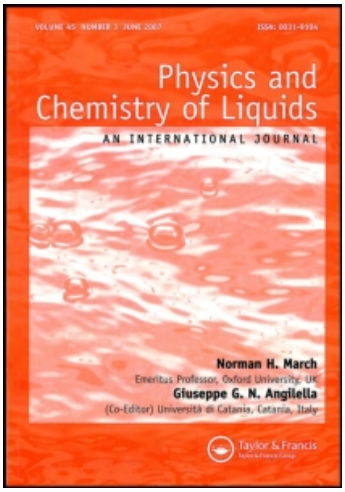

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Thermodynamics of Binary Mixtures Containing Cyclic Ethers 1. Excess Volumes of Tetrahydrofuran Chloroethanes or Chloroethenes

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THERMODYNAMICS OF BINARY MIXTURES CONTAINING CYCLIC ETHERS 1. EXCESS VOLUMES OF TETRAHYDROFURAN + CHLOROETHANES OR + CHLOROETHENES

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Excess volumes of mixing, V^E, for binary mixtures of tetrahydrofuran (THF) with 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, trichloroethene and tetrachloroethene have been measured dilatometrically at 303.15 K over the entire composition range. Values of V^E are negative in all the mixtures except in the system, THF + 1,2-dichloroethane, wherein an inversion in sign of V^E is observed. The experimental results are interpreted in terms of molecular interactions.

KEY WORDS: Excess volumes, tetrahydrofuran, chloro-ethanes and ethenes.

INTRODUCTION

This work is part of a programme on the investigation of binary non-electrolyte mixtures containing cyclic ethers in order to characterize the behaviour of "ether" group with respect to chloroethanes and chloroethenes. We report here experimental excess volume data at 303.15 K for mixtures formed by chloroethanes (1,2-dichloro-, 1,1,1-trichloro- and 1,1,2,2-tetrachloro-) and chloroethenes (trichloro- and tetrachloro-) with THF. The main purpose of this study is to predict the type and magnitude of molecular interactions in these mixtures. The secondary aspect is to study the effect of successive chlorination and unsaturation of ethane molecule on excess volumes of these mixtures.

EXPERIMENTAL SECTION

Tetrahydrofuran (BDH) was kept over sodium hydroxide pellets for twenty-four hours, then refluxed three times for ten hours over sodium metal and then distilled.

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

Component	*Density, g cm^{-3}*		*Boiling point, K*	
	Present work	*Literature*	*Present work*	*Literature*
Tetrahydrofuran	0.87914	0.87910	339.05	339.15
1,2-dichloroethane	1.23828	1.23831	356.70	356.63
1,1,1-trichloroethane	1.32092	1.32096	347.00	347.15
1,1,2,2-tetrachloroethane	1.57857	1.57860	419.25	419.35
Trichloroethene	1.45134	1.45140	360.40	360.34
Tetrachloroethene	1.60636	1.60640	394.45	394.35

Table 2 Excess volumes of tetrahydrofuran with chloroethanes and chloroethenes at 303.15 K

x	V^E / $cm^3\ mol^{-1}$	x_1	V^E / $cm^3\ mol^{-1}$
Tetrahydrofuran + 1,2-dichloroethane			
0.0815	0.038	0.5015	0.040
0.1436	0.060	0.6095	0.020
0.2474	0.072	0.7289	−0.003
0.3055	0.072	0.8142	−0.016
0.4137	0.061	0.9176	−0.015
Tetrahydrofuran + 1,1,1-trichloroethane			
0.0731	−0.126	0.5677	−0.391
0.1231	−0.184	0.6475	−0.368
0.2262	−0.294	0.7415	−0.316
0.3894	−0.376	0.8139	−0.245
0.4716	−0.393	0.8660	−0.194
Tetrahydrofuran + 1,1,2,2-tetrachloroethane			
0.0912	−0.154	0.5426	−0.638
0.1846	−0.304	0.6763	−0.610
0.2753	−0.425	0.7791	−0.493
0.3389	−0.512	0.8994	−0.270
0.4617	−0.609	0.9513	−0.146
Tetrahydrofuran + trichloroethene			
0.0614	−0.091	0.5166	−0.357
0.1057	−0.140	0.6400	−0.315
0.2281	−0.255	0.7608	−0.252
0.3529	−0.331	0.8813	−0.137
0.4929	−0.360	0.9421	−0.073
Tetrahydrofuran + tetrachloroethene			
0.0667	−0.027	0.5309	−0.148
0.1429	−0.055	0.6897	−0.150
0.2457	−0.085	0.7605	−0.138
0.3692	−0.121	0.8435	−0.114
0.4384	−0.137	0.9213	−0.071

