

## Excess molar volumes and viscosities of binary mixtures of 1,2-diethoxyethane with chloroalkanes at 298.15 K

AMALENDU PAL\*<sup>a</sup> and RAKESH KUMAR BHARDWAJ<sup>b</sup>

<sup>a</sup>Department of Chemistry, Kurukshetra University, Kurukshetra 136 119, India

<sup>b</sup>Department of Chemistry, Dyal Singh College, Karnal 132 001, India  
e-mail: search@vidya.kuk.ernet.in

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**Abstract.** Excess molar volumes ( $V_m^E$ ) and viscosities ( $\eta$ ) of the binary mixtures of 1,2-diethoxyethane with di-, tri- and tetrachloromethane have been measured at 298.15 K and atmospheric pressure over the entire mole fraction range. The deviations in viscosities ( $\Delta \ln \eta$ ) and excess energies of activation ( $\Delta G^{*E}$ ) for viscous flow have been calculated from the experimental data. The Prigogine–Flory–Patterson (PFP) model has been used to calculate  $V_m^E$ , and the results have been compared with experimental data. The Bloomfield and Dewan model has been used to calculate viscosity coefficients and these have also been compared with experimental data for the three mixtures. The results have been discussed in terms of dipole–dipole interactions between 1,2-diethoxyethane and chloroalkanes and their magnitudes decreasing with the dipole character of the molecules. A short comparative study with results for mixtures with polyethers and chloroalkanes is also described.

**Keywords.** Excess volumes; viscosity deviations; binary mixtures; 1,2-diethoxyethane; chloroalkanes.

### 1. Introduction

In our previous paper<sup>1</sup> we have studied the excess molar volumes and viscosities of 1,2-dimethoxyethane with chloroalkanes at 298.15 K. In continuation of these investigations on the thermodynamic and transport properties of some mixtures of polyethers with organic solvents<sup>2,3</sup>, the present paper reports the excess molar volumes ( $V_m^{*E}$ ), deviation in viscosity ( $\Delta \ln \eta$ ) and excess energies of activation ( $\Delta G^{*E}$ ) for viscous flow for mixtures containing 1,2-diethoxyethane (DEE) with dichloromethane (DCM), trichloromethane (TCM) or tetrachloromethane (TC) over the entire mole fraction range at atmospheric pressure and 298.15 K, for characterizing their possible interactions. This will be useful in developing a further complete treatment of the present mixtures. Investigations into the literature have shown that excess properties of binary mixtures containing chloroalkanes have previously been studied by several authors<sup>4–7</sup>. The present study was therefore undertaken in order to compare the excess molar volumes and deviations in viscosity of 1,2-diethoxyethane + chloroalkanes with those of our previous results for 1,2-dimethoxyethane + chloroalkanes<sup>1</sup> by an enlargement of the alkyl group, that is, by the addition of an CH<sub>2</sub> unit, for species with a common polar head group. An attempt is also

\*For correspondence

made to rationalize the results by collecting the data on polyethers + chloroalkanes. We are not aware of any study on the excess properties of binary mixtures of 1,2-diethoxyethane with chloroalkanes.

The Prigogine–Flory–Patterson (PFP) model<sup>8–13</sup> has been used successfully in describing  $V_m^E$  of binary mixtures. Viscosities of the mixtures have also been analysed by means of the Bloomfield and Dewan<sup>14</sup> method, based both on the free-volume theory and the absolute reaction rate theory.

## 1. Experimental

### 2.1 Materials

Materials are of the same origin and purity as used in earlier studies<sup>15</sup>. The samples of dichloromethane (Qualigens, HPLC grade, minimum assay 99.8%) and 1,2-diethoxyethane (Lancaster, UK, 98%) were used without further purification. The densities and viscosities of these liquids were measured and compared at 298.15 ( $\pm 0.01$ ) K and atmospheric pressure with their corresponding literature values<sup>4,16–22</sup> as shown in table 1. All liquids were kept in dark bottles over 4 Å molecular sieves, to reduce the water content, and protected against atmospheric moisture and CO<sub>2</sub>. Prior to the measurements, all liquids were partially degassed under vacuum.

