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Viscosities of Nonelectrolyte Liquid Mixtures. I. Binary Mixtures Containing *p*-Dioxane

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Viscosity measurements are reported for *p*-dioxane with cyclohexane, *n*-hexane, benzene, toluene, carbon tetrachloride, tetrachloroethane, chloroform, pentachloroethane, and ethyl acetate at 303.15 K. Excess Gibbs energies of activation ΔG^{*E} of viscous flow have been calculated with Eyring's theory of absolute reaction rates. The deviations of the viscosities from a linear dependence on the mole fraction and values of ΔG^{*E} for binary mixtures have been explained in terms of molecular interactions between unlike pairs. The Prigogine–Flory–Patterson theory has been used to estimate the excess viscosity, $\Delta \ln \eta$, and corresponding enthalpy $\ln \eta_H$, entropy $\ln \eta_S$, and free volume $\ln \eta_V$ terms for binary mixtures of *p*-dioxane with cyclohexane, *n*-hexane, benzene, toluene, carbon tetrachloride, and chloroform. Estimates of excess viscosities from this theory for *p*-dioxane with benzene, toluene, and carbon tetrachloride are good, while for the other three mixtures they are poor. The local-composition thermodynamic model of Wei and Rowley estimates the excess viscosity quite well even for *p*-dioxane mixtures with cyclohexane and *n*-hexane.

KEY WORDS: activation energy; aromatic hydrocarbons; chloroalkanes; *p*-dioxane; molecular interactions; viscosity.

1. INTRODUCTION

There exists considerable interest in the investigation of excess thermodynamic functions of cyclic ethers in polar and nonpolar solvents [1–6]. Cyclic ethers are of technical importance as solvents. In addition, cyclic polyethers have attracted interest as model substances for biosystems and for their use in synthetic methods in organic chemistry [7, 8]. From the thermodynamic studies, it has been observed that there exist specific interactions between cyclic ethers and aromatic hydrocarbons and between

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cyclic ethers and haloalkanes [2–4, 6]. The measurement of viscosity is also an important technique for studying structural changes associated with liquids. It also reveals information about the molecular packing, molecular motion, and various types of intermolecular interactions as related to size, shape, and chemical nature of the component molecules [9–12]. In view of this, the present paper deals with the viscosity of binary mixtures containing *p*-dioxane as one of the components so as to gain further insight into the molecular interactions in like and unlike molecules. The excess viscosities are also analyzed in terms of the Prigogine–Flory–Patterson (PFP) theory [13–15] and the Wei–Rowley local-composition thermodynamic (LCT) model [16, 17] of liquid mixtures.

2. EXPERIMENTAL

2.1. Method

The viscosity η measurements were made with a modified Ubbelhode suspended-level viscometer [18]. The viscometer was so designed to reduce surface-tension effects to negligible values as recommended by Gonçalves et al. [19]. It had a capillary of very fine uniform bore of 0.15-mm diameter and 35-cm length. The capillary had a sudden enlargement at the exist. The efflux time of a definite volume (about 5 cm^3) of doubly distilled water, measured with an accurate stopwatch with a resolution of 0.1 s, was more than 210 s. In the experiment the viscometer was suspended vertically for a sufficient time in a constant-temperature bath maintained within 0.02 K. Doubly distilled water and purified benzene were used for the calibration of the viscometer. The required densities ρ for the measurements of viscosity were determined with a calibrated glass pycnometer. The details of the procedure of measuring the viscosity and density have been described previously [11, 12]. The errors of η and ρ are estimated to be 0.4% and 0.01%, respectively.

2.2. Source and Purity of Samples

p-Dioxane (BDH, AR), cyclohexane (Merck, GR), *n*-hexane (Fluka, AG), benzene (Merck, GR), toluene (Merck, GR), carbon tetrachloride (BDH, AR), 1,1,2,2-tetrachloroethane (Ridel-Dehaenat Seelze-Hannover) chloroform (BDH, AR), pentachloroethane (Fluka, AG), and ethyl acetate (BDH, AR) were used after further purification and drying by standard procedures [20]. Details of the purification procedures have been discribed previously [4, 21]. The purified samples have densities, refractive indices, and viscosities that are in close agreement with the literature values [20–24] as shown in Table I.

Table I. Density, Refractive Index, and Viscosity of Liquid Components at 303.15 K

	Density ($g \cdot cm^{-3}$)		Refractive index		Viscosity ($mPa \cdot s$)	
Component	Expt.	Lit.[a,b]	Expt.	Lit.[a]	Expt.	Lit.[a]
p-Dioxane	1.0223	1.0223	1.4180	1.4180	1.090	1.087
Cyclohexane	0.7692	0.7693 0.76914	1.4210	1.4214	0.818	0.819
n-Hexane	0.6502	0.65018	1.3704	1.3697	0.279	0.278
Benzene	0.8684	0.86831 0.86843	1.4951	1.4947	0.559	0.562
Toluene	0.8578	0.8577	1.4910	1.4913	0.520	0.520
CTC	1.5747	1.5748	1.4575	1.4546	0.844	0.845
Chloroform	1.4684	1.4706	1.4399	1.4400	0.507	0.514
TCE	1.5790	1.5786	1.4899	1.4888	1.459	1.456
PCE	1.6651	1.6643	1.5003	1.4980	1.971	2.070
EA	0.8886	0.8886	1.3700	1.3672	0.402	0.400

[a] From Ref. 20.
[b] From Ref. 22–24.

