

## **Viscosity of Nonelectrolyte Liquid Mixtures. IV. Binary Mixtures Containing *p*-Dioxane**

**S. L. Oswal,<sup>1,2</sup> P. Oswal,<sup>3</sup> and R. P. Phalak<sup>1</sup>**

*Received January 16, 1996*

---

Measurements of the viscosity  $\eta$  and density  $\rho$  are reported for eight binary mixtures of *p*-dioxane with methylcyclohexane, 1-chlorohexane, 1-bromohexane, *p*-xylene, propylbenzene, methyl acetate, butyl acetate, and amyl acetate at 303.15 K. The viscosity data have been correlated with the equations of Grunberg–Nissan, of McAllister, and of Auslaender. The relation among the excess viscosity  $\Delta \ln \eta$ , excess Gibbs energy of activation  $\Delta G^{*E}$  of viscous flow, and intermolecular interaction in these mixtures is discussed.

---

**KEY WORDS:** alkyl acetates; aromatic hydrocarbons; liquid mixtures; methylcyclohexane; densities; *p*-dioxane; haloalkanes; viscosities.

### **1. INTRODUCTION**

We have been engaged in a systematic study of the thermodynamic, acoustic, and transport properties of binary mixtures containing cyclic ethers [1–6], as the latter are industrially important solvents. In previous papers we have reported viscosity [5], speed of sound, and isentropic compressibility measurements [6] for nine binary mixtures of *p*-dioxane with hexane, cyclohexane, benzene, toluene, carbon tetrachloride, chloroform, tetrachloroethane, pentachloroethane, and ethyl acetate. The results on excess properties of volume, isentropic compressibility, and viscosity were explained by considering the specific interactions between *p*-dioxane and aromatic hydrocarbons or chloroalkanes. As an extension of our studies we

---

<sup>1</sup> Department of Chemistry, South Gujarat University, Surat 395007, India.

<sup>2</sup> To whom correspondence should be addressed.

<sup>3</sup> Department of Chemistry, Meera Girls Government College, Udaipur 313001, India.

report in this paper the viscosities and densities of eight binary mixtures of *p*-dioxane with methylcyclohexane, 1-chlorohexane, 1-bromohexane, *p*-xylene, propylbenzene, methyl acetate, butyl acetate, and amyl acetate.

## 2. EXPERIMENTS

### 2.1. Method

The details of the methods and techniques used to determine viscosity and density have been described in previous publications [5, 7, 8]. The measurements of the kinematic viscosity  $\eta/\rho$  were obtained with a modified suspended-level Ubbelohde viscometer [9, 10]. The apparatus was submerged in a thermostatic bath at 303.15 K with a resolution of  $\pm 0.05$  K. The viscometer has been calibrated so as to determine the two constants  $C$  and  $B$  in the equation  $\eta/\rho = Ct - (B/t)$ , obtained by measuring the flow time  $t$  with pure water, benzene, and cyclohexane at  $(303.15 \pm 0.05)$  K [11]. Four or five sets of readings for the flow times were taken for each pure liquid or liquid mixture and the arithmetic mean was taken for the calculations. The densities  $\rho$  of pure components and mixtures required for converting kinematic viscosities into absolute viscosities were measured with an Anton Paar vibrating-tube digital densimeter (Model DMA 60/602) with a thermostated bath controlled to  $\pm 0.01$  K.

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 the 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 viscosity  $\eta$  and the density  $\rho$  were reproducible to within  $\pm 0.002$  mPa·s and  $\pm 0.1$  kg·m<sup>-3</sup>, respectively.

### 2.2. Source and Purity of Samples

*p*-Dioxane ( $\text{pC}_4\text{H}_8\text{O}_2$ ) of BDH, AR was refluxed for several hours over sodium metal wire until free from peroxide and, finally, distilled over sodium [11]. Methylcyclohexane ( $\text{C}_6\text{H}_{11}\text{CH}_3$ ) of BDH, AR, 1-chlorohexane ( $\text{C}_6\text{H}_{13}\text{Cl}$ ), 1-bromohexane ( $\text{C}_6\text{H}_{13}\text{Br}$ ), and propylbenzene ( $\text{C}_6\text{H}_5\text{C}_3\text{H}_7$ ) from E. Merck, Bombay, >99 mol%, were dried over a 4A-type molecular sieve (Fluka) and then fractionally distilled before use. *p*-Xylene [ $\text{C}_6\text{H}_4(\text{CH}_3)_2$ ] from E. Merck, >99 mol%, was treated with  $\text{H}_2\text{SO}_4$  until free from thiophene [11], then washed, dried, and fractionally distilled. Methyl acetate ( $\text{CH}_3\text{COOCH}_3$ ), butyl acetate ( $\text{CH}_3\text{COOC}_4\text{H}_9$ ), and amyl acetate ( $\text{CH}_3\text{COOC}_5\text{H}_{11}$ ) from BDH, AR, were kept over

