# Densities, Viscosities, and Excess Molar Enthalpies of 2-Pyrrolidone + Butanol Isomers at T = (293.15, 298.15, and 303.15) K

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The experimental densities  $\rho$ , and viscosities  $\eta$ , of binary mixtures of 2-pyrrolidone with butanol isomers: 1-butanol, 2-methyl-1-propanol, 2-butanol, and 2-methyl-2-propanol have been measured at T = (293.15, 298.15, and 303.15) K and atmospheric pressure over the whole mole fraction range. From these data, excess molar volumes,  $V^{\rm E}$ , and viscosity deviations,  $\eta$ , have been calculated at various temperatures. Both excess molar volumes and viscosity deviations are negative for all investigated systems. The excess molar enthalpies,  $H^{\rm E}$ , measured at 298.15 K and at atmospheric pressure for the four systems are positive over the whole mole fraction range. The experimental results have been correlated using Redlich–Kister polynomial equation, and parameters from least-squares analysis have been reported.

## Introduction

The physicochemical properties of liquid mixtures have attracted much attention from both theoretical and engineering applications points of view. 2-Pyrrolidone has an important industrial applications, as a solvent for surface treatment of textiles, metal coating plastics, paint removing, and intermediate for the synthesis of agrochemicals, pharmaceuticals, plasticizers, polymer solvents, and stabilizers specially inks. Mixtures of 2-pyrrolidone with other solvents are also of particular interest. Understanding the mixing behavior of 2-pyrrolidone with alkanols is therefore important and has applications in many engineering industries. Many engineering applications require quantitative data on the density of liquid mixtures. It is also provides information about the nature and molecular interactions between liquid mixture components.

This work continues our systematic studies for determination of the thermodynamic properties of the binary mixtures containing 2-pyrrolidone as one component.<sup>1,2</sup> In recent publication,<sup>2</sup> we have presented the volumetric properties for mixtures of 2-pyrrolidone + aromatic hydrocarbons at various temperatures. A survey of the literature shows that Blumenshine and Sears<sup>3</sup> have measured the dielectric constants, viscosities, densities, and refractive indices of aqueous solution of 2-pyrrolidone at temperatures from (31 to 50) °C. Garcia et al.<sup>4–6</sup> studied excess viscosities, excess volumes, free energies of activation for viscous flow, enthalpies, and entropies of the binary mixtures of 2-pyrrolidone + methanol, + ethanol, + 1-propanol, + 1-butanol, + 1-pentanol, + hexan-1-ol, + heptan-1-ol, octan-1-ol, + nonan-1-ol, and decan-1-ol at temperatures from (298.15 to 318.15) K. Recently. Mehta et al.<sup>7</sup> reported the excess molar volumes, speed of sound, transport parameter viscosity, and IR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectroscopic parameters for the mixtures of  $\alpha, \omega$ -alkanediols in 2-pyrrolidone at T = 308 K.

To examine the effect of branching in alkanols on mixing properties of mixtures of 2-pyrrolidone and butanol isomers,

Table 1. Densities,  $\rho$ , and Viscosities,  $\eta$ , of Pure Liquids at T = (293.15 to 303.15) K

|                     |        | $\rho/g \cdot m^{-3}$ |                     | η/mPa∙s |                      |
|---------------------|--------|-----------------------|---------------------|---------|----------------------|
| liquid              | T/K    | exptl                 | lit.                | exptl   | lit.                 |
| 1-butanol           | 293.15 | 0.80952               |                     | 2.941   |                      |
|                     | 298.15 | 0.80554               | $0.8059^{a}$        | 2.572   | $2.560^{b}$          |
|                     | 303.15 | 0.80192               | $0.8019^{a}$        | 2.275   | $2.560^{\circ}$      |
| 2-butanol           | 293.15 | 0.80554               | $0.80648^{d}$       | 3.625   | 3.6316 <sup>d</sup>  |
|                     | 298.15 | 0.80206               | $0.80206^{b}$       | 2.998   | $3.068^{b}$          |
|                     | 303.15 | 0.79845               |                     | 2.489   |                      |
| 2-methyl-1-propanol | 293.15 | 0.80128               | $0.80168^{d}$       | 3.943   | $4.0336^{d}$         |
|                     | 298.15 | 0.79774               | $0.79742^{b}$       | 3.332   | $3.410^{b}$          |
|                     | 303.15 | 0.79432               |                     | 2.884   |                      |
| 2-methyl-2-propanol | 293.15 | 0.79568               | $0.80961^{d}$       | 5.486   | $5.108^{d}$          |
|                     | 298.15 | 0.78065               | $0.78049^{b}$       | 4.436   | $4.444^{b}$          |
|                     | 303.15 | 0.77576               | $0.77573^{b}$       | 3.378   | 3.361 <sup>b</sup>   |
| 2-pyrrolidone       | 293.15 | 1.10984               |                     | 15.842  |                      |
| 1.*                 | 298.15 | 1.10698               | $1.1080^{a}$        | 13.068  | 13.0927 <sup>a</sup> |
|                     | 303.15 | 1.10338               | 1.1034 <sup>a</sup> | 10.687  | 10.6983 <sup>a</sup> |

<sup>a</sup> Reference 6. <sup>b</sup> Reference 8. <sup>c</sup> Reference 9. <sup>d</sup> Reference 10.

we report in the present paper, the density  $\rho$ , excess molar volumes  $V^{\rm E}$ , viscosity  $\eta$ , viscosity deviations  $\eta$ , and excess molar enthalpies  $H^{\rm E}$  for the binary mixtures of 2-pyrrolidone + 1-butanol, + 2-methyl-1-propanol, + 2-butanol, and + 2-methyl-2-propanol over the whole mole fraction range at temperatures from (293.15 to 303.15) K.

