CHAPTER IX

Thermodynamic and Transport Behavior of Non-Aqueous Binary Mixtures of Benzene with Carbon-tetrachloride and Chloroform at Different Temperatures

Density and viscosity of pure benzene and its binary mixtures with carbontetrachloride and chloroform have been measured as a function of composition over the entire range at 298.15, 308.15 and 318.15 K. The excess volume, viscosity deviations, excess free energy of activation of viscous flow and interaction parameter of Grunberg and Nissan have been calculated from the experimental data as a function of composition. All the excess functions are found to be either negative or positive over the entire range of composition depending on the molecular interactions and the nature of liquid mixtures. These properties are discussed in terms of nature of the molecular interactions between the component molecules.

Keywords: Density; viscosity; viscosity deviations; excess molar volume; excess activation of viscous flow; interaction parameter.

9.1. Introduction

In continuation of our earlier Study [1, 2] on binary systems, we now report here the density and viscosity data of binary mixtures formed by benzene, carbontetrachloride and chloroform at various temperatures. There has been a recent upsurge of interest [3-5] in the thermodynamic properties of binary liquid mixtures. These have been extensively used to obtain information on the intermolecular interactions and geometrical effects in these systems [5]. The various thermodynamic properties such as excess molar volume (V^E), viscosity deviations ($\Delta\eta$) etc. obtained from experimental observations have been predicted. The main aim of the study is to correlate the data with the

nature and type of interactions between the mixing components. In this paper the nature of various types of interactions in these binary systems are discussed.

9.2. Experimental

Chemicals

Extrapure AR grade AN, benzene, chloroform and carbontetrachloride procured from Sisco Research Laboratories, Bombay, were purified further as describer earlier[14].

Apparatus and Procedure

The densities (ρ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at (298.15, 308.15 and 318.15) K with doubly distilled water and benzene. The pycnometer with the test solution was equilibrated in a water bath maintained at ± 0.01^0C of the desired temperature by means of a mercury glass thermo regulator and the temperature was determined by a calibrated thermometer and Muller bridge. The pycnometer was then removed from the thermostatic bath, properly dried and weighed. The evaporation losses remained insignificant during the time of actual measurements. An average of triplicate measurements was taken into account. The density values are reproducible to ± 3×10^{-5} g cm^{-3}. Details have been described earlier [1, 15].

The viscosities were measured by means of suspended level Ubbelohde [16] viscometer at the desired temperature (accuracy ±0.01^0C). The precision of the viscosity measurements was ± 0.05%. Details have been discussed earlier [1].

9.2. Results and Discussion

The physical properties such as density and viscosity of pure benzene, carbontetrachloride and chloroform are reported in table II. These results are in excellent agreement with the literature values [17, 9].

The excess functions V^E, $\Delta\eta$, G^{*E} and d were calculated from the experimentally determined ρ and η using equations [9].

$$V^E = V - (x_1V_1 + x_2V_2) \quad (1)$$

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \quad (2)$$

$$G^{*E} = RT(\ln\eta V - x_1 \ln\eta_1V_1 - x_2 \ln\eta_2V_2) \quad (3)$$

$$\ln\eta = x_1\ln\eta_1 + x_2\ln\eta_2 + x_1x_2d \quad (4)$$

where x, V and η represent mole-fraction, molar volume and viscosity respectively, and subscripts 1, 2 represent the pure components. The values of these functions and d are recorded in Table I along with the values of ρ, η and mole fraction. The molar value (V) of pure liquid/mixture is calculated using the following equation.

$$V = M/\rho \quad (5)$$

where M is the molar mass of liquid and for mixture is given by $x_1M_1 + x_2M_2$.

The plots of η versus x_1 for binary liquid mixtures of benzene with Carbontetrachloride and chloroform are shown in 1 and 5.

From Table I and figures 3 and 7, it is found that the value of V^E for benzene and carbon tetrachloride mixture is negative where it is positive for benzene and chloroform mixture at various temperatures over the entire

composition .The negative contribution to V^E due to the difference in size and shape of component molecules in the mixture [6]. The molar volume of benzene is much smaller than that of carbontetrachloride shown in Table1. Because of much appreciable difference in the molar volumes of the components, benzene will fit into the structures of the carbontetrachloride molecule thereby reducing the volume of the mixture [7]. Muller [8] made a similar report from the V^E studies of binary liquid mixtures.

The observed positive value of V^E for benzene and chloroform mixture over the entire composition range shown in Table I and fig.7 indicate the mutual dissociation of the component molecules. Because of the small difference in the molar volumes of the components, benzene will not fit into the structure of chloroform thereby increasing the volume of the mixture.

A correlation between the sign of $\Delta\eta$ and V^E has been observed for a number of binary solvent systems [9-10], i.e. if $\Delta\eta$ is positive then V^E is negative and *vice versa*. In the present observation this is found to hold good which evident from Table I and figs. 2-3 and 6-7.

The value of G^{*E} for the mixture of Benzene + Carbontetrachloride is positive whereas it is negative for the mixture of benzene + chloroform (Table I and figs. 4 and 8). This indicates that intermolecular complex is formed between benzene and carbontetrachloride through non-covalent bonds and this is not favorable in the mixture of benzene and chloroform. Subha *et al* [6] made a similar observation from their G^{*E} studies for the mixtures of propionic acid and alcohols.

