*International Journal of Thermophysics, Vol. 21, No. 3, 2000*

# Viscosities and Excess Molar Volumes of Binary Mixtures of Alkyl Acetates with Di-, Tri-, and Tetrachloroethane

**S. L. Oswal,[1,4] I. N. Patel,[1,2] P. S. Modi,[1,3] and S. A. Barad[1]**

*Received June 24, 1999*

The excess molar volume $V^{E}$, viscosity deviation $\Delta\eta$, excess viscosity $\eta^{E}$, and excess Gibbs energy of activation $\Delta G^{*E}$ of viscous flow have been investigated from density $\rho$ and viscosity $\eta$ measurements of nine binary mixtures of methyl acetate, ethyl acetate, and amyl acetate with dichloroethane, trichloroethane, and tetrachloroethane at 303.15 K. The results were fitted to polynomials of variable degree. The viscosity data have been correlated with the equations of Grunberg and Nissan, Hind, McLaughlin, and Ubbelohde, Tamura and Kurata, Katti and Chaudhri, McAllister, Heric, and Auslaender. The results have been analyzed in terms of molecular interactions between alkyl acetates and chloroethanes.

**KEY WORDS:** alkyl acetates; binary liquid mixtures; chloroethanes; correlating equations; densities; excess molar volumes; Gibbs energy of activation; molecular interactions; viscosities.

## 1. INTRODUCTION

In previous papers [1–3] measurements on the viscosities $\eta$ and the excess molar volumes $V^{E}$ for binary mixtures of methyl acetate, ethyl acetate, amyl acetate, and isoamyl acetate with hexane, tetrachloromethane, and trichloromethane have been reported. The results were explained by considering the disruption of dipolar order in acetates and the specific interactions between acetates and chloromethanes. As an extension of our studies,

---

[1] Department of Chemistry, South Gujarat University, Surat 395 007, India.

[2] Present address: Department of Chemistry, B.K.M. Science College, Valsad 396 001, India.

[3] Present address: Department of Chemistry, Jayendrapuri Arts and Science College, Bharuch, India.

[4] To whom correspondence should be addressed.

in this paper we report measurements on viscosities $\eta$ and excess molar volumes $V^E$ for binary mixtures of methyl acetate (MA), ethyl acetate (EA), and *n*-amyl acetate (nAA) with 1,2-dichloroethane (diCE), 1,1,1-trichloroethane (triCE), and 1,1,2,2-tetrachloroethane (tetCE).

## 2. EXPERIMENTAL

### 2.1. Materials

The source and purification process of the pure liquids methyl acetate, ethyl acetate, amyl acetate, dichloroethane, trichloroethane, and tetrachloroethane have been described in our earlier papers [1, 4]. The purity of the liquid samples was checked by gas–liquid chromatography and by measuring their physical properties. The measured values of the densities, refractive indices, and viscosities are in very good agreement with literature values. The estimated purity was better than 99.8 mol% for all samples.

### 2.2. Method

Densities $\rho$ at 303.15 K were measured with an Anton Paar vibrating-tube densimeter (Model DMA 60/602) with a thermostated bath controlled to $\pm 0.01$ K. The viscosities $\eta$ were measured at the same temperature with a modified suspended-level Ubbelohde viscometer [5]. The viscometer was designed so as to minimize surface tension effects [6]. The details of the methods and techniques used to determine $\rho$ and $\eta$ have been described previously [7, 8].

The mixtures were prepared by mixing known masses of pure liquids in airtight, narrow-mouth ground stoppered bottles taking due precautions to minimize the evaporation losses. All mass measurements were performed on an electronic balance (Mettler AE 163, Switzerland) accurate to 0.01 mg. The possible error in the mole fraction is estimated to be less than $\pm 1 \times 10^{-4}$. The errors in viscosity $\eta$ and the density $\rho$ were estimated to be less than $\pm 2 \times 10^{-3}\ \mathrm{mPa \cdot s}$ and $\pm 2 \times 10^{-2}\ \mathrm{kg \cdot m^{-3}}$, respectively.

## 3. CORRELATING EQUATIONS

Several semiempirical relations have been proposed to estimate the dynamic viscosity $\eta$ of liquid mixtures in terms of pure-component data [9–11]. We have examined equations proposed by Grunberg and Nissan [12], Tamura and Kurata [13], Hind et al. [14], Katti and Chaudhri [15], McAllister [16], Heric [17], and Auslaender [18]. These equations are presented as Eqs. (5)–(11) in Ref. 3.

The correlating ability of each of Eqs. (5)–(11) in Ref. 3 was tested by calculating the standard percentage deviations $\sigma(\%)$ between the experimental and the calculated viscosity as

$$\sigma(\%)=\left[\frac{1}{n-k}\sum\left\{\frac{100(\eta_{\exp}-\eta_{\mathrm{cal}})}{\eta_{\exp}}\right\}^{2}\right]^{1/2} \tag{1}$$

where $n$ represents the number of data points and $k$ is the number of numerical coefficients in the respective equations. The values of the standard deviations $\sigma(\%)$ were obtained from the experimental viscosity data by the method of least squares, with equal weights assigned to each point.

## 4. RESULTS

The viscosity $\eta$ and density $\rho$ for pure liquids and binary mixtures were measured as a function of mole fraction at 303.15 K, and the results are given in Table I. For a compact and smooth representation, the values of $\eta$ were fitted to a polynomial equation of the form

$$\eta=\sum_{i=0}^{m} A_i x_i \tag{2}$$

where $x_i$ is the mole fraction of component $i$. The coefficients $A_i$ obtained from a least-squares fit with equal weights assigned to each point are listed in Table II together with the standard deviations $\sigma$.

