*J. Chem. Eng. Data* **2009,** *54,* 2895–2901

# Molar Heat Capacity of Aqueous Sulfolane, 4-Formylmorpholine, 1-Methyl-2-pyrrolidinone, and Triethylene Glycol Dimethyl Ether Solutions from (303.15 to 353.15) K

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The present study has focused on the experimental measurements of the molar heat capacities of four aqueous physical solvents of importance in natural gas sweetening: (1) tetramethylene sulfone (sulfolane), (2) 4-formylmorpholine (NFM), (3) 1-methyl-2-pyrrolidinone (NMP), and (4) triethylene glycol dimethyl ether (TEGDME). The measurements of the molar heat capacities were carried out in the temperature range of (303.15 to 353.15) K and for the entire range of mole fractions. Fractional deviations of the measured molar heat capacities from literature data were less than 1 %, and at worst 2 %. Molar excess heat capacities were calculated from the measurements and correlated as a function of mole fraction and temperature employing the Redlich−Kister equation. The excess partial molar quantities ($C_i^{\circ} - C_i^{*}$) were calculated by extrapolating the reduced excess heat capacity ($C_p^{E}/x_1x_2$) function at $x_1 = 0$ and $x_1 = 1$.

## Introduction

Physical solvents have been extensively studied during the last 25 years because of their industrial importance in the removal of $CO_2$ and $H_2S$ from high-pressure gas streams. Knowledge of various thermodynamic properties such as molar heat capacities ($C_p$) and enthalpies ($H$) is required for engineering design and subsequent operations.[1]

Physical solvents are nonreactive organic polar solvents that physically dissolve the acid gases. Solvent regeneration is done by reducing the pressure and requires less energy than chemical solvents. Physical solvents are also less corrosive than chemical solvents as no chemical reaction takes place with the acid gases.

Physical solvents such as tetramethylene sulfone (sulfolane), 4-formylmorpholine (NFM), 1-methyl-2-pyrrolidinone (NMP), and triethylene glycol dimethyl ether (TEGDME) are widely used as absorbents to remove acid gases from the high-pressure natural gas streams. Molar heat capacities for physical solvents are required for the calculation of heat balances around the absorbers, regenerators, and heat exchangers used in gas-treating industries. The molar heat capacities of aqueous sulfolane solutions were measured by Steele et al.,[2] Castagnolo et al.,[3] and Ho.[4] Becker and Gmehling[5] published the heat capacities for pure TEGDME. For the three aqueous systems of TEGDME, NMP, and NFM, the heat capacities were not found in the literature. The aim of this study was to experimentally determine the heat capacities of these physical solvents. The experimental $C_p$ values were used to calculate the molar excess heat capacities ($C_p^{E}$) and correlated as a function of mole fraction and temperature employing the Redlich−Kister equation. For the sake of completeness, the partial molar quantities $C_i^{\circ} - C_i^{*}$ were calculated by extrapolating the reduced excess heat capacity ($C_p^{E}/x_1x_2$) function at $x_1 = 0$ and $x_1 = 1$. Reduced excess heat capacity ($C_p^{E}/x_1x_2$) functions serve as sensitive indicators of phase transition and are also used to understand the changes in the structure of liquid solutions. Previously published data on excess volumes and viscosity deviations were combined with the present work to draw some conclusions on the intermolecular interactions with water.

## Materials

Triethylene glycol dimethyl ether (Fluka, 99.0 %), 1-methyl-2-pyrrolidinone (Fluka, 99.5 %), 4-formylmorpholine (Fluka, 99.0 %), and tetramethylene sulfone (Fluka, 99.0 %) were used without further purification. A standard reference material, synthetic sapphire ($\alpha$-$Al_2O_3$, 99.99 %), was purchased from the National Institute of Standards and Technology, Gaithersburg. All purities reported were on a mass basis.

## Experimental Section

Aqueous solutions were prepared on the basis of mole fractions. An analytical balance manufactured by Ohaus (model AP250D, Florham Park, NJ) with a precision of ± 0.1 mg was used to prepare gravimetrically the binary mixtures of solvent and deionized water. The overall possible uncertainty in the mole fractions was ± 0.0002.

The measurements of the molar heat capacities were carried out in a C-80 heat flow calorimeter manufactured by SETARAM Instrumentation (France). The C-80 calorimeter, working on the Tian-Calvet heat flow principle, was described in detail by Calvet et al.[6] To obtain precise measurements of the molar heat capacity of a sample, the sensitivity and the temperature scale of the C80 calorimeter were first calibrated. The calibration was performed for the entire temperature range of the C80 calorimeter, i.e., (303.15 to 573.15) K, at a scanning rate of 0.1 $K\cdot min^{-1}$. Two specially designed Joule-effect calibration cells and a calibration unit (EJ3), supplied by SETARAM with all the necessary accessories, were used for the sensitivity calibration. A detailed description of the sensitivity calibration was given elsewhere.[7] The temperature calibration was performed

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10.1021/je800999s CCC: $40.75

by measuring the displayed temperature of a phase change of a substance (indium), which has a well-documented precise (fixed) transition temperature. A sample of pure indium was encapsulated in aluminum foil and placed inside the standard cell. The melting point was found by measuring the rate of the heat flow into a sample as a function of temperature at melting time. The difference between the observed and actual transition temperature determined the amount of necessary adjustment. The manufacturer uncertainty in the measured temperature was given as ± 0.0001 K. The detailed description of the temperature calibration was also given elsewhere.[7]