# **Experimental Section**

*Materials.* 1-Butanol (stated purity 99.8 %), 2-methyl-1propanol (stated purity 99.5 %), 2-butanol (stated purity 99.5 %), and 2-methyl-2-propanol (stated purity 99.5 %) were obtained Aldrich and 2-pyrrolidone (stated purity 99 %) from Fluka AG and used without further purification. All liquids were kept over activated molecular sieves of type 4A (Union Carbide) and filtered before use. The purity of liquids was confirmed by gas-liquid chromatographic analysis. The measured density and viscosity data of the pure liquids at temperatures from (293.15 to 303.15) K are shown in Table 1 together with literature data. Binary mixtures were prepared by mass using a Mettler balance (model AE-240) with a precision of  $\pm$  0.01 mg.

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*Measurements.* The densities of the pure component liquids and their binary mixtures were measured with a high precision vibrating-tube digital densimeter (model DMA 60/602) whose measurement cell temperature was controlled automatically within  $\pm$  0.01 K of the selected value. Before each series of measurements, the densimeter was calibrated at atmospheric pressure with double distilled water and dry air. Densities, both water and dry air, at the various working temperatures were given by the manufacturer in the instruction manual. The uncertainty in the density measurements was within  $\pm$  3  $\cdot$  10<sup>-5</sup> g  $\cdot$  cm<sup>-3</sup>.

Kinematic viscosities  $\nu$  of pure liquids and the binary mixtures were determined using an Ubbelohde viscometer with a Schott-Gerate automatic measuring unit model AVS-300. The temperature was kept constant within  $\pm$  0.01 K by means of a Schott-Gerate CT-1150 thermostat. The viscometer was calibrated with deionized doubly distilled water. Ubbelohde viscometer of relatively long flow > 300 s was used to minimize the kinetic energy corrections. Experiments were repeated at least three times at each temperature for all mixtures, and the results were averaged. The uncertainty of flow time measurements was  $\pm$  0.01 s. The uncertainty in the viscosity measurements was found to be within  $\pm$  3·10<sup>-3</sup> mPa·s.

Excess molar enthalpies  $H^{\rm E}$  for 2-pyrrolidone (1) + butanol isomers (2) mixtures were measured using LKB model 2107 flow microcalorimeter (LKB, Sweden). Electrical calibrations, details of the instrument, and the operating procedure have been described elswhere.<sup>11</sup> Before measurements, the apparatus performance was checked by measuring the excess molar enthalpies of the standard mixtures cyclohexane + *n*-hexane and benzene + carbontetrachloride. Results were in good agreement with the reported data in the literature.<sup>12</sup> The experimental errors of H<sup>E</sup> were estimated to be better than  $\pm 1 \%$ .

Binary mixtures were prepared by mixing known masses of pure liquids in airtight-stoppered bottles to minimize the evaporation losses. All measurements of mass were performed on a Mettler balance (model AE-240) with a precision of  $\pm$  0.01 mg. The uncertainty in the mole fractions of the mixtures was estimated to be lower than  $\pm 2 \cdot 10^{-4}$ .

# **Results and Discussion**

The experimental values of density  $\rho$  for 2-pyrrolidone (1) + butanol isomers (2) mixtures at T = (293.15, 298.15, and 303.15) K over the whole mole fraction range are listed in Table 2. The excess molar volumes  $V^{\text{E}}$  for these binary mixtures were obtained from the following relation:

$$V_{\rm m}^{\rm E} = \frac{x_1 M_1 + x_2 M_2}{\rho} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} \tag{1}$$

where  $x_1$  and  $x_2$  are the mole fractions,  $M_1$  and  $M_2$  are molar masses, and  $\rho_1$  and  $\rho_2$  are the densities of the pure component liquids 1 and 2, respectively.  $\rho$  is the density of the binary mixtures. The experimental  $\rho$  and  $V^E$  data of 2-pyrrolidone (1) + butanol isomers (2) mixtures at T = (293.15, 298.15, 303.15)K are presented in Table 2.

Table 3 presents viscosity and viscosity deviations  $\eta$  of 2-pyrrolidone (1) + butanol isomers (2) mixtures at T = (293.15, 298.15,and 303.15) K. Dynamic viscosity  $\eta$  and viscosity deviations  $\eta$ were calculated according to the following equations:

$$\eta = \nu \rho \tag{2}$$

$$\Delta \eta = \eta - (x_1 \eta_1 + x_2 \eta_2) \tag{3}$$

where  $\nu$  and  $\eta$  are the kinematic and the dynamic viscosity of the mixtures and subscripts 1 and indicate 2-pyrrolidone and butanol isomers, respectively.

Table 2. Densities,  $\rho$ , and Excess Molar Volumes,  $V^{E}$ , for 2-Pyrrolidone (1) + Butanol Isomers (2) at T = (293.15 to 303.15) K

