

## VISCOSITIES OF BINARY MIXTURES OF TRICHLOROETHYLENE WITH SOME ALIPHATIC, ALICYCLIC AND SUBSTITUTED AROMATIC HYDROCARBONS

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Viscosities of binary mixtures of trichloroethylene with *n*-hexane, *n*-heptane, cyclohexane, methylcyclohexane, toluene, chlorobenzene, bromobenzene and nitrobenzene were measured at 303.15 K. The values of  $\eta^E$  are negative in all the systems except in mixtures containing toluene and chlorobenzene. An inversion of sign is observed in the case of trichloroethylene + chlorobenzene and positive in the case of trichloroethylene + toluene. The viscosity data were analysed in terms of absolute reaction rate and the free volume theories of liquid viscosity. Further the study was extended to evaluate interaction parameter, (d).

*Key words:* Viscosity, Absolute reaction rate theory, Free volume theory.

### INTRODUCTION

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

### EXPERIMENTAL

Viscosity of liquids and liquid mixtures were determined at 303.15 K by 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 agree with in  $\pm 0.5$  % with those reported in the literature [1,2]. Mixtures of various compositions were prepared by mass. A constant volume of the mixture was transferred into the viscometer and then inserted into a thermostat controlled at  $303.15 \pm 0.01$  K. The viscosities were computed from flow time (*t*), density ( $\rho$ ), and the constant of the viscometer (*k*) using the equation

$$\eta = k\rho t \quad \dots \dots \dots (1)$$

Densities of pure components were determined using pycnometer. In the case of mixtures, densities were obtained from excess volumes [3] using the relation

$$= \frac{xM_1 + (1-x)M_2}{V^O + V^E} \quad \dots \dots \dots (2)$$

where *x* stands for mole fraction of trichloroethylene.  $M_1$  and  $M_2$  are the molecular weights of trichloroethylene and the non-common component respectively.  $V^O$  and  $V^E$  stand for the ideal molar volume and excess molar volume respectively.

### MATERIALS

Trichloroethylene (BDH) was purified by the method described by Jagannath and Dubey [4]. Cyclohexane (BDH), methylcyclohexane (BDH) were purified by the method described by Rao and Naidu [5], *n*-hexane (BDH), *n*-heptane (BDH) were purified by following the procedure described by Krishnaiah *et al.* [6]. Toluene (AR) was purified by the method described by Rastogi and co-workers [7]. Chlorobenzene (BDH) and nitrobenzene (BDH) were purified by the procedure described elsewhere [8]. Bromobenzene (AR) was dried with calcium chloride and fractionally distilled under reduced pressure. The purity of the samples is checked by comparing the measured densities and boiling points with those reported in the literature [1,2]. The data are given in Table 1.

*Theoretical aspects.* Excess viscosity ( $\eta^E$ ) at each composition is obtained from the equation

$$\eta^E = \eta_{mix} - x\eta_1 - (1-x)\eta_2 \quad \dots \dots \dots (3)$$

where  $\eta_{mix}$ ,  $\eta_1$  and  $\eta_2$  are the viscosities of the mixture and pure components respectively.

Two major semi-empirical theories which can be used to predict liquid viscosity are the absolute reaction rate

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

Compound	Boiling point, °K		Density $\rho$ , g/cm <sup>3</sup>	
	Expt.	Lit [1,2]	Expt.	Lit [1,2]
Trichloroethylene	360.2	360.3	1.45136	1.45140
<i>n</i> -Hexane	341.6	341.9	0.65064	0.65070
<i>n</i> -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
Bromobenzene	429.1	429.1	1.48154	1.48150
Chlorobenzene	404.8	404.8	1.09552	1.09550
Nitrobenzene	483.7	483.9	1.19346	1.19341

theory of Eyring and co-workers 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)

$$\ln \eta_{\text{mix}} = x \ln \eta_1 + (1-x) \ln \eta_2 - \frac{\Delta H_M}{RT} - \frac{\Delta S^R}{R} + \frac{1}{\tilde{V}-1} - \frac{x}{\tilde{V}_1-1} - \frac{(1-x)}{\tilde{V}_2-1} = \ln \eta_{\text{id}} + \ln \eta_H + \ln \eta_S + \ln \eta_V \quad (4)$$

