

# Densities and Surface Tensions of Trimethylbenzene + Dimethyl Carbonate or + Diethyl Carbonate at 298.15 K and 313.15 K

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Densities and surface tensions for binary systems of (1,2,4-trimethylbenzene or 1,3,5-trimethylbenzene + dimethyl carbonate or diethyl carbonate) have been measured under normal atmospheric pressure over the entire mole fraction range at 298.15 K and 313.15 K. The excess molar volumes and the surface tension deviation have been calculated. The excess molar volumes and the values of the surface tension deviation are fitted to the Redlich–Kister polynomial equation. The excess molar volumes for all the binary systems are positive over the whole composition range, and the surface tension deviations are negative.

## Introduction

The surface tension and density of liquid mixtures are very important physical properties for understanding and interpreting the nature of interactions between the molecules of the mixtures. They also affect most separation procedures, such as liquid–liquid extraction, gas absorption, and distillation. In the study of separating mixed xylene and trimethylbenzene, our group has developed a high-performance separation method named urging rectification,<sup>1</sup> which involves adding some special solvent (named urging solvent) to the rectification system to aid light component separation. The determination of excess functions of the mixtures involved is vital for selecting an urging solvent. In previous papers, the excess molar volumes and surface tensions at 298.15 K were presented for xylene + alkane (acetone or 2-butanone), xylene + ether (isopropyl ether or methyl *tert*-butyl ether), trimethylbenzene + ethylene glycol ester (ethylene glycol monomethyl ether or ethylene glycol dimethyl ether), trimethylbenzene + alkanol (1-butanol, or 2-methyl-1-propanol, 2-butanol, 2-methyl-2-propanol), trimethylbenzene + tetrahydrofuran, tetrachloromethane, or dimethyl sulfoxide.<sup>2–6</sup> Herein, excess molar volumes and surface tensions for 1,2,4-trimethylbenzene or 1,3,5-trimethylbenzene + dimethyl carbonate or diethyl carbonate at 298.15 K and 313.15 K are determined.

## Experimental Section

Dimethyl carbonate, diethyl carbonate, 1,2,4-trimethylbenzene, and 1,3,5-trimethylbenzene were commercially available (Acros Organics). All the chemicals were stored over molecular sieve before use. The mass fraction of the substances, determined by PE auto system XL gas chromatograph, were as follows: dimethyl carbonate (99.57 %), diethyl carbonate (99.79 %), 1,2,4-trimethylbenzene (99.20 %), 1,3,5-trimethylbenzene (99.30 %). The mole fraction of each mixture was obtained by measuring the masses of the components using an Ohaus E12140 balance; the uncertainty of the mole fraction is estimated to be less than  $1 \times 10^{-4}$ .

Densities of the pure liquids and their mixtures were measured with an Anton Paar DMA 4500 vibrating-tube densimeter,

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Table 1. Physical Properties of the Pure Components

| substance              | $\rho/\text{g}\cdot\text{cm}^{-3}$ |   | $\sigma/\text{mN}\cdot\text{m}^{-1}$ |   |
|------------------------|------------------------------------|---|--------------------------------------|---|
|                        | exptl                              | lit.  | exptl                                | lit.                                      |
| $T = 298.15 \text{ K}$ |                                    |   |                                      |   |
| dimethyl carbonate     | 1.06297                            | 1.06295 <sup>11</sup><br>1.06335 <sup>12</sup>                          | 28.63                                | 28.58 <sup>18</sup>                       |
| diethyl carbonate      | 0.96912                            | 0.96900 <sup>13</sup><br>0.96923 <sup>14</sup><br>0.96926 <sup>15</sup> | 25.92                                | 25.87 <sup>18</sup>                       |
| 1,2,4-trimethylbenzene | 0.87164                            | 0.87174 <sup>16</sup><br>0.87164 <sup>5</sup>                           | 29.29                                | 29.19 <sup>18</sup><br>29.25 <sup>5</sup> |
| 1,3,5-trimethylbenzene | 0.86104                            | 0.86109 <sup>17</sup><br>0.86103 <sup>5</sup>                           | 28.09                                | 27.54 <sup>18</sup><br>28.09 <sup>5</sup> |
| $T = 313.15 \text{ K}$ |                                    |   |                                      |   |
| dimethyl carbonate     | 1.04463                            | 1.04319 <sup>19</sup><br>1.04301 <sup>20</sup>                          | 26.62                                | 26.57 <sup>18</sup>                       |
| diethyl carbonate      | 0.95215                            | 0.95232 <sup>11</sup><br>0.9522 <sup>21</sup>                           | 24.26                                | 24.22 <sup>18</sup>                       |
| 1,2,4-trimethylbenzene | 0.85950                            |   | 27.67                                | 27.66 <sup>18</sup>                       |
| 1,3,5-trimethylbenzene | 0.84873                            | 0.84880 <sup>22</sup>   | 26.82                                | 26.20 <sup>18</sup>                       |

thermostated at  $(298.15 \pm 0.01) \text{ K}$  and  $(313.15 \pm 0.01) \text{ K}$ . The uncertainty of the density is about  $5 \times 10^{-5} \text{ g}\cdot\text{cm}^{-3}$ . The surface tensions of the pure liquids and their mixtures were determined by the pendant drop method, using a Dataphysics OCA20 contact angle and surface tension measuring device. This instrument provides a computer-controlled display video camera (CCD) to take pictures and an electronic syringe unit to inject samples, so the surface tension of the sample can be determined rapidly. The surface tension was given by<sup>7</sup>

