# Excess Volumes, Dielectric Constants, Refractive Indexes, and Viscosities for Anisole + Methylene Chloride, 1,2-Dichloroethane, Trichloroethene, Tetrachloroethene, and Cyclohexane 

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#### Abstract

Dilatometric measurements of excess volumes, $V_{m}{ }^{\mathrm{E}}$, have been made for anisole + methylene chloride and trichloroethene at 293.15 and 303.15 K , for anisole $+1,2$-dichloroethane at 298.15 and 308.15 K , for anisole + tetrachloroethene at 303.15 and 313.15 K , and for anisole + cyclohexane at 308.15 K . Dielectric constants, refractive indexes, and dynamic viscosities have also been measured for anisole + methylene chloride, 1,2dichloroethane, trichloroethene, tetrachloroethene, and cyclohexane at 303.15 K . The quantities $\Delta \epsilon$ and $\Delta \eta$, which refer, respectively, to the deviations of the dielectric constants and viscosities of the mixtures from the values arising from the mole fraction mixture law, have been calculated. The results of $V_{\mathrm{m}} \mathrm{E}, \Delta \eta$, and refractive indexes for the various systems have been fitted by the method of least squares to the various smoothing equations.


## Introduction

Mixtures of anisole ( $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}$ ) with methylene chloride ( $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ), 1,2-dichloroethane $\left(\mathrm{CH}_{2} \mathrm{ClCH}_{2} \mathrm{Cl}\right)$, trichloroethene $\left(\mathrm{CHClCCl}_{2}\right)$, tetrachloroethene $\left(\mathrm{CCl}_{2} \mathrm{CCl}_{2}\right)$, and cyclohexane $\left(\mathrm{c}-\mathrm{C}_{6} \mathrm{H}_{12}\right)$ are of considerable interest from the viewpoint of the existence of a specific interaction between the components. As described by Mulliken (1), $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}$, which contains a $-\mathrm{OCH}_{3}$ group, can act as a $n \pi$-type donor. Due to the presence of Cl and H atoms in $\mathrm{CHClCCl}_{2}, \mathrm{CH}_{2} \mathrm{ClCH}_{2} \mathrm{Cl}$, and $\mathrm{CH}_{2} \mathrm{Cl}_{2}$, these compounds can act as a $\sigma$-acceptor toward, and be involved in the formation of a hydrogen bond with, $\mathrm{C}_{6} \mathrm{H}_{5}$ $\mathrm{OCH}_{3}$. Also $\mathrm{CCl}_{2} \mathrm{CCl}_{2}$ can act as a $\sigma$-acceptor toward $\mathrm{C}_{6} \mathrm{H}_{5^{-}}$ $\mathrm{OCH}_{3}$. The system $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}+\mathrm{c}-\mathrm{C}_{6} \mathrm{H}_{12}$, in which only nonspecific forces between the components are believed to be present, can be considered as a reference system (2-4). In this work we present excess volumes, $V_{m}{ }^{E}$, dielectric constants, $\epsilon$, refractive indexes, $n$, and viscosities for $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}+\mathrm{CH}_{2}$ $\mathrm{Cl}_{2}, \mathrm{CH}_{2} \mathrm{ClCH}_{2} \mathrm{Cl}, \mathrm{CHClCCl}_{2}, \mathrm{CCl}_{2} \mathrm{CCl}_{2}$, and $\mathrm{c}-\mathrm{C}_{6} \mathrm{H}_{12}$.

## Experimental Section

Materials. Methylene chloride (SRL), cyclohexane (SRL), and tetrachloroethene (E. Merck, Darmstadt, FRG), all spectral grade chemicals, were dried over anhydrous calcium chloride prior to use. 1,2-Dichloroethane (SRL, A.R.) was washed with an aqueous solution of sodium hydrogen carbonate, dried over anhydrous calcium chloride, and then fractionally distilled from phosphorus pentoxide. Trichloroethene (SRL, A.R.) was shaken with an aqueous solution of potassium carbonate, washed with water, dried over anhydrous potassium carbonate and calcium chloride, and then subjected to fractional distillations. Anisole (SRL, A.R.) was distilled from sodium.

Methods. (i) Excess volumes, $V_{m}$ E, were measured with an accuracy of $\pm 0.002 \mathrm{~cm}^{3} \mathrm{~mol}^{-1}$, using a two-limbed Pyrex glass dilatometer (5-7). Known amounts of the two liquid components were confined over mercury in the absence of air spaces in the two limbs of the dilatometer. The dilatometer


