

# Densities and Viscosities for Binary Mixtures of Ethyl Lactate with Methacrylic Acid, Benzyl Methacrylate, and 2-Hydroxyethyl Methacrylate at (298.15, 308.15, and 318.15) K

Jui-Tang Chen\* and Hsiao-Pei Chu

Department of Chemical Engineering, Ming-Hsin University of Science and Technology, Hsin-chu, Hsin-feng 304, Taiwan, Republic of China

Densities and viscosities at (298.15, 308.15, and 318.15) K are presented as a function of mixture composition for the binary mixtures of ethyl lactate with methacrylic acid, benzyl methacrylate, and 2-hydroxyethyl methacrylate. From the experimental data, the excess molar volumes  $V^E$  and viscosity deviations  $\delta\eta$  have been calculated. These results have been correlated with the Redlich–Kister type polynomial to derive the coefficients and standard deviation  $\sigma$ . McAllister's three-body and four-body interaction models were also used to correlate the kinematic viscosities. These model's parameters were treated to be temperature dependent.

## Introduction

Color filter is one of essential parts of color liquid crystal display, and the pigment dispersed color resist (PDCR) is the most important materials for manufacture of this part. We are interested in investigating the photolithography processes, transport properties, and storage stability of new color resists. The thermophysical properties of a binary mixture such as density and viscosity are useful in design of many types of process and transport equipment in chemical industries. Methacrylic acid (MAA), benzyl methacrylate (BzMA), 2-hydroxyethyl methacrylate (2-HEMA), and ethyl lactate (EL) are the key compounds in the manufacturing of the PDCR industries. A series of density and viscosity measurements have been made recently in our laboratory.<sup>1–3</sup> This paper reports on the binary systems composed of EL with MMA, BzMA, and 2-HEMA at (298.15, 308.15, and 318.15) K and over the entire composition range. No literature data were found at comparable conditions. From the new experimental data, the excess molar volumes  $V^E$  and viscosity deviations  $\delta\eta$  have been calculated. These results have been correlated with the Redlich–Kister type polynomial to derive the coefficients and standard deviation  $\sigma$ . McAllister's three-body and four-body interaction models were also used to correlate the kinematic viscosities. In this paper, the parameters of these models were also treated to be temperature dependent.

## Experimental Section

Methacrylic acid (mass fraction 99 %) was obtained from Sigma-Aldrich. 2-Hydroxyethyl methacrylate (mass fraction 98 %) was supplied by Acros Organics. Benzyl methacrylate (mass fraction 98 %) was purchased from Showa Chemical Co. Ltd. Ethyl lactate (mass fraction 99 %) was obtained from Fluka Chemicals (Germany). The purities of these substances were checked with gas chromatography before use. All reagents were used without further purification.

**Density Measurement.** The densities were determined with a pycnometer having a nominal internal volume of 10 cm<sup>3</sup>. The internal volume of the pycnometer was calibrated with pure

water<sup>4</sup> at each temperature. The sample mixture was prepared by mass with an uncertainty of  $\pm 0.0001$  in mole fraction. To minimize evaporation during the sample preparation, the less volatile component was charged first. Three loaded pycnometers were immersed in a thermostatic bath (Neslab GP-500), which was controlled to within  $\pm 0.03$  K. A precision digital thermometer (model 1560, Hart Scientific) with a thermistor probe was used to read the temperature with an uncertainty of  $\pm 0.015$  K. The mixture densities were obtained by averaging the results from these three replications. The uncertainty of reported densities was estimated to be less than  $\pm 0.1$  %. The sample compositions were frequently checked with a gas chromatography at the end of measurements, indicating that there was no change in the compositions.

**Viscosity Measurement.** The kinematic viscosities  $\nu$  were measured using Cannon-Fenske routine viscometers (size 75, supplied by Cannon Instrument Co.). The viscometer was placed in a thermostatic water bath (TV-4000, TAMSON), in which the temperature was regulated to within  $\pm 0.01$  K. An electronic stop watch was used to measure the flow times. Triplicates or more measurements of flow times were reproducible within  $\pm 0.2$  % or less. The kinematic viscosities  $\nu/\text{cm}^2\cdot\text{s}^{-1}$  were obtained from the relation

$$\nu = kt \quad (1)$$

where  $k/\text{cm}^2\cdot\text{s}^{-2}$  is the capillary constant of viscometer and  $t/s$  is the flow time. The viscometer was calibrated with double-distilled water at each working temperature, and the capillary constant at each specific temperature was determined by averaging 10 calibration runs. The uncertainty of viscosity measurements was estimated to within  $\pm 1.0$  %, and the values of absolute viscosities  $\eta/\text{mPa}\cdot\text{s}$  were calculated by using the equation of  $\eta = \rho\nu$ .

Since there are no available data for the methacrylates and only one literature datum for pure EL, the measurements of pure 1-butanol and EL were conducted to test the validity of the experimental procedure. Table 1 compares the experimental results with the literature values. It shows that our measurements agree with literature values within the experimental uncertainties.

\* Corresponding author. E-mail: dale\_chen@must.edu.tw. Fax: +886-3-6007577.