$$\sigma = \frac{g\Delta\rho d_e^2}{H} \quad (1)$$

In eq 1,  $g$  is the gravitational acceleration;  $\Delta\rho$  is the density difference between the droplet and the surroundings;  $d_e$  is the largest diameter of the drop; and  $H$  is a correction factor, which depends on the shape of the drop, and is calculated by the Young-Laplace equation and performed via the computer. The software needs only the density data and a picture of the drop of liquid to calculate the surface tension. The uncertainty of the surface tension measured here is about  $\pm 0.05 \text{ mN}\cdot\text{m}^{-1}$ . The densities and surface tensions of the pure compounds are given in Table 1 and compared with the literature values.

Table 2. Experimental Density  $\rho$  and Excess Molar Volumes  $V^E$ 

| $x$  | $\rho$<br>g·cm <sup>-3</sup> | $V^E$<br>cm <sup>3</sup> ·mol <sup>-1</sup> | $x$    | $\rho$<br>g·cm <sup>-3</sup> | $V^E$<br>cm <sup>3</sup> ·mol <sup>-1</sup> | $x$    | $\rho$<br>g·cm <sup>-3</sup> | $V^E$<br>cm <sup>3</sup> ·mol <sup>-1</sup> | $x$    | $\rho$<br>g·cm <sup>-3</sup> | $V^E$<br>cm <sup>3</sup> ·mol <sup>-1</sup> | $x$    | $\rho$<br>g·cm <sup>-3</sup> | $V^E$<br>cm <sup>3</sup> ·mol <sup>-1</sup> |
|--|------------------------------|---|--------|------------------------------|---|--------|------------------------------|---|--------|------------------------------|---|--------|------------------------------|---|
| $T = 298.15 \text{ K}$   |                              |   |        |                              |   |        |                              |   |        |                              |   |        |                              |   |
| (CH <sub>3</sub> O) <sub>2</sub> CO ( $x$ ) + 1,2,4-C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>3</sub> (1 - $x$ )               |                              |   |        |                              |   |        |                              |   |        |                              |   |        |                              |   |
| 0  | 0.87164                      | 0   | 0.2498 | 0.90122                      | 0.404                                       | 0.4500 | 0.93135                      | 0.527                                       | 0.6500 | 0.96890                      | 0.502                                       | 0.8501 | 1.01710                      | 0.293                                       |
| 0.0499   | 0.87693                      | 0.106                                       | 0.2995 | 0.90807                      | 0.454                                       | 0.5000 | 0.93996                      | 0.534                                       | 0.6999 | 0.97971                      | 0.476                                       | 0.8999 | 1.03125                      | 0.209                                       |
| 0.0999   | 0.88255                      | 0.196                                       | 0.3502 | 0.91553                      | 0.485                                       | 0.5500 | 0.94904                      | 0.535                                       | 0.7497 | 0.99122                      | 0.435                                       | 0.9498 | 1.04657                      | 0.104                                       |
| 0.1500   | 0.88853                      | 0.267                                       | 0.4001 | 0.92326                      | 0.506                                       | 0.5998 | 0.95857                      | 0.531                                       | 0.7997 | 1.00368                      | 0.370                                       | 1      | 1.06297                      | 0   |
| 0.2000   | 0.89476                      | 0.336                                       |        |                              |   |        |                              |   |        |                              |   |        |                              |   |
| (CH <sub>3</sub> O) <sub>2</sub> CO ( $x$ ) + 1,3,5-C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>3</sub> (1 - $x$ )               |                              |   |        |                              |   |        |                              |   |        |                              |   |        |                              |   |
| 0  | 0.86104                      | 0   | 0.2491 | 0.89185                      | 0.429                                       | 0.4499 | 0.92332                      | 0.587                                       | 0.6488 | 0.96247                      | 0.575                                       | 0.8500 | 1.01367                      | 0.351                                       |
| 0.0540   | 0.86708                      | 0.114                                       | 0.3001 | 0.89928                      | 0.475                                       | 0.4999 | 0.93232                      | 0.600                                       | 0.7000 | 0.97417                      | 0.544                                       | 0.8999 | 1.02884                      | 0.251                                       |
| 0.1048   | 0.87295                      | 0.229                                       | 0.3496 | 0.90677                      | 0.525                                       | 0.5508 | 0.94203                      | 0.602                                       | 0.7514 | 0.98683                      | 0.490                                       | 0.9499 | 1.04518                      | 0.138                                       |
| 0.1518   | 0.87880                      | 0.303                                       | 0.4001 | 0.91484                      | 0.565                                       | 0.5977 | 0.95157                      | 0.587                                       | 0.7999 | 0.99960                      | 0.426                                       | 1      | 1.06297                      | 0   |
| 0.1998   | 0.88510                      | 0.366                                       |        |                              |   |        |                              |   |        |                              |   |        |                              |   |
| (C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> CO ( $x$ ) + 1,2,4-C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>3</sub> (1 - $x$ ) |                              |   |        |                              |   |        |                              |   |        |                              |   |        |                              |   |
| 0  | 0.87164                      | 0   | 0.2518 | 0.89323                      | 0.114                                       | 0.4496 | 0.91154                      | 0.140                                       | 0.6497 | 0.93130                      | 0.122                                       | 0.8499 | 0.95236                      | 0.069                                       |
| 0.0501   | 0.87581                      | 0.027                                       | 0.2998 | 0.89755                      | 0.127                                       | 0.5000 | 0.91638                      | 0.142                                       | 0.6998 | 0.93641                      | 0.116                                       | 0.9000 | 0.95782                      | 0.053                                       |
| 0.1005   | 0.88010                      | 0.047                                       | 0.3499 | 0.90217                      | 0.132                                       | 0.5494 | 0.92122                      | 0.138                                       | 0.7505 | 0.94172                      | 0.102                                       | 0.9500 | 0.96345                      | 0.025                                       |
| 0.1497   | 0.88428                      | 0.075                                       | 0.4004 | 0.90689                      | 0.136                                       | 0.5997 | 0.92624                      | 0.131                                       | 0.8001 | 0.94700                      | 0.085                                       | 1      | 0.96912                      | 0   |
| 0.1994   | 0.88862                      | 0.092                                       |        |                              |   |        |                              |   |        |                              |   |        |                              |   |
| (C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> CO ( $x$ ) + 1,3,5-C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>3</sub> (1 - $x$ ) |                              |   |        |                              |   |        |                              |   |        |                              |   |        |                              |   |
| 0  | 0.86104                      | 0   | 0.2501 | 0.88412                      | 0.198                                       | 0.4499 | 0.90428                      | 0.261                                       | 0.6498 | 0.92607                      | 0.249                                       | 0.8490 | 0.94964                      | 0.156                                       |
| 0.0500   | 0.86543                      | 0.058                                       | 0.2999 | 0.88901                      | 0.220                                       | 0.5006 | 0.90964                      | 0.266                                       | 0.7007 | 0.93190                      | 0.234                                       | 0.9001 | 0.95606                      | 0.113                                       |
| 0.1000   | 0.86994                      | 0.104                                       | 0.3498 | 0.89396                      | 0.242                                       | 0.5497 | 0.91493                      | 0.267                                       | 0.7495 | 0.93762                      | 0.214                                       | 0.9501 | 0.96249                      | 0.064                                       |