For the measurement of the molar heat capacity, a sample weighting about (5.5 to 6) g was placed inside the sample cell. The cell was positioned into the measurement chamber of the calorimeter. The reference cell placed in the reference chamber of the calorimeter remained empty. Both the sample and reference cells were allowed to come to an isothermal condition over a period of (3 to 4) h. After allowing sufficient time to reach the isothermal condition at $T = 298.15$ K, the temperature of both cells was increased at the scanning rate of $0.1\ \text{K}\cdot\text{min}^{-1}$. During this time, the calorimetric signal increased as a function of time. On attainment of the set temperature, the calorimeter automatically reverted to an isothermal mode, causing the calorimetric signal to return to the baseline. To obtain the most precise values of $C_p$, the three-step method was employed. Becker and Gmehling[5] and also Becker et al.[8] have used this method to measure the heat capacity for 12 and 9 organic substances, respectively. In this method, two additional runs were performed with (1) both cells empty and (2) the reference material before running the sample run; i.e., the measurements of the molar heat capacities were conducted with (1) blank run, (2) reference run, and (3) sample run. For the reference run, a standard sapphire was used as a reference material. All runs were performed under the same experimental conditions. The heat flow values of all runs were noted for the desired temperature, and the molar heat capacity values were then calculated using the following equation.

$$C_p(T)/(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) = \left(\frac{H^{\text{F}}_{\text{sample}} - H^{\text{F}}_{\text{blank}}}{H^{\text{F}}_{\text{reference}} - H^{\text{F}}_{\text{blank}}}\right) \times \left(\frac{m_{\text{reference}}}{m_{\text{sample}}}\right) C_{p,\text{reference}}(T) \quad (1)$$

where $C_p(T)$ and $C_{p,\text{reference}}(T)$ are the molar heat capacity of the sample and reference substance (sapphire) at the desired temperature $T$, respectively; $H^{\text{F}}_{\text{sample}}$, $H^{\text{F}}_{\text{reference}}$, and $H^{\text{F}}_{\text{blank}}$ are the heat flows of the sample, reference (sapphire), and blank runs, respectively, at temperature $T$; and $m_{\text{sample}}$ and $m_{\text{reference}}$ are the masses of the sample and reference substance (sapphire), respectively. The values of the $C_{p,\text{reference}}(T)$ in eq 1 were taken from ref 9.

## Results and Discussion

To assess the accuracy of the calorimeter, the molar heat capacities of several systems over a large temperature range were measured. The molar heat capacity measurements of sapphire were conducted over the temperature range of (298.15 to 360.15) K at a scanning rate of $0.1\ \text{K}\cdot\text{min}^{-1}$. About 5 g of sapphire was used in the run. Ginnings and Furukawa,[10] Inaba,[11] and Xu[12] have also measured the molar heat capacity of sapphire. The values of the $C_p$ obtained in this study were in excellent agreement with values found in the literature as shown in Figure 1. If data from Ginnings and Furukawa[10] were not included, the deviations would be less than 1 %. Monoethanolamine (MEA) was also used, using the three-step method described earlier, to test the precision of the calorimeter. Heat capacity measurements of MEA were carried out over the temperature range of (303.15 to 353.15) K. Figure 2 shows the comparison between $C_p$ of MEA measured in the present study and the literature values. The values of $C_p$ obtained in this study were in excellent agreement with values obtained by Chiu et al.[13] Figures 3 and 4 show the comparison of the molar heat capacities measured in the present study for both pure sulfolane and TEGDME with those available in the literature. As shown in Figures 3 and 4, the values of the $C_p$ obtained in this study were in excellent agreement for sulfolane and TEGDME.[2,8] The deviations in all four systems were less than 1 %.

The obtained values of $C_p$ for all pure physical solvents are expressed as a function of temperature for all four studied systems. The values of $C_p$ for the binary systems sulfolane + $H_2O$, NMP + $H_2O$, NFM + $H_2O$, and TEGDME + $H_2O$ were measured from (303.15 to 353.15) K and are listed in Tables 1, 2, 3, and 4, respectively.

An excess molar heat capacity for a mixture is defined as[14]

$$C_p^{\text{E}} = C_p - x_{\text{w}} C^{\text{o}}_{p,\text{w}} - (1 - x_{\text{w}}) C^{\text{o}}_{p,\text{s}} \quad (2)$$

where $C_p^{\text{E}}$ is the molar excess molar heat capacity; $C^{\text{o}}_{p,\text{w}}$ is the molar heat capacity of water; $C^{\text{o}}_{p,\text{s}}$ is the molar heat capacity of solvent; and $x_{\text{w}}$ is the mole fraction of water. The Redlich−Kister equation was employed to represent the compositional dependence of the excess molar heat capacity for all four binary mixtures as follows

$$C_p^{\text{E}}\ (\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) = x_1(1 - x_1) \sum_{i=1}^{n} A_i (x_1 - x_2)^{i-1} \quad (3)$$

The temperature dependence of $A_i$ was assumed to follow the following relation

$$A_i = a_{i,0} + a_{i,1}(T/\text{K}) \quad (4)$$

The number of terms ($A_i$) in eq 3 used to represent the excess molar heat capacity depended on the degree of complexity of the binary systems. The number of coefficients was set according to the results of the F-test and is shown in Table 5.

The partial molar excess quantities for physical solvents $C_1^{\text{o}} - C_1^{*}$ and water $C_2^{\text{o}} - C_2^{*}$ were calculated by extrapolating $(C_p^{\text{E}}/x_1x_2)$ at $x_1 = 0$ and $x_1 = 1$, respectively. According to Desnoyers and Perron,[15] the reduced molar excess heat capacity functions would give a better picture of the nonideality in the mixtures.

Table 6 shows that the values of $C_1^{\text{o}} - C_1^{*}$ and $C_2^{\text{o}} - C_2^{*}$ increased with temperatures for all the physical solvents studied (except TEGDME). It is important to observe that the values of the excess partial molar quantities varied linearly with temperature.