Table I. Density  $\rho$ , Refractive Index  $n_D$ , and Viscosity  $\eta$  for Pure Liquids at 303.15 K

Component	$\rho$ (kg · m <sup>-3</sup> )		$n_D$		$\eta$ (mPa · s)	
	Exptl.	Lit.	Exptl.	Lit.	Exptl.	Lit.
<i>p</i> C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	1022.3	1222.3 [11]	1.4180	1.4180 [11]	1.0900	1.087 [11]
<i>c</i> C <sub>6</sub> H <sub>11</sub> CH <sub>3</sub>	760.5	760.3 [11] 760.65 [12]	1.4200	1.4182 [11]	0.6407	0.639 [11]
C <sub>6</sub> H <sub>13</sub> Cl	878.2 <sup>a</sup>	878.5 [3] <sup>a</sup>	1.4205 <sup>a</sup>	1.4199 [3] <sup>a</sup>	0.6856	0.6859 [14]
	873.5 <sup>b</sup>	873.5 [5] <sup>b</sup>	1.4178	1.4174 [8] <sup>b</sup>		
		873.9 [16] <sup>b</sup>		1.4177 [15, 17] <sup>b</sup>		
		874.5 [17] <sup>b</sup>				
C <sub>6</sub> H <sub>13</sub> Br	1174.2 <sup>a</sup>	1174.4 [13] <sup>a</sup>	1.4485 <sup>a</sup>	1.4478 [3] <sup>a</sup>		
C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub>	852.3	852.3 [11]	1.4909	1.4907 [11]	0.5669	0.566 [11]
C <sub>6</sub> H <sub>5</sub> C <sub>3</sub> H <sub>7</sub>	853.3	853.8 [16]	1.4828	1.4828 [16]	0.7500	0.746 [16]
CH <sub>3</sub> COOCH <sub>3</sub>	920.3	920.4 [19]	1.3610	1.3614 [11]	0.3430	0.3440 [11]
CH <sub>3</sub> COOC <sub>4</sub> H <sub>9</sub>	870.8	871.29 [11]	1.3896	1.3892 [11]	0.6453	0.6444 [11]
CH <sub>3</sub> COOC <sub>5</sub> H <sub>11</sub>	865.7	865.7 [11]	1.4020	1.4028 [11]	0.8618 <sup>b</sup>	0.862 [11] <sup>b</sup>

<sup>a</sup> At 293.15 K.<sup>b</sup> At 298.15 K.

anhydrous K<sub>2</sub>CO<sub>3</sub> for more than 72 h and were fractionally distilled. The middle fraction of the distillate was used.

The purities of the liquid samples were checked by gas-liquid chromatography and they were better than 99.8 mol%. The measured values of the densities  $\rho$ , the refractive indexes  $n_D$ , and the viscosities  $\eta$  are compared with the literature values in Table I. The agreement between the experimentally determined values and those found in the literature was considered satisfactory, since the greatest deviation found was smaller than 0.1% for  $\rho$  and  $n_D$  and 0.5% for  $\eta$ .

### 3. RESULTS

The measured viscosities  $\eta$  and densities  $\rho$  for binary mixtures at number of mole fractions at 303.15 K are given in Table II. The viscosities  $\eta$  were fitted to a polynomial,

$$\eta = \sum_{i=0}^m A_i x_1^i \quad (1)$$

The coefficients  $A_i$  obtained from a least-squares fit with equal weights assigned to each point are listed in Table III together with the standard deviations  $\sigma$ . No published viscosity measurements were found for the present systems for comparison with the present results.

