Acknowledgment

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Glossary

F	fluid phase
Δh^f	heat of fusion
L	liquid phase
P	pressure, bar
R	gas constant
S	solid phase
T	temperature, K
x	condensed-phase mole fraction
y	fluid-phase mole fraction

Subscripts

M	melting point
m	methyl *m*-nitrobenzoate
o	methyl *o*-nitrobenzoate
p	methyl *p*-nitrobenzoate
5	5-methoxy-1-tetralone
6	6-methoxy-1-tetralone
7	7-methoxy-1-tetralone

Registry No. Carbon dioxide, 124-38-9; naphthalene, 91-20-3; 5-methoxy-1-tetralone, 33892-75-0; 6-methoxy-1-tetralone, 1078-19-9; 7-methoxy-1-tetralone, 6836-19-7; methyl *o*-nitrobenzoate, 606-27-9; methyl *m*-nitrobenzoate, 618-95-1; methyl *p*-nitrobenzoate, 619-50-1.

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Excess Volumes of Binary Mixtures of 1,1,2,2-Tetrachloroethane with *n*-Alkanes (C_6–C_9)

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Excess volumes for binary mixtures of 1,1,2,2-tetrachloroethane with *n*-hexane, *n*-heptane, *n*-octane, and *n*-nonane have been determined at 303.15 and 313.15 K. V^E is negative over the whole range of composition in the mixtures of 1,1,2,2-tetrachloroethane with *n*-hexane and the function is positive over the whole range of composition in the remaining mixtures. The results have been ascribed to interstitial accommodation of *n*-hexane between the aggregates of self-associated chloroalkane and the structure-breaking effects of *n*-heptane, *n*-octane, and *n*-nonane. The results also have been used to show that increase in chain length of the alkane leads to an increase in the algebraic values of the excess function.

Introduction

The present work forms a part of the program to measure excess volumes and isentropic compressibilities for several binary mixtures (*1-9*) containing chloroalkanes as a common component. The work was taken up to gain insight into the nature and degree of interaction between like and unlike molecules. The binary mixtures studied in the present work include 1,1,2,2-tetrachloroethane + *n*-hexane, + *n*-heptane, + *n*-octane, and + *n*-nonane at 303.15 and 313.15 K.

Experimental Section

Excess volumes were measured by using a single composition per loading type dilatometer described by Rao and Naidu (*10*). The mixing cell contained two bulbs of different capacities that were connected through a U-tube having mercury to separate the two compartments. One end of the first bulb was fitted with a capillary outlet and the opposite end of the second bulb was closed with a ground-glass stopper. Four dilatometers of this type were used to cover the whole range of composition. The composition of each mixture was determined directly by weighing. All weights were corrected for buoyancy. Measurements were made by using a thermostatic bath controlled to within ±0.01 K. The excess volumes were reproducible to ±0.003 $cm^3\ mol^{-1}$.

Table I. Densities, ρ, of Pure Liquids at 303.15 K

component	$\rho/(g\ cm^{-3})$ present work	$\rho/(g\ cm^{-3})$ lit.
1,1,2,2-tetrachloroethane	1.578 51	1.578 60
n-hexane	0.650 64	0.650 70
n-heptane	0.675 30	0.675 38
n-octane	0.694 59	0.694 50
n-nonane	0.709 98	0.709 99

Purification of Materials. 1,1,2,2-Tetrachloroethane (Riedel) was purified by the method described earlier (*7*). *n*-Hexane and *n*-heptane supplied by BDH (England) and *n*-octane and *n*-nonane supplied by Veb (West Germany) were purified by the methods described by Reddick and Bunger (*11*). *n*-Hexane was shaken several times with concentrated sulfuric acid, then with a 0.1 N solution of potassium permanganate in 10% sulfuric acid, and finally with a 0.1 N solution of permanganate in 10% sodium hydroxide. The sample was washed with water, dried over sodium wire, and fractionally distilled. *n*-Heptane was shaken twice with concentrated sulfuric acid and washed with

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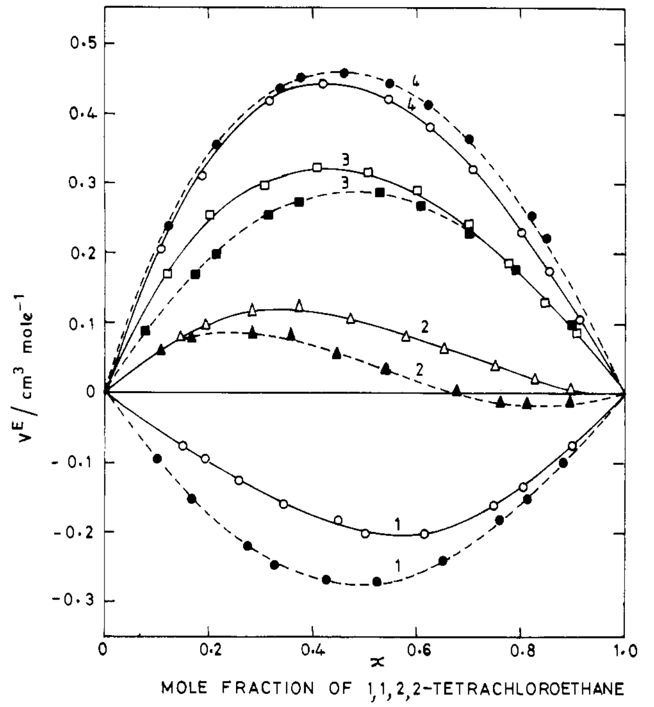