Figure 1. $V_{m}{ }^{\mathrm{E}}$ versus $x_{1}$ for the following systems: $\odot, \mathrm{C}_{6} \mathrm{H}_{5^{-}}$ $\mathrm{OCH}_{3}(1)+\mathrm{c}-\mathrm{C}_{6} \mathrm{H}_{12}$ (2) at 308.15 K ; 口, $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{CH}_{2}-$ $\mathrm{ClCH}_{2} \mathrm{Cl}$ (2) at $298.15 \mathrm{~K} ; \nabla, \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{CCl}_{2} \mathrm{CCl}_{2}$ (2) at 313.15 K ; ©, $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}$ (1) $+\mathrm{CH}_{2} \mathrm{Cl}_{2}$ (2) at 293.15 K ; $\mathbf{\Delta}$, $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{CHClCCl}_{2}$ (2) at 293.15 K .
(mounted on a stand) was immersed in a thermostat bath which was controlled to $\pm 0.01 \mathrm{~K}$. The mixing of the components was achieved by rocking the cell back and forth through a defined angle, and the mercury levels in the capillary of the dilatometer were noted with a cathetometer which could read correct to $\pm 0.001 \mathrm{~cm}$.
(ii) Dielectric constants, $\epsilon$, were measured at $303.15 \pm 0.01$ K and at a frequency of 1.8 MHz with a dekameter (type $\mathrm{DK}_{03}$, Wissenschaftlich-Technische, Werkstätten, Germany), using two cells: cell MFL 1/S, no. 2078, for mixtures having $\epsilon<7.0$ and cell MFL 2/S, no. 2084, for mixtures having $\epsilon>$ 7.0, as described previously (4). The precision in $\epsilon$ is $\sim \pm 0.005$ unit for mixtures of $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}+\mathrm{c}-\mathrm{C}_{6} \mathrm{H}_{12}, \mathrm{CHClCCl}_{2}$, and

Table I. Experimental Values of Excess Volumes, $V_{m} \mathbf{E}$, for $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}+\mathrm{CH}_{2} \mathrm{Cl}_{2}, \mathrm{CH}_{2} \mathrm{ClCH}_{2} \mathrm{Cl}, \mathrm{CHClCCl}_{2}, \mathrm{CCl}_{2} \mathrm{CCl}_{2}$, and c- $\mathrm{C}_{6} \mathrm{H}_{12}$ at Various Temperatures

|  | $V_{\mathrm{m}}^{\mathrm{E}} /$ <br> $\left(\mathrm{cm}^{3} \mathrm{~mol}^{-1}\right)$ | $\boldsymbol{x}_{1}$ <br> $\left(\mathrm{~cm}^{3} \mathrm{~mol}^{-1}\right)$ | $x_{1}$ | $V_{\mathrm{m}}^{\mathrm{E}} /$ <br> $\left(\mathrm{cm}^{3} \mathrm{~mol}^{-1}\right)$ |
| :---: | :---: | :---: | :---: | :---: |


| $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{CH}_{2} \mathrm{Cl}_{2}(2)$ |  |  |  |  |  |
| :--- | :--- | :--- | :--- | :--- | :--- |
| $T=293.15 \mathrm{~K}$ |  |  |  |  |  |
| 0.0217 | 0.013 | 0.3647 | 0.097 | 0.6495 | 0.097 |
| 0.1133 | 0.052 | 0.4112 | 0.100 | 0.8333 | 0.064 |
| 0.1789 | 0.073 | 0.4676 | 0.103 | 0.9136 | 0.039 |
| 0.2255 | 0.082 | 0.5542 | 0.100 |  |  |
| 0.3040 | 0.092 | 0.6044 | 0.101 |  |  |
| $T=303.15 \mathrm{~K}$ |  |  |  |  |  |
| 0.0616 | 0.017 | 0.2929 | 0.071 | 0.6278 | 0.090 |
| 0.1421 | 0.037 | 0.3585 | 0.080 | 0.6966 | 0.081 |
| 0.1882 | 0.050 | 0.4036 | 0.082 | 0.8308 | 0.054 |

$\begin{array}{llllll}0.1882 & 0.050 & 0.4036 & 0.082 & 0.8308 & 0.054\end{array}$

| $\mathrm{C}_{8} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{CH}_{2} \mathrm{ClCH}_{2} \mathrm{Cl}$ (2) |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | $T=$ | .15 K |  |  |
| 0.0820 | 0.075 | 0.3290 | 0.188 | 0.6500 | 0.166 |
| 0.1180 | 0.101 | 0.3782 | 0.200 | 0.7083 | 0.145 |
| 0.1674 | 0.131 | 0.4292 | 0.198 | 0.8000 | 0.109 |
| 0.2395 | 0.163 | 0.4859 | 0.198 | 0.8517 | 0.085 |
| 0.2882 | 0.181 | 0.6068 | 0.178 | 0.9008 | 0.057 |
| $T=308.15 \mathrm{~K}$ |  |  |  |  |  |
| 0.0486 | 0.049 | 0.3707 | 0.195 | 0.7131 | 0.137 |
| 0.1616 | 0.136 | 0.4041 | 0.195 | 0.7426 | 0.127 |
| 0.2380 | 0.169 | 0.4518 | 0.195 | 0.8413 | 0.089 |
| 0.2790 | 0.182 | 0.5465 | 0.183 |  |  |
| 0.3411 | 0.192 | 0.6711 | 0.149 |  |  |
| $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{CHClCCl}_{2}(2)$ |  |  |  |  |  |


| $T=293.15 \mathrm{~K}$ |  |  |  |  |  |
| :--- | :--- | :--- | :--- | :--- | :--- |
| 0.0935 | -0.015 | 0.2494 | -0.026 | 0.4754 | -0.020 |
| 0.1533 | -0.020 | 0.2883 | -0.028 | 0.5794 | -0.017 |
| 0.1767 | -0.025 | 0.3344 | -0.022 | 0.6614 | -0.011 |
| 0.2224 | -0.027 | 0.4193 | -0.021 | 0.8873 | -0.004 |
| $T=303.15 \mathrm{~K}$ |  |  |  |  |  |
| 0.0714 | -0.007 | 0.2874 | -0.028 | 0.6057 | -0.018 |
| 0.0993 | -0.010 | 0.3038 | -0.028 | 0.7644 | -0.009 |
| 0.1419 | -0.018 | 0.3332 | -0.030 | 0.8222 | -0.007 |
| 0.1643 | -0.021 | 0.4643 | -0.030 | 0.8728 | -0.005 |
| 0.2345 | -0.023 | 0.5050 | -0.026 |  |  |