**Table II.** Density and Viscosity of Binary Mixtures of *p*-Dioxane with Various Solvents at 303.15 K

$x_1$	$\rho$ ( $\text{kg} \cdot \text{m}^{-3}$ )	$\eta$ ( $\text{mPa} \cdot \text{s}$ )
(i) $p\text{C}_4\text{H}_8\text{O}_2 + c\text{C}_6\text{H}_{11}\text{CH}_3$		
0.0000	760.5	0.6407
0.1001	776.5	0.6334
0.2013	794.2	0.6394
0.2960	812.7	0.6530
0.3948	833.8	0.6802
0.5046	859.8	0.7196
0.5993	884.6	0.7612
0.7003	913.9	0.8213
0.7956	944.6	0.8868
0.8960	980.4	0.9775
1.0000	1022.3	1.0900
(ii) $p\text{C}_4\text{H}_8\text{O}_2 + \text{C}_6\text{H}_{13}\text{Cl}$		
0.0000	868.8	0.6544
0.1087	878.4	0.6686
0.2953	897.6	0.7084
0.5004	923.6	0.7719
0.6974	955.1	0.8637
0.9013	997.1	1.0037
1.0000	1022.3	1.0900
(iii) $p\text{C}_4\text{H}_8\text{O}_2 + \text{C}_6\text{H}_{13}\text{Br}$		
0.0000	1162.6	0.9030
0.1105	1150.8	0.8848
0.3021	1128.9	0.8777
0.4972	1104.1	0.9007
0.6980	1075.0	0.9470
0.8997	1041.2	1.0302
1.0000	1022.3	1.0900
(iv) $p\text{C}_4\text{H}_8\text{O}_2 + \text{C}_6\text{H}_4(\text{CH}_3)_2$		
0.0000	852.3	0.5669
0.0997	864.1	0.6005
0.1975	876.4	0.6365
0.3004	890.3	0.6742
0.3991	904.7	0.7184
0.5041	921.2	0.7664
0.5999	937.4	0.8195
0.7030	956.4	0.8792
0.7976	975.9	0.9400
0.8972	997.3	1.0105
1.0000	1022.3	1.0900

Table II. (Continued)

$x_1$	$\rho$ ( $\text{kg} \cdot \text{m}^{-3}$ )	$\eta$ ( $\text{mPa} \cdot \text{s}$ )
(v) $p\text{C}_4\text{H}_8\text{O}_2 + \text{C}_6\text{H}_5\text{C}_3\text{H}_7$		
0.0000	853.3	0.7500
0.1061	864.4	0.7763
0.1984	874.9	0.8007
0.2968	887.0	0.8298
0.3990	900.7	0.8589
0.4945	914.9	0.8922
0.5985	932.1	0.9278
0.7003	950.9	0.9648
0.8026	972.2	1.0048
0.9025	995.9	1.0454
1.0000	1022.3	1.0900
(vi) $p\text{C}_4\text{H}_8\text{O}_2 + \text{CH}_3\text{COOCH}_3$		
0.0000	920.3	0.3430
0.1026	931.6	0.3813
0.3032	953.2	0.4727
0.5004	973.7	0.5895
0.7187	995.6	0.7642
0.8981	1012.8	0.9562
1.0000	1022.3	1.0900
(vii) $p\text{C}_4\text{H}_8\text{O}_2 + \text{CH}_3\text{COOC}_4\text{H}_9$		
0.0000	870.8	0.6453
0.1002	880.8	0.6618
0.1988	891.4	0.6820
0.2997	903.1	0.7051
0.3963	915.2	0.7333
0.4977	929.1	0.7684
0.6024	944.9	0.8090
0.7009	961.2	0.8590
0.7968	978.7	0.9174
0.9016	1000.0	0.9976
1.0000	1022.3	1.0900
(viii) $p\text{C}_4\text{H}_8\text{O}_2 + \text{CH}_3\text{COOC}_5\text{H}_{11}$		
0.0000	865.7	0.7573
0.0981	874.7	0.7721
0.2981	895.7	0.8134
0.5050	922.5	0.8719
0.7018	954.6	0.9452
0.9003	996.4	1.0368
1.0000	1022.3	1.0900

Table III. Parameters  $A_i$  of Eqs. (1) and (3) and Standard Deviations  $\sigma$ 