The excess molar volumes $V^{\mathrm{E}}$ were calculated from the molar masses $M_i$ and the densities of the pure liquids $\rho_i$ and the mixtures $\rho$ as

$$V^{\mathrm{E}}=\sum_{i=1}^{2} x_i M_i[(1/\rho)-(1/\rho_i)] \tag{3}$$

The viscosity deviations from a linear dependence on mole fraction were calculated by

$$\Delta\eta=\eta-\sum_{i=1}^{2} x_i\eta_i \tag{4}$$

Quantitatively, according to the absolute reaction rates theory [19], the deviations of the viscosities from the ideal mixture values (i.e., the excess viscosity $\eta^{\mathrm{E}}$) can be calculated as [20, 21]

$$\eta^{\mathrm{E}}=\eta-\exp\left(\sum_{i=1}^{2} x_i \ln(\eta_i)\right) \tag{5}$$

**Table I.** Densities, Viscosities, Excess Molar Volumes, Excess Viscosity, and Gibbs Energy of Activation of Viscous Flow for Alkyl Acetate + Chloroethane at 303.15 K

| $x_1$ | $\rho$ $(\mathrm{kg \cdot m^{-3}})$ | $\eta$ $(\mathrm{mPa \cdot s})$ | $V^E$ $(\mathrm{cm^3 \cdot mol^{-1}})$ | $\eta^E$ $(\mathrm{mPa \cdot s})$ | $\Delta G^{*E}$ $(\mathrm{J \cdot mol^{-1}})$ |
|---|---|---|---|---|---|
| | | (1) Methyl acetate + 1,2-dichloroethane | | | |
| 0.0000 | 1238.37 | 0.7239 | | | |
| 0.1016 | 1204.34 | 0.6754 | 0.1046 | 0.0040 | 18 |
| 0.1990 | 1172.06 | 0.6342 | 0.1901 | 0.0096 | 44 |
| 0.2978 | 1139.53 | 0.5940 | 0.2698 | 0.0136 | 66 |
| 0.4014 | 1106.02 | 0.5517 | 0.3179 | 0.0142 | 75 |
| 0.4966 | 1075.82 | 0.5168 | 0.3234 | 0.0159 | 89 |
| 0.5959 | 1044.75 | 0.4819 | 0.2995 | 0.0166 | 97 |
| 0.6976 | 1013.25 | 0.4445 | 0.2513 | 0.0130 | 82 |
| 0.8973 | 952.24 | 0.3780 | 0.0865 | 0.0059 | 42 |
| 1.0000 | 920.85 | 0.3448 | | | |
| | | (2) Ethyl acetate + 1,2-dichloroethane | | | |
| 0.0000 | 1238.37 | 0.7239 | | | |
| 0.0990 | 1195.76 | 0.6790 | 0.0436 | −0.0037 | −6 |
| 0.2036 | 1153.04 | 0.6354 | 0.0788 | −0.0063 | −12 |
| 0.3005 | 1115.42 | 0.6020 | 0.1010 | −0.0039 | 0 |
| 0.3976 | 1079.51 | 0.5686 | 0.1100 | −0.0035 | 1 |
| 0.4996 | 1043.54 | 0.5353 | 0.1081 | −0.0033 | 2 |
| 0.6025 | 1008.92 | 0.5057 | 0.0964 | −0.0010 | 11 |
| 0.6983 | 978.16 | 0.4784 | 0.0703 | −0.0004 | 11 |
| 0.7998 | 946.81 | 0.4505 | 0.0466 | −0.0004 | 8 |
| 0.9034 | 916.19 | 0.4236 | 0.0121 | −0.0005 | 2 |
| 1.0000 | 888.55 | 0.4005 | | | |
| | | (3) *n*-Amyl acetate + 1,2-dichloroethane | | | |
| 0.0000 | 1238.37 | 0.7239 | | | |
| 0.1052 | 1171.60 | 0.7366 | −0.0449 | 0.0098 | 88 |
| 0.1960 | 1122.51 | 0.7444 | −0.0921 | 0.0150 | 138 |
| 0.3030 | 1072.60 | 0.7582 | −0.1508 | 0.0258 | 197 |
| 0.4004 | 1033.03 | 0.7651 | −0.1887 | 0.0300 | 220 |
| 0.4924 | 999.87 | 0.7693 | −0.2112 | 0.0316 | 225 |
| 0.5994 | 965.54 | 0.7716 | −0.2146 | 0.0309 | 212 |
| 0.7020 | 936.23 | 0.7686 | −0.1971 | 0.0249 | 174 |
| 0.8050 | 909.82 | 0.7620 | −0.1622 | 0.0154 | 117 |
| 0.8946 | 888.86 | 0.7597 | −0.1034 | 0.0105 | 73 |
| 1.0000 | 866.28 | 0.7522 | | | |