| $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{CCl}_{2} \mathrm{CCl}_{2}$ (2) |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $T=303.15 \mathrm{~K}$ |  |  |  |  |  |
| 0.1772 | 0.132 | 0.4340 | 0.195 | 0.7229 | 0.147 |
| 0.1878 | 0.139 | 0.4583 | 0.200 | 0.8093 | 0.114 |
| 0.2036 | 0.148 | 0.5845 | 0.180 | 0.8839 | 0.077 |
| $T=313.15 \mathrm{~K}$ |  |  |  |  |  |
| 0.0866 | 0.088 | 0.3217 | 0.178 | 0.8400 | 0.068 |
| 0.1558 | 0.131 | 0.6863 | 0.122 | 0.9202 | 0.033 |
| 0.2468 | 0.171 | 0.7736 | 0.091 |  |  |
| $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{c}-\mathrm{C}_{6} \mathrm{H}_{12}(2)$ |  |  |  |  |  |
| $T=308.15 \mathrm{~K}$ |  |  |  |  |  |
| 0.1313 | 0.412 | 0.5092 | 0.634 | 0.6744 | 0.503 |
| 0.1621 | 0.477 | 0.5608 | 0.603 | 0.7263 | 0.433 |
| 0.2970 | 0.644 | 0.6228 | 0.552 |  |  |
| 0.3304 | 0.653 | 0.6695 | 0.504 |  |  |

$\mathrm{CCl}_{2} \mathrm{CCl}_{2}$ and $\sim \pm 0.01$ units for mixtures of $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}+$ $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and $\mathrm{CH}_{2} \mathrm{ClCH}_{2} \mathrm{Cl}$.
(iii) Refractive indexes, $n$, were measured at the $\mathrm{Na}{ }^{\mathrm{D}}$ line with an accuracy of $\pm 0.0002$ units at $303.15 \pm 0.01 \mathrm{~K}$ using a thermostated Abbe refractometer (Carl Zeiss).
(iv) The viscosities, $\eta$, which are accurate to $\pm 0.02 \times 10^{-4}$ $\mathrm{kg} \mathrm{m}^{-1} \mathrm{~s}^{-1}$, were measured at $303.15 \pm 0.01 \mathrm{~K}$, by measuring the flow times in a viscometer similar to that described by Tuan and Fuoss (8). The viscometer was calibrated with $\mathrm{CHCl}_{3}$ and $\mathrm{C}_{8} \mathrm{H}_{5} \mathrm{Cl}$. The results were used to calculate constants $A$ and $B$ from the equation

$$
\begin{equation*}
\eta / \rho=A t-B / t \tag{1}
\end{equation*}
$$



Figure 2. $\Delta \epsilon$ versus $x_{1}$ for the following systems at 303.15 $\mathrm{K}: \nabla, \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{CH}_{2} \mathrm{Cl}_{2}$ (2); 回, $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{CH}_{2}$ $\mathrm{ClCH}_{2} \mathrm{Cl}$ (2); $\odot, \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}$ (1) $+\mathrm{CHClCCl}_{2}$ (2); ©, $\mathrm{C}_{6} \mathrm{H}_{5^{-}}$ $\mathrm{OCH}_{3}(1)+\mathrm{CCl}_{2} \mathrm{CCl}_{2}$ (2); $\Delta, \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}$ (1) $+\mathrm{c}-\mathrm{C}_{6} \mathrm{H}_{12}$ (2).
Table 1I. Dielectric Constants \& for $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}+\mathrm{CH}_{2} \mathrm{Cl}_{2}$, $\mathrm{CH}_{2} \mathrm{ClCH}_{2} \mathrm{Cl}_{1} \mathrm{CHClCCl}_{2}, \mathrm{CCl}_{2} \mathrm{CCl}_{2}$, and $\mathrm{c}-\mathrm{C}_{8} \mathrm{H}_{12}$ at 303.15 K