### 2.2 Apparatus and procedure

Excess molar volumes were measured by means of a continuous dilution dilatometer in fashion similar to that described by Dickinson *et al*<sup>23</sup>. Details of its calibration, experimental set up and operational procedure have been described previously<sup>24</sup>. The excess molar volumes are reproducible to  $\pm 0.003 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ . Each run covered just over half of the mole fraction range so as to give an overlap between two runs. The composition of each mixture was obtained from the measured apparent masses of the components with an accuracy of  $1 \times 10^{-4}$ . All masses were corrected for buoyancy.

**Table 1.** Densities and viscosities of pure components at 298.15 K.

Substance	$\rho$ (kg m <sup>-3</sup> )		$\eta$ (mPa s)	
	Exp.	Lit.	Exp.	Lit.
1,2-Diethoxyethane	836.2	836.2 <sup>16</sup> 836.07 <sup>17</sup>	0.602	
Dichloromethane	1316.3	1316.2 <sup>4</sup> 1316.78 <sup>19</sup> 1316.8 <sup>20</sup>	0.406	0.410 <sup>4</sup> 0.4043 <sup>19</sup>
Trichloromethane	1479.4	1479.1 <sup>4</sup> 1479.70 <sup>19</sup> 1478.55 <sup>21</sup> 1479.7 <sup>22</sup>	0.532	0.537 <sup>4</sup> 0.5357 <sup>18</sup> 0.5357 <sup>19</sup>
Tetrachloromethane	1584.3	1584.3 <sup>4</sup> 1584.36 <sup>19</sup> 1584.3 <sup>20</sup>	0.905	0.900 <sup>4</sup> 0.9004 <sup>19</sup>

The kinematic viscosities ( $\mathbf{n}$ ) of both the pure liquids and the mixtures were determined at atmospheric pressure and 298.15 K with a calibrated Ubbelohde suspended level viscometer. Experimental details have been given previously<sup>25,26</sup>. Care was taken to prevent evaporation during the measurements. An average of four or five sets of flow time for each fluid was taken for the purpose of the calculation of viscosity. The flow time measurements were made with an electronic stopwatch having a precision of  $\pm 0.01$  s. After multiplication by the density, the dynamic viscosity,  $\mathbf{h}$ , was deduced with a relative error of  $3 \times 10^{-3}$  mPa s. The performance of the viscometer was checked by measuring and comparing the viscosities of the pure liquids with the values reported in the literature<sup>19,27</sup>. The densities of pure liquids were measured with a bicapillary pycnometer, which gave an error of  $\pm 0.3$  kg m<sup>-3</sup>. All measurements were made in a thermostatically controlled, well-stirred water-bath whose temperature was controlled to  $\pm 0.01$  K. Densities of liquid mixtures were computed from the excess volume and composition according to the relation:

$$\mathbf{r} = (x_1 M_1 + x_2 M_2) / (V_m^E + x_1 V_1 + x_2 V_2), \quad (1)$$

where  $x_1$  and  $x_2$  are mole fractions,  $M_1$  and  $M_2$  are molar masses, and  $V_1$  and  $V_2$  are molar volumes of 1,2-diethoxyethane and chloroalkanes respectively.

### 3. Result and discussion

Results of measurements of excess molar volumes for all the binary mixtures over a range of mole fractions at 298.15 K and atmospheric pressure are given in table 2 and are graphically represented in figure 1.

The viscosities were fitted to a polynomial of type:

$$\mathbf{h} = \sum_{i=1}^k a_i x_i^{i-1}, \quad (2)$$

by the method of least squares with equal weights assigned to each point. The values of coefficients  $a_i$  and standard deviation  $\mathbf{s}$  are listed in table 3a.

The deviation in viscosity has been calculated from the following relationship<sup>28,29</sup>:

$$\Delta \ln \mathbf{h} = \ln \mathbf{h} - x_1 \ln \mathbf{h}_1 - x_2 \ln \mathbf{h}_2, \quad (3)$$

where the additivity law in logarithmic form on mole fraction average was taken into account for ideal mixtures.

On the basis of the theory of absolute reaction rates<sup>30</sup>, the excess energies of activation for viscous flow were obtained with the expression:

$$\Delta G^{*E} = RT(\ln \mathbf{h} V - x_1 \ln \mathbf{h}_1 V_1 - x_2 \ln \mathbf{h}_2 V_2), \quad (4)$$

where  $V$  is the molar volume of the mixtures.  $R$  and  $T$  have their usual meaning. Data on derived densities, viscosities and excess energies of activation for viscous flow for the three systems at 298.15 K are given in table 4.

