

## Density, Viscosity, Refractive Index and Excess Properties of Binary and Ternary Solutions of Poly (Ethylene Glycol), Sulfate Salts and Water at 298.15 K

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The refractive index ( $n_D$ ), viscosity ( $\eta$ ) and density ( $\rho$ ) values of the poly (ethylene glycol) (PEG)300, 400 and 600 + water, zinc sulfate, magnesium sulfate and aluminum sulfate + water binary and their ternary solutions have been measured at 298.15 K and atmospheric pressure. In this work, the effect of concentration (0.05-0.3 %w/w), PEG molecular weight and type of cation on the  $n_D$ ,  $\eta$  and  $\rho$  of the mentioned binary and ternary mixtures have been explored. Furthermore, the experimental measurements were applied to compute the refractive index deviation ( $\Delta n_D$ ), viscosity deviation ( $\Delta \eta$ ), the apparent specific volume ( $V_\phi$ ), excess molar volume ( $V^E$ ) and excess Gibbs energy of activation for viscous flow ( $\Delta G^{*E}$ ) for the analysis of the behavior of the solutions.  $\Delta n_D$  and  $V^E$  were fitted to the Cibulka and a third-order Redlich-Kister polynomial models to estimate the interaction parameters. The intermolecular interactions between the mixing components were demonstrated by the obtained data from the calculated functions.

**Keywords:** Refractive index, Density, Excess properties, Poly (ethylene glycol), Aluminum sulfate

### INTRODUCTION

Today, physicochemical and thermodynamic features of solutions are a main part of the engineering computations to design industrial unit operations in terms of the transport phenomena and interpreting the liquid state [1]. Thus, investigations on liquid solution behavior of the industrially significant chemicals have been favored by researchers [2-4]. Aqueous solutions involving poly (ethylene glycol) (PEG), inorganic salts (found in an extensive range of molecular masses), and salt types with uncommon features such as high water solubility, low operational cost, low toxicity and low flammability were explored in terms of an extensive range of applications in the biotechnology [5,6], pharmaceutical, and cosmetic products [7]. Refractive index, density, and viscosity are of tremendous significance in terms of the physical properties and understanding them

comprehensively would shed light on the basic behavior of liquid systems regarding mass transport and fluid flow.

As a water-soluble hydrophilic and biocompatible polymer, PEG has several applications in chemical partitioning [8,9]; in recent years, researchers have extensively used crystallization of inorganic salts [10]. Moreover, tartrate salts are not poisonous [11] and some of them are of great worth and it is possible to recycle them too [12]. Various fields including medicine [13], electronics [14], industry [15] have benefited from their application and it is possible to use them as an appropriate green substitute for traditional inorganic salts [16]. In addition to their significant involvement in partitioning biological materials, the release of tartrate into the biological wastewater is not dangerous for the environment and the plants [17,18]. To the best of our knowledge, no report has been published on the physical and thermophysical features of binary and ternary solutions of PEG300, 400, 600 + water and zinc sulfate, magnesium sulfate and aluminum sulfate + water.

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**Table 1.** Specifications of Pure Components Used in this Work

| Chemical name     | CAS number | Source        | Initial mole fraction purity | Final mole fraction purity | Purification method        |
|-------------------|------------|---------------|------------------------------|----------------------------|----------------------------|
| PEG300            | 25322-68-3 | Merck         | 0.99                         | 0.999                      | Crystallization            |
| PEG400            | 25322-68-3 | Merck         | 0.99                         | 0.999                      | Crystallization            |
| PEG600            | 25322-68-3 | Merck         | 0.99                         | 0.999                      | Crystallization            |
| Zinc sulfate      | 7446-20-0  | Sigma Aldrich | 0.99                         | 0.9997                     | Fractional crystallization |
| Magnesium sulfate | 7487-88-9  | Sigma Aldrich | 0.99                         | 0.9997                     | Fractional crystallization |
| Aluminum sulfate  | 10043-01-3 | Sigma Aldrich | 0.99                         | 0.9999                     | Fractional crystallization |

The thermophysical features consisting of PEG and various chemicals have been investigated by a large number of researchers. Cruz *et al.* [19] determined kinematic viscosities of various molecular weight of PEG(200, 400, 600, 1000, 1500 and 3350) by the application of different temperatures ranging from 293.15-363.15 K. Li *et al.* [20] explored excess features for the binary system of PEG 200 + 1,2-ethanediamine at (303.15-323.15) K and the spectroscopic studies of system. Mousavi *et al.* [3] focused on some thermophysical features of PEG200 binary solutions using different temperatures. Also, Eliassi *et al.* [21] have measured densities of aqueous solutions of PEG(400, 4000 and 6000) at 300.15, 310.15, 313.15, 318.15, 323.15 and 328.15 K.

The current study focused on the experimental values of the refractive index, density, and viscosity of binary and ternary mixtures of PEG300, 400, 600, water and zinc sulfate, magnesium sulfate and aluminum sulfate at 298.15 K and atmospheric pressure. Deviations from ideality were explored with refractive indices deviations, excess molar volumes, viscosity deviations, the apparent specific volumes and excess Gibbs energy of activation. Furthermore, the Redlich-Kister and Cibulka equations were used to correlate and predict the obtained thermophysical data by driving adjustable parameters.

## MATERIALS AND METHODS

### Material

To prepare the materials, PEG with average of 300, 400

and 600 g mol<sup>-1</sup> and zinc sulfate, magnesium sulfate, and aluminum sulfate with minimum purity of 99.5% of mass percentage were supplied from Merck (Darmstadt, Germany) and Sigma, respectively. They were used with no further purification. Distilled deionized water (conductivity = 17.5  $\mu\text{s cm}^{-1}$ ) was used for the preparation of solutions. All other materials were in analytical grade. The chemical name, purification method, purity, and analytical method are reported in Table 1.

The densities of the studied pure PEGs were compared with the available literature [22-37] (Table 2). In the majority of cases, a good agreement between the studied and literature values was observed. In Table 2, the density data shows that the average absolute deviation percent (AAD%) between experimental and literature values are between 0.040136 (for PEG300 [22], 0.007487 for PEG400 [26,34] and 0.035616 for PEG600 [36]. The maximum AAD% = 0.820549 was found for PEG300 [24]. Taking into account that these agreements are satisfactory, no further purification was performed.

### Preparation of Solution

The mass fractions of 0.05-0.3 for the PEG or salt are used for density, viscosity and refractive index measurements and the range is selected in accordance with the conventional values used in industries. 10 grams of specific amounts of PEG or salt with water were mixed in a 15 ml scaled tube. All binary were prepared by mass using an analytical balance (A&D; model GF300; Japan) with an accuracy of  $\pm 10^{-4}$  g. The samples are then stirred well in a

**Table 2.** Densities  $\rho$  of the Pure PEG Studied in this Work at 298.15 K and Pressure of 0.1 MPa<sup>a</sup>

| Component   | $\rho_{\text{exp}}$<br>(g cm <sup>-3</sup> ) | $\rho_{\text{lit}}$<br>(g cm <sup>-3</sup> ) | <i>AAD</i> % <sup>a</sup> |
|-------------|--|--|---------------------------|
| PEG300      | 1.1212                                       | 1.12165 [22]                                 | 0.040136                  |
|             |  | 1.1217 [23]                                  | 0.044595                  |
|             |  | 1.1304 [24]                                  | 0.820549                  |
|             |  | 1.1233 [25]                                  | 0.187299                  |
| PEG400      | 1.1219                                       | 1.12225 [22]                                 | 0.031197                  |
|             |  | 1.121984 [26]                                | 0.007487                  |
|             |  | 1.1218 [27]                                  | 0.008913                  |
|             |  | 1.12162 [28]                                 | 0.024958                  |
|             |  | 1.12249 [29]                                 | 0.052589                  |
|             |  | 1.1223 [30]                                  | 0.035654                  |
|             |  | 1.1224 [31]                                  | 0.044567                  |
|             |  | 1.121984 [32]                                | 0.007487                  |
|             |  | 1.12249 [29]                                 | 0.052589                  |
|             |  | 1.1223 [33]                                  | 0.035654                  |
|             |  | 1.1218 [27]                                  | 0.008913                  |
|             |  | 1.12162 [28]                                 | 0.024958                  |
|             |  | 1.123835 [34]                                | 0.172475                  |
|             |  | 1.1231 [35]                                  | 0.106961                  |
| 1.1226 [36] | 0.062394                                     |  |                           |
| 1.1218 [27] | 0.008913                                     |  |                           |
| 1.1231 [34] | 0.106961                                     |  |                           |
| PEG600      | 1.1214                                       | 1.12177 [28]                                 | 0.118422                  |
|             |  | 1.122 [37]                                   | 0.097943                  |
|             |  | 1.1225 [24]                                  | 0.053424                  |
|             |  | 1.1235 [36]                                  | 0.035616                  |

The standard uncertainties,  $u$ , of P and T are  $u(P) = 0.1$  kPa and  $u(T) = 0.1$  K.

$$^a \text{AAD}\% = \frac{100}{N} \sum_{i=1}^N \left| \frac{A_i^{\text{exp}} - A_i^{\text{cal}}}{A_i^{\text{exp}}} \right|$$

magnetic stirrer to ensure that the PEG or salt is completely dissolved in water. When stirring was being applied, the samples were closed tightly and the glass tube was equipped with an external jacket put in a thermostatic bath (Mettler, Germany, model INE400) to have an uncertainty of  $\pm 0.1$  K. To thoroughly confirm the miscibility, retention was permitted at a desired temperature for 2 h. A CETI refractometer (Belgium) with an accuracy of  $0.0001 n_D$ , an Anton Paar oscillation U-tube densitometer (model: DMA 500) (DMA 500) with a precision of  $\pm 10^{-4} \text{ g cm}^{-3}$  and an Anton Paar Lovis 2000 M viscometer of various capillary sizes (1.59-1.8 mm) with an accuracy of up to 0.5% were employed to measure the refractive index, viscosity and density values of the solutions.

