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VISCOSITIES AND ACTIVATION ENERGIES OF FLOW OF MIXTURES CONTAINING 1,2-DIBROMOETHANE

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ABSTRACT

The viscosities of the mixtures of 1,2-dibromoethane + cyclohexane, + benzene, + toluene, + *o*-xylene, + *m*-xylene, and + *p*-xylene have been measured at 298.15 and 308.15 K as a function of composition. The viscosity data have been analysed in the light of approaches developed by Hind et al. and Grunberg et al. Using Eyring kinematic scheme the viscosity data have been employed to calculate activation energies of flow.

INTRODUCTION

Excess volumes of mixing for the above-mentioned mixtures have been reported earlier[1]. Viscosity data may provide valuable information regarding the molecular interactions in the mixtures[2–4]. Viscosity data coupled with Eyring kinematic scheme[5] may be used to compute activation energies of flow which in turn are related to excess free energies of mixing. Therefore we measured the viscosities of the above-mentioned mixtures at 298.15 and 308.15 K as a function of composition to get information about intermolecular forces and to obtain excess thermodynamic functions.

EXPERIMENTAL

Cyclohexane, benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene (all B.D.H.) and 1,2-dibromoethane (Reidel) were purified as described earlier[1].

Viscosities of the mixtures were determined with a modified Ubbelohde kinematic viscometer[6]. The viscometer was calibrated against liquids of known viscosities. The viscometer containing the liquid was placed in a water-filled thermostat controlled to within ±0.01 K with the help of an electronic relay and toluene regulator. The characteristic constants *a* and *b* of the viscometer were evaluated from the measured time of flow for several liquids at 298.15 and 308.15 K using the known

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viscosities[7–9] by the relation[10]

$$\nu = \eta/\rho = at - b/t \tag{1}$$

where ν is the kinematic viscosity, η is the viscosity, ρ the density and t is the time of flow of the liquid in seconds. The constants a and b were determined by the least-squares method. The values of a and b at 298.15 and 308.15 K are recorded below:

Temp. (K)	*a*	*b*
298.15	0.001318	5.3604
308.15	0.001317	5.3038

The viscosities of the mixtures of 1,2-dibromoethane + cyclohexane, + benzene, + toluene, + *o*-xylene, + *m*-xylene, and + *p*-xylene have been measured by noting the time of flow at 298.15 and 308.15 K. The densities of the mixtures were taken from excess volume data[1]. The measured viscosities were correct to 1.0%.

RESULTS AND DISCUSSION

The viscosities and kinematic viscosities of the mixtures at 298.15 and 308.15 K are recorded in Table 1. The viscosity data have been plotted in Fig. 1.

TABLE 1

VISCOSITIES AND αG^{E} VALUES FOR MIXTURES CONTAINING 1,2-DIBROMOETHANE

x	ν *(centistokes)*	η *(centipoise)*	η_{12}	d	αG^{E} *(cal mol^{-1})*
x 1,2-Dibromoethane + (1 − x) cyclohexane at 298.15 K					
1.0000	0.7459	1.6159			
0.9100	0.7205	1.4505	0.6415	−0.6676	+31.48
0.8327	0.6965	1.3106	0.5920	−0.8050	62.24
0.7406	0.6924	1.2075	0.6782	−0.7226	80.27
0.6465	0.6991	1.1048	0.6932	−0.7601	91.0
0.5537	0.7098	1.0091	0.6763	−0.8500	101.84
0.4599	0.7295	0.9659	0.7141	−0.8013	107.88
0.3514	0.7732	0.9260	0.7623	−0.7806	103.28
0.2453	0.8838	0.8556	0.6634	−1.0256	78.46
0.1283	0.9415	0.8597	0.6669	−1.0888	39.76
0.0000	1.1644	0.9009			
x 1,2-Dibromoethane + (1 − x) cyclohexane at 308.15 K					
1.0000	0.6452	1.3843			
0.9281	0.6231	1.2856	0.6691	−0.4581	29.48
0.8334	0.6144	1.1447	0.5842	−0.6446	50.49
0.7424	0.6124	1.0552	0.6327	−0.6065	66.35