## Sulfolane System

Experimentally measured molar heat capacities of binary aqueous solutions of sulfolane from $T = (303.15 \text{ to } 353.15)$ K are presented in Table 1 with an interval of 5 K throughout the whole concentration range. The continuous method has provided reproducible results with an overall absolute deviation of 0.3 %. The obtained values for the molar heat capacity of pure sulfolane ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) were correlated with a linear function of the temperature in the range from (303.15 to 353.15) K

$$C_{p,\text{sulfolane}} = 0.3255(T/\text{K}) + 82.989 \quad (5)$$

The equation correlated the data with a standard deviation of 0.0045 %. The molar heat capacity for pure sulfolane increased as temperature increased.

**Table 1. Molar Heat Capacity ($C_p$) for Sulfolane (1) + $H_2O$ (2) from $T$ = (303.15 to 353.15) K as a Function of Mole Fraction $x_1$**

| | $C_p$/(J·mol$^{-1}$·K$^{-1}$) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $x_1$ | $T$/K = 303.15 | $T$/K = 308.15 | $T$/K = 313.15 | $T$/K = 318.15 | $T$/K = 323.15 | $T$/K = 328.15 | $T$/K = 333.15 | $T$/K = 338.15 | $T$/K = 343.15 | $T$/K = 348.15 | $T$/K = 353.15 |
| 0.0999 | 87 | 88 | 88 | 88 | 89 | 89 | 89 | 90 | 90 | 91 | 91 |
| 0.1998 | 100 | 100 | 101 | 102 | 102 | 103 | 104 | 104 | 105 | 106 | 107 |
| 0.2987 | 112 | 113 | 114 | 114 | 115 | 116 | 117 | 118 | 119 | 120 | 121 |
| 0.3995 | 124 | 125 | 126 | 127 | 128 | 129 | 130 | 131 | 132 | 133 | 135 |
| 0.4945 | 135 | 136 | 137 | 138 | 139 | 141 | 142 | 143 | 144 | 146 | 148 |
| 0.5987 | 145 | 147 | 148 | 149 | 150 | 152 | 153 | 155 | 156 | 158 | 160 |
| 0.6984 | 155 | 156 | 157 | 159 | 160 | 162 | 164 | 165 | 167 | 169 | 171 |
| 0.7904 | 164 | 166 | 167 | 168 | 170 | 172 | 173 | 175 | 177 | 179 | 181 |
| 0.8865 | 173 | 175 | 176 | 177 | 179 | 181 | 183 | 184 | 186 | 188 | 191 |
| 1.0000 | 182 | 184 | 185 | 186 | 188 | 189 | 191 | 193 | 194 | 197 | 199 |

**Table 2. Molar Heat Capacity ($C_p$) for NFM (1) + $H_2O$ (2) from $T$ = (303.15 to 353.15) K as a Function of Mole Fraction $x_1$**

| | $C_p$/(J·mol$^{-1}$·K$^{-1}$) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $x_1$ | $T$/K = 303.15 | $T$/K = 308.15 | $T$/K = 313.15 | $T$/K = 318.15 | $T$/K = 323.15 | $T$/K = 328.15 | $T$/K = 333.15 | $T$/K = 338.15 | $T$/K = 343.15 | $T$/K = 348.15 | $T$/K = 353.15 |
| 0.0997 | 86 | 86 | 87 | 87 | 88 | 88 | 89 | 90 | 91 | 91 | 92 |
| 0.1998 | 98 | 99 | 100 | 100 | 101 | 102 | 103 | 104 | 106 | 107 | 107 |
| 0.2992 | 111 | 111 | 113 | 114 | 115 | 116 | 117 | 118 | 120 | 121 | 122 |
| 0.3993 | 123 | 124 | 125 | 126 | 127 | 129 | 130 | 131 | 133 | 135 | 135 |
| 0.4975 | 134 | 135 | 137 | 138 | 140 | 141 | 142 | 144 | 146 | 147 | 148 |
| 0.5978 | 145 | 146 | 148 | 149 | 150 | 152 | 153 | 155 | 157 | 158 | 159 |
| 0.6954 | 154 | 156 | 158 | 159 | 161 | 162 | 164 | 166 | 168 | 169 | 170 |
| 0.7988 | 164 | 166 | 168 | 169 | 171 | 173 | 174 | 176 | 178 | 180 | 181 |
| 0.8946 | 174 | 176 | 178 | 179 | 181 | 183 | 184 | 186 | 189 | 190 | 191 |
| 1.0000 | 185 | 186 | 188 | 189 | 191 | 193 | 195 | 197 | 200 | 201 | 202 |

**Table 3. Molar Heat Capacity ($C_p$) for NMP (1) + $H_2O$ (2) from $T$ = (303.15 to 353.15) K as a Function of Mole Fraction $x_1$**

| | $C_p$/(J·mol$^{-1}$·K$^{-1}$) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $x_1$ | $T$/K = 303.15 | $T$/K = 308.15 | $T$/K = 313.15 | $T$/K = 318.15 | $T$/K = 323.15 | $T$/K = 328.15 | $T$/K = 333.15 | $T$/K = 338.15 | $T$/K = 343.15 | $T$/K = 348.15 | $T$/K = 353.15 |
| 0.0999 | 90 | 90 | 91 | 91 | 92 | 92 | 93 | 93 | 94 | 95 | 95 |
| 0.1998 | 102 | 103 | 104 | 105 | 105 | 106 | 107 | 108 | 109 | 110 | 110 |
| 0.2984 | 113 | 114 | 115 | 116 | 118 | 119 | 120 | 121 | 122 | 123 | 124 |
| 0.3979 | 122 | 123 | 124 | 125 | 127 | 128 | 129 | 131 | 132 | 133 | 134 |
| 0.4961 | 129 | 131 | 132 | 133 | 135 | 136 | 138 | 139 | 141 | 142 | 142 |
| 0.5981 | 137 | 138 | 140 | 141 | 142 | 144 | 145 | 147 | 149 | 150 | 151 |
| 0.6917 | 144 | 146 | 147 | 148 | 150 | 151 | 153 | 154 | 156 | 157 | 158 |
| 0.799 | 152 | 153 | 154 | 155 | 157 | 158 | 160 | 161 | 163 | 164 | 165 |
| 0.8946 | 158 | 160 | 161 | 162 | 164 | 165 | 166 | 168 | 169 | 170 | 170 |
| 1.0000 | 166 | 167 | 168 | 169 | 170 | 172 | 174 | 175 | 176 | 177 | 178 |