| 0.1500   | 0.87461                      | 0.135                                       | 0.3999 | 0.89908                      | 0.253                                       | 0.6001 | 0.92047                      | 0.262                                       | 0.8004 | 0.94371                      | 0.186                                       | 1      | 0.96912                      | 0   |
| 0.1999   | 0.87930                      | 0.169                                       |        |                              |   |        |                              |   |        |                              |   |        |                              |   |
| $T = 313.15 \text{ K}$   |                              |   |        |                              |   |        |                              |   |        |                              |   |        |                              |   |
| (CH <sub>3</sub> O) <sub>2</sub> CO ( $x$ ) + 1,2,4-C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>3</sub> (1 - $x$ )               |                              |   |        |                              |   |        |                              |   |        |                              |   |        |                              |   |
| 0  | 0.85950                      | 0   | 0.2491 | 0.88796                      | 0.425                                       | 0.4509 | 0.91726                      | 0.563                                       | 0.6500 | 0.95333                      | 0.552                                       | 0.8502 | 1.00000                      | 0.328                                       |
| 0.0505   | 0.86472                      | 0.104                                       | 0.3003 | 0.89487                      | 0.466                                       | 0.5008 | 0.92559                      | 0.569                                       | 0.6995 | 0.96385                      | 0.506                                       | 0.8976 | 1.01308                      | 0.239                                       |
| 0.1012   | 0.87023                      | 0.199                                       | 0.3498 | 0.90176                      | 0.518                                       | 0.5507 | 0.93432                      | 0.575                                       | 0.7505 | 0.97523                      | 0.464                                       | 0.9504 | 1.02872                      | 0.127                                       |
| 0.1500   | 0.87575                      | 0.288                                       | 0.4010 | 0.90943                      | 0.541                                       | 0.5998 | 0.94346                      | 0.565                                       | 0.7994 | 0.98699                      | 0.402                                       | 1      | 1.04463                      | 0   |
| 0.2008   | 0.88192                      | 0.354                                       |        |                              |   |        |                              |   |        |                              |   |        |                              |   |
| (CH <sub>3</sub> O) <sub>2</sub> CO ( $x$ ) + 1,3,5-C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>3</sub> (1 - $x$ )               |                              |   |        |                              |   |        |                              |   |        |                              |   |        |                              |   |
| 0  | 0.84873                      | 0   | 0.2489 | 0.87845                      | 0.461                                       | 0.4498 | 0.90893                      | 0.630                                       | 0.6488 | 0.94686                      | 0.622                                       | 0.8479 | 0.99611                      | 0.375                                       |
| 0.0505   | 0.85419                      | 0.111                                       | 0.2985 | 0.88542                      | 0.512                                       | 0.5001 | 0.91776                      | 0.636                                       | 0.6992 | 0.95818                      | 0.574                                       | 0.8997 | 1.01133                      | 0.271                                       |
| 0.1046   | 0.86031                      | 0.226                                       | 0.3500 | 0.89295                      | 0.568                                       | 0.5492 | 0.92676                      | 0.647                                       | 0.7489 | 0.96998                      | 0.526                                       | 0.9501 | 1.02737                      | 0.148                                       |
| 0.1500   | 0.86569                      | 0.315                                       | 0.3983 | 0.90054                      | 0.594                                       | 0.5999 | 0.93676                      | 0.632                                       | 0.7995 | 0.98291                      | 0.452                                       | 1      | 1.04463                      | 0   |
| 0.2007   | 0.87213                      | 0.386                                       |        |                              |   |        |                              |   |        |                              |   |        |                              |   |
| (C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> CO ( $x$ ) + 1,2,4-C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>3</sub> (1 - $x$ ) |                              |   |        |                              |   |        |                              |   |        |                              |   |        |                              |   |
| 0  | 0.85950                      | 0   | 0.2507 | 0.87988                      | 0.128                                       | 0.4499 | 0.89737                      | 0.161                                       | 0.6481 | 0.91593                      | 0.148                                       | 0.8473 | 0.93587                      | 0.086                                       |
| 0.0508   | 0.86346                      | 0.039                                       | 0.3007 | 0.88417                      | 0.139                                       | 0.4981 | 0.90179                      | 0.159                                       | 0.6990 | 0.92093                      | 0.132                                       | 0.9001 | 0.94145                      | 0.054                                       |
| 0.1005   | 0.86743                      | 0.068                                       | 0.3520 | 0.88861                      | 0.154                                       | 0.5498 | 0.90660                      | 0.157                                       | 0.7499 | 0.92598                      | 0.118                                       | 0.9499 | 0.94674                      | 0.028                                       |
| 0.1486   | 0.87136                      | 0.089                                       | 0.4006 | 0.89294                      | 0.157                                       | 0.597  | 0.91106                      | 0.151                                       | 0.8002 | 0.93106                      | 0.101                                       | 1      | 0.95215                      | 0   |
| 0.2012   | 0.87571                      | 0.111                                       |        |                              |   |        |                              |   |        |                              |   |        |                              |   |
| (C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> CO ( $x$ ) + 1,3,5-C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>3</sub> (1 - $x$ ) |                              |   |        |                              |   |        |                              |   |        |                              |   |        |                              |   |
| 0  | 0.84873                      | 0   | 0.2480 | 0.87064                      | 0.201                                       | 0.4487 | 0.88994                      | 0.276                                       | 0.6510 | 0.91105                      | 0.262                                       | 0.8501 | 0.93370                      | 0.152                                       |
| 0.0502   | 0.85295                      | 0.059                                       | 0.2987 | 0.87533                      | 0.234                                       | 0.5005 | 0.89518                      | 0.282                                       | 0.6995 | 0.91640                      | 0.244                                       | 0.9001 | 0.93969                      | 0.111                                       |
| 0.1001   | 0.85731                      | 0.099                                       | 0.3417 | 0.87945                      | 0.248                                       | 0.5501 | 0.90030                      | 0.280                                       | 0.7495 | 0.92197                      | 0.226                                       | 0.9501 | 0.94576                      | 0.071                                       |
| 0.1497   | 0.86170                      | 0.137                                       | 0.4009 | 0.88520                      | 0.266                                       | 0.5995 | 0.90552                      | 0.274                                       | 0.8004 | 0.92784                      | 0.191                                       | 1      | 0.95215                      | 0   |
| 0.2010   | 0.86626                      | 0.182                                       |        |                              |   |        |                              |   |        |                              |   |        |                              |   |