TABLE 1 (*continued*)

x	ν (*centistokes*)	η (*centipoise*)	η_{12}	d	αG^E (*cal mol*$^{-1}$)
x 1'2-Dibromoethane + $(1-x)$ cyclohexane at 308.15 K					
0.6741	0.6305	1.0209	0.7089	−0.4907	72.34
0.5559	0.6278	0.9064	0.6670	−0.6295	86.47
0.4545	0.6466	0.8447	0.6725	−0.6643	92.26
0.3629	0.6813	0.8116	0.6964	−0.6462	85.23
0.2398	0.7374	0.7673	0.6863	−0.7198	76.37
0.1562	0.7973	0.7122	0.5290	−1.1782	60.19
0.0000	0.9899	0.7570			
x 1,2-Dibromoethane + $(1-x)$ benzene at 298.15 K					
1.0000	0.7459	1.6159			
0.9005	0.6991	1.4225	0.5926	−0.3290	17.53
0.8038	0.6563	1.2527	0.5879	−0.3891	36.85
0.7101	0.6349	1.1159	0.6081	−0.4122	41.29
0.6073	0.6215	1.0336	0.7223	−0.2533	40.27
0.5099	0.6067	0.8941	0.6581	−0.4377	44.92
0.4109	0.5919	0.8428	0.7445	−0.2933	53.63
0.3120	0.5899	0.8229	0.8847	−0.0114	54.38
0.2016	0.6087	0.6889	0.7404	−0.4137	41.09
0.0999	0.6402	0.6395	0.7461	−0.4548	23.79
0.0000	0.6911	0.6038			
x 1,2-Dibromoethane + $(1-x)$ benzene at 308.15 K					
1.0000	0.6452	1.3843			
0.9019	0.6050	1.2190	0.4968	−0.3665	20.93
0.8028	0.5890	1.1280	0.6801	−0.0903	34.17
0.7019	0.5473	0.9610	0.5548	−0.3684	52.06
0.6088	0.5283	0.8569	0.5525	−0.4276	63.64
0.5068	0.5189	0.7767	0.5860	−0.4064	67.17
0.4086	0.5160	0.7026	0.5942	−0.4363	67.50
0.3146	0.5203	0.6379	0.5874	−0.5233	63.90
0.2078	0.5419	0.6034	0.6466	−0.3967	47.05
0.1052	0.5715	0.5588	0.6455	−0.4569	30.07
0.0000	0.6265	0.5270			
x 1,2-Dibromoethane + $(1-x)$ toluene at 298.15 K					
1.0000	0.7459	1.6159			
0.9171	0.6951	1.3810	0.1189	−0.9063	22.34
0.8331	0.6617	1.2682	0.4716	−0.4658	33.31
0.7460	0.6302	1.1052	0.4484	−0.5789	45.04
0.6537	0.6148	1.0153	0.5695	−0.4257	43.68
0.5548	0.5919	0.9001	0.5914	−0.4519	51.74
0.4549	0.5866	0.8563	0.7182	−0.2227	45.89
0.3480	0.5846	0.7383	0.6732	−0.3958	40.29
0.2578	0.5919	0.6736	0.6769	−0.4472	30.69
0.1229	0.6047	0.6433	0.8803	−0.1103	23.36
0.0000	0.6469	0.5578			

(*Table continued on p. 348*)

