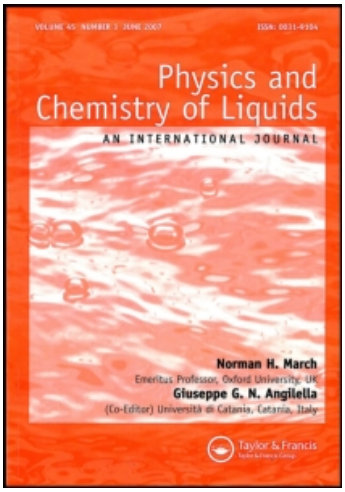

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Excess Volumes of Tetrachloroethylene with Some Aliphatic, Alicyclic and Substituted Aromatic Hydrocarbons

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EXCESS VOLUMES OF TETRACHLOROETHYLENE WITH SOME ALIPHATIC, ALICYCLIC AND SUBSTITUTED AROMATIC HYDROCARBONS

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Excess volumes for binary mixtures of tetrachloroethylene with hexane, heptane, cyclohexane, methylcyclohexane, toluene, bromobenzene, chlorobenzene and nitrobenzene have been determined dilatometrically at 303.15 K. The measured V^E values are negative for the mixtures of tetrachloroethylene with hexane, heptane and nitrobenzene and are positive for the systems containing cyclohexane, methylcyclohexane and toluene. In case of tetrachloroethylene + bromobenzene and + chlorobenzene systems inversion of sign of V^E is observed. The data are interpreted in terms of (1) loss of dipolar association, difference in size and shape of the molecules and (2) specific interactions between unlike molecules.

KEY WORDS: π-electron density, cyclic compound.

INTRODUCTION

The present paper forms a part of our programme on the measurement of thermodynamic properties of non-electrolyte solutions. In this work we report excess volumes of tetrachloroethylene with hexane, heptane, cyclohexane, methylcyclohexane, toluene, bromobenzene, chlorobenzene and nitrobenzene at 303.15 K. We have undertaken this work to investigate the effect of cyclization and aromatization and also the influence of different substituents over aromatic ring on excess volumes.

EXPERIMENTAL

Apparatus

The dilatometer used for measuring excess volumes in the present work is similar to that described by Rao and Naidu.[1] The mixing cell contains two bulbs of different capacities that are connected through a U-tube containing mercury to separate the

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two bulbs. One end of the bulb is closed with a ground glass stopper. Five dilatometers with different capacities were used to cover the entire composition range. The composition of each mixture was determined directly by weighing. The dilatomers were kept in a thermostat controlled to ± 0.01 K. The excess volumes were reproducible to $\pm 0.003\ cm^3\ mol^{-1}$. The dilatometers were standardised with a cyclohexane + benzene system at 298.15 K. The measured excess volumes for the standard system are in good agreement with the earlier values reported in the literature.[2]

Material

Analytical reagent grade tetrachloroethylene was dried over sodium carbonate and fractionally distilled. Cyclohexane (BDH), methylcyclohexane (BDH), were washed several times with a cold mixture of concentrated sulphuric acid and nitric acid until the acid layer gave no more yellow colour. Then these were washed with dilute alkali solution to remove the acid. After repeated washings with water the products were dried over fused calcium chloride for two days and distilled. Finally the products were refluxed with metallic sodium for twelve hours and then fractionally distilled over sodium. Hexane (BDH), heptane (Veb) were purified using the methods described earlier.[3] Toluene was purified by the method described by Rastogi and coworkers.[4] Chlorobenzene, nitrobenzene were purified by the procedure described previously.[5] Bromobenzene was dried with calcium chloride and fractionally distilled under reduced pressure. The purity of the chemicals were checked by densities and boiling points. The densities were measured by using a bicapillary pycnometer which gave an accuracy of 5 parts in 10^5. The boiling points were measured using a Swietoslawski[6] type ebulliometer which gave an accuracy of ± 0.2 K. The measured values are included in Table 1 along with the literature values reported by Timmermans[7] and Riddick *et al.*[8]

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

Compound	*Boiling point, K*		*Density, g cm*$^{-3}$	
	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	0.77394	0.77389*
Methylcyclohexane	373.8	374.0	0.76512	0.76506*
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

* 298.15 K.