**Table I.** *(Continued)*

| $x_1$ | $\rho$ $(\mathrm{kg \cdot m^{-3}})$ | $\eta$ $(\mathrm{mPa \cdot s})$ | $V^{\mathrm{E}}$ $(\mathrm{cm^3 \cdot mol^{-1}})$ | $\eta^{\mathrm{E}}$ $(\mathrm{mPa \cdot s})$ | $\Delta G^{*\mathrm{E}}$ $(\mathrm{J \cdot mol^{-1}})$ |
|---|---|---|---|---|---|
| (4) Methyl acetate + 1,1,1-trichloroethane | | | | | |
| 0.0000 | 1321.40 | 0.7275 | | | |
| 0.0993 | 1287.77 | 0.6661 | 0.0986 | −0.0094 | −27 |
| 0.2042 | 1251.25 | 0.6072 | 0.1666 | −0.0174 | −56 |
| 0.3008 | 1216.47 | 0.5599 | 0.2083 | −0.0213 | −75 |
| 0.4008 | 1179.35 | 0.5182 | 0.2190 | −0.0211 | −79 |
| 0.5039 | 1139.46 | 0.4792 | 0.2200 | −0.0202 | −81 |
| 0.6038 | 1099.26 | 0.4462 | 0.1996 | −0.0173 | −74 |
| 0.6968 | 1060.27 | 0.4186 | 0.1680 | −0.0138 | −62 |
| 0.7992 | 1015.34 | 0.3921 | 0.1275 | −0.0085 | −39 |
| 0.9020 | 968.17 | 0.3668 | 0.0631 | −0.0042 | −20 |
| 1.0000 | 920.85 | 0.3448 | | | |
| (5) Ethyl acetate + 1,1,1-trichloroethane | | | | | |
| 0.0000 | 1321.40 | 0.7275 | | | |
| 0.1006 | 1277.48 | 0.6668 | 0.0848 | −0.0183 | −66 |
| 0.1989 | 1235.06 | 0.6158 | 0.1206 | −0.0303 | −117 |
| 0.2986 | 1192.13 | 0.5731 | 0.1387 | −0.0356 | −148 |
| 0.4038 | 1146.85 | 0.5366 | 0.1431 | −0.0351 | −155 |
| 0.4965 | 1106.85 | 0.5101 | 0.1434 | −0.0308 | −144 |
| 0.5999 | 1062.26 | 0.4831 | 0.1265 | −0.0254 | −126 |
| 0.7003 | 1018.75 | 0.4579 | 0.1141 | −0.0211 | −110 |
| 0.7974 | 976.74 | 0.4366 | 0.0785 | −0.0154 | −85 |
| 0.9008 | 931.75 | 0.4167 | 0.0469 | −0.0082 | −48 |
| 1.0000 | 888.55 | 0.4005 | | | |
| (6) *n*-Amyl acetate + 1,1,1-trichloroethane | | | | | |
| 0.0000 | 1321.40 | 0.7275 | | | |
| 0.1040 | 1255.78 | 0.7366 | −0.1209 | 0.0066 | 40 |
| 0.1989 | 1201.41 | 0.7441 | −0.2605 | 0.0118 | 68 |
| 0.2995 | 1148.34 | 0.7518 | −0.3975 | 0.0170 | 92 |
| 0.4018 | 1098.36 | 0.7568 | −0.4950 | 0.0195 | 104 |
| 0.5014 | 1053.05 | 0.7653 | −0.5368 | 0.0255 | 124 |
| 0.5996 | 1011.21 | 0.7667 | −0.5148 | 0.0245 | 118 |
| 0.6961 | 972.61 | 0.7663 | −0.4340 | 0.0217 | 104 |
| 0.7935 | 936.18 | 0.7658 | −0.3253 | 0.0188 | 86 |
| 0.8993 | 899.12 | 0.7589 | −0.1615 | 0.0092 | 44 |
| 1.0000 | 866.28 | 0.7522 | | | |

**Table I.** *(Continued)*

| $x_1$ | $\rho$ $(\mathrm{kg \cdot m^{-3}})$ | $\eta$ $(\mathrm{mPa \cdot s})$ | $V^{\mathrm{E}}$ $(\mathrm{cm^3 \cdot mol^{-1}})$ | $\eta^{\mathrm{E}}$ $(\mathrm{mPa \cdot s})$ | $\Delta G^{*\mathrm{E}}$ $(\mathrm{J \cdot mol^{-1}})$ |
|---|---|---|---|---|---|
| (7) Methyl acetate + 1,1,2,2-tetrachloroethane | | | | | |
| 0.0000 | 1578.66 | 1.4845 | | | |
| 0.1030 | 1528.59 | 1.3792 | −0.1704 | 0.1019 | 197 |
| 0.1999 | 1478.88 | 1.2678 | −0.3283 | 0.1590 | 344 |
| 0.3012 | 1423.75 | 1.1470 | −0.4746 | 0.1907 | 465 |
| 0.3998 | 1366.36 | 1.0292 | −0.5713 | 0.2011 | 555 |
| 0.5031 | 1302.06 | 0.8951 | −0.6260 | 0.1829 | 583 |
| 0.6017 | 1236.16 | 0.7640 | −0.6131 | 0.1473 | 546 |
| 0.6999 | 1165.97 | 0.6464 | −0.5431 | 0.1120 | 485 |
| 0.8014 | 1088.42 | 0.5324 | −0.4146 | 0.0716 | 368 |
| 0.9019 | 1006.28 | 0.4308 | −0.2267 | 0.0329 | 202 |
| 1.0000 | 920.85 | 0.3448 | | | |
| (8) Ethyl acetate + 1,1,2,2-tetrachloroethane | | | | | |
| 0.0000 | 1578.66 | 1.4845 | | | |
| 0.1500 | 1483.68 | 1.3576 | −0.1805 | 0.1380 | 266 |
| 0.2009 | 1450.94 | 1.3058 | −0.2423 | 0.1648 | 335 |
| 0.3141 | 1376.93 | 1.1802 | −0.3624 | 0.1965 | 451 |
| 0.3963 | 1322.14 | 1.0802 | −0.4332 | 0.1969 | 498 |
| 0.4968 | 1253.75 | 0.9507 | −0.4839 | 0.1764 | 506 |
| 0.5996 | 1182.17 | 0.8225 | −0.4886 | 0.1458 | 481 |
| 0.7128 | 1101.56 | 0.6857 | −0.4416 | 0.1022 | 397 |
| 0.8056 | 1034.05 | 0.5773 | −0.3538 | 0.0606 | 271 |
| 0.9246 | 945.64 | 0.4625 | −0.1684 | 0.0204 | 109 |
| 1.0000 | 888.55 | 0.4005 | | | |
| (9) *n*-Amyl acetate + 1,1,2,2-tetrachloroethane | | | | | |
| 0.0000 | 1578.66 | 1.4845 | | | |
| 0.1051 | 1479.94 | 1.4730 | −0.2023 | 0.0909 | 171 |
| 0.2031 | 1394.63 | 1.4456 | −0.3826 | 0.1525 | 298 |
| 0.3044 | 1312.35 | 1.4012 | −0.5408 | 0.1942 | 397 |
| 0.4008 | 1238.98 | 1.3396 | −0.6521 | 0.2092 | 451 |
| 0.5038 | 1165.24 | 1.2562 | −0.7068 | 0.2022 | 465 |
| 0.5980 | 1101.68 | 1.1647 | −0.6969 | 0.1761 | 435 |
| 0.7002 | 1036.59 | 1.0605 | −0.6195 | 0.1383 | 370 |
| 0.7935 | 980.48 | 0.9582 | −0.4942 | 0.0926 | 270 |
| 0.8927 | 924.05 | 0.8565 | −0.3052 | 0.0474 | 151 |
| 1.0000 | 866.28 | 0.7522 | | | |