|        | $\rho/g \cdot cm^{-3}$ |            |                | $V^{\rm E}/{\rm cm}^3 \cdot {\rm mol}^{-1}$ |          |          |
|--------|------------------------|------------|----------------|---|----------|----------|
| $X_1$  | 293.15 K               | 298.15 K   | 303.15 K       | 293.15 K                                    | 298.15 K | 303.15 K |
|        |                        | 2-Pyrro    | lidone $(1)$ + | 1-Butanol                                   |          |          |
| 0.0956 | 0.83448                | 0.83055    | 0.82697        | -0.058                                      | -0.060   | -0.067   |
| 0.1784 | 0.85672                | 0.85286    | 0.84930        | -0.102                                      | -0.108   | -0.120   |
| 0.2445 | 0.87489                | 0.87115    | 0.86757        | -0.134                                      | -0.147   | -0.158   |
| 0.3055 | 0.89200                | 0.88827    | 0.88473        | -0.158                                      | -0.169   | -0.184   |
| 0.3874 | 0.91545                | 0.91187    | 0.90831        | -0.181                                      | -0.200   | -0.215   |
| 0.4434 | 0.93179                | 0.92829    | 0.92472        | -0.190                                      | -0.210   | -0.224   |
| 0.4996 | 0.94845                | 0.94503    | 0.94150        | -0.192                                      | -0.214   | -0.231   |
| 0.5944 | 0.97719                | 0.97395    | 0.97039        | -0.185                                      | -0.211   | -0.226   |
| 0.6573 | 0.99667                | 0.99350    | 0.99011        | -0.169                                      | -0.193   | -0.212   |
| 0.7236 | 1.01757                | 1.01453    | 1.01105        | -0.142                                      | -0.170   | -0.187   |
| 0.7983 | 1.04170                | 1.03872    | 1.03532        | -0.112                                      | -0.133   | -0.155   |
| 0.8554 | 1.06058                | 1.05759    | 1.05415        | -0.087                                      | -0.100   | -0.117   |
| 0.9121 | 1.07961                | 1.07671    | 1.07326        | -0.055                                      | -0.065   | -0.080   |
| 0.9778 | 1.10222                | 1.09935    | 1.09578        | -0.022                                      | -0.024   | -0.028   |
| 0.0005 | 0.02150                | 2-Pyrrolia | done $(1) + 2$ | -Butanol (2                                 | )        | 0.051    |
| 0.0995 | 0.83158                | 0.82813    | 0.82455        | -0.041                                      | -0.044   | -0.051   |
| 0.1675 | 0.84993                | 0.84653    | 0.84294        | -0.073                                      | -0.079   | -0.088   |
| 0.2444 | 0.87114                | 0.86780    | 0.86423        | -0.101                                      | -0.110   | -0.122   |
| 0.2996 | 0.88673                | 0.88342    | 0.87983        | -0.121                                      | -0.132   | -0.142   |
| 0.3945 | 0.91418                | 0.91092    | 0.90730        | -0.146                                      | -0.159   | -0.167   |
| 0.4531 | 0.93154                | 0.92830    | 0.92468        | -0.156                                      | -0.168   | -0.1//   |
| 0.4967 | 0.94464                | 0.94143    | 0.93781        | -0.158                                      | -0.170   | -0.179   |
| 0.5546 | 0.96232                | 0.95915    | 0.95553        | -0.157                                      | -0.169   | -0.178   |
| 0.6402 | 0.98906                | 0.98596    | 0.98236        | -0.148                                      | -0.160   | -0.170   |
| 0.7126 | 1.01223                | 1.00919    | 1.00562        | -0.130                                      | -0.143   | -0.153   |
| 0.7895 | 1.03738                | 1.03441    | 1.03084        | -0.100                                      | -0.111   | -0.120   |
| 0.8438 | 1.05557                | 1.05266    | 1.04912        | -0.078                                      | -0.089   | -0.098   |
| 0.9096 | 1.07809                | 1.0/519    | 1.0/164        | -0.049                                      | -0.055   | -0.061   |
| 0.9/6/ | 1.10154                | 1.09873    | 1.09514        | -0.012                                      | -0.018   | -0.020   |
|        | 2-F                    | yrrolidone | (1) + 2-Met    | hyl-1-propai                                | nol (2)  |          |
| 0.0889 | 0.82477                | 0.82128    | 0.81786        | -0.044                                      | -0.048   | -0.052   |
| 0.1776 | 0.84894                | 0.84547    | 0.84204        | -0.086                                      | -0.090   | -0.097   |
| 0.2378 | 0.86574                | 0.86231    | 0.85886        | -0.108                                      | -0.115   | -0.122   |
| 0.3009 | 0.88375                | 0.88034    | 0.87686        | -0.131                                      | -0.139   | -0.145   |
| 0.3978 | 0.91212                | 0.90880    | 0.90528        | -0.156                                      | -0.167   | -0.172   |
| 0.4456 | 0.92649                | 0.92319    | 0.91966        | -0.168                                      | -0.179   | -0.184   |
| 0.5106 | 0.94636                | 0.94311    | 0.93959        | -0.177                                      | -0.187   | -0.194   |
| 0.5844 | 0.96946                | 0.96629    | 0.96276        | -0.180                                      | -0.193   | -0.201   |
| 0.6489 | 0.99011                | 0.98700    | 0.98349        | -0.176                                      | -0.190   | -0.200   |
| 0.7126 | 1.01087                | 1.00783    | 1.00440        | -0.162                                      | -0.176   | -0.192   |
| 0.7943 | 1.03814                | 1.03518    | 1.03180        | -0.134                                      | -0.148   | -0.167   |
| 0.8564 | 1.05936                | 1.05643    | 1.05304        | -0.107                                      | -0.117   | -0.134   |
| 0.9126 | 1.07891                | 1.07598    | 1.07253        | -0.074                                      | -0.079   | -0.091   |
| 0.9755 | 1.10098                | 1.09814    | 1.09458        | -0.020                                      | -0.024   | -0.028   |
| 0.0706 | 2-F                    | yrrolidone | (1) + 2-Metl   | hyl-2-propa                                 | nol (2)  | 0.021    |
| 0.0786 | 0.80696                | 0.80200    | 0.79713        | -0.030                                      | -0.031   | -0.031   |
| 0.1832 | 0.83627                | 0.83145    | 0.82669        | -0.065                                      | -0.0/1   | -0.079   |
| 0.2489 | 0.85532                | 0.85057    | 0.84586        | -0.090                                      | -0.094   | -0.102   |
| 0.3105 | 0.8/359                | 0.86894    | 0.86429        | -0.107                                      | -0.112   | -0.123   |
| 0.38/3 | 0.89703                | 0.89252    | 0.88/93        | -0.124                                      | -0.131   | -0.140   |
| 0.4330 | 0.91830                | 0.91393    | 0.90939        | -0.130                                      | -0.139   | -0.14/   |
| 0.5003 | 0.93255                | 0.92828    | 0.92380        | -0.131                                      | -0.141   | -0.149   |
| 0.5/34 | 0.95636                | 0.95227    | 0.94/8/        | -0.126                                      | -0.138   | -0.145   |
| 0.6544 | 0.98351                | 0.9/959    | 0.97532        | -0.112                                      | -0.121   | -0.129   |
| 0.7236 | 1.00/30                | 1.00303    | 0.99949        | -0.093                                      | -0.102   | -0.110   |
| 0.7995 | 1.05428                | 1.05079    | 1.026/4        | -0.068                                      | -0.076   | -0.080   |
| 0.80/2 | 1.03906                | 1.055/3    | 1.05185        | -0.046                                      | -0.049   | -0.052   |
| 0.923/ | 1.08026                | 1.0//13    | 1.0/33/        | -0.024                                      | -0.026   | -0.030   |
| 0.9823 | 1.10287                | 1.09993    | 1.09031        | -0.005                                      | -0.005   | -0.000   |