Excess molar heat capacities of binary aqueous sulfolane mixtures are shown in Figure 5. All the excess molar heat capacity values were positive with a maximum value at 0.5 mol fraction of sulfolane for all temperatures. The $C_p^E$ values also increased with increasing temperature.

Figure 6 shows the concentration dependency of the reduced molar excess heat capacity ($C_p^E/x_1x_2$) function of the sulfolane + water system at various temperatures. It also shows a sharp change in the reduced molar heat capacity function in both the water- and solvent-rich regions. ($C_p^E/x_1x_2$) values reached a maximum at around $x_1 = 0.5$. On the basis of the shape of $C_p^E$ and ($C_p^E/x_1x_2$) plots, Desnoyers and Perron[15] suggested that for this kind of system there is a possibility of formation of a complex. Measurements of density and viscosity of aqueous sulfolane solutions, and the study of the resulting excess volumes and viscosity deviations by Elmahmudi,[16] could not confirm the presence of a complex formation as suggested by Desnoyers and Perron.

## NFM System

Experimentally measured molar heat capacities of aqueous solutions of NFM from $T$ = (303.15 to 353.15) K with an interval of 5 K are listed in Table 2. The obtained values of the molar heat capacity of pure NFM (J·mol$^{-1}$·K$^{-1}$) were correlated with a linear function of temperature in the range from (303.15 to 353.15) K

$$C_{p,\mathrm{NFM}} = 0.3672(T/\mathrm{K}) + 72.984 \qquad (6)$$

The equation correlated the data with a standard deviation of 0.003 %. Table 2 shows the increase in the molar heat capacity of the mixture after the addition of NFM. The effect of the composition on the molar heat capacity increased with the increase in temperature. No experimental $C_p$ values were available in the literature for NFM.

The excess molar heat capacities of the aqueous NFM mixtures are shown in Figure 7. All the excess molar heat capacities were positive for the entire range of the mole fraction and temperature, except for $x = 0.1$ at 303.15 K, where the value of the excess molar heat capacity became negative. The minimum value of the molar excess heat capacity was found at 303.15 K and for 0.1 mol fraction. The $C_p^E$ value became more positive with increasing temperature and reached a maximum for 0.4 mol fraction at 353.15 K. Desnoyers and Perron[15] suggested that for this kind of shape of the reduced excess molar heat capacity (Figure 8) there is a possible formation of a complex. Since the calculated excess volumes from density

**Table 4. Molar Heat Capacity ($C_p$) for TEGDME (1) + $H_2O$ (2) from $T$ = (303.15 to 353.15) K as a Function of Mole Fraction $x_1$**

| | $C_p$/(J·mol$^{-1}$·K$^{-1}$) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $x_1$ | $T$/K = 303.15 | $T$/K = 308.15 | $T$/K = 313.15 | $T$/K = 318.15 | $T$/K = 323.15 | $T$/K = 328.15 | $T$/K = 333.15 | $T$/K = 338.15 | $T$/K = 343.15 | $T$/K = 348.15 | $T$/K = 353.15 |
| 0.0999 | 109 | 110 | 111 | 112 | 112 | 113 | 114 | 114 | 115 | 116 | 116 |
| 0.1997 | 141 | 143 | 144 | 145 | 146 | 147 | 148 | 149 | 150 | 151 | 152 |
| 0.2967 | 171 | 173 | 174 | 175 | 176 | 177 | 179 | 180 | 181 | 183 | 184 |
| 0.3977 | 198 | 200 | 202 | 203 | 204 | 206 | 207 | 208 | 210 | 211 | 212 |
| 0.4983 | 224 | 227 | 228 | 229 | 231 | 232 | 233 | 235 | 237 | 238 | 239 |
| 0.5918 | 250 | 253 | 254 | 255 | 256 | 258 | 259 | 261 | 263 | 264 | 265 |
| 0.6926 | 275 | 278 | 279 | 281 | 282 | 283 | 285 | 286 | 289 | 290 | 291 |
| 0.7941 | 300 | 304 | 306 | 307 | 309 | 310 | 312 | 313 | 316 | 318 | 318 |
| 0.8686 | 328 | 332 | 334 | 335 | 337 | 339 | 341 | 342 | 345 | 347 | 348 |
| 1.0000 | 359 | 364 | 366 | 368 | 370 | 371 | 373 | 375 | 379 | 381 | 382 |

measurements for aqueous NFM mixtures were all negative, and the calculated Grunberg−Nissan parameters were positive, Henni et al.[17] concluded the predominance of interaction forces through hydrogen bonding. Viscosity deviations were also positive and reached a maximum (also) around 0.4 mol fraction.

## NMP System

Experimentally measured molar heat capacities of binary aqueous solutions of NMP from (303.15 to 353.15) K with an interval of 5 K are listed in Table 3.