3. RESULTS AND DISCUSSION

3.1. General

The measured viscosities η for the nine binary mixtures of *p*-dioxane with cyclohexane, *n*-hexane, benzene, toluene, carbon tetrachloride (CTC), 1,1,2,2-tetrachloroethane (TCE), chloroform, pentachloroethane (PCE), and ethyl acetate (EA) at 303.15 K as a function of composition are presented in Table II.

The densities ρ of the mixtures required for the calculation of the viscosities for seven binary mixtures, *p*-dioxane with cyclohexane, *n*-hexane, benzene, toluene, CTC, chloroform, and EA, were calculated from accurate excess volume V^E data [3, 9, 25]:

$$\rho = \sum_{1}^{2} x_i M_i \bigg/ \left(\sum_{1}^{2} x_i V_i^0 + V^E \right) \tag{1}$$

where V_i^0 and M_i are the molar volume and molar mass of pure component i. For the remaining two mixtures, *p*-dioxane + TCE and *p*-dioxane + PCE, the densities ρ were determined with a calibrated glass pycnometer. The viscosity values in Table II can be represented by

$$\eta = \sum_{i=0}^{m} A_i x_1^i \tag{2}$$

Table II. Viscosity of Mixtures of p-Dioxane with Various Solvents at 303.15 K as a Function of the Mole Fraction x_1 of p-Dioxane

x_1	η (mPa · s)	x_1	η (mPa · s)	x_1	η (mPa · s)
Cyclohexane		n-Hexane		Benzene	
0.0000	0.818	0.0000	0.279	0.0000	0.559
0.1001	0.793	0.1110	0.297	0.1009	0.603
0.2073	0.783	0.1961	0.317	0.2035	0.645
0.3007	0.785	0.3001	0.348	0.3017	0.687
0.4018	0.787	0.4033	0.389	0.4005	0.736
0.5018	0.815	0.4962	0.436	0.4969	0.787
0.5983	0.841	0.5966	0.498	0.6000	0.841
0.6997	0.882	0.7169	0.601	0.7019	0.895
0.7992	0.934	0.8008	0.700	0.8015	0.961
0.8901	1.000	0.8988	0.854	0.8993	1.024
1.0000	1.090	1.0000	1.090	1.0000	1.090
Toluene		CTC		TCE	
0.0000	0.520	0.0000	0.844	0.0000	1.459
0.0992	0.556	0.0983	0.901	0.0967	1.633
0.1993	0.591	0.2040	0.957	0.1938	1.742
0.2925	0.628	0.2994	1.011	0.2925	1.801
0.3999	0.676	0.4025	1.055	0.3925	1.818
0.4961	0.623	0.4985	1.086	0.4926	1.761
0.5981	0.778	0.6001	1.114	0.5951	1.661
0.6985	0.843	0.6996	1.132	0.6928	1.528
0.8009	0.918	0.8023	1.129	0.7950	1.397
0.8967	0.998	0.8984	1.129	0.8962	1.245
1.0000	1.090	1.0000	1.090	1.0000	1.090
Chloroform		PCE		EA	
0.0000	0.506	0.0000	1.971	0.0000	0.402
0.0995	0.590	0.0967	2.052	0.1021	0.435
0.1981	0.672	0.1938	2.133	0.2024	0.466
0.2998	0.750	0.2925	2.141	0.2982	0.505
0.3953	0.801	0.3925	2.108	0.4026	0.553
0.4992	0.857	0.4926	2.011	0.4968	0.602
0.5971	0.910	0.5951	1.851	0.6025	0.668
0.6993	0.956	0.6928	1.650	0.6970	0.742
0.8015	0.997	0.7950	1.463	0.8007	0.834
0.9021	1.044	0.8962	1.289	0.9003	0.948
1.0000	1.090	1.0000	1.090	1.0000	1.090

Table III. Parameters of Eq. (2), Standard Deviations σ, and Largest Deviations $\delta_{\max}$ for the Viscosity of p-Dioxane (1) + Component (2) at 303.15 K in mPa · s

Component (2)	A_0	A_1	A_2	A_3	A_4	σ	$\delta_{\max}$
Cyclohexane	0.8176	−0.2965	0.6686	−0.3032	0.2042	0.003	−0.005
n-Hexane	0.2802	0.0360	0.9998	−1.5398	1.3120	0.003	−0.004
Benzene	0.5601	0.3933	0.1016	0.0361		0.002	−0.004
Toluene	0.5200	0.3629	−0.0825	0.4022	−0.1120	0.001	0.001
CTC	0.8434	0.5989	−0.0829	−0.2691		0.002	0.003
TCE	1.4582	2.0992	−3.1336	−0.2158	0.8854	0.008	0.013
Chloroform	0.5046	0.9399	−0.4738	−0.0426	0.1623	0.004	0.006
PCE	1.9643	1.2084	−1.3437	−3.0999	2.3705	0.015	0.023
EA	0.4028	0.2653	0.2965	−0.2097	0.3348	0.002	0.002

The parameters A_i, obtained from a least-squares analysis with equal weights assigned to each point, are given in Table III, together with the standard deviations σ and largest deviations $\delta_{\max}$.

