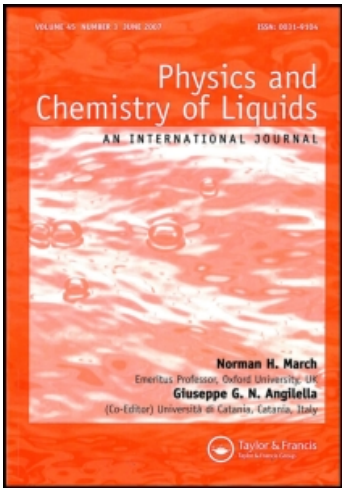

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Viscosities of Binary Liquid Mixtures of Tetrachloroethylene with Some Aliphatic, Alicyclic and Substituted Aromatic Hydrocarbons

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VISCOSITIES OF BINARY LIQUID MIXTURES OF TETRACHLOROETHYLENE WITH SOME ALIPHATIC, ALICYCLIC AND SUBSTITUTED AROMATIC HYDROCARBONS

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Viscosities of binary mixtures of tetrachloroethylene with hexane, heptane, cyclohexane, methylcyclohexane, toluene, chlorobenzene, bromobenzene and nitrobenzene were measured at 303.15 K. The values of η^E are negative in all the systems except in tetrachloroethylene + bromobenzene system. An inversion in sign from positive to negative is observed in the system, tetrachloroethylene + bromobenzene. The viscosity data were analysed in terms of absolute reaction rate and free volume theories of liquid viscosity. Further, Grunberg and Nissan Parameter has also been evaluated.

KEY WORDS: Viscosities, binary mixtures, absolute reaction rate, free volume.

1 INTRODUCTION

The present paper forms a part of our programme on the measurement of transport properties of non-electrolyte solutions containing chlorosubstituted hydrocarbon as a common component. We report here new experimental data for excess viscosities of the systems: tetrachloroethylene + hexane, + heptane, + cyclohexane, + methylcyclohexane, + toluene, + chlorobenzene, + bromobenzene and + nitrobenzene. We have undertaken this work to investigate the effects of cyclization and aromatization and also the influence of different substituents in the aromatic ring on viscosity.

2 EXPERIMENTAL SECTION

Materials

Analytical reagent grade tetrachloroethylene was dried over sodium carbonate and fractionally distilled. Cyclohexane (BDH, AR) and methylcyclohexane (BDH, LR) were purified by the method described by Rao and Naidu[1]. Hexane (BDH, AR), and

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Table 1 Boiling points and densities of pure components at 303.15 K.

Compound	*Boiling point, K*		*Density, g/cm³*	
	Expt.	*Lit.*	*Expt.*	*Lit.*
Tetrachloroethylene	394.3	394.4	1.60634	1.60640
Hexane	341.6	341.9	0.65064	0.65070
Heptane	371.8	371.6	0.67530	0.67538
Cyclohexane	353.7	353.9	0.76937	0.76928
Methylcyclohexane	373.8	374.0	0.76024	0.76030
Toluene	383.7	383.8	0.85772	0.85766
Chlorobenzene	404.8	404.8	1.09552	1.09550
Bromobenzene	429.1	429.1	1.48154	1.48150
Nitrobenzene	483.7	483.9	1.19346	1.19341

heptane (Veb, LR) were purified using the methods described earlier[2]. Toluene (BDH, AR) was purified by the method described by Rastogi and co-workers[3]. Chlorobenzene (BDH, LR) and nitrobenzene (BDH, LR) were purified by the procedure described elsewhere[4]. Bromobenzene (BDH, LR) was dried with calcium chloride and fractionally distilled under reduced pressure. The purity of the chemicals were checked by comparing the measured densities and boiling points with those reported in the literature[5,6]. The data are given in Table 1.

