the Grumberg-Nissan constant. In the presence of a polymer and according to the quasi-binary system hypothesis, the interaction between unlike molecules is quantified by a pseudo Grumberg-Nissan constant. An expression of the deviation of the Grumberg-Nissan constant due to the presence of a polymer was theoretically established. The application of the established method has determined the effect of the presence of polyvinylpyrrolidone on the mixture of water and methanol at 25 °C.

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