TABLE 1 (*continued*)

x	ν (*centistokes*)	η (*centipoise*)	η_{12}	d	αG^E (*cal mol*$^{-1}$)
x 1,2'Dibromoethane + (1 − x) toluene at 308.15 K					
1.0000	0.6452	1.3843			
0.9144	0.6104	1.2333	0.4611	−0.4195	15.88
0.8319	0.5889	1.1107	0.4953	−0.4138	21.95
0.7416	0.5688	0.9937	0.5190	−0.4277	27.69
0.6520	0.5573	0.9069	0.5680	−0.3827	26.96
0.5524	0.5526	0.8275	0.6161	−0.3327	29.31
0.4489	0.5338	0.7283	0.6006	−0.4447	32.80
0.3568	0.5257	0.6572	0.5962	−0.5394	33.12
0.2377	0.5405	0.6000	0.6363	−0.5509	22.11
0.1176	0.5634	0.5499	0.6764	−0.6846	6.35
0.0000	0.5884	0.5011			
x 1,2-Dibromoethane + (1 − x) o-xylene at 298.15 K					
1.0000	0.7459	1.6159			
0.9267	0.7265	1.4870	0.7010	−0.4079	14.41
0.8472	0.7238	1.3736	0.7573	−0.4962	20.26
0.7597	0.7198	1.2630	0.7849	−0.3545	26.29
0.6829	0.7105	1.1817	0.8124	−0.3380	37.27
0.5850	0.7238	1.0980	0.8338	−0.3263	31.83
0.4919	0.7332	1.0317	0.8899	−0.2682	30.94
0.3856	0.7465	0.9602	0.9149	−0.2363	29.98
0.2610	0.7659	0.8771	0.9143	−0.2712	25.19
0.1292	0.8085	0.7932	0.8484	−0.4729	12.55
0.0000	0.8658	0.7587			
x 1,2-Dibromoethane + (1 − x) o-xylene at 308.15 K					
1.0000	0.5452	1.3843			
0.9258	0.6318	1.2729	0.6074	−0.2007	26.19
0.8499	0.6137	1.1541	0.5568	−0.3139	37.88
0.7647	0.5782	1.0178	0.4961	−0.4736	38.34
0.6798	0.5634	0.9216	0.5208	−0.4791	53.34
0.5874	0.5553	0.8292	0.5385	−0.5059	54.21
0.4845	0.5560	0.7526	0.5732	−0.4897	56.76
0.3821	0.5620	0.6992	0.6176	−0.4199	53.58
0.2566	0.5728	0.6257	0.6217	−0.4804	44.32
0.1371	0.5903	0.5822	0.6573	−0.4292	31.92
0.0000	0.6345	0.5381			
x 1,2-Dibromoethane + (1 − x) m-xylene at 298.15 K					
1.0000	0.7459	1.6159			
0.9257	0.7118	1.4466	0.4266	−0.5095	17.75
0.8458	0.6804	1.3073	0.5268	−0.4214	34.50
0.7684	0.6617	1.1907	0.5767	−0.3911	42.16
0.6789	0.6603	1.0641	0.6007	−0.4063	47.10
0.5776	0.6650	1.0017	0.7345	−0.1976	50.25
0.4852	0.6369	0.8843	0.6989	−0.3155	48.17
0.3835	0.6402	0.8095	0.7400	−0.2694	43.73
0.2690	0.6349	0.7069	0.7068	−0.4204	30.19
0.1391	0.6523	0.6538	0.7924	−0.2382	17.18
0.0000	0.6777	0.5839			

TABLE 1 (*continued*)