Table 2 Excess volumes V^E ($cm^3\ mol^{-1}$) of tetrachloroethylene with some aliphatic, alicyclic and substituted aromatic hydrocarbons at 303.15 K

Mole fraction of tetrachloroethylene X	V^E	*Mole fraction of tetrachloroethylene* X	V^E
Tetrachloroethylene + hexane		Tetrachloroethylene + heptane	
0.1642	−0.218	0.1960	−0.136
0.2468	−0.297	0.3642	−0.214
0.3538	−0.366	0.4421	−0.236
0.4336	−0.391	0.4713	−0.244
0.4782	−0.396	0.5272	−0.249
0.5140	−0.396	0.6106	−0.242
0.6460	−0.354	0.6939	−0.214
0.7236	−0.304	0.7237	−0.204
0.8072	−0.230	0.8091	−0.166
0.9346	−0.091	0.9254	−0.082
Tetrachloroethylene + cyclohexane		Tetrachloroethylene + methylcyclohexane	
0.1695	0.270	0.1166	0.007
0.2698	0.387	0.2246	0.056
0.3794	0.475	0.3047	0.101
0.4197	0.496	0.4335	0.145
0.4966	0.519	0.5554	0.149
0.5532	0.507	0.6523	0.136
0.6182	0.476	0.7700	0.087
0.7242	0.390	0.8108	0.067
0.8383	0.256	0.8864	0.030
0.9204	0.134	0.9342	0.012
Tetrachloroethylene + toluene		Tetrachloroethylene + bromobenzene	
0.1502	0.036	0.1026	−0.007
0.2612	0.066	0.1749	−0.010
0.3745	0.084	0.2799	−0.015
0.4715	0.096	0.3996	−0.015
0.5666	0.098	0.4574	−0.012
0.6428	0.091	0.5408	−0.008
0.6905	0.085	0.6270	−0.004
0.7529	0.072	0.7273	0.001
0.8376	0.051	0.8585	0.004
0.9336	0.020	0.9426	0.002
Tetrachloroethylene + chlorobenzene		Tetrachloroethylene + nitrobenzene	
0.1496	−0.016	0.1516	−0.054
0.2048	−0.019	0.2128	−0.079
0.2727	−0.020	0.2966	−0.111
0.3562	−0.019	0.3642	−0.134
0.4651	−0.013	0.4582	−0.153
0.5412	−0.006	0.5496	−0.159
0.6279	0.002	0.6451	−0.149
0.7180	0.009	0.7624	−0.116
0.8422	0.012	0.8428	−0.082
0.9302	0.008	0.9206	−0.043

RESULTS AND DISCUSSION

The excess volume data at 303.15 K for all the mixtures are listed in Table 2. The results are graphically represented in Figure 1 for mixtures of tetrachloroethylene with hexane, cyclohexane and methylcyclohexane and in Figure 2 for mixtures containing toluene, bromobenzene chlorobenzene and nitrobenzene. The V^E values are fitted to an empirical equation of the form