Experimental excess molar enthalpies  $H^{\rm E}$  for 2-pyrrolidone (1) + butanol isomers (2) mixtures at 298.15 K are shown in Table 4.

The values of  $V^{\text{E}}$ ,  $\eta$ , and  $H^{\text{E}}$  for each mixture were fitted to the Redlich–Kister polynomial equation<sup>13</sup>

$$Q = x_1 x_2 \sum_{i=0}^{n} A_i (x_1 - x_2)^i$$
(4)

where Q denotes  $V^{E}$  or  $\eta$  or  $H^{E}$ .  $A_{i}$  are adjustable parameters.

In each case, the optimum number of coefficients  $A_i$  was determined from an examination of the variation of the standard deviation  $\sigma(Q)$ :

$$\sigma Q = \left[\sum (Q_{\rm exp} - Q_{\rm cal})^2 / (n - m)\right]^{1/2}$$
(5)

where *n* is the total number of experimental points and *m* is the number of parameters. The fitting coefficients and the standard deviations values  $\sigma(Q)$  for binary mixtures of 2-pyrrolidone (1) + butanol isomers (2) at T = (293.15, 298.15, and 303.15) K are given in Table 5.

It can be observed from the experimental results in Table 2 and Figure 1 that  $V^{\rm E}$  values are negative over the whole mole fraction range at T = (293.15, 298.15, and 303.15) K for binary mixtures of 2-pyrrolidone + 1-butanol, + 2-butanol, + 2-methyl-1-propanol, and + 2-methyl-2-propanol. The negative  $V^{\rm E}$ values indicate that there is a volume contraction on mixing. Such behavior is a result of several opposing effects: dipolardipolar interactions between 2-PY molecules and butanol isomers, hydrogen bond breaking in 2-pyrrolidone and butanol isomers structures, and a new hydrogen bond formation between -NH or -C-O groups in 2-PYwith hydroxyl groups -OH in butanol isomers, changes of free volume in the real mixtures, interstitial accommodation effect, and sterically hindered effect. The less negative  $V^{\rm E}$  values for 2-methyl-2-propanol mixtures serves as evidence that the interactions between 2-PY and 2-methyl-2-propanol are weaker than those between the three butanol isomers and 2-PY. Such behavior may be due to the larger steric hindrance of the methyl groups -CH<sub>3</sub> in 2-methyl-2-propanol. The negative  $V^{\rm E}$  values at equimolar concentrations of the binary mixtures follow the order: 1-butanol > 2-methyl-1-propanol > 2-butanol > 2-methyl-2-propanol, Figure 1.

Viscosity deviations  $\Delta \eta$  for the mixtures containing 2-PY and butanol isomers present negative values at T = (293.15, 298.15, and 303.15) K.  $\Delta \eta$  becomes less negative following the sequence 2-methyl-2-propanol < 2-butanol < 2-methyl-1propanol < 1-butanol, Figure 2. The minimum  $\Delta \eta$  values for all mixtures appear in the 2-pyrrolidone-rich region, around  $x_1$ 

Table 4. Experimental Excess Molar Enthalpies,  $H^{\rm E}$ , for 2-Pyrrolidone (1) + Butanol Isomers (2) at T = 298.15 K and at Atmospheric Pressure

