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EXCESS VOLUMES OF HOMOLOGOUS SERIES OF ALIPHATIC ALCOHOLS WITH TETRACHLOROETHYLENE AT 303.15 AND 313.15 K

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ABSTRACT

Excess volume data on the mixing of binary mixtures of alcohols in tetrachloroethylene have been determined at 303.15 and 313.15 K, using a dilatometer. The mixtures include: (1) 1-propanol + tetrachloroethylene; (2) 1-butanol + tetrachloroethylene; (3) 1-pentanol + tetrachloroethylene; (4) 1-hexanol + tetrachloroethylene; (5) 1-heptanol + tetrachloroethylene; (6) 1-octanol + tetrachloroethylene. The V^E values are found to be positive over the whole range of composition in all six mixtures at both temperatures, and are increasingly positive with the higher homologues. V^E becomes more positive on increasing temperature. The positive values of the excess volume have been attributed to the breaking of hydrogen bonds of associated species of alcohols by dilution with tetrachloroethylene.

INTRODUCTION

Since alcohols are strongly associated by hydrogen bonding, it has been beneficial to consider changes in the thermodynamic functions occurring on the dilution of an alcohol with a nonpolar solvent to consist partly of the breaking of hydrogen bonds and partly of the mixing of the alcohol homorph with the solvent. In continuation of earlier work on excess volumes of binary mixtures of alcohols in a common solvent [1], V^E values for mixtures of *n*-alcohols ($C_3 - C_8$) with tetrachloroethylene at 303.15 and 313.15 K are reported here.

Tetrachloroethylene was chosen for its approximately spherical geometry and because its chlorine atoms are symmetrically disposed. However, in tetrachloroethylene the molecular π orbital is almost entirely screened by the chlorine atoms and has scarcely any direct influence on the intermolecular forces, although there is some indirect influence through its effect on the chlorine atoms.

EXPERIMENTAL

Analytical reagent grade tetrachloroethylene was dried over sodium carbonate and fractionally distilled. 1-Propanol, 1-butanol, 1-pentanol and 1-hexanol were purified by the methods described by Rao and Naidu [2]. 1-Heptanol (Koch Light Laboratories) and 1-octanol (BDH) were fractionated.

The purity of the compounds were checked by measuring densities and boiling points. The densities were measured using a bi-capillary pycnometer with an accuracy of 5 parts in 10^5. The boiling points at 760 mm Hg were measured using a Swietoslawski-type ebulliometer which gave an accuracy of $\pm 0.2\,^\circ$C. The measured values are reported in Table 1 along with the literature values [3,4].

Excess volumes were determined directly to an accuracy of ± 0.003 cm^3 mol^{-1} using the dilatometer described earlier [5]. The benzene + cyclohexane system at 298.15 K was used as a standard for dilatometry. The measured excess volumes for the standards are in good agreement with values reported in the literature [6].

RESULTS

The excess volumes of mixing, covering the complete range of mole fraction of tetrachloroethylene at 303.15 and 313.15 K, are presented in Table 2 and graphically represented in Fig. 1. These mixtures have positive values of V^E over the entire range of composition with maxima occurring at 0.6–0.75 and 0.55–0.70 mole fraction of tetrachloroethylene at 303.15 and 313.15 K, respectively. The V^E values for all the binary mixtures with tetrachloroethylene decrease from 1-octanol to 1-propanol. This order is similar to that observed for trichloroethylene with *n*-alcohols reported earlier

TABLE 1

Boiling points and densities of the pure components at 303.15 K

	Boiling point (K)		Density, ρ (g cm^{-3})	
	Present work	Literature [3,4]	Present work	Literature [3]
Tetrachloroethylene	394.28	394.4	1.60634	1.60640
1-Propanol	370.25	370.34	0.79596	0.79600
1-Butanol	390.75	390.87	0.80201	0.80206
1-Pentanol	411.0	411.21	0.80755	0.80764
1-Hexanol	430.88	431.00	0.81195	0.81201
1-Heptanol	499.00	499.15	0.81572	—
1-Octanol	467.45	467.6	0.82188	0.82192