The positive value of Grunberg and Nissan parameter (*d*) gives an indication of strong molecular interactions between unlike molecules due to appreciable diple-diploe and dipole-induced dipole interactions [12]. This parameter *d* is found to be positive in the mixture of benzene and carbontetrachloride and negative in case of benzene and chloroform mixture (Table I and figs.9 and 10). This indicates that there is formation of inter-

molecular complexes between benzene and carbontetrachloride through non-covalent bonds in their mixture whereas such complex formation is not favorable in the mixture of benzene and chloroform. These conclusions are in excellent agreement with that draw from G^{*E} values as reported [6, 11] earlier. A similar result was reported by the workers [13] in the case of thermodynamic studies of formamide with various glycols at 308.15 K.

References

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Table-I: Density (ρ), Viscosity (η), viscosity Deviations($\Delta\eta$), Volume (V), Excess Volume (V^E), Excess Free Energy of Activation of Viscous Flow (G^{*E}), Interactions Parameters (d), and Mole Fraction of Benzene (x_1) with Carbontetrachloride and Chloroform at 298.15, 308.15 and 318.15 K

x_1	ρ x 10^{-3} (kg.m^{-3})	η x 10^3 (Pa. s)	$\Delta\eta$ x 10^6 (Pa. s)	V x 10^6 (m^3.mol^{-1})	V^E x 10^8 (m^3.mol^{-1})	G^{*E} (J. mol^{-1})	d
Benzene + Carbontetrachloride							
298.15 K							
0.00000	1.58522	0.91284	0.000	103.34212	0.000	0.00000	0.00000
0.18899	1.47057	0.88139	25.045	100.38398	-34.129	94.29401	0.26041
0.27013	1.41938	0.86261	30.521	99.10473	-49.704	117.82761	0.25647
0.34397	1.37121	0.84496	34.941	97.97036	-60.898	136.97908	0.262280
0.47336	1.28305	0.80843	37.092	96.05881	-72.894	151.95467	0.26604
0.58302	1.20449	0.77512	36.565	94.52053	-74.881	154.57804	0.27868
0.63181	1.16821	0.76013	36.161	93.87636	-71.741	154.59647	0.29049
0.67714	1.13395	0.74553	35.112	93.28686	-67.925	151.64939	0.30264
0.71937	1.10169	0.73086	33.061	92.731280	-64.857	144.21095	0.31229
0.75880	1.07101	0.71756	31.547	92.23338	-60.202	138.13864	0.32958
0.83033	1.01433	0.69173	27.101	91.34345	-50.151	119.08712	0.36937
0.89349	0.96332	0.66704	21.292	90.56053	-40.989	92.30070	0.42818
0.92239	0.93950	0.65666	19.551	90.22011	-35.015	82.81818	0.51028
0.94969	0.91652	0.64245	13.502	89.92904	-26.321	57.17201	0.53333
1.00000	0.87278	0.61391	0.000	89.49563	0.000	0.00000	0.00000

			308.15 K				
0.00000	1.57396	0.78877	0.000	104.08143	0.000	0.00000	0.00000
0.18899	1.45826	0.75179	10.123	101.23160	-20.091	59.75659	0.15504
0.27013	1.40632	0.73548	14.044	100.02518	-27.006	81.85908	0.16559
0.34397	1.35777	0.72016	17.126	98.94018	-32.011	99.19281	0.17568
0.47336	1.26961	0.69188	21.098	97.07574	-37.100	121.66077	0.19546
0.58302	1.19190	0.66515	21.704	95.51904	-39.068	126.64292	0.20969
0.63181	1.15613	0.65237	21.088	94.85476	-37.111	124.61643	0.21540
0.67714	1.12262	0.63913	19.145	94.22843	-36.209	116.02392	0.21416
0.71937	1.09072	0.62697	17.509	93.66561	-33.301	108.20761	0.21622
0.75880	1.06055	0.61585	16.219	93.14384	30.212	101.03189	0.22255
0.83033	1.00479	0.59394	12.140	92.21036	-23.302	78.53985	0.22483
0.89349	0.95465	0.57527	9.216	91.38292	-17.520	58.49386	0.24929
0.92239	0.93123	0.56608	7.221	91.02143	-13.162	45.91814	0.25978
0.94969	0.90897	0.55730	5.2510	90.67660	-9.381	32.83340	0.27908
1.00000	0.86726	0.53951	0.000	90.06526	0.000	0.00000	0.00000
			318.15 K				
0.00000	1.55478	0.67879	0.000	105.36539	0.000	0.00000	0.00000
0.18899	1.43995	0.64829	7.301	102.51830	-15.066	53.16862	0.13052
0.27013	1.38848	0.63458	9.923	101.31017	-20.112	71.42070	0.13673
0.34397	1.34047	0.62170	11.711	100.21725	-24.052	85.08949	0.14283
0.47336	1.25355	0.59903	14.922	98.31969	-29.200	105.54218	0.16148
0.58302	1.17693	0.57748	15.311	96.93410	-31.301	109.09294	0.17236
0.63181	1.14176	0.56648	14.066	96.05098	-30.002	103.31145	0.17067