$$V^E = x(1 - x)[a_0 + a_1(2x - 1) + a_2(2x - 1)^2] \quad (1)$$

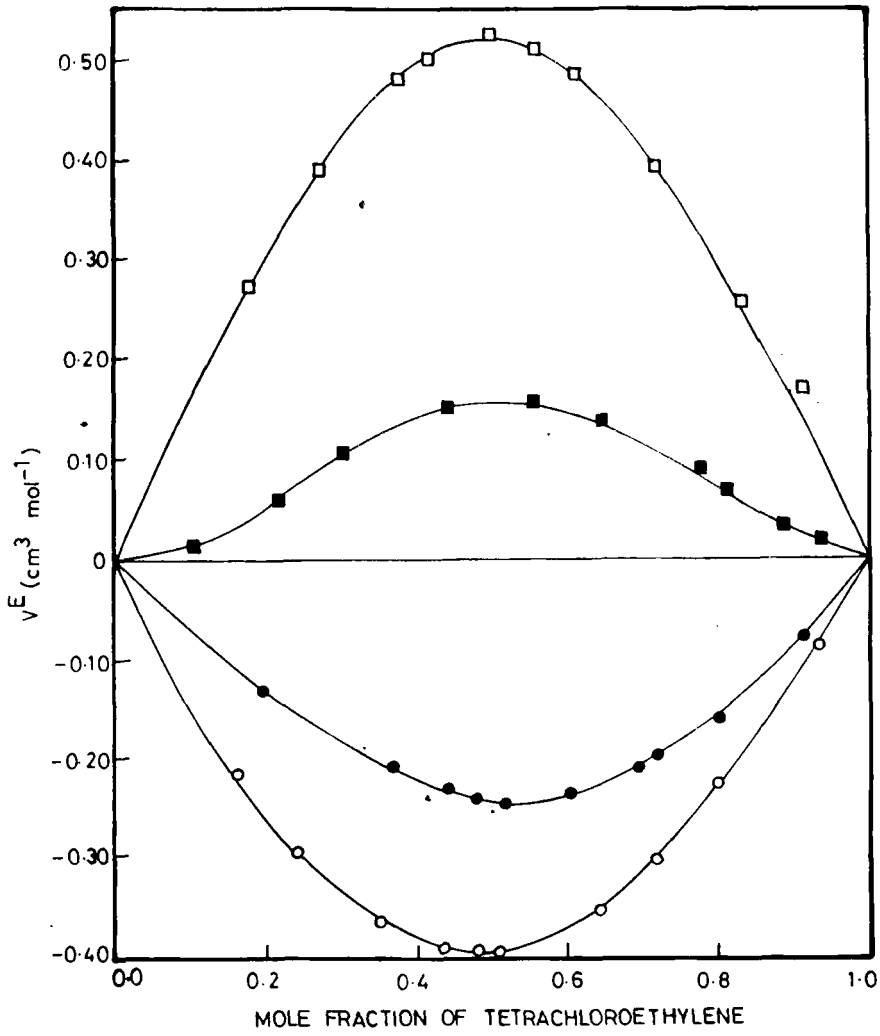

Figure 1 Tetrachloroethylene + hexane (○), + heptane (●), + cyclohexane (□), + methylcyclohexane (■).