Viscosities

Viscosity of liquids and liquid mixtures were determined at 303.15 K using Ostwald viscometers with an accuracy of $\pm 0.5\%$. The accuracy of the viscometer was checked by measuring the viscosities of pure benzene and cyclohexane. The results show very good agreement with those reported in the literature. Mixtures of various compositions were prepared by weight. A constant volume of the mixture transferred into the viscometer and then inserted into a thermostat controlled at 303.15 ± 0.01 K. The viscosities were computed from flow time (t), density (ρ) and the constant of the viscometer (k) using the equation

$$\eta = k\rho t \tag{1}$$

Densities of pure components were determined using a pycnometer. In the case of mixtures, densities were obtained from excess volumes[7] using the relation

$$\rho = \frac{xM_1 + (1-x)M_2}{V^0 + V^E} \tag{2}$$

where x stands for mole fraction of tetrachloroethylene. M_1 and M_2 are the molecular weights of tetrachloroethylene and the non-common component respectively. V^0 and V^E stand for the molar volume and excess molar volume respectively. Excess viscosity (η^E) was calculated using the relation suggested by Fort and Moore[8].

$$\eta^E = \eta_{\text{mix}} - [x\eta_1 + (1-x)\eta_2] \tag{3}$$

where η_{mix}, η_1 and η_2 are the viscosities of the mixture, and pure components 1 and 2 respectively.

3 THEORETICAL ASPECTS

Two major semi-empirical theories which can be used to predict liquid viscosity are the absolute reaction rate theory of Eyring and coworkers and the free volume theory. Combining the absolute reaction rate and the free volume theories of liquid viscosity, Bloomfield and Dewan[9] have obtained Eq. (4)

$$\ln \eta = x \ln \eta_1 + (1-x) \ln \eta_2 - \frac{\Delta H_m}{RT} + \frac{\Delta S^R}{R} + \left(\frac{1}{\tilde{v}-1} - \frac{x}{\tilde{v}_1 - 1} - \frac{(1-x)}{\tilde{v}_2 - 1} \right) \quad (4)$$

$$= \ln \eta_{id} + \ln \eta_H + \ln \eta_S + \ln \eta_V \quad (5)$$

Where ΔH_M is the enthalpy of mixing per mole of the solution, ΔS^R is the residual entropy per mole, R is the gas constant, T is the absolute temperature and $\tilde{V}$, $\tilde{V}_1$ and $\tilde{V}_2$ are the reduced volumes of the mixture, component 1 and component 2 respectively. $\ln \eta_{id}$, $\ln \eta_H$, $\ln \eta_S$ and $\ln \eta_V$ are the ideal mixture viscosity and enthalpy, entropy and the free volume contributions respectively. In order to estimate the contributions to mixture viscosity from $\Delta H_M/RT$ and $\Delta S^R/R$ in Eq. (4), we use Flory's[10] equations for ΔH_M and ΔS^R, which can be written in the following form.

$$\frac{\Delta H_M}{RT} = \frac{xC_1}{\tilde{T}_1}\left(\frac{1}{\tilde{V}_1} - \frac{1}{\tilde{V}}\right) + \frac{(1-x)C_2}{\tilde{T}_2}\left(\frac{1}{\tilde{V}_2} - \frac{1}{\tilde{V}}\right) + \frac{xC_1C_2X_{12}}{\tilde{V}\tilde{T}_1P_1^*} \quad (6)$$

$$\frac{\Delta S^R}{R} = -3xC_1 \ln \frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}^{1/3} - 1} - 3(1-x)C_2 \ln \frac{\tilde{V}_2^{1/3} - 1}{\tilde{V}^{1/3} - 1} \quad (7)$$

The parameter C_i for a component i is related to the characteristic pressure P_i^*, the characteristic temperature T_i^*, and the hard-core volume per mole v_i^* of component i as described earlier[9,10]. The characteristic Parameters P_i^*, T_i^*, and V_i^*, and the reduced Temperature $\tilde{T}_i$ and the reduced volume $\tilde{v}_i$ of the pure component i, used in

Table 2 Parameters of the pure components at 303.15 K.

