A Theoretical Justification for Viscosity Models & Prediction of Excess Thermodynamic Functions for Binary Liquid Mixtures†

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Viscosities and densities of twenty-two binary mixtures measured at $35 \pm 0.1°C$ over the entire composition range of 0-100% have been used to theoretically justify the validity of the viscosity models. Several useful thermodynamic parameters such as excess Gibbs free energy, excess volume, excess viscosity and density increments have been calculated. The results are discussed in terms of thermodynamic interactions of the individual components in the mixture.

As a part of an ongoing research programme[1-4] concerning the physicochemical properties of binary liquid mixtures, herein we present a theoretical analysis of the validity of several viscosity models based on density and viscosity data of twenty two binary mixtures at 35°C over the entire composition range. Furthermore, an attempt has been made to predict a few thermodynamic quantities so as to discuss the results in terms of the nature of the interacting components of the mixtures.

Materials and Methods

The binary mixtures consisted of bromoform (BF), carbon tetrachloride (CTC), dimethyl sulphoxide (DMSO), dimethylformamide (DMF), bromobenzene (BB), cyclohexane (CH), ethyl acetate (EA), methyl ethyl ketone (MEK), methanol (MET), benzene (B), xylene (Xy) and nitromethane (NM).

All solvents were of reagent grade and purified by standard procedures[5], and their purities checked against literature values of densities and viscosities. Mixtures were prepared for several compositions from 0-100%. To minimize preferential evaporation of one of the solvents in the mixture, densities and viscosities of pure liquids and their mixtures were measured as reported earlier[2], on the same day on which mixtures were prepared. All calculations were done using a DCM microcomputer with programmes written in machine language.

Viscosity models

A number of workers have proposed a number of equations for the calculation of the viscosity of

mixtures. For example, for mixtures with small volume changes during mixing, viscosity (η) is given by Tamura-Kurata relation[6](1).

$$\eta = x_1 \phi_1 \eta_1 + x_2 \phi_2^{\eta_2} + 2(x_1 x_2 \phi_1 \phi_2)^{1/2} T_{12} \qquad \ldots (1)$$

where T_{12} is the interaction parameter which depends on temperature and composition of the mixture; η_1 and η_2 refer to viscosities of pure components 1 and 2 respectively; x_1 and ϕ_1 are respectively the mol fractions and volume fractions.

Hind *et al*[7]. proposed Eq. (2) which is formally similar to Eq. (1),

$$\eta = x_1^2 \eta_1 + x_2^2 \eta_2 + 2 x_1 x_2 H_{12} \qquad \ldots (2)$$

where H_{12} is an interaction parameter.
Grunberg and Nissan[8] suggested a logarithmic relation (3)

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12} \qquad \ldots (3)$$

where G_{12} is a measure of the strength of interaction between the mixing species.

Based on a three-body interaction model, McAllister[9] proposed Eq. (4)

$$\ln \eta = x_1^3 \ln \eta_1 + 3 x_1^2 x_2 \ln Z_{12} + 3 x_1 x_2^2 \ln Z_{21}$$

$$+ x_2^3 \ln \eta_2 - \ln \left[x_1 + x_2 \frac{M_2}{M_1} \right] +$$

$$3 x_1^2 x_2 \ln [(2 + M_2/M_1)/3] +$$

$$3 x_1 x_2^2 \ln [(1 + 2 M_2/M_1)/3] + x_2 \ln (M_2/M_1)$$
$$\ldots (4)$$

where Z_{12} and Z_{21} are the parameters to be evaluated; M_1 and M_2 are molecular weights of components 1 and 2 respectively.

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A three-parameter relation (Eq. 5) was proposed by Auslaender[10]

$$x_1(x_1 + B_{12}x_2)(\eta - \eta_1) + A_{21}x_2(B_{21}x_1 + x_2)(\eta - \eta_2) = 0 \qquad \ldots(5)$$

where the interaction terms A_{21}, B_{12} and B_{21} are to be evaluated from a least-squares method.