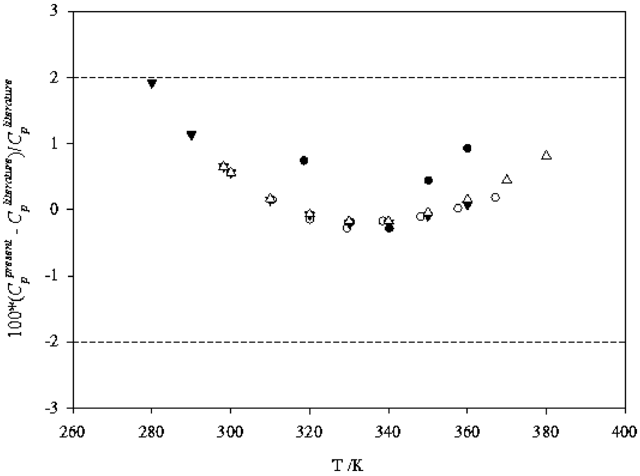

**Figure 1.** Fractional deviations [$(C_p - C_p^{\text{cal}})/C_p^{\text{cal}}$] of the experimental molar heat capacities of sapphire in the literature ($C_p$) from values obtained with polynomial correlation of the measurements obtained in this study ($C_p^{\text{cal}}$): ●, Xu;[12] Δ, Ditmars et al.;[9] ○, Inaba,;[11] ▼, Ginnings and Furukawa.[10]

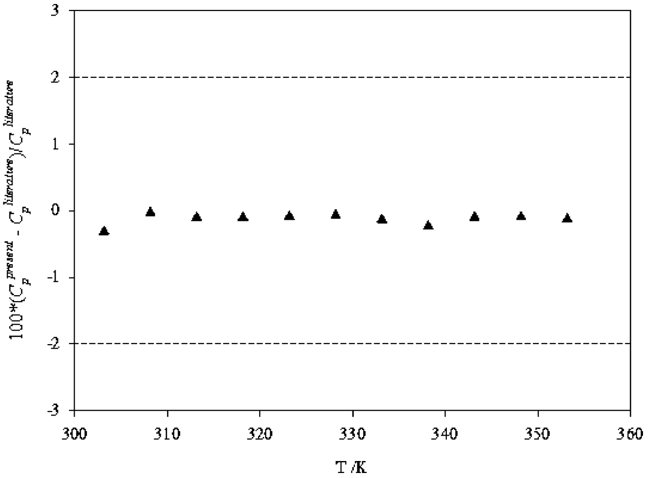

**Figure 2.** Fractional deviations [$(C_p - C_p^{\text{cal}})/C_p^{\text{cal}}$] of the experimental molar heat capacities of MEA in the literature ($C_p$) from values obtained with polynomial correlation of the measurements obtained in this study ($C_p^{\text{cal}}$): ▲, Chiu et al.[12]

The obtained values of heat capacity of pure NMP (J·mol$^{-1}$·K$^{-1}$) were expressed as a polynomial, which was a function of temperature in the range from (303.15 to 353.15) K.

$$C_{p,\text{NMP}} = -0.0005(T/\text{K})^2 + 0.7584(T/\text{K}) + 36.62 \tag{7}$$

The equation correlated the data with a standard deviation of 0.005 %. Table 3 shows an increase in the molar heat capacity

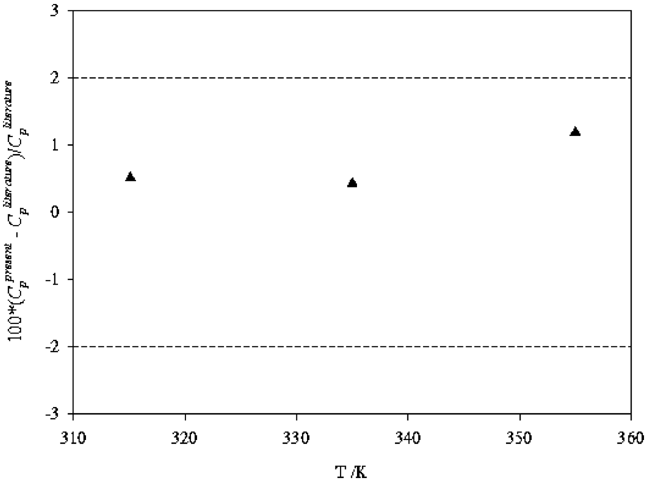

**Figure 3.** Fractional deviations [$(C_p - C_p^{\text{cal}})/C_p^{\text{cal}}$] of the experimental molar heat capacities of sulfolane in the literature ($C_p$) from values obtained with polynomial correlation of the measurements obtained in this study ($C_p^{\text{cal}}$): ▲, Steele et al.[2]

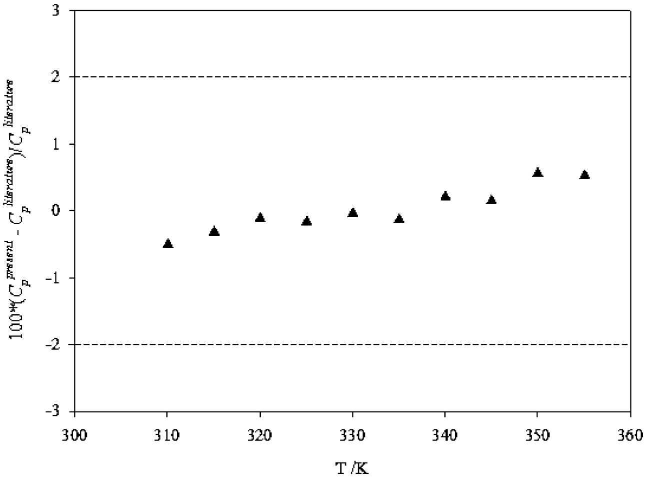

**Figure 4.** Fractional deviations [$(C_p - C_p^{\text{cal}})/C_p^{\text{cal}}$] of the experimental molar heat capacity of TEGDME in the literature ($C_p$) from values obtained with polynomial correlation of the measurements obtained in this study ($C_p^{\text{cal}}$): ▲, Becker and Gmehling.[5]