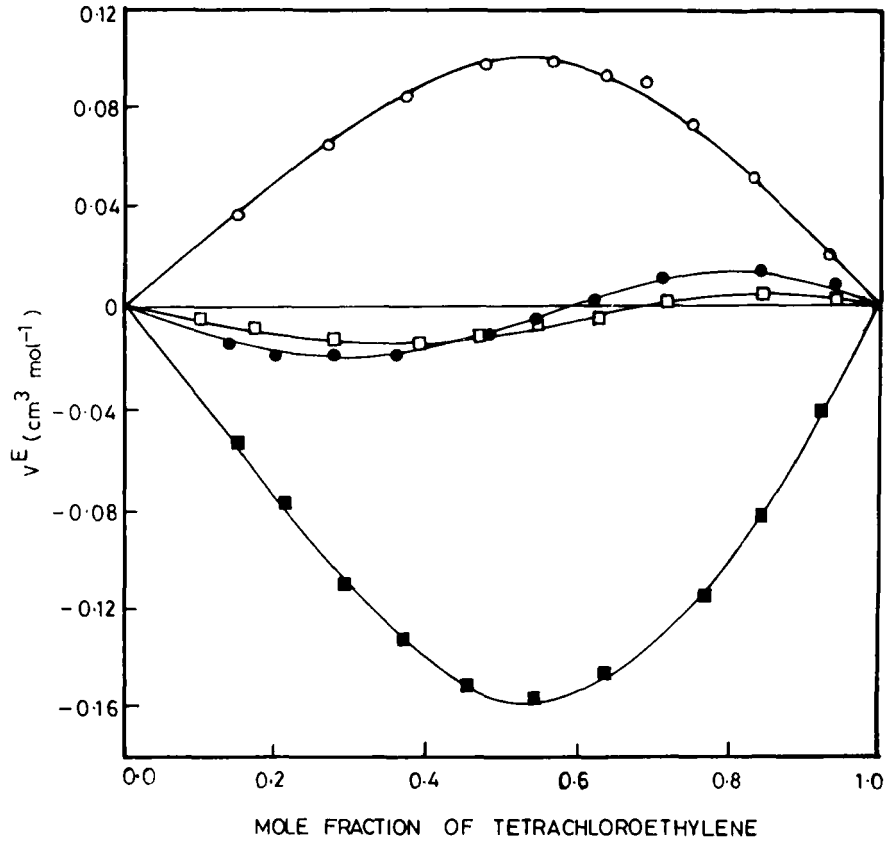

Figure 2 Tetrachloroethylene + toluene (○), + chlorobenzene (●), + bromobenzene (□), + nitrobenzene (■).

where x refers the mole fraction of tetrachloroethylene. The values of the coefficients a_0, a_1 and a_2, obtained by the least square method, are included in Table 3 along with the standard deviation, $\sigma(V^E)$.

The data included in Table 2 show that the V^E values are positive in mixtures of tetrachloroethylene with cyclohexane, methylcyclohexane and toluene and the quantity becomes negative in the systems containing hexane, heptane and nitrobenzene. An inversion in the sign of V^E is observed for the systems made up of bromobenzene and chlorobenzene. V^E is positive for mixtures rich in tetrachloroethylene and is negative at lower concentrations. The negative values of V^E for tetrachloroethylene with hexane is greater than that of heptane. In the case of cycloalkanes, the values for the mixtures of tetrachloroethylene with cyclohexane is larger than that of methylcyclohexane. The data indicate that the inversion of the sign of V^E takes place when the straight chain compound is replaced by cyclic compound with the same number of

Table 3 Values of the parameters a_0, a_1 and a_2 of the Eq. (1) and the standard deviation $\sigma(V^E)$ at 303.15 K.

System	a_0	a_1	a_2	σV^E
	$cm^3\ mol^{-1}$			
Tetrachloroethylene + hexane	−1.568	0.050	0.062	0.005
Tetrachloroethylene + heptane	−0.968	−0.159	−0.056	0.005
Tetrachloroethylene + cyclohexane	2.043	−0.001	−0.319	0.004
Tetrachloroethylene + methylcyclohexane	0.645	0.160	−0.799	0.003
Tetrachloroethylene + toluene	0.392	0.023	−0.124	0.003
Tetrachloroethylene + bromobenzene	−0.041	0.072	0.030	0.002
Tetrachloroethylene + chlorobenzene	−0.037	0.158	0.038	0.001
Tetrachloroethylene + nitrobenzene	−0.630	−0.142	0.220	0.001

carbon atoms. The V^E values in mixtures made up of tetrachloroethylene and substituted benzenes fall in the order

$$\text{toluene} > \text{bromobenzene} \approx \text{chlorobenzene} > \text{nitrobenzene}$$

This order may be attributed to the decrease in π-electron density on benzene ring as the methyl groups is replaced by nitro group. The existence of electron donor-acceptor interaction between tetrachloroethylene and alkyl substituted benzenes has been reported by Handa and Benson.[9]

Acknowledgements

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