Figures 1 and 2 show the viscosity as a function of the mole fractions x_1 for all binary mixtures. Figure 2 also includes the results obtained by

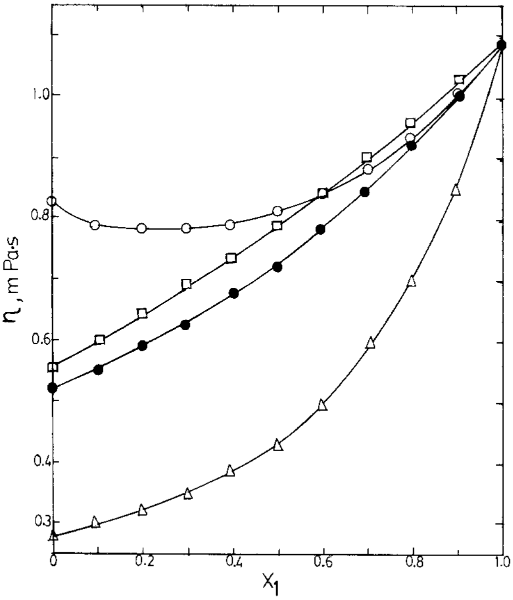

Fig. 1. Dependence of viscosity η at 303.15 K on mole fraction x_1 for binary mixtures containing p-dioxane, cyclohexane (○), n-hexane (△), benzene (□), and toluene (●).

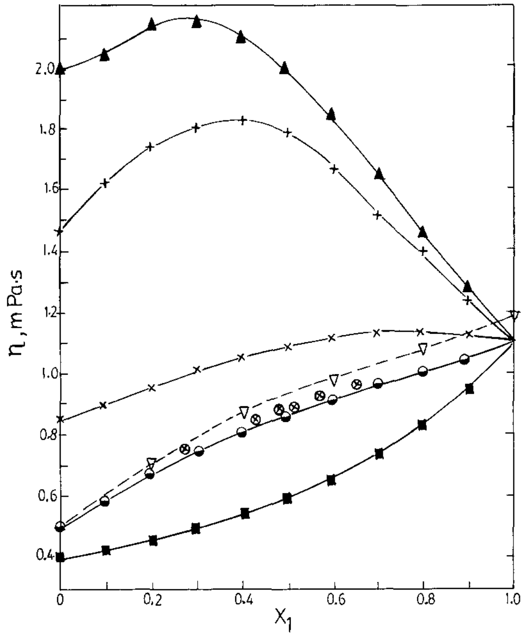

Fig. 2. Dependence of viscosity η at 303.15 K on mole fraction x_1 for binary mixtures containing *p*-dioxane, CTC (×), chloroform (present work, ◒ ; Nigam and Mahl [10], ▽; Fort and Moore [9] at 298.15 K, ⊗), TCE (+), PCE (▲), and EA (■).

Nigam and Mahl [10] at 303.15 K and by Fort and Moore [9] at 298.15 K for the *p*-dioxane + chloroform. The results of Nigam and Mahl [10] exceed the present values by about 1%. However, the pattern of the variation of the viscosity with composition is the same, i.e., both results show a similar positive deviation from a linear dependence on the mole fraction.

Figures 1 and 2 show that the viscosities exhibit large and negative deviations from a linear dependence on the mole fraction ($\delta\eta = \eta - x_1\eta_1^0 - x_2\eta_2^0$) for the binary mixtures of *p*-dioxane with cyclohexane, *n*-hexane, and EA; large and positive deviations for the mixtures of *p*-dioxane with CTC, TCE, chloroform, and PCE; and very small deviations in the case of *p*-dioxane + benzene and *p*-dioxane + toluene mixtures. For the *p*-dioxane + benzene mixture a slight positive deviation is observed at low mole fractions of *p*-dioxane which changes sign at higher mole fractions, while for the *p*-dioxane + toluene mixture, the deviation is small but negative throughout.

The *p*-dioxane + cyclohexane mixture shows minima which occur between 0.2 and 0.3 mole fraction of *p*-dioxane. There are no minima for the mixtures of *p*-dioxane either with *n*-hexane or with EA. All four binary mixtures of *p*-dioxane with chloroalkanes show positive deviations and the maxima occur for the mixtures containing CTC, TCE, and PCE around 0.7, 0.4, and 0.3 mole fractions x_1 of *p*-dioxane, respectively.