**Table 5. Parameters of Excess Molar Heat Capacity ($C_p^E$) for the Four Binary Systems Using Equations 4 and 5 and the Standard Deviations**

| systems | $i$ | $a_{i,0}$ | $a_{i,1}$ | no. data points | AAD % | AAPD % | rmsd % |
|---|---|---|---|---|---|---|---|
| Sulfolane (1) + $H_2O$ (2) | 1 | −81.251 | 0.349 | 99 | 0.08 | 1.56 | 0.11 |
| | 2 | −18.591 | 0.059 | | | | |
| | 3 | −78.337 | 0.213 | | | | |
| NFM (1) + $H_2O$ (2) | 1 | −101.215 | 0.389 | 99 | 0.22 | 8.35 | 0.29 |
| | 2 | 133.807 | −0.413 | | | | |
| | 3 | −110.183 | 0.268 | | | | |
| NMP (1) + $H_2O$ (2) | 1 | −142.387 | 0.589 | 99 | 0.30 | 3.82 | 0.41 |
| | 2 | 51.368 | −0.257 | | | | |
| | 3 | 54.521 | −0.149 | | | | |
| TEGDME (1) + $H_2O$ (2) | 1 | −56.0315 | 0.2744 | 99 | 0.12 | 3.87 | 0.14 |
| | 2 | 140.6671 | −0.6570 | | | | |
| | 3 | −93.9153 | 0.2475 | | | | |
| overall 396 | | | | | 0.18 | 4.40 | 0.24 |

**Table 6. Extrapolated Excess Partial Molar Quantities for Physical Solvents ($C_1^\circ - C_1^*$) and Water ($C_2^\circ - C_2^*$)**

| | sulfolane + $H_2O$ | | NFM + $H_2O$ | | NMP + $H_2O$ | | TEGDME + $H_2O$ | |
|---|---|---|---|---|---|---|---|---|
| $T$/K | $C_1^\circ - C_1^*$ | $C_2^\circ - C_2^*$ | $C_1^\circ - C_1^*$ | $C_2^\circ - C_2^*$ | $C_1^\circ - C_1^*$ | $C_2^\circ - C_2^*$ | $C_1^\circ - C_1^*$ | $C_2^\circ - C_2^*$ |
| 303.15 | 9 | 8 | −21 | −4 | 72 | 19 | 70 | −47 |
| 308.15 | 12 | 10 | −15 | −2 | 75 | 20 | 76 | −48 |
| 313.15 | 16 | 16 | −10 | −1 | 79 | 21 | 82 | −48 |
| 318.15 | 19 | 19 | −5 | 0 | 82 | 22 | 88 | −49 |
| 323.15 | 21 | 22 | 0.6 | 1 | 86 | 23 | 94 | −50 |
| 328.15 | 24 | 25 | 6 | 2 | 89 | 23 | 100 | −50 |
| 333.15 | 27 | 29 | 11 | 4 | 93 | 24 | 106 | −51 |
| 338.15 | 29 | 32 | 17 | 5 | 96 | 25 | 111 | −51 |
| 343.15 | 32 | 35 | 22 | 6 | 100 | 26 | 117 | −52 |
| 348.15 | 34 | 38 | 27 | 7 | 103 | 27 | 123 | −53 |
| 353.15 | 37 | 41 | 33 | 8 | 107 | 28 | 129 | −53 |

of the mixture after the addition of NMP. The effect of the composition on the molar heat capacity increased with the increase in temperature. The excess molar heat capacities of binary aqueous NMP mixtures are presented in Figure 9. All the excess molar heat capacities were positive. The maximum values were at 0.3 mol fraction. Desnoyers and Perron[15] suggested that this kind of system, with reduced excess molar heat capacity values varying as a function of mole fractions as shown in Figure 10, is observed with mixtures of different sizes and polarities. Henni et al.[18] suggested, from an excess volume and viscosity deviation study, the formation of a stable complex between two water molecules and one NMP molecule. This is the same mole fraction (0.3) as that found for the maximum values of excess molar heat capacities.

## TEGDME System

Experimentally measured molar heat capacities of binary aqueous solutions of TEGDME from (303.15 to 353.15) K are listed in Table 4. All obtained data for the molar heat capacity of pure TEGDME ($J \cdot mol^{-1} \cdot K^{-1}$) were correlated with a linear equation as a function of temperature in the range from (303.15 to 353.15) K.

$$C_{p,\mathrm{TEGDME}} = 0.4309(T/\mathrm{K}) + 230.24 \qquad (8)$$

The equation correlated the data with a standard deviation of 0.0043 %. The excess molar heat capacities of aqueous TEGDME solutions are presented in Figure 11. The $C_p^E$ curves were positive from 0 to 0.7 mol fractions and became negative between $x_1 = 0.7$ and $x_1 = 1$.

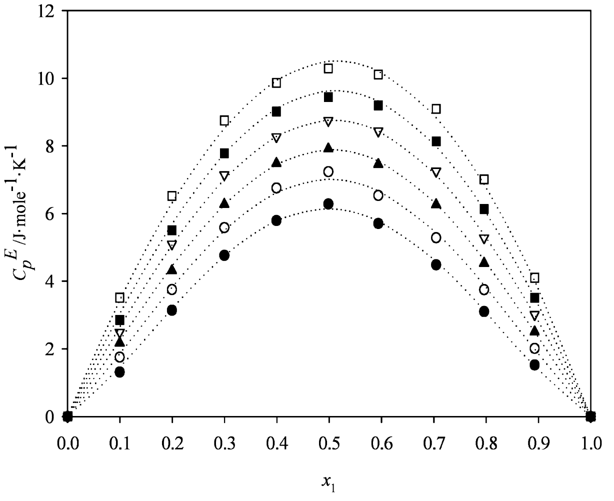

**Figure 5.** Excess molar heat capacity of (sulfolane + $H_2O$): ●, 303.15 K; ○, 313.15 K; ▲, 323.15 K; ▽, 333.15 K; ■, 343.15 K; □, 353.15 K; ····, Redlich−Kister.

