# Densities and Excess Molar Volumes of 2,2,4-Trimethylpentane + Linear and Cyclic Ethers at 298.15 K

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Densities and excess molar volumes of the five systems containing 2,2,4-trimethylpentane + dimethoxymethane, + 1,2-dimethoxyethane, + 2,2-dimethoxypropane, + 1,4-dioxane, and + oxane have been determined at 298.15 K using an Anton Paar density meter. The experimental data were correlated by means of the Redlich–Kister equation. Excess volumes are positive for all systems except for 2,2,4-trimethylpentane + oxane, where the values are negative, and small in magnitude.

## Introduction

The present paper forms a part of the program to measure excess properties for binary mixtures (*1–7*) containing linear or cyclic ethers as a common component. We present here measurements of the excess molar volumes $V_m^E$ at 298.15 K of the binary systems containing 2,2,4-trimethylpentane (component 1) + three linear ethers and two cyclic ethers (component 2), namely, dimethoxymethane, 1,2-dimethoxyethane, 2,2-dimethoxypropane, 1,4-dioxane, and oxane.

Results for the binary systems containing isooctane + 1,3-dioxolane or + oxolane, studied in a previous paper (*7*), are also reported in Figure 1 and are considered in the conclusions of this paper.

These works were taken up to gain insight into the nature of interaction of the molecules.

No measurements on the densities or excess volumes for these systems have been found in the literature.

## Experimental Section

***Materials.*** The purification of the linear and cyclic ethers is the same as reported in ref 3, with the exception of 2,2-dimethoxypropane. 2,2-Dimethylpropane (Aldrich), analytical grade 98 + mol %, was treated with lithium aluminum hydride and fractionally distilled.

2,2,4-Trimethylpentane, (Aldrich) analytical grade 99.7 mol %, was used as received. Before use, all liquids were stored in dark bottles over molecular sieves (Union Carbide Type 4A, 1/16-in. pellets). Density values of the pure components are reported in Table I and compared with literature data.

***Measurements.*** Densities $\rho$ were measured by means of an Anton Paar DMA 60/602 density meter with resolution of $\pm 1.5 \times 10^{-6}$ g cm$^{-3}$. Water and dry air have been used to calibrate the apparatus, and the constancy of the parameters of the vibrating tube has been checked using results for benzene + cyclohexane, for which the densities are accurately known from the literature (*8*). Our value of $V_m^E$ at $x_1 = 0.5$ is 0.652 cm$^3$ mol$^{-1}$ compared with a literature value of 0.6514 (*8*). The mean estimated uncertainty of $V_m^E$ is $\pm 3 \times 10^{-3}$ cm$^3$ mol$^{-1}$.

The temperature of the water bath containing the oscillator tube was kept constant within 0.005 K by means of a Heto bath circulator (Hetotherm Type 01 DBT 623). Details on the apparatus and procedure are the same as described in our previous works following the method given by Fermeglia and Lapasin (*9*).

Samples were prepared by mass, with a precision of $\pm 1 \times 10^{-4}$ g, by means of a Mettler balance (model A 160), and all measurements were corrected for buoyancy and for evaporation of components. This latter correction implied knowledge of the vapor pressure $P^\circ$ of the pure components at room temperature. We report in Table II only the vapor

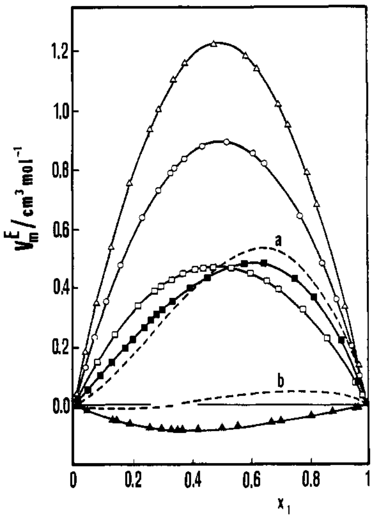

**Figure 1.** Excess molar volumes at 298.15 K for 2,2,4-trimethylpentane + dimethoxymethane (△), + 1,2-dimethoxyethane (○), + 2,2-dimethoxypropane (□), + 1,4-dioxane (■), + oxane (▲), + 1,3-dioxolane (- - -) (a) (ref 7), and + oxolane (- - -) (b) (ref 7). The solid curve was calculated from eq 1, using parameters $a_k$ of Table IV.