Component	$\alpha \times 10^3$ deg^{-1}	k_T TPa^{-1}	$\tilde{V}$	V $cm^3\ mol^{-1}$	V^* $cm^3\ mol^{-1}$	P^* $J\ cm^{-3}$	$\tilde{T}$
Tetrachloroethylene	1.025	807.0	1.256	103.25	82.21	607.2	0.05825
Hexane	1.404	1792.0	1.329	132.45	99.65	419.5	0.06820
Heptane	1.260	1526.0	1.303	148.39	113.88	425.0	0.06480
Cyclohexane	1.229	1173.3	1.297	109.36	84.32	534.2	0.06402
Methylcyclohexane	0.954	1105.4	1.242	129.16	103.99	403.6	0.05611
Toluene	1.079	948.5	1.267	107.43	84.79	553.6	0.05986
Chlorobenzene	0.986	786.8	1.248	102.75	82.33	591.7	0.05704
Bromobenzene	0.904	701.7	1.231	105.99	86.10	591.8	0.05437
Nitrobenzene	0.828	526.0	1.214	103.15	84.97	703.3	0.05156

Table 3 Values of experimental and calculated viscosities (cp) and the parameter, d for tetrachloroethylene with some aliphatic, alicyclic and substituted aromatic hydrocarbons at 303.15 K.

x_1	n_{exp}	n_{id}	n_H	n_S	n_V	n_G	$n_{id}n_H$	$n_{id}n_S$	$n_{id}n_G$	$n_{id}n_V$	$n_{id}n_Hn_V$	$n_{id}n_Hn_Vn_S$	d
						Tetrachloroethylene + hexane							
0.0000	0.309	—	—	—	—	—	—	—	—	—	—	—	—
0.1642	0.358	0.362	0.924	0.986	0.996	0.911	0.334	0.357	0.330	0.361	0.334	0.329	−0.08
0.2468	0.388	0.392	0.895	0.981	0.994	0.878	0.351	0.384	0.344	0.390	0.349	0.342	−0.06
0.3358	0.432	0.435	0.875	0.974	0.995	0.852	0.381	0.424	0.371	0.433	0.379	0.369	−0.03
0.4336	0.471	0.470	0.868	0.969	0.996	0.841	0.408	0.455	0.395	0.468	0.406	0.393	−0.01
0.4782	0.494	0.491	0.864	0.968	0.997	0.836	0.424	0.475	0.410	0.490	0.423	0.409	0.02
0.5140	0.515	0.508	0.866	0.966	0.998	0.837	0.440	0.491	0.425	0.507	0.439	0.424	0.05
0.6464	0.591	0.578	0.875	0.966	1.000	0.845	0.506	0.558	0.488	0.578	0.506	0.489	0.10
0.7236	0.643	0.623	0.890	0.970	1.000	0.863	0.554	0.604	0.538	0.623	0.554	0.537	0.16
0.8072	0.697	0.675	0.910	0.977	1.001	0.889	0.614	0.659	0.600	0.676	0.615	0.601	0.20
0.9346	0.776	0.764	0.965	0.990	1.001	0.955	0.737	0.756	0.730	0.765	0.738	0.731	0.26
1.0000	0.814	—	—	—	—	—	—	—	—	—	—	—	—
						Tetrachloroethylene + heptane							
0.0000	0.388	—	—	—	—	—	—	—	—	—	—	—	—
0.1960	0.442	0.449	0.945	0.973	1.000	0.919	0.424	0.437	0.413	0.449	0.424	0.413	−0.10
0.3642	0.497	0.508	0.924	0.956	1.003	0.883	0.469	0.486	0.449	0.510	0.471	0.450	−0.09
0.4421	0.529	0.538	0.921	0.948	1.006	0.873	0.495	0.510	0.470	0.541	0.498	0.472	−0.07
0.4713	0.543	0.550	0.919	0.947	1.006	0.870	0.505	0.521	0.479	0.553	0.508	0.481	−0.05
0.5272	0.568	0.573	0.923	0.943	1.009	0.870	0.529	0.540	0.499	0.578	0.533	0.503	−0.04
0.6106	0.610	0.610	0.927	0.943	1.010	0.874	0.565	0.575	0.533	0.616	0.571	0.538	0.00
0.6939	0.653	0.649	0.931	0.950	1.009	0.884	0.604	0.617	0.574	0.655	0.610	0.580	0.03
0.7237	0.668	0.663	0.935	0.951	1.009	0.889	0.620	0.631	0.589	0.669	0.626	0.595	0.04
0.8091	0.714	0.707	0.952	0.960	1.009	0.914	0.673	0.679	0.646	0.713	0.679	0.652	0.06
0.9254	0.775	0.770	0.981	0.977	1.007	0.958	0.755	0.752	0.738	0.775	0.760	0.743	0.09
1.0000	0.814	—	—	—	—	—	—	—	—	—	—	—	—