## RESULTS AND DISCUSSION

### Density, Excess Molar Volume and the Apparent Specific Volume

For understanding the intermolecular interactions in our binary solutions excess molar volume ( $V^E$ ), set as the deviation of ideality of density, was defined as follows [38]:

$$V^E = V_m - \sum_{i=1}^I X_i V_i \quad (1)$$

where  $V_m$  is the molar volume of the solution,  $V_i$  indicates the molar volume for the pure component  $i$ , and  $X_i$  denotes the mole fraction of component  $i$ . The molar volumes of the solution were calculated from the experimental densities using Eq. (2) [38]:

$$V_m = \frac{\sum_{i=1}^I M_i X_i}{\rho} \quad (2)$$

where  $M_i$  is the molecular weight of the pure component  $i$ ,  $X_i$  denotes the mole fraction of the component  $i$ , and  $\rho$  indicates the experimental density values of the solution. The apparent specific volumes of the polymer  $V_\phi$  in water was obtained based on the equation below [39]:

$$V_\phi = \frac{1}{W \left( \frac{1}{\rho} - \frac{1-W}{\rho_w} \right)} \quad (3)$$

where the terms  $\rho$ ,  $\rho_w$  and  $w$  denote the densities of the solution and solvent, and mass fraction of PEG, respectively.

### Binary System

According to Tables 3 and 4, the density of aqueous solutions of PEG and salt is increased by increasing the mass fraction of polymer and salt. The densities of aqueous polymer solutions are  $1.0473$ ,  $1.04790$  and  $1.0486 \text{ g cm}^{-3}$  for 0.3 mass fraction of PEG300, 400 and 600, respectively, and the density is higher for the salt solution. For 0.3 mass fraction of zinc, aluminum and magnesium sulfate are  $1.1947$ ,  $1.1822$  and  $1.1531 \text{ g cm}^{-3}$ , respectively.

Also, a comparison was made between the experimental density data and the available literature values [25,27,31,36]. Considering the different concentrations selected in this study compared to the other studies, the density values of this study were first correlated as a function of mixtures composition as described by Eq. (4) which involves the nonlinear effect of mixtures composition on the density values:

$$\rho = \frac{a}{1 + \exp(b - cx_p)} \quad (4)$$

where  $\rho$  is density of binary mixture, and  $X_p$  are the mole fraction of PEG and the fitting parameters are denoted by  $a$ ,  $b$  and  $c$ . The respective coefficients and statistical parameters are shown in Table 5.

Therefore, density values were correlated as a function of mixtures composition as described by Eq. (4) which involves the nonlinear effect of mixtures composition on the density values. The experimental mole fraction data were fitted to Eq. (4) model. Model constants were computed using Curve Expert Professional software. The trained version of the models were used to predict the literature density reported in Table S1. In Table S1, the density data show that the average absolute deviation percent between experimental and predicted values at  $T = 298.15$  K are 0.2098 for PEG300 [24], 0.1377 for PEG400 [27], 0.1567 for PEG400 [31] and 0.1022 for PEG600 [36]. The excellent agreement were observed between experimental density data and predicted data.

The apparent specific volumes of PEG in water ( $V_\phi$ ) reduced when the polymer mass was increased by up to

**Table 3.** Experimental Density ( $\rho$ ), Molar Volume ( $V_m$ ), Excess Molar Volume ( $V^E$ ) and Apparent Specific Volume ( $V_\phi$ ) and Mass Fraction ( $w$ ) of PEG300, 400, 600 (1) + Water (2) Solution at 298.15 K and 0.1 MPa

| $w_1$         | $x_1$   | $\rho(\pm 0.0001)$<br>(g cm <sup>3</sup> ) | $V_m$<br>(cm <sup>3</sup> mol <sup>-1</sup> ) | $V^E$<br>(cm <sup>3</sup> mol <sup>-1</sup> ) | $V_\phi$<br>(cm <sup>3</sup> g <sup>-1</sup> ) |
|---------------|---------|--|---|---|--|
| PEG300 +water |         |  |   |   |  |
| 0.00          | 0.00000 | 0.9970                                     | 0.000   | 0.000   | -  |
| 0.05          | 0.00315 | 1.0046                                     | 0.956   | -0.038  | 0.8512   |
| 0.10          | 0.00663 | 1.0128                                     | 1.955   | -0.090  | 0.8465   |
| 0.15          | 0.01049 | 1.0205                                     | 3.087   | -0.135  | 0.8490   |
| 0.20          | 0.01479 | 1.0294                                     | 4.313   | -0.207  | 0.8170   |
| 0.25          | 0.01962 | 1.0374                                     | 5.668   | -0.266  | 0.8468   |
| 0.30          | 0.02509 | 1.0473                                     | 7.190   | -0.372  | 0.8473   |
| 1.00          | 1.00000 | 1.1212                                     | 267.57  | 0.000   | -  |
| PEG400 +water |         |  |   |   |  |
| 0.00          | 0.0000  | 0.9970                                     | 0.000   | 0.000   | -  |
| 0.05          | 0.00236 | 1.0045                                     | 0.956   | -0.036  | 0.8532   |
| 0.10          | 0.00498 | 1.0130                                     | 1.974   | -0.093  | 0.8349   |
| 0.15          | 0.00789 | 1.0211                                     | 3.095   | -0.145  | 0.8197   |
| 0.20          | 0.01113 | 1.0288                                     | 4.316   | -0.193  | 0.8072   |
| 0.25          | 0.01479 | 1.0377                                     | 5.705   | -0.270  | 0.7929   |
| 0.30          | 0.01894 | 1.0479                                     | 7.219   | -0.370  | 0.7656   |
| 1.00          | 1.00000 | 1.1219                                     | 356.538                                       | 0.000   | -  |
| PEG600 +water |         |  |   |   |  |
| 0.00          | 0.00000 | 0.9970                                     | 0.000   | 0.000   | -  |
| 0.05          | 0.00158 | 1.0052                                     | 0.637   | -0.048  | 0.8394   |
| 0.10          | 0.00333 | 1.0120                                     | 1.304   | -0.072  | 0.8543   |
| 0.15          | 0.00527 | 1.0210                                     | 2.076   | -0.141  | 0.8458   |
| 0.20          | 0.00745 | 1.0297                                     | 2.913   | -0.209  | 0.8437   |
| 0.25          | 0.00991 | 1.0386                                     | 3.813   | -0.286  | 0.8423   |
| 0.30          | 0.01270 | 1.0486                                     | 4.849   | -0.373  | 0.8415   |
| 1.00          | 1.00000 | 1.1231                                     | 356.157                                       | 0.000   | -  |

Standard uncertainties:  $u(w_i) = 0.001$ ;  $u(P) = 5$  kPa;  $u(T) = 0.05$  K.

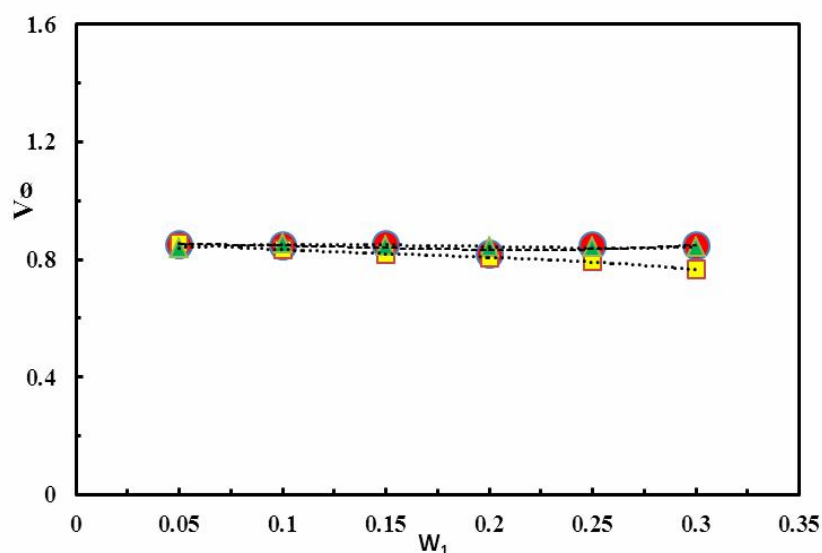
**Table 4.** Experimental Density ( $\rho$ ), Molar Volume ( $V_m$ ), Excess Molar Volume ( $V^E$ ) and Apparent Specific Volume ( $V_\phi$ ) and Mass Fraction ( $w$ ) of Magnesium Sulfate, Zinc Sulfate and Aluminum Sulfate (1) + Water (2) Solution<sup>a</sup> at 298.15 K and 0.1 MPa