**Table I. Densities, $\rho$, of Pure Liquids**

| component | T/K | $\rho$/(g cm$^{-3}$) present paper | $\rho$/(g cm$^{-3}$) lit. |
|---|---|---|---|
| 2,2,4-trimethylpentane | 298.15 | 0.687 69 | 0.687 81 (*19*) |
| dimethoxymethane | 288.15 | 0.866 48 | 0.866 45 (*19*) |
| | 298.15 | 0.856 89 | |
| 1,2-dimethoxyethane | 298.15 | 0.861 90 | 0.862 08 (*20*) |
| 2,2-dimethoxypropane | 293.15 | 0.845 12 | 0.844 8 (*21*) |
| | 298.15 | 0.844 93 | |
| 1,4-dioxane | 298.15 | 1.028 07 | 1.027 97 (*19*) |
| oxane | 298.15 | 0.878 92 | 0.879 16 (*22*) |

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**Table II. Experimental Vapor Pressure of 2,2-Dimethoxypropane**

| $T$/K | $p°$/kPa | $T$/K | $p°$/kPa |
|---|---|---|---|
| 292.6 | 9.6 | 330.4 | 48.1 |
| 296.4 | 11.5 | 335.8 | 58.5 |
| 298.2 | 12.6 | 340.5 | 69.2 |
| 306.4 | 18.3 | 344.3 | 78.7 |
| 316.6 | 28.2 | 349.2 | 92.5 |
| 324.3 | 38.4 | | |

pressure of 2,2-dimethoxypropane; the other ones are known from previous works. An equilibrium still (Fritz GmbH, Normag, Hoffheim, Germany) was used for the determination of the vapor pressure of 2,2-dimethoxypropane. For details and operation, see ref 10.

## Discussion of the Results and Conclusions

The excess molar volumes $V_m^E$ for the five binary systems are given in Table III and graphically represented in Figure 1.

The composition dependence of $V_m^E$ was correlated by the Redlich–Kister polynomial

$$(V_m^E/(\mathrm{cm^3\ mol^{-1}}))/x_1x_2 = \sum_{k\geq0} a_k(x_1 - x_2)^k \qquad (1)$$

where $x_1$ and $x_2$ are the molar fractions of 2,2,4-trimethylpentane and linear or cyclic ether, respectively.

The adjustable parameters $a_k$ were obtained by the method of least squares and are collected in Table IV with the standard deviation $\sigma(V_m^E)$.

As can be seen from Figure 1, all mixtures show positive values of $V_m^E$, with the exception of 2,2,4-trimethylpentane + oxane, which shows a small negative value, of order −0.1 cm$^3$ mol$^{-1}$. The mixture 2,2,4-trimethylpentane + oxolane shows a small $V_m^E$ with a sign inversion. $V_m^E$ increases in passing from oxane and oxolane to the corresponding diethers where it is slightly influenced by the ring size. Instead, the increase of the chain length of linear diethers is accompanied by a decrease in the excess volume at $x_1 = 0.5$.

In the attempt of interpreting the results shown in Figure 1, three theories, namely, of Flory (*11,12*), Sanchez and Lacombe (*13, 14*), and Graph (*15, 16*), were used to calculate the values of $V_m^E$. Unfortunately, only a poor agreement was obtained with the experimental $V_m^E$. However, a qualitative description of the trend of curves in Figure 1 may be achieved by considering that (1) only physical intermolecular forces are involved in the liquids and mixtures, since both hydrogen bonding and weak chemical bonds (between electron donor and acceptor) are absent, (2) the molecular size of the liquid compounds is quite similar (the mean distances between molecules, calculated with the formula of Kohler (*17*), are in the range $4.9 < r \times 10^8/\mathrm{cm} < 6.5$), and (3) the main molecular interactions are those between similar molecules of ethers (due to electronegative O atoms).