| $x_{1}$ | $\epsilon$ | $x_{1}$ | $\epsilon$ | $x_{1}$ | $\epsilon$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{CH}_{2} \mathrm{Cl}_{2}(2)$ |  |  |  |  |  |
| 0.0000 | 8.704 | 0.3104 | 6.57 | 0.8431 | 4.61 |
| 0.0268 | 8.42 | 0.3365 | 6.43 | 0.8511 | 4.58 |
| 0.0767 | 8.02 | 0.4670 | 5.77 | 0.9199 | 4.422 |
| 0.1111 | 7.77 | 0.5520 | 5.45 | 0.9256 | 4.397 |
| 0.1442 | 7.55 | 0.5885 | 5.31 | 0.9784 | 4.258 |
| 0.1896 | 7.26 | 0.6441 | 5.14 | 1.0000 | 4.247 |
| 0.2587 | 6.85 | 0.7993 | 4.72 |  |  |
| $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{CH}_{2} \mathrm{ClCH}_{2} \mathrm{Cl}$ (2) |  |  |  |  |  |
| 0.0000 | 10.072 | 0.3811 | 6.93 | 0.8373 | 4.768 |
| 0.0281 | 9.85 | 0.4266 | 6.68 | 0.8830 | 4.616 |
| 0.0732 | 9.39 | 0.4755 | 6.40 | 0.9118 | 4.515 |
| 0.1099 | 9.02 | 0.5182 | 6.19 | 0.9604 | 4.363 |
| 0.1477 | 8.67 | 0.5504 | 6.03 | 0.9879 | 4.279 |
| 0.1939 | 8.27 | 0.5900 | 5.843 | 1.0000 | 4.247 |
| 0.2294 | 7.99 | 0.7122 | 5.223 |  |  |
| 0.2868 | 7.56 | 0.7907 | 4.932 |  |  |
| $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{CHClCCl}_{2}(2)$ |  |  |  |  |  |
| 0.0000 | 3.347 | 0.2961 | 3.738 | 0.6870 | 4.049 |
| 0.0102 | 3.367 | 0.3483 | 3.761 | 0.7762 | 4.088 |
| 0.0450 | 3.415 | 0.4242 | 3.826 | 0.8023 | 4.112 |
| 0.0841 | 3.468 | 0.4589 | 3.867 | 0.8213 | 4.119 |
| 0.1227 | 3.519 | 0.4724 | 3.888 | 0.9072 | 4.177 |
| 0.1590 | 3.573 | 0.5439 | 3.942 | 0.8121 | 4.179 |
| 0.1983 | 3.621 | 0.5592 | 3.955 | 1.0000 | 4.247 |
| 0.2215 | 3.649 | 0.6292 | 4.005 |  |  |
| 0.2680 | 3.692 | 0.6647 | 4.030 |  |  |
| $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{CCl}_{2} \mathrm{CCl}_{2}$ (2) |  |  |  |  |  |
| 0.0000 | 2.296 | 0.1861 | 2.629 | 0.6418 | 3.547 |
| 0.0044 | 2.304 | 0.2258 | 2.731 | 0.6846 | 3.653 |
| 0.0055 | 2.306 | 0.2765 | 2.832 | 0.7565 | 3.779 |
| 0.0069 | 2.307 | 0.3289 | 2.915 | 0.8213 | 3.904 |
| 0.0184 | 2.321 | 0.3879 | 3.050 | 0.8796 | 4.002 |
| 0.0573 | 2.405 | 0.4188 | 3.111 | 0.8830 | 4.036 |
| 0.0805 | 2.441 | 0.4887 | 3.237 | 0.9603 | 4.159 |
| 0.1038 | 2.478 | 0.5235 | 3.316 | 0.9959 | 4.226 |
| 0.1477 | 2.554 | 0.5668 | 3.405 | 1.0000 | 4.247 |
| $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{c}-\mathrm{C}_{6} \mathrm{H}_{12}(2)$ |  |  |  |  |  |
| 0.0000 | 2.007 | 0.2192 | 2.430 | 0.6733 | 3.466 |
| 0.0039 | 2.015 | 0.2623 | 2.519 | 0.7232 | 3.580 |
| 0.0123 | 2.036 | 0.2984 | 2.622 | 0.7324 | 3.602 |
| 0.0506 | 2.115 | 0.3302 | 2.694 | 0.7641 | 3.677 |
| 0.0637 | 2.126 | 0.3899 | 2.822 | 0.8474 | 3.879 |
| 0.0756 | 2.145 | 0.4731 | 3.002 | 0.8564 | 3.901 |
| 0.1055 | 2.199 | 0.4850 | 3.160 | 0.9385 | 4.102 |
| 0.1267 | 2.243 | 0.5643 | 3.210 | 1.0000 | 4.247 |
| 0.1950 | 2.393 | 0.6049 | 3.301 |  |  |

The values of $\eta$ and $\rho$ of $\mathrm{CHCl}_{3}$ and $\mathrm{C}_{6} \mathrm{H}_{6} \mathrm{Cl}$, needed to evaluate $A$ and $B$ from eq 1, were obtained from the data available in

Table III. Refractive Indexes for $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}+\mathrm{CH}_{2} \mathrm{Cl}_{2}$, $\mathrm{CH}_{2} \mathrm{ClCH}_{2} \mathrm{Cl}, \mathrm{CHClCCl}_{2}, \mathrm{CCl}_{2} \mathrm{CCl}_{2}$, and $\mathrm{c}-\mathrm{C}_{6} \mathrm{H}_{12}$ at 303.15 K