In addition, the excess viscosity $\Delta \ln \eta$ can be calculated from the Arrhenius equation [26],

$$\Delta \ln \eta = \ln(\eta/\eta_2^0) - x_1 \ln(\eta_1^0/\eta_2^0) \qquad (3)$$

where η_1^0 and η_2^0 represent the viscosity of pure components 1 and 2, respectively. The values of the $\Delta \ln \eta$ have been fitted to a Redlich–Kister polynomial equation,

$$\Delta \ln \eta = x_1 x_2 \sum_{i=0}^{m} B_i (1 - 2x_1)^i \qquad (4)$$

The parameters B_i and the standard deviations σ are listed in Table IV. The dependence of $\Delta \ln \eta$ on the mole fraction x_1 is shown in Fig. 3.

3.2. Activation Energy of Viscous Flow

On the basis of the theory of absolute reaction rates [27] and following Katti and Chaudhri [28], the excess Gibbs energy of activation ΔG^{*E} of viscous flow may be calculated from

$$\Delta G^{*E} = RT[\ln(\eta V/\eta_2^0 V_2^0) - x_1 \ln(\eta_1^0 V_1^0/\eta_2^0 V_2^0)] \qquad (5)$$

Table IV. Parameters of Eq. (4) and Standard Deviations σ of $\Delta \ln \eta$ for the Binary Mixtures *p*-Dioxane (1) + Component (2) at 303.15 K

Component (2)	B_0	B_1	B_2	B_3	$10^3\,\sigma$
Cyclohexane	−0.6109	−0.0022	0.001	−0.081	4.0
n-Hexane	−0.9323	−0.1726	−0.131	−0.057	1.6
Benzene	0.0215	−0.0056	0.068	0.021	3.6
Toluene	−0.1581	0.0395	0.077	−0.014	1.6
CTC	0.5043	−0.0530	0.018	0.056	2.5
TCE	1.3338	0.3199	0.003	0.009	9.6
Chloroform	0.5961	0.3882	0.042	−0.124	5.3
PCE	1.2230	0.2684	−0.124	−0.405	8.3
EA	−0.3703	0.0608	0.022	0.092	2.7

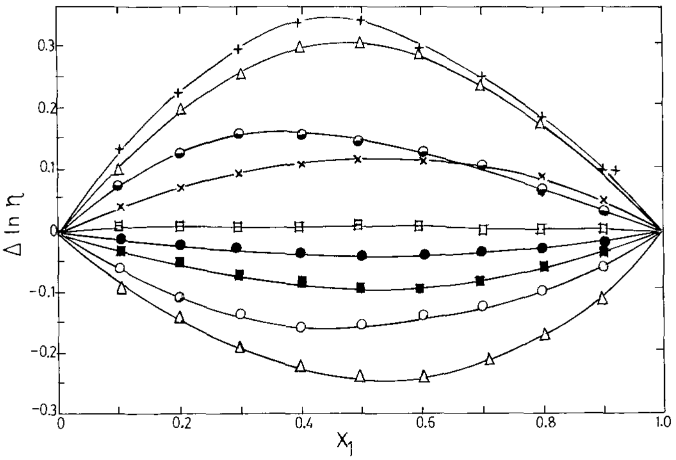

Fig. 3. Dependence of excess viscosity $\Delta \ln \eta$ at 303.15 K on mole fraction x_1 for binary mixtures containing *p*-dioxane. Symbols as in the legends to Figs. 1 and 2.

where η and V are the viscosity and molar volume of the mixture and η_i^0 and V_i^0 are the viscosity and molar of the pure component *i*, respectively. The values of $\Delta G^{*E}/RT$ were fitted to a polynomial expression similar to Eq. (4). The parameters B_i and standard deviations σ are given in Table V.

The dependence of ΔG^{*E} on the mole fraction x_1 of *p*-dioxane is shown in Fig. 4. The estimated accuracy of ΔG^{*E} is about 25 J · mol^{-1}. The values of ΔG^{*E} for *p*-dioxane with cyclohexane, *n*-hexane, and EA are large and negative, and those for *p*-dioxane with CTC, TCE, chloroform,

Table V. Parameters of Eq. (4) and Standard Deviations σ of $\Delta G^{*E}/RT$ for the Binary Mixtures *p*-Dioxane (1) + Component (2) at 303.15 K

Component (2)	B_0	B_1	B_2	B_3	$10^3 \sigma$
Cyclohexane	−0.5331	−0.0655	−0.0677	0.0388	3.8
n-Hexane	−0.8163	0.1491	−0.1613	0.0161	1.7
Benzene	0.0233	−0.0117	0.0567	0.0471	2.2
Toluene	−0.1132	0.0351	0.0764	−0.0079	1.6
CTC	0.4820	−0.0278	−0.0094	−0.0492	2.7
TCE	1.3427	0.3243	0.0077	−0.0134	9.5
Chloroform	0.5924	0.3745	0.0331	−0.1040	5.3
PCE	1.2655	0.2505	−0.1146	−0.3887	7.1
EA	−0.3622	0.0763	−0.0267	0.0287	2.0