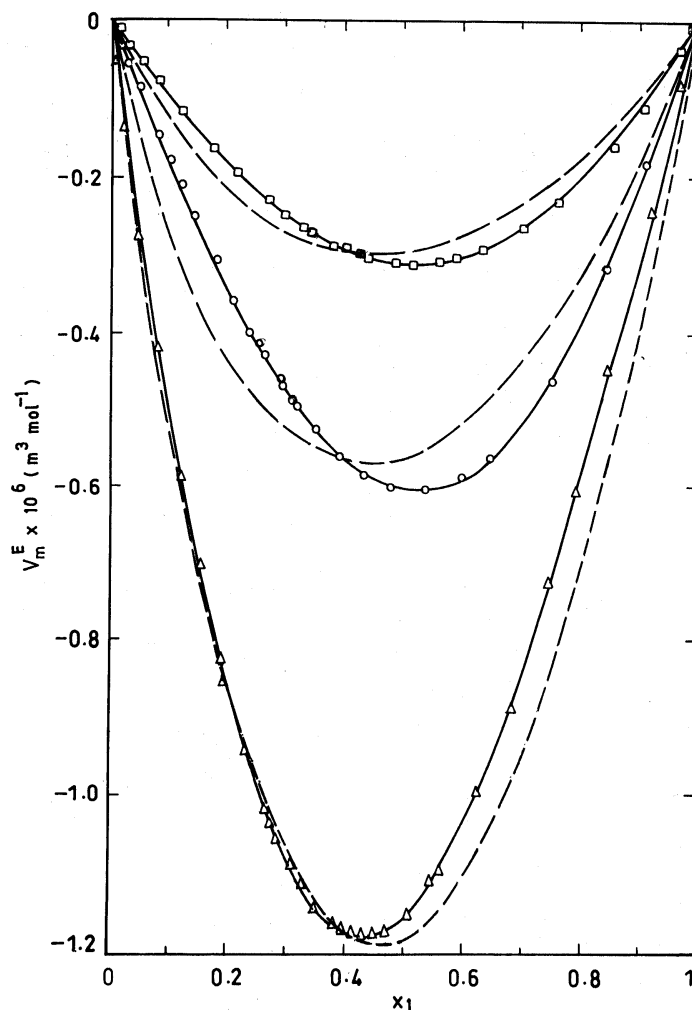
Each set of values has been fitted to the Redlich–Kister type equation:

**Table 2.** Excess molar volumes for 1,2-diethoxyethane + chloroalkane systems at 298.15 K.

$x_1$	$V_m^E \times 10^6$ ( $\text{m}^3 \text{mol}^{-1}$ )	$x_1$	$V_m^E \times 10^6$ ( $\text{m}^3 \text{mol}^{-1}$ )	$x_1$	$V_m^E \times 10^6$ ( $\text{m}^3 \text{mol}^{-1}$ )
<i>1,2-Diethoxyethane + dichloromethane</i>					
0.0044	-0.006	0.1839	-0.305	0.4308	-0.580
0.0092	-0.015	0.2157	-0.356	0.4833	-0.602
0.0199	-0.032	0.2430	-0.394	0.5430	-0.604
0.0332	-0.052	0.2619	-0.412	0.5990	-0.586
0.0503	-0.082	0.2657	-0.426	0.6474	-0.560
0.0695	-0.111	0.2963	-0.460	0.7500	-0.458
0.0852	-0.140	0.3140	-0.487	0.8442	-0.314
0.1060	-0.174	0.3204	-0.490	0.9155	-0.180
0.1256	-0.207	0.3540	-0.520		
0.1466	-0.243	0.3942	-0.555		
<i>1,2-Diethoxyethane + trichloromethane</i>					
0.0084	-0.046	0.2928	-1.054	0.4751	-1.174
0.0243	-0.126	0.3132	-1.091	0.5046	-1.153
0.0538	-0.270	0.3313	-1.116	0.5575	-1.102
0.0868	-0.419	0.3566	-1.145	0.6298	-0.994
0.1265	-0.581	0.3884	-1.169	0.6842	-0.883
0.1591	-0.699	0.3911	-1.173	0.7496	-0.724
0.1966	-0.820	0.4165	-1.174	0.7936	-0.605
0.2388	-0.942	0.4271	-1.176	0.8495	-0.444
0.2729	-1.016	0.4469	-1.177	0.9182	-0.238
0.2810	-1.035	0.4700	-1.178	0.9716	-0.081
<i>1,2-Diethoxyethane + tetrachloromethane</i>					
0.0035	-0.001	0.3363	-0.259	0.5575	-0.305
0.0134	-0.012	0.3435	-0.269	0.5838	-0.299
0.0334	-0.029	0.3687	-0.275	0.6303	-0.289
0.0596	-0.052	0.3801	-0.284	0.7022	-0.260
0.0852	-0.074	0.4067	-0.286	0.7608	-0.225
0.1234	-0.108	0.4353	-0.296	0.8526	-0.155
0.1800	-0.159	0.4362	-0.300	0.9063	-0.104
0.2239	-0.189	0.4770	-0.299	0.9657	-0.036
0.2733	-0.225	0.4859	-0.306	0.9978	-0.002
0.3028	-0.244	0.5153	-0.311		