**Table II.** Coefficients $A_i$ and Standard Deviations $\sigma(\eta)$ of Eq. (2) for the Viscosity $\eta$ (in mPa · s) of Binary Mixtures

| Mixture | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $\sigma(\eta)$ |
|---|---|---|---|---|---|
| MA + diCE | 0.7233 | −0.4748 | 0.1399 | −0.0439 | 0.0009 |
| EA + diCE | 0.7232 | −0.4631 | 0.2099 | −0.0703 | 0.0010 |
| nAA + diCE | 0.7224 | 0.1534 | −0.1228 | −0.0021 | 0.0022 |
| MA + triCE | 0.7278 | −0.6675 | 0.4072 | −0.1227 | 0.0004 |
| EA + triCE | 0.7267 | −0.6439 | 0.5031 | −0.1870 | 0.0017 |
| nAA + triCE | 0.7275 | 0.0863 | 0.0034 | −0.0656 | 0.0012 |
| MA + tetCE | 1.4831 | −0.9302 | −0.7678 | 0.5595 | 0.0030 |
| EA + tetCE | 1.4842 | −0.6841 | −1.1502 | 0.7507 | 0.0014 |
| nAA + tetCE | 1.4799 | 0.1265 | −1.4504 | 0.5928 | 0.0047 |

On the basis of the theory of absolute reaction rates [19], the excess Gibbs energy of activation $\Delta G^{*E}$ of viscous flow was calculated from

$$\Delta G^{*E}/RT = [\ln(\eta V/\eta_2 V_2) - x_1 \ln(\eta_1 V_1/\eta_2 V_2)] \tag{6}$$

where $V$ is the molar volume of the mixture and $V_i$ is the molar volume of the pure component $i$. $V^E$, $\eta^E$, and $\Delta G^{*E}$ data are included in Table I. The estimated uncertainties of $V^E$ and $\Delta G^{*E}$ are about 0.005 $\text{cm}^3 \cdot \text{mol}^{-1}$ and 15 $\text{J} \cdot \text{mol}^{-1}$, respectively.

The values of $V^E$, $\Delta\eta$, $\eta^E$, and $\Delta G^{*E}/RT$ for each mixture were fitted by the Redlich–Kister polynomial equation

$$Y^E = x_1(1-x_1) \sum_{i=0}^{m} A_i(1-2x_1)^I \tag{7}$$

The coefficients $A_i$ in Eq. (7), and the standard deviations $\sigma$ are given in Table III.

The results of the correlating equations [Eqs. (5)–(11) in Ref. 3] are compiled in Tables IV and V. In Table IV results of Eqs. (5)–(8) in Ref. 3, each containing a single adjustable parameter, are presented, while Table V lists the results of the two-parameter McAllister equation [Eq. (9) in Ref. 3] and the Heric equation [Eq. (10) in Ref. 3] and of the three-parameter Auslaender equation [Eq. (11) in Ref. 3]. The values of the different parameters and the percentage standard deviations $\sigma(\%)$ listed in Tables IV and V were obtained from the experimental viscosity data using the method of least squares.