where  $\Delta H_M$  is the enthalpy of mixing per mole of the solution,  $\Delta S^R$  is the residual entropy per mole,  $R$  is the gas constant,  $T$  is the absolute temperature and  $\tilde{V}_1$ ,  $\tilde{V}_2$  and  $\tilde{V}$  are the reduced volumes of component 1, component 2, and the mixture respectively.  $\ln \eta_{\text{id}}$ ,  $\ln \eta_H$ ,  $\ln \eta_S$  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 the mixture viscosity from  $\frac{\Delta H_M}{RT}$  and  $\frac{\Delta S^R}{R}$  in eq. (4) we used Flory's equations [10] for  $\Delta H_M$  and  $\Delta S^R$ , which can be written in the following form

$$\frac{\Delta H_M}{RT} = \frac{x C_1}{\tilde{T}_1} \left( \frac{1}{\tilde{V}_1} - \frac{1}{\tilde{V}} \right) + \frac{(1-x) C_2}{\tilde{T}_2} \left( \frac{1}{\tilde{V}_2} - \frac{1}{\tilde{V}} \right) + \frac{x C_1 \theta_2 x_{12}}{\tilde{V} \tilde{T}_1 P_i^*} \dots \dots \dots (5)$$

$$\frac{\Delta S^R}{R} = -3x C_1 \ln \frac{\tilde{V}_1^{Y_3}}{\tilde{V}^{Y_3-1}} - 1 - 3(1-x) C_2 \ln \frac{\tilde{V}_2^{1/3-1}}{\tilde{V}^{Y_3-1}} \dots \dots (6)$$

The parameter  $C_i$  for component  $i$  is related to the characteristic pressure  $P_i^*$ , the characteristic temperature  $T_i^*$ , and the hardcore 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 the calculations are obtained from the values of the molar volume  $V$ , thermal expansion coefficient,  $\alpha$  and the isothermal compressibility,  $K_T$  by using the methods described by the 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. (5) 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  $\tilde{V}$ , the reduced volumes of mixtures, need in eq. (5) and (6) were also obtained from the relations of Abe and Flory by using the experimental data for excess volumes.

## RESULTS AND DISCUSSION

Contributions of various terms involved in the eq.(4) have been shown in columns 3-6 of Table 3, whereas the

Table 2. Parameters of the pure components at 303.15 K.

	$\alpha \times 10^3$ deg <sup>-1</sup>	$K_T$ Tpa <sup>-1</sup>	$\tilde{V}$	$\frac{V}{\text{cm}^3 \text{mol}^{-1}}$	$\frac{V^*}{\text{cm}^3 \text{mol}^{-1}}$	$\frac{P^*}{\text{J cm}^{-3}}$	$\tilde{T}$
Trichloroethylene	1.170	976.7	1.285	90.53	70.45	599.6	0.06240
<i>n</i> -Hexane	1.404	1792.0	1.329	132.45	99.65	419.5	0.06820
<i>n</i> -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
Bromobenzene	0.904	701.7	1.231	105.99	86.10	591.8	0.05437
Chlorobenzene	0.986	786.8	1.248	102.75	82.33	591.7	0.05704
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 trichloroethylene with some aliphatic, alicyclic and substituted aromatic hydrocarbons at 303.15 K.