$$F(x) = x_1 x_2 \sum_{i=1}^k a_i (x_1 - x_2)^{i-1}, \quad (5)$$

where  $a_i$  is the polynomial coefficient and  $k$  is the polynomial degree. The values of the coefficients  $a_i$  are summarized in table 3b along with standard deviations  $\mathbf{s}$ .  $F(x)$  represents  $V_m^E$ ,  $\Delta \ln \mathbf{h}$  or  $\Delta G^{*E}$ . For all mixtures,  $\mathbf{s}(V_m^E)/V_{m(\min)}^E < 0.010$ , where  $V_{m(\min)}^E$  denotes the minimum value of the excess molar volume. There are no literature values of either  $V_m^E$  or  $\mathbf{h}$  for these mixture available for comparison.



**Figure 1.** Experimental excess molar volumes for 1,2-diethoxyethane + dichloromethane, O; + trichloromethane,  $\Delta$ ; + tetrachloromethane,  $\square$ ; PFP theory, -----. Continuous curves were calculated from (5) for experimental data.

Figure 1 shows that  $V_m^E$  values are negative for all the three binary mixtures over the whole range of mole fraction. The behaviour is similar for 1,2-dimethoxyethane with chloroalkanes<sup>1</sup> but with a marked decrease in  $V_m^E$ . The value of  $V_m^E$  decreases with increasing alkyl chain length in the molecule of 1,2-dimethoxyethane. The behaviour is consistent with that of the  $V_m^E$  for mono- and polyethers with chloroalkanes<sup>1-4</sup>:  $V_m^E$  increases in magnitude in the positive direction with increase of the polar head group of polyethers when the alkyl chain end of the polyether is fixed. The negative values of  $V_m^E$  can be explained by considering the chemical or specific interactions which have resulted from differences in molecular volumes and free volumes<sup>31</sup>, possible association by hydrogen bonds and/or dipole-dipole interactions leading to weak complex formation.

**Table 3a.** Coefficients  $a_i$  from (2) for viscosity  $h$  (mPa s) and standard deviation  $s$ .

1,2-Diethoxyethane +	$a_1$	$a_2$	$a_3$	$a_4$	$a_5$	$s$
Dichloromethane	0.405	0.633	-0.191	-0.592	0.349	0.002
Trichloromethane	0.524	1.103	-0.417	-2.055	1.458	0.003
Tetrachloromethane	0.905	-0.094	-0.588	0.592	-0.213	0.002

**Table 3b.** Coefficients  $a_i$  from (5) and standard deviation  $\sigma$  determined by the method of least squares.

1,2-Diethoxyethane +		$a_1$	$a_2$	$a_3$	$a_4$	$a_5$	$s$
Dichloromethane	$V_m^E \times 10^6 (\text{m}^3 \text{mol}^{-1})$	-2.413	-0.268	0.499	-0.091		0.002
	$\Delta \ln(h/\text{mPa s})$	0.910	-0.248	-0.045	0.049		0.003
	$\Delta G^{*E} (\text{J mol}^{-1})$	2933	-794	114	186	-338	8
Trichloromethane	$V_m^E \times 10^6 (\text{m}^3 \text{mol}^{-1})$	-4.641	1.350	0.563	-0.159		0.003
	$\Delta \ln(h/\text{mPa s})$	1.407	-0.655	-0.255	0.238		0.003
	$\Delta G^{*E} (\text{J mol}^{-1})$	3740	-1682	-186	563	-752	9
Tetrachloromethane	$V_m^E \times 10^6 (\text{m}^3 \text{mol}^{-1})$	-1.226	-0.099	0.198	-0.080		0.003
	$\Delta \ln(h/\text{mPa s})$	0.181	-0.073	0.066	0.015		0.002
	$\Delta G^{*E} (\text{J mol}^{-1})$	604	-200	41	48	238	6