| $x_1$                                     | $H^{\mathrm{E}}/\mathrm{J} \cdot \mathrm{mol}^{-1}$ | $x_1$             | $H^{\mathrm{E}}/\mathrm{J} \cdot \mathrm{mol}^{-1}$ |  |  |  |  |
|---|---|-------------------|---|--|--|--|--|
| 2-Pyrrolidone $(1) + 1$ -Butanol $(2)$    |   |                   |   |  |  |  |  |
| 0.0564                                    | 97.7  | 0.5022            | 232.6   |  |  |  |  |
| 0.1225                                    | 163.3   | 0.5963            | 206.2   |  |  |  |  |
| 0.1877                                    | 207.5   | 0.6844            | 172.4   |  |  |  |  |
| 0.2452                                    | 235.6   | 0.7452            | 144.8   |  |  |  |  |
| 0.3266                                    | 250.2   | 0.8553            | 94.9  |  |  |  |  |
| 0.3884                                    | 252.3   | 0.9278            | 52.7  |  |  |  |  |
| 0.4453                                    | 243.1   |                   |   |  |  |  |  |
|   | 2-Pyrrolidone (1)                                   | ) + 2-Butanol (2) | )   |  |  |  |  |
| 0.0555                                    | 169.2   | 0.4998            | 384.9   |  |  |  |  |
| 0.1212                                    | 277.5   | 0.5887            | 337.2   |  |  |  |  |
| 0.1842                                    | 344.4   | 0.6799            | 278.4   |  |  |  |  |
| 0.2443                                    | 388.5   | 0.7389            | 236.4   |  |  |  |  |
| 0.3301                                    | 413.4   | 0.8478            | 154.6   |  |  |  |  |
| 0.3903                                    | 416.7   | 0.9309            | 89.9  |  |  |  |  |
| 0.4444                                    | 404.3   |                   |   |  |  |  |  |
|   | 2-Pyrrolidone $(1) + 2$ -                           | Methyl-1-Propa    | nol (2)   |  |  |  |  |
| 0.0522                                    | 121.2   | 0.5022            | 277.5   |  |  |  |  |
| 0.1222                                    | 214.3   | 0.5912            | 243.6   |  |  |  |  |
| 0.1812                                    | 272.1   | 0.6807            | 204.4   |  |  |  |  |
| 0.2451                                    | 298.9   | 0.7402            | 179.8   |  |  |  |  |
| 0.3296                                    | 312.8   | 0.8466            | 119.8   |  |  |  |  |
| 0.4043                                    | 309.7   | 0.9233            | 71.4  |  |  |  |  |
| 0.4535                                    | 297.4   |                   |   |  |  |  |  |
| 2-Pyrrolidone $(1)$ + 2-Methyl-2-propanol |   |                   |   |  |  |  |  |
| 0.0498                                    | 144.5   | 0.4943            | 432.3   |  |  |  |  |
| 0.1189                                    | 243.6   | 0.5766            | 396.1   |  |  |  |  |
| 0.1932                                    | 322.2   | 0.6806            | 338.9   |  |  |  |  |
| 0.2551                                    | 377.4   | 0.7422            | 287.4   |  |  |  |  |
| 0.3309                                    | 424.8   | 0.8435            | 172.9   |  |  |  |  |
| 0.3946                                    | 444.5   | 0.9312            | 107.4   |  |  |  |  |
| 0.4411                                    | 444.4   |                   |   |  |  |  |  |

= 0.6. A comparison of viscosity behavior with temperature indicates that  $\Delta \eta$  values decrease in absolute value with temperature. Figure 2 shows the less negative  $\Delta \eta$  values for

Table 3. Viscosities for 2-Pyrrolidone (1) + Butanol Isomers (2) at T = (293.15 to 303.15) K

|  | η/mPa•s   |          |  |   | η/mPa•s  |          |          |  |
|--|---|----------|--|---|----------|----------|----------|--|
| $x_1$                                  | 293.15 K  | 298.15 K | 303.15 K                               | $x_1$   | 293.15 K | 298.15 K | 303.15 K |  |
| 2-Pyrrolidone $(1) + 1$ -Butanol $(2)$ |   |          | 2-Pyrrolidone $(1) + 2$ -Butanol $(2)$ |   |          |          |          |  |
| 0.0956                                 | 3.300   | 2.884    | 2.456                                  | 0.0995  | 3.409    | 2.829    | 2.300    |  |
| 0.1784                                 | 3.346   | 3.050    | 2.431                                  | 0.1675  | 3.108    | 2.409    | 1.896    |  |
| 0.2445                                 | 3.373   | 3.071    | 2.433                                  | 0.2444  | 3.034    | 2.443    | 1.707    |  |
| 0.3055                                 | 3.548   | 3.028    | 2.504                                  | 0.2996  | 2.840    | 2.461    | 1.724    |  |
| 0.3874                                 | 3.595   | 3.119    | 2.638                                  | 0.3945  | 2.982    | 2.561    | 1.834    |  |
| 0.4434                                 | 3.893   | 3.426    | 2.899                                  | 0.4531  | 3.084    | 2.698    | 2.068    |  |
| 0.4996                                 | 4.198   | 3.740    | 3.211                                  | 0.4967  | 3.237    | 2.856    | 2.348    |  |
| 0.5944                                 | 5.167   | 4.682    | 3.921                                  | 0.5546  | 3.668    | 3.241    | 2.702    |  |
| 0.6573                                 | 6.087   | 5.497    | 4.578                                  | 0.6402  | 4.673    | 4.125    | 3.405    |  |
| 0.7236                                 | 7.353   | 6.572    | 5.384                                  | 0.7126  | 5.995    | 5.238    | 4.304    |  |
| 0.7983                                 | 9.017   | 8.117    | 6.428                                  | 0.7895  | 7.928    | 6.821    | 5.519    |  |
| 0.8554                                 | 10.754  | 9.560    | 7.469                                  | 0.8438  | 9.691    | 8.277    | 6.842    |  |
| 0.9121                                 | 12.573  | 11.006   | 8.726                                  | 0.9096  | 11.741   | 10.096   | 8.162    |  |
| 0.9778                                 | 14.883  | 12.699   | 10.305                                 | 0.9767  | 14.726   | 12.474   | 10.148   |  |
| 1                                      | 2-Pyrrolidone $(1)$ + 2-Methyl-1-propanol $(2)$ |          |  | 2-Pyrrolidone $(1)$ + 2-Methyl-2-propanol $(2)$ |          |          |          |  |
| 0.0889                                 | 3.624   | 3.033    | 2.921                                  | 0.0786  | 4.778    | 3.771    | 3.586    |  |
| 0.1776                                 | 3.381   | 2.802    | 2.596                                  | 0.1832  | 3.931    | 3.230    | 2.732    |  |
| 0.2378                                 | 2.987   | 2.570    | 2.409                                  | 0.2489  | 3.399    | 2.698    | 2.053    |  |
| 0.3009                                 | 2.870   | 2.483    | 2.167                                  | 0.3105  | 2.824    | 2.109    | 1.481    |  |
| 0.3978                                 | 2.787   | 2.487    | 1.789                                  | 0.3875  | 2.167    | 1.547    | 0.786    |  |
| 0.4456                                 | 2.833   | 2.483    | 1.750                                  | 0.4556  | 1.857    | 1.333    | 0.464    |  |
| 0.5106                                 | 3.145   | 2.736    | 1.783                                  | 0.5003  | 1.665    | 1.232    | 0.271    |  |
| 0.5844                                 | 3.686   | 3.262    | 2.118                                  | 0.5734  | 1.870    | 1.496    | 0.414    |  |
| 0.6489                                 | 4.428   | 3.966    | 2.645                                  | 0.6544  | 2.478    | 2.049    | 1.049    |  |
| 0.7126                                 | 5.569   | 4.938    | 3.369                                  | 0.7236  | 3.648    | 3.252    | 2.120    |  |
| 0.7943                                 | 7.610   | 6.753    | 4.876                                  | 0.7995  | 5.671    | 5.011    | 3.681    |  |
| 0.8564                                 | 9.460   | 8.552    | 6.388                                  | 0.8672  | 8.035    | 7.463    | 5.849    |  |
| 0.9126                                 | 11.566  | 10.271   | 8.021                                  | 0.9237  | 10.941   | 9.609    | 8.042    |  |
| 0.9753                                 | 14.552  | 12.909   | 10.152                                 | 0.9823  | 14.335   | 12.116   | 9.894    |  |