x	ν (*centistokes*)	η (*centipoise*)	η_{12}	d	αG^E (*cal mol*$^{-1}$)
x 1,2-Dibromoethane + (1 − x) m-xylene at 308.15 K					
1.0000	0.6452	1.3843			
0.9254	0.6204	1.2589	0.5108	−0.3212	15.60
0.8516	0.6077	1.1426	0.5032	−0.3727	20.68
0.7697	0.5862	1.0176	0.4789	−0.4685	35.13
0.6796	0.5755	0.9345	0.5548	−0.3689	39.21
0.5883	0.5694	0.8526	0.5885	−0.3426	39.75
0.4834	0.5594	0.7640	0.6031	−0.3618	45.49
0.3771	0.5607	0.7044	0.6494	−0.2889	41.10
0.2621	0.5694	0.6362	0.6644	−0.2973	31.30
0.1463	0.6003	0.5870	0.7089	−0.2002	12.01
0.0000	0.6117	0.5218			
x 1,2-Dibromoethane + (1 − x) p-xylene at 298.15 K					
1.0000	0.7459	1.6159			
0.9211	0.7098	1.4592	0.5810	−0.3408	20.89
0.8555	0.6871	1.3092	0.4606	−0.0907	33.66
0.7685	0.6717	1.1692	0.5124	−0.5449	39.39
0.6809	0.6583	1.0818	0.6209	−0.4091	44.64
0.5921	0.6577	1.0013	0.6909	−0.3282	49.63
0.4898	0.6449	0.8870	0.6829	−0.4015	46.47
0.39098	0.6335	0.7899	0.6676	−0.5014	54.24
0.2783	0.6456	0.7322	0.7240	−0.4236	42.43
0.1435	0.6590	0.6686	0.7728	−0.3579	33.55
0.0000	0.7085	0.6071			
x 1,2-Dibromoethane + (1 − x) p-xylene at 308.15 K					
1.0000	0.6452	1.3843			
0.9258	0.6318	1.2729	0.6074	−0.2007	26.19
0.8499	0.6137	1.1541	0.5568	−0.3139	37.88
0.7647	0.5782	1.10178	0.4961	−0.4736	48.34
0.6798	0.5634	0.9216	0.5208	−0.4791	53.34
0.5874	0.5553	0.8292	0.5385	−0.5059	54.21
0.4845	0.5560	0.7526	0.5732	−0.4897	56.76
0.3821	0.5620	0.6992	0.6176	−0.4199	53.58
0.2566	0.5728	0.6257	0.6217	−0.4804	44.32
0.1371	0.5903	0.5822	0.6573	−0.4292	31.92
0.0000	0.6345	0.5381			

The plots of η_{mix} against composition exhibiting maximum or positive deviations from rectilinear dependence on the mole fraction should indicate the presence of specific interactions resulting in the formation of complexes between them[3]. The negative deviations from rectilinear behaviour should mean on the other hand the presence of dominant dispersion forces in the mixtures. Fig. 1 shows negative deviations from linear behaviour and hence mainly dispersive forces may be present in these mixtures.

The approach of Hind et al.[11], Tamara and Kurata[12], and Tamara and Sata[13] may give an estimate of the extent of interactions present in the mixtures in terms of