x	$\eta_{\text{mix}}$	$\eta_{\text{id}}$	$\eta_{\text{H}}$	$\eta_{\text{S}}$	$\eta_{\text{V}}$	$\eta_{\text{G}}$	$\eta_{\text{id}}\eta_{\text{H}}$	$\eta_{\text{id}}\eta_{\text{S}}$	$\eta_{\text{id}}\eta_{\text{G}}$	$\eta_{\text{id}}\eta_{\text{V}}$	$\eta_{\text{id}}\eta_{\text{H}}\eta_{\text{V}}$	$\eta_{\text{id}}\eta_{\text{H}}\eta_{\text{V}}\eta_{\text{S}}$	d $\eta$
Trichloroethylene + <i>n</i> -hexane													
0.0000	0.309	-	-	-	-	-	-	-	-	-	-	-	-
0.1367	0.329	0.333	0.966	0.933	0.996	0.959	0.322	0.331	0.319	0.332	0.321	0.319	-0.10
0.2452	0.346	0.353	0.951	0.986	0.995	0.938	0.336	0.348	0.331	0.351	0.334	0.329	-0.09
0.3359	0.364	0.370	0.942	0.980	0.996	0.923	0.349	0.363	0.342	0.369	0.348	0.341	-0.07
0.4720	0.391	0.398	0.936	0.972	0.998	0.910	0.373	0.387	0.362	0.397	0.372	0.362	-0.07
0.5529	0.409	0.416	0.936	0.971	0.999	0.909	0.389	0.404	0.378	0.416	0.389	0.378	-0.07
0.6264	0.426	0.433	0.942	0.968	1.002	0.912	0.408	0.419	0.395	0.434	0.409	0.396	-0.07
0.7076	0.447	0.452	0.948	0.971	1.002	0.921	0.428	0.439	0.416	0.453	0.429	0.417	-0.05
0.7648	0.462	0.466	0.956	0.973	1.003	0.930	0.445	0.453	0.433	0.467	0.446	0.434	-0.05
0.8161	0.477	0.479	0.961	0.978	1.002	0.940	0.460	0.468	0.450	0.480	0.461	0.451	-0.03
0.9282	0.508	0.509	0.982	0.991	1.001	0.973	0.500	0.504	0.495	0.510	0.501	0.496	-0.03
1.0000	0.529	-	-	-	-	-	-	-	-	-	-	-	-
Trichloroethylene + <i>n</i> -heptane													
0.0000	0.388	-	-	-	-	-	-	-	-	-	-	-	-
0.1564	0.402	0.407	0.972	1.000	0.995	0.972	0.396	0.407	0.396	0.405	0.394	0.394	-0.09
0.2406	0.411	0.418	0.956	1.002	0.992	0.958	0.400	0.419	0.400	0.415	0.397	0.398	-0.09
0.3549	0.424	0.433	0.945	1.003	0.989	0.948	0.409	0.434	0.410	0.428	0.404	0.405	-0.09
0.4994	0.444	0.453	0.936	1.005	0.987	0.941	0.424	0.455	0.426	0.447	0.418	0.420	-0.08
0.6271	0.464	0.471	0.936	1.006	0.987	0.942	0.441	0.474	0.444	0.465	0.435	0.438	-0.06
0.6529	0.469	0.475	0.937	1.006	0.987	0.943	0.445	0.478	0.448	0.469	0.439	0.442	-0.06
0.7365	0.483	0.488	0.946	1.003	0.990	0.949	0.462	0.489	0.463	0.483	0.457	0.458	-0.05