Table 5. Coefficients  $(A_i)$  of Redlich-Kister Equation and Standard Deviations ( $\sigma$ ) for 2-Pyrrolidone (1) + Butanol Isomers (2) at T = (293.15 to 303.15) K

| <u>(</u>  |  |  |   |  |  |  |  |  |
|---|--|--|---|--|--|--|--|--|
|   | $A_0$  | $A_1$  | $A_2$   | $A_3$  | σ  |  |  |  |
| 2-Pyrrolidone (1) + 1-Butanol (2)               |  |  |   |  |  |  |  |  |
| $V^{\rm E}$                                     | -0.763   | -0.028   | 0.137   | -0.070   | 0.002  |  |  |  |
| $\Delta \eta$                                   | -20.52   | -9.179   | 2.409   | -3.02  | 0.014  |  |  |  |
| $V^{\dot{E}}$                                   | -0.858   | -0.049   | 0.172   | 0.741  | 0.003  |  |  |  |
| $\Delta \eta$                                   | -16.76   | -7.48  | 6.576   | 3.115  | 0.011  |  |  |  |
| $H^{\dot{E}}$                                   | 916.3  | -424.2   | 451.6   | -188.3   | 3.1  |  |  |  |
| $V^{E}$   | -0.919   | -0.067   | 0.073   | -0.097   | 0.002  |  |  |  |
| $\Delta \eta$                                   | -13.64   | -7.54  | 4.343   | 6.463  | 0.015  |  |  |  |
|   | 2-Pyrrol   | idone $(1) + 2$  | -Butanol (2   | !)   |  |  |  |  |
| $V^{E}$   | -0.663.  | -0.066   | 0.175   | -0.008   | 0.003  |  |  |  |
| $\Delta \eta$                                   | -25.76   | -11.54   | 0.313   | -0.310   | 0.011  |  |  |  |
| $V^{\dot{E}}$                                   | -0.678   | -0.010   | 0.126   | -0.198   | 0.002  |  |  |  |
| $\Delta \eta$                                   | -21.21   | -9.986   | 1.668   | 4.401  | 0.013  |  |  |  |
| $H^{\dot{E}}$                                   | 1107.6   | -661.5   | 701.9   | -11.5  | 1.8  |  |  |  |
| $V^{\rm E}$                                     | -0.716   | -0.016   | 0.065   | -0.182   | 0.004  |  |  |  |
| $\Delta \eta$                                   | -17.74   | -7.04  | 3.059   | 4.798  | 0.011  |  |  |  |
| 2   | 2-Pyrrolidone  | (1) + 2-Meth   | nyl-1-propa   | nol (2)  |  |  |  |  |
| $V^{E}$   | -0.705   | -0.244   | -0.012  | 0.082  | 0.001  |  |  |  |
| $\Delta \eta$                                   | -27.35   | -13.84   | -1.331  | -0.093   | 0.011  |  |  |  |
| $V^{\dot{E}}$                                   | -0.749   | -0.245   | -0.053  | 0.026  | 0.003  |  |  |  |
| $\Delta \eta$                                   | -23.85   | -13.8  | 1.067   | 7.075  | 0.014  |  |  |  |
| $H^{\dot{\mathrm{E}}}$                          | 1493.7   | -707.2   | 858.8   | -376.7   | 1.2  |  |  |  |
| $V^{E}$   | -0.779   | -0.327   | -0.164  | 0.067  | 0.004  |  |  |  |
| $\Delta \eta$                                   | -20.76   | -16.76   | 7.714   | 13.97  | 0.013  |  |  |  |
| 2-Pyrrolidone $(1)$ + 2-Methyl-2-propanol $(2)$ |  |  |   |  |  |  |  |  |
| $V^{E}$   | -0.522   | 0.002  | 0.215   | 0.061  | 0.002  |  |  |  |
| $\Delta \eta$                                   | -34.78   | -18.24   | -9.36   | -11.166  | 0.014  |  |  |  |
| $V^{\dot{E}}$                                   | -0.561   | -0.009   | 0.227   | 0.053  | 0.004  |  |  |  |
| $\Delta \eta$                                   | -27.94   | -15.74   | -7.942  | -4.715   | 0.022  |  |  |  |
| $H^{\dot{\mathrm{E}}}$                          | 1695.3   | -448.9   | 441.3   | -215.0   | 1.6  |  |  |  |
| $V^{\rm E}$                                     | -0.599   | 0.024  | 0.243   | -0.016   | 0.015  |  |  |  |
| $\Delta \eta$                                   | -27.13   | -14.744  | 10.277  | -3.715   | 0.013  |  |  |  |
|   | $V^{E} \\ \Delta \eta \\ V^{E} \\ \Delta \eta \\ $ | $\begin{array}{rrrr} & A_0 \\ & 2 \text{-Pyrrol} \\ V^{\text{E}} & -0.763 \\ \Delta \eta & -20.52 \\ V^{\text{E}} & -0.858 \\ \Delta \eta & -16.76 \\ H^{\text{E}} & 916.3 \\ V^{\text{E}} & -0.919 \\ \Delta \eta & -13.64 \\ & 2 \text{-Pyrrol} \\ V^{\text{E}} & -0.663. \\ \Delta \eta & -25.76 \\ V^{\text{E}} & -0.678 \\ \Delta \eta & -25.76 \\ V^{\text{E}} & -0.678 \\ \Delta \eta & -25.76 \\ V^{\text{E}} & -0.716 \\ \Delta \eta & -17.74 \\ & 2 \text{-Pyrrolidone} \\ V^{\text{E}} & -0.716 \\ \Delta \eta & -17.74 \\ & 2 \text{-Pyrrolidone} \\ V^{\text{E}} & -0.705 \\ \Delta \eta & -27.35 \\ V^{\text{E}} & -0.749 \\ \Delta \eta & -23.85 \\ H^{\text{E}} & 1493.7 \\ V^{\text{E}} & -0.779 \\ \Delta \eta & -20.76 \\ & 2 \text{-Pyrrolidone} \\ V^{\text{E}} & -0.522 \\ \Delta \eta & -34.78 \\ V^{\text{E}} & -0.591 \\ \Delta \eta & -27.94 \\ H^{\text{E}} & 1695.3 \\ V^{\text{E}} & -0.599 \\ \Delta \eta & -27.13 \\ \end{array}$ | $\begin{array}{c ccccccccccccccccccccccccccccccccccc$ | $\begin{array}{c c c c c c c c c c c c c c c c c c c $ | $\begin{array}{c c c c c c c c c c c c c c c c c c c $ |  |  |  |