Tetrachloroethylene + cyclohexane

0.0000	0.786	—	—	—	—	—	—	—	—	—	—	—	—
0.1695	0.762	0.791	0.904	1.085	0.952	0.981	0.715	0.858	0.776	0.753	0.681	0.739	−0.27
0.2698	0.750	0.793	0.867	1.123	0.932	0.974	0.686	0.891	0.772	0.739	0.641	0.720	−0.28
0.3794	0.742	0.797	0.837	1.156	0.915	0.968	0.771	0.921	0.771	0.729	0.610	0.705	−0.30
0.4194	0.740	0.798	0.831	1.164	0.911	0.967	0.663	0.929	0.772	0.727	0.604	0.703	−0.31
0.4966	0.738	0.800	0.823	1.173	0.906	0.965	0.658	0.938	0.772	0.725	0.597	0.700	−0.32
0.5532	0.741	0.801	0.823	1.173	0.906	0.965	0.659	0.940	0.773	0.726	0.597	0.700	−0.32
0.6182	0.746	0.803	0.831	1.165	0.909	0.968	0.667	0.935	0.777	0.730	0.607	0.707	−0.31
0.7242	0.764	0.806	0.857	1.136	0.922	0.974	0.691	0.916	0.785	0.743	0.638	0.725	−0.27
0.8383	0.781	0.809	0.901	1.089	0.946	0.981	0.729	0.881	0.794	0.765	0.689	0.750	−0.26
0.9204	0.800	0.812	0.945	1.048	0.970	0.990	0.767	0.851	0.804	0.788	0.745	0.781	−0.20
1.0000	0.814	—	—	—	—	—	—	—	—	—	—	—	—

Tetrachloroethylene + methylcyclohexane

0.0000	0.627	—	—	—	—	—	—	—	—	—	—	—	—
0.1166	0.637	0.646	0.928	0.995	0.998	0.923	0.599	0.643	0.596	0.645	0.598	0.595	−0.14
0.2246	0.648	0.665	0.871	1.002	0.989	0.873	0.579	0.666	0.581	0.658	0.573	0.574	−0.15
0.3047	0.658	0.679	0.838	1.011	0.980	0.847	0.569	0.686	0.575	0.665	0.557	0.563	−0.15
0.4335	0.679	0.702	0.805	1.014	0.973	0.816	0.565	0.712	0.573	0.683	0.550	0.558	−0.14
0.5554	0.708	0.725	0.799	1.024	0.971	0.818	0.579	0.742	0.593	0.704	0.562	0.575	−0.10
0.6523	0.734	0.743	0.813	1.022	0.974	0.831	0.604	0.759	0.617	0.724	0.589	0.602	−0.05
0.7700	0.762	0.767	0.850	1.014	0.982	0.862	0.652	0.778	0.661	0.753	0.640	0.649	−0.04
0.8108	0.773	0.775	0.868	1.012	0.985	0.878	0.673	0.784	0.680	0.763	0.662	0.670	−0.02
0.8864	0.790	0.790	0.916	1.004	0.993	0.920	0.724	0.793	0.727	0.784	0.718	0.721	0.00
0.9342	0.801	0.800	0.949	0.999	0.997	0.948	0.759	0.799	0.758	0.798	0.757	0.756	0.02
1.0000	0.814	—	—	—	—	—	—	—	—	—	—	—	—

(continued over page)