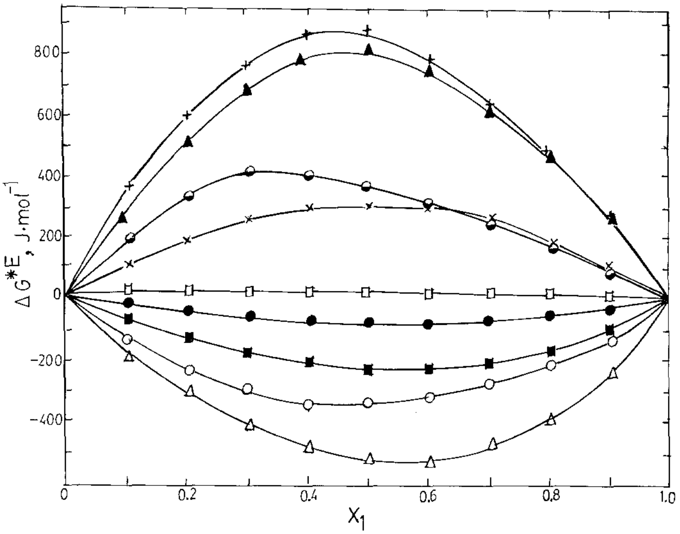

Fig. 4. Dependence of excess Gibbs energy of activation ΔG^{*E} of viscous flow at 303.15 K on mole fraction x_1 for binary mixtures containing *p*-dioxane. Symbols as the legends to Figs. 1 and 2.

and PCE are large and positive. For the mixtures *p*-dioxane with benzene and toluene, the values of ΔG^{*E} are very small. For the former mixture ΔG^{*E} is within 25 $J \cdot mol^{-1}$, while for the latter it is negative throughout, with a maximum value of $-84\ J \cdot mol^{-1}$ at $x_1 = 0.6$.

The absolute values of ΔG^{*E} for *p*-dioxane mixtures increase in the sequence *n*-hexane < cyclohexane < EA < toluene < benzene < CTC < chloroform < PCE and < TCE.

3.3. Molecular Interactions

For an analysis of the results in terms of molecular interactions, the maximum values of the $\Delta \ln \eta$ and the ΔG^{*E} of viscous flow are summarized in Table VI. The values of the excess enthalpy H^E_{max} and the excess volume V^E_{max} from the literature [1,3,9,25,29–31] have also been included in Table VI.

3.3.1. *Mixtures with Aliphatic Hydcrocarbon*

For the two mixtures *p*-dioxane with cyclohexane and *n*-hexane, the large and negative values of ΔG^{*E} and $\Delta \ln \eta$ indicate that the forces between pairs of unlike molecules are far less than the forces between pairs of like molecules, and that is why the mixtures are less viscous. This is

Table VI. Maximum Values of Excess Properties of *p*-Dioxane (1) + Component (2) Mixtures at 303.15 K

Component (2)	$\Delta \ln \eta_{\max}$	$\Delta G^{*E}_{\max}$ ($J \cdot mol^{-1}$)	$H^{E}_{\max}$ ($J \cdot mol^{-1}$)	$V^{E}_{\max}$ ($cm^3 \cdot mol^{-1}$)
Cyclohexane	−0.154	−350	1600[a]	0.965[b]
n-Hexane	−0.233	−519	1595[c]	0.502[c]
Benzene	0.010	24	−48 (at $x_1 = 0.3$)[a] 6 (at $x_1 = 0.9$)[a]	0.090[b]
Toluene	−0.040	−84	126[d]	−0.021[b]
CTC	0.124	299	−237[c]	−0.245[b]
TCE	0.349	887		−0.382[e]
Chloroform	0.163	408	−1820[f,g]	−0.180[h]
PCE	0.314	813		−0.591[e]
EA	−0.094	−234		−0.093[e]

[a] From Ref. 1.
[b] From Ref. 3.
[c] From Ref. 25.
[d] From Ref. 29.
[e] From Ref. 30.
[f] From Ref. 31.
[g] At 323 K.
[h] From Ref. 9.

probable in view of the large dispersion forces in these mixtures as evidenced by the large and positive values of both H^E and V^E as shown in Table VI.

3.3.2. Mixtures with Aromatic Hydrocarbons

Table VI shows that the numerical values of ΔG^{*E} and $\Delta \ln \eta$ for the mixtures of *p*-dioxane with benzene and toluene are very small compared to the values for the mixtures of *p*-dioxane with aliphatic hydrocarbons. According to Fort and Moore [9] and Nigam and Mahl [10], such viscosity behavior indicates moderate specific interactions between *p*-dioxane and the aromatic hydrocarbons.

Slight differences between the values of ΔG^{*E} and $\Delta \ln \eta$ for the mixtures with benzene and with toluene are attributable to the introduction of a $-CH_3$ group in benzene which reduces the delocalization of π-electrons in the aromatic ring, hence reducing specific interactions. This graded behavior is consistent with the excess enthalpy [1, 5], excess volume [1, 3] excess Gibbs free energy [4], and excess heat capacity [1].