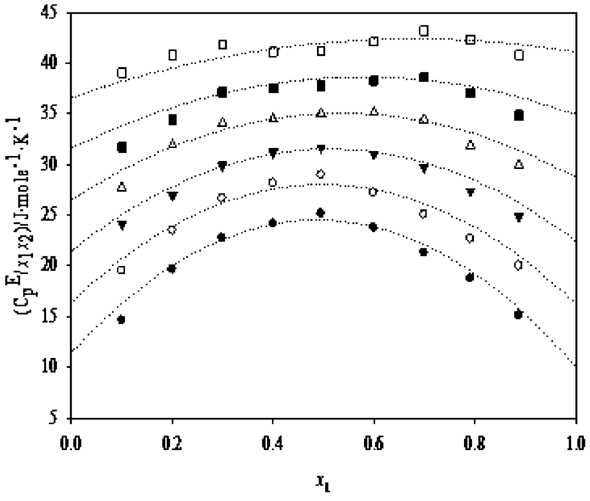

**Figure 6.** Reduced excess molar heat capacity ($C_p^E/x_1x_2$) of aqueous sulfolane solutions: ●, 303.15 K; ○, 313.15 K; ▼, 323.15 K; Δ, 333.15 K; ■, 343.15 K; □, 353.15 K; ····, Redlich−Kister.

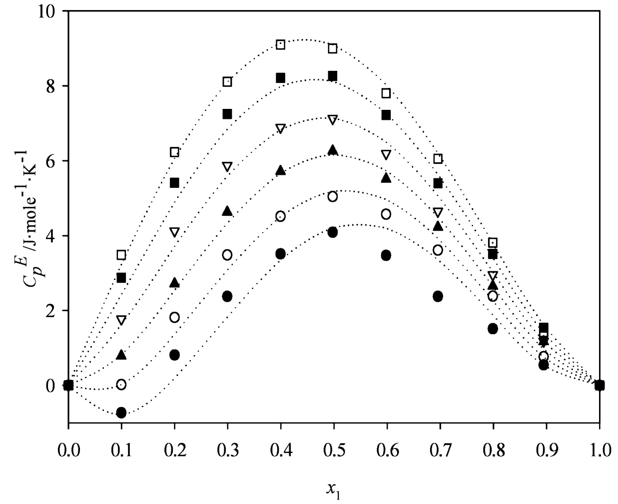

**Figure 7.** Excess molar heat capacity of (NFM + $H_2O$): ●, 303.15 K; ○, 313.15 K; ▲, 323.15 K; ▽, 333.15 K; ■, 343.15 K; □, 353.15 K; ····, Redlich−Kister.

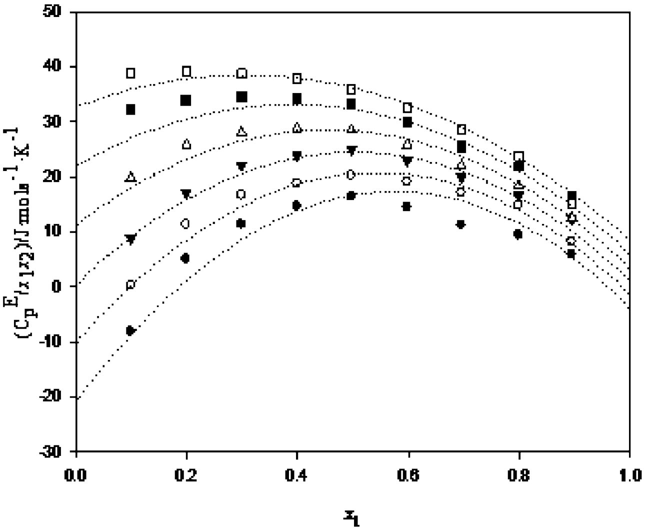

**Figure 8.** Reduced excess molar heat capacity ($C_p^E/x_1x_2$) of aqueous NFM solutions: ●, 303.15 K; ○, 313.15 K; ▼, 323.15 K; Δ, 333.15 K; ■, 343.15 K; □, 353.15 K; ····, Redlich−Kister.

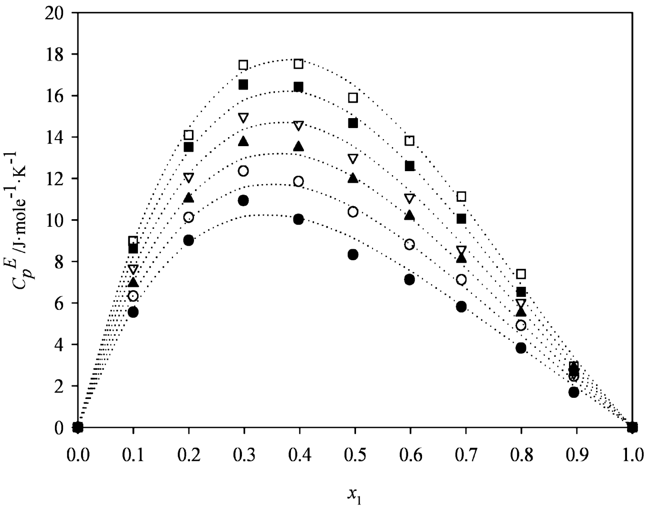

**Figure 9.** Excess molar heat capacity of (NMP + $H_2O$): ●, 303.15 K; ○, 313.15 K; ▲, 323.15 K; ▽, 333.15 K; ■, 343.15 K; □, 353.15 K; ····, Redlich−Kister.