Heric and Brewer[11] proposed an equation for the kinematic viscosity $\lambda (= \eta/\rho)$ of the mixture (Eq. 6 or 7)

$$\lambda = x_1\lambda_1 + x_2\lambda_2 + x_1x_2[A + B(x_1 - x_2) + C(x_1 - x_2)^2] \qquad \ldots(6)$$

or

$$\ln \lambda = x_1\ln \lambda_1 + x_2\ln \lambda_2 + x_1\ln M_1 + x_2\ln M_2$$
$$- \ln(x_1M_1 + x_2M_2) + x_1x_2[A' + B'$$
$$(x_1 - x_2) + C'(x_1 - x_2)^2] \qquad \ldots(7)$$

Excess functions

The excess Gibbs free energy of flow (G^{*E}) is given by Eyring's[12] relation (8)

$$G^{*E} = RT[\ln \eta V - x_1 \ln \eta_1 V_1 - x_2 \ln \eta_2 V_2] \qquad \ldots(8)$$

where V_i is the molar volume of i-th component and the term RT has its usual meaning.

Excess volume and excess viscosity are calculated from Eqs (9) and (10),

$$V^E = (M_1\phi_1 + M_2\phi_2)/\rho - M_1\phi_1/\rho_1 - M_2\phi_2/\rho_2 \qquad \ldots(9)$$

$$\eta^E = \eta - \eta_1\phi_1 - \eta_2\phi_2 \qquad \ldots(10)$$

Density increments

Recently Aminabhavi *et al.*[13,14] proposed Eq. (11) to predict the density increments of solvent mixtures,

$$(\partial\rho/\partial\phi_1)_{P,T} = \frac{(\rho_1 - \rho_2) - \rho\left[A_{12}(\phi_2 - \phi_1) + \dfrac{dA_{12}}{d\phi_1}(\phi_1\phi_2)\right]}{(1 + A_{12}\phi_1\phi_2)} \qquad \ldots(11)$$

Here, the composition-dependent binary contact interaction parameter A_{12} is given[15] by Eq. (12)

$$A_{12} = \frac{(\phi_1\rho_1 + \phi_2\rho_2 - \rho)}{\phi_1\phi_2\rho} \qquad \ldots(12)$$

The parameter A_{12} can be calculated using densities of pure components and their mixtures. However, to calculate the derivative $(dA_{12}/d\phi_1)$, Eq. (13) was used with the numerical values of a_0, a_1, and a_2 as computed from a least-squares method.

$$A_{12} = a_0 + a_1(\phi_2 - \phi_1) + a_2(\phi_2 - \phi_1)^2 \qquad \ldots(13)$$

Results and Discussion

A few calculated parameters are given in Table 1. Figure 1 depicts the dependence of mixture viscosity on volume fraction (ϕ_1) for a few typical mixtures. Of all the mixtures, BF(1)-