3.3.3. *Mixtures with Chloroalkanes*

The values of ΔG^{*E} and $\Delta \ln \eta$ for the four mixtures of *p*-dioxane with CTC, TCE, chloroform, and PCE are all large and positive, over the entire range of composition (Table VI and Fig. 3). All these results point to the presence of specific interaction between *p*-dioxane and the chloroalkanes in the liquid state. There are earlier reports that open-chain and cyclic ethers interact strongly with chloroalkanes, forming complexes [31–35].

The specific interaction of *p*-dioxane with CTC can be visualized as an electron donor and an acceptor type, and further, it is possible to imagine a 1:2 complex in the mixture. In fact, Kennard and McCusker [36] and Ott et al. [37] have shown the existence of a compouond $C_4H_8O_2 \cdot 2CCl_4$. Positive values of C_P^E [25, 32] for this mixture are also consistent with the formation of a mixed complex. Viscosities of *p*-dioxane + chloroform have been explained by Fort and Moore [9] and Nigam and Mahl [10] in terms of H-bonding between *p*-dioxane and chloroform. The large negative values of the excess enthalpy [31], also support this view. Maxima in ΔG^{*E} for this system occur at about $x_1 = 0.3$, an indication of a $C_4H_8O_2 \cdot 2CHCl_3$ mixed complex.

The present results for *p*-dioxane + TCE and *p*-dioxane + PCE can be explained in a similar manner. But apart from H-bonding, $O \cdots Cl$ interaction in these two mixtures is not less significant. However, at present we have no method to estimate the strength of each interaction, separately.

3.3.4. *Mixtures with Ethyl Acetate*

For *p*-dioxane + EA moderate negative values of ΔG^{*E} and $\Delta \ln \eta$ are found. Such results may be explained by considering the fact that *p*-dioxane molecules are destroying dipolar order in EA molecules, similar to the cyclohexane in the cyclohexane + EA mixture [12, 38]. However, the magnitude of the negative values of ΔG^{*E} and $\Delta \ln \eta$ for *p*-dioxane + EA is somewhat smaller than that for the cyclohexane + EA, which further points to the existence of a weak dipole–dipole interaction between *p*-dioxane and EA.

From the foregoing discussion of the results derived from the viscosity, it can be concluded that specific interactions leading to mixed complex formation occur between *p*-dioxane and chloroalkanes or aromatic hydrocarbons. The interactions are stronger with the chloroalkanes than those with the aromatic hydrocarbons.

4. THEORETICAL ANALYSIS OF EXCESS VISCOSITY

The excess viscosities of a number of mixtures have recently been analyzed [13, 39–41] in terms of the PFP theory [13–15] in combination with expressions developed by Bloomfield and Dewan [42] and in terms of the LCT model by Wei and Rowley [16, 17]. In the present study an attempt to check these two approaches from our viscosity measurements is being made.

4.1. PFP Theory

Following Bloomfield and Dewan [42], we represent the excess viscosity $\Delta \ln \eta_{\mathrm{PFP}}$ as a sum of three contributions:

$$\Delta \ln \eta_{\mathrm{PFP}} = \ln \eta_{\mathrm{H}} + \ln \eta_{\mathrm{S}} + \ln \eta_{\mathrm{V}} \tag{6}$$

where

$$\ln \eta_{\mathrm{H}} = -H^{\mathrm{E}}/RT \tag{7}$$

$$\ln \eta_{\mathrm{S}} = S^{\mathrm{E}}/R \tag{8}$$

$$\ln \eta_{\mathrm{V}} = (\tilde{V}-1)^{-1} - \sum_{i=1}^{2} x_i(\tilde{V}_i - 1)^{-1} \tag{9}$$

The terms $\ln \eta_{\mathrm{H}}$, $\ln \eta_{\mathrm{S}}$, and $\ln \eta_{\mathrm{V}}$ represent enthalpy, entropy, and free-volume contributions, respectively, to $\Delta \ln \eta_{\mathrm{PFP}}$. According to the PFP theory, the excess entropy S^{E} is given by

$$S^{\mathrm{E}} = 3 \sum_{i=1}^{2} x_i P_i^* V_i^* / T_i^* \ln[(\tilde{V}_i^{1/3} - 1)/(\tilde{V}^{1/3} - 1)] \tag{10}$$

Here, P_i^*, V_i^*, and T_i^* are the Flory's reduction parameters and $\tilde{V}_i$ is the reduced volume. The reduced volume $\tilde{V}$ for the mixture is defined as

$$\tilde{V}^{-1} = \sum_i \psi_i / \tilde{V}_i \tag{11}$$

where ψ_i, the contact-energy, fraction is defined as

$$\psi_i = x_i P_i^* V_i^* \Big/ \sum_i x_i P_i^* V_i^* \tag{12}$$

In the present investigation, the PFP theory for the excess viscosity is considered for binary mixtures of *p*-dioxane with cyclohexane, *n*-hexane, benzene, toluene, CTC, and chloroform as H^{E} data for these mixtures are available [1, 25, 29, 31]. The values of the Flory reduction parameters of $\tilde{V}$, V^*, P^*, and T^* used in the present work are listed in Table VII. The theoretical estimates, based on the PFP theory of the excess viscosity