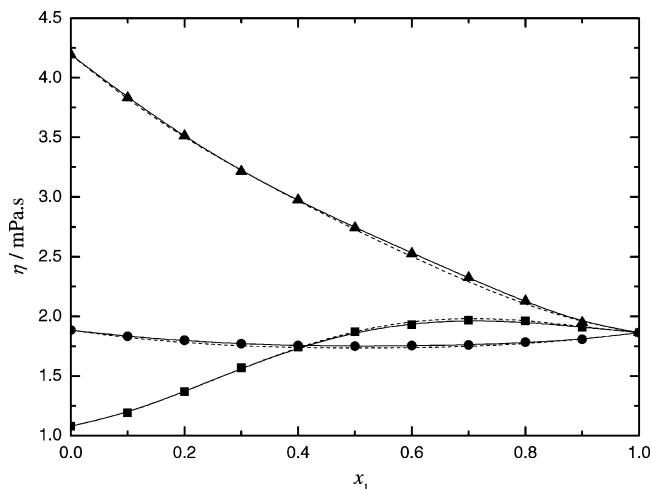
**Table 1. Densities  $\rho$  and Viscosities  $\eta$  of 1-Butanol and Ethyl Lactate at Different Temperatures**

| component     | $T/K$  | $\rho/g\cdot cm^{-3}$ |                        | $\eta/mPa\cdot s$    |                    |
|---------------|--------|-----------------------|------------------------|----------------------|--------------------|
|               |        | exptl                 | lit.                   | exptl                | lit.               |
| 1-butanol     | 298.15 | 0.8056                | 0.80575 <sup>b,e</sup> | 2.566                | 2.571 <sup>a</sup> |
|               |        |                       | 0.8060 <sup>e</sup>    | 2.571 <sup>b,c</sup> |                    |
|               |        |                       | 0.80576 <sup>a</sup>   | 2.509 <sup>d</sup>   |                    |
|               |        |                       | 0.8057 <sup>d</sup>    | 2.578 <sup>e</sup>   |                    |
|               |        |                       | 0.8060 <sup>f</sup>    | 2.570 <sup>f</sup>   |                    |
|               |        |                       | 0.8059 <sup>g</sup>    | 2.506 <sup>g</sup>   |                    |
|               |        |                       | 0.8077 <sup>h</sup>    | 2.564 <sup>h</sup>   |                    |
|               |        |                       | 0.8058 <sup>a</sup>    | 2.550 <sup>i</sup>   |                    |
|               |        |                       | 0.80581 <sup>i,j</sup> | 2.550 <sup>j</sup>   |                    |
|               |        |                       |                        | 2.563 <sup>k</sup>   |                    |
|               |        |                       |                        | 2.550 <sup>l</sup>   |                    |
|               |        |                       |                        | 1.929 <sup>d</sup>   |                    |
|               |        |                       |                        | 1.982 <sup>m</sup>   |                    |
|               |        |                       |                        | 1.982 <sup>n</sup>   |                    |
|               |        |                       |                        | 1.927 <sup>g</sup>   |                    |
|               |        |                       |                        | 2.000 <sup>h</sup>   |                    |
| ethyl lactate | 318.15 | 0.7905                | 0.79821 <sup>a</sup>   | 1.998                | 1.981 <sup>a</sup> |
|               |        |                       | 0.7980 <sup>d</sup>    | 2.000 <sup>c</sup>   |                    |
|               |        |                       | 0.7985 <sup>m,n</sup>  | 1.929 <sup>d</sup>   |                    |
|               |        |                       | 0.8002 <sup>f</sup>    | 1.982 <sup>m</sup>   |                    |
|               |        |                       | 0.7981 <sup>g</sup>    | 1.982 <sup>n</sup>   |                    |
|               |        |                       | 0.8001 <sup>h</sup>    | 2.000 <sup>f</sup>   |                    |
|               |        |                       |                        | 1.493 <sup>g</sup>   |                    |
|               |        |                       |                        | 2.440 <sup>b</sup>   |                    |
|               | 298.15 | 1.0289                | 1.0272 <sup>b</sup>    | 2.398                | 2.440 <sup>b</sup> |

<sup>a</sup> Nikam et al.<sup>5</sup> <sup>b</sup> Riddick et al.<sup>6</sup> <sup>c</sup> TRC Tables.<sup>7</sup> <sup>d</sup> Aminabhavi and Bindu.<sup>8</sup> <sup>e</sup> Fermeglia and Lapasin.<sup>9</sup> <sup>f</sup> Sastry and Valand.<sup>10</sup> <sup>g</sup> Aminabhavi and Bindu.<sup>11</sup> <sup>h</sup> Rattan et al.<sup>12</sup> <sup>i</sup> Franjo et al.<sup>13</sup> <sup>j</sup> Franjo et al.<sup>14</sup> <sup>k</sup> Nikam et al.<sup>15</sup> <sup>l</sup> Nikam et al.<sup>16</sup>

## Results and Discussion

Experimental results for the three binary systems of EL with MAA, BzMA, and 2-HEMA are listed in Tables 2 to 4, respectively. Figure 1 shows the variations of the absolute viscosities with the mole fraction of EL for these three investigated systems at 308.15 K. In the MAA system, the viscosity increases with the mole fraction of EL, reaching a weak maximum at about  $x_1 = 0.7$  and then decreasing slightly to the value of pure EL. In the BzMA system, the viscosity decreases with the mole fraction of EL, reaching a weak minimum at about  $x_1 = 0.5$  and then increasing slightly to the



**Figure 1.** Viscosity  $\eta$  at 308.15 K: ■, ethyl lactate (1) + MAA (2); ●, ethyl lactate (1) + BzMA (2); ▲, ethyl lactate (1) + 2-HEMA (2); —, calculated from eq 7; - - -, calculated from eq 7 with temperature-dependent parameters of eq 12.