Table 1—Calculated Parameters for Various Binary Mixtures at 35°C

x_1	T_{12}	H_{12}	G_{12}	$A_{12}10^3$	G^{*E} (J/mol)
(I) Bromoform(1)-carbon tetrachloride(2)					
0.16	0.114	0.113	10.66	− 2.1	− 6.62
0.32	0.114	0.111	5.44	− 3.5	− 16.09
0.52	0.110	0.108	3.27	− 3.2	− 44.55
0.67	0.110	0.108	2.55	− 2.0	− 34.22
0.86	0.113	0.109	2.01	− 4.9	− 5.76
(II) Bromoform (1)-dimethyl sulphoxide (2)					
0.13	0.279	0.288	15.28	12.0	403.13
0.26	0.032	0.308	8.24	8.0	752.97
0.45	0.338	0.338	5.57	3.9	1076.49
0.55	0.342	0.339	4.86	3.7	1075.12
0.60	0.341	0.336	4.56	1.4	1025.82
0.83	0.311	0.301	3.53	− 1.2	528.79
(III) Bromoform(1)-cyclohexane(2)					
0.18	0.100	0.096	9.71	12.9	− 71.31
0.35	0.100	0.096	4.85	5.7	− 89.39
0.55	0.100	0.094	3.02	7.9	− 81.41
0.70	0.100	0.092	2.36	2.1	− 68.85
0.88	0.097	0.089	1.83	− 1.0	− 39.09
(IV) Bromoform(1)-bromobenzene(2)					
0.18	0.137	0.133	10.19	0.8	66.27
0.34	0.136	0.132	5.26	0.5	86.96
0.55	0.136	0.132	3.33	113.8	166.68
0.69	0.138	0.133	2.67	0.1	88.59
0.87	0.142	0.138	2.19	0.0	57.90
(V) Bromoform(1)-dimethyl formamide(2)					
0.14	0.157	0.161	14.12	2.5	406.69
0.27	0.172	0.176	7.82	2.9	720.28
0.47	0.196	0.199	5.21	2.0	954.11
0.62	0.211	0.212	4.33	− 0.3	913.92
0.73	0.215	0.215	3.87	− 0.2	748.28
0.84	0.217	0.216	3.50	− 2.3	492.04
(VI) Bromoform(1)-methyl ethyl ketone(2)					
0.15	0.083	0.082	12.11	− 19.0	242.09
0.30	0.085	0.084	6.51	− 28.1	388.11
0.51	0.090	0.089	4.20	− 22.3	461.00
0.65	0.094	0.093	3.43	− 21.7	419.55
0.85	0.102	0.101	2.82	− 18.0	239.15
(VII) Bromoform(1)-ethyl acetate(2)					
0.27	0.085	0.082	5.936	− 12.6	220.97
0.53	0.091	0.086	3.810	− 10.6	315.16
0.77	0.099	0.094	2.820	− 6.3	250.89
(VIII) Bromoform(1)-methanol(2)					
0.17	0.126	0.149	12.537	− 28.7	837.33
0.32	0.126	0.145	7.111	− 24.8	1039.60
0.46	0.127	0.142	5.122	− 26.1	1008.18
0.73	0.119	0.131	3.316	− 25.0	586.12
0.90	0.098	0.113	2.554	− 42.1	193.43

(contd)