0.67714	1.10857	0.55655	13.209	95.42202	-28.223	98.46345	0.17310
0.71937	1.07721	0.54690	12.006	94.84031	-26.142	91.27643	0.17384
0.75880	1.04756	0.53731	10.304	94.29805	-24.111	80.90671	0.17031
0.83033	0.99266	0.52092	8.221	93.33758	-18.102	65.57513	0.17861
0.89349	0.94326	0.50531	5.242	92.48625	-13.121	43.40566	0.17642
0.92239	0.92030	0.49921	4.926	92.10301	-10.212	38.10922	0.20580
0.94969	0.89801	0.49204	3.221	91.74340	-7.222	25.21784	0.20504
1.00000	0.85743	0.47876	0.000	91.09782	0.000	0.00000	0.00000
Benzene + Chloroform							
298.15 K							
0.00000	1.47393	0.54268	0.000	80.99435	0.000	0.00000	0.00000
0.14517	1.37566	0.54309	-9.93046	82.42514	19.666	-35.00007	-0.13819
0.21242	1.33167	0.54573	-12.085	83.06369	26.350	-41.04441	-0.12311
0.27646	1.29010	0.54783	-14.542	83.69168	34.707	-48.27207	-0.12323
0.39577	1.21502	0.55323	-17.645	84.81081	45.191	-57.01902	-0.12713
0.54068	1.14903	0.55904	-19.593	85.76952	48.474	-63.49582	-0.13017
0.55565	1.11897	0.56204	-20.216	86.19365	47.556	-66.19287	-0.13558
0.60449	1.09040	0.56598	-19.754	86.60387	47.058	-64.12259	-0.13599
0.65132	1.06339	0.57025	-18.827	86.98563	45.423	-60.49306	-0.13550
0.69628	1.03783	0.57512	-17.156	87.34018	42.656	-54.20199	-0.13152
0.78100	0.99060	0.58438	-13.935	87.97603	34.218	-43.49345	-0.13031
0.85942	0.94773	0.59431	-9.584	88.53954	23.902	-29.47952	-0.12506
0.89649	0.92827	0.60021	-6.326	88.74784	13.218	-19.47952	-0.10564
0.93223	0.90900	0.60443	-4.654	89.00848	8.598	-14.69747	-0.11404
1.00000	0.87278	0.61391	0.000	89.49563	0.000	0.00000	0.00000

			308.15 K				
0.00000	1.45991	0.48812	0.00000	81.77216	0.000	0.00000	0.00000
0.14517	1.36404	0.49175	-3.83029	83.12732	15.125	-12.05804	-0.05739
0.21242	1.32082	0.49388	-5.15374	83.74621	21.243	-15.86915	-0.05698
0.27646	1.28021	0.49580	-6.52721	84.33843	27.356	-20.14491	-0.06030
0.39577	1.20681	0.50010	-8.35961	85.38522	33.090	26.53942	-0.06427
0.54068	1.14181	0.50495	-9.10254	86.31221	35.469	-29.03089	-0.06649
0.55565	1.11210	0.50767	-9.00564	86.72594	34.572	-28.70186	-0.06622
0.60449	1.08396	0.51083	-8.35240	87.11829	33.303	-25.85351	-0.06288
0.65132	1.05741	0.51360	-7.98992	87.47791	30.429	-25.04433	-0.06303
0.69628	1.03208	0.51680	-7.04568	87.82682	28.034	-21.29448	-0.05908
0.78100	0.98514	0.52247	-5.78559	88.46250	21.343	-17.85518	-0.05947
0.85942	0.94241	0.52821	-4.07559	89.03923	13.981	-12.73463	-0.05873
0.89649	0.92254	0.53113	-3.06210	89.29913	9.229	-9.82571	-0.05704
0.93223	0.90331	0.53355	-2.47300	89.56693	6.369	-8.51867	-0.06845
1.00000	0.86726	0.53951	0.00000	90.06526	0.000	0.000	0.00000
			318.15 K				
0.00000	1.44510	0.44869	0.00000	82.64394	0.000	0.00000	0.00000
0.14517	1.35045	0.45096	-2.10021	83.96374	9.255	-7.04657	-0.04004
0.21242	1.30799	0.45198	-3.09654	84.56712	12.741	-10.99165	-0.03869
0.27646	1.26810	0.45319	-3.81023	85.14341	16.231	-13.44011	-0.03976
0.39577	1.19539	0.45577	-4.82001	86.20360	21.387	-16.89676	-0.04189
0.54068	1.13083	0.45873	-5.13224	87.15030	23.986	-17.62623	-0.04243
0.55565	1.10122	0.46020	-5.20051	87.58315	24.181	-17.93445	-0.04340

0.60449	1.07319	0.46177	-5.10005	87.99255	23.829	-17.55326	-0.04382
0.65132	1.04665	0.46347	-4.80221	88.37682	22.970	-16.40578	-0.04333
0.69628	1.02139	0.46517	-4.45623	88.74631	21.610	-14.98282	-0.04301
0.78100	0.97442	0.46854	-3.63297	89.43625	18.983	-11.76751	-0.04310
0.85942	0.93182	0.47202	-2.51106	90.05024	14.087	-7.75642	-0.04187
0.89649	0.91193	0.47383	-1.82231	90.38824	11.548	-5.09829	-0.03919
0.93223	0.89298	0.47552	-1.20011	90.60279	7.789	-3.28636	-0.03790
1.00000	0.85743	0.47876	0.00000	91.09782	0.000	0.00000	0.00000