Table 3 (*continued*)

x_1	n_{exp}	n_{id}	n_H	n_S	n_V	n_G	$n_{id}n_H$	$n_{id}n_S$	$n_{id}n_G$	$n_{id}n_V$	$n_{id}n_Hn_V$	$n_{id}n_Hn_Vn_S$	d
						Tetrachloroethylene + toluene							
0.0000	0.521	—	—	—	—	—	—	—	—	—	—	—	—
0.1502	0.551	0.557	0.982	1.011	0.994	0.993	0.547	0.563	0.553	0.554	0.544	0.550	−0.08
0.2612	0.574	0.585	0.968	1.023	0.988	0.990	0.566	0.598	0.579	0.578	0.560	0.573	−0.10
0.3745	0.599	0.616	0.958	1.030	0.984	0.987	0.590	0.634	0.608	0.606	0.581	0.598	−0.12
0.4715	0.629	0.643	0.956	1.032	0.983	0.987	0.615	0.664	0.635	0.632	0.604	0.623	−0.09
0.5666	0.662	0.671	0.953	1.036	0.980	0.987	0.639	0.695	0.662	0.658	0.627	0.650	−0.06
0.6428	0.691	0.694	0.955	1.032	0.983	0.986	0.663	0.716	0.684	0.682	0.651	0.672	−0.02
0.6905	0.708	0.709	0.960	1.030	0.984	0.989	0.681	0.730	0.701	0.698	0.670	0.690	−0.01
0.7529	0.730	0.729	0.964	1.026	0.986	0.989	0.703	0.748	0.721	0.719	0.693	0.711	0.01
0.8376	0.760	0.757	0.972	1.021	0.988	0.992	0.736	0.773	0.751	0.748	0.727	0.742	0.03
0.9336	0.793	0.790	0.990	1.006	0.997	0.996	0.782	0.795	0.787	0.788	0.780	0.785	0.06
1.0000	0.814	—	—	—	—	—	—	—	—	—	—	—	—
						Tetrachloroethylene + chlorobenzene							
0.0000	0.712	—	—	—	—	—	—	—	—	—	—	—	—
0.1416	0.716	0.726	1.006	0.994	0.997	1.000	0.730	0.722	0.726	0.724	0.728	0.724	−0.11
0.2048	0.717	0.732	1.005	0.994	0.995	0.999	0.736	0.728	0.731	0.728	0.732	0.728	−0.13
0.2727	0.718	0.738	1.004	0.994	0.995	0.998	0.741	0.734	0.737	0.734	0.737	0.733	−0.14
0.3562	0.720	0.747	1.003	0.993	0.993	0.996	0.749	0.742	0.744	0.742	0.744	0.739	−0.16
0.4651	0.728	0.758	1.003	0.993	0.992	0.996	0.760	0.753	0.755	0.752	0.754	0.749	−0.16
0.5412	0.739	0.765	1.002	0.995	0.991	0.997	0.767	0.761	0.763	0.758	0.760	0.756	−0.14
0.6279	0.751	0.774	1.000	0.998	0.990	0.998	0.774	0.772	0.772	0.766	0.766	0.764	−0.13
0.7180	0.766	0.784	0.998	1.000	0.991	0.998	0.782	0.784	0.782	0.777	0.775	0.775	−0.11
0.8422	0.786	0.797	0.996	1.003	0.993	0.999	0.794	0.799	0.796	0.791	0.788	0.790	−0.10
0.9302	0.802	0.806	0.998	1.001	0.997	0.999	0.804	0.807	0.805	0.804	0.802	0.803	−0.08
1.0000	0.814	—	—	—	—	—	—	—	—	—	—	—	—