**Table III.** Coefficients $A_i$ and Standard Deviations $\sigma$ of Eq. (7)

| Mixture | Property | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $\sigma$ |
|---|---|---|---|---|---|---|
| MA + diCE | $V^E$ ($cm^3 \cdot mol^{-1}$) | 1.2969 | 0.1233 | −0.4118 |  | 0.0035 |
|  | $\Delta\eta$ (mPa · s) | −0.0778 | −0.0260 |  |  | 0.0011 |
|  | $\eta^E$ (mPa · s) | 0.0615 | −0.0086 |  |  | 0.0010 |
|  | $\Delta G^{*E}/RT$ | 0.1399 | −0.0580 |  |  | 0.0017 |
| EA + diCE | $V^E$ ($cm^3 \cdot mol^{-1}$) | 0.4391 | 0.1408 | −0.1812 | 0.1114 | 0.0025 |
|  | $\Delta\eta$ (mPa · s) | −0.1109 | −0.0344 |  |  | 0.0013 |
|  | $\eta^E$ (mPa · s) | −0.0157 | −0.0246 |  |  | 0.0012 |
|  | $\Delta G^{*E}/RT$ | 0.0017 | −0.0314 |  |  | 0.0019 |
| nAA + diCE | $V^E$ ($cm^3 \cdot mol^{-1}$) | −0.8439 | 0.2764 | 0.0935 | 0.1953 | 0.0018 |
|  | $\Delta\eta$ (mPa · s) | 0.1140 | −0.0030 |  |  | 0.0026 |
|  | $\eta^E$ (mPa · s) | 0.1144 | −0.0029 |  |  | 0.0026 |
|  | $\Delta G^{*E}/RT$ | 0.3446 | 0.0414 |  |  | 0.0029 |
| MA + triCE | $V^E$ ($cm^3 \cdot mol^{-1}$) | 0.8806 | 0.2268 | 0.0534 |  | 0.0029 |
|  | $\Delta\eta$ (mPa · s) | −0.2217 | −0.0580 |  |  | 0.0005 |
|  | $\eta^E$ (mPa · s) | −0.0801 | −0.0400 |  |  | 0.0006 |
|  | $\Delta G^{*E}/RT$ | −0.1215 | −0.0253 |  |  | 0.0017 |
| EA + triCE | $V^E$ ($cm^3 \cdot mol^{-1}$) | 0.5544 | 0.1449 | 0.2567 | 0.1813 | 0.0040 |
|  | $\Delta\eta$ (mPa · s) | −0.2331 | −0.0852 |  |  | 0.0022 |
|  | $\eta^E$ (mPa · s) | −0.1360 | −0.0755 |  |  | 0.0021 |
|  | $\Delta G^{*E}/RT$ | −0.2345 | −0.0624 | −0.0327 |  | 0.0025 |
| nAA + triCE | $V^E$ ($cm^3 \cdot mol^{-1}$) | −2.1370 | 0.1908 | 0.9432 | 0.1975 | 0.0033 |
|  | $\Delta\eta$ (mPa · s) | 0.0918 | −0.0263 |  |  | 0.0013 |
|  | $\eta^E$ (mPa · s) | 0.0923 | −0.0259 |  |  | 0.0013 |
|  | $\Delta G^{*E}/RT$ | 0.1870 | −0.0229 |  |  | 0.0016 |
| MA + tetCE | $V^E$ ($cm^3 \cdot mol^{-1}$) | −2.4924 | 0.4503 | 0.4562 |  | 0.0021 |
|  | $\Delta\eta$ (mPa · s) | −0.0778 | 0.2679 |  |  | 0.0032 |
|  | $\eta^E$ (mPa · s) | 0.7281 | 0.4605 |  |  | 0.0028 |
|  | $\Delta G^{*E}/RT$ | 0.9135 | −0.0414 | −0.0608 |  | 0.0028 |
| EA + tetCE | $V^E$ ($cm^3 \cdot mol^{-1}$) | −1.9301 | 0.5632 | 0.1344 | 0.1668 | 0.0016 |
|  | $\Delta\eta$ (mPa · s) | 0.0238 | 0.3700 |  |  | 0.0014 |
|  | $\eta^E$ (mPa · s) | 0.7155 | 0.5168 |  |  | 0.0017 |
|  | $\Delta G^{*E}/RT$ | 0.8151 | 0.1050 | −0.1353 |  | 0.0026 |
| nab tetCE | $V^E$ ($cm^3 \cdot mol^{-1}$) | −2.8034 | 0.4411 | 0.2422 | 0.3427 | 0.0048 |
|  | $\Delta\eta$ (mPa · s) | 0.5605 | 0.2833 | −0.1335 |  | 0.0018 |
|  | $\eta^E$ (mPa · s) | 0.8070 | 0.3111 | −0.1311 |  | 0.0018 |
|  | $\Delta G^{*E}/RT$ | 0.7370 | 0.0625 | −0.1057 |  | 0.0009 |

**Table IV.** Values of the Parameters of Eqs. (5)–(8) from Ref. 3 and Percent Standard Deviations $\sigma(\%)$ in Correlating Viscosity of Binary Mixtures at 303.15 K

| | Eq. (5) | | Eq. (6) | | Eq. (7) | | Eq. (8) | |
|---|---|---|---|---|---|---|---|---|
| Mixture | $G_{12}$ | $\sigma(\%)$ | $C$ | $\sigma(\%)$ | $\eta_{12}$ | $\sigma(\%)$ | $W_{\text{vis}}/RT$ | $\sigma(\%)$ |
| MA + diCE | 0.12 | 0.43 | 0.50 | 0.39 | 0.49 | 0.39 | 0.14 | 0.43 |
| EA + diCE | −0.03 | 0.34 | 0.53 | 0.38 | 0.51 | 0.55 | 0.00 | 0.32 |
| nAA + diCE | 0.15 | 0.31 | 0.83 | 0.52 | 0.80 | 0.32 | 0.34 | 0.43 |
| MA + triCE | −0.16 | 0.27 | 0.41 | 1.44 | 0.43 | 0.99 | −0.12 | 0.27 |
| EA + triCE | −0.25 | 0.66 | 0.45 | 1.45 | 0.45 | 1.42 | −0.24 | 0.64 |
| nAA + triCE | 0.12 | 0.33 | 0.80 | 0.53 | 0.79 | 0.35 | 0.19 | 0.26 |
| MA + tetCE | 0.88 | 0.53 | 0.81 | 3.07 | 0.88 | 3.05 | 0.90 | 0.49 |
| EA + tetCE | 0.79 | 0.93 | 0.93 | 3.70 | 0.95 | 3.67 | 0.78 | 0.97 |
| nAA + tetCE | 0.67 | 0.63 | 1.46 | 1.53 | 1.38 | 2.10 | 0.71 | 0.67 |

