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Excess Volumes of 1,1,2,2-Tetrachloroethane + Normal Alkanols (C_3–C_8)

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Excess volumes for the binary mixtures of 1,1,2,2-tetrachloroethane with 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol have been determined at 303.15 K. The excess function is negative in mixtures rich in alcohols and it becomes positive at different mole fractions of the chloroalkane. The results have been explained in terms of depolymerization of hydrogen-bonded alcohol aggregates, interstitial accommodation of halogenated hydrocarbon in the polymers of alcohols, and weak hydrogen-bond interactions between unlike molecules.

Introduction

We report here new excess volume data for six binary mixtures of 1,1,2,2-tetrachloroethane with 1-alkanols. The alcohols include 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol. The results are examined in the light of depolymerization of alcohols, interstitial accommodation of chloroalkane in hydrogen-bonded alcohol aggregates, possible hydrogen-bond interactions of the type Cl···H–O, between unlike molecules, and the influence of chain length of the alcohol on the aforesaid factors.

Experimental Section

Excess volumes were measured by using the dilatometer described by Rao and Naidu (*1*). The mixing cell contained two bulbs of different capacities which were connected through a U-tube having mercury to separate the two components. One end of the bulb was fitted with a capillary (1-mm i.d.) and the other end of the second bulb was fixed with a ground-glass stopper. The V^E values were accurate to ± 0.003 cm^3 mol^{-1}.

Purification of Materials. All the materials were purified by the methods described by Reddick and Bunger (*2*). 1,1,2,2-Tetrachloroethane (Riedel) was shaken with concentrated sulfuric acid for 10 min at 80–90 °C. The operation was repeated until the acid developed no more color. The chloroalkane was then washed with water, steam distilled, dried with potassium carbonate, and fractionally distilled. 1-Propanol (J. T. Baker) and 1-butanol (BDH) were refluxed over freshly ignited calcium oxide for 6 h and distilled with a fractionating column. 1-Pentanol (J. T. Baker) was dried over Drierite and fractionally distilled. 1-Hexanol (BDH England), 1-heptanol (Koch-Light Laboratories Ltd., England), and 1-octanol (BDH England) were fractionally distilled. A fractionating column that contained 30 theoretical plates was used in all cases. The purity of the samples was checked by comparing the measured densities of the compounds with those reported in the literature (*3*). Densities were determined by using a bicapillary-type pycnometer which offered an accuracy of 2 parts in 10^5.

Results

The experimental excess volumes of the six binary mixtures are given in Table I and are also graphically represented in Figure 1. The dependence of V^E on composition may be expressed by an empirical equation of the form

$$V^E/(\text{cm}^3\ \text{mol}^{-1}) = x(1-x)\{a_0 + a_1(2x-1) + a_2(2x-1)^2\} \quad (1)$$

where a_0, a_1, and a_2 are adjustable parameters and x is the mole fraction of 1,1,2,2-tetrachloroethane. The values of the parameters obtained by the least-squares method are included in Table II along with the standard deviation $\sigma(V^E)$. The values of $\sigma(V^E)$ were obtained by using the equation

$$\sigma(V^E) = \left[\frac{\sum(V^E_{\text{calcd}} - V^E_{\text{exptl}})^2}{(n-P)}\right]^{1/2}$$

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Table I. Experimental V^E Values for the Mixtures of 1,1,2,2-Tetrachloroethane with Six Alcohols at 303.15 K[a]