| $w_1$                             | $x_1$   | $\rho(\pm 0.0001)$<br>( $\text{g cm}^3$ ) | $V_m$<br>( $\text{cm}^3 \text{mol}^{-1}$ ) | $V^E$<br>( $\text{cm}^3 \text{mol}^{-1}$ ) |
|-----------------------------------|---------|---|--|--|
| Magnesium sulfate (1) + water (2) |         |   |  |  |
| 0.00                              | 0.00000 | 0.9970                                    | 0.00                                       | 0.000                                      |
| 0.05                              | 0.00782 | 1.0216                                    | 0.921                                      | -0.130                                     |
| 0.10                              | 0.01636 | 1.0473                                    | 1.880                                      | -0.269                                     |
| 0.15                              | 0.02573 | 1.0728                                    | 2.887                                      | -0.395                                     |
| 0.20                              | 0.03607 | 1.0990                                    | 3.950                                      | -0.523                                     |
| 0.25                              | 0.04752 | 1.1256                                    | 5.081                                      | -0.649                                     |
| 0.30                              | 0.06028 | 1.1531                                    | 6.292                                      | -0.781                                     |
| Zinc sulfate (1) + water (2)      |         |   |  |  |
| 0.00                              | 0.00000 | 0.9970                                    | 0.000                                      | 0.000                                      |
| 0.05                              | 0.00584 | 1.0272                                    | 0.918                                      | -0.179                                     |
| 0.10                              | 0.01224 | 1.0579                                    | 1.869                                      | -0.350                                     |
| 0.15                              | 0.01931 | 1.0905                                    | 2.859                                      | -0.540                                     |
| 0.20                              | 0.02714 | 1.1229                                    | 3.902                                      | -0.710                                     |
| 0.25                              | 0.03586 | 1.1573                                    | 5.003                                      | -0.900                                     |
| 0.30                              | 0.04563 | 1.1947                                    | 6.168                                      | -1.128                                     |
| Aluminum sulfate(1) + water (2)   |         |   |  |  |
| 0.00                              | 0.00000 | 0.9970                                    | 0.000                                      | 0.000                                      |
| 0.05                              | 0.00276 | 1.0255                                    | 0.922                                      | -0.139                                     |
| 0.10                              | 0.00582 | 1.055                                     | 1.886                                      | -0.279                                     |
| 0.15                              | 0.00921 | 1.0852                                    | 2.903                                      | -0.417                                     |
| 0.20                              | 0.01299 | 1.1149                                    | 3.987                                      | -0.530                                     |
| 0.25                              | 0.01725 | 1.1492                                    | 5.135                                      | -0.710                                     |
| 0.30                              | 0.02207 | 1.1822                                    | 6.387                                      | -0.851                                     |

Standard uncertainties:  $u(w_i) = 0.001$ ;  $u(P) = 5 \text{ kPa}$ ;  $u(T) = 0.05 \text{ K}$ .

**Table 5.** Coefficients and Statistical Parameters of Eq. (4) for the Density ( $\text{g cm}^{-3}$ ) of {Polyethylene Glycol + Water} Mixtures as a Function of Temperature and Composition

| Mixture        | Constant |           |           | Coefficient of determination ( $R^2$ ) | Standard error |
|----------------|----------|-----------|-----------|--|----------------|
|                | a        | b         | c         |  |                |
| PEG300 + water | 1.121206 | -2.083076 | 22.428674 | 0.999940                               | 0.00035        |
| PEG400 + water | 1.121911 | -2.077462 | 29.797536 | 0.999940                               | 0.00049        |
| PEG600 + water | 1.123101 | -2.068312 | 44.318894 | 0.999966                               | 0.00038        |

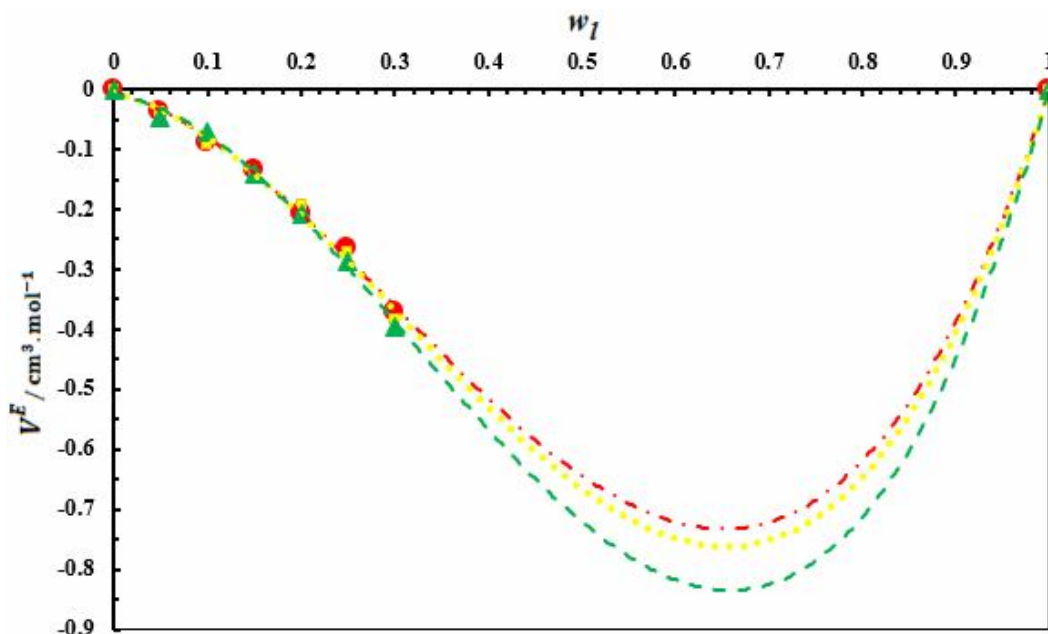
**Fig. 1.** The apparent specific volume of PEG in water ( $V_\phi$ ) against the mass fraction of component ( $w$ ): (●), PEG300 (1) + water (2), (■), PEG400 (1) + water (2), (▲), PEG600 (1) + water (2) at 298.15 K and 0.1 MPa.

$0.8 \text{ cm}^3 \text{ g}^{-1}$  (Fig. 1). At low PEG concentrations, the apparent specific volumes of PEG in water decreased with increasing the polymer mass fraction. Furthermore, it was observed that for low concentration of PEG, the value of  $V_\phi$  decreases as the concentration of PEG increases and for a high concentration of PEG, the value of  $V_\phi$  is independent of the PEG concentration.

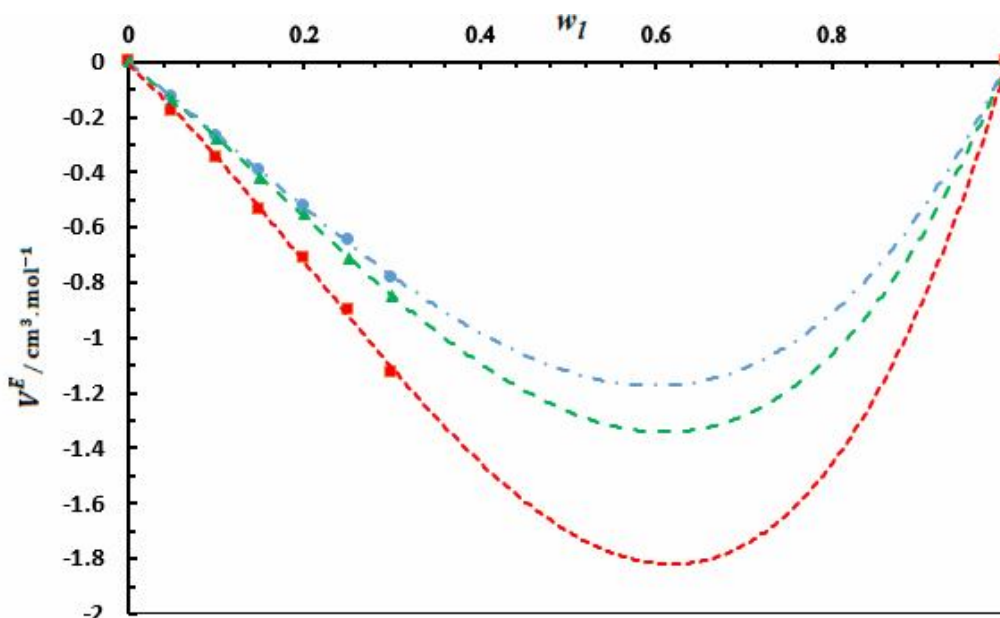
According to Table 3 and Fig. 2, the excess volume of the polymer solution in water ( $V^E$ ) had a negative deviation from ideality probably due to increased interactions such as

hydrogen bonding and/or large differences in molar volumes of components [25]. In all cases, the excess volumes are negative indicating contraction in volume after mixing.

In this way, according to Fort and Moore [25,31,40] a negative excess volume is an indication of strong heteromolecular interactions in the liquid mixtures that is attributed to charge transfer, dipole-dipole, dipole-induced dipole interactions, and hydrogen bonding between the unlike components, while a positive sign indicates a weak



**Fig. 2.** Excess molar volume ( $V^E$ ) against the mass fraction of the components ( $w$ ): (●), PEG300 (1) + water (2), (■), PEG400 (1) + water (2), (▲), PEG600 (1) + water (2) at 298.15 K and 0.1 MPa. Values obtained from fitting to Equation 8 are represented by dash lines (- -).



**Fig. 3.** Excess molar volume ( $V^E$ ) against the mass fraction of the components ( $w$ ): (●),  $MgSO_4$  (1) + water (2), (■),  $ZnSO_4$  (1) + water (2), (▲),  $(Al)_2(SO_4)_3$  (1) + water (2) at 298.15 K and 0.1 MPa. Values obtained from fitting to Equation 8 are represented by dash lines (- -).