The above assumptions allow application of the one-dimensional model of solutions in the version of Prigogine and Lafleur (*18*). According to this theory, the sign and magnitude of the excess volume are determined by

$$\frac{2}{E_{AB}} - \frac{1}{E_{AA}} - \frac{1}{E_{BB}} \qquad (2)$$

$E_{ij}$ being proportional to the intermolecular energies between molecules $i$ and $j$. Equation 2 predicts that the more positive are the values of $V_m^E$ the larger is $E_{AA}$ (ether–ether interactions).

This conclusion agrees with the values of $V_m^E$ being larger for the cyclic diethers than the corresponding monoethers and explains why the values of $V_m^E$ for dioxolane and dioxane or oxolane and oxane are practically the same. Furthermore, in linear diethers, the electronegative O atoms will cause positive polarization of the nearest H atoms, with a consequent electrostatic attraction between molecules, and this effect

**Table III. Experimental Densities, $\rho$, and Excess Molar Volumes, $V^E$, for Binary Mixtures of 2,2,4-Trimethylpentane + Linear and Cyclic Ethers at 298.15 K**

| $x_1$ | $\rho$/ (g cm$^{-3}$) | $V^E$/ (cm$^3$ mol$^{-1}$) | $x_1$ | $\rho$/ (g cm$^{-3}$) | $V^E$/ (cm$^3$ mol$^{-1}$) |
|---|---|---|---|---|---|
| 2,2,4-Trimethylpentane (1) + Dimethoxymethane (2) | | | | | |
| 0.0088 | 0.853 76 | 0.037 | 0.4860 | 0.741 64 | 1.220 |
| 0.0406 | 0.842 78 | 0.186 | 0.5888 | 0.727 29 | 1.182 |
| 0.0790 | 0.830 46 | 0.347 | 0.6244 | 0.722 82 | 1.146 |
| 0.1278 | 0.816 06 | 0.537 | 0.6977 | 0.714 89 | 1.023 |
| 0.1935 | 0.798 69 | 0.752 | 0.7332 | 0.710 60 | 0.951 |
| 0.2617 | 0.782 69 | 0.938 | 0.7936 | 0.704 62 | 0.793 |
| 0.2916 | 0.776 81 | 1.001 | 0.8292 | 0.701 83 | 0.684 |
| 0.3469 | 0.765 80 | 1.098 | 0.9240 | 0.693 36 | 0.338 |
| 0.3883 | 0.757 67 | 1.155 | 0.9689 | 0.689 93 | 0.147 |
| 2,2,4-Trimethylpentane (1) + 1,2-Dimethoxyethane (2) | | | | | |
| 0.0103 | 0.858 73 | 0.041 | 0.4430 | 0.759 61 | 0.875 |
| 0.0373 | 0.850 73 | 0.133 | 0.5246 | 0.746 12 | 0.891 |
| 0.0693 | 0.841 67 | 0.232 | 0.6099 | 0.733 27 | 0.859 |
| 0.1117 | 0.830 24 | 0.356 | 0.6497 | 0.727 69 | 0.824 |
| 0.1591 | 0.818 24 | 0.456 | 0.7718 | 0.712 00 | 0.649 |
| 0.2369 | 0.800 38 | 0.643 | 0.8462 | 0.703 40 | 0.486 |
| 0.2893 | 0.788 78 | 0.729 | 0.8928 | 0.698 36 | 0.360 |
| 0.3349 | 0.779 57 | 0.789 | 0.9427 | 0.693 25 | 0.203 |
| 0.3466 | 0.777 29 | 0.802 | 0.9715 | 0.690 43 | 0.101 |
| 0.3815 | 0.770 65 | 0.836 | | | |
| 2,2,4-Trimethylpentane (1) + 2,2-Dimethoxypropane (2) | | | | | |
| 0.0095 | 0.842 80 | 0.019 | 0.4758 | 0.755 96 | 0.470 |