| $x_{1}$ | $n$ | $x_{1}$ | $n$ | $x_{1}$ | $n$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{CH}_{2} \mathrm{Cl}_{2}$ (2) |  |  |  |  |  |
| 0.0000 | 1.4184 | 0.1431 | 1.4372 | 0.4884 | 1.4758 |
| 0.0335 | 1.4235 | 0.2214 | 1.4478 | 0.7009 | 1.4932 |
| 0.0475 | 1.4248 | 0.2785 | 1.4540 | 0.8911 | 1.5058 |
| 0.0688 | 1.4282 | 0.3051 | 1.4572 | 1.0000 | 1.5116 |
| 0.0923 | 1.4320 | 0.3622 | 1.4632 |  |  |
| $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{CH}_{2} \mathrm{ClCH}_{2} \mathrm{Cl}$ (2) |  |  |  |  |  |
| 0.0000 | 1.4394 | 0.2670 | 1.4618 | 0.5997 | 1.4864 |
| 0.0267 | 1.4418 | 0.2918 | 1.4638 | 0.7783 | 1.4980 |
| 0.0564 | 1.4444 | 0.3427 | 1.4680 | 0.8070 | 1.5002 |
| 0.0725 | 1.4454 | 0.3642 | 1.4692 | 1.0000 | 1.5116 |
| 0.1781 | 1.4546 | 0.3974 | 1.4718 |  |  |
| 0.2160 | 1.4578 | 0.5292 | 1.4815 |  |  |
| $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{CHClCCl}_{2}(2)$ |  |  |  |  |  |
| 0.0000 | 1.4712 | 0.3720 | 1.4880 | 0.5967 | 1.4972 |
| 0.0435 | 1.4732 | 0.4456 | 1.4906 | 0.6428 | 1.4988 |
| 0.0647 | 1.4742 | 0.4896 | 1.4925 | 0.7860 | 1.5043 |
| 0.0813 | 1.4748 | 0.5332 | 1.4942 | 0.8680 | 1.5066 |
| 0.1660 | 1.4792 | 0.5539 | 1.4948 | 0.9260 | 1.5088 |
| 0.2139 | 1.4812 | 0.5822 | 1.4958 | 1.0000 | 1.5116 |
| $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{CCl}_{2} \mathrm{CCl}_{2}(2)$ |  |  |  |  |  |
| 0.0000 | 1.5002 | 0.2537 | 1.5028 | 0.6133 | 1.5072 |
| 0.0414 | 1.5010 | 0.3072 | 1.5034 | 0.6322 | 1.5074 |
| 0.0717 | 1.5014 | 0.4719 | 1.5056 | 0.7074 | 1.5082 |
| 0.1086 | 1.5018 | 0.5101 | 1.5060 | 0.8111 | 1.5096 |
| 0.1386 | 1.5020 | 0.5341 | 1.5062 | 0.9509 | 1.5110 |
| 0.2159 | 1.5026 | 0.5657 | 1.5067 | 1.0000 | 1.5116 |
| $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{c}-\mathrm{C}_{6} \mathrm{H}_{12}(2)$ |  |  |  |  |  |
| 0.0000 | 1.4202 | 0.1688 | 1.4338 | 0.7863 | 1.4898 |
| 0.0553 | 1.4252 | 0.1957 | 1.4360 | 0.8308 | 1.4948 |
| 0.0999 | 1.4285 | 0.3563 | 1.4502 | 0.9068 | 1.5028 |
| 0.1029 | 1.4286 | 0.4247 | 1.4558 | 1.0000 | 1.5116 |
| 0.1272 | 1.4302 | 0.6306 | 1.4752 |  |  |

Table IV. Dynamic Viscosities for $\mathrm{C}_{6} \mathrm{H}_{5} \mathbf{O C H}_{3}+\mathrm{CH}_{2} \mathrm{Cl}_{2}$, $\mathrm{CH}_{2} \mathrm{ClCH}_{2} \mathrm{Cl}^{2} \mathrm{CHClCCl}_{2}, \mathrm{CCl}_{2} \mathrm{CCl}_{2}$, and $\mathrm{c}-\mathrm{C}_{6} \mathrm{H}_{12}$ at 303.15 K

| $x_{1}$ | $\begin{gathered} \eta /\left(10^{-4}\right. \\ \left.\mathbf{k g ~ m} \mathrm{m}^{-1} \mathrm{~s}^{-1}\right) \end{gathered}$ | $x_{1}$ | $\begin{gathered} \eta /\left(10^{-4}\right. \\ \left.\mathrm{kg} \mathrm{~m}^{-1} \mathrm{~s}^{-1}\right) \end{gathered}$ | $x_{1}$ | $\begin{gathered} \eta /\left(10^{-4}\right. \\ \left.\mathrm{kg} \mathrm{~m}^{-1} \mathrm{~s}^{-1}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{CCl}_{2} \mathrm{CCl}_{2}(2)$ |  |  |  |  |  |
| 0.0000 | 7.99 | 0.2742 | 7.83 | 0.7292 | 8.56 |
| 0.0193 | 7.93 | 0.3317 | 7.87 | 0.7745 | 8.62 |
| 0.0390 | 7.90 | 0.3643 | 7.90 | 0.8665 | 8.78 |
| 0.0561 | 7.92 | 0.4286 | 8.01 | 0.8991 | 8.85 |
| 0.1158 | 7.81 | 0.4726 | 8.12 | 0.9485 | 8.99 |
| 0.1890 | 7.76 | 0.6096 | 8.31 | 1.0000 | 9.15 |
| 0.2303 | 7.78 | 0.6829 | 8.48 |  |  |
| $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{CHClCCl}_{2}(2)$ |  |  |  |  |  |
| 0.0000 | 5.09 | 0.2818 | 5.77 | 0.6480 | 7.30 |
| 0.1234 | 5.23 | 0.4018 | 6.23 | 0.7243 | 7.65 |
| 0.1791 | 5.41 | 0.5204 | 6.72 | 0.8135 | 8.14 |
| 0.2335 | 5.61 | 0.5501 | 6.82 | 1.0000 | 9.15 |
| $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}$ (1) $+\mathrm{CH}_{2} \mathrm{ClCH}_{2} \mathrm{Cl}$ (2) |  |  |  |  |  |
| 0.0000 | 7.30 | 0.3833 | 7.40 | 0.6717 | 7.97 |
| 0.0479 | 7.08 | 0.5479 | 7.76 | 0.9751 | 8.96 |
| 0.2944 | 7.26 | 0.6192 | 7.85 | 1.0000 | 9.15 |
| $\mathrm{C}_{8} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{CH}_{2} \mathrm{Cl}_{2}(2)$ |  |  |  |  |  |
| 0.0000 | 3.94 | 0.3570 | 5.40 | 0.6580 | 6.88 |
| 0.0690 | 4.25 | 0.4045 | 5.67 | 0.8807 | 8.20 |
| 0.3210 | 5.27 | 0.6109 | 6.65 | 1.0000 | 9.15 |
| $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{c}-\mathrm{C}_{6} \mathrm{H}_{12}(2)$ |  |  |  |  |  |
| 0.0000 | 8.21 | 0.4829 | 7.08 | 0.7744 | 7.92 |
| 0.0224 | 7.99 | 0.5172 | 7.14 | 0.8952 | 8.46 |
| 0.0385 | 7.83 | 0.5409 | 7.20 | 0.9478 | 8.84 |
| 0.0614 | 7.73 | 0.5731 | 7.29 | 1.0000 | 9.15 |