Table II. Physical Properties of Benzene, Carbontetrachloride and Chloroform

T / (K)	ρ x 10^{-3} / (kg. m^{-3})		η x 10^{3} / (Pa. s)	
	This Work	Literature	This Work	Literature
		Benzene		
298.15	0.87278	0.87278[a]	0.61391	0.61391[a]
308.15	0.86726	0.86726[a]	0.53951	0.53950[a]
318.15	0.85743	0.85742[a]	0.47876	0.47876[a]
		Carbontetrachloride		
298.15	1.58522	1.58522[a]	0.91284	0.91284[a]
308.15	1.57396	1.57396[a]	0.78877	0.78877[a]
318.15	1.55478	1.55479[a]	0.67879	0.67879[a]
		Chloroform		
298.15	1.47393	1.47393[a]	0.54268	0.54628[a]
308.15	1.45991	1.45990[a]	0.48812	0.48812[a]
318.15	1.44451	1.44452[a]	0.44869	0.44868[a]

[a]Refs. From (1) and (9)

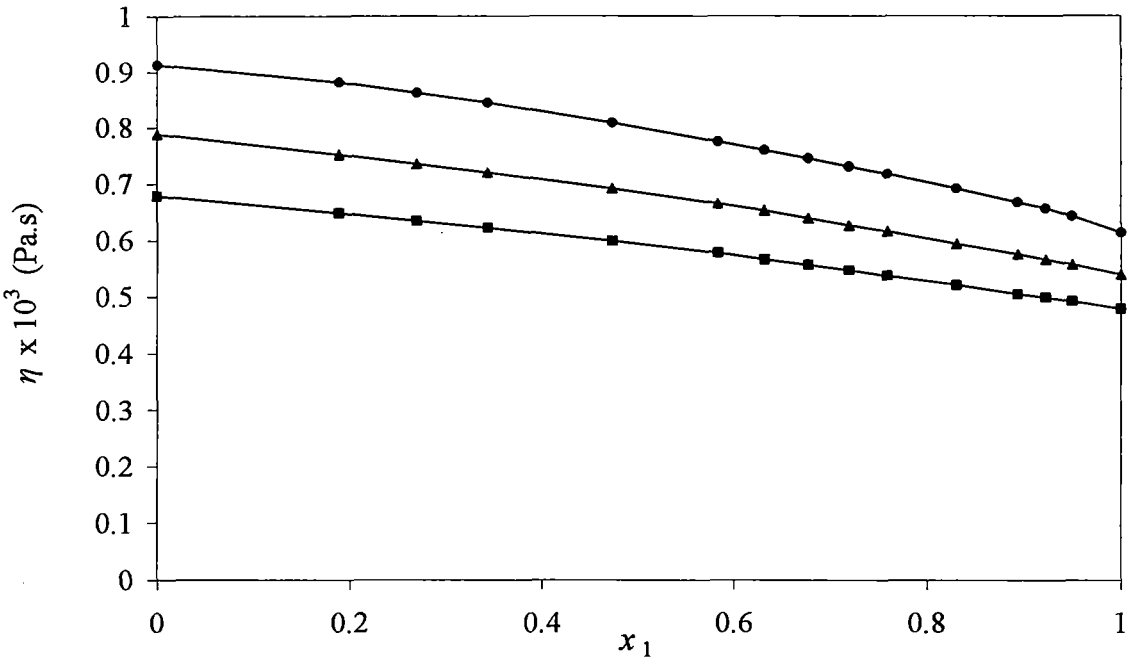

Fig. 1. The plots of viscosity η *versus* mole fraction of benzene x_1 for benzene + carbontetrachloride. Experimental points: 298.15 K (●), 308.15 K (▲), 318.15 K (■).

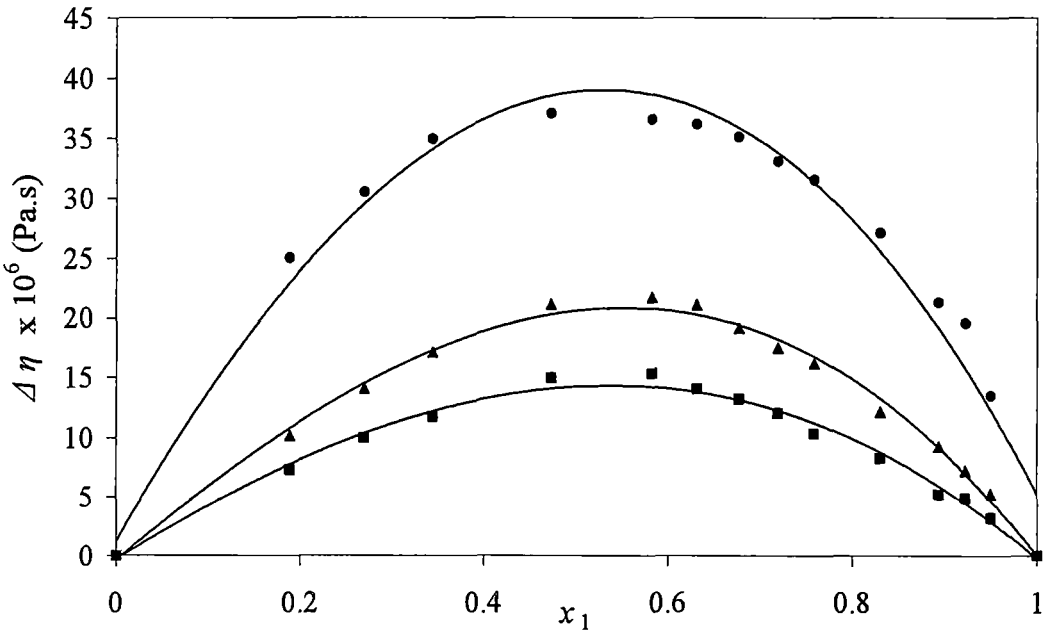

Fig. 2. The plots of excess viscosity $\Delta\eta$ *versus* mole fraction of benzene x_1 for benzene + carbontetrachloride. Experimental points: 298.15 K (●), 308.15 K (▲), 318.15 K (■).