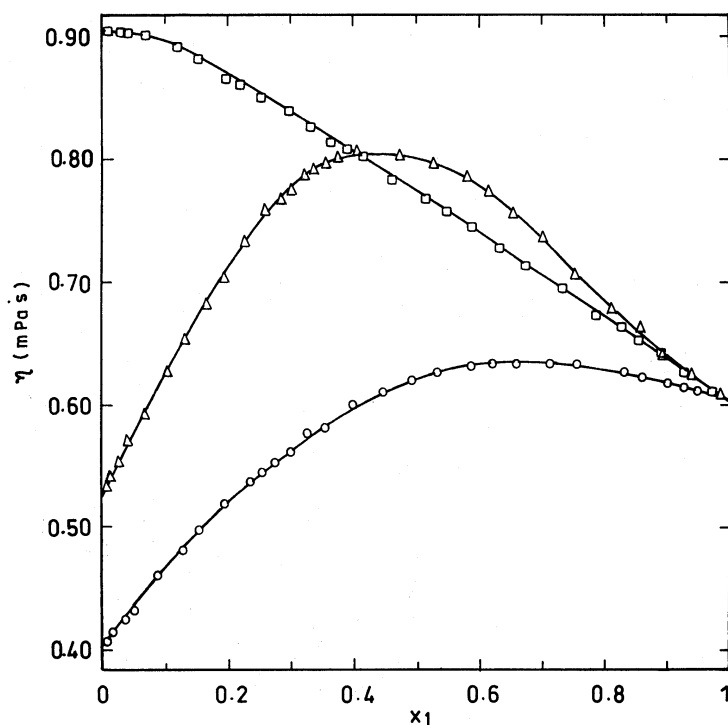
The algebraic values of  $V_m^E$  for all the three binary systems with 1,2-diethoxyethane are in the order, TCM > DCM > TC. The negative contribution to the  $V_m^E$  of the TCM and DCM is due to the strong interactions between the ether oxygen and the more polarized hydrogen(s) of these solvents<sup>32-35</sup> in addition to the disruption of the dipole structure of both the components when they are mixed<sup>36,37</sup>. Moreover, there is clear evidence of the effect of the position of the hydrogen atom in the chloroalkane structure: asymmetrical trichloromethane has a higher negative  $V_m^E$  than symmetrical dichloromethane.

The Prigogine-Flory-Patterson (PFP) theory<sup>8-13</sup> was used to correlate the  $V_m^E$  results for the present mixtures. The various parameters involved in the PFP theory for the pure components are listed in table 5. In the prediction of  $V_m^E$  values by PFP theory, the interaction parameter  $c_{12}$  is needed; this can be evaluated using  $H^E$  values. Since excess functions other than the excess volumes of mixing of our systems are not known, the  $c_{12}$  parameter was adjusted by fitting the experimental  $V_m^E$  results over the whole mole fraction range. Values of  $c_{12}$  obtained from PFP theory are listed in the last column of table 5 and figure 1 presents the results together with the experimental values. The much larger negative values of the  $c_{12}$  parameter for the 1,2-diethoxyethane (DEE) + trichloromethane (TCM) system indicates the possible chemical interaction as suggested from the  $V_m^E$  results.

We have determined  $h$  and calculated  $\Delta \ln h$  and  $\Delta G^{*E}$  values at 298.15 K and these are shown in figures 2-4. There is a maximum in the 1,2-diethoxyethane (DEE) + trichloromethane (TCM) system (figure 2), indicating specific interactions. This behaviour also finds support from the negative values of excess molar volumes and  $c_{12}$ . Positive values of  $\Delta \ln h$  would imply that (i) the mixture is more viscous than the corresponding ideal mixtures, and (ii) the specific interactions<sup>38</sup> corroborated by the

**Table 4.** Densities, viscosities and excess energies of activation for viscous flow for the (1,2-diethoxyethane + chloroalkanes) system at 298.15 K.