Table 1 — Calculated Parameters for Various Binary Mixtures at 35°C — *Contd*

x_1	T_{12}	H_{12}	G_{12}	$A_{12} 10^3$	G^{*E} (J/mol)
(IX) Carbon tetrachloride(1)-methanol(2)					
0.15	0.086	0.093	17.32	8.6	522.67
0.30	0.087	0.091	9.31	−2.7	707.14
0.43	0.088	0.089	6.50	−3.8	735.02
0.56	0.088	0.086	5.15	−7.0	660.13
0.71	0.081	0.079	3.97	−2.5	422.00
0.89	0.075	0.073	3.08	−7.9	147.46
(X) Carbon tetrachloride(1)-benzene(2)					
0.14	0.068	0.068	17.85	2.4	29.67
0.28	0.068	0.068	8.84	2.0	51.52
0.48	0.067	0.068	5.24	3.0	44.97
0.63	0.068	0.069	4.02	1.4	54.08
0.84	0.069	0.069	3.06	1.1	36.67
(XI) Carbon tetrachloride(1)-ethyl acetate(2)					
0.1	0.056	0.056	16.56	4.3	−7.23
0.3	0.055	0.055	8.09	3.6	−24.44
0.50	0.054	0.054	4.85	5.1	−46.54
0.65	0.052	0.052	3.71	4.0	−60.93
0.85	0.051	0.051	2.79	4.5	−38.89
(XII) Carbon tetrachloride(1)-dimethyl formamide(2)					
0.12	0.093	0.094	20.86	−25.7	120.76
0.25	0.093	0.094	10.20	−26.1	206.68
0.44	0.092	0.092	5.97	−26.9	236.51
0.60	0.091	0.091	4.49	−26.9	206.86
0.82	0.089	0.088	3.29	−26.9	98.90
(XIII) Carbon tetrachloride(1)-cyclohexane(2)					
0.17	0.072	0.071	14.77	12.2	−64.81
0.33	0.072	0.071	7.44	9.7	−104.80
0.53	0.073	0.072	4.51	8.7	−98.42
0.67	0.073	0.072	3.51	7.6	−86.47
0.86	0.073	0.073	2.72	5.5	−42.85
(XIV) Carbon tetrachloride(1)-bromobenzene(2)					
0.16	0.089	0.089	15.36	−6.8	−1.83
0.32	0.087	0.088	7.66	−8.9	−23.38
0.52	0.088	0.088	4.74	−9.2	−19.22
0.67	0.087	0.088	3.67	−9.4	−25.45
0.86	0.089	0.089	2.87	−10.1	−5.40
(XV) Carbon tetrachloride(1)-methyl ethyl ketone(2)					
0.14	0.055	0.055	17.97	−2.0	49.10
0.28	0.054	0.055	8.94	−8.1	60.91
0.48	0.053	0.053	5.24	−5.4	45.06
0.63	0.052	0.053	3.99	−5.1	30.56
0.84	0.048	0.050	2.94	−4.9	−8.78
(XVI) Carbon tetrachloride(1)-dimethyl sulphoxide(2)					
0.12	0.134	0.127	21.59	−9.7	74.78
0.24	0.137	0.130	10.66	−17.7	155.30
0.42	0.135	0.128	6.15	−22.7	201.20
0.58	0.135	0.128	4.63	−26.0	212.94
0.81	0.132	0.124	3.35	−28.3	122.66
(XVII) Carbon tetrachloride(1)-nitromethane(2)					
0.09	0.061	0.059	27.72	17.7	−18.13
0.19	0.063	0.062	12.64	15.3	4.44
0.36	0.064	0.065	6.80	10.1	44.08
0.51	0.066	0.066	4.81	13.7	78.11
0.76	0.061	0.063	3.12	17.3	16.71
(XVIII) Dimethyl sulphoxide(1)-dimethyl formamide(2)					
0.16	0.093	0.092	11.44	0.5	−64.75
0.32	0.091	0.090	5.58	1.2	−112.87
0.52	0.089	0.087	3.32	2.2	−132.48
0.67	0.088	0.085	2.54	0.6	−115.84
0.86	0.084	0.081	1.92	2.8	−63.96
(XIX) Dimethyl sulphoxide(1)-nitromethane(2)					
0.12	0.082	0.085	15.53	5.0	3.63
0.25	0.079	0.083	7.34	3.7	−4.79
0.43	0.073	0.079	4.15	10.0	−44.23
0.59	0.069	0.076	3.01	11.8	−53.49
0.81	0.060	0.069	2.09	16.0	−47.10
(XX) Benzene(1)-ethyl acetate(2)					
0.16	0.044	0.044	17.88	6.0	−58.11
0.32	0.044	0.044	8.91	2.8	−81.48
0.53	0.044	0.043	5.39	3.3	−102.22
0.67	0.043	0.043	4.16	5.3	−104.44
0.86	0.043	0.043	3.20	1.8	−51.53
(XXI) Benzene(1)-p-xylene(2)					
0.20	0.054	0.053	14.74	7.9	8.53
0.38	0.052	0.053	7.73	9.6	3.06
0.58	0.052	0.052	4.92	7.7	−21.83
0.72	0.053	0.052	3.96	9.3	−12.27
0.89	0.052	0.051	3.17	7.7	−12.68
(XXII) Cyclohexane(1)-methyl ethyl ketone(2)					
0.13	0.041	0.041	20.20	30.7	−113.92
0.26	0.038	0.039	9.43	35.5	−225.13
0.45	0.035	0.036	5.19	39.4	−317.30
0.60	0.032	0.034	3.71	40.1	−331.52
0.83	0.022	0.026	2.40	51.4	−253.18