Tetrachloroethylene + bromobenzene

0.0000	0.992	—	—	—	—	—	—	—	—	—	—	—	—
0.1026	0.978	0.972	1.000	0.999	0.997	0.999	0.972	0.971	0.971	0.969	0.969	0.968	0.07
0.1749	0.971	0.958	0.998	0.999	0.995	0.997	0.956	0.957	0.955	0.953	0.951	0.950	0.09
0.2799	0.960	0.939	0.998	0.996	0.995	0.994	0.937	0.935	0.933	0.934	0.932	0.928	0.11
0.3996	0.945	0.917	0.998	0.996	0.993	0.994	0.915	0.913	0.911	0.911	0.909	0.905	0.13
0.4574	0.933	0.906	0.997	0.997	0.992	0.994	0.903	0.903	0.901	0.899	0.896	0.893	0.12
0.5408	0.916	0.891	0.996	0.998	0.991	0.994	0.887	0.889	0.886	0.883	0.879	0.877	0.11
0.6276	0.894	0.876	0.993	1.001	0.990	0.994	0.870	0.877	0.871	0.867	0.861	0.862	0.09
0.7273	0.871	0.859	0.993	1.001	0.991	0.994	0.853	0.860	0.854	0.851	0.845	0.846	0.07
0.8585	0840	0.837	0.994	1.004	0.993	0.998	0.832	0.840	0.835	0.831	0.826	0.829	0.03
0.9426	0.822	0.823	0.998	1.001	0.997	0.998	0.821	0.824	0.822	0.821	0.819	0.820	−0.02
1.0000	0.814	—	—	—	—	—	—	—	—	—	—	—	—

Tetrachloroethylene + Nitrobenzene

0.0000	1.639	—	—	—	—	—	—	—	—	—	—	—	—
0.1516	1.446	1.462	0.962	1.007	0.993	0.969	1.406	1.472	1.417	1.452	1.397	1.407	−0.09
0.2128	1.376	1.412	0.955	1.003	0.995	0.958	1.348	1.416	1.353	1.405	1.342	1.346	−0.15
0.2966	1.288	1.332	0.948	1.001	0.995	0.949	1.263	1.333	1.264	1.325	1.256	1.257	−0.16
0.3642	1.221	1.270	0.947	0.996	0.998	0.943	1.203	1.265	1.198	1.267	1.200	1.195	−0.17
0.4582	1.144	1.189	0.946	0.993	1.000	0.939	1.125	1.181	1.116	1.189	1.125	1.117	−0.16
0.5496	1.074	1.116	0.946	0.992	1.000	0.938	1.056	1.107	1.047	1.116	1.056	1.048	−0.16
0.6451	1.012	1.044	0.950	0.992	1.001	0.942	0.992	1.036	0.983	1.045	0.993	0.985	−0.14
0.7624	0.941	0.961	0.960	0.994	1.000	0.954	0.923	0.955	0.917	0.961	0.923	0.917	−0.12
0.8428	0.896	0.909	0.967	0.997	0.999	0.964	0.879	0.906	0.876	0.908	0.878	0.875	−0.11
0.9206	0.856	0.861	0.980	1.001	0.998	0.981	0.844	0.862	0.845	0.859	0.842	0.843	−0.08
1.0000	0.814	—	—	—	—	—	—	—	—	—	—	—	—

the calculations, were obtained from the values of the molar volume (V), thermal expansion co-efficient ($\propto$), and the isothermal compressibility (K_T) by using the methods described by Abe and Flory[11]. The data are given in Table 2. The parameter $\theta_2 X_{12}$ (characteristic of a system) used to calculate $\Delta H_m/RT$ from Eq. (6) at all concentrations for each system, was estimated from the reduced excess volumes $\tilde{v}^E$ by using the experimental excess volumes and by employing the relations described by Abe and Flory. The values of the reduced volumes of mixtures, needed in Eqs (6, 7) were also obtained from relations of Abe and Flory by using the experimental data for excess volumes.

According to Grunberg and Nissan[12] the viscosity of a binary mixture can be expressed by Eq. (8).

$$\ln \eta = x \ln \eta_1 + (1 - x)\ln \eta_2 + x(1 - x)d \tag{8}$$

In Eq. (8) the parameter d has been regarded as a measure of the strength of the interaction between the components[8,12].