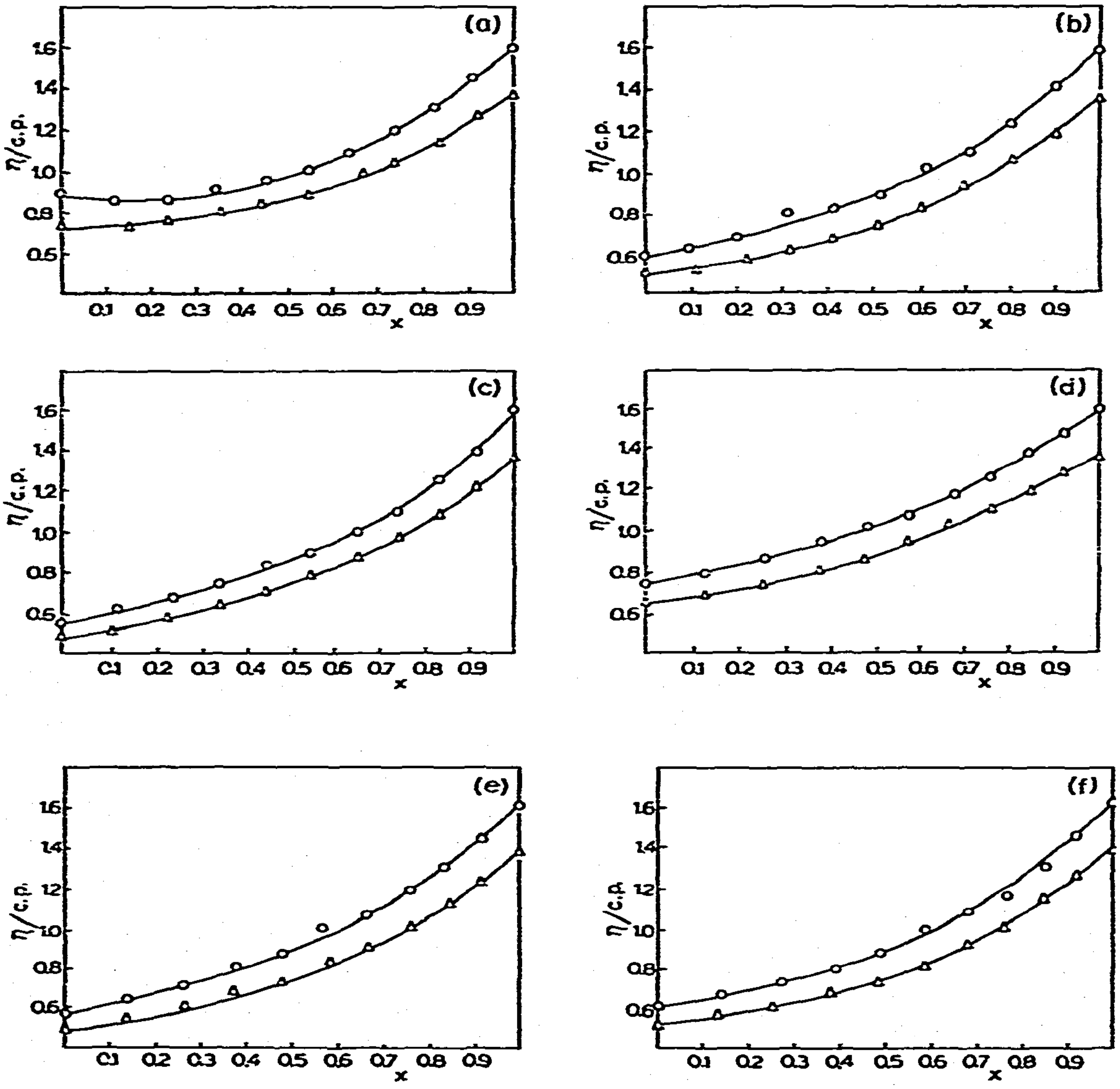

Fig. 1. Plots of surface tensions of mixtures against mole fraction x.

a. O—O x 1,2-Dibromoethane+$(1-x)$ cyclohexane at 298.15 K
Δ—Δ x 1,2-dibromoethane+$(1-x)$ cyclohexane at 308.15 K

b. x 1,2-Dibromoethane+$(1-x)$ benzene.
O—O 298.15 K; Δ—Δ 308.15 K.

c. x 1,2-Dibromoethane+$(1-x)$ toluene.
O—O 298.15 K; Δ—Δ 308.15 K.

d. x 1,2-Dibromoethane+$(1-x)$ *o*-xylene.
O—O 298.15 K; Δ—Δ 308.15 K.

e. x 1,2-Dibromoethane+$(1-x)$ *m*-xylene.
O—O 298.15 K; Δ—Δ 308.15 K.

f. x 1,2-Dibromoethane+$(1-x)$ *p*-xylene.
O—O 298.15 K; Δ—Δ 308.15 K.

η_{12}. Hind et al. represented viscosity data by the relation:

$$\eta_{\mathrm{mix}} = x_1^2\eta_1 + 2x_1x_2\eta_{12} + x_2^2\eta_2 \qquad (2)$$

where x_1 and x_2 are the mole fractions, η_1 and η_2 are the viscosities of the pure components. η_{12} is found to be independent of composition. The values of η_{12} are recorded in Table 1.

The knowledge about the strength of interactions in the mixtures may be provided by the Grunberg and Nissan approach[14]. Accordingly, the viscosity of the mixture is related to the viscosity of pure components by the relation:

$$\ln \eta_{\mathrm{mix}} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1x_2d \qquad (3)$$

where d is the interaction parameter which is proportional to w/RT, w is the interchange energy. This parameter d has the same significance as given by Guggenheim[15] in the treatment of regular solution theory. The values of the interaction parameter d have been calculated and are recorded in Table 1. It was observed that the values of d are independent of the composition for all the mixtures at 298.15 and 308.15 K, but it has a negative value for all the mixtures. The negative values of d indicate the presence of dispersion forces and the absence of specific interactions in these mixtures.