The source and method of purification of chloroethanes and chloroethenes are given elsewhere[1]. The purity of the sample was checked by comparing the measured densities and boiling points with those reported in the literature[2]. The data are given in Table 1. Molar excess volumes were measured directly following the procedure described by Krishnaiah *et al.*[3] at 303.15 ± 0.01 K. The values of V^E are accurate to ±0.003 cm^3 mol^{-1}.

RESULTS AND DISCUSSION

The molar excess volumes, V^E, at 303.15 K for mixtures of THF with 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, trichloroethene and tetrachloroethene are reported in Table 2. Dependence of V^E on composition of THF is graphically represented in Figure 1. The data are fitted to an empirical equation of the form,

$$V^E/\text{cm}^3\ \text{mol}^{-1} = x(1-x)\sum_{i=0}^{2} a_i(2x-1)^i \qquad (1)$$

where x is the mole fraction of THF and a_i's are the empirical parameters. Values of the parameters, obtained by the method of least squares, are included in Table 3 along with the standard deviation, $\sigma(V^E)$.

Values of V^E are negative over the entire composition range in all the mixtures except in the system, THF + 1,2-dichloroethane, wherein an inversion in sign is observed from positive to negative at around 0.7 mole fraction of THF. Similar change in sign of V^E has been reported by Suri and Chawla[4] in mixtures of THF with 1,2-dichloroethane at 298.15 K. The equimolar V^E for the system, THF + 1,1,1-trichloroethane, at 303.15 K reported here is slightly less negative than that observed for the same system at 298.15 K by Inglese *et al.*[5]. The experimental negative excess volumes may be mainly attributed to the dominant nature of specific n-σ type interactions between oxygen (n-donor) and chloro (σ-acceptor) over the dispersive forces in all the systems except in THF + 1,2-dichloroethane below 0.7 mole fraction of THF. In this region V^E values may be determined by the loss of dipolar association of THF on the addition of 1,2-dichloroethane and difference in the size and shape of the molecules. The existence of an O(ether) — — — Cl interaction is reported on the basis of molecular polarization[6], spectroscopic[7] and excess enthalpy[8] studies.

The negative values of V^E follow the sequence in mixtures of THF with chloroethanes.