Property	$A_0$	$A_1$	$A_2$	$A_3$	$\sigma \times 10^4$
(i) $x_1 pC_4H_8O_2 + x_2 cC_6H_{11}CH_3$					
$\eta$ (mPa · s)	0.6382	-0.0579	0.3323	0.1752	30
$\Delta \ln \eta$	-0.6156	-0.0800	-0.535		17
$\Delta G^{*E}/RT$	-0.5035	-0.0936	-0.506		17
(ii) $x_1 pC_4H_8O_2 + x_2 C_6H_{13}Cl$					
$\eta$ (mPa · s)	0.6537	0.1384	0.0892	0.2086	11
$\Delta \ln \eta$	-0.3573	0.0121			17
$\Delta G^{*E}/RT$	-0.2254	-0.0119			18
(iii) $x_1 pC_4H_8O_2 + x_2 cC_6H_{13}Br$					
$\eta$ (mPa · s)	0.9033	-0.2044	0.3879		28
$\Delta \ln \eta$	-0.3901	-0.0043	-0.0454		14
$\Delta G^{*E}/RT$	-0.2571	-0.3220			27
(iv) $x_1 pC_4H_8O_2 + x_2 C_6H_4(CH_3)_2$					
$\eta$ (mPa · s)	0.5675	0.3145	0.1224	0.0860	11
$\Delta \ln \eta$	-0.1055	0.0039	0.0296		14
$\Delta G^{*E}/RT$	-0.0321	-0.0072	0.0316		15
(v) $x_1 pC_4H_8O_2 + x_2 C_6H_5C_3H_7$					
$\eta$ (mPa · s)	0.7504	0.2326	0.1059		9
$\Delta \ln \eta$	-0.0512				10
$\Delta G^{*E}/RT$	0.0768	-0.0249			10
(vi) $x_1 pC_4H_8O_2 + x_2 CH_3COOCH_3$					
$\eta$ (mPa · s)	0.3425	0.3737	0.1009	0.2725	8
$\Delta \ln \eta$	-0.1438				8
$\Delta G^{*E}/RT$	-0.1440				8
(vii) $x_1 pC_4H_8O_2 + x_2 CH_3COOC_4H_9$					
$\eta$ (mPa · s)	0.6438	0.1975	-0.0554	0.3027	18
$\Delta \ln \eta$	-0.3559	0.0767			13
$\Delta G^{*E}/RT$	-0.2478	0.0431			6
(viii) $x_1 pC_4H_8O_2 + x_2 CH_3COOC_5H_{11}$					
$\eta$ (mPa · s)	0.7558	0.1186	0.2127		9
$\Delta \ln \eta$	-0.1699				16
$\Delta G^{*E}/RT$	-0.0108				6

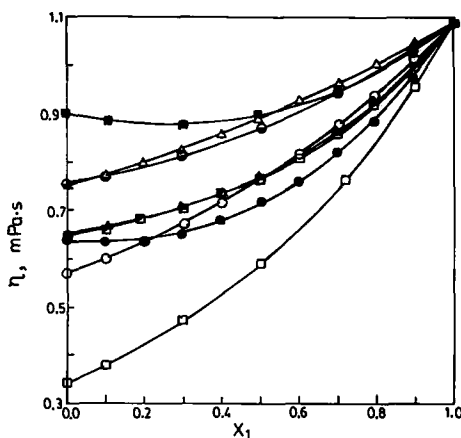
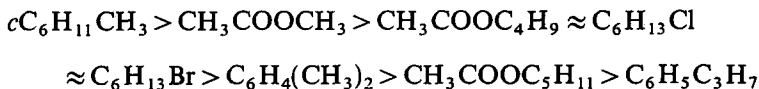


Fig. 1. Viscosity  $\eta$  for *p*-dioxane (1) + component (2) at 303.15 K. Experimental points:  $cC_6H_{11}CH_3$  ( $\bullet$ ),  $C_6H_{13}Cl$  ( $\blacktriangle$ ),  $C_6H_{13}Br$  ( $\blacksquare$ ),  $C_6H_4(CH_3)_2$  ( $\circ$ ),  $C_6H_5C_3H_7$  ( $\triangle$ ),  $CH_3COOCH_3$  ( $\square$ ),  $CH_3COOC_4H_9$  ( $\blacksquare$ ), and  $CH_3COOC_5H_{11}$  ( $\ominus$ ). (—) Calculated with Eq. (1).