CALCULATION OF EXCESS THERMODYNAMIC FUNCTIONS

According to Andrade[16], Arrhenius[17] and Guzman[18], the viscosity of a liquid is related with its temperature by the relation:

$$\eta = A\mathrm{e}^{B/T} \qquad (4)$$

where A and B are constants. This expression was modified by Glasstone et al.[5] to give it a theoretical bearing and was represented by

$$\eta = (\lambda_1 h/\lambda_2\lambda_3\lambda^2)\,\mathrm{e}^{\Delta G^*/RT} \qquad (5)$$

If $\lambda = \lambda_1$ and $\lambda_1\lambda_2\lambda_3 =$ molecular volume, the above equation may be written as

$$\eta = (hN/V)\,\mathrm{e}^{\Delta G^*/RT} \qquad (6)$$

or

$$\nu = \eta/\rho = (hN/M)\,\mathrm{e}^{\Delta G^*/RT} \qquad (7)$$

where ν is the kinematic viscosity in centistokes.

Consequently, the kinematic viscosity of pure components would be given by

$$\nu_1 = (hN/M_1)\,\mathrm{e}^{\Delta G_1^*/RT} \qquad (8)$$

$$\nu_2 = (hN/M_2)\,\mathrm{e}^{\Delta G_2^*/RT} \qquad (9)$$

An analogous expression for binary liquid mixtures can be written after accounting for non-ideality, as given below:

$$\nu_{\mathrm{mix}} = [hN/(x_1M_1 + x_2M_2)] \exp [(x_1 G_1^* + x_2 G_2^* - \alpha G_{\mathrm{mix}}^{\mathrm{E}})/RT] \qquad (10)$$