x	$V^E/(\mathrm{cm^3\ mol^{-1}})$	x	$V^E/(\mathrm{cm^3\ mol^{-1}})$	x	$V^E/(\mathrm{cm^3\ mol^{-1}})$	x	$V^E/(\mathrm{cm^3\ mol^{-1}})$	x	$V^E/(\mathrm{cm^3\ mol^{-1}})$
				1,1,2,2-Tetrachloroethane + 1-Propanol					
0.0999	−0.158	0.2394	−0.219	0.4212	−0.153	0.6107	−0.040	0.8188	0.042
0.1723	−0.205	0.3141	−0.206	0.5188	−0.098	0.7185	0.012	0.8924	0.040
				1,1,2,2-Tetrachloroethane + 1-Butanol					
0.1160	−0.156	0.2810	−0.189	0.4811	−0.104	0.6573	−0.005	0.8464	0.051
0.1347	−0.167	0.3612	−0.170	0.5692	−0.052	0.7508	0.035	0.9068	0.046
				1,1,2,2-Tetrachloroethane + 1-Pentanol					
0.1284	−0.136	0.3223	−0.132	0.5007	−0.039	0.6937	0.055	0.8556	0.071
0.1861	−0.155	0.3948	−0.100	0.6090	0.019	0.7824	0.075	0.9142	0.058
				1,1,2,2-Tetrachloroethane + 1-Hexanol					
0.1246	−0.083	0.2832	−0.071	0.5346	0.059	0.7257	0.121	0.8897	0.100
0.2168	−0.087	0.4433	0.006	0.6393	0.101	0.8468	0.115	0.3316	−0.051
				1,1,2,2-Tetrachloroethane + 1-Heptanol					
0.1412	−0.033	0.2748	0.013	0.4665	0.130	0.6678	0.213	0.8603	0.166
0.2069	−0.020	0.3535	0.059	0.5623	0.181	0.7458	0.215	0.9277	0.107
				1,1,2,2-Tetrachloroethane + 1-Octanol					
0.1009	−0.011	0.2348	0.044	0.4805	0.205	0.6972	0.276	0.8761	0.189
0.1893	0.022	0.3849	0.143	0.6003	0.260	0.7760	0.260	0.9188	0.140

[a] x = mole fraction of 1,1,2,2-tetrachloroethane.

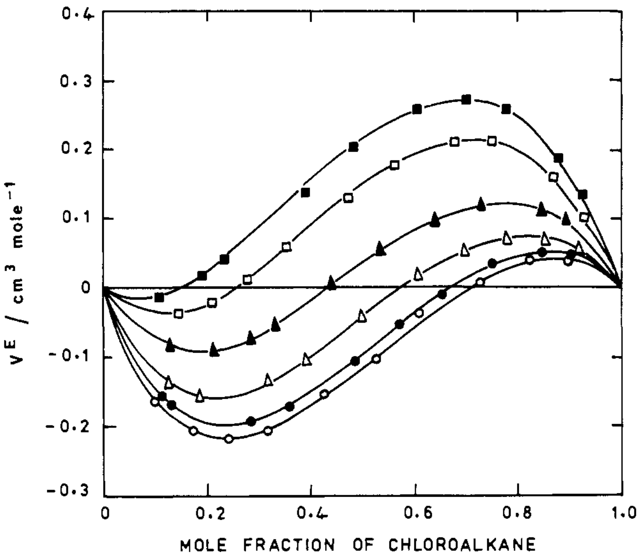

Figure 1. Excess volumes V^E plotted against mole fraction of 1,1,2,2-tetrachloroethane at 303.15 K for the mixtures of 1,1,2,2-tetrachloroethane with alcohols: (○) 1-propanol, (●) 1-butanol, (△) 1-pentanol, (▲) 1-hexanol, (□) 1-heptanol, (■) 1-octanol.

where n is the number of experimental data and P is the number of parameters.

Discussion

The results included in Figure 1 show that V^E is negative in mixtures rich in alcohols. The negative values of V^E decrease with an increase in the chain length of the alcohol. Further, the excess quantity tends to become positive as the concentration of chloroalkane increases. The results may be explained in terms of two opposing contributions: (1) expansion in volume due to depolymerization of alcohol aggregates, (2) contraction in volume due to interstitial accommodation of chloroalkane in the aggregates of alcohols and weak hydrogen-bond interactions of the type Cl···H–O between unlike molecules. The experimental results suggest that the two opposing contributions balance each other to varying degrees over the composition range studied. Furthermore, the depolymerization effect becomes dominant with an increase in the chain length of the alcohols.

Table II. Standard Deviation $\sigma(V^E)$ and Values of the Constants in Eq 1 at 303.15 K

system	a_0	a_1	a_2	$\sigma(V^E)$/ (cm^3 mol^{-1})
1,1,2,2-tetrachloroethane + 1-propanol	−0.4280	1.3329	−0.3562	0.004
1,1,2,2-tetrachloroethane + 1-butanol	−0.3783	1.2784	−0.2195	0.005
1,1,2,2-tetrachloroethane + 1-pentanol	−0.1661	1.2266	−0.2169	0.004
1,1,2,2-tetrachloroethane + 1-hexanol	0.1450	1.1317	−0.0663	0.004
1,1,2,2-tetrachloroethane + 1-heptanol	0.5844	1.1648	−0.0299	0.003
1,1,2,2-tetrachloroethane + 1-octanol	0.8727	1.1871	−0.0464	0.004

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