Figure 1 shows the dependence of  $\eta$  on  $x_1$ , the mole fraction of *p*-dioxane for all binary mixtures. Figure 1 reveals that  $\eta$  increases with increases in the mole fraction  $x_1$  of *p*-dioxane for all mixtures except for  $pC_4H_8O_2 + cC_6H_{11}CH_3$  and for  $pC_4H_8O_2 + C_6H_{13}Br$  mixtures. In the case of the latter two mixtures, a minimum around 0.1 and 0.3 mole fraction  $x_1$ , respectively, is observed. The eight mixtures show negative deviations ( $\Delta\eta = \eta - x_1\eta_1^0 - x_2\eta_2^0$ ) from a linear dependence on mole fraction. The negative deviations in binary mixtures with *p*-dioxane as a common component follow the sequence:



Quantitatively, the deviations of the viscosities from the ideal mixture values can be calculated from an Arrhenius equation,

$$\Delta \ln \eta = \ln(\eta/\eta_2^0) - x_1 \ln(\eta_1^0/\eta_2^0) \quad (2)$$

where  $\eta_i^0$  represents the viscosities of pure components  $i$ . The dependence of the excess viscosities  $\Delta \ln \eta$  on composition is shown in Fig. 2. The

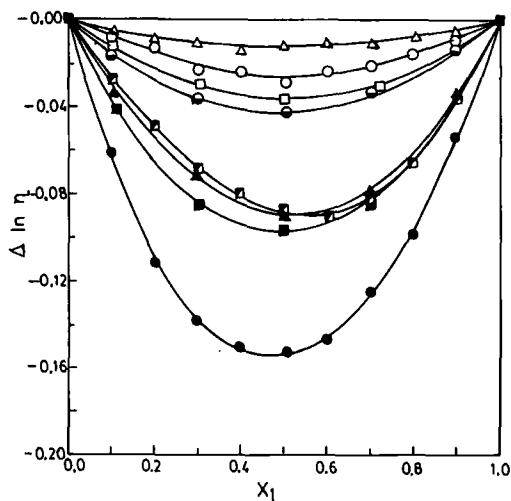


Fig. 2. Excess viscosity  $\Delta \ln \eta$  for *p*-dioxane (1) + component (2) at 303.15 K. Symbols are the same as in Fig. 1. (—) Calculated with Eq. (3).

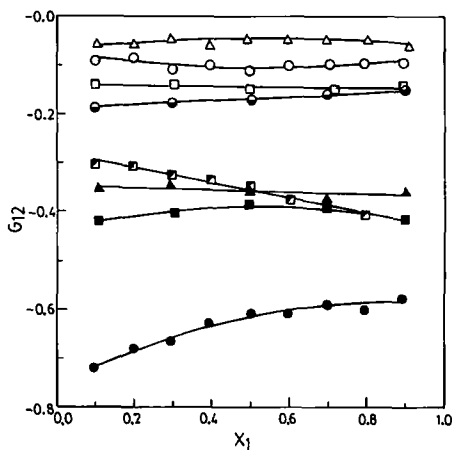


Fig. 3. Variation of Grunberg-Nissan parameter  $G_{12}$  in Eq. (4) with mole fraction  $x_1$  of *p*-dioxane in binary mixtures *p*-dioxane (1) + component (2). Symbols are the same as in Fig. 1.

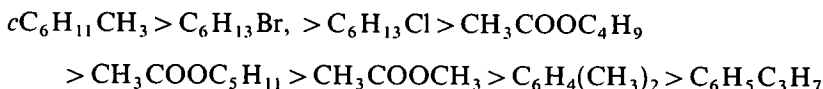


values of  $\Delta \ln \eta$  have been fitted to the Redlich-Kister [20] polynomial equation

$$\Delta \ln \eta = x_1(1 - x_1) \sum_{i=0}^m A_i(1 - 2x_1)^i \quad (3)$$

The coefficients  $A_i$  of Eq. (3), obtained by the method of least-squares with all points weighted equally, and the standard deviations  $\sigma$  are given in Table III.

Figure 3 shows that the negative values of  $\Delta \ln \eta$  at  $x_1 = 0.5$  for *p*-dioxane mixtures decrease in the sequence



#### 4. CORRELATING EQUATIONS

Several semiempirical relations have been proposed to estimate the dynamic viscosity  $\eta$  of liquid mixtures in terms of pure-component data. The Grunberg-Nissan equation [21] reads

$$\ln \eta = x_1 \ln \eta_1^0 + x_2 \ln \eta_2^0 + x_1 x_2 G_{12} \quad (4)$$

where  $G_{12}$  is a parameter proportional to the interchange energy. We have analyzed Eq. (4) in two ways, namely, (i) by calculating  $G_{12}$  for each of the binary mixtures at each individual composition and (ii) by calculating one optimum value of  $G_{12}$  for each of binary mixtures using all the experimental points.