**Table 6.** Experimental Refractive Index ( $n_D$ ), Refractive Index Deviation ( $\Delta n_D$ ) of PEG300, 400, 600 (1) + Water (2) Solution<sup>a</sup> at 298.15 K and 0.1 MPa

| $w_1$          | $n_D(\pm 0.0001)$ | $\Delta n_D$ |
|----------------|-------------------|--------------|
| PEG300 + water |                   |              |
| 0.00           | 1.3327            | 0.0000       |
| 0.05           | 1.3385            | 0.0058       |
| 0.10           | 1.3455            | 0.0127       |
| 0.15           | 1.3521            | 0.0192       |
| 0.20           | 1.3585            | 0.0256       |
| 0.25           | 1.3658            | 0.0328       |
| 0.30           | 1.3734            | 0.0404       |
| 1.00           | 1.4650            | 0.0000       |
| PEG400 + water |                   |              |
| 0.00           | 1.3327            | 0.0000       |
| 0.05           | 1.3386            | 0.0058       |
| 0.10           | 1.3442            | 0.0114       |
| 0.15           | 1.3508            | 0.0179       |
| 0.20           | 1.3588            | 0.0259       |
| 0.25           | 1.3653            | 0.0324       |
| 0.30           | 1.3716            | 0.0386       |
| 1.00           | 1.4670            | 0.0000       |
| PEG600 + water |                   |              |
| 0.00           | 1.3327            | 0.0000       |
| 0.05           | 1.3391            | 0.0063       |
| 0.10           | 1.3458            | 0.0130       |
| 0.15           | 1.3527            | 0.0198       |
| 0.20           | 1.3592            | 0.0263       |
| 0.25           | 1.3657            | 0.0328       |
| 0.30           | 1.3731            | 0.0401       |
| 1.00           | 1.4690            | 0.0000       |

Standard uncertainties:  $u(w_i) = 0.001$ ;  $u(P) = 5$  kPa;  $u(T) = 0.05$  K.

**Table 7.** Experimental Refractive Index ( $n_D$ ), Refractive Index Deviation ( $\Delta n_D$ ) of Zinc Sulfate, Magnesium Sulfate and Aluminum Sulfate (1) + Water (2) at 298.15 K and 0.1 MPa

| $w_1$                         | $n_D(\pm 0.0001)$ | $\Delta n_D$ |
|-------------------------------|-------------------|--------------|
| Zinc sulfate (1) + water      |                   |              |
| 0.00                          | 1.3327            | 0.0000       |
| 0.05                          | 1.3373            | 0.0001       |
| 0.10                          | 1.3424            | 0.0010       |
| 0.15                          | 1.3477            | 0.0025       |
| 0.20                          | 1.3527            | 0.0039       |
| 0.25                          | 1.3576            | 0.0054       |
| 0.30                          | 1.3625            | 0.0072       |
| 1.00                          | 1.4369            | 0.0000       |
| Magnesium sulfate (1) + water |                   |              |
| 0.00                          | 1.3327            | 0.0000       |
| 0.05                          | 1.3370            | 0.0011       |
| 0.10                          | 1.3421            | 0.0032       |
| 0.15                          | 1.3472            | 0.0055       |
| 0.20                          | 1.3524            | 0.0080       |
| 0.25                          | 1.3568            | 0.0099       |
| 0.30                          | 1.3613            | 0.0119       |
| 1.00                          | 1.4299            | 0.0000       |
| Aluminum sulfate (1) + water  |                   |              |
| 0.00                          | 1.3327            | 0.0000       |
| 0.05                          | 1.3383            | -0.0049      |
| 0.10                          | 1.3442            | -0.0079      |
| 0.15                          | 1.3501            | -0.0096      |
| 0.20                          | 1.3558            | -0.0105      |
| 0.25                          | 1.3623            | -0.0098      |
| 0.30                          | 1.3687            | -0.0086      |
| 1.00                          | 1.4532            | 0.0000       |

Standard uncertainties:  $u(w_i) = 0.001$ ;  $u(P) = 5$  kPa;  $u(T) = 0.05$  K.

interaction and is attributed to dispersion forces (London interactions), which are operative in all cases.

According to Table 4 and Fig. 3, the excess volume of the sulfate salts solution in water are negative. Most probably, the different molecular sizes and shapes of sulfate salts resulted in interstitial accommodation in the solutions. At the same time, considering the disturbance of hydrogen-bonded structures seems essential upon mixing.

### Refractive Index and Excess Refractive Index

The refractive index deviation ( $\Delta n_D$ ) is defined as [39]:

$$\Delta n_D = n_D - \sum_{i=1}^I X_i n_{Di} \quad (5)$$

where  $n_D$  denotes the refractive index of the solution,  $x_i$  shows the mole fraction of component  $i$ , and the refractive index (for each pure component of the solution) is represented as  $n_{Di}$ . Experimental refractive index and refractive index deviation of PEG300, 400, 600 + water, zinc sulfate, magnesium sulfate and aluminum sulfate + water, binary systems at 298.15 K and 0.1 MPa are reported in Tables 6 and 7. Also, Figs. 4 and 5 show the refractive indices deviations of mention binary systems. There is a positive deviation from ideality in the refractive index deviation of PEG 300, 400, 600 + water binary system. Yet, the refractive index deviation in binary solutions of sulfate salts were only positive for two magnesium sulfate and zinc sulfate salts, and for aluminum sulfate salt, this deviation was negative as compared to the ideal state. The reason for this negative deviation is that the solution of aluminum sulfate in water in real mode occupies more volume than the ideal state.

### Redlich-Kister Polynomial and Cibulka Equations Model

The refractive index and density for PEG 300, 400, 600 + water and zinc sulfate, magnesium sulfate and aluminum sulfate + water solutions were measured at different concentrations at 298.15 K. The refractive index and the densities of PEG300, 400 and 600 (1) + water (2) are shown in Table 6 and Table 7. Table 7 and Table 3 show the refractive indices and densities of sulfate salts (1) + water (2). To determine the mathematical relationship between the

features and compositions of the solutions, both features were adjusted to a polynomial mass fraction expansion model and the fitting lines were determined by the following equation [39]:

$$Q = \sum_{k=1}^K \sum_{i=1}^I A_{ik} W_i^k \quad (6)$$

where  $Q$  is  $n_D$ ,  $\eta$  (mPa s), or  $\rho$  in  $\text{g cm}^{-3}$ ,  $A_{ik}$  denotes the adjustment coefficients of the model,  $I$  shows the number of components,  $w_i$  denotes the mass fraction of component  $i$ , and  $K$  is the polynomial degree. Adjustments were made to the refractive index and density to obtain a third-order polynomial expansion model and a second-order polynomial expansion equation. The Curve Expert Professional software was also used to calculate easily the coefficients.

The standard deviation( $s$ ) for each adjustment [39] was calculated using Eq. (7):

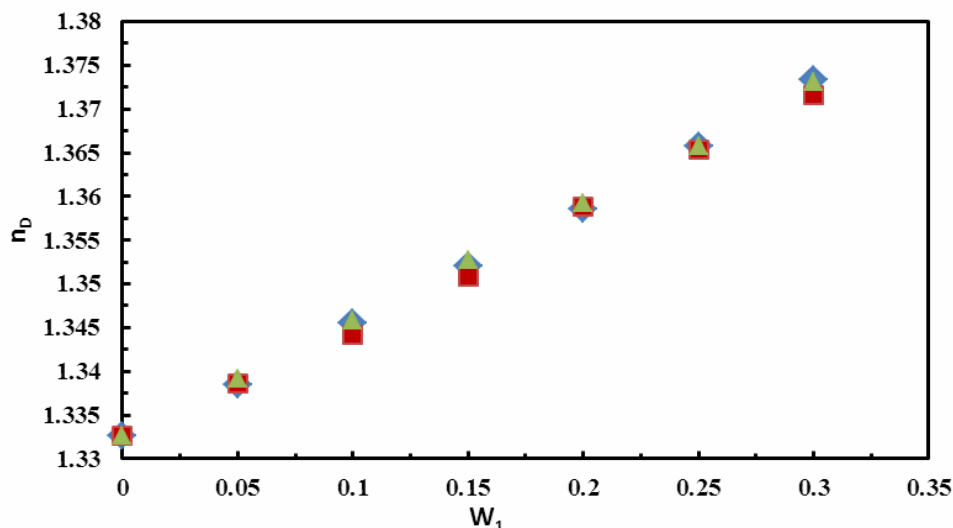
$$s = \sqrt{\frac{1}{N-1} \sum_{N=1}^N (Q_{\text{exp}} - Q_{\text{cal}})^2} \quad (7)$$

where  $Q_{\text{cal}}$  indicates the adjusted property values,  $Q_{\text{exp}}$  indicates the experimental property values, and  $N$  indicates the number of measurements. Fitting parameters ( $A_{ik}$ ) (Eq. (5)) of PEG300,400,600 + water, and sulfate salts + water are reported in Tables 8 and 9, respectively.