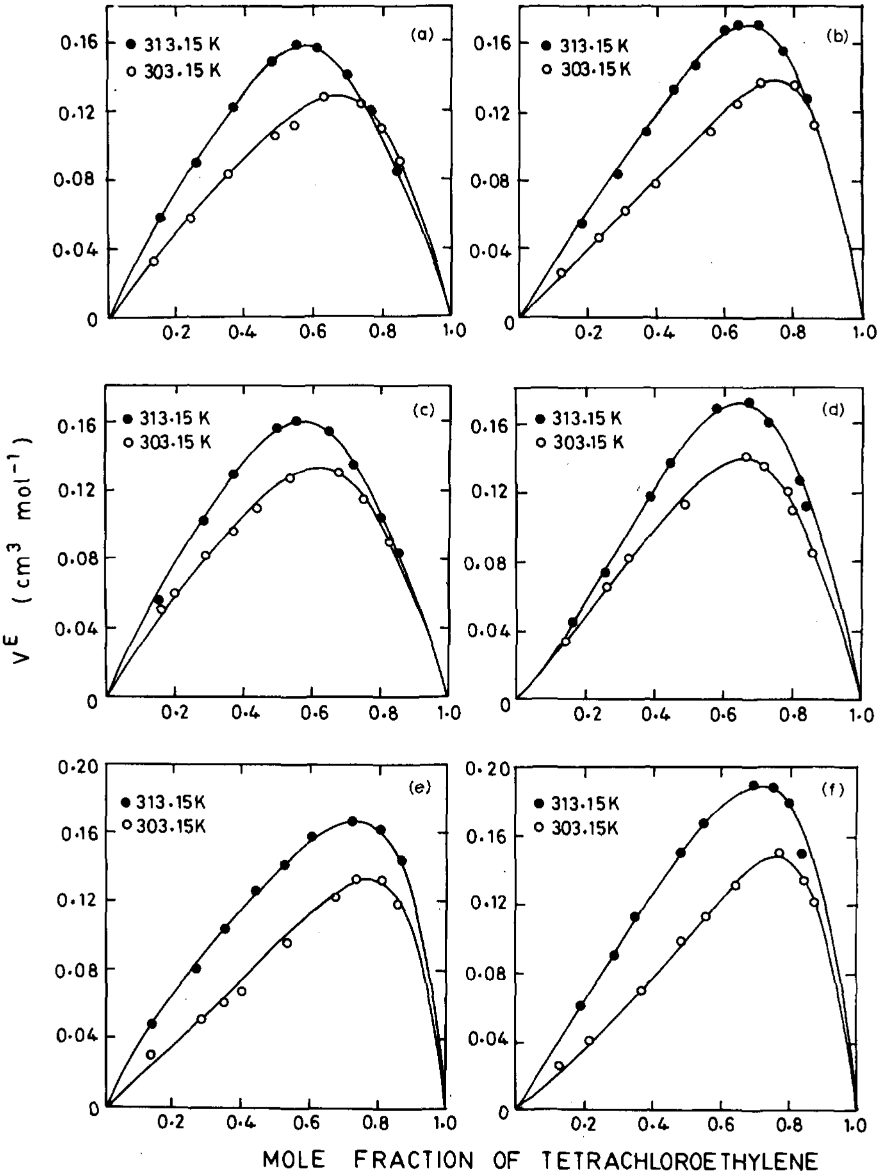

Fig. 1. Excess volume–composition curves for tetrachloroethylene with (a) 1-propanol; (b) 1-butanol; (c) 1-pentanol; (d) 1-hexanol; (e) 1-heptanol; (f) 1-octanol at 303.15 and 313.15 K.

[1]. V^E values become more positive on increasing temperature for all the six systems.

The experimental values of V^E may be represented by an empirical equation of the form

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

TABLE 2

Excess volumes of mixing, V^E (cm^3 mol^{-1}) for the binary mixtures of tetrachloroethylene with *n*-alcohols at 303.15 and 313.15 K

303.15 K		313.15 K	
Mole fraction of tetrachloroethylene, x	V^E (cm^3 mol^{-1})	Mole fraction of tetrachloroethylene, x	V^E (cm^3 mol^{-1})
Tetrachloroethylene(1) + 1-propanol			
0.1443	0.033	0.1593	0.058
0.2515	0.057	0.2626	0.090
0.3666	0.083	0.3714	0.122
0.4906	0.105	0.4809	0.148
0.5433	0.113	0.5515	0.158
0.6275	0.127	0.6113	0.155
0.7420	0.123	0.7005	0.139
0.7966	0.110	0.7729	0.120
0.8509	0.090	0.8444	0.085
Tetrachloroethylene(1) + 1-butanol(2)			
0.1653	0.051	0.1505	0.057
0.2004	0.059	0.2771	0.103
0.2952	0.082	0.3664	0.130
0.3716	0.096	0.4916	0.157
0.4420	0.110	0.5513	0.160
0.5421	0.128	0.6502	0.154
0.6805	0.130	0.7243	0.135
0.7521	0.115	0.8014	0.105
0.8331	0.090	0.8515	0.084
Tetrachloroethylene(1) + 1-pentanol(2)			
0.1392	0.030	0.1404	0.047
0.2765	0.051	0.2666	0.079
0.3555	0.060	0.3507	0.103
0.4029	0.067	0.4454	0.126
0.5324	0.095	0.5233	0.141
0.6729	0.122	0.6002	0.157
0.7273	0.132	0.7180	0.165
0.8016	0.132	0.7954	0.161
0.9553	0.118	0.8551	0.143
Tetrachloroethylene(1) + 1-hexanol(2)			
0.1223	0.026	0.1775	0.055
0.2304	0.046	0.2853	0.083
0.3107	0.062	0.3704	0.108
0.3988	0.078	0.4526	0.132
0.5565	0.108	0.5121	0.146
0.6410	0.125	0.6029	0.168
0.7103	0.136	0.6415	0.170
0.8056	0.134	0.7028	0.169
0.8613	0.112	0.7725	0.155
		0.8354	0.128