4 RESULTS AND DISCUSSION

Contributions of various terms involved in Eq. (4) have been shown in columns 3-6 of Table 3. Whereas the values of the free energy contribution, defined by $\eta_G = \eta_H \eta_s$ are given in column 7. It is not clear that the contributions of all terms to the mixture viscosity are equally important in Eq. (4). In the absence of this information, the various combinations of the calculated contributions from different terms to n, combining them multiplicatively in accordance with the additive logarithmic relation are tabulated in columns 8-11 of Table 3. The absolute reaction rate theory which takes into account free energy contributions to ideal mixture viscosity η_{id}, corresponds to the multiplicate term $\eta_{id}\eta_G$, whereas the free volume theory which takes into account free volume corrections to the ideal mixture viscosity corresponds $\eta_{id}\eta_v$. Further, according to Macedo and Litvovit[13] which accounts for enthalpic and free volume corrections to ideal mixture viscosity corresponds to $\eta_{id}\eta_H\eta_v$ which is given in column 12 of the Table 3, whereas the values of the complete product $\eta_{id}\eta_H\eta_v\eta_s$ are given in column 13. Table 3 shows that the experimental viscosities are best reproduced by the contributions of $\eta_{id}\eta_v$ in the mixtures of tetrachloroethylene with hexane, heptane, cyclohexane and methylcyclohexane. $\eta_{id}\eta_H\eta_v$ and $\eta_{id}\eta_H\eta_v\eta_s$ predict mixture viscosity in tetrachloroethylene + nitrobenzene system. All combinations i.e. $\eta_{id}\eta_H$, $\eta_{id}\eta_s$, $\eta_{id}\eta_G$, $\eta_{id}\eta_v$, $\eta_{id}\eta_H\eta_v$ and $\eta_{id}\eta_H\eta_v\eta_s$ contribute to the mixture viscosity in the systems, tetrachloroethylene + toluene, + chlorobenzene and + bromobenzene to the same extent.

The dependence ofη^E on composition is shown in Figures 1 and 2. Figures 1 and 2 show that the values of η^E are negative in all the systems except tetrachloroethylene + bromobenzene. An inversion in sign from positive to negative is observed at around 0.85 mole fraction of tetrachloroethylene in the system, tetrachloroethylene + bromobenzene.

The η^E values may be interpreted in terms of two opposing effects (1) loss of dipolar association, difference in size and shape of the component molecules and (2) specific interaction between unlike molecules such as dipole-dipole, dipole-induced dipole and electron-donor-acceptor interactions. The curves in Figures 1 and 2 suggest that the former effect is contributing to viscosity in all the systems except in the system, tetrachloroethylene + bromobenzene. The latter effect determines the viscosity data up to 0.85 mole fraction in tetrachloroethylene + bromobenzene system. As the η^E values are smaller above 0.85 mole fraction of tetrachloroethylene, no conclusion can be drawn from the data.

The values of d calculated for the various mixtures from Eq. (8) by using the viscosity data are given in the last column of Table 3. The values of d are negative in the mixtures of tetrachloroethylene with cyclohexane, chlorobenzene and nitroben-