value of pure EL. However, the viscosities in the 2-HEMA systems decrease monotonically with the mole fraction of EL. In this paper, the measured densities for pure fluids are presented as functions of temperature by

$$\rho = a_0 + a_1(T/K) \quad (2)$$

where  $a_0$  and  $a_1$  are the undetermined parameters. The viscosities for pure fluids are also presented as functions of temperature by an Orbey–Sandler viscosity expression:<sup>17</sup>

$$\ln(\eta/\eta_{\text{ref}}) = c_0[-1.6866 + 1.4010(T_b/T) + 0.2406(T_b/T)^2] \quad (3)$$

where  $T_b/K$  is the normal boiling point of pure fluids. In this research, we estimated  $T_b$  for pure substances by an advanced group contribution method<sup>18</sup> based on the UNIFAC groups.  $\eta_{\text{ref}}/$

**Table 2. Density  $\rho$  and Viscosity  $\eta$  for Ethyl Lactate (1) + MAA (2)**

| $x_1$  | $\rho/g\cdot cm^{-3}$ |                |                | $\eta/mPa\cdot s$ |                |                |
|--------|-----------------------|----------------|----------------|-------------------|----------------|----------------|
|        | $T/K = 298.15$        | $T/K = 308.15$ | $T/K = 318.15$ | $T/K = 298.15$    | $T/K = 308.15$ | $T/K = 318.15$ |
| 0.0    | 1.0095                | 0.9994         | 0.9892         | 1.267             | 1.078          | 0.945          |
| 0.1000 | 1.0121                | 1.0020         | 0.9917         | 1.422             | 1.190          | 1.020          |
| 0.2000 | 1.0146                | 1.0046         | 0.9945         | 1.660             | 1.368          | 1.154          |
| 0.3000 | 1.0170                | 1.0074         | 0.9973         | 1.933             | 1.567          | 1.306          |
| 0.3999 | 1.0198                | 1.0102         | 0.9999         | 2.181             | 1.742          | 1.430          |
| 0.5000 | 1.0225                | 1.0127         | 1.0022         | 2.378             | 1.870          | 1.520          |
| 0.6000 | 1.0247                | 1.0148         | 1.0042         | 2.465             | 1.929          | 1.551          |
| 0.6999 | 1.0265                | 1.0165         | 1.0058         | 2.532             | 1.967          | 1.579          |
| 0.8000 | 1.0279                | 1.0178         | 1.0072         | 2.539             | 1.962          | 1.567          |
| 0.9001 | 1.0287                | 1.0186         | 1.0082         | 2.471             | 1.907          | 1.526          |
| 1.0    | 1.0291                | 1.0187         | 1.0075         | 2.398             | 1.863          | 1.494          |

**Table 3. Density  $\rho$  and Viscosity for Ethyl Lactate (1) + BzMA (2)**

| $x_1$  | $\rho/g\cdot cm^{-3}$ |                |                | $\eta/mPa\cdot s$ |                |                |
|--------|-----------------------|----------------|----------------|-------------------|----------------|----------------|
|        | $T/K = 298.15$        | $T/K = 308.15$ | $T/K = 318.15$ | $T/K = 298.15$    | $T/K = 308.15$ | $T/K = 318.15$ |
| 0.0    | 1.0347                | 1.0258         | 1.0170         | 2.302             | 1.885          | 1.580          |
| 0.1000 | 1.0337                | 1.0243         | 1.0151         | 2.219             | 1.832          | 1.530          |
| 0.1999 | 1.0327                | 1.0233         | 1.0139         | 2.166             | 1.800          | 1.493          |
| 0.3000 | 1.0321                | 1.0226         | 1.0129         | 2.153             | 1.770          | 1.458          |
| 0.4000 | 1.0316                | 1.0219         | 1.0121         | 2.149             | 1.753          | 1.437          |
| 0.5000 | 1.0311                | 1.0212         | 1.0112         | 2.161             | 1.749          | 1.426          |
| 0.6000 | 1.0307                | 1.0206         | 1.0104         | 2.179             | 1.753          | 1.426          |
| 0.7000 | 1.0302                | 1.0200         | 1.0095         | 2.209             | 1.761          | 1.431          |
| 0.7999 | 1.0298                | 1.0194         | 1.0087         | 2.250             | 1.782          | 1.447          |
| 0.9000 | 1.0294                | 1.0189         | 1.0080         | 2.303             | 1.807          | 1.464          |
| 1.0    | 1.0291                | 1.0187         | 1.0075         | 2.398             | 1.863          | 1.494          |

**Table 4.** Density  $\rho$  and Viscosity  $\eta$  for Ethyl Lactate (1) + 2-HEMA (2)

| $x_1$  | $\rho/\text{g}\cdot\text{cm}^{-3}$ |                       |                       | $\eta/\text{mPa}\cdot\text{s}$ |                       |                       |
|--------|------------------------------------|-----------------------|-----------------------|--------------------------------|-----------------------|-----------------------|
|        | $T/\text{K} = 298.15$              | $T/\text{K} = 308.15$ | $T/\text{K} = 318.15$ | $T/\text{K} = 298.15$          | $T/\text{K} = 308.15$ | $T/\text{K} = 318.15$ |
|        | 0.0                                | 1.0671                | 1.0577                | 1.0486                         | 5.784                 | 4.194                 |
| 0.1000 | 1.0639                             | 1.0547                | 1.0456                | 5.230                          | 3.833                 | 2.938                 |
| 0.2000 | 1.0606                             | 1.0514                | 1.0422                | 4.750                          | 3.513                 | 2.710                 |
| 0.3000 | 1.0571                             | 1.0479                | 1.0385                | 4.360                          | 3.215                 | 2.493                 |
| 0.4000 | 1.0535                             | 1.0443                | 1.0346                | 3.989                          | 2.975                 | 2.311                 |
| 0.5000 | 1.0498                             | 1.0404                | 1.0306                | 3.663                          | 2.742                 | 2.141                 |
| 0.6000 | 1.0459                             | 1.0364                | 1.0264                | 3.343                          | 2.526                 | 1.985                 |
| 0.7000 | 1.0418                             | 1.0322                | 1.0220                | 3.041                          | 2.323                 | 1.834                 |
| 0.8000 | 1.0377                             | 1.0279                | 1.0175                | 2.767                          | 2.127                 | 1.689                 |
| 0.9000 | 1.0334                             | 1.0234                | 1.0128                | 2.524                          | 1.949                 | 1.556                 |
| 1.0    | 1.0291                             | 1.0187                | 1.0075                | 2.398                          | 1.863                 | 1.494                 |