The McAllister equation [22] based on Eyring's theory of absolute reaction rates [23] and the three-body interaction model is

$$\begin{aligned} \ln v = & x_1^3 \ln v_1^0 + 3x_1^2 x_2 \ln Z_{12} + 3x_1 x_2^2 \ln Z_{21} + x_2^3 \ln v_2^0 \\ & - \ln(x_1 + x_2 M_2/M_1) + 3x_1^2 x_2 \ln(2/3 + M_2/3M_1) \\ & + 3x_1 x_2^2 \ln(1/3 + 2M_2/3M_1) + x_2^3 \ln(M_2/M_1) \end{aligned} \quad (5)$$

where  $Z_{12}$  and  $Z_{21}$  are interaction parameters and  $M_i$  and  $v_i^0$  are the molecular mass and kinematic viscosity of pure component  $i$ .

The less complicated three-parameter Auslaender [24] equation has the form

$$x_1(x_1 + B_{12}x_2)(\eta - \eta_1^0) + A_{21}x_2(B_{21}x_1 + x_2)(\eta - \eta_2^0) = 0 \quad (6)$$

Table IV. Parameters of Eqs. (4) to (6) and Percentage Standard Deviations ( $\sigma\%$ ) for *p*-Dioxane (1) + Component (2) Mixtures at 303.15 K

Component (2)	Eq. (4)		Eq. (5)			Eq. (6)			
	$G_{12}$	$\sigma\%$	$Z_{12}$	$Z_{21}$	$\sigma\%$	$B_{12}$	$B_{21}$	$A_{21}$	$\sigma\%$
$cC_6H_{11}CH_3$	-0.630	0.64	0.855	0.744	0.26	-0.275	3.271	0.844	0.16
$C_6H_{13}Cl$	-0.358	0.19	0.875	0.776	0.15	0.192	2.603	0.876	0.18
$C_6H_{13}Br$	-0.404	0.24	0.850	0.753	0.19	-1.043	4.299	0.831	0.13
$C_6H_4(CH_3)_2$	-0.098	0.17	0.903	0.768	0.19	-0.555	-1.793	-0.892	0.32
$C_6H_5C_3H_7$	-0.051	0.10	1.007	0.975	0.80	-0.310	-3.193	-0.433	0.14
$CH_3COOCH_3$	-0.144	0.07	0.712	0.504	0.06	1.199	0.740	2.561	0.05
$CH_3COOC_4H_9$	-0.356	0.60	0.842	0.777	0.11	0.331	2.441	1.055	0.12
$CH_3COOC_5H_{11}$	-0.172	0.14	0.993	0.901	0.05	0.439	1.540	1.095	0.02

where  $B_{12}$ ,  $A_{21}$ , and  $B_{21}$  are the parameters representing binary interactions.

The results of the three correlating equations, Eqs. (4)–(6), are compiled in Table IV. In Table IV, the second column provides  $G_{12}$  in Eq. (4) and the fourth and fifth columns list  $Z_{12}$  and  $Z_{21}$  in Eq. (5), while the seventh to ninth columns present the values of  $B_{12}$ ,  $B_{21}$ , and  $A_{21}$  in Eq. (6). The values of the different parameters listed in Table IV were obtained from the experimental viscosity data with the method of least squares, with equal weights assigned to each point.

The values calculated for  $G_{12}$  in Eq. (4) as a function of composition  $x_1$  for each of the binary mixtures are plotted in Fig. 3. In general,  $G_{12}$  is constant for the mixtures, except for  $pC_4H_8O_2 + cC_6H_{11}CH_3$ ,  $pC_4H_8O_2 + C_6H_{13}Br$ , and  $pC_4H_8O_2 + CH_3COOC_4H_9$ , where  $G_{12}$  is dependent on the composition of the mixture.

Furthermore, the correlating ability of each of the Eqs. (4)–(6) was tested by calculating the standard percentage deviations  $\sigma(\%)$  between the experimental and the calculated viscosity. The values of the percentage standard deviations for each of the equations are also given in the Table IV. The values of  $\sigma$  are in the range from 0.07 to 0.64% for Eq. (4), from 0.05 to 0.80% for Eq. (5), and from 0.02 to 0.32% for Eq. (6) for the present mixtures. The average values of  $\sigma$  for Eqs. (4), (5), and (6) are  $0.27 \pm 0.21$ ,  $0.22 \pm 0.23$ , and  $0.14 \pm 0.09\%$ . From this study, it can be concluded that the correlating ability for all three equations is very good. However, the correlating ability for the Auslaender equation, Eq. (6), is better than for the other two equations considered.