0.8106	0.496	0.499	0.956	1.002	0.992	0.958	0.477	0.500	0.478	0.495	0.473	0.474	-0.04
0.8994	0.511	0.513	0.973	1.001	0.995	0.974	0.499	0.514	0.500	0.510	0.495	0.496	-0.04
0.9326	0.517	0.518	0.983	1.000	0.997	0.983	0.509	0.518	0.509	0.516	0.507	0.507	-0.03
1.0000	0.529	-	-	-	-	-	-	-	-	-	-	-	-
Trichloroethylene + cyclohexane													
0.0000	0.786	-	-	-	-	-	-	-	-	-	-	-	-
0.1126	0.721	0.752	0.958	1.042	0.976	0.998	0.720	0.784	0.750	0.734	0.703	0.773	-0.42
0.1815	0.683	0.731	0.932	1.070	0.961	0.997	0.681	0.782	0.729	0.702	0.654	0.700	-0.46
0.2710	0.640	0.706	0.902	1.104	0.944	0.996	0.637	0.779	0.703	0.666	0.601	0.664	-0.50
0.3216	0.621	0.692	0.887	1.120	0.936	0.993	0.614	0.775	0.687	0.648	0.575	0.644	-0.50
0.4267	0.586	0.664	0.868	1.143	0.924	0.992	0.576	0.759	0.659	0.614	0.533	0.609	-0.51
0.5408	0.565	0.634	0.862	1.151	0.920	0.992	0.547	0.730	0.629	0.583	0.503	0.579	-0.46
0.6646	0.560	0.604	0.878	1.131	0.928	0.993	0.530	0.683	0.600	0.561	0.493	0.558	-0.34
0.7803	0.559	0.577	0.901	1.105	0.946	0.996	0.520	0.638	0.575	0.546	0.492	0.544	-0.18
0.8157	0.559	0.569	0.923	1.081	0.953	0.998	0.525	0.615	0.568	0.542	0.500	0.541	-0.12
0.9306	0.541	0.544	0.970	1.029	0.982	0.998	0.528	0.560	0.543	0.534	0.518	0.533	-0.09
1.0000	0.529	-	-	-	-	-	-	-	-	-	-	-	-
Trichloroethylene + methylcyclohexane													
0.0000	0.627	-	-	-	-	-	-	-	-	-	-	-	-
0.1426	0.600	0.612	0.925	1.016	0.973	0.940	0.566	0.622	0.575	0.595	0.551	0.560	-0.16
0.2282	0.585	0.604	0.887	1.030	0.957	0.914	0.536	0.622	0.552	0.578	0.553	0.560	-0.18
0.3341	0.569	0.593	0.851	1.045	0.942	0.889	0.505	0.620	0.527	0.559	0.527	0.551	-0.19
0.4126	0.560	0.585	0.834	1.053	0.937	0.878	0.488	0.616	0.514	0.548	0.513	0.540	-0.18
0.4708	0.554	0.579	0.826	1.059	0.933	0.875	0.478	0.613	0.507	0.540	0.504	0.534	-0.18
0.5625	0.547	0.570	0.824	1.060	0.934	0.873	0.470	0.604	0.498	0.532	0.497	0.527	-0.17
0.7118	0.538	0.556	0.849	1.049	0.947	0.891	0.472	0.583	0.495	0.527	0.499	0.523	-0.16
0.8119	0.534	0.546	0.886	1.033	0.963	0.915	0.484	0.564	0.500	0.526	0.507	0.524	-0.15