$x_1$	$\rho$ (kg m <sup>-3</sup> )	$\eta$ (mPa s)	$\Delta G^{*E}$ (J mol <sup>-1</sup> )	$x_1$	$\rho$ (kg m <sup>-3</sup> )	$\eta$ (mPa s)	$\Delta G^{*E}$ (J mol <sup>-1</sup> )
<i>1,2-Diethoxyethane + dichloromethane</i>							
0.0038	1312.5	0.408	13	0.3993	1038.1	0.599	747
0.0150	1301.5	0.412	38	0.4481	1015.2	0.609	740
0.0331	1284.2	0.424	101	0.4935	995.3	0.621	743
0.0480	1270.5	0.431	140	0.5299	980.2	0.627	727
0.0899	1234.2	0.459	285	0.5834	959.3	0.630	680
0.1265	1204.9	0.481	387	0.6180	946.5	0.632	646
0.1563	1182.6	0.496	452	0.6610	931.4	0.634	604
0.1936	1156.3	0.515	528	0.7109	914.9	0.632	533
0.2340	1129.8	0.535	598	0.7565	900.6	0.632	474
0.2543	1117.2	0.543	622	0.8304	879.1	0.625	344
0.2729	1106.0	0.555	659	0.8513	873.3	0.623	305
0.3032	1088.4	0.562	669	0.8999	860.5	0.617	210
0.3260	1075.8	0.577	716	0.9247	854.2	0.613	159
0.3522	1061.8	0.580	709	0.9441	849.4	0.610	120
<i>1,2-Diethoxyethane + trichloromethane</i>							
0.0058	1473.2	0.533	5	0.3619	1170.0	0.797	962
0.0149	1463.6	0.541	41	0.3710	1163.8	0.799	963
0.0237	1454.4	0.552	94	0.4043	1141.5	0.805	973
0.0407	1437.0	0.569	170	0.4746	1096.7	0.803	947
0.0680	1409.9	0.592	267	0.5244	1066.8	0.796	907
0.1050	1374.7	0.628	414	0.5774	1036.3	0.787	859
0.1317	1350.3	0.653	507	0.6107	1017.9	0.774	806
0.1652	1321.0	0.682	613	0.6557	993.9	0.756	729
0.1908	1299.3	0.705	690	0.7019	970.1	0.736	642
0.2254	1271.1	0.732	780	0.7508	945.9	0.708	524
0.2624	1242.2	0.759	861	0.8141	916.0	0.680	397
0.2864	1224.0	0.768	887	0.8503	899.5	0.662	313
0.2972	1216.0	0.775	907	0.8965	879.2	0.641	208
0.3259	1195.2	0.786	934	0.9391	861.1	0.625	126
0.3334	1189.9	0.790	947	0.9887	840.7	0.609	36
<i>1,2-Diethoxyethane + tetrachloromethane</i>							
0.0062	1577.7	0.905	6	0.4135	1208.6	0.806	167
0.0184	1564.8	0.902	14	0.4589	1174.1	0.784	146
0.0315	1551.1	0.901	27	0.5115	1135.5	0.768	146
0.0412	1541.0	0.900	35	0.5443	1112.1	0.757	145
0.0729	1508.7	0.898	67	0.5879	1081.9	0.742	137
0.1232	1459.2	0.886	94	0.6317	1052.5	0.728	133
0.1550	1428.9	0.879	104	0.6710	1026.8	0.713	118
0.1998	1387.5	0.865	115	0.7336	987.3	0.694	110
0.2226	1367.0	0.862	130	0.7846	956.3	0.674	88
0.2532	1340.0	0.849	128	0.8240	933.0	0.662	78
0.3028	1297.6	0.840	155	0.8520	916.8	0.653	69
0.3320	1273.4	0.828	149	0.8965	891.8	0.639	56
0.3689	1243.6	0.814	146	0.9338	871.3	0.626	38
0.3885	1228.0	0.812	161	0.9711	851.3	0.613	19



**Figure 2.** Experimental viscosity for 1,2-diethoxyethane + dichloromethane, O; + trichloromethane, Δ; + tetrachloromethane, □. Continuous curves were calculated from (2) for experimental data.