## Result and Discussion

Excess molar volumes were determined from the density data:<sup>8</sup>

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - x_1 \frac{M_1}{\rho_1} - x_2 \frac{M_2}{\rho_2} \quad (2)$$

where  $M_i$  are the molar mass of component  $i$ ,  $\rho$  and  $\rho_i$  are the densities of the mixture and component  $i$ , and  $x_i$  is the mole fraction of component  $i$ . Experimental  $\rho$  and  $V^E$  for four binary mixtures (dimethyl carbonate + 1,2,4-trimethylbenzene, dimethyl carbonate + 1,3,5-trimethylbenzene, diethyl carbonate + 1,2,4-trimethylbenzene, and diethyl carbonate + 1,3,5-trimethylbenzene) at 298.15 K are listed in Table 2, and the  $V^E \sim x$  values are graphically presented in Figure 1. The values of  $\rho$  and  $V^E$  for these mixtures at 313.15 K are also listed in Table 2, and the  $V^E \sim x$  values are graphically presented in Figure 2. The experimental results were fitted by the method

of least squares with all points weighted equally to the smoothing equation:<sup>9,10</sup>

$$V^E/\text{cm}^3 \cdot \text{mol}^{-1} = x(1-x) \sum_{i=0}^k A_i (1-2x)^i \quad (3)$$

The parameters  $A_0, A_1, A_2, A_3$ , and  $A_4$  and the standard deviations are given in Table 3.