the literature $(9,10)$. The values of $A$ and $B$ for the viscometer used for the present measurements were found to be 0.030952 $\times 10^{-7} \mathrm{~m}^{2} \mathrm{~s}^{-2}$ and $80.298727 \times 10^{-7} \mathrm{~m}^{2}$, respectively. The densities of the mixtures were calculated using the excess volume values reported in this paper.

## Results and Discussion

The excess volumes $V_{m}{ }^{\mathrm{E}}$ for $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}+\mathrm{CH}_{2} \mathrm{Cl}_{2}, \mathrm{CH}_{2}$ $\mathrm{ClCH}_{2} \mathrm{Cl}, \mathrm{CHClCCl}_{2}, \mathrm{CCl}_{2} \mathrm{CCl}_{2}$, and $\mathrm{c}-\mathrm{C}_{6} \mathrm{H}_{12}$ at various temperatures are given in Table I, and the dielectric constants $\epsilon$ at 303.15 K are given in Table II. The refractive indexes $n$ for the same systems at 303.15 K are given in Table III, and dynamic viscosities $\eta$ are given in Table IV. The experimental values of $\epsilon$ for $\mathrm{CH}_{2} \mathrm{Cl}_{2}, \mathrm{CH}_{2} \mathrm{ClCH}_{2} \mathrm{Cl}, \mathrm{CHClCCl}_{2}, \mathrm{CCl}_{2} \mathrm{CCl}_{2}$, $\mathrm{c}-\mathrm{C}_{6} \mathrm{H}_{12}$, and $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}$ at 303.15 K are found to be 8.704, $10.072,3.347,2.296,2.0070$, and 4.247 , respectively, which are in good agreement with the literature $(2,11)$ values 8.712 , $10.076,3.340,2.290,2.0070$, and 4.250 , respectively. The experimental values of the refractive indexes $n$ for the pure liquids are in good agreement with the literature $(9,10)$ values. The values of $10^{4} \eta$ for $\mathrm{CH}_{2} \mathrm{Cl}_{2}, \mathrm{CH}_{2} \mathrm{ClCH}_{2} \mathrm{Cl}, \mathrm{CCl}_{2} \mathrm{CCl}_{2}$, and $\mathrm{c}-\mathrm{C}_{6} \mathrm{H}_{12}$ at 303.15 K are found to be $3.94,7.30,7.99$, and 8.21 $\mathrm{kg} \mathrm{m}^{-1} \mathrm{~s}^{-1}$, respectively, which are in good agreement with the literature $(9,10)$ values of $3.93,7.30,7.98$, and $8.20 \mathrm{~kg} \mathrm{~m}^{-1} \mathrm{~s}^{-1}$, respectively. The value of $\eta$ for $\mathrm{CHClCCl}_{2}$ at 303.15 K is 5.09 $\times 10^{-4} \mathrm{~kg} \mathrm{~m}^{-1} \mathrm{~s}^{-1}$, whereas the literature (10) value of $\eta$ for $\mathrm{CHClCCl}_{2}$ is $5.66 \times 10^{-4} \mathrm{~kg} \mathrm{~m}^{-1} \mathrm{~s}^{-1}$ at 293.15 K and $5.32 \times 10^{-4}$ $\mathrm{kg} \mathrm{m} \mathrm{m}^{-1} \mathrm{~s}^{-1}$ at 298.15 K . The value of $\eta$ for $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}$ at 303.15 K , as reported by Timmermann (9) is $7.89 \times 10^{-4} \mathrm{~kg} \mathrm{~m}^{-1} \mathrm{~s}^{-1}$, whereas our value of $\eta$ for $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}$ at 303.15 K is $9.15 \times$ $10^{-4} \mathrm{~kg} \mathrm{~m}^{-1} \mathrm{~s}^{-1}$, which is in very good agreement with the value $9.15 \times 10^{-4} \mathrm{~kg} \mathrm{~m}^{-1} \mathrm{~s}^{-1}$ based on the viscosity data for $\mathrm{C}_{6} \mathrm{H}_{5}-$ $\mathrm{OCH}_{3}$ as available in the literature (12). The value of $\eta$ for $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}$ at 303.15 K , as reported by Geddes and Bingham (13), is $9.28 \times 10^{-4} \mathrm{~kg} \mathrm{~m}^{-1} \mathrm{~s}^{-1}$.