## 5. DISCUSSION

The values of $\sigma$ are in the range from 0.26 to 3.70% for the single-parameter Eqs. (5) to (8) from Ref. 3, from 0.16 to 0.62% for the two-parameter Eqs. (9) and (10) from Ref. 3, and from 0.15 to 0.45% for the three-parameter Eq. (11) from Ref. 3. The average percentage standard deviations $\langle\sigma(\%)\rangle$ for Eqs. (5)–(8) with a single parameter are 0.49, 1.44, 1.42, and 0.50, respectively; for Eqs. (9) and (10) with two parameters, $\langle\sigma(\%)\rangle$ is 0.31; and for the three-parameter Eq. (11), $\langle\sigma(\%)\rangle$ is 0.26. From an analysis of the results in Table IV, the Tamura and Kurata

**Table V.** Values of the Parameters of Eqs. (9)–(11) from Ref. 3 and Percent Standard Deviations $\sigma(\%)$ in Correlating Viscosities of Binary Mixtures at 303.15 K

| | Eq. (9) | | | Eq. (10) | | | Eq. (11) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Mixtures | $Z_{12}$ | $Z_{21}$ | $\sigma(\%)$ | $\alpha_{12}$ | $\alpha_{21}$ | $\sigma(\%)$ | $B_{12}$ | $A_{21}$ | $B_{21}$ | $\sigma(\%)$ |
| MA + diCE | 0.46 | 0.51 | 0.16 | 0.14 | 0.06 | 0.16 | 0.04 | 0.02 | 33.70 | 0.17 |
| EA + diCE | 0.50 | 0.53 | 0.19 | 0.00 | 0.03 | 0.19 | −0.12 | −0.09 | −8.23 | 0.42 |
| nAA + diCE | 0.84 | 0.75 | 0.29 | 0.34 | −0.04 | 0.29 | 2.94 | 0.72 | −3.05 | 0.19 |
| MA + triCE | 0.40 | 0.44 | 0.17 | −0.12 | 0.02 | 0.17 | −0.14 | −0.08 | −7.09 | 0.16 |
| EA + triCE | 0.44 | 0.46 | 0.30 | −0.24 | 0.06 | 0.30 | −0.40 | −0.19 | −2.52 | 0.39 |
| nAA + triCE | 0.80 | 0.68 | 0.16 | 0.19 | 0.02 | 0.16 | 4.80 | 1.36 | −2.33 | 0.17 |
| MA + tetCE | 0.64 | 0.86 | 0.41 | 0.90 | 0.04 | 0.41 | 0.78 | 0.93 | 0.79 | 0.45 |
| EA + tetCE | 0.68 | 0.95 | 0.62 | 0.78 | −0.12 | 0.62 | 0.65 | 0.97 | 0.73 | 0.24 |
| nAA + tetCE | 1.10 | 1.18 | 0.49 | 0.71 | −0.06 | 0.49 | 0.05 | 1.07 | 1.19 | 0.15 |

Eq. (6) and Hind et al. Eq. (7) have very large values of $\sigma(\%)$, whereas the other two Eqs. (5) and (8) of Grunberg and Nissan and of Katti and Chaudhri, respectively, have comparatively low values of $\sigma(\%)$. The use of two-parameter equations [Eqs. (9) and (10)] reduces the values of $\sigma(\%)$ significantly below those of single-parameter equations. In most systems the three-parameter equation [Eqs. (11)] proposed by Auslaender [18] gives very good results. Thus, the correlating ability increases in the following sequence: Tamura and Kurata $\approx$ Hind et al. $<$ Grunberg–Nissan $\approx$ Katti–Chaudhri $<$ McAllister $\approx$ Heric $<$ Auslaender equations.

The experimental results for $\eta$, $\eta^{\mathrm{E}}$, $V^{\mathrm{E}}$, and $\Delta G^{*\mathrm{E}}$ at 303.15 K are shown in Figs. 1 to 4. Figure 1 reveals that the viscosities exhibit negative deviations from linear dependence on the mole fraction over the entire range of composition for mixtures of methyl and ethyl acetates with di- and trichloroethanes, but the deviations are positive for amyl acetate mixtures with di- and trichloroethanes. Maxima in the viscosity curves are observed for the latter mixtures. For the common component diCE or triCE, the values of $\Delta\eta$ increase with the chain length of alkyl acetate. In the case of alkyl acetates + tetrachloroethane mixtures, both small positive as well as small negative deviations in the viscosity curves are found for mixtures involving methyl and ethyl acetates. The inversion of sign from positive to negative occurs as the mole fraction of ester is increased. On the other hand, for nAA + tetCE, the deviations are large and positive over the entire range of composition. It can be seen from Fig. 2 that the excess viscosities $\eta^{\mathrm{E}}$, as from Eq. (5) are positive for MA + diCE, nAA + diCE, nAA + triCE, MA + tetCE, EA + tetCE, and nAA + tetCE and negative for EA + diCE, MA + triCE, and EA + triCE. The values of $\eta^{\mathrm{E}}$ are very large for alkyl acetates + tetrachloroethane mixtures.

It can be seen from Fig. 3 that the $V^{\mathrm{E}}$ are positive for mixtures of methyl and ethyl acetate with di- and trichloroethane, but they are negative for amyl acetate with di- or trichloroethane mixtures. The $V^{\mathrm{E}}$ values are large and negative for all three alkyl acetates + tetrachloroethane mixtures. For the common component chloroethane, $V^{\mathrm{E}}$ varies as MA $>$ EA $>$ AA except for EA + tetCE whose $V^{\mathrm{E}}$ is larger than for MA + tetCE. The $V^{\mathrm{E}}$ values for EA + diCE, EA + triCE, and EA + tetCE have been reported in the literature [22]. Our equimolar $V^{\mathrm{E}}$ results for EA + tetCE are in agreement within $0.02\ \mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$, but the $V^{\mathrm{E}}$ values are higher by 0.08 $\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$ for EA + diCE and lower by $0.065\ \mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$ for EA + triCE than those reported by Reddy et al. [22]. The values of $\Delta G^{*\mathrm{E}}$ (Fig. 4) for the common ester component fall in the order tetCE $>$ diCE $>$ triCE, and for the common chloroalkane component, the sequence is AA $>$ EA $>$ MA.