DMSO(2) is particularly interesting because it displays a large positive deviation. The critical composition at which maximum in the curve occurs is around $\phi_1 \approx 0.5$. Such a behaviour is not seen with BF(1)-DMF(2) mixture for which viscosity increases steadily upto $\phi_1 = 0.6$ reaching a maximum at $\phi_1 = 0.7$ beyond which only a slight decrease is noticed. Such deviations from a rectilinear dependence on volume fraction and maxima are attributed to strong specific interactions between the components of the binary mixtures leading to complex formation[16]. Thus, the two mixtures represent the non-ideal behaviour. The mixture BF(1)-BB(2) exhibits almost a linear dependence of viscosity on volume fraction. This is expected because the vacant 3d-orbitals in bromine atom of
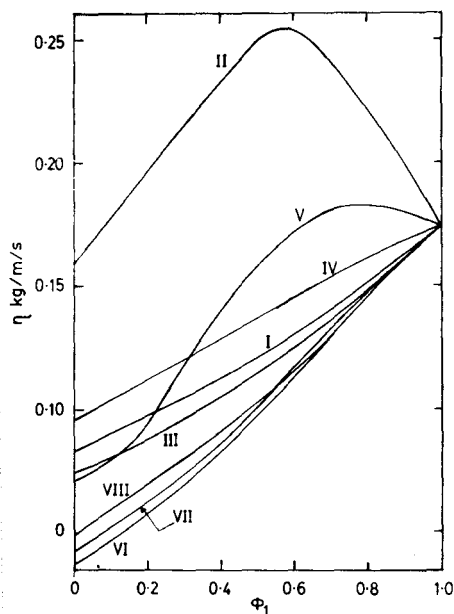
Fig. 1—Viscosity versus composition plots for various binary mixtures [I, bromoform (BF)-carbon tetrachloride (CTC); II, BF-dimethyl suphoxide (DMSO); III, BF-cyclohexane (CH); IV, BF-bromobenzene (BB); V, BF-dimethylformamide (DMF); VI, BF-methyl ethyl ketone (MEK); VII, BF-ethyl acetate (EA); and VIII, BF-methanol (MET)]
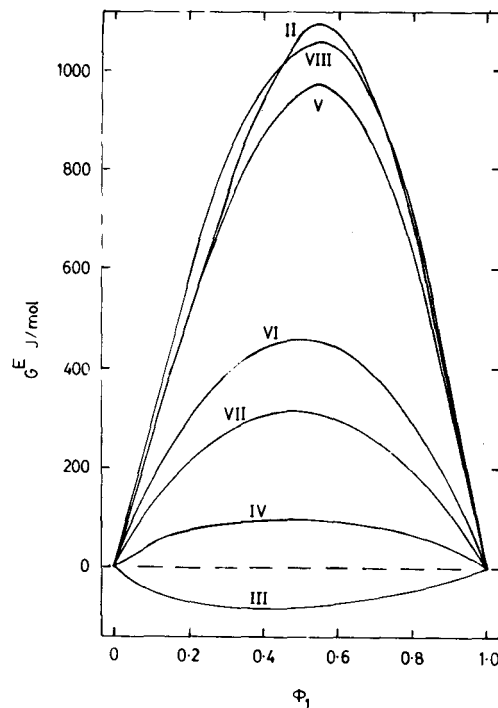

Fig. 2—Excess Gibbs free energy versus composition plots for mixtures (II-VIII) listed in Fig. 1.

bromoform(BF) accomodates the π-electron charge of bromobenzene. Further, because of its high density, bromoform has a comparatively small volume, and should thus behave as an ideal component in binary mixtures with aromatic hydrocarbons. Similarly, a least interaction is observed in the binary mixtures BF(1)-CTC(2), B(1)-CTC(2) and B(1)-Xy(2). On the other hand, CTC(1)-DMF(2) and CTC(1)-MET(2) exhibit small positive deviations. The systems BF(1)-CTC(2), BF(1)-CH(2), BF(1)-MEK(2), BF(1)-EA(2), DMSO(1)-NM(2), DMSO(1)-DMF(2), CTC(1)-NM(2), CTC(1)-EA(2), B(1)-EA(2) and CH(1)-MEK(2) show small negative deviations. Such deviations occur in systems where dispersion forces are primarily responsible for interaction and also with components which interact strongly[17].