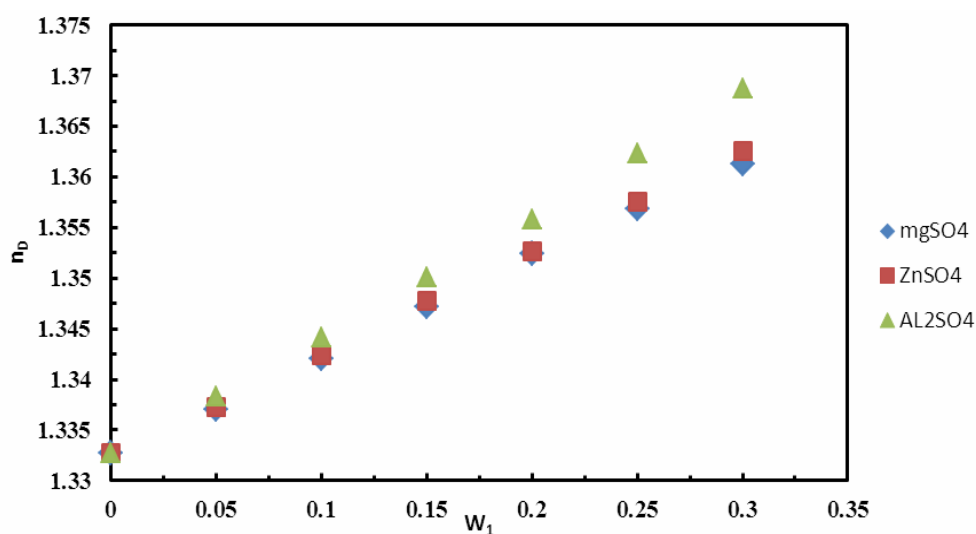
The refractive index deviation and excess molar volumes were adjusted to determine the Redlich-Kister model for binary solutions, corresponding to [39]:

$$Q_{ij} = W_i W_j \sum_{k=0}^K A_k (2W_i - 1)^k \quad (8)$$

where  $Q_{ij}$  denotes the excess property,  $w_i$  and  $w_j$  are the mass fractions of the components  $i$  and  $j$  in the binary solutions, and  $A_k$  is related to the fitting parameters, and  $K$  is the order of the fit. Tables 4-7 show the refractive index deviations, molar volumes and excess molar volumes, and the fitting parameters ( $A_{ik}$ ) (Eq. (8)) of PEG300, 400, 600 + water, and sulfate salts +water are shown in Tables 10 and 11, respectively.



**Fig. 4.** Refractive index ( $n_D$ ) against the mass fraction of the polymers ( $w_p$ ): (♦), PEG300 (1) + water (2), (■), PEG400 (1) + water (2), (▲), PEG600 (1) + water (2) at 298.15 K 0.1 MPa.



**Fig. 5.** Refractive index ( $n_D$ ) against the mass fraction of the polymers ( $w_p$ ): (♦),  $MgSO_4$  (1) + water (2), (■),  $ZnSO_4$  (1) + water (2), (▲),  $(Al)_2(SO_4)_3$  (1) + water (2) at 298.15 K 0.1 MPa.

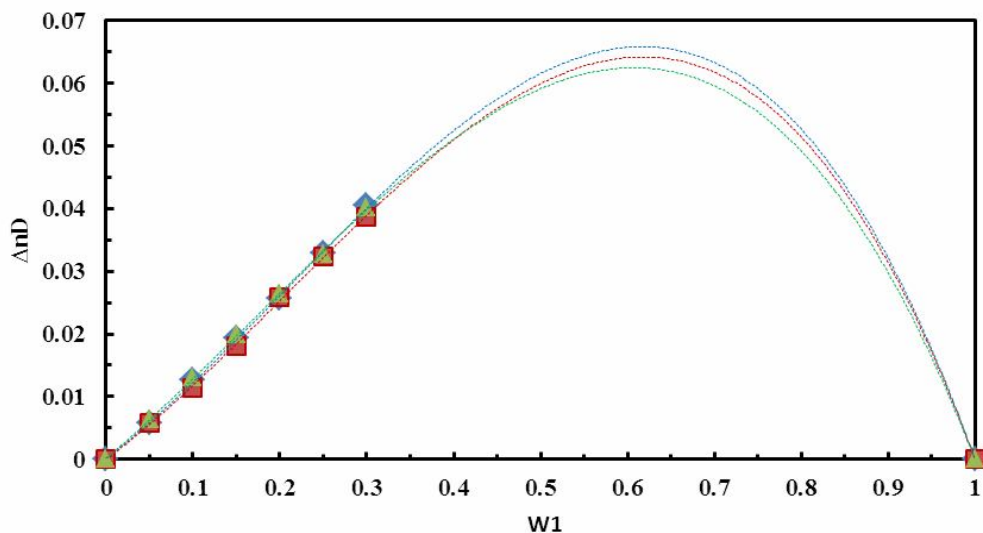
### Viscosity, Viscosity Deviation and Excess Gibbs Energy of Activation for Viscous Flow

The viscosity deviation ( $\Delta\eta$ ) is defined as [39]:

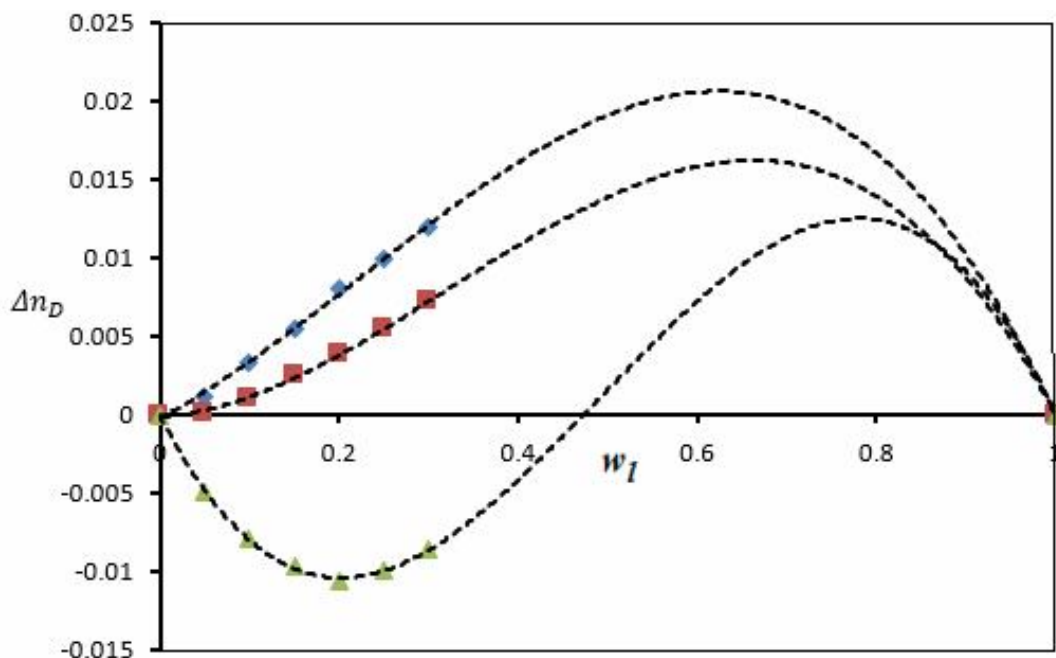
$$\Delta\eta = \eta - \sum_{i=1}^j X_i \eta_i \quad (9)$$

where  $\eta$  shows the viscosity of the solution,  $X_i$  shows the mole fraction of component  $i$ , and the viscosity of each pure component of the solution is shown by  $\eta_i$ .

Viscosity determines the internal resistance of a liquid to shear or flow, which is a significant physical character of fluid. Table 12 and Figs. 8 and 9 reveal the dependence of



**Fig. 6.** Refractive index deviation ( $\Delta n_D$ ) against the mass fraction of the components ( $w$ ): ( $\blacklozenge$ ), PEG300 (1) + water (2), ( $\blacksquare$ ), PEG400 (1) + water (2), ( $\blacktriangle$ ), PEG600 (1) + water (2) at 298.15 K 0.1 MPa. Values obtained from fitting to Eq. (8) are represented by dash lines (- -).



**Fig. 7.** Refractive index deviation ( $\Delta n_D$ ) against the mass fraction of the salt ( $w_s$ ): ( $\blacklozenge$ ),  $\text{MgSO}_4$  (1) + water (2), ( $\blacksquare$ ),  $\text{ZnSO}_4$  (1) + water (2), ( $\blacktriangle$ ),  $\text{Al}_2(\text{SO}_4)_3$  (1) + water (2) at 298.15 K 0.1 MPa. Values obtained from fitting to Eq. (8) are represented by dash lines (- -).

**Table 8.** Refractive Index ( $n_D$ ) and Density ( $\rho$ ) Fitting Parameters ( $A_{ik}$ ) of PEG300, 400, 600 (1) + Water (2) at 298.15 K and 0.1 MPa

| Property                     | Component (i) | Order (k)  |            |           | S      |
|------------------------------|---------------|------------|------------|-----------|--------|
|                              |               | (1)        | (2)        | (3)       |        |
| PEG300( 1) + water (2)       |               |            |            |           |        |
| $n_D$                        | 1             | -384.0807  | 433.4236   | -39.01682 | 0.0003 |
|                              | 2             | -3567.5803 | 751.9804   | -39.5209  |        |
| $\rho$ (g cm <sup>-3</sup> ) | 1             | -280.5569  | 27.9287    |           | 0.0006 |
|                              | 2             | 280.9793   | -28.0880   |           |        |
| PEG400 ( 1) + water (2)      |               |            |            |           |        |
| $n_D$                        | 1             | 9379.0823  | -3079.6096 | 213.1409  | 0.0004 |
|                              | 2             | 12044.360  | -3346.7362 | 214.2313  |        |
| $\rho$ (g cm <sup>-3</sup> ) | 1             | 673.4609   | -66.8129   |           | 0.0007 |
|                              | 2             | -673.1723  | 67.2272    |           |        |
| PEG600 (1) + water (2)       |               |            |            |           |        |
| $n_D$                        | 1             | 9256.4544  | -1142.5179 | 89.0209   | 0.0004 |
|                              | 2             | 4911.2962  | -1307.8489 | 81.6733   |        |
| $\rho$ (g cm <sup>-3</sup> ) | 1             | 1195.9814  | -108.5164  |           | 0.0006 |
|                              | 2             | -1198.6283 | 119.8744   |           |        |

deviation of viscosity,  $\Delta\eta$ , on composition.  $\Delta\eta$  of all binary solutions have a positive deviation from ideality. If the solution in the flow process were more ordered than expected from ideality, it would have a positive  $\Delta\eta$  value. Earlier studies revealed positive  $\Delta\eta$  displayed by solution with strong interactions among various molecules. The major contributing factor to the positive  $\Delta\eta$  values of

aqueous PEG is the more efficient packing in the solution than in the pure PEGs [39]. Also, this behavior can be attributed to the degree of self-association among the PEG molecules which are more than the degree of hetero-association between PEG and the solvent molecules. Moreover, the interaction in solution is in relation with the H-bonding between the solute-solvent molecules.