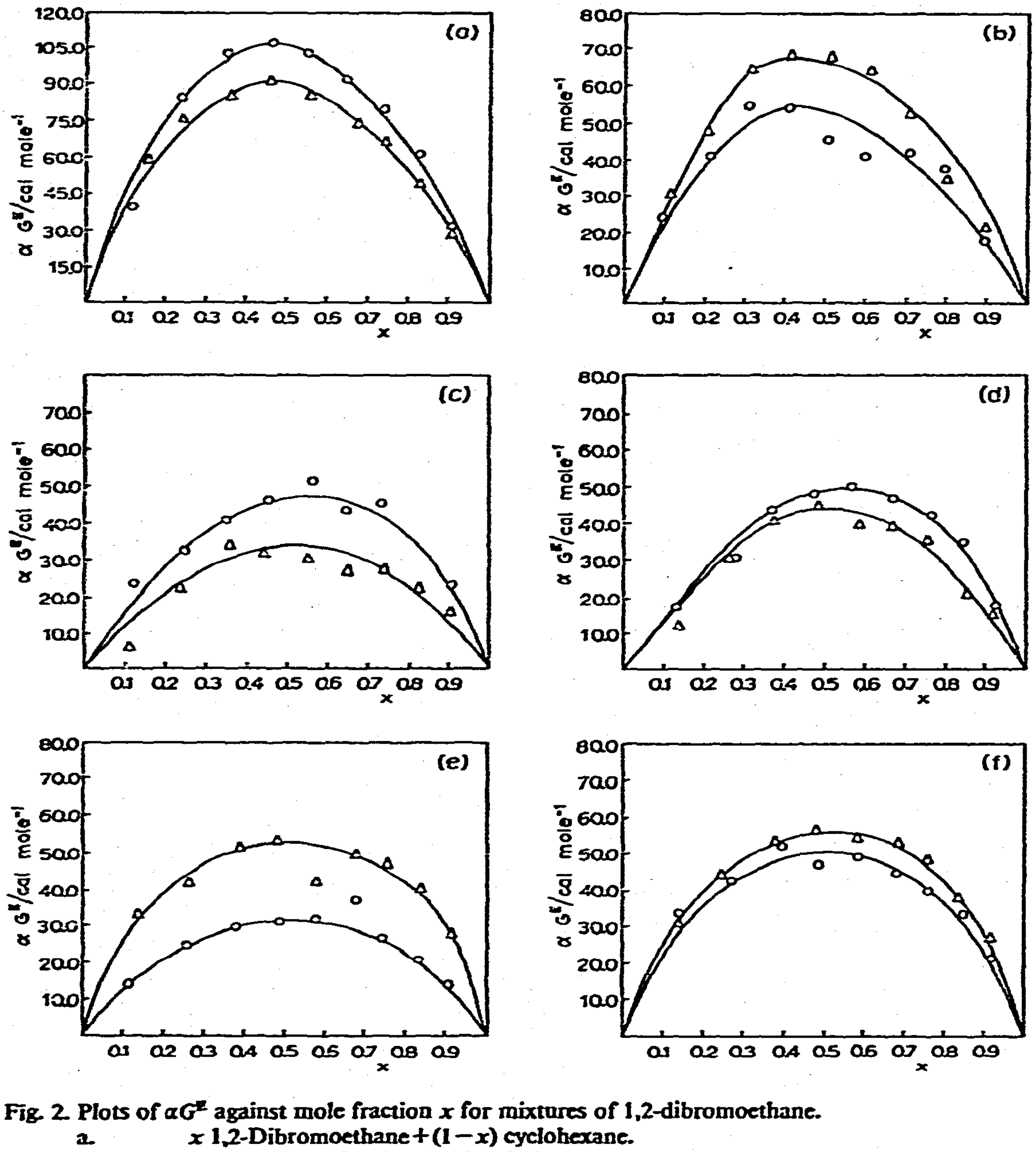

Fig. 2. Plots of αG^E against mole fraction x for mixtures of 1,2-dibromoethane.

a. x 1,2-Dibromoethane + $(1-x)$ cyclohexane.
O—O 298.15 K; Δ—Δ 308.15 K.

b. x 1,2-Dibromoethane + $(1-x)$ benzene.
O—O 298.15 K; Δ—Δ 308.15 K.

c. x 1,2-Dibromoethane + $(1-x)$ toluene.
O—O 298.15 K; Δ—Δ 308.15 K.

d. x 1,2-Dibromoethane + $(1-x)$ *o*-xylene.
O—O 298.15 K; Δ—Δ 308.15 K.

e. x 1,2-Dibromoethane + $(1-x)$ *m*-xylene.
O—O 298.15 K; Δ—Δ 308.15 K.

f. x 1,2-Dibromoethane + $(1-x)$ *p*-xylene.
O—O 298.15 K; Δ—Δ 308.15 K.

where G^E is the excess free energy of mixing representing the departure from Rault's law and α is the fraction of this energy affecting the viscosity of solution. α was designated a value of 0.4082. This value was based on the work of Reseveare et al.[19] who analysed the data for 22 liquid systems in terms of the plot of deviations from Rault's law. The scattering of points in their graph were too much and no reliance can be made on this value. Krishnan and Laddha[20] have suggested $\alpha = 1$ which was not based on any sound footing and was merely a conjecture. Recently[21], we have suggested that α can take up any value between 0.4082 and 1.0000 which will be characteristic of the system. So α varies from system to system, independent of temperature and is dependent on the nature of the system[21]. Due to the uncertainty in the value of α, we computed αG^E values for these mixtures. The values of αG^E are recorded in Table 1 and are plotted in Fig. 2. The uncertainity in the value of αG^E is 2.5%.

On analysis of Fig. 2, it is evident that the sign of αG^E is positive for all these mixtures at 298.15 and 308.15 K. Regardless of the value of α (between 0.4082 and 1.0000) the sign of G^E is positive for these mixtures. The positive values of excess free energies rule out the possibility of complexes in these mixtures. It indicates the presence of dispersion forces in these mixtures.

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