Viscosities and densities were fitted to Eqs (1-3) to evaluate T_{12}, H_{12} and G_{12}. A close resemblance could be seen between the parameters T_{12} and H_{12} for the majority of mixtures. This is expected because of the somewhat identical functional dependence of either T_{12} or H_{12}. The values of T_{12} or H_{12} show some variation with composition although this is large for systems in which there is strong specific interaction between the components and/or one component is likely to be associated. There is a tendency for the values of T_{12} and H_{12} at a given composition to increase with the strength of the interaction between the components but this is not well-defined and therefore the parameters T_{12} and H_{12} cannot generally be regarded as a measure of the strength of interaction. However, the values of G_{12} would seem to provide a better measure. Their variation with composition is large; the function steadily decreases with increase in the mol fraction of the mixture. Furthermore, Eqs. (1-3) do not reproduce the experimental viscosities within the limits of experimental errors. Errors upto 5-7% are seen with Hind *et al.*, and Grunberg-Nissan models.

In an effort to test the validity of other empirical relations proposed to predict the viscosities of the mixtures we have chosen McAllister, Auslander and Heric models. Computer analyses of the results i.e. evaluated coefficients of Eqs. (4-7) are given in Table 2. This analysis suggests that McAllister model fits the data better than the other two. For instance, with McAllister relation the standard error is about 0.9% whereas Auslaender and Heric relations give the standard errors upto 1.5%. As has been suggested earlier[11] we have not found it worthwhile to test McAllister's four-body equation because of the inconsistent relationship between the molecular size ratios and the errors in applying the three-body relation.

Table 2—Computer Analysis of Parameters of Eqs (4-7) at 35°C

System*	McAllister (Eq. 4)		Auslaender (Eq. 5)			Heric (Eq. 6)			Heric (Eq. 7)		
	Z_{12}	Z_{21}	B_{12}	A_{21}	B_{21}	A	B	C	A'	B'	C'
(I)	0.134	0.108	−1.505	−2.271	−6.586	−0.011	−0.001	0.005	−0.063	−0.022	0.099
(II)	0.296	0.317	13.429	0.972	−13.546	0.075	−0.003	−0.092	1.697	−0.009	−0.588
(III)	0.127	0.104	0.039	0.154	11.508	−0.059	0.031	−0.020	−0.133	0.044	−0.074
(IV)	0.151	0.124	−1.462	−1.538	−0.666	0.006	0.003	0.007	0.211	0.030	−0.102
(V)	0.216	0.180	1.552	1.055	−0.697	0.057	0.021	−0.037	1.504	0.056	−0.257
(VI)	0.134	0.094	1.123	1.767	0.551	−0.003	0.017	−0.002	0.717	0.014	0.040
(VII)	0.135	0.086	1.156	1.980	0.534	−0.004	0.016	0.000	0.487	0.117	0.025
(VIII)	0.119	0.264	−5.718	−3.437	−0.152	−0.018	0.013	−0.029	1.504	−0.986	0.323
(IX)	0.073	0.118	−1.648	−0.543	−0.714	−0.003	−0.004	−0.016	1.088	−0.643	0.017
(X)	0.075	0.067	−1.156	−1.171	−0.851	−0.002	0.013	−0.008	0.195	0.166	−0.122
(XI)	0.064	0.054	0.315	0.418	4.000	−0.012	−0.003	0.000	−0.076	−0.076	0.007
(XII)	0.087	0.094	1.010	0.298	−1.618	0.002	−0.005	−0.003	0.362	−0.317	−0.032
(XIII)	0.078	0.074	−0.653	0.630	3.864	−0.037	0.014	−0.005	−0.163	0.038	−0.009
(XIV)	0.086	0.091	−0.467	-0.379	−2.043	−0.003	0.000	0.003	−0.040	-0.007	0.046
(XV)	0.064	0.055	1.528	1.886	0.827	−0.011	−0.003	−0.002	0.072	−0.118	−0.015
(XVI)	0.117	0.147	−0.255	−0.253	−4.372	-0.036	0.009	−0.009	0.334	0.001	−0.058
(XVII)	0.074	0.067	−0.252	−0.472	−3.426	−0.015	0.006	−0.017	0.113	0.009	−0.282
(XVIII)	0.114	0.088	0.467	0.980	1.903	−0.044	−0.010	−0.001	−0.206	−0.008	0.014
(XIX)	0.106	0.081	−0.134	−0.270	−7.034	−0.057	−0.021	−0.003	−0.077	−0.094	0.044
(XX)	0.047	0.044	−0.095	−0.062	−35.012	−0.011	−0.003	−0.011	−0.162	−0.025	−0.019
(XXI)	0.052	0.054	4.322	1.966	−2.197	−0.004	−0.004	0.002	−0.017	−0.053	0.028
(XXII)	0.046	0.041	−0.223	−0.653	−4.991	−0.051	−0.027	−0.016	−0.511	−0.186	−0.101