**Table 9.** Refractive Index ( $n_D$ ) and Density ( $\rho$ ) Fitting Parameters ( $A_{ik}$ ) of Zinc Sulfate, Magnesium Sulfate and Aluminum Sulfate (1) + Water (2) at 298.15 K and 0.1 MPa

| Property  | Component (i) | Order (k)  |            |          | S      |
|---|---------------|------------|------------|----------|--------|
|   |               | (1)        | (2)        | (3)      |        |
| <b>MgSO<sub>4</sub> (1) + water (2)</b>                           |               |            |            |          |        |
| $n_D$   | 1             | 341.3110   | -416.1531  | 38.0452  | 0.0003 |
|   | 2             | 3479.9517  | -730.0715  | 38.2089  |        |
| $\rho$ (g cm <sup>-3</sup> )                                      | 1             | -75.7735   | 7.7322     |          | 0.0006 |
|   | 2             | 76.4643    | -7.6364    |          |        |
| <b>ZnSO<sub>4</sub> (1) + water (2)</b>                           |               |            |            |          |        |
| $n_D$   | 1             | 1150.5715  | -773.0112  | 65.7690  | 0.0004 |
|   | 2             | 5429.6280  | -1200.9322 | 65.7982  |        |
| $\rho$ (g cm <sup>-3</sup> )                                      | 1             | -561.2181  | 56.4790    |          | 0.0007 |
|   | 2             | 561.9835   | -56.1884   |          |        |
| <b>Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (1) + water (2)</b> |               |            |            |          |        |
| $n_D$   | 1             | 8620.0167  | 1736.3396  | -87.2531 | 0.0004 |
|   | 2             | -123.3333  | 886.7207   | -87.4374 |        |
| $\rho$ (g cm <sup>-3</sup> )                                      | 1             | 1408.4670  | -140.5404  |          | 0.0006 |
|   | 2             | -1407.7259 | 140.7826   |          |        |

Consequently, by increasing the PEG mole fraction, the H-bonding between the solute and the solvent in the solutions is exchanged gradually by the intermolecular force between the PEG particles [3]. Furthermore, an increase in  $\Delta\eta$  was observed for salt + water and PEG + water by increased mass fraction of sulfate salts and PEG. According to this figure, the concentration of PEG had a greater influence

than that of sulfate salts on the  $\Delta\eta$  magnitude. This behavior was as predictable since the aqueous solutions of PEG regularly show the viscosity values greater than those of aqueous solutions of electrolytes at the same concentration.

The excess Gibbs energy of activation for viscous flow ( $\Delta G^{*E}$ ) was calculated through Eq. (10) [41]:

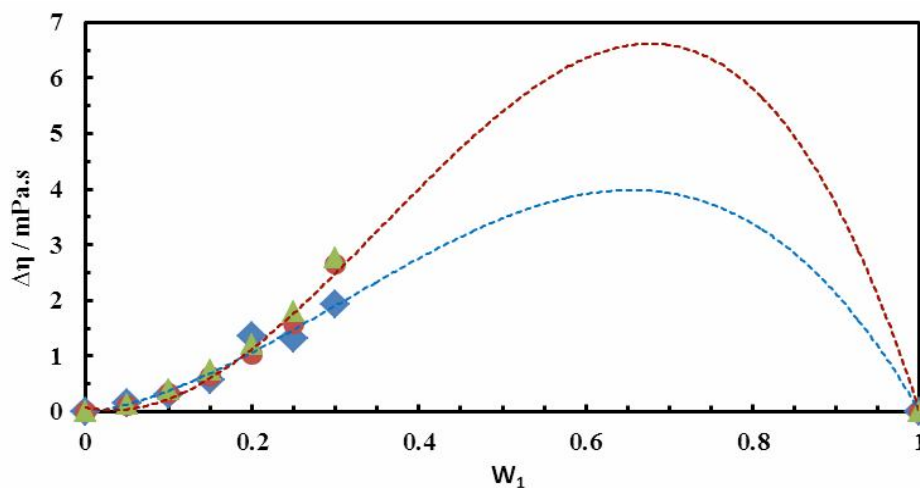
**Table 10.** Fitting Parameters of Refractive Index Deviation ( $n_D$ ), and Excess Molar Volumes ( $V^E$ ) of PEG (1) + Water (2) at 298.15 K and 0.1 MPa

| Excess property                            | Order (k) |         |         |         | S     |
|--|-----------|---------|---------|---------|-------|
|  | (0)       | (1)     | (2)     | (3)     |       |
| PEG300 + water                             |           |         |         |         |       |
| $\Delta n_D$                               | 0.0232    | 0.0455  | 0.0709  | 0.0382  | 0.004 |
| $V^E$ (cm <sup>3</sup> mol <sup>-1</sup> ) | -0.1792   | 0.1839  | -0.3437 | -0.5412 | 0.002 |
| PEG400 + water                             |           |         |         |         |       |
| $\Delta n_D$                               | 0.0004    | -0.0668 | -0.1084 | -0.0529 | 0.002 |
| $V^E$ (cm <sup>3</sup> mol <sup>-1</sup> ) | -1.0573   | -2.9014 | -4.0161 | -2.0025 | 0.003 |
| PEG600 + water                             |           |         |         |         |       |
| $\Delta n_D$                               | 0.0224    | 0.0442  | 0.0712  | 0.0382  | 0.003 |
| $V^E$ (cm <sup>3</sup> mol <sup>-1</sup> ) | -0.4619   | -1.0592 | -2.0939 | -1.2863 | 0.004 |

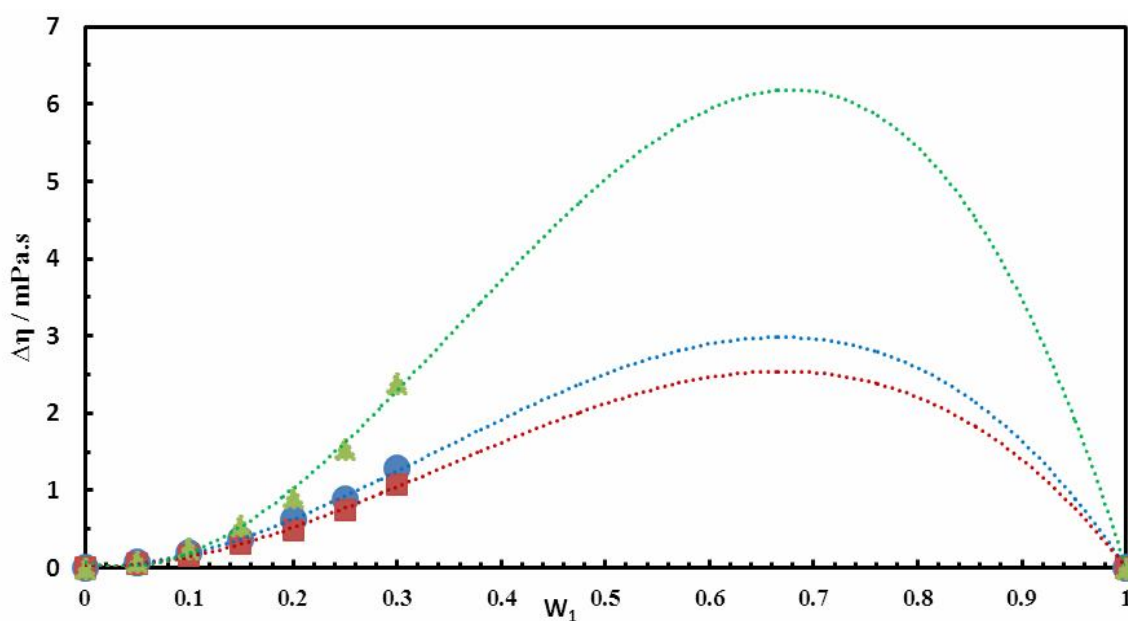
**Table 11.** Refractive Index Deviation ( $n_D$ ), and Excess Molar Volumes ( $V^E$ ) of Zinc Sulfate, Magnesium Sulfate and Aluminum Sulfate (1) + Water (2) + Water (2) at 298.15 K and 0.1 MPa

| Excess property   | Order (k) |          |         |         | S     |
|---|-----------|----------|---------|---------|-------|
|   | (0)       | (1)      | (2)     | (3)     |       |
| MgSO <sub>4</sub> + water                               |           |          |         |         |       |
| $\Delta n_D$  | 0.0066    | 0.0158   | 0.0332  | 0.0233  | 0.004 |
| $V^E$ (cm <sup>3</sup> mol <sup>-1</sup> )              | 1.5835    | -0.5475  | -0.6080 | -0.3524 | 0.002 |
| ZnSO <sub>4</sub> + water                               |           |          |         |         |       |
| $\Delta n_D$  | 0.0059    | 0.0179   | 0.0307  | 0.0199  | 0.002 |
| $V^E$ (cm <sup>3</sup> mol <sup>-1</sup> )              | 0.2649    | -5.3517  | -3.4538 | -2.6024 | 0.003 |
| Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + water |           |          |         |         |       |
| $\Delta n_D$  | 0.0026    | 0.0177   | 0.0139  | 0.0104  | 0.003 |
| $V^E$ (cm <sup>3</sup> mol <sup>-1</sup> )              | 4.0524    | -11.9550 | -0.2003 | -7.9442 | 0.004 |





**Fig. 8.** Viscosity deviation ( $\Delta\eta$ ) against the mass fraction of the components ( $w$ ): ( $\blacklozenge$ ), PEG300(1) + water (2), ( $\bullet$ ), PEG400 (1) + water (2), ( $\blacktriangle$ ), PEG600 (1) + water (2) at 298.15 K and 0.1 MPa. Values obtained from fitting to Eq. (8) are represented by dash lines (- -).