The $V_{\mathrm{m}}{ }^{\mathrm{E}}$ for $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}+\mathrm{CH}_{2} \mathrm{Cl}_{2}, \mathrm{CH}_{2} \mathrm{ClCH}_{2} \mathrm{Cl}, \mathrm{CHClCCl}_{2}$, $\mathrm{CCl}_{2} \mathrm{CCl}_{2}$, and $\mathrm{c}-\mathrm{C}_{6} \mathrm{H}_{12}$ at various temperatures have been fitted by the method of least squares to the equation

$$
\begin{align*}
V_{\mathrm{m}}^{\mathrm{E}} /\left(\mathrm{cm}^{3} \mathrm{~mol}^{-1}\right) & = \\
& x_{1} x_{2}\left[A_{0}+A_{1}\left(x_{1}-x_{2}\right)+A_{2}\left(x_{1}-x_{2}\right)^{2}\right] \tag{2}
\end{align*}
$$

where $x_{1}$ and $x_{2}$ refer to the mole fractions of $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}$ and the second component, respectively, and $A_{0}, A_{1}$, and $A_{2}$ are constants characteristic of a system at a given temperature. The values of the constants $A_{0}, A_{1}$, and $A_{2}$ of eq 2 , and those of the standard deviations $\delta\left(V_{m}{ }^{E}\right)$ for the various systems are given in Table $V$. The values of $V_{m}{ }^{E}$ for each system at one temperature have been plotted against $x_{1}$ in Figure 1. The experimental values of the refractive indexes $n_{12}$ of the various present mixtures have been fitted by the method of least squares to the equation

$$
\begin{equation*}
n_{12}=a+b x_{1}+c x_{1}^{2} \tag{3}
\end{equation*}
$$

where $a, b$, and $c$ are constants. The values of the constants along with those of the standard deviations $\delta(n)$ for the various systems are given in Table VI. The dielectric constants $\epsilon$ of the various mixtures have been used to calculate the quantity $\Delta \epsilon$ (see Figure 2) from the relation

$$
\begin{equation*}
\Delta \epsilon=\epsilon-x_{1} \epsilon_{1}-x_{2} \epsilon_{2} \tag{4}
\end{equation*}
$$

where $\epsilon_{1}$ and $\epsilon_{2}$ refer to the dielectric constants of the two pure components 1 and 2.

The experimental values of the dynamic viscosities $\eta$ of the various mixtures have been used to calculate the quantity $\Delta \eta$

Table V. Values of the Constants $A_{0}, A_{1}$, and $A_{2}$ of Equation 2 and the Standard Deviations $\delta\left(V_{\mathrm{m}} \mathbf{E}\right)$ for $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{\mathbf{3}}+\mathrm{CH}_{2} \mathrm{Cl}_{2}$, $\mathrm{CH}_{2} \mathrm{ClCH}_{2} \mathrm{Cl}, \mathrm{CHClCCl}_{2}, \mathrm{CCl}_{2} \mathrm{CCl}_{2}$, and $\mathrm{c}-\mathrm{C}_{6} \mathrm{H}_{12}$

| system | $T / \mathrm{K}$ | $A_{0}$ | $A_{1}$ | $A_{2}$ | $\delta\left(V_{\mathrm{m}} \mathrm{E}\right) /\left(\mathrm{cm}^{3} \mathrm{~mol}^{-1}\right)$ |
| :--- | :---: | ---: | ---: | ---: | ---: |
| $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{CH}_{2} \mathrm{Cl}_{2}(2)$ | 293.15 | 0.3978 | -0.0251 | 0.2055 | 0.0026 |
| $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{CH}_{2} \mathrm{ClCH}_{2} \mathrm{Cl}(2)$ | 303.15 | 0.3656 | 0.0541 | -0.0324 | 0.0016 |
|  | 298.15 | 0.1827 | -0.2006 | 0.0535 | 0.0014 |
| $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{CHClCCl}_{2}(2)$ | 308.15 | 0.7760 | -0.2589 | 0.0527 | 0.0034 |
| $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{CCl}_{2} \mathrm{CCl}_{2}(2)$ | 293.15 | -0.0773 | 0.0910 | -0.0523 | 0.0018 |
| $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{c}-\mathrm{C}_{6} \mathrm{H}_{12}(2)$ | 303.15 | -0.1120 | 0.0663 | 0.0575 | 0.0023 |
|  | 303.15 | 0.7750 | -0.1381 | 0.1291 | 0.0027 |
|  | 313.15 | 0.6790 | -0.3798 | 0.1516 | 0.0026 |