*See Table 1 for the components of the various binary systems.
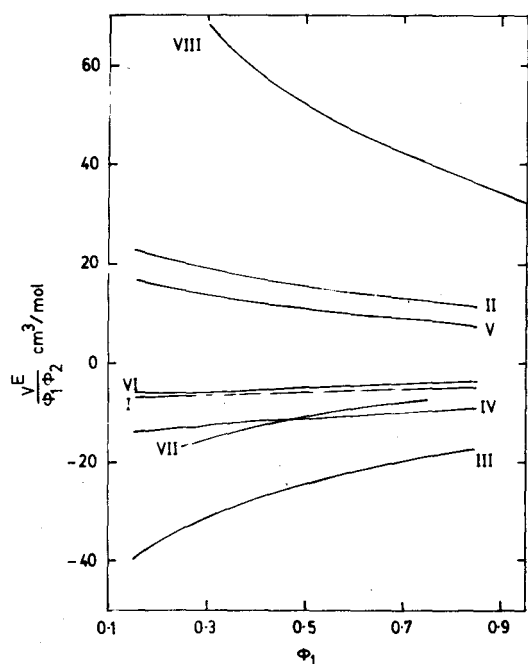
Fig. 3—Excess volume versus composition plots for mixtures (I-VIII) listed in Fig. 1.

Fig. 4—Excess viscosity versus composition plots for mixtures (I-VIII) listed in Fig. 1 [Curve for mixture VII is not drawn]

Excess quantities namely, G^{*E}, V^E and η^E have been calculated using Eqs. (8-10) respectively. For a few representative systems their dependences on composition of the binaries are shown in Figs. 2-4. G^{*E} is negative for BF(1)-CTC(2), BF(1)-CH(2), CTC(1)-EA(2), CTC(1)-CH(2), CTC(1)-BB(2), DMSO(1)-DMF(2), DMSO(1)-NM(2), B(1)-EA(2), BB(1)-CH(2) and CH(1)-MEK(2) systems. Positive G^{*E} is observed for the remaining mixtures except B(1)-Xy(2), wherein both positive and negative values are prevalent. It is noticed that either the maxima or the minima in

Table 3—Estimated Parameters of Eq (13) at 35°C

System	$A_{12}.10^3$		
	a_0	a_1	a_2
(I)	−3	−1	−2
(II)	4	9	2
(III)	5	9	0
(IV)	55	−1	−130
(V)	2	4	−3
(VI)	−24	−3	11
(VII)	−11	−6	4
(VIII)	−24	−5	−24
(IX)	3	19	33
(X)	2	1	−1
(XI)	4	0	0
(XII)	−27	1	1
(XIII)	9	4	1
(XIV)	−9	−2	2
(XV)	−6	1	5
(XVI)	−23	13	8
(XVII)	12	1	12
(XVIII)	1	−1	0
(XIX)	9	−9	3
(XX)	4	2	0
(XXI)	9	0	−2
(XXII)	38	−13	6