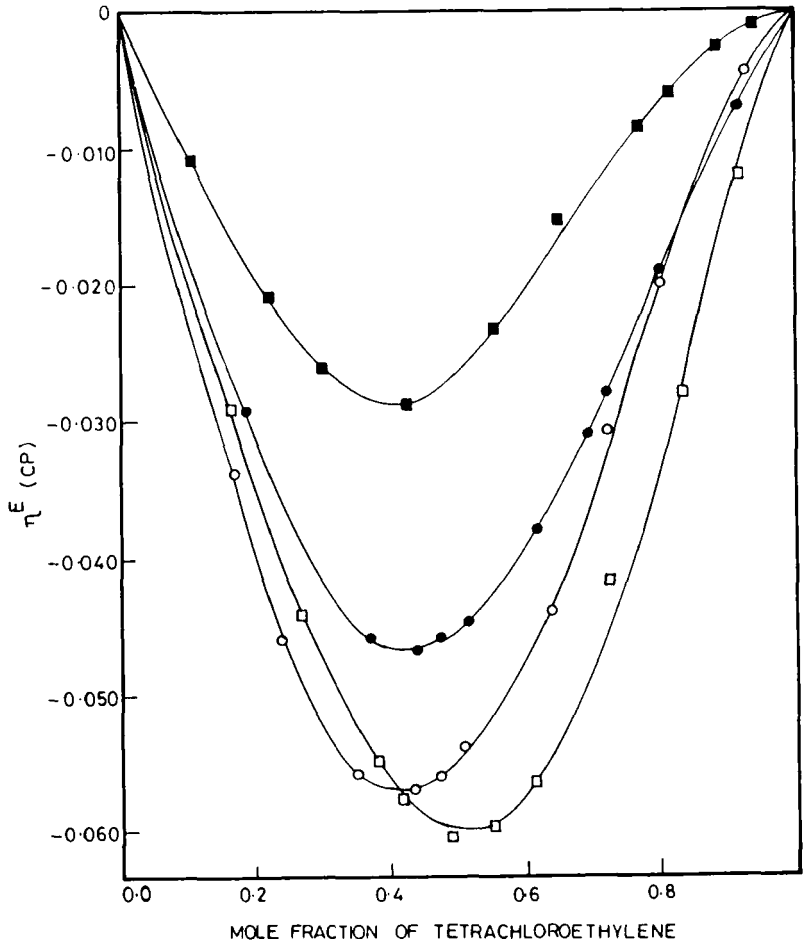

Figure 1 Tetrachloroethylene + hexane (○), + heptane (●), + cyclohexane (□), + methylcyclohexane (■).

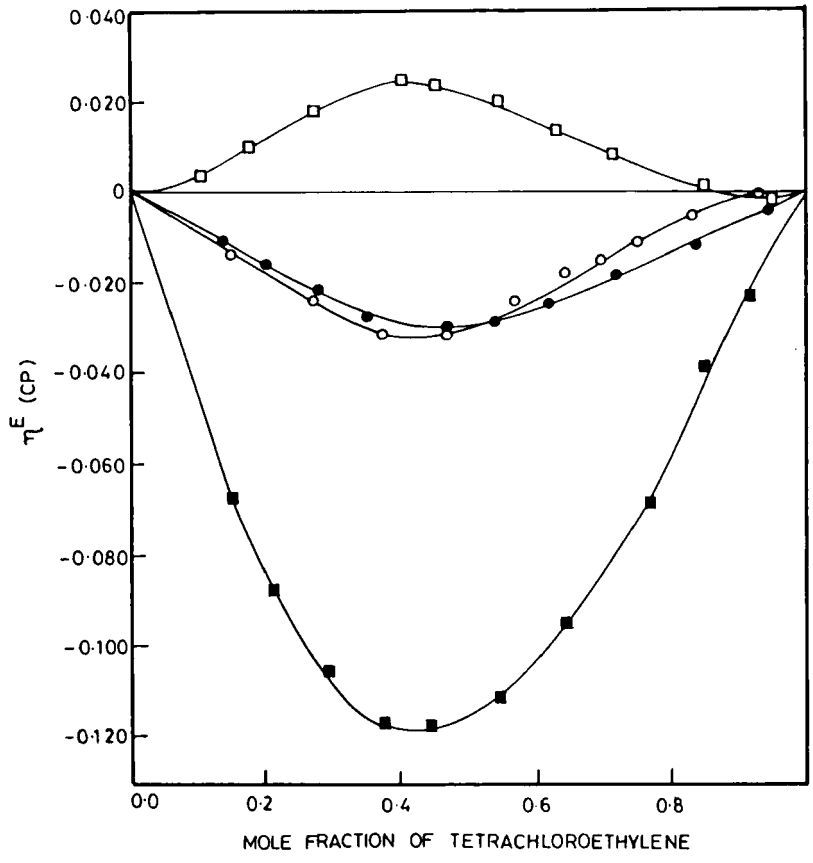

Figure 2 Tetrachloroethylene + Toluene (○), + Chlorobenzene (●), + Bromobenzene (□), + Nitrobenzene (■).

zene over the entire mole fraction range. An inversion in sign of d is observed in the remaining systems. A comparision between the values of η^E and d suggests the variation of these two parameters with composition is not similar.

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