Table VII. Flory's Reduction Parameters at 303.15 K

Component	$\tilde{V}$	V^* ($cm^3 \cdot mol^{-1}$)	P^* ($J \cdot cm^{-3}$)	T^* (K)
p-Dioxane	1.2725	67.74	707.8	4998
Cyclohexane	1.2925	84.33	529.3	4730
n-Hexane	1.3282	99.76	421.0	4460
Benzene	1.2975	69.33	623.0	4730
Toluene	1.2677	84.74	542.5	5055
CTC	1.2998	75.16	567.0	4708
Chloroform	1.3075	62.09	610.0	4636

$\Delta \ln \eta_{PFP}$ and the three contribution terms $\ln \eta_H$, $\ln \eta_S$, and $\ln \eta_V$ at equimolar compositions are given in Table VIII. Table VIII also gives the $\Delta \ln \eta_{exp}$ and its difference $\delta = (\Delta \ln \eta_{exp} - \Delta \ln \eta_{PFP})$. A comparison between $\Delta \ln \eta_{PFP}$ and $\Delta \ln \eta_{exp}$ results at all mole fractions is shown in Fig. 5.

A study of Table VIII indicates that values of each term are comparatively quite large for the mixtures containing containing cyclohexane, *n*-hexane, and chloroform, whereas they are much smaller for the remaining three mixtures containing benzene, toluene, and CTC. In the case of *p*-dioxane + cyclohexane and *p*-dioxane + *n*-hexane, the $\ln \eta_H$ and $\ln \eta_V$ contributions are negative, while the $\ln \eta_S$ contribution is opposite. The $\ln \eta_H$ contribution is dominant, while the contributions $\ln \eta_S$ and $\ln \eta_V$

Table VIII. Experimental $\Delta \ln \eta_{exp}$, PFP Theory Estimates of $\ln \eta_H$, $\ln \eta_S$, $\ln \eta_V$, $\Delta \ln \eta_{PFP}$, and δ_{PFP} and LCT Model Estimates of $\Delta \ln \eta_{LCT}$ and δ_{LCT} for Equimolar Composition at 303.15 K

		PFP theory					LCT model	
Mixture	$\Delta \ln \eta_{exp}$	$\ln \eta_H$	$\ln \eta_S$	$\ln \eta_V$	$\Delta \ln \eta_{PFP}$	δ_{PFP}[a]	$\Delta \ln \eta_{LCT}$	δ_{LCT}[b]
p-Dioxane +								
Cyclohexane	−0.153	−0.635	0.168	−0.183	−0.651	0.498	−0.173	0.020
n-Hexane	−0.233	−0.632	0.165	−0.181	−0.649	0.416	−0.327	0.086
Benzene	0.005	0.013	−0.006	0.007	0.014	−0.009	−0.046	0.051
Toluene	−0.040	−0.049	0.012	−0.015	−0.052	+0.012	−0.082	0.042
CTC	0.126	0.094	0.028	0.033	0.099	0.027	+0.018	0.108
Chloroform	0.163	0.722	−0.189	0.225	0.773	−0.610	—	—

[a] $\delta_{PFP} = \Delta \ln \eta_{exp} - \Delta \ln \eta_{PFP}$.

[b] $\delta_{LCT} = \Delta \ln \eta_{exp} - \Delta \ln \eta_{LCT}$.

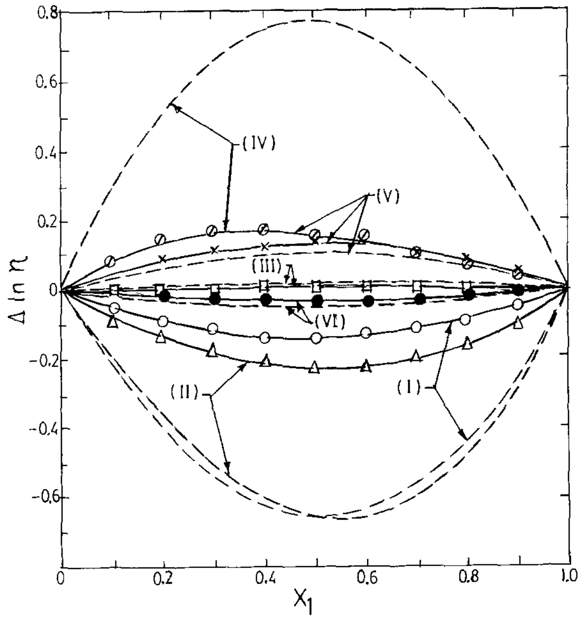

Fig. 5. Comparison of experimental and PFP theory excess viscosity $\Delta \ln \eta$ for binary mixtures containing *p*-dioxane. Experimental (——); PFP theory (----); (I) cyclohexane (○); (II) *n*-hexane (△); (III) benzene (□); (IV) toluene (∅); (V) CTC (×); (VI) chloroform (●).

are almost equal but opposite. The difference $\delta \equiv (\Delta \ln \eta_{\mathrm{exp}} - \Delta \ln \eta_{\mathrm{PFP}})$ for the cyclohexane and *n*-hexane mixtures is large and positive. The reason may be that in *p*-dioxane there exists a small local dipolar order which is destroyed by the addition of cyclohexane or *n*-hexane molecules. As suggested by Delmas et al. [40], this contribution is not taken into account in the PFP theory.