**Table 5.** Parameters in Equations 2 and 3 for Density and Viscosity Data of Pure Fluids

|               | $a_0$   | $a_1 \times 10^4$ | $T_b/\text{K}$ | $\eta_{\text{ref}}/\text{mPa}\cdot\text{s}$ | $c_0$  |
|---------------|---------|-------------------|----------------|---|--------|
| ethyl lactate | 1.3472  | -10.70            | 452.72         | 0.2310                                      | 2.3508 |
| MAA           | 1.31214 | -10.20            | 435.77         | 0.3314                                      | 1.5327 |
| BzMA          | 1.29855 | -8.85             | 515.21         | 0.2352                                      | 1.5703 |
| 2-HEMA        | 1.34284 | -9.25             | 476.71         | 0.2268                                      | 2.7717 |

mPa·s and  $c_0$  are the undetermined parameters. The best-fit values of the parameters for pure fluids are given in Table 5. According to eqs 2 and 3 and the parameters of pure fluids in Table 5, the average absolute deviations (AAD) of the calculated densities and viscosities for pure fluids are approximately close to zero.

Excess volumes  $V^E$  and viscosity deviations  $\delta\eta$  were calculated from the experimental results by the following equations, respectively:

$$V^E = V_M - (x_1 V_1 + x_2 V_2) \quad (4)$$

$$\delta\eta = \eta_M - (x_1 \eta_1 + x_2 \eta_2) \quad (5)$$

where  $x_1$  and  $x_2$  are the mole fractions,  $V_1$  and  $V_2$  are the molar volumes, and  $\eta_1$  and  $\eta_2$  are the viscosities of components 1 and 2, respectively. The subscript M represents mixture properties. The excess volumes and viscosity deviations were correlated by a Redlich–Kister type polynomial:<sup>19</sup>

$$V^E/\text{cm}^3\cdot\text{mol}^{-1} = x_1 x_2 \sum_{k=0}^2 A_k (x_1 - x_2)^k \quad (6)$$

$$\delta\eta/\text{mPa}\cdot\text{s} = x_1 x_2 \sum_{k=0}^2 B_k (x_1 - x_2)^k \quad (7)$$

The coefficients of  $A_k$  and  $B_k$  were obtained by fitting the equations to the experimental values with a least-squares method. The correlated results for excess volumes and viscosity deviations are given respectively in Tables 6 and 7, in which the tabulated standard deviation  $\sigma$  was defined as

$$\sigma = \left[ \frac{\sum (Y_{\text{exp}} - Y_{\text{calcd}})^2}{n - p} \right]^{1/2} \quad (8)$$

where  $Y$  refers to  $V^E$  or  $\delta\eta$ ,  $n$  is the number of data points, and  $p$  is the number of coefficients. The subscripts exp and calcd denote the experimental value and the calculated value, respectively.

The variations of  $V^E$  and  $\delta\eta$  with the mole fraction of EL at 308.15 K are presented in Figures 2 and 3, respectively. Figure 2 shows that the excess molar volumes are negative in EL + MAA and + 2-HEMA systems and positive in the EL + BzMA system over the entire composition range. They imply that

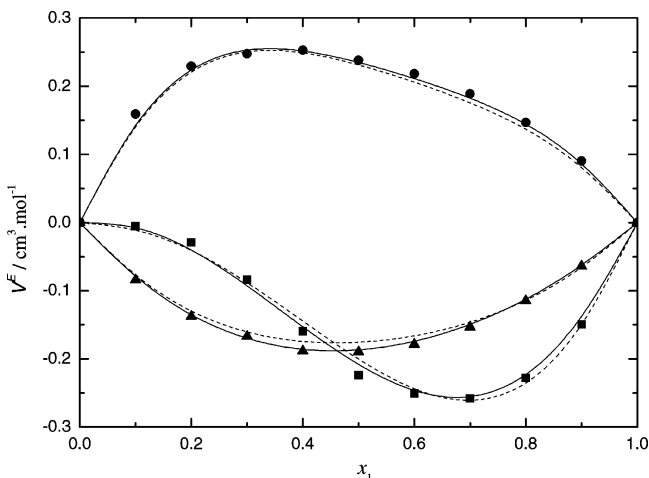
**Table 6.** Correlated Results of Excess Molar Volume  $V^E$ 

| mixture                | $T/\text{K}$ | $A_0$   | $A_1$   | $A_2$   | $\sigma/\text{cm}^3\cdot\text{mol}^{-1}$ |
|------------------------|--------------|---------|---------|---------|--|
| ethyl lactate + MAA    | 298.15       | -0.6233 | -0.9192 | -0.0791 | 0.0163                                   |
|                        | 308.15       | -0.8437 | -1.0140 | 0.0115  | 0.0072                                   |
|                        | 318.15       | -0.9611 | -1.3037 | -0.5685 | 0.0266                                   |
| ethyl lactate + BzMA   | 298.15       | 0.7438  | -0.3672 | 0.2264  | 0.0068                                   |
|                        | 308.15       | 0.9435  | -0.4419 | 0.6761  | 0.0054                                   |
|                        | 318.15       | 1.1027  | -0.5890 | 0.9567  | 0.0103                                   |
| ethyl lactate + 2-HEMA | 298.15       | -0.5068 | 0.1301  | 0.0742  | 0.0038                                   |
|                        | 308.15       | -0.7555 | 0.1269  | -0.1008 | 0.0025                                   |
|                        | 318.15       | -0.8658 | 0.0089  | -0.5740 | 0.0072                                   |