**Fig. 9.** Excess molar volume ( $V^E$ ) against the mass fraction of the components ( $w$ ): ( $\bullet$ ),  $\text{MgSO}_4$  (1) + water (2), ( $\blacksquare$ ),  $\text{ZnSO}_4$  (1) + water (2), ( $\blacktriangle$ ),  $(\text{Al})_2(\text{SO}_4)_3$  (1) + water (2) at 298.15 K and 0.1 MPa. Values obtained from fitting to Eq. (8) are represented by dash lines (- -).

$$\Delta G^{*E} = RT \left[ \ln(V_m \eta) - \sum_{i=1}^n x_i \ln(V_i \eta_i) \right]$$

where  $X$ ,  $\eta$  and  $V$  are the mole fraction, dynamic viscosity and the mole volume, respectively.

(10) According to Tables 13, 14 and Figs. 10 and 11, the

**Table 12.** Experimental Viscosity ( $\eta$ ) and Mass Fraction ( $w$ ) and Calculated Viscosity Deviation ( $\Delta\eta$ ) of PEG300, 400 and 600 (1) + Water (2) <sup>a</sup>Solutions at 298.15 K and 0.1 MPa

| $w_1$                  | $\eta(\pm 0.001)$<br>(mPa s) | $\Delta\eta$<br>(mPa s) |
|------------------------|------------------------------|-------------------------|
| PEG300 (1) + water (2) |                              |                         |
| 0.00                   | 0.8940                       | 0.0000                  |
| 0.05                   | 1.0620                       | 0.1476                  |
| 0.10                   | 1.2478                       | 0.3127                  |
| 0.15                   | 1.5308                       | 0.5749                  |
| 0.20                   | 2.3340                       | 1.3571                  |
| 0.25                   | 2.3190                       | 1.3709                  |
| 0.30                   | 2.9398                       | 1.9203                  |
| PEG400 (1) + water (2) |                              |                         |
| 0.00                   | 0.8940                       | 0.0000                  |
| 0.05                   | 1.0291                       | 0.1074                  |
| 0.10                   | 1.2860                       | 0.3364                  |
| 0.15                   | 1.6217                       | 0.6440                  |
| 0.20                   | 2.0419                       | 1.0357                  |
| 0.25                   | 2.6089                       | 1.5740                  |
| 0.30                   | 3.7222                       | 2.6583                  |
| PEG600 (1) + water (2) |                              |                         |
| 0.00                   | 0.8940                       | 0.0000                  |
| 0.05                   | 1.0718                       | 0.1371                  |
| 0.10                   | 1.3690                       | 0.3933                  |
| 0.15                   | 1.7570                       | 0.7398                  |
| 0.20                   | 2.2613                       | 1.2023                  |
| 0.25                   | 2.8899                       | 1.7887                  |
| 0.30                   | 3.9068                       | 2.7629                  |

<sup>a</sup>Standard uncertainties:  $u(w_i) = 0.001$ ;  $u(P) = 5$  kPa;  $u(T) = 0.05$  K.

**Table 13.** Mass Fraction (w) and Calculated Excess Gibbs Energy of Activation for Viscous Flow ( $\Delta G^E$ ) of PEG300, 400 and 600 (1) + Water (2) <sup>a</sup>Solutions at 298.15 K and 0.1 MPa

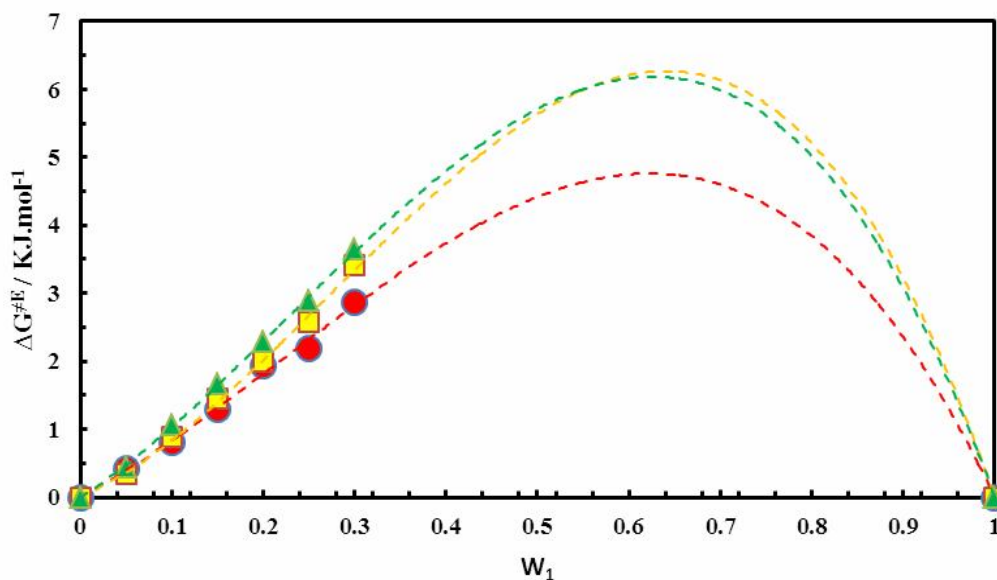
| $w_1$                  | $\Delta G^E$<br>(kJ mol <sup>-1</sup> ) |
|------------------------|---|
| PEG300 (1) + water (2) |   |
| 0.00                   | 0.00                                    |
| 0.05                   | 0.41                                    |
| 0.10                   | 0.80                                    |
| 0.15                   | 1.29                                    |
| 0.20                   | 1.94                                    |
| 0.25                   | 2.19                                    |
| 0.30                   | 2.87                                    |
| 1.00                   | 0.00                                    |
| PEG400 (1) + water (2) |   |
| 0.00                   | 0.00                                    |
| 0.05                   | 0.34                                    |
| 0.10                   | 0.88                                    |
| 0.15                   | 1.44                                    |
| 0.20                   | 1.99                                    |
| 0.25                   | 2.57                                    |
| 0.30                   | 3.41                                    |
| 1.00                   | 0.00                                    |
| PEG600 (1) + water (2) |   |
| 0.00                   | 0.00                                    |
| 0.05                   | 0.45                                    |
| 0.10                   | 1.05                                    |
| 0.15                   | 1.67                                    |
| 0.20                   | 2.29                                    |
| 0.25                   | 2.90                                    |
| 0.30                   | 3.64                                    |
| 1.00                   | 0.00                                    |

<sup>a</sup>Standard uncertainties  $u$  are  $u(w_i) = 0.01$ ,  $u(\Delta G^E) = 0.01$  kJ mol<sup>-1</sup>,  $u(T) = 0.05$  K and  $u(P) = 5$  kPa.

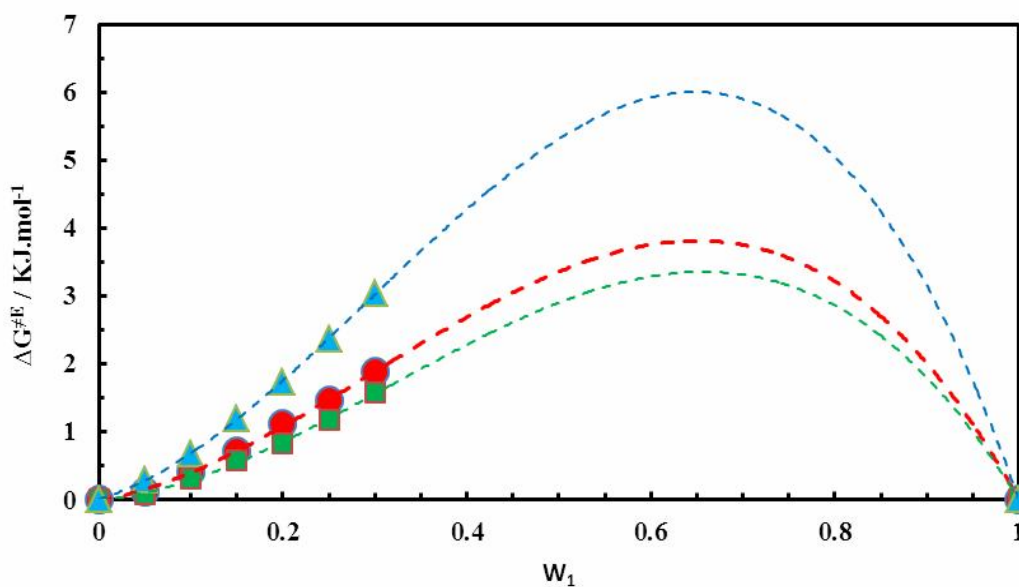
**Table 14.** Mass Fraction (w) and Calculated Excess Gibbs Energy of Activation for Viscous Flow ( $\Delta G^E$ ) of Zinc Sulfate, Magnesium Sulfate and Aluminum Sulfate (1)+ Water (2)  
<sup>a</sup>Solutions at 298.15 K and 0.1 MPa