As stated earlier, each of the three contributions is quite small for the *p*-dioxane mixture with benzene, toluene, and CTC. The sign of $\ln \eta_{\mathrm{H}}$ is always the same as that of $\ln \eta_{\mathrm{V}}$, while it is opposite to that of $\ln \eta_{\mathrm{S}}$. The agreement of the $\Delta \ln \eta_{\mathrm{PFP}}$ with $\Delta \ln \eta_{\mathrm{exp}}$ is quite satisfactory for these mixtures.

In the case of *p*-dioxane + chloroform the enthalpy contribution $\ln \eta_{\mathrm{H}}$ is quite large and positive, while the other two contributions, $\ln \eta_{\mathrm{S}}$ and $\ln \eta_{\mathrm{V}}$, are relatively small. The difference $\delta \equiv (\Delta \ln \eta_{\mathrm{exp}} - \Delta \ln \eta_{\mathrm{PFP}})$ for this mixture is large and negative and has the opposite sign to that for the mixture of *p*-dioxane containing cyclohexane or *n*-hexane. This is attributed to the formation of a mix complex through strong H-bonding.

4.2 LCT Model

The LCT model of Wei and Rowley [16, 17] also estimates $\Delta \ln \eta$ for binary mixtures. The LCT model estimates with $\sigma = 0.25$, of $\Delta \ln \eta_{\text{LCT}}$ and their difference $\delta_{\text{LCT}} = (\Delta \ln \eta_{\text{exp}} - \Delta \ln \eta_{\text{LCT}})$ at equimolar composition for *p*-dioxane mixtures with cyclohexane, *n*-hexane, benzene, toluene, and CTC, are listed in the eighth and ninth columns of Table VIII. A comparison of $\Delta \ln \eta_{\text{LCT}}$ with $\Delta \ln \eta_{\text{exp}}$ at all the mole fractions for these mixtures is shown in Fig. 6.

Study of columns 8 and 9 in Table VIII and Fig. 6 clearly shows that all trends are correctly predicted by the LCT model for these mixtures, especially for *p*-dioxane mixtures with cyclohexane and *n*-hexane. For the latter two mixtures δ_{PFP} values 0.498 and 0.416 are quite large compared to δ_{LCT} values, which are only, 0.020 and 0.086, respectively.

In conclusion, the PFP theory in combination with the Bloomfield and Dewan expressions provides good estimates of the excess viscosities for

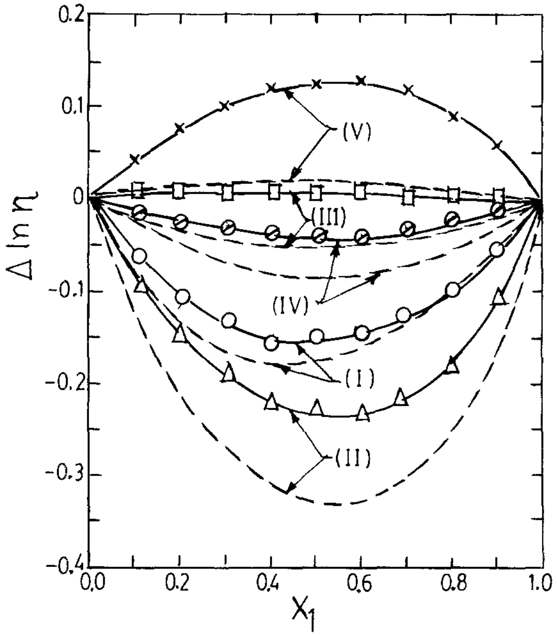

Fig. 6. Comparison of experimental and estimated for LCT model (with $\sigma = 0.25$) excess viscosity $\Delta \ln \eta$ for binary mixtures containing *p*-dioxane. Experimental (——); LCT model (----); (I) cyclohexane (○); (II) *n*-hexane (△(; (III) benzene (□); (IV) toluene (⊘); (V) CTC (×).

p-dioxane with benzene, toluene, and CTC, but the estimates of the excess viscosity are very poor for *p*-dioxane with cyclohexane, *n*-hexane, and chloroform. On the other hand, the LCT model of Wei and Rowley predicts the excess viscosity reasonably well, even for *p*-dioxane mixtures containing cyclohexane and *n*-hexane.

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