**Table 5.** Parameters of pure components and Prigogine-Flory-Patterson theory ( $c_{12}$ ) at 298.15 K.

	$a \times 10^{-4}$ ( $k^{-1}$ )	$k_T \times 10^7$ ( $k Pa^{-1}$ )	$V^* \times 10^6$ ( $m^3 mol^{-1}$ )	$P^* \times 10^{-6}$ ( $J m^{-3}$ )	$T^*$	$\bar{h}$	$\bar{t}$	$c_{12} \times 10^6$ ( $J m^{-3}$ )
1,2-Diethoxyethane	10.28 <sup>a</sup>	10.03	112.74	480 <sup>b</sup>	5149	1.2535	0.0579	
Dichloromethane	13.91 <sup>4</sup>	10.26 <sup>4</sup>	48.78	707	4430	1.3227	0.0673	-58.74
Trichloromethane	12.60 <sup>4</sup>	9.98 <sup>4</sup>	62.13	635	4644	1.2987	0.0642	-83.70
Tetrachloromethane	12.29 <sup>4</sup>	10.80 <sup>4</sup>	75.10	567	4695	1.2928	0.0635	-22.70

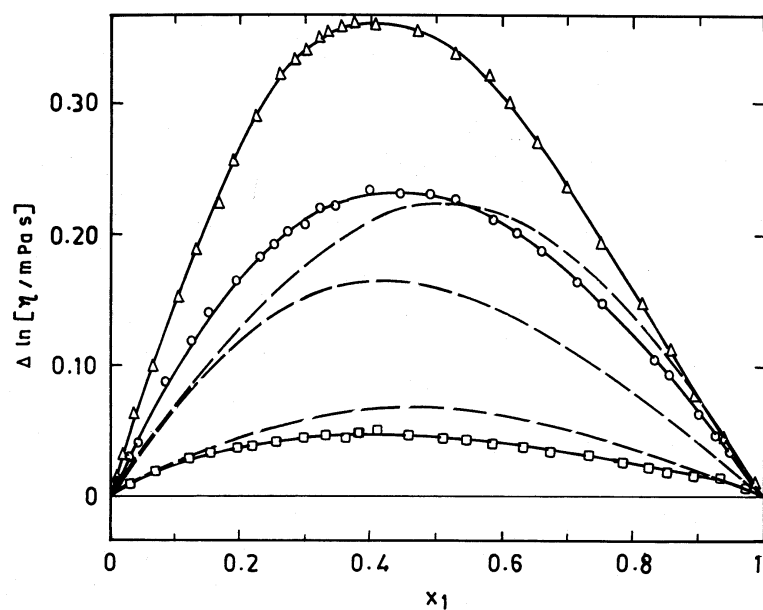
<sup>a</sup>Calculated from our measured densities; <sup>b</sup>calculated from the relation<sup>42</sup>;  $P^* = (\Delta H_{vap} \times V)/(V^*)^2$ ;  $\Delta H_{vap}$  (heat of vaporization from ref. 43)

negative  $V_m^E$  and positive  $\Delta G^{*E}$  values. The  $\Delta G^{*E}$  parameter may be considered<sup>39,40</sup> to be a useful indicator of the presence of specific interaction<sup>38</sup> between molecules. Different expressions are available in the literature to calculate  $\mathbf{h}$ . In the present work, we have applied the method of Bloomfield and Dewan<sup>14</sup>.