The surface tensions  $\sigma$  and surface tension deviations  $\delta\sigma$  for four binary mixtures (dimethyl carbonate + 1,2,4-trimethylbenzene, dimethyl carbonate + 1,3,5-trimethylbenzene, diethyl carbonate + 1,2,4-trimethylbenzene, and diethyl carbonate + 1,3,5-trimethylbenzene) at 298.15 K and 313.15 K are listed in Table 4. The values of surface tension deviations for these mixtures at 298.15 K and 313.15 K are graphically presented in Figures 3 and 4. The surface tension deviations  $\delta\sigma$  are defined by<sup>8</sup>

$$\delta\sigma = \sigma - x_1\sigma_1 - x_2\sigma_2 \quad (4)$$

**Table 3. Least-Squares Parameters and Standard Deviations for Excess Molar Volumes from Equation 3**

|   | $A_0$ | $A_1$  | $A_2$  | $A_3$  | $A_4$  | $\frac{\sigma}{\text{cm}^3 \cdot \text{mol}^{-1}}$ |
|---|-------|--------|--------|--------|--------|--|
| $T = 298.15 \text{ K}$                      |       |        |        |        |        |  |
| dimethyl carbonate + 1,2,4-trimethylbenzene | 2.144 | -0.193 | 0.402  | 0.148  | -0.450 | 0.005  |
| dimethyl carbonate + 1,3,5-trimethylbenzene | 2.395 | -0.362 | 0.216  | 0.135  | 0.127  | 0.005  |
| diethyl carbonate + 1,2,4-trimethylbenzene  | 0.560 | 0.004  | 0.059  | -0.130 | -0.107 | 0.002  |
| diethyl carbonate + 1,3,5-trimethylbenzene  | 1.069 | -0.092 | 0.012  | 0.012  | 0.306  | 0.002  |
| $T = 313.15 \text{ K}$                      |       |        |        |        |        |  |
| dimethyl carbonate + 1,2,4-trimethylbenzene | 2.294 | -0.229 | 0.305  | -0.027 | -0.205 | 0.004  |
| dimethyl carbonate + 1,3,5-trimethylbenzene | 2.562 | -0.339 | 0.239  | -0.034 | -0.027 | 0.006  |
| diethyl carbonate + 1,2,4-trimethylbenzene  | 0.641 | 0.037  | 0.068  | 0.050  | -0.005 | 0.002  |
| diethyl carbonate + 1,3,5-trimethylbenzene  | 1.127 | -0.073 | -0.002 | -0.027 | 0.181  | 0.004  |