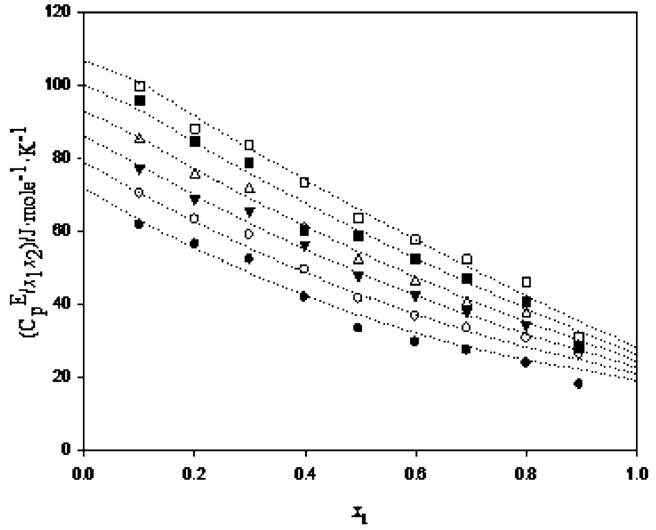

**Figure 10.** Reduced excess molar heat capacity ($C_p^E/x_1x_2$) of aqueous NMP solutions: ●, 303.15 K; ○, 313.15 K; ▼, 323.15 K; Δ, 333.15 K; ■, 343.15 K; □, 353.15 K; ····, Redlich−Kister.

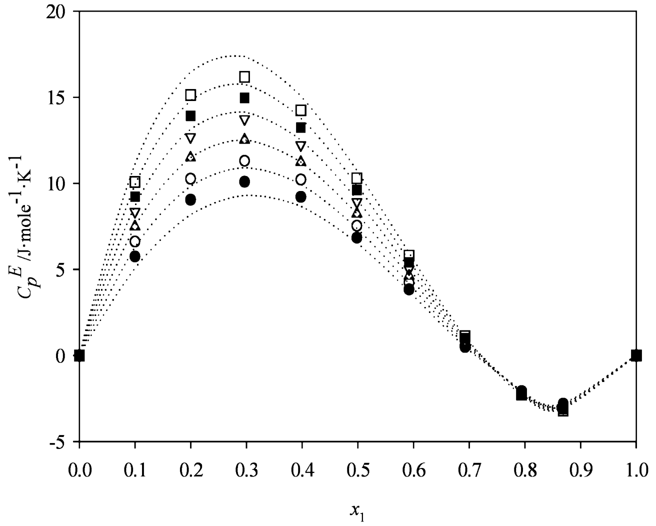

**Figure 11.** Excess molar heat capacity of (TEGDME + $H_2O$): ●, 303.15 K; ○, 313.15 K; ▼, 323.15 K; Δ, 333.15 K; ■, 343.15 K; □, 353.15 K; ····, Redlich−Kister.

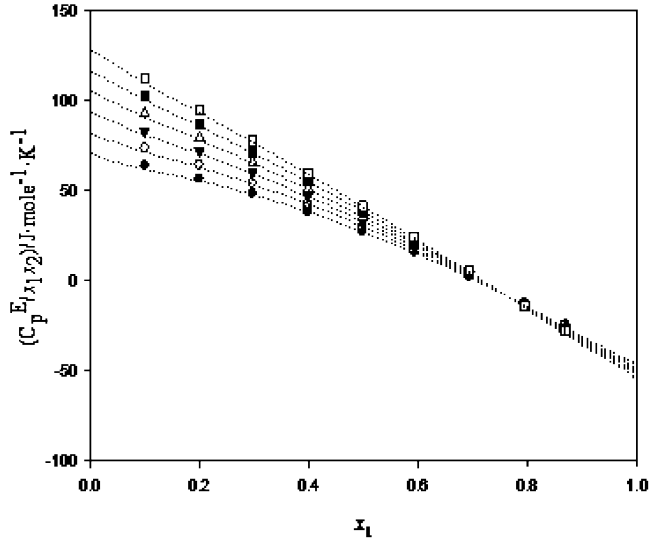

**Figure 12.** Reduced excess molar heat capacity ($C_p^E/x_1x_2$) of aqueous TEGDME solutions: ●, 303.15 K; ○, 313.15 K; ▼, 323.15 K; Δ, 333.15 K; ■, 343.15 K; □, 353.15 K; ····, Redlich−Kister.

Desnoyers and Perron[15] suggested that for this kind of system shown in Figure 12 $C_1^\circ - C_1^*$ and $C_2^\circ - C_2^*$ have opposite signs. This affirmation was confirmed by values shown in Table 6. On the basis of a density and viscosity study, Henni et al.[19] suggested the probable formation of a complex at $x_1 = 0.15$, a value close to the maximum excess molar heat capacity found in this study.

## Conclusions

The values of the molar heat capacity of the four physical solvents measured by the continuous three-step method were in the order of TEGDME > NFM > sulfolane > NMP. For all systems, the values of the molar heat capacity increased with an increase in temperature and mole fraction of the solvents. Excess molar heat capacities of the four systems were correlated with the Redlich−Kister equations.

The interactions between water and the physical solvents were interpreted using suggestions made by Desnoyers and Perron[15] and previous measurements of density and viscosity done by Elmahmudi[16] and Henni et al.[17−19] The interpretations did not seem to be in agreement in terms of possible formation of complexes.

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Received for review December 25, 2008. Accepted July 6, 2009.

JE800999S