Results for the present alkyl acetate + chloroethane mixtures can also be explained in a similar manner as has been done for alkyl acetate +

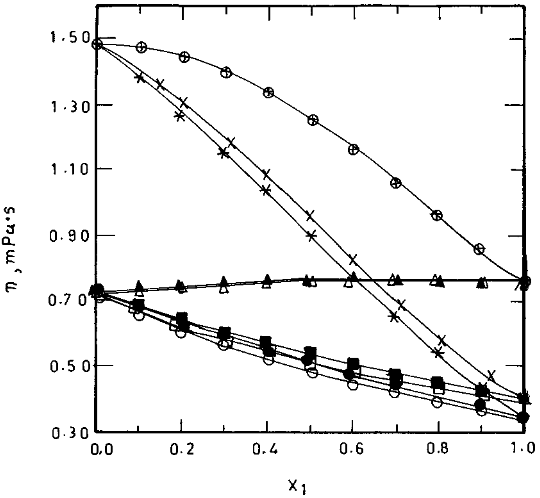

**Fig. 1.** Viscosity $\eta$ for alkyl acetate + chloroethane at 303.15 K. Experimental points: (●) MA + diCE; (■) EA + diCE; (▲) nAA + diCE; (○) MA + triCE; (□) EA + triCE; (△) nAA + triCE; (∗) MA + tetCE, (×), EA + tetCE; (⊕) nAA + tetCE. (——) Calculated with Eq. (2).

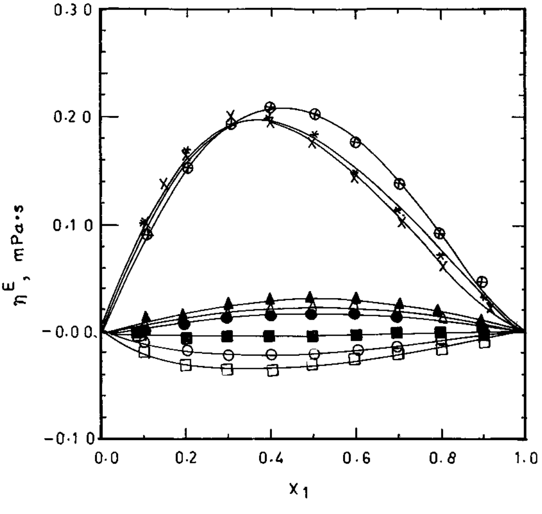

**Fig. 2.** Excess viscosity $\eta^E$ for alkyl acetate + chloroethane at 303.15 K. (——) Calculated with Eq. (7). Symbols are the same as in Fig. 1.

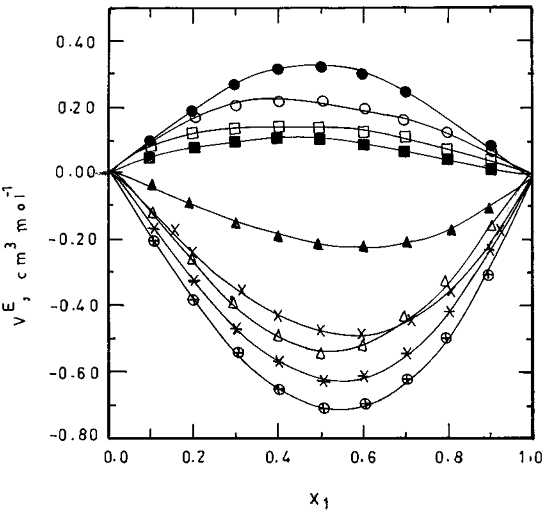

**Fig. 3.** Excess molar volumes $V^E$ of alkyl acetate + chloroethane at 303.15 K. (——) Calculated with Eq. (7). Symbols are the same as in Fig. 1.

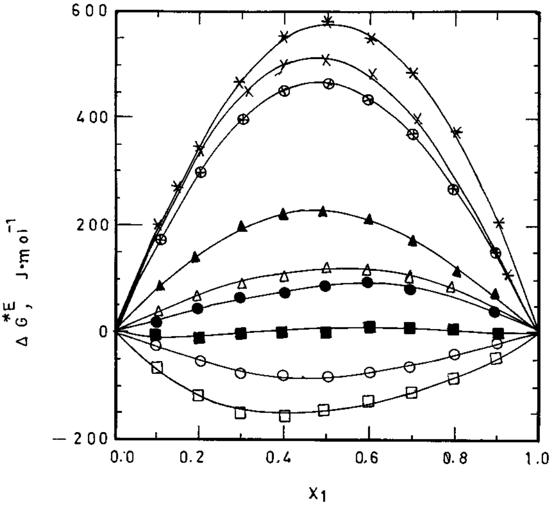

**Fig. 4.** Excess Gibbs energy of activation $\Delta G^{*E}$ of viscous flow for alkyl acetate + chloroethane at 303.15 K. (——) Calculated with Eq. (7). Symbols are the same as in Fig. 1.

chloromethane [1, 3, 5, 23]. In these mixtures, apart from dipole–dipole interactions, the O ··· H and O ··· Cl interactions are of equal significance. The volumetric and compressibility behavior for *p*-dioxane + dichloroethane was explained by proposing the formation of dioxane–dichloroethane adduct [24, 25]. O ··· Cl interactions between oxygen of alkyl acetate and chlorine of diCE as well as O ··· H interactions between oxygen of alkyl acetate and hydrogen of diCE are likely. At present we have no method to separate the two effects.