**Table 7.** Correlated Results of Viscosity Deviation  $\delta\eta$ 

| mixture                | $T/\text{K}$ | $B_0$   | $B_1$   | $B_2$   | $\sigma/\text{mPa}\cdot\text{s}$ |
|------------------------|--------------|---------|---------|---------|----------------------------------|
| ethyl lactate + MAA    | 298.15       | 2.1272  | 0.9825  | -1.3355 | 0.0131                           |
|                        | 308.15       | 1.5855  | 0.6011  | -1.0968 | 0.0096                           |
|                        | 318.15       | 1.1905  | 0.4225  | -0.9106 | 0.0103                           |
| ethyl lactate + BzMA   | 298.15       | -0.7552 | 0.0869  | -0.3728 | 0.0035                           |
|                        | 308.15       | -0.4895 | -0.0343 | -0.1616 | 0.0039                           |
|                        | 318.15       | -0.4385 | 0.0218  | 0.0079  | 0.0022                           |
| ethyl lactate + 2-HEMA | 298.15       | -1.7124 | 0.1204  | -1.0343 | 0.0106                           |
|                        | 308.15       | -1.1302 | -0.0176 | -0.5913 | 0.0146                           |
|                        | 318.15       | -0.7717 | -0.1176 | -0.3432 | 0.0128                           |

volume expansion takes place when EL mixes with BzMA and that the magnitude of volume contraction in the EL + MAA system is similar to the EL + 2-HEMA system. Figure 2 also shows that the  $V^E$  profile of the EL + MAA system is asymmetric and sigmoid with initial almost zero value followed by negative values in the EL-rich region. The above results can be discussed in terms of several effects, which may be simply divided into dispersion forces and hydrogen bond contributions. The positive  $V^E$  values may be attributed to from dispersion



**Figure 2.** Excess volumes  $V^E$  at 308.15 K: ■, ethyl lactate (1) + MAA (2); ●, ethyl lactate (1) + BzMA (2); ▲, ethyl lactate (1) + 2-HEMA (2); —, calculated from eq 6; ---, calculated from eq 6 with temperature-dependent parameters of eq 11.

**Table 8. Correlated Results of McAllister's Models**

| mixture                        | T/K    | three-body model |            |                                   | four-body model |              |              |                                   |
|--------------------------------|--------|------------------|------------|-----------------------------------|-----------------|--------------|--------------|-----------------------------------|
|                                |        | $\nu_{12}$       | $\nu_{21}$ | AAD <sup>a</sup> ·10 <sup>2</sup> | $\nu_{1112}$    | $\nu_{1122}$ | $\nu_{2221}$ | AAD <sup>a</sup> ·10 <sup>2</sup> |
| ethyl lactate (1) + MAA (2)    | 298.15 | 2.8416           | 2.2011     | 1.65                              | 2.4622          | 3.1688       | 1.6299       | 0.66                              |
|                                | 308.15 | 2.1837           | 1.7865     | 1.61                              | 1.9017          | 2.4554       | 1.3570       | 0.60                              |
|                                | 318.15 | 1.7458           | 1.4824     | 1.63                              | 1.5238          | 1.9942       | 1.1434       | 0.67                              |
| ethyl lactate (1) + BzMA (2)   | 298.15 | 2.1016           | 1.9854     | 0.39                              | 2.0994          | 2.1335       | 1.9898       | 0.08                              |
|                                | 308.15 | 1.6856           | 1.6845     | 0.17                              | 1.7014          | 1.7096       | 1.7038       | 0.12                              |
|                                | 318.15 | 1.3920           | 1.3886     | 0.13                              | 1.4239          | 1.3657       | 1.4407       | 0.09                              |
| ethyl lactate (1) + 2-HEMA (2) | 298.15 | 2.9251           | 4.0046     | 0.81                              | 2.5962          | 3.8076       | 4.0806       | 0.26                              |
|                                | 308.15 | 2.2713           | 2.9671     | 0.65                              | 2.0489          | 2.7647       | 3.1229       | 0.40                              |
|                                | 318.15 | 1.7952           | 2.3534     | 0.53                              | 1.6475          | 2.1493       | 2.4676       | 0.42                              |

$$^a \text{AAD} = (1/n) \sum_{k=1}^n |v_k^{\text{cal}} - v_k^{\text{exp}}| / v_k^{\text{exp}}$$