**Table 4. Surface Tensions  $\sigma$** 

| $x$   | $\frac{\sigma}{\text{mN} \cdot \text{m}^{-1}}$ | $\frac{d\sigma}{\text{mN} \cdot \text{m}^{-1}}$ | $x$    | $\frac{\sigma}{\text{mN} \cdot \text{m}^{-1}}$ | $\frac{d\sigma}{\text{mN} \cdot \text{m}^{-1}}$ | $x$   | $\frac{\sigma}{\text{mN} \cdot \text{m}^{-1}}$ | $\frac{d\sigma}{\text{mN} \cdot \text{m}^{-1}}$ | $x$    | $\frac{\sigma}{\text{mN} \cdot \text{m}^{-1}}$ | $\frac{d\sigma}{\text{mN} \cdot \text{m}^{-1}}$ |
|---|--|---|--------|--|---|---|--|---|--------|--|---|
| $T = 298.15 \text{ K}$  |  |   |        |  |   |   |  |   |        |  |   |
| $(\text{CH}_3\text{O})_2\text{CO}(x) + 1,2,4\text{-C}_6\text{H}_3(\text{CH}_3)_3(1-x)$          |  |   |        |  |   | $(\text{CH}_3\text{O})_2\text{CO}(x) + 1,3,5\text{-C}_6\text{H}_3(\text{CH}_3)_3(1-x)$          |  |   |        |  |   |
| 0   | 29.29  | 0   | 0.5998 | 28.12  | -0.77   | 0   | 28.09  | 0   | 0.6003 | 27.44  | -0.97   |
| 0.0999  | 28.93  | -0.29   | 0.6999 | 28.15  | -0.68   | 0.1048  | 27.91  | -0.24   | 0.7000 | 27.65  | -0.82   |
| 0.2000  | 28.64  | -0.52   | 0.7997 | 28.26  | -0.50   | 0.1998  | 27.60  | -0.60   | 0.7999 | 28.01  | -0.51   |
| 0.3001  | 28.34  | -0.75   | 0.8999 | 28.43  | -0.27   | 0.3001  | 27.43  | -0.83   | 0.8999 | 28.35  | -0.23   |
| 0.4001  | 28.21  | -0.82   | 1      | 28.63  | 0   | 0.3999  | 27.32  | -0.99   | 1      | 28.63  | 0   |
| 0.5000  | 28.08  | -0.88   |        |  | 0.4999  | 27.34   | -1.03  |   |        |  |   |
| $(\text{C}_2\text{H}_5\text{O})_2\text{CO}(x) + 1,2,4\text{-C}_6\text{H}_3(\text{CH}_3)_3(1-x)$ |  |   |        |  |   | $(\text{C}_2\text{H}_5\text{O})_2\text{CO}(x) + 1,3,5\text{-C}_6\text{H}_3(\text{CH}_3)_3(1-x)$ |  |   |        |  |   |
| 0   | 29.29  | 0   | 0.5997 | 26.94  | -0.32   | 0   | 28.09  | 0   | 0.6001 | 26.41  | -0.37   |
| 0.1005  | 28.85  | -0.10   | 0.6998 | 26.66  | -0.27   | 0.1000  | 27.71  | -0.16   | 0.7007 | 26.26  | -0.31   |
| 0.1994  | 28.41  | -0.21   | 0.8001 | 26.39  | -0.20   | 0.1999  | 27.37  | -0.29   | 0.8004 | 26.14  | -0.21   |
| 0.2998  | 27.98  | -0.30   | 0.9000 | 26.13  | -0.13   | 0.2999  | 27.01  | -0.43   | 0.9001 | 26.01  | -0.13   |
| 0.4001  | 27.58  | -0.37   | 1      | 25.92  | 0   | 0.3999  | 26.76  | -0.47   | 1      | 25.92  | 0   |
| 0.5000  | 27.23  | -0.38   |        |  | 0.5006  | 26.56   | -0.45  |   |        |  |   |
| $T = 313.15 \text{ K}$  |  |   |        |  |   |   |  |   |        |  |   |
| $(\text{CH}_3\text{O})_2\text{CO}(x) + 1,2,4\text{-C}_6\text{H}_3(\text{CH}_3)_3(1-x)$          |  |   |        |  |   | $(\text{CH}_3\text{O})_2\text{CO}(x) + 1,3,5\text{-C}_6\text{H}_3(\text{CH}_3)_3(1-x)$          |  |   |        |  |   |
| 0   | 27.67  | 0   | 0.5996 | 26.06  | -0.98   | 0   | 26.82  | 0   | 0.5998 | 25.62  | -1.08   |
| 0.1008  | 27.23  | -0.33   | 0.6993 | 26.08  | -0.86   | 0.1009  | 26.42  | -0.39   | 0.6999 | 25.86  | -0.82   |
| 0.1999  | 26.82  | -0.64   | 0.7998 | 26.16  | -0.67   | 0.1994  | 26.04  | -0.74   | 0.7994 | 26.08  | -0.58   |
| 0.2996  | 26.51  | -0.85   | 0.9000 | 26.37  | -0.36   | 0.2996  | 25.80  | -0.96   | 0.9000 | 26.38  | -0.26   |
| 0.3991  | 26.29  | -0.96   | 1      | 26.62  | 0   | 0.4016  | 25.63  | -1.12   | 1      | 26.62  | 0   |
| 0.5000  | 26.11  | -1.04   |        |  | 0.5004  | 25.55   | -1.17  |   |        |  |   |
| $(\text{C}_2\text{H}_5\text{O})_2\text{CO}(x) + 1,2,4\text{-C}_6\text{H}_3(\text{CH}_3)_3(1-x)$ |  |   |        |  |   | $(\text{C}_2\text{H}_5\text{O})_2\text{CO}(x) + 1,3,5\text{-C}_6\text{H}_3(\text{CH}_3)_3(1-x)$ |  |   |        |  |   |
| 0   | 27.67  | 0   | 0.6003 | 25.23  | -0.39   | 0   | 26.82  | 0   | 0.5996 | 24.71  | -0.57   |
| 0.1000  | 27.16  | -0.17   | 0.6996 | 24.99  | -0.30   | 0.0997  | 26.36  | -0.208  | 0.7004 | 24.56  | -0.47   |
| 0.2002  | 26.69  | -0.30   | 0.8002 | 24.75  | -0.20   | 0.1995  | 25.95  | -0.355  | 0.8000 | 24.44  | -0.34   |
| 0.3005  | 26.23  | -0.42   | 0.8999 | 24.51  | -0.09   | 0.2997  | 25.57  | -0.482  | 0.8996 | 24.31  | -0.20   |
| 0.3997  | 25.81  | -0.50   | 1      | 24.26  | 0   | 0.4001  | 25.22  | -0.578  | 1      | 24.26  | 0   |
| 0.5001  | 25.49  | -0.48   |        |  | 0.5001  | 24.93   | -0.615   |   |        |  |   |

**Table 5. Least-Squares Parameters and Standard Deviations for Surface Tensions from Equation 5**

|   | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $A_4$ | $\frac{\sigma}{\text{mN} \cdot \text{m}^{-1}}$ |
|---|-------|-------|-------|-------|-------|--|
| $T = 298.15 \text{ K}$                      |       |       |       |       |       |  |
| dimethyl carbonate + 1,3,5-trimethylbenzene | -3.42 | -0.43 | 0.57  | 0.53  | -0.08 | 0.03   |
| dimethyl carbonate + 1,2,4-trimethylbenzene | -4.11 | -0.26 | 0.81  | 0.15  | 2.74  | 0.02   |
| diethyl carbonate + 1,3,5-trimethylbenzene  | -1.49 | -0.38 | 1.01  | 0.90  | -1.11 | 0.01   |
| diethyl carbonate + 1,2,4-trimethylbenzene  | -1.79 | -0.87 | 0.56  | 1.15  | -0.33 | 0.01   |
| $T = 313.15 \text{ K}$                      |       |       |       |       |       |  |
| dimethyl carbonate + 1,3,5-trimethylbenzene | -4.07 | 0.09  | -0.13 | 0.10  | 0.73  | 0.02   |
| dimethyl carbonate + 1,2,4-trimethylbenzene | -4.64 | -0.69 | 2.05  | -0.34 | -0.85 | 0.03   |
| diethyl carbonate + 1,3,5-trimethylbenzene  | -1.90 | -0.90 | 1.37  | 0.74  | -1.05 | 0.02   |
| diethyl carbonate + 1,2,4-trimethylbenzene  | -2.46 | -0.10 | 1.54  | 0.06  | -1.99 | 0.01   |