the mixtures of 2-pyrrolidone (1) + 1-butanol (2) and the more negative for the mixtures of 2-methyl-2-propanol (2), which may result from the sterically hindered effect. A reasonable agreement between our experimental values of  $V^{\rm E}$  and  $\Delta\eta$  and those published in the literature.  $V^{\rm E}$  and  $\Delta\eta$  values for the binary mixtures of 2-pyrrolidone (1) + 1-butanol (2) at 298.15 K and  $x_1 = 0.5$  are -0.2145 and -4.19, respectively, and those reported by Garcia et al.<sup>6</sup> are -0.2272 and -4.047.

From Figure 3, it can be seen that  $H^{\rm E}$  values are positive (endothermic) in the mixture of 2-PY with butanol isomers at 298.15 K over the whole mole fraction range. The maximum  $H^{\rm E}$  values are observed around 0.3 to 0.5 mol fraction of 2-PY for these binary mixtures. The hydrogen bonds in 2-pyrrolidone and butanol isomers, the strong dipole–dipole interactions in



**Figure 1.** Excess molar volumes against mole fraction of 2-pyrrolidone (1) + butanol isomers (2) at 298.15 K:  $\blacklozenge$ , 2-pyrrolidone (1) + 1-butanol (2);  $\Box$ , 2-pyrrolidone + 2-methyl-1-propanol (2);  $\Delta$ , 2-pyrrolidone (1) + 2-butanol (2);  $\bigcirc$ , 2-pyrrolidone (1) + 2-methyl-2-propanol (2).



**Figure 2.** Viscosity deviations against mole fraction of 2-pyrrolidone (1) + butanol isomers (2) at 298.15 K:  $\blacklozenge$ , 2-pyrrolidone (1) + 1-butanol (2);  $\Box$ , 2-pyrrolidone + 2-methyl-1-propanol (2);  $\blacktriangle$ , 2-pyrrolidone (1) + 2-butanol (2);  $\diamondsuit$ , 2-pyrrolidone (1) + 2-methyl-2-propanol (2).