**Table 9. Temperature-Dependent Parameters in the Redlich–Kister Type Polynomial and the McAllister's Model**

| Ethyl Lactate (1) + MAA (2)                          |                    |  |                    |   |                        |                          |                          |
|--|--------------------|--|--------------------|---|------------------------|--------------------------|--------------------------|
| $A_0^0 = 4.3949$                                     | $A_1^0 = -0.0169$  | $B_0^0 = 16.0661$                            | $B_1^0 = -0.0468$  | $\nu_{12}^0 = 19.5431$                    | $\nu_{12}^1 = -0.0560$ | $\nu_{1112}^0 = 16.1172$ | $\nu_{1112}^1 = -0.0460$ |
| $A_1^0 = 4.8452$                                     | $A_2^0 = 7.3264$   | $B_1^0 = 9.2979$                             | $B_2^0 = -7.6597$  | $\nu_{21}^0 = 12.7339$                    | $\nu_{21}^1 = -0.0355$ | $\nu_{1122}^0 = 19.7938$ | $\nu_{1122}^1 = -0.0558$ |
| $A_2^0 = 7.3264$                                     | $A_3^0 = -0.0245$  | $B_2^0 = -7.6597$                            | $B_3^0 = 0.0212$   | AAD <sup>a</sup> ·10 <sup>2</sup> = 1.988 |                        | $\nu_{2221}^0 = 8.2998$  | $\nu_{2221}^1 = -0.0225$ |
| $\sigma = 0.0187 \text{ cm}^3 \cdot \text{mol}^{-1}$ |                    | $\sigma = 0.0134 \text{ mPa} \cdot \text{s}$ |                    | AAD <sup>a</sup> ·10 <sup>2</sup> = 1.233 |                        |                          |                          |
| Ethyl Lactate (1) + BzMA (2)                         |                    |  |                    |   |                        |                          |                          |
| $A_0^0 = -4.6010$                                    | $A_1^0 = 0.0179$   | $B_0^0 = -5.4409$                            | $B_1^0 = 0.0158$   | $\nu_{12}^0 = 12.8240$                    | $\nu_{12}^1 = -0.0360$ | $\nu_{1112}^0 = 11.8794$ | $\nu_{1112}^1 = -0.0329$ |
| $A_1^0 = 2.9521$                                     | $A_2^0 = -10.6306$ | $B_1^0 = 1.0272$                             | $B_2^0 = -6.0397$  | $\nu_{21}^0 = 10.8493$                    | $\nu_{21}^1 = -0.0297$ | $\nu_{1122}^0 = 14.0108$ | $\nu_{1122}^1 = -0.0397$ |
| $A_2^0 = -10.6306$                                   | $A_3^0 = 0.0365$   | $B_2^0 = -6.0397$                            | $B_3^0 = 0.0190$   | AAD <sup>a</sup> ·10 <sup>2</sup> = 0.541 |                        | $\nu_{2221}^0 = 9.9005$  | $\nu_{2221}^1 = -0.0266$ |
| $\sigma = 0.0086 \text{ cm}^3 \cdot \text{mol}^{-1}$ |                    | $\sigma = 0.0120 \text{ mPa} \cdot \text{s}$ |                    | AAD <sup>a</sup> ·10 <sup>2</sup> = 0.512 |                        |                          |                          |
| Ethyl Lactate (1) + 2-HEMA (2)                       |                    |  |                    |   |                        |                          |                          |
| $A_0^0 = 4.8226$                                     | $A_1^0 = -0.0180$  | $B_0^0 = -15.6989$                           | $B_1^0 = 0.0470$   | $\nu_{12}^0 = 19.9017$                    | $\nu_{12}^1 = -0.0570$ | $\nu_{1112}^0 = 15.7705$ | $\nu_{1112}^1 = -0.0445$ |
| $A_1^0 = 1.9564$                                     | $A_2^0 = 9.7843$   | $B_1^0 = 3.6616$                             | $B_2^0 = -11.3028$ | $\nu_{21}^0 = 28.0192$                    | $\nu_{21}^1 = -0.0807$ | $\nu_{1122}^0 = 27.7679$ | $\nu_{1122}^1 = -0.0803$ |
| $A_2^0 = 9.7843$                                     | $A_3^0 = -0.0324$  | $B_2^0 = -11.3028$                           | $B_3^0 = 0.0345$   | AAD <sup>a</sup> ·10 <sup>2</sup> = 1.477 |                        | $\nu_{2221}^0 = 29.2704$ | $\nu_{2221}^1 = -0.0845$ |
| $\sigma = 0.0072 \text{ cm}^3 \cdot \text{mol}^{-1}$ |                    | $\sigma = 0.0178 \text{ mPa} \cdot \text{s}$ |                    | AAD <sup>a</sup> ·10 <sup>2</sup> = 1.396 |                        |                          |                          |

$$^a \text{AAD} = (1/n) \sum_{k=1}^n |v_k^{\text{cal}} - v_k^{\text{exp}}| / v_k^{\text{exp}}$$

forces contribution between EL and BzMA molecules. On the other hand, the negative  $V^E$  values for binary mixtures of EL with MAA or 2-HEMA may be attributed to hydrogen bond formation through dipole–dipole interactions between EL and MAA or 2-HEMA molecules. Figure 3 illustrates that the viscosity deviations are negative in the EL + BzMA system as well as in the EL + 2-HEMA system but positive in the EL + MAA system over the entire composition range.

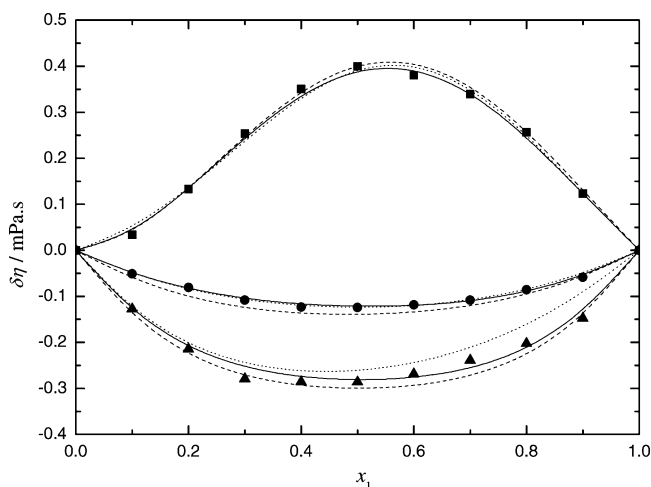
McAllister's multi-body interaction model<sup>20</sup> was widely used to correlate kinematic viscosity  $\nu$  data. The three-body McAllister model was defined as