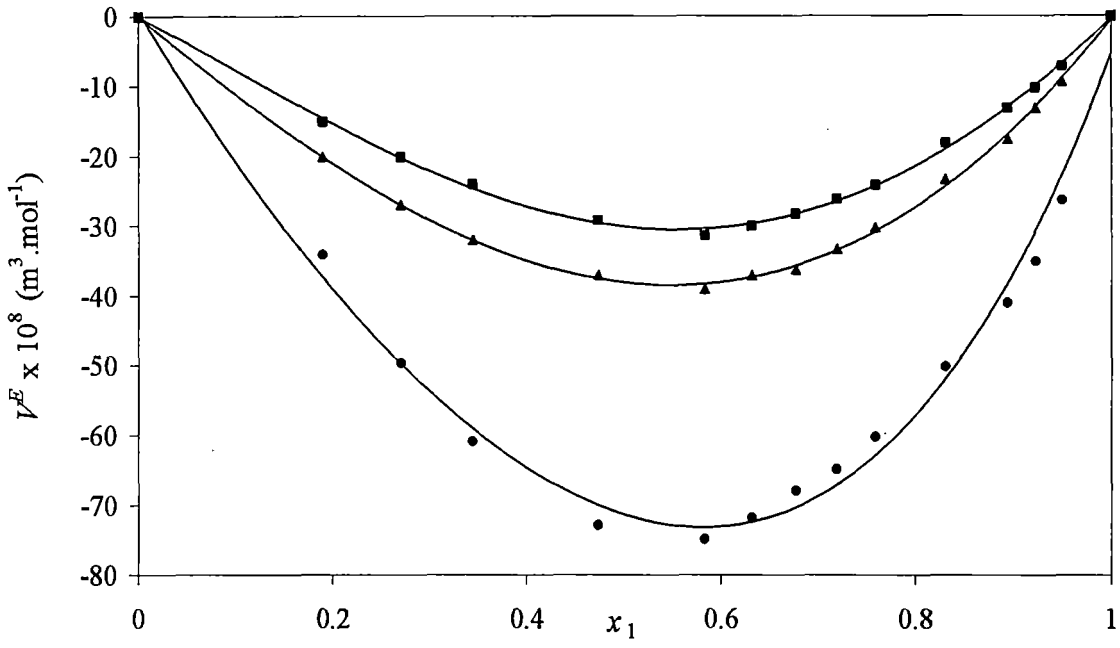

Fig. 3. The plots of excess volumes V^E *versus* mole fraction x_1 of benzene for benzene + carbontetrchloride. Experimental points: 298.15 K (●), 308.15 K (▲), 318.15 K (■).

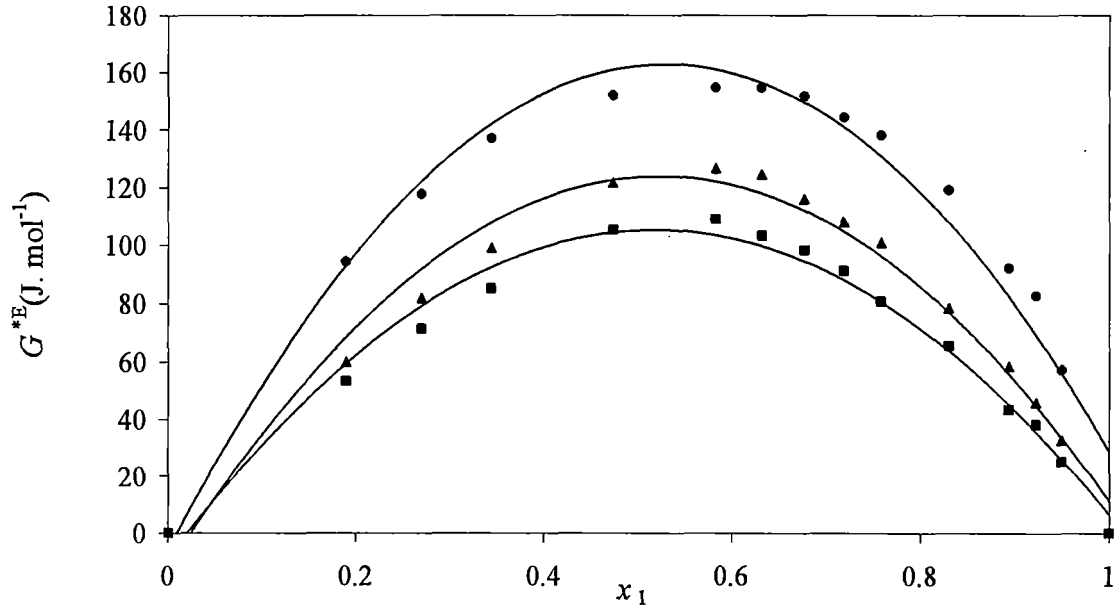

Fig. 4. The plots of excess free energy of activation of viscous flow G^{*E} *versus* mole fraction of benzene x_1 for benzene + carbontetrachloride. Experimental points: 298.15 K (●), 308.15 K (▲), 318.15 K (■).