(Continued . . . . .)



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 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  $\eta$ , 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 corrections to ideal mixture viscosity,  $\eta_{id}$ , corresponds to the multiplicative term  $\eta_{id} \eta_G$ , whereas the free volume theory which takes into account free volume corrections to the ideal mixture viscosity, corresponds to  $\eta_{id} \eta_V$ . Further Macedo-Litovitz theory [12] 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 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 contribution of  $\eta_{id} \eta_V$  or  $\eta_{id} \eta_S$  and the viscosities reproduced by other contributions are less satisfactory in these mixtures.

The dependence of  $\eta^E$  on composition is shown in Fig. 1 and 2. The  $\eta^E$  values may be interpreted in terms of two opposing effects: (1) loss of dipolar association, and difference in size and shape of component molecules, (2) and specific interactions between unlike molecules such as dipole-dipole, dipole-induced dipole and electron-donor-acceptor interactions. The curves in Fig. 1 and 2 suggest

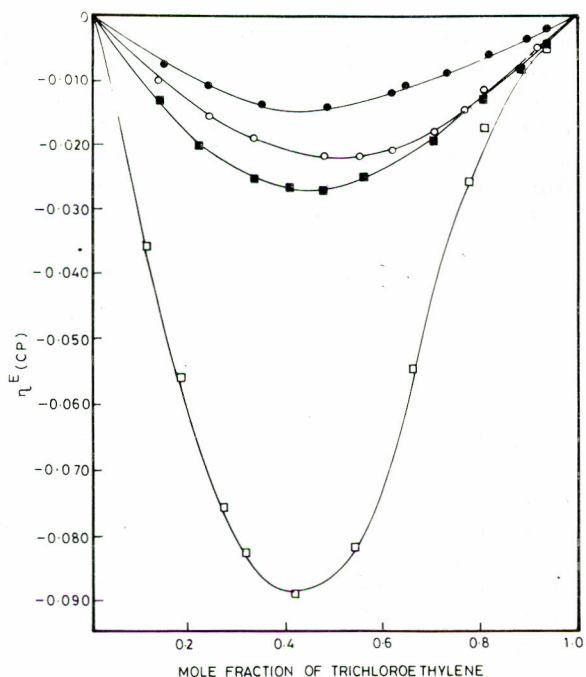


Fig. 1. Trichloroethylene + Hexane (o), + Heptane (●), + Cyclohexane (□), + Methylcyclohexane (■), + Methylcyclohexane (■).

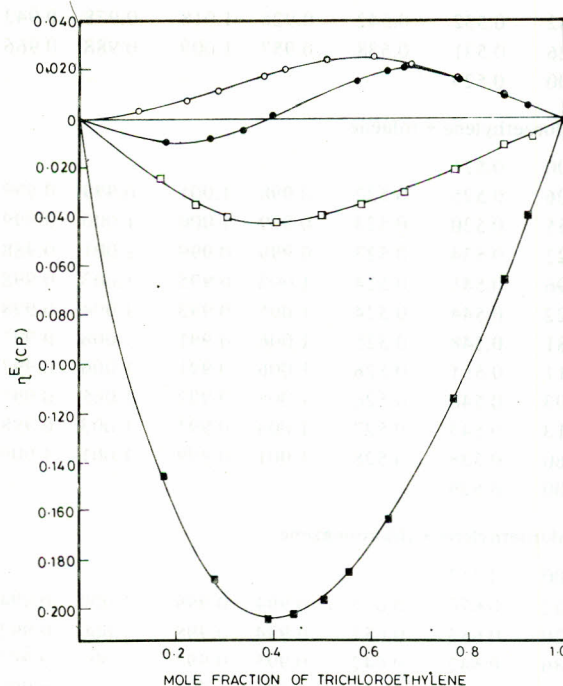


Fig. 2. Trichloroethylene + Toluene (o), + Chlorobenzene (●), + Bromobenzene (□), + Nitrobenzene (■).

that the former effect may be contributing to viscosity in all the mixtures except in mixtures containing toluene and chlorobenzene. In trichloroethylene + toluene system the latter effect may be dominant. The former effect operates at lower concentrations of trichloroethylene + chlorobenzene system and the latter effect at higher concentrations.

The negative deviations in viscosity with cyclohexane is much greater than that of with *n*-hexane, and with methylcyclohexane is much greater than that of with *n*-heptane. This indicates that  $\eta^E$  becomes more negative when the straight chain compound is replaced by a cyclic one with the same number of carbon atoms. The  $\eta^E$  values in mixtures made up of trichloroethylene and substituted benzenes fall in the order.

Toluene > chlorobenzene > bromobenzene > nitrobenzene. This trend in the values of  $\eta^E$  gives evidence in favour of decreasing extent of specific interactions of trichloroethylene with aromatics when the methyl group is replaced by chloro, bromo and nitro groups. The existence of electron-donor-acceptor type interactions between trichloroethylene and aromatic hydrocarbons has been reported earlier [13,14].

According to Grunberg and Nissan [15] the viscosity of a binary mixture can be expressed by eq. (7).

$$\ln \eta_{\text{mix}} = x \ln \eta_1 + (1-x) \ln \eta_2 + x(1-x) d \dots \dots \dots (7)$$

In eq. (7) the parameter  $d$  has been regarded as a measure of the strength of the interaction between the components [15,16]. The values of  $d$  calculated for the various mixtures from eq.(7) by using the viscosity data are given in the last column of Table 3. The variation of  $d$  with composition is not large. At any fixed composition, the variation of the  $d$  with the strength of interaction is similar to that of  $\eta^E$ , being negative in the case of systems in which the dispersion forces are predominant between the components, being less negative and then becoming positive as the strength of interaction increases.

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