TABLE 2 (continued)

303.15 K		313.15 K	
Mole fraction of tetrachloroethylene, x	V^E (cm^3 mol^{-1})	Mole fraction of tetrachloroethylene, x	V^E (cm^3 mol^{-1})
Tetrachloroethylene(1) + 1-heptanol(2)			
0.1407	0.035	0.1578	0.045
0.2729	0.067	0.2604	0.074
0.3331	0.083	0.3926	0.118
0.4856	0.113	0.4452	0.137
0.6668	0.140	0.5759	0.168
0.7219	0.135	0.6720	0.172
0.7766	0.120	0.7304	0.160
0.8013	0.110	0.8152	0.127
0.8616	0.085	0.8425	0.112
Tetrachloroethylene(1) + 1-octanol(2)			
0.1354	0.027	0.1937	0.062
0.2162	0.042	0.2804	0.091
0.3673	0.070	0.3526	0.113
0.4901	0.100	0.4752	0.151
0.5614	0.113	0.5453	0.167
0.6377	0.132	0.6851	0.192
0.7664	0.149	0.7502	0.189
0.8402	0.135	0.7954	0.179
0.8729	0.122	0.8421	0.150

TABLE 3

Parameters of eqn. (1) and standard deviation $\sigma(V^E)$ of experimental values for the binary mixtures of tetrachloroethylene with *n*-alcohols at 303.15 and 313.15 K

System (1)+(2)	Temperature (K)	Parameters of eqn. (1) (cm^3 mol^{-1})			
		a_0	a_1	a_2	$\sigma(V^E)$
Tetrachloroethylene + 1-propanol	303.15	0.4369	0.3284	0.1179	0.002
	313.15	0.6046	0.1896	−0.1408	0.004
Tetrachloroethylene + 1-butanol	303.15	0.4830	0.2294	0.0608	0.003
	313.15	0.6281	0.1648	−0.1600	0.002
Tetrachloroethylene + 1-pentanol	303.15	0.3201	0.4734	0.6351	0.005
	313.15	0.5433	0.5088	0.4368	0.004
Tetrachloroethylene + 1-hexanol	303.15	0.3954	0.4764	0.3881	0.003
	313.15	0.5864	0.4511	0.1474	0.003
Tetrachloroethylene + 1-heptanol	303.15	0.4900	0.3264	0.0300	0.005
	313.15	0.6098	0.4153	−0.0253	0.005
Tetrachloroethylene + 1-octanol	303.15	0.3978	0.5619	0.4861	0.003
	313.15	0.6365	0.5667	0.2872	0.003

where x refers to mole fraction of tetrachloroethylene and a_0, a_1 and a_2 are adjustable constants which have been evaluated by the principle of least-squares.

The values of the three parameters obtained by a least-squares analysis are given in Table 3 along with the standard deviation, $\sigma(V^E)$ which is evaluated from the equation

$$\sigma = \left[\frac{\Sigma(\Delta V^E)^2}{(n-p)} \right]^{1/2}$$

where n is the number of results.

DISCUSSION

Alcohols are strongly associated through hydrogen bonding. When alcohols are diluted with solvents like tetrachloroethylene, changes in the thermodynamic functions can be due to: (i) the break-up of hydrogen bonds with diluent; and (ii) the formation of new species acting as an adduct between the alcohols and the tetrachloroethylene.

The dissociation of alcohols leads to an increase in the excess volume while the formation of an adduct leads to a decrease in the excess volume. The observed positive excess volume on mixing indicates that the dissociation of the associated species of the alcohol, on dilution with tetrachloroethylene, is the dominating force.

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