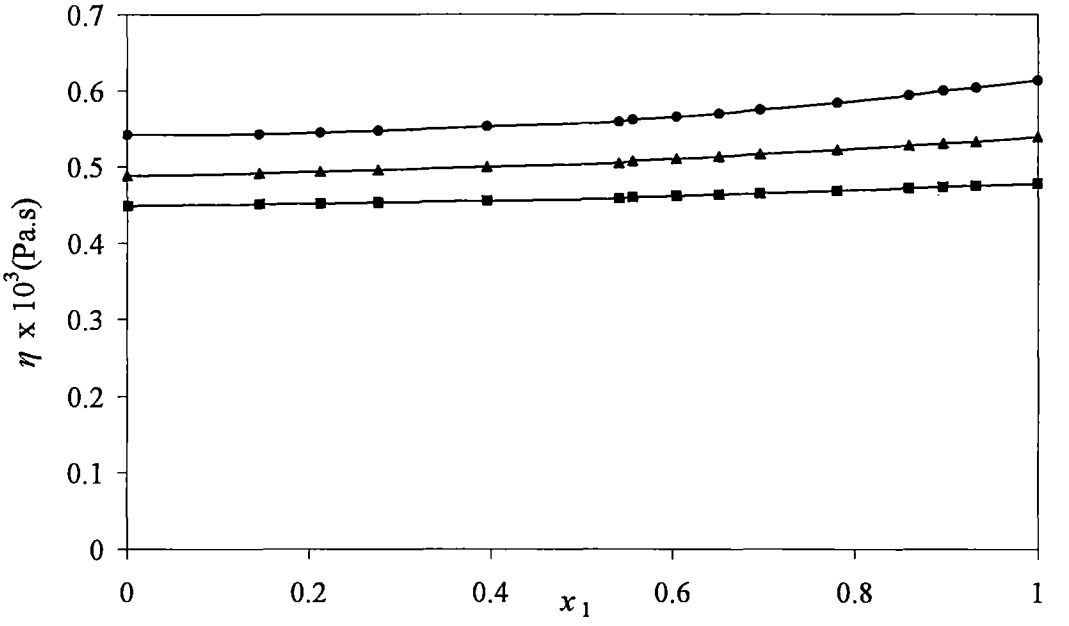

Fig. 5. The plots of viscosity η *versus* mole fraction of benzene x_1 for benzene + chloroform. Experimental points: 298.15 K (●), 308.15 K (▲), 318.15 K (■).

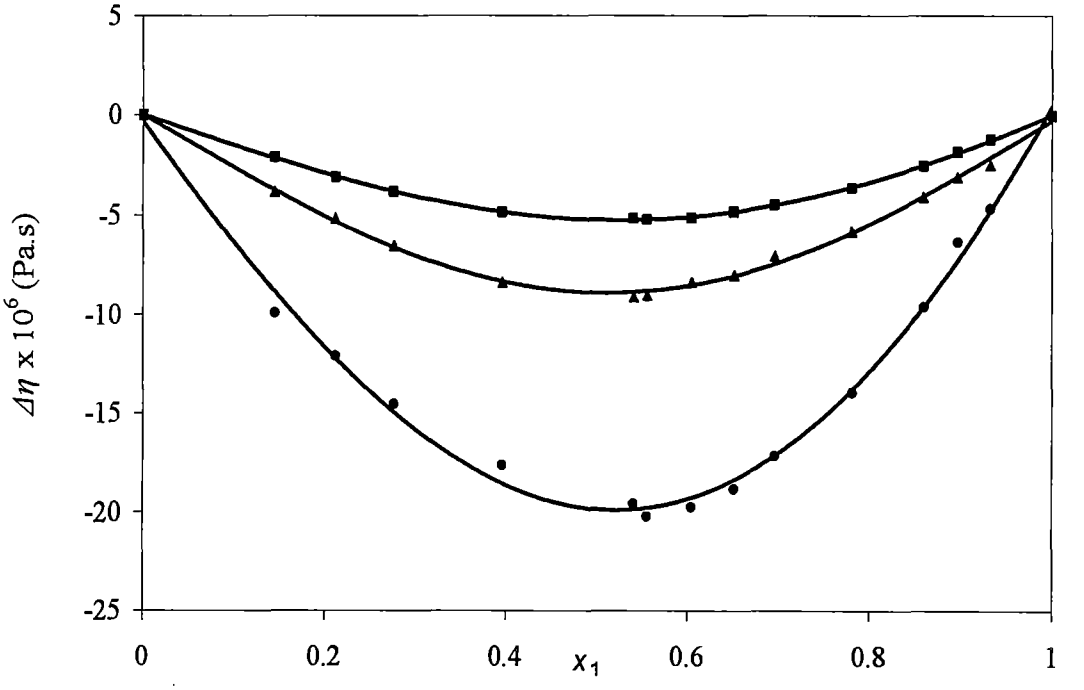

Fig. 6. The plots of excess viscosity $\Delta\eta$ *versus* mole fraction of benzene x_1 for benzene + chloroform. Experimental points: 298.15 K (●), 308.15 K (▲), 318.15 K (■).