| 0.0815 | 0.827 18 | 0.148 | 0.5357 | 0.746 86 | 0.466 |
| 0.1427 | 0.814 62 | 0.240 | 0.5997 | 0.737 56 | 0.449 |
| 0.2218 | 0.799 26 | 0.340 | 0.6523 | 0.730 22 | 0.425 |
| 0.2742 | 0.789 62 | 0.387 | 0.6963 | 0.724 27 | 0.397 |
| 0.2966 | 0.785 63 | 0.404 | 0.7741 | 0.714 20 | 0.324 |
| 0.3355 | 0.778 87 | 0.424 | 0.8576 | 0.703 93 | 0.230 |
| 0.3717 | 0.772 73 | 0.441 | 0.9533 | 0.692 87 | 0.080 |
| 0.4138 | 0.765 80 | 0.457 | 0.9790 | 0.690 00 | 0.039 |
| 0.4397 | 0.761 63 | 0.465 | | | |
| 2,2,4-Trimethylpentane (1) + 1,4-Dioxane (2) | | | | | |
| 0.0103 | 1.021 20 | 0.012 | 0.3412 | 0.854 87 | 0.353 |
| 0.0508 | 0.995 46 | 0.058 | 0.3981 | 0.834 07 | 0.393 |
| 0.0926 | 0.970 82 | 0.101 | 0.4550 | 0.814 81 | 0.432 |
| 0.1276 | 0.951 52 | 0.140 | 0.5835 | 0.776 50 | 0.475 |
| 0.1780 | 0.925 62 | 0.196 | 0.6448 | 0.760 39 | 0.476 |
| 0.2043 | 0.912 96 | 0.223 | 0.7492 | 0.735 65 | 0.431 |
| 0.2413 | 0.896 02 | 0.264 | 0.8138 | 0.721 86 | 0.370 |
| 0.2609 | 0.887 43 | 0.282 | 0.9087 | 0.703 50 | 0.217 |
| 0.2851 | 0.877 19 | 0.307 | 0.9634 | 0.693 81 | 0.096 |
| 0.3077 | 0.867 98 | 0.327 | | | |
| 2,2,4-Trimethylpentane (1) + Oxane (2) | | | | | |
| 0.0098 | 0.875 78 | −0.001 | 0.4239 | 0.773 29 | −0.080 |
| 0.0473 | 0.865 26 | −0.020 | 0.5077 | 0.757 7 | −0.076 |
| 0.1360 | 0.839 06 | −0.051 | 0.5541 | 0.749 64 | −0.071 |
| 0.1448 | 0.836 71 | −0.055 | 0.6701 | 0.731 01 | −0.057 |
| 0.1914 | 0.824 65 | −0.064 | 0.7064 | 0.725 61 | −0.052 |
| 0.2572 | 0.808 71 | −0.074 | 0.8033 | 0.712 00 | −0.036 |
| 0.2972 | 0.799 63 | −0.079 | 0.8742 | 0.702 76 | −0.024 |
| 0.3314 | 0.792 14 | −0.081 | 0.9540 | 0.693 04 | −0.013 |
| 0.3505 | 0.788 09 | −0.081 | 0.9599 | 0.692 33 | −0.010 |
| 0.3672 | 0.784 61 | −0.081 | | | |

**Table IV. Values of the Parameters $a_k$ According to Equation 1 and Standard Deviations $\sigma(V^E)$ for 2,2,4-Trimethylpentane (1) + Linear and Cyclic Ethers (2) at 298.15 K**

| ether | $a_0$ | $a_1$ | $a_2$ | $\sigma(V^E)$/ (cm$^3$ mol$^{-1}$) |
|---|---|---|---|---|
| dimethoxymethane | 4.8790 | 0.0155 | −0.1275 | 0.0022 |
| 1,2-dimethoxyethane | 3.5660 | 0.1211 | 0.1711 | 0.0022 |
| 2,2-dimethoxypropane | 1.8798 | −0.0724 | 0.0927 | 0.0024 |
| 1,4-dioxane | 1.8211 | 0.8521 | 0.1704 | 0.0024 |
| oxane | −0.3058 | 0.1502 | −0.0439 | 0.0015 |

should be more efficient when the H atoms are less distant from the O atoms. The $E_{AA}$ values will then increase in the order 2,2-dimethoxypropane, 1,2-dimethoxyethane, and dimethoxymethane, in agreement with the $V_m^E$ values.

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