*See Table 1 for the components of the binary systems

the curves occurred around the middle of the composition scale (i.e., $\phi \approx 0.5$). The negative G^{*E} suggests the presence of complex formation, by an exothermic process, between the components. The maxima or minima in the G^{*E} versus ϕ_1 plots indicate that the specific interactions occur only around these regions (see Fig. 2). Several researchers[18-20] have attempted to relate G^{*E} to chemical interactions. The flow process in a mixture depends to a large extent on the shape and size of the moving molecules. For instance, when a rigid symmetrical molecule such as carbon tetrachloride is mixed with a rigid planar molecule such as benzene, then such a mixture may produce local fluctuations of the density due to n-π interactions leading to positive deviations[21]. On the other hand, when we consider the mixture of carbon tetrachloride with cyclohexane, a negative deviation is seen. This is due to the greater flexibility of the cyclohexane molecules which can oscillate between the *cis* and *trans* configurations. It is, however, very difficult to predict exactly which of the two configurations leads to complex formation.

Excess molar volumes and excess viscosities (see Figs 3 and 4) are negative for BF(1)-CTC(2), BF(1)-CH(2), BF(1)-MEK(2), BF(1)-EA(2), CTC(1)-EA(2), CTC(1)-CH(2), CTC(1)-BB(2) and DMSO(1)-DMF(2) mixtures. However, BF(1)-DMF(2), BF(1)-DMSO(2), BF(1)-BB(2), CTC(1)-MET(2), CTC(1)-DMF(2) and CTC(1)-DMSO(2)

exhibit positive values of both V^E and η^E. Mixtures such as CTC(1)-B(2), CTC(1)-MEK(2), CTC(1)-NM(2), DMSO(1)-NM(2), B(1)-EA(2), and CH(1)-MEK(2) exhibit positive V^E and negative η^E. No systematic behaviour is seen with B(1)-Xy(2) wherein both negative and positive values are observed for V^E but η^E is negative over the entire composition range. It may be seen from the data presented in Figs. 3 and 4, that the scatter in experimental points from the smooth curve is within the limits of experimental precision ($<2\%$). Generally, positve values of V^E suggests the presence of dipole-dipole type attractive interactions[22]. The negative V^E values are known for systems in which hydrogen-bond formation occurs[26]. It appears that even the systems wherein H-bonding occurs have positive η^E values.

The dependence of excess viscosity on ϕ_1 for a few representative systems is shown in Fig. 4. It may be noticed that the systems which involve hydrogen-bonding exhibit positve η^E whereas negative η^E are exhibited by systems involving weak dipole interaction[23,24]. Differences in molecular size of the components may also be important[25] and perhaps molecular size differences may even account for negative values of η^E. Maxima in these curves suggest the formation of stable complexes. In other cases of complex formation, the contribution of the complex may be insufficient to lead to a maximum or even, if complex formation is weak, to a positive value of η^E; but its effect may be seen in a smaller negative value of η^E than would be obtained in its absence.

The binary contact interaction parameter (A_{12}) as calculated from Eq. (12) is negative for BF(1)-CTC(2), BF(1)-MEK(2), BF(1)-EA(2), BF(1)-MET(2), CTC(1)-MET(2), CTC(1)-DMF(2), CTC(1)-BB(2), CTC(1)-MEK(2) and CTC(1)-DMSO(2); no systematic trend is seen for BF(1)-DMF(2). For the remaining mixtures A_{12} is positive. Using the estimated coefficients from Eq. (13) (see Table 3), the derivative, $(dA_{12}/d\phi_1)$, is obtained from which the density increment, $(\partial \rho / \partial \phi_1)_{P,T}$, of the mixture is computed which is also a function of composition of the mixture. It is negative for three systems namely, DMSO(1)-NM(2), B(1)-EA(2) and B(1)-Xy(2) whereas for the remaining mixtures it is positive.

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