It is interesting to note that the equimolar $H^E$ [26] for MA + triCE is positive (170.7 $J \cdot mol^{-1}$), while for EA + triCE, $H^E$ is negative ($-101.5$ $J \cdot mol^{-1}$). Thus, $V^E$ and $H^E$ have the same trend, i.e., they become smaller as the size of the ester is increased. The volumetric and viscosity results indicate that H of trichloroethane is not involved in H-bond formation with the alkyl acetate molecule, since the 1,1,1-trichloroethane molecule contains no active hydrogen. The specific interactions in these systems can be visualized as due to (a) donor (O) and acceptor (Cl) and (b) dipole–dipole interactions between alkyl acetate and trichloroethane molecule.

From large negative values of $V^E$, and large positive values of $\Delta\eta$ and $\Delta G^{*E}$, it can be said that analogous to the alkyl acetate + chloroform system [1, 3], the specific interactions between alkyl acetates and tetrachloroethane are very strong. Studies of the acetone + tetrachloroethane system concerning excess molar volume, compressibility, viscosity, and dielectric properties were reported by Nath and Tripathi [27, 28]. They concluded that tetrachloroethane forms a molecular complex with acetone, where tetrachloroethane acts as an acceptor, while acetone acts as a donor. Tetrachloroethane also forms complexes with *p*-dioxane [29, 30]. Similar complexation may occur between alkyl acetate and tetrachloroethane. Thus, it may be inferred that the net combined effect of (i) donor–acceptor type interactions, (ii) H-bond formations, and (iii) closer molecular arrangements in alkyl acetates + tetrachloroethane mixtures dominate over the breaking of dipole associations.

The size effect is reflected in the amyl acetate mixtures, where all three mixtures with diCE, triCE, and tetCE have larger positive $\Delta\eta$ and $\Delta G^{*E}$ and larger negative $V^E$ than those observed for the methyl and ethyl acetate mixtures.

## REFERENCES

1. S. L. Oswal and I. N. Patel, *Fluid Phase Equil.* **149**:249 (1998).
2. S. L. Oswal, P. Oswal, and J. P. Dave, *Fluid Phase Equil.* **98**:225 (1994)
3. S. L. Oswal, J. P. Dave, and I. N. Patel, *Int J. Thermophys.* **20**:1449 (1999).
4. S. L. Oswal and I. N. Patel, *Indian J. Chem. Sect. A* **29**:870 (1990.).

5. L. Ubbelohde, *Ind. Eng. Chem. Anal. Educ.* **9**:85 (1937).
6. F. A. Goncalves, J. Kestin, and J. V. Sengers, *Int. J. Thermophys.* **12**:1013 (1991).
7. S. G. Patel and S. L. Oswal, *J. Chem. Soc. Faraday Trans.* **88**:2497 (1992).
8. S. L. Oswal and H. S. Desai, *Fluid Phase Equil.* **149**:359(1998).
9. J. B. Irving, *Viscosity of Liquid Mixtures*, NEL Report Nos. 630 and 631 (National Engineering Laboratory, East Kilbride, Glasgow, 1977).
10. R. C. Reid, J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, 4th ed. (McGraw–Hill, New York, 1987).
11. W. Cao, A. Fredenslund, and P. Rasmussen, *Ind. Eng. Chem. Res.* **31**:2603 (1992).
12. L. Grunberg and A. H. Nissan, *Nature* **164**:799 (1949).
13. M. Tamura and M. Kurata, *Bull. Chem. Soc. Japan* **25**:32 (1952).
14. R. K. Hind, E. McLaughlin, and A. R. Ubbelohde, *Trans. Faraday Soc.* **56**:328 (1960).
15. P. K. Katti and M. M. Chaudhri, *J. Chem. Eng. Data* **9**:442 (1964).
16. R. A. McAllister, *AIChE J.* **6**:427 (1960).
17. E. L. Heric and J. C. Brewer, *J. Chem. Eng. Data* **12**:574 (1967).
18. G. Auslaender, *Brit. Chem. Eng.* **10**:196 (1965).
19. S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Process* (McGraw–Hill, New York, 1941), p. 514.
20. I. L. Acevedo, G. C. Pedrosa, and M. Katz, *Can. J. Chem.* **69**:1006 (1991).
21. D. S. Gill, T. S. Kaur, H. Kaur, I. M. Joshi, and J. Singh, *J. Chem. Soc. Faraday Trans.* **89**:1737 (1993).
22. D. V. B. Reddy, K. Ramanjaneyulu, and A. Krishnaiah, *Indian J. Pure Appl. Phys.* **28**:107 (1990).
23. T. Ohta, H. Asomo, and I. Nagata, *Fluid Phase Equil.* **4**:105 (1980).
24. J. Nath and Rashmi, *Fluid Phase Equil.* **58**:319 (1990).
25. J. Nath and Rashmi, *J. Chem. Soc. Faraday Trans.* **86**:3399 (1990).
26. J. Gmehling, *J. Chem. Eng. Data* **38**:143 (1993).
27. J. Nath and A. D. Tripathi, *J. Chem. Eng. Data* **28**:263 (1983).
28. J. Nath and A. D. Tripathi, *J. Chem. Soc. Faraday Trans.* **80**:1517 (1984).
29. S. L. Oswal, *Indian J. Tech.* **27**:101 (1989).
30. S. L. Oswal and R. P. Phalak, *J. Solution Chem.* **22**:43 (1993).