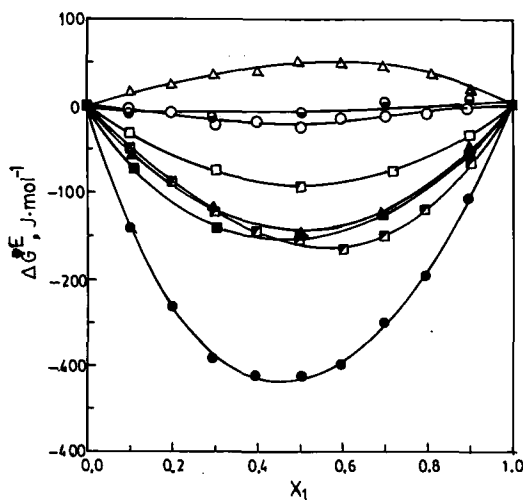


Fig. 4. Excess Gibbs energy of activation  $\Delta G^{*E}$  of viscous flow for binary mixtures *p*-dioxane (1) + component (2). Symbols are the same as in Fig. 1. (—) Calculated with Eq. (3).

## 5. ACTIVATION ENERGY OF VISCOUS FLOW

On the basis of the theory of absolute reaction rates [23], the excess Gibbs energy of activation  $\Delta G^{*E}$  of viscous flow may be calculated from

$$\Delta G^{*E}/RT = \{ \ln(\eta V/\eta_2^0 V_2^0) - x_1 \ln(\eta_1^0 V_1^0/\eta_2^0 V_2^0) \} \quad (7)$$

where  $\eta$  and  $V$  are the viscosity and molar volume of the mixture and  $\eta_i^0$  and  $V_i^0$  are the viscosity and molar volume of the pure component  $i$ , respectively. The estimated accuracy of  $\Delta G^{*E}$  is about  $15 \text{ J mol}^{-1}$ . A polynomial of type Eq. (3) was fitted to the  $\Delta G^{*E}/RT$  results of each mixture. The values of coefficients  $A_i$  in Eq. (3), and the standard deviations  $\sigma$  are included in Table III. The plots of the results of  $\Delta G^{*E}$  for the present systems, and their representation by Eq. (3), are shown in Fig. 4.

## 6. MOLECULAR INTERACTIONS

The large and negative values of  $\Delta \ln \eta$ ,  $\Delta G^{*E}$ , and  $G_{12}$  for  $p\text{C}_4\text{H}_8\text{O}_2 + c\text{C}_6\text{H}_{11}\text{CH}_3$  are similar to those obtained for the system  $p\text{C}_4\text{H}_8\text{O}_2 + c\text{C}_6\text{H}_{12}$  [5]. They are indicative of the fact that the cohesive forces between pairs of unlike molecules are far less than the forces between

the pairs of like molecules. This is consistent with the view of the large dispersion forces in the mixture  $pC_4H_8O_2 + cC_6H_{11}CH_3$  as evidenced by the large and positive values of excess enthalpy and excess volume [25, 26].

For the systems  $pC_4H_8O_2 + C_6H_{13}Cl$  and  $+C_6H_{13}Br$ , the negative values of  $\Delta \ln \eta$  and  $\Delta G^{*E}$  are comparatively much smaller than those observed for  $pC_4H_8O_2 + nC_6H_{14}$ , [5] which suggests enhanced interaction between *p*-dioxane and haloheptane.

The viscosity behavior of the present mixtures  $pC_4H_8O_2 + C_6H_4(CH_3)_2$  and  $pC_4H_8O_2 + C_6H_5C_3H_7$  is not much different from that of  $pC_4H_8O_2 + C_6H_6$  and  $pC_4H_8O_2 + C_6H_5CH_3$ , studied earlier [5]. The values of  $\Delta \ln \eta$  and  $\Delta G^{*E}$  are very small, having either sign. This indicates that the dispersive forces are counter-balanced by the specific interaction. The slight variation in the values of  $\Delta \ln \eta$  and  $\Delta G^{*E}$  for aromatic hydrocarbon mixtures is attributable to the difference in the polarity of aromatic hydrocarbons and substitution in the benzene ring.