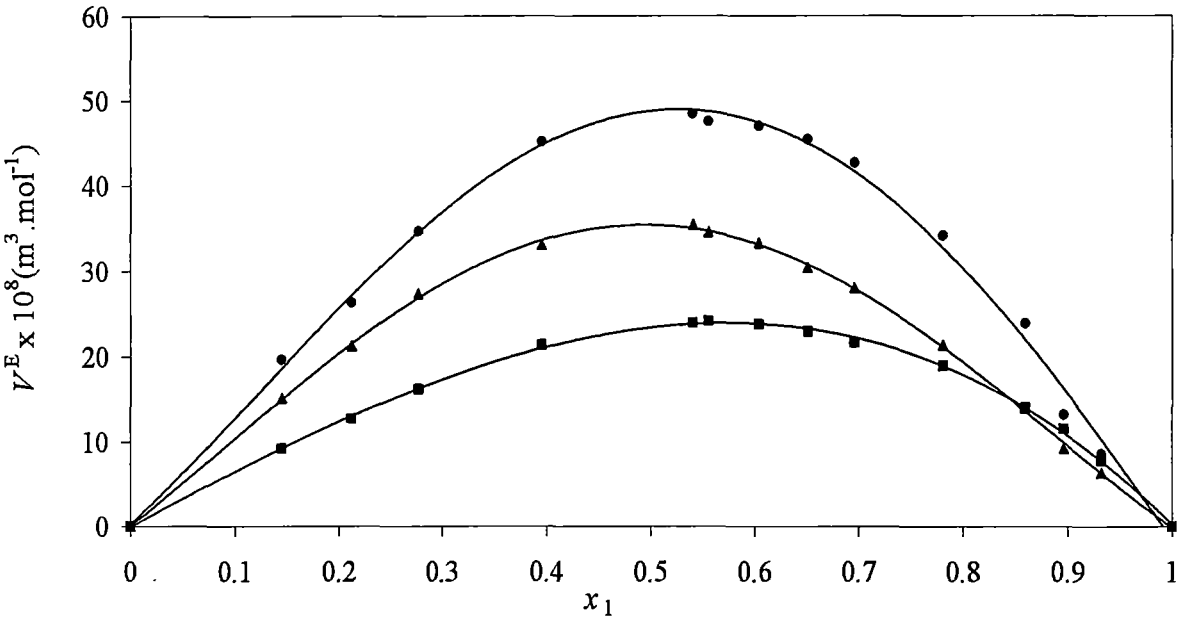

Fig.7. The plots of excess volumes V^E *versus* mole fraction of benzene x_1 for benzene + chloroform. Experimental points: 298.15 K (●), 308.15 K (▲), 318.15 K (■)

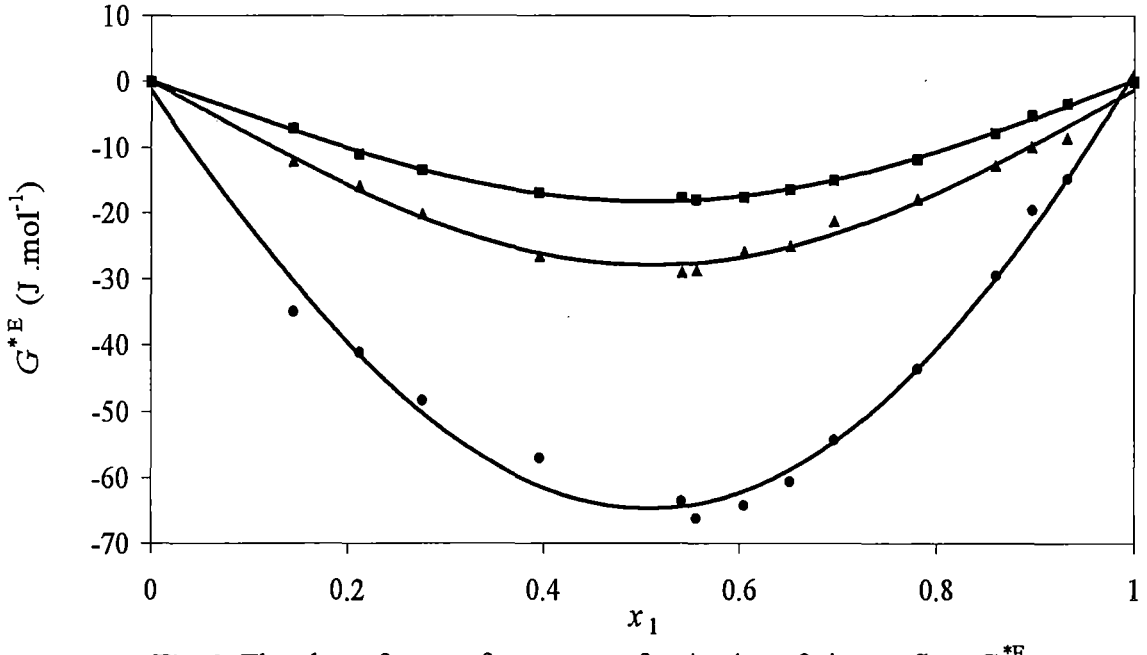

Fig. 8. The plots of excess free energy of activation of viscous flow G^{*E} *versus* mole fraction of benzene x_1 for benzene + chloroform. Experimental points: 298.15 K (●), 308.15 K (▲), 318.15 K (■)