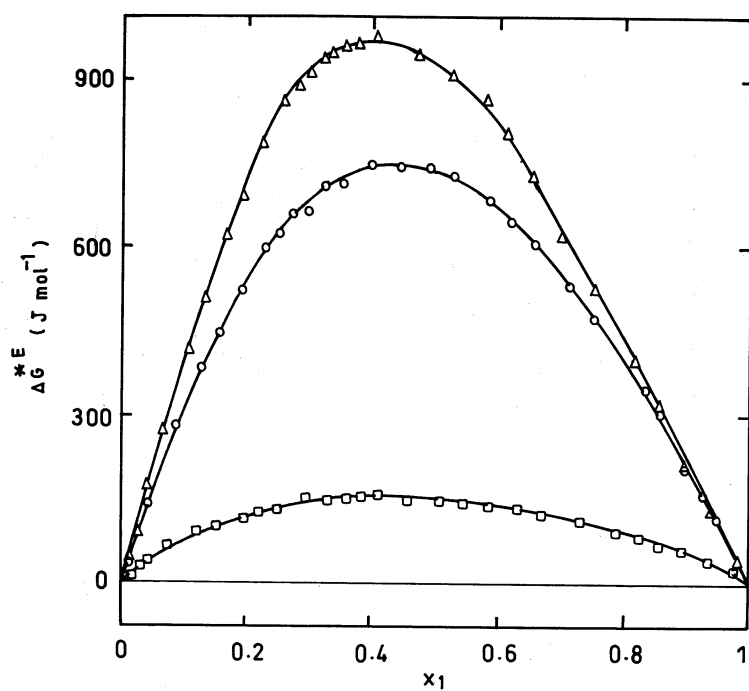
Bloomfield and Dewan developed an expression from the combination of the theories of free volumes and absolute reaction rate. The expression is given by:

$$\Delta \ln \mathbf{h} = f(\tilde{v}) - \Delta G^R / RT, \quad (6)$$





**Figure 3.** Experimental viscosity deviations for 1,2-diethoxyethane + dichloromethane, O; + trichloromethane, Δ; + tetrachloromethane, □; Bloomfield and Dewan, -----. Continuous curves were calculated from (5) for experimental data.



**Figure 4.** Excess energy of activation for viscous flow for 1,2-diethoxyethane + dichloromethane, O; + trichloromethane, Δ; + tetrachloromethane, □. Continuous curves were calculated from (5) for experimental data.

where  $f(\tilde{v})$  is the characteristic function of the free volume defined by,

$$f(\tilde{v}) = 1/(\tilde{v} - 1) - x_1/(\tilde{v}_1 - 1) - x_2/(\tilde{v}_2 - 1), \quad (7)$$

and  $\Delta G^R$  is the residual energy of mixing, calculated with the following expression<sup>41</sup>:

$$\Delta G^R = \Delta G^E + RT\{x_1 \ln(x_1/j_1) + x_2 \ln(x_2/j_2)\}. \quad (8)$$

The excess free energy can be obtained from Flory's theory<sup>10,11</sup> as given by the following expression:

$$\begin{aligned} \Delta G^E = & x_1 P_1^* V_1^* [1/(\tilde{v}_1) - 1/(\tilde{v}) + 3\tilde{T}_1 \ln\{\tilde{v}_1^{1/3} - 1\}/(\tilde{v}^{1/3} - 1)] + x_2 P_2^* V_2^* \\ & [1/(\tilde{v}_2) - 1/(\tilde{v}) + 3\tilde{T}_2 \ln\{\tilde{v}_2^{1/3} - 1\}/(\tilde{v}^{1/3} - 1)] + (x_1 q_2 V_1^* c_{12})/\tilde{v}, \end{aligned} \quad (9)$$

where the various symbols used have their usual meanings.

Using the  $\chi_{12}$  values from the fitting values of  $V_m^E$  and table 5, we have calculated  $\Delta G^E$  and  $f(\tilde{v})$  and finally  $\Delta \ln h$ , according to the Bloomfield and Dewan relationship<sup>14</sup>, which is compared with the experimental data as shown in figure 3.

#### 4. Conclusions

It is interesting to note that in going from tetrachloromethane to trichloromethane the absolute values of  $V_m^E$  become about four times larger. Since interaction between chloroalkanes and the ether DEE cannot imply hydrogen bonding, the high value of dipole moment of trichloromethane ( $m=1.15$  compared with  $m=1.14$  and 0 of dichloromethane and tetrachloromethane) may be responsible for a decrease in the negative contribution in  $V_m^E$ .

Further, an analysis of each of the three contributions to the  $V_m^E$ ,  $\Delta \ln h$ , and  $\Delta G^{*E}$  of the present mixtures suggests the presence of dipole-dipole interactions in the DEE + TCM or DCM mixtures. Finally, it should be noted that in spite of strong interactions existing between species, the PFP theory correctly predicts the sign of  $V_m^E$  for all the mixtures. However, some deviations in estimation of  $\Delta \ln h$ , based on the Bloomfield and Dewan theory, obtained from the present analysis of viscosity were observed.

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