Table VI. Values of the Constants $a, b$, and $c$ of Equation 3 and the Standard Deviations $\delta(n)$ for $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}+\mathrm{CH}_{2} \mathrm{Cl}_{2}$, $\mathrm{CH}_{2} \mathrm{ClCH}_{2} \mathrm{Cl}, \mathrm{CHClCCl}_{2}, \mathrm{CCl}_{2} \mathrm{CCl}_{2}$, and c-C $\mathrm{C}_{6} \mathrm{H}_{12}$ at 303.15 K

| system | $a$ | $b$ | $c$ | $\delta(n)$ |
| :--- | :--- | :--- | :--- | :--- |
| $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{CH}_{2} \mathrm{Cl}_{2}(2)$ | 1.418651 | 0.140364 | -0.047629 | 0.00033 |
| $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{CH}_{2} \mathrm{ClCH}_{2} \mathrm{Cl}(2)$ | 1.439118 | 0.090148 | -0.018176 | 0.00028 |
| $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{CHCClCl}_{2}(2)$ | 1.471549 | 0.044811 | -0.04605 | 0.00032 |
| $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{CCl}_{2} \mathrm{CCl}_{2}(2)$ | 1.50054 | 0.009610 | 0.001691 | 0.00018 |
| $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{c}_{6} \mathrm{C}_{6} \mathrm{H}_{12}(2)$ | 1.420589 | 0.076499 | 0.015101 | 0.00036 |

Table VII. Values of the Constants $B_{0}, B_{1}$, and $B_{2}$ of Equation 6, the Standard Deviations $\delta(\Delta \eta)$, Maximum Percentage Deviations $\Delta_{\text {max }} / \%$, Average Percentage Deviations $\Delta_{\text {av }} / \%$, and the Average Values of the Parameter $d$ for $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}+$ $\mathrm{CH}_{2} \mathrm{Cl}_{2}, \mathrm{CH}_{2} \mathrm{ClCH}_{2} \mathrm{Cl}^{2}, \mathrm{CHClCCl}_{2}, \mathrm{CCl}_{2} \mathrm{CCl}_{2}$, and $\mathrm{c}-\mathrm{C}_{6} \mathrm{H}_{12}$ at 303.15 K

| system | $B_{0}$ | $B_{1}$ | $B_{2}$ | $\delta(\Delta \eta) /\left(10^{-4} \mathrm{~kg} \mathrm{~m}^{-1} \mathrm{~s}^{-1}\right)$ | $\Delta_{\max } / \%$ | $\Delta_{\mathrm{av}} / \%$ | $d_{\mathrm{av}}$ |
| :--- | :---: | ---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{CCl}_{2} \mathrm{CCl}_{2}(2)$ | -1.7237 | 0.8383 | -1.2381 | 0.026 | 0.58 | 0.21 | -0.26 |
| $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{CHCCCl}_{2}(2)$ | -1.9659 | 0.8120 | -0.7777 | 0.027 | 0.57 | 0.32 | -0.17 |
| $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{CH}_{2} \mathrm{ClCH}_{2} \mathrm{Cl}(2)$ | -1.9793 | 0.3055 | -5.7162 | 0.059 | 0.69 | 0.52 | -0.43 |
| $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{CH}_{2} \mathrm{Cl}_{2}(2)$ | -1.8648 | -0.5608 | 0.5064 | 0.041 | 0.73 | 0.38 | +0.02 |
| $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}(1)+\mathrm{c}-\mathrm{C}_{6} \mathrm{H}_{12}(2)$ | -6.3214 | 2.5780 | -2.3120 | 0.036 | 0.65 | 0.31 | -0.90 |

from the relation

$$
\begin{equation*}
\Delta \eta=\eta-x_{1} \eta_{1}-x_{2} \eta_{2} \tag{5}
\end{equation*}
$$

The values of the quantity $\Delta \eta$ for the various mixtures have been fitted by the method of least squares to the equation

$$
\begin{align*}
& \Delta \eta /\left(10^{-4} \mathrm{~kg} \mathrm{~m}^{-1} \mathrm{~s}^{-1}\right)= \\
& \qquad x_{1} x_{2}\left[B_{0}+B_{1}\left(x_{1}-x_{2}\right)+B_{2}\left(x_{1}-x_{2}\right)^{2}\right] \tag{6}
\end{align*}
$$

The values of $B_{0}, B_{1}$, and $B_{2}$ of eq 6 , along with the standard deviations $\delta(\Delta \eta)$ are given in Table VII. The maximum percentage deviations, $\Delta_{\max } / \%$, and average percentage deviations, $\Delta_{\mathrm{av}} / \%$, of the experimental values of $\Delta \eta$ from those obtained from eq 6 are also given in Table VII. Attempts have been made to describe the viscosities of the mixtures in terms of the viscosities of the pure components and a parameter attributed to the intermolecular interaction between them. According to Grunberg and Nissan (14), the viscosity $\eta$ of a binary mixture is represented by the equation

$$
\begin{equation*}
\ln \eta=x_{1} \ln \eta_{1}+x_{2} \ln \eta_{2}+x_{1} x_{2} d \tag{7}
\end{equation*}
$$

In eq $7, d$ is a parameter proportional to $\omega / R T$, where $\omega$ is an interchange energy. The average values of $d$ for the various systems are given in Table VII.

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Registry No. $\mathrm{CH}_{2} \mathrm{Cl}_{2}, 75-09-2$; $\mathrm{C}_{2} \mathrm{Cl}_{4}$, 127-18-4; anisole, $100-$ 66-3; 1,2-dichloroethane, 107-06-2; trichloroethene, 79-01-6; cyclohexane, 110-82-7.