The values of  $\Delta \ln \eta$  and  $\Delta G^{*E}$  for the three ester mixtures are negative except for  $pC_4H_8O_2 + CH_3COOC_5H_{11}$ , where  $\Delta G^{*E}$  changes the sign from small negative to small positive as the concentration of *p*-dioxane is increased. The small to moderate negative values of  $\Delta \ln \eta$  and  $\Delta G^{*E}$  may be explained by considering the fact that destruction of dipolar order in pure esters is counter-balanced by weak electrostatic attraction energy between unlike pairs [5, 6]. The variation in the values of  $\Delta \ln \eta$  and  $\Delta G^{*E}$  is presumably due to the difference in alkyl chain length of ester molecules.

## 7. CONCLUSIONS

From this study, it may be concluded that specific interactions exist in *p*-dioxane + aromatic hydrocarbon, + haloalkane, and + ester mixtures. Further, it can be said that all three equations, due to Grunberg–Nissan, McAllister, and Auslaender, correlate the viscosities of the present binary mixtures very well.

## REFERENCES

1. D. D. Deshpande and S. L. Oswal, *J. Chem. Soc. Faraday Trans I* **68**:1059 (1972).
2. D. D. Deshpande and S. L. Oswal, *J. Chem. Thermodyn.* **7**:155 (1975).
3. S. L. Oswal and D. D. Deshpande, *Indian J. Chem. Sec. A* **16**:798 (1978).
4. S. L. Oswal and D. D. Deshpande, *Int. Data Ser. Sel. Data Ser. A* **1**:7–36 (1988).
5. S. L. Oswal and R. P. Phalak, *Int. J. Thermophys.* **13**:251 (1992).
6. S. L. Oswal and R. P. Phalak, *J. Soln. Chem.* **22**:43 (1993).
7. S. L. Oswal and J. P. Dave, *Int. J. Thermophys.* **13**:943 (1992).
8. S. G. Patel and S. L. Oswal, *J. Chem. Soc. Faraday Trans.* **88**:2497 (1992).
9. L. Ubbelohde, *Ind. Eng. Chem. Anal. Edn.* **9**:85 (1937).

10. F. A. Concalves, J. Kestin, and J. V. Sengers, *Int. J. Thermophys.* **12**:1013 (1991).
11. J. A. Riddick, W. B. Bunger, and T. K. Sakano, *Organic Solvents: Physical Properties and Method of Purifications*, 4th ed. (Wiley Interscience, New York, 1986).
12. K. Tamura, S. Murakami, and S. Doi, *J. Chem. Thermodyn.* **17**:325 (1985).
13. R. C. Weast, *Hand Book of Chemistry and Physics*, 59th ed. (Chemical Rubber Co., Cleveland, OH, 1979).
14. P. J. Petrino, Y. H. Gaston-Bonhomme, and J. L. E. Chevalier, *J. Chem. Eng. Data* **40**:136 (1995).
15. J. Ortega, *Ber. Bunsenges. Phys. Chem.* **93**:730 (1989).
16. J. Timmermans, *Physico-Chemical Constants of Pure Organic Compounds*, Vol. 2 (Elsevier, Amsterdam, 1965).
17. R. R. Dreisbach, *Physical Properties of Chemical Compounds II and III* (Am. Chem. Soc., Washington, DC, 1961).
18. J. Ortega, J. S. Matos, M. I. Paz-Andrade, and J. Fernandez, *J. Chem. Eng. Data* **32**:464 (1987).
19. *TRC Data Bases for Chemistry and Engineering*, TRC Thermodynamics Tables; (Research Center, Texas A&M University System, College Station, 1994).
20. O. Redlich and A. T. Kister, *Ind. Eng. Chem.* **40**:345 (1948).
21. L. Grunberg and A. H. Nissan, *Trans. Faraday Soc.* **45**:125 (1949).
22. P. A. McAllister, *AIChE J.* **6**(3):427 (1960).
23. S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Process* (McGraw-Hill, New York, 1941).
24. G. Auslaender, *Br. Chem. Eng.* **9**:610 (1964).
25. S. C. Sharma, M. L. Lakhanpal, and M. L. Rumpul, *Indian J. Chem. Sect. A* **21**:67 (1982).
26. D. V. S. Jain, V. K. Singh, S. B. Saini, and R. S. Sidhu, *J. Chem. Thermodyn.* **15**:1105 (1983).