$$\ln(\nu/\text{cm}^2 \cdot \text{s}^{-1}) = x_1^3 \ln \nu_1 + 3x_1^2 x_2 \ln \nu_{12} + 3x_1 x_2^2 \ln \nu_{21} + x_2^3 \ln \nu_2 - \ln[x_1 + x_2(M_2/M_1)] + 3x_1^2 x_2 \ln[(2 + M_2/M_1)/3] + 3x_1 x_2^2 \ln[(1 + 2M_2/M_1)/3] + x_2^3 \ln(M_2/M_1) \quad (9)$$

and the four-body McAllister model was given by

$$\ln(\nu/\text{cm}^2 \cdot \text{s}^{-1}) = x_1^4 \ln \nu_1 + 4x_1^3 x_2 \ln \nu_{1112} + 6x_1^2 x_2^2 \ln \nu_{1122} + 4x_1 x_2^3 \ln \nu_{2221} + x_2^4 \ln \nu_2 - \ln[x_1 + x_2(M_2/M_1)] + 4x_1^3 x_2 \ln[(3 + M_2/M_1)/4] + 6x_1^2 x_2^2 \ln[(1 + M_2/M_1)/2] + 4x_1 x_2^3 \ln[(1 + 3M_2/M_1)/4] + x_2^4 \ln(M_2/M_1) \quad (10)$$

where  $\nu_{12}$ ,  $\nu_{21}$ ,  $\nu_{1112}$ ,  $\nu_{1122}$ , and  $\nu_{2221}$  are model parameters. The calculated results are presented in Table 8. As seen from Table 8, the calculated values of AAD from the McAllister's four-body interaction model are smaller than those from the three-body model.



**Figure 3.** Viscosity deviations  $\delta\eta$  at 308.15 K: ■, ethyl lactate (1) + MAA (2); ●, ethyl lactate (1) + BzMA (2); ▲, ethyl lactate (1) + 2-HEMA (2); —, calculated from eq 7; - - -, calculated from eq 7 with temperature-dependent parameters of eq 12; ···, calculated from eq 10.

The parameters in eqs 6, 7, 9, and 10 were also treated to be temperature dependent, as given by the following equations, respectively:

$$A_k = A_k^0 + A_k^1 T/K \quad (k = 0 \text{ to } 2) \quad (11)$$

$$B_k = B_k^0 + B_k^1 T/K \quad (k = 0 \text{ to } 2) \quad (12)$$

$$\nu_{ij} = \nu_{ij}^0 + \nu_{ij}^1 T/K \quad (ij = 12 \text{ or } 21) \quad (13)$$

$$v_{ijj} = v_{ijj}^0 + v_{ijj}^1 T/K \quad (iii\ j = 1112 \text{ or } 2221) \quad (14)$$

$$v_{1122} = v_{1122}^0 + v_{1122}^1 T/K \quad (15)$$

where  $A_k^0$ ,  $A_k^1$ ,  $B_k^0$ ,  $B_k^1$ ,  $v_{ij}^0$ ,  $v_{ij}^1$ ,  $v_{iii\ j}^0$ ,  $v_{iii\ j}^1$ ,  $v_{1122}^0$ , and  $v_{1122}^1$  are the undetermined parameters. The best-fit values of the parameters together with the standard deviations  $\sigma$  of the calculated excess volumes and viscosity deviations and the AADs of the calculated kinematic viscosities for EL + MAA, EL + BzMA, and EL + 2-HEMA are given in Table 9. As seen from Tables 6, 7, and 9, the standard deviations of the calculated excess volumes and viscosity deviations are approximately similar, regardless of the parameters treating as temperature-specific or temperature-dependent in the Redlich–Kister type polynomial. However, from Tables 8 and 9, the McAllister's multi-body interaction model with temperature-specific parameters yielded better calculated results than with temperature-dependent parameters did for those three investigated systems. These calculated results are also illustrated in Figures 1 to 3.

## Conclusion

In this study, the densities and viscosities of binary mixtures of EL with MAA, BzMA, and 2-HEMA were measured at (298.15, 308.15, and 318.15) K over the entire composition range. The excess molar volumes are negative in ethyl lactate + MAA and + 2-HEMA systems and positive in ethyl lactate + BzMA system. They imply that volume expansion takes place when ethyl lactate mixes with benzyl methacrylate and volume contraction in the EL + MAA system and in the EL + 2-HEMA system. Moreover, the excess volumes were found to increase with increasing temperature, while the viscosity deviation decreased with increasing temperature for all investigated systems. The excess volumes and viscosity deviations were correlated by a Redlich–Kister type polynomial. From the correlated results, the standard deviations of the calculated excess volumes and viscosity deviations are very small and approximately similar, regardless of the parameters treating as temperature-specific or temperature-dependent in the Redlich–Kister type polynomial. McAllister's three-body and four-body interaction models were also used to correlate the kinematic viscosities. In this study, the McAllister's multi-body interaction model with temperature-specific parameters yielded better calculated results than with temperature-dependent parameters did for those three investigated systems.