The surface tensions data were fitted by the method of least squares with all points weighted equally to the smoothing equation:<sup>10</sup>

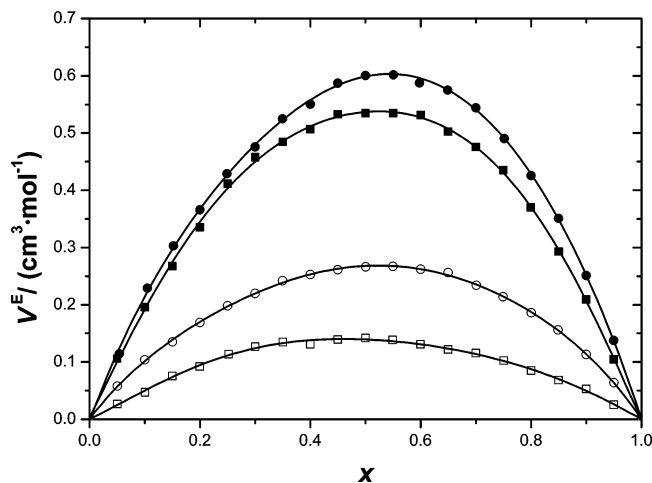
$$\delta\sigma/\text{mN} \cdot \text{m}^{-1} = x(1-x) \sum_{i=0}^k A_i(1-2x)^i \quad (5)$$

The parameters  $A_0$ ,  $A_1$ ,  $A_2$ ,  $A_3$ , and  $A_4$  and the standard deviations are given in Table 5.

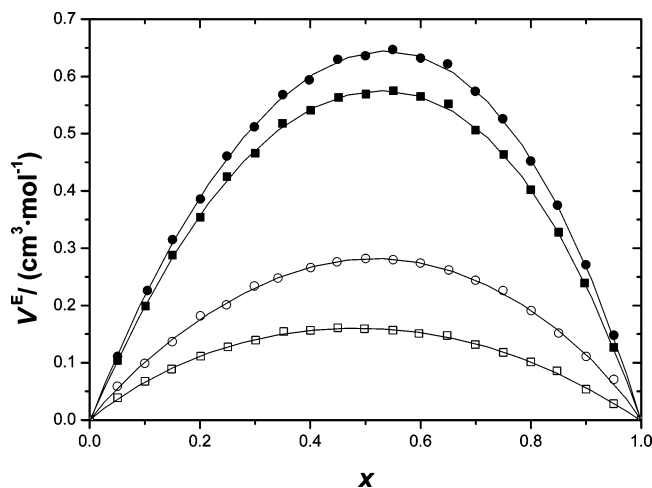
Figures 1 and 2 show that  $V^E$  values are all positive for these binary mixtures at 298.15 K and 313.15 K. The maximum values of  $V^E$  follow the order: diethyl carbonate + 1,2,4-trimethyl-

benzene < diethyl carbonate + 1,3,5-trimethylbenzene < dimethyl carbonate + 1,2,4-trimethylbenzene < dimethyl carbonate + 1,3,5-trimethylbenzene. At the same time it can be seen that  $V^E$  curves are shifted in a regular way with increasing temperature (i.e.,  $V^E$  becomes more positive at higher temperature).

It was suggested that  $V^E$  is the result of the contributions from several opposing effects, which may be divided into three types: physical, chemical, and structural effect. Physical effects make a positive contribution to  $V^E$ ; chemical and structural effects make a negative contribution.<sup>23</sup> The  $V^E$  values are all positive for these binary mixtures. It indicates that the physical



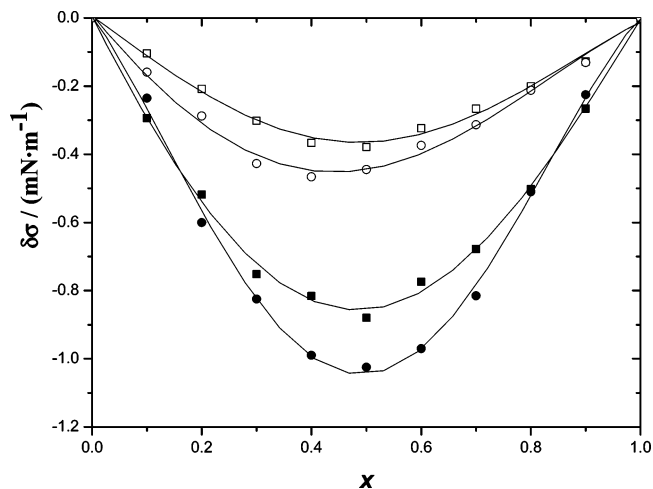
**Figure 1.** Excess molar volumes  $V^E$  for dimethyl carbonate ( $x$ ) + ■, 1,2,4-trimethylbenzene ( $1-x$ ); + ●, 1,3,5-trimethylbenzene ( $1-x$ ) or for diethyl carbonate ( $x$ ) + □, 1,2,4-trimethylbenzene; + ○, 1,3,5-trimethylbenzene ( $1-x$ ) at 298.15 K.