1,1,2,2-tetrachloroethane > 1,1,1-trichloroethane > 1,2-dichloroethane,

and in case of mixtures containing chloroethenes the order is,

trichloroethene > tetrachloroethene

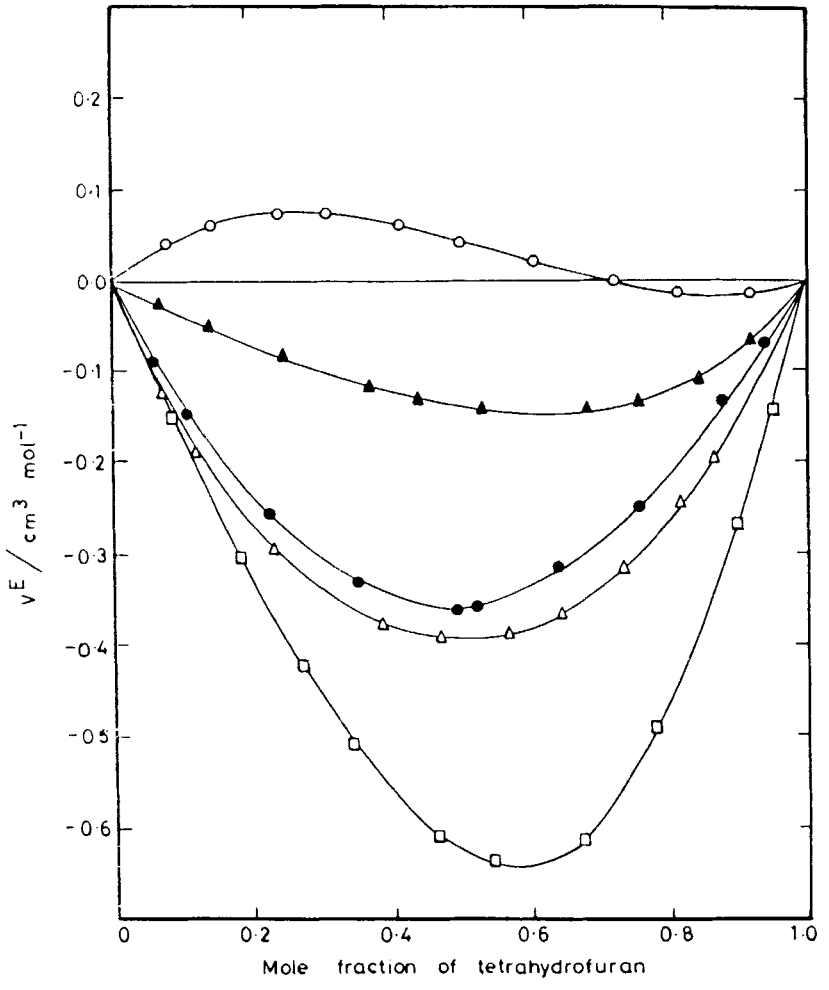

Figure 1 Excess volumes (V^E) for tetrahydrofuran + 1,2-dichloroethane (○), + 1,1,1-trichloroethane (△), + 1,1,2,2-tetrachloroethane (□), + trichloroethene (●), and + tetrachloroethene (▲) at 303.15 K.

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

System	a_0	a_1	a_2	$\sigma(V^E)$
		$cm^3\ mol^{-1}$		
Tetrahydrofuran + 1,2-dichloroethane	0.176	−0.429	−0.021	0.002
Tetrahydrofuran + 1,1,1-trichloroethane	−1.583	0.052	−0.253	0.005
Tetrahydrofuran + 1,1,2,2-tetrachloroethane	−2.512	−0.734	0.088	0.005
Tetrahydrofuran + Trichloroethene	−1.416	0.115	−0.017	0.004
Tetrahydrofuran + Tetrachloroethene	−0.574	−0.306	−0.177	0.003

The order in V^E suggest that V^E decreases linearly with number of chlorine atoms on ethane molecule in mixtures containing chloroethanes. Similar behaviour of decreasing V^E with number of chlorine atoms on alkanes was observed by Bolinga *et al.*[8] and Suri and Chawla[4]. In case of mixtures containing chloroethenes V^E increases with increase of number of chlorine atoms. Further, the experimental data suggest that the interaction between THF and chloroethane is stronger compared to that between THF and chloroethene, with the same number of chlorine atoms.

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References

1. K. N. Surendranath, K. Ramanjaneyulu and A. Krishnaiah, *Indian J. Chem.*, **27A,** 275 (1988).
2. J. A. Riddick and W. B. Bunger, Techniques of Chemistry, Vol. II, Organic Solvents, 3rd edn. (Wiley Interscience, New York), (1970).
3. A. Krishnaiah, M. Sreenivasulu and P. R. Naidu, *Can. J. Chem.*, **57,** 1915 (1979).
4. S. K. Suri and B. Chawla, *J. Chem. Eng. Data*, **26,** 269 (1981).
5. A. Inglese, M. Castagnolo and A. Dellatti, *Thermochim. Acta*, **47,** 165 (1981).
6. B. Castagna, M. Bumas Jean, M. Guerin and M. Gomel, *J. Chim. Phys. Phys.-Chim. Biol.*, **70,** 960 (1973).
7. C. Geron and M. Gomel, *J. Chim. Phys. Phys.-Chim. Biol.*, **75,** 241 (1978).
8. R. Bolinga, M. Gracia and G. Losa, *J. Chem. Thermodyn.* **10,** 667 (1978).