## Literature Cited

- (1) Chen, J. T.; Chang, W. C. Densities and viscosities of binary mixtures of propylene glycol monomethyl ether acetate with methacrylic acid, benzyl methacrylate, and 2-hydroxyethyl methacrylate between 298.15 K and 318.15 K. *J. Chem. Eng. Data* **2005**, *50*, 1753–1756.
- (2) Chen, J. T.; Chang, W. C. Density and viscosity for ethyl 3-ethoxypropionate + methacrylic acid, + benzyl methacrylate, and + 2-hydroxyethyl methacrylate. *J. Chem. Eng. Data* **2005**, *50*, 1991–1994.
- (3) Chen, J. T.; Chang, W. C. Excess molar volumes and viscosities for binary mixtures of cyclohexanone with methacrylic acid, benzyl methacrylate, and 2-hydroxyethyl methacrylate at (298.15, 308.15, and 318.15) K. *J. Chem. Eng. Data* **2006**, *51*, 88–92.
- (4) Wagner, W.; Pruss, The, A., IAPWS Formulation for the thermodynamic properties of ordinary water substance for general and scientific use. *J. Phys. Chem. Ref. Data* **2002**, *31*, **1995**, *2*, 387–494.
- (5) Nikam, P. S.; Shirsat, L. N.; Hasan, M. Density and viscosity studies of binary mixtures of acetonitrile with methanol, ethanol, propan-1-ol, butan-1-ol, 2-methylpropan-1-ol, and 2-methylpropan-2-ol at (298.15, 303.15, 308.15, and 313.15) K. *J. Chem. Eng. Data* **1998**, *43*, 732–737.
- (6) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents: Physical Properties and Methods of Purifications*, 4th ed.; Wiley-Interscience: New York, 1986.
- (7) TRC. *Data Bases for Chemistry and Engineering. TRC Thermodynamic Tables*, Ver. 1996-1S, Jan 1996; Thermodynamic Research Center, Texas A&M University: College Station, TX, 1996.
- (8) Aminabhavi, T. M.; Bindu, G., Densities, viscosities, and refractive indices of bis(2-methoxyethyl) ether + Cyclohexane or + 1,2,3,4-Tetrahydronaphthalene and of 2-Ethoxyethanol + Propan-1-ol, + Propan-2-ol, or + Butan-1-ol. *J. Chem. Eng. Data* **1995**, *40*, 462–467.
- (9) Fermeleglia, M.; Lapasin, R. Excess volumes and viscosities of binary mixtures of organics. *J. Chem. Eng. Data* **1988**, *33*, 415–417.
- (10) Sastry, N. V.; Valand, M. K. Densities, speeds of sound, viscosities, and relative permittivities for 1-propanol + and 1-butanol + heptane at 298.15 K and 308.15 K. *J. Chem. Eng. Data* **1996**, *41*, 1421–1425.
- (11) Aminabhavi, T. M.; Bindu, G. Densities, viscosities, and refractive indices of the binary mixtures of bis(2-methoxyethyl) ether with 1-propanol, 1-butanol, 2-methyl-1-propanol, and 2-methyl-2-propanol. *J. Chem. Eng. Data* **1994**, *39*, 865–867.
- (12) Rattan, V. K.; Singh, S.; Sethi, B. P. S. Viscosities, densities, and ultrasonic velocities of binary mixtures of ethylbenzene with ethanol, 1-propanol, and 1-butanol at (298.15 and 308.15) K. *J. Chem. Eng. Data* **2004**, *49*, 1074–1077.
- (13) Franjo, C.; Jimenez, E.; Iglesias, T. P.; Legido, J. L.; Andrade, M. I. P. Viscosities and densities of hexane + butan-1-ol, + hexan-1-ol, and + octan-1-ol at 298.15 K. *J. Chem. Eng. Data* **1995**, *40*, 68–70.
- (14) Franjo, C.; Menaut, C. P.; Jimenez, E.; Legido, J. L.; Andrade, M. I. P. Viscosities and densities of octane + butan-1-ol, hexan-1-ol, and octan-1-ol at 298.15 K. *J. Chem. Eng. Data* **1995**, *40*, 992–994.
- (15) Nikam, P. S.; Jagdale, B. S.; Sawant, A. B.; Hasan, M. Densities and viscosities for binary mixtures of benzonitrile with methanol, ethanol, propan-1-ol, butan-1-ol, pentan-1-ol, and 2-methylpropan-2-ol at (303.15, 308.15, and 313.15) K. *J. Chem. Eng. Data* **2000**, *45*, 214–218.
- (16) Nikam, P. S.; Jagdale, B. S.; Sawant, A. B.; Hasan, M. Densities and viscosities of binary mixtures of toluene with methanol, ethanol, propan-1-ol, butan-1-ol, pentan-1-ol, and 2-methylpropan-2-ol at (303.15, 308.15, 313.15) K. *J. Chem. Eng. Data* **2000**, *45*, 559–563.
- (17) Orbey, H.; Sandler, S. I. The prediction of the viscosity of liquid hydrocarbons and their mixtures as a function of temperature and pressure. *Can. J. Chem. Eng.* **1993**, *71*, 437–446.
- (18) Constantinou, L.; Gani, R. New group contribution method for estimating properties of pure compounds. *AIChE J.* **1994**, *40*, 1697–1710.
- (19) Redlich, O.; Kister, A. T. Algebraic representation of thermodynamics properties and the classification of solutions. *Ind. Eng. Chem.* **1948**, *40*, 345–348.
- (20) McAllister, R. A. The viscosity of liquid mixtures. *AIChE J.* **1960**, *6*, 427–431.

Received for review December 14, 2006. Accepted December 15, 2006. Financial support from the National Science Council, ROC, through Grant NSC 93-2216-E-159-001 is gratefully acknowledged.

JE600568W