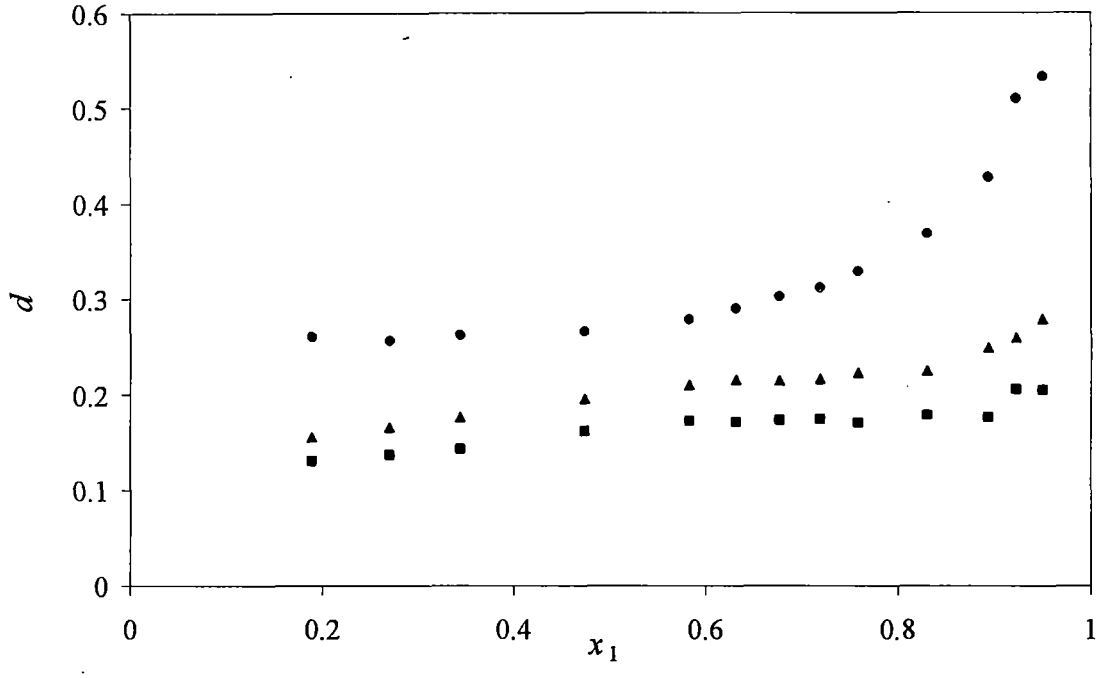

Fig.9. The plots of *d versus* mole fraction of benzene x_1 for benzene + carbontetrachloride. Experimental points: 298.15 K (●), 308.15 K (▲), 318.15 K (■)

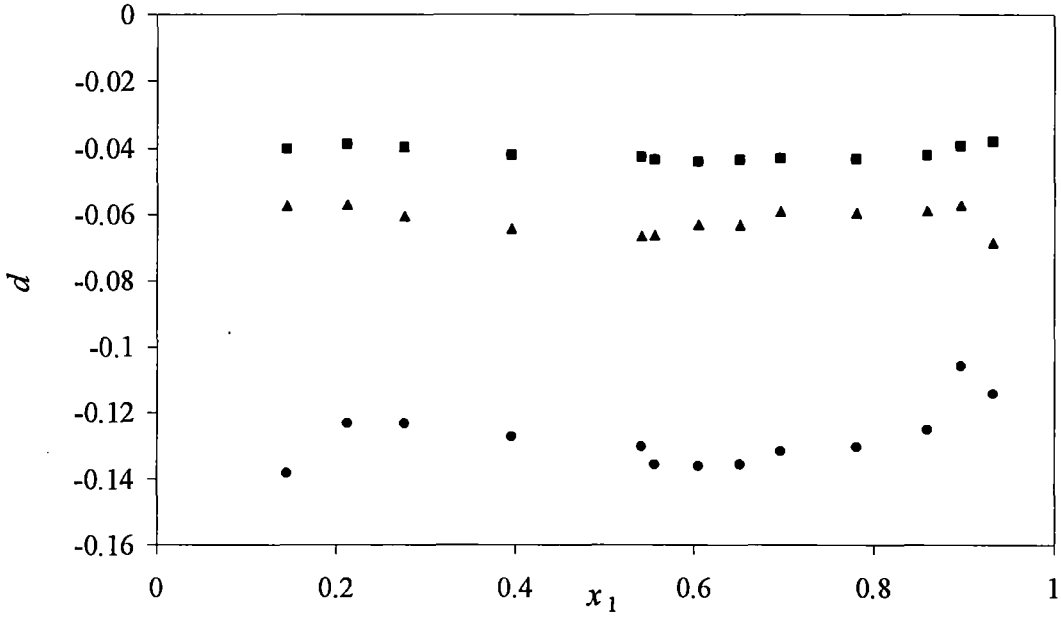

Fig.10. The plots of *d versus* mole fraction of benzene x_1 for benzene + chloroform. Experimental points: 298.15 K (●), 308.15 K (▲), 318.15 K (■)