| $w_1$                             | $\Delta G^E$<br>(kJ mol <sup>-1</sup> ) |
|-----------------------------------|---|
| Magnesium sulfate (1) + water (2) |   |
| 0.00                              | 0.00                                    |
| 0.05                              | 0.12                                    |
| 0.10                              | 0.40                                    |
| 0.15                              | 0.71                                    |
| 0.20                              | 1.11                                    |
| 0.25                              | 1.46                                    |
| 0.30                              | 1.88                                    |
| 1.00                              | 0.00                                    |
| Zinc sulfate (1) + water (2)      |   |
| 0.00                              | 0.00                                    |
| 0.05                              | 0.08                                    |
| 0.10                              | 0.30                                    |
| 0.15                              | 0.57                                    |
| 0.20                              | 0.83                                    |
| 0.25                              | 1.18                                    |
| 0.30                              | 1.57                                    |
| 1.00                              | 0.00                                    |
| Aluminum sulfate (1) + water (2)  |   |
| 0.00                              | 0.00                                    |
| 0.05                              | 0.29                                    |
| 0.10                              | 0.67                                    |
| 0.15                              | 1.20                                    |
| 0.20                              | 1.74                                    |
| 0.25                              | 2.37                                    |
| 0.30                              | 3.03                                    |
| 1.00                              | 0.00                                    |

<sup>a</sup>Standard uncertainties u are  $u(w_i) = 0.01$ ,  $u(\Delta G^E) = 0.01$  kJ mol<sup>-1</sup>,  $u(T) = 0.05$  K and  $u(P) = 5$  kPa.



**Fig. 10.** Excess Gibbs energy ( $\Delta G^E$ ) against the mass fraction of the components ( $w$ ): (●), PEG300 (1) + water (2), (■) PEG400 (1) + water (2), (▲) PEG600 (1) + water (2) at 298.15 K and 0.1 MPa. Values obtained from fitting to equation 8 are represented by dashed lines (- -).



**Fig. 11.** Excess Gibbs energy ( $\Delta G^E$ ) against the mass fraction of the salt ( $w_s$ ): (●), magnesium sulfate (1) + water (2), (■) zinc sulfate (1) + water (2), (▲) aluminum sulfate (1) + water (2) at 298.15 K and 0.1 MPa. Values obtained from fitting to Eq. (8) are represented by dashed lines (- -).

**Table 15.** Experimental Refractive Index ( $n_D$ ) and Density ( $\rho$ ) and Calculated Refractive Index Deviation ( $\Delta n_D$ ), Molar Volume ( $V_m$ ), and Excess Molar Volume ( $V^E$ ) of the PEG300 (1) + Zinc Sulfate, Magnesium Sulfate and Aluminum Sulfate (2) + Water (3) Systems at 298.15 K and 0.1 MPa

| $w_1$                                      | $w_2$ | $n_D(\pm 0.0001)$ | $\rho(\pm 0.0001)$<br>( $\text{g cm}^{-3}$ ) | $\Delta n_D$ | $V_m$   | $V^E$   |
|--|-------|-------------------|--|--------------|---------|---------|
| PEG300 + aluminum sulfate (1) + water (2)  |       |                   |  |              |         |         |
| 0.05                                       | 0.05  | 1.4548            | 1.1322                                       | 0.01242      | 17.5549 | -1.9153 |
| 0.10                                       | 0.05  | 1.4599            | 1.1455                                       | 0.01879      | 18.3008 | -2.1149 |
| 0.15                                       | 0.05  | 1.4600            | 1.1866                                       | 0.02494      | 18.6900 | -2.7808 |
| 0.20                                       | 0.05  | 1.4612            | 1.2261                                       | 0.0310       | 19.1997 | -3.4558 |
| 0.25                                       | 0.05  | 1.4632            | 1.3256                                       | 0.0370       | 18.9217 | -5.0738 |
| PEG300 + magnesium sulfate (1) + water (2) |       |                   |  |              |         |         |
| 0.05                                       | 0.15  | 1.3383            | 1.1455                                       | 0.0948       | 18.6374 | -1.6382 |
| 0.10                                       | 0.15  | 1.3422            | 1.1566                                       | 0.0963       | 19.0892 | -1.7983 |
| 0.15                                       | 0.15  | 1.3462            | 1.2685                                       | 0.1085       | 18.4561 | -3.6497 |
| 0.20                                       | 0.15  | 1.3505            | 1.3325                                       | 0.1145       | 18.6987 | -4.7453 |
| 0.25                                       | 0.15  | 1.3540            | 1.4565                                       | 0.1217       | 17.1415 | -6.7766 |
| PEG300 + zinc sulfate (1) + water (2)      |       |                   |  |              |         |         |
| 0.05                                       | 0.10  | 1.4388            | 1.1899                                       | 0.1049       | 16.9523 | -2.4906 |
| 0.10                                       | 0.10  | 1.4466            | 1.2885                                       | 0.1121       | 16.1659 | -3.9241 |
| 0.15                                       | 0.10  | 1.4496            | 1.3588                                       | 0.1145       | 16.2112 | -4.9680 |
| 0.20                                       | 0.10  | 1.4533            | 1.3855                                       | 0.1174       | 16.8691 | -5.5012 |
| 0.25                                       | 0.10  | 1.4630            | 1.5577                                       | 0.1263       | 15.9794 | -7.8550 |

Standard uncertainties:  $u(w_i) = 0.001$ ;  $u(P) = 5$  kPa;  $u(T) = 0.05$  K.

excess Gibbs energy of activation for viscous flow ( $\Delta G^{zE}$ ) values, for PEG + water and Salt + water binary system, are positive. Moreover, the excess Gibbs energy showed a deviation from ideality that was positive. Experimental data on excess Gibbs energy show a maximum deviation near to 30% PEG mass fraction.

### Ternary System

At 298.15 K, measurements of the refractive index and

density of the zinc sulfate, magnesium sulfate and aluminum sulfate + PEG300 + water ternary system were performed. The experimental properties are reported in Table 15 and the experimental data were adjusted to a model following Eq. (10) for the three component.

According to Table 15, these properties showed both a slightly greater influence of mass %PEG compared with the concentration of sulfate salts on the refractive index value of the ternary solutions. The opposite happens with density.

**Table 16.** Refractive Index Deviation ( $\Delta n_D$ ) and Excess Molar Volume ( $V^E$ ) Fitting Parameters of Sulfate Salt (1) + PEG (2) + Water (3) System to the Cibulka Equation at 298.15 K and 0.1 MPa

| Thermophysical properties                      | Constant parameter |            |            | Standard error |
|--|--------------------|------------|------------|----------------|
|  | $C_1$              | $C_2$      | $C_3$      |                |
| PEG300 (1) + aluminum sulfate (2) + water (3)  |                    |            |            |                |
| $V^E$ (cm <sup>3</sup> mol <sup>-1</sup> )     | -24.6748           | 3022.3534  | -1265.9962 | 0.0002         |
| $\Delta n_D$                                   | 1.0805             | -3005.2411 | 1.0682     | 0.0042         |
| PEG300 (1) + magnesium sulfate (2) + water (3) |                    |            |            |                |
| $V^E$ (cm <sup>3</sup> mol <sup>-1</sup> )     | -258.1612          | -2320.8271 | -478.1679  | 0.0005         |
| $\Delta n_D$                                   | 1.4401             | -2925.9591 | 1.4868     | 0.0022         |
| PEG300 (1) + zinc sulfate (2) + water (3)      |                    |            |            |                |
| $V^E$ (cm <sup>3</sup> mol <sup>-1</sup> )     | 143.4058           | -3064.7191 | -879.6234  | 0.0025         |
| $\Delta n_D$                                   | -71.0082           | 1452.0124  | -6.3541    | .00577         |

The Cibulka equation (Eq. (10)) for the excess properties was used to correlate the results of the ternary system PEG (1) + zinc sulfate, magnesium sulfate and aluminum sulfate (2) + water (3):

$$Q_{123} = Q_{\text{bin}} + w_1 w_2 (1 - w_1 - w_2) (C_1 + C_2 w_1 + C_3 w_2) \quad (11)$$

where

$$Q_{\text{bin}} = Q_{23} + Q_{13} \quad (12)$$

The adjustment coefficients  $C_1$ ,  $C_2$  and  $C_3$  are shown in Table 16.

## CONCLUSIONS

The present study specified new experimental densities, viscosities, and refractive indices for the binary and ternary systems of PEG with different molecular weights, sulfate salts and water at 298.15 K. For analyzing the thermodynamic behavior of the solutions, the excess molar volumes, refractive indices deviations, viscosity deviations,

the apparent specific volumes, and excess Gibbs energy of activation for viscous flow were computed from the experimental measurements. Refractive indices deviation, viscosity deviations, excess molar volumes and Gibbs energy of all binary solutions had a positive deviation from ideality. However, in the ternary systems, refractive indices deviation had a positive deviation and excess molar volumes had a negative deviation from ideality. Difference in the refractive index was positive, also, the excess molar volumes were positive for sulfate salts + water, and negative for PEG + water. Moreover, the excess molar volumes and difference in refractive indices of binary and ternary solutions correlated reliably with the Redlich-Kister and Cibulka equations, respectively.

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