**Figure 3.** Excess molar enthalpies against mole fraction of 2-pyrrolidone (1) + butanol isomers (2) at 298.15 K:  $\blacklozenge$ , 2-pyrrolidone (1) + 1-butanol (2);  $\bigtriangleup$ , 2-pyrrolidone + 2-methyl-1-propanol (2);  $\blacksquare$ , 2-pyrrolidone (1) + 2-butanol (2);  $\diamondsuit$ , 2-pyrrolidone (1) + 2-methyl-2-propanol (2).

both components and the hydrogen bonds association of 2-pyrrolidone with butanol isomers affect considerably the properties of the mixtures with endothermic as well as exothermic contributions. The positive experimental  $H^{\rm E}$  values suggest that the absorption of heat to depolmerization of selfassociated butanol isomers and 2-pyrrolidone is stronger than the liberation of heat as a result of possible hydrogen bonding interaction between -NH or -C-O groups in 2-PY with hydroxyl groups -OH in butanol isomers. The positive values of  $H^{\rm E}$  over the whole mole fraction range may be attributed to the dominance on molecular dissociation over associations.  $H^{\rm E}$ is less negative for the mixtures of 2-pyrrolidone (1) + 1-butanol (2) and more negative for the mixtures 2-pyrrolidone (1) + 2-methyl-2-propanol (2); this may be closely related with increasing difficulty to produce heteromolecular interactions with increasing of branching in the carbon atom carrying the -OH group.

#### Conclusion

This paper reports new experimental data for the densities and viscosities of the binary mixtures of 2-pyrrolidone (1) + 1-butanol (2), 2-pyrrolidone (1) + 2-butanol (2), 2-pyrrolidone (1) + 2-methyl-1-propanol (2), and 2-pyrrolidone (1) + 2-methyl-2-propanol (2) measured at temperatures from (293.15 to 303.15) K and at atmospheric pressure over the whole mole fraction range. The excess molar volumes,  $V^{\rm E}$ , and viscosity deviations,  $\Delta \eta$  for these mixtures determined from the experimental results of density and viscosity and the measured excess molar enthalpies,  $H^{\rm E}$ , at T = 298.15 K were fitted to the Redlich–Kister polynomial equation. All excess functions  $V^{\rm E}$ , and  $\Delta \eta$ , are negative, while  $H^{\rm E}$  is positive for all binary mixtures of the 2-pyrrolidone (1) + butanol isomers (2) over the whole mole fraction range and investigated temperatures, The excess molar volumes, viscosity deviations, and excess molar enthalpies behavior of the binary mixtures of 2-pyrrolidone (1) + butanol isomers (2) is a result of several opposing effects: dipolar–dipolar interactions, hydrogen bond breaking in butanol isomers, hydrogen bond formation between the –NH or –CO of 2-pyrrolidone and the –OH of butanols, and the sterically hindered effect.

## Literature Cited

- Al-Azzawi, S. F.; Awwad, A. M.; Al-Dujaili, A. H.; Al-Noori, M. K. Dielectric Constants and Excess Volumes of 2 - Pyrrolidone + Water at Several Temperatures. J. Chem. Eng. Data 1990, 35, 463–466.
- (2) Awwad, A. M.; Farhan, A. M. Volumetric Properties of 2-Pyrrolidone with Aromatic Hydrocarbons at *T* = (293.15, 303.15, 313.15, 333.15, and 343.15. *J. Chem. Thermodyn.* **2009**, *41*, 205–211.
- (3) Blumenshine, R. L.; Sears, P. G. Several Properties of the 2-Pyrrolidone - Water System as Functions of Composition and Temperature. *J. Chem. Eng. Data* **1966**, *11*, 141–143.
- (4) Garcia, B.; Herrera, C. A.; Leal, J. M. Thermodynamics of 2-Pyrrolidinone + n-Alkanol, Binary Mixtures: Activation Properties. *Thermochim. Acta* **1991**, *180*, 159–167.

- (5) Hoyuelos, F. J.; Garcia, B.; Alcalde, R. S.; Ibeas, S.; Leal, J. M. Shear Viscosities of Binary Mixtures of Pyrrolidin-2-one with C<sub>6</sub>-C<sub>10</sub> n-Alkan-1-ols. J. Chem. Soc., Faraday Trans. 2 1996, 92, 219–215.
- (6) Garcia, B.; Herrera, C. A.; Leal, J. M. Shear Viscosities of Binary Liquid Mixtures: 2-Pyrrolidone with 1-Alkanols. J. Chem. Eng. Data 1991, 36, 269–274.
- (7) Mehta, S. K.; Ram, G.; Bhasin, K. K. Molecular Interactions of α, ω-Alkanediols in Pyrrolidin-2-one: Thermophysical and Spectroscopic Measurements. J. Chem. Thermodyn. 2008, 40, 498–508.
- (8) Martinez, S.; Garriga, R.; Pérez, P.; Gracia, M. Densities and Viscosities of Binary Mixtures of Butanone and Butanol Isomers at Different Temperatures. *Fluid Phase Equilib.* 2000, *168*, 267–279.
- (9) Ansón, A.; Garriga, R.; Martinez, S.; Pérez, P.; Garcia, M. Densities and Viscosities of Binary Mixtures of 1- Chlorobutane and Butanol Isomers at Several Temperatures. J. Chem. Eng. Data 2005, 50, 677– 682.
- (10) Lomte, S. B.; Bawa, M. J.; Lande, M. S.; Arbad, R. Densities and Viscosities of Binary Liquid Mixtures of 2-Butanone with Branched Alcohols at (293.15 to 313.15) K. J. Chem. Eng. Data. DOI: 10.1021/ je800571y.
- (11) Francesconi, R.; Comelli, F. Liquid-Phase Enthalpy of Mixing for the System 1,3-Dioxolane-Chlorobenzene in the Temperature Range 288.15-313. K. J. Chem. Eng. Data 1986, 31, 250-253.
- (12) Gmehling, I. Excess Enthalpies for 1, 1, 1-Trichloroethane with Alkanes, Ketones, and Esters. J. Chem. Eng. Data 1993, 38, 143– 146.
- (13) Redlich, O.; Kister, A. T. Algebric Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* **1948**, 40, 345–348.

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