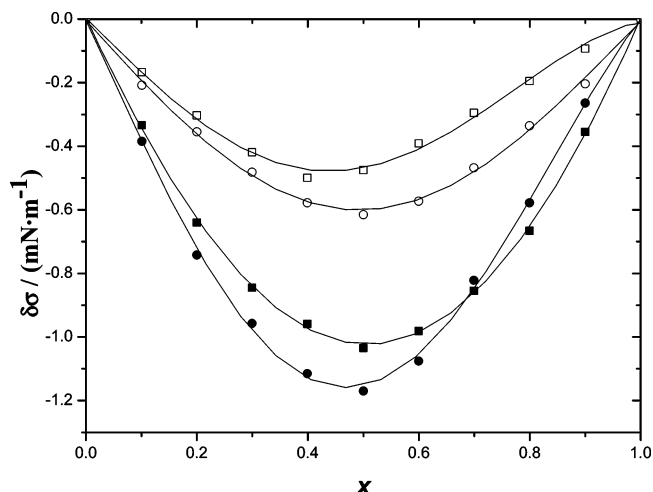
**Figure 2.** Excess molar volumes  $V^E$  for dimethyl carbonate ( $x$ ) + ■, 1,2,4-trimethylbenzene ( $1-x$ ); + ●, 1,3,5-trimethylbenzene ( $1-x$ ) or for diethyl carbonate ( $x$ ) + □, 1,2,4-trimethylbenzene; + ○, 1,3,5-trimethylbenzene ( $1-x$ ) at 313.15 K.

contributions are dominant. Figures 1 and 2 show that the  $V^E$  values for dimethyl carbonate + trimethylbenzene are more positive than diethyl carbonate + trimethylbenzene. It may be explained as follows: the structures of dimethyl carbonate and diethyl carbonate are similar and the molecular weight of dimethyl carbonate is smaller than that of diethyl carbonate; however, the value of density of dimethyl carbonate is larger than that of diethyl carbonate. In a sense, it shows that the packing of molecules inside the dimethyl carbonate is more compact than in diethyl carbonate. After adding the trimethylbenzene, the structures of the binary systems become incompact, so the increase of the  $V^E$  for dimethyl carbonate + trimethylbenzene should be more than diethyl carbonate + trimethylbenzene. The  $V^E$  values for dimethyl carbonate or diethyl carbonate + 1,3,5-trimethylbenzene are more positive than dimethyl carbonate or diethyl carbonate + 1,2,4-trimethylbenzene. This is similar to our previous result of trimethylbenzene + ethylene glycol ester or butanol.<sup>2,5</sup> It is possibly because 1,3,5-trimethylbenzene is symmetrical and nonpolar. The dipole-dipole interaction is weaker than 1,2,4-trimethylbenzene.

Figures 3 and 4 show that the surface tension deviations  $\delta\sigma$  at 298.15 K and 313.15 K are negative for these binary systems. The minimum values of  $\delta\sigma$  follow the order: dimethyl carbonate



**Figure 3.** Surface tension deviation  $\delta\sigma$  dimethyl carbonate ( $x$ ) + ■, 1,2,4-trimethylbenzene ( $1-x$ ); + ●, 1,3,5-trimethylbenzene ( $1-x$ ) or for diethyl carbonate ( $x$ ) + □, 1,2,4-trimethylbenzene; + ○, 1,3,5-trimethylbenzene ( $1-x$ ) at 298.15 K.



**Figure 4.** Surface tension deviation  $\delta\sigma$  dimethyl carbonate ( $x$ ) + ■, 1,2,4-trimethylbenzene ( $1-x$ ); + ●, 1,3,5-trimethylbenzene ( $1-x$ ) or for diethyl carbonate ( $x$ ) + □, 1,2,4-trimethylbenzene; + ○, 1,3,5-trimethylbenzene ( $1-x$ ) at 313.15 K.

+ 1,3,5-trimethylbenzene < dimethyl carbonate + 1,2,4-trimethylbenzene < diethyl carbonate + 1,3,5-trimethylbenzene < diethyl carbonate + 1,2,4-trimethylbenzene. The surface tension deviations  $\delta\sigma$  can be considered to be the result of two aspects: one is the surface region, and the other is the bulk region. For the surface region, the surface tension deviations indicate different distributions of unlike components between the surface and the bulk region. The negative value of  $\delta\sigma$  indicates that the surface concentration of the lower surface tension component is higher than its bulk concentration. For the bulk region, the surface tension deviations relate to chemical effects, physical effects, and dipolar-dipolar interaction. The physical effects and dipolar-dipolar interaction make negative contribution to the surface tension deviations, and the chemical effects make positive contribution. For these binary systems, the physical effects are more dominant than the chemical effects, which results in a decrease in surface tension. It can also be observed from Figures 3 and 4 that  $\delta\sigma$  curves are shifted in a regular way with increasing temperature (i.e.,  $\delta\sigma$  becomes more negative at higher temperature). This is similar to our previous result of trimethylbenzene + ethylene glycol ester.<sup>2</sup>

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**Supporting Information Available:**

Two tables showing the experimental density data at 298.15 K and 313.15 K. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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