Figure 1. Excess volumes V^E plotted against mole fraction of 1,1,2,2-tetrachloroethane at 303.15 (—) and 313.15 (- - -) K for the mixtures of 1,1,2,2-tetrachloroethane with *n*-alkanes: (1) *n*-hexane, (2) *n*-heptane, (3) *n*-octane, (4) *n*-nonane.

water, with dilute potassium hydroxide solution, and again with water. The sample was kept over potassium hydroxide and finally fractionated. *n*-Octane was passed through silica gel and then fractionated. *n*-Nonane was fractionally distilled. The purity of the samples was checked by comparing the measured densities of the compounds with those reported in the literature (*12*). Densities were determined by using a bicapillary type pycnometer which offered an accuracy of 2 parts in 10^5. The measured density data are reported in Table I along with those reported in the literature.

Results and Discussion

The experimental excess volumes of the four binary mixtures are graphically represented in Figure 1 and are also given in Table II. 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 III along with the standard deviation $\sigma(V^E)$. The values of $\sigma(V^E)$ were obtained by using the equation

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

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

Table II. Excess Volumes of 1,1,2,2-Tetrachloroethane + *n*-Alkanes at 303.15 and 313.15 K

303.15 K		313.15 K	
x	V^E/(cm^3 mol^{-1})	x	V^E/(cm^3 mol^{-1})
	1,1,2,2-Tetrachloroethane + *n*-Hexane		
0.1515	−0.075	0.1006	−0.096
0.1928	−0.094	0.1675	−0.150
0.2567	−0.127	0.2723	−0.218
0.3451	−0.155	0.3270	−0.247
0.4350	−0.179	0.4283	−0.268
0.5003	−0.201	0.5202	−0.272
0.6141	−0.199	0.6493	−0.241
0.7446	−0.162	0.7534	−0.182
0.8090	−0.135	0.8141	−0.149
0.9021	−0.077	0.8813	−0.101
	1,1,2,2-Tetrachloroethane + *n*-Heptane		
0.1352	0.081	0.1068	0.056
0.1935	0.102	0.1661	0.078
0.2849	0.121	0.2880	0.086
0.3773	0.123	0.3613	0.078
0.4738	0.107	0.4477	0.061
0.5807	0.082	0.5405	0.036
0.6799	0.066	0.6757	0.003
0.7442	0.043	0.7637	−0.011
0.8310	0.022	0.8152	−0.012
0.8951	0.002	0.8917	−0.010
	1,1,2,2-Tetrachloroethane + *n*-Octane		
0.1208	0.181	0.0833	0.092
0.2011	0.259	0.1748	0.171
0.3081	0.301	0.2123	0.198
0.4071	0.326	0.3142	0.255
0.5082	0.317	0.3730	0.276
0.6009	0.290	0.5262	0.288
0.7005	0.241	0.6081	0.271
0.7816	0.188	0.7003	0.232
0.8478	0.142	0.7916	0.178
0.9096	0.090	0.8945	0.100
	1,1,2,2-Tetrachloroethane + *n*-Nonane		
0.1108	0.208	0.1210	0.244
0.1853	0.312	0.2137	0.357
0.3160	0.417	0.3352	0.436
0.4111	0.445	0.3755	0.450
0.5396	0.422	0.4603	0.457
0.6243	0.379	0.5481	0.442
0.7035	0.320	0.6997	0.365
0.8000	0.231	0.8200	0.258
0.8502	0.177	0.8479	0.224
0.9153	0.109	0.6206	0.416

Table III. Values of Parameters for Eq 1 Calculated by the Method of Least Squares along with the Standard Deviation $\sigma(V^E)$

T/K	a_0[a]	a_1[a]	a_2[a]	$\sigma(V^E)$[a]
		1,1,2,2-Tetrachloroethane + *n*-Hexane		
303.15	−0.783	−0.212	0.117	0.004
313.15	−1.091	0.082	0.141	0.003
		1,1,2,2-Tetrachloroethane + *n*-Heptane		
303.15	0.429	−0.409	−0.074	0.005
313.15	0.192	−0.475	0.073	0.003
		1,1,2,2-Tetrachloroethane + *n*-Octane		
303.15	1.266	−0.401	0.233	0.004
313.15	1.155	−0.090	−0.047	0.003
		1,1,2,2-Tetrachloroethane + *n*-Nonane		
303.15	1.735	−0.480	0.040	0.003
313.15	1.813	0.347	0.366	0.006

[a] Units: cm^3 mol^{-1}.

The curves in Figure 1 show that V^E is positive over the whole range of composition in all the mixtures except in that which contains *n*-hexane. In the mixture of *n*-hexane with chloroalkane V^E is negative over the whole mole fraction range. These results point out that the addition of *n*-heptane, *n*-octane, and *n*-nonane to 1,1,2,2-tetrachloroethane results in the loss of self-association (*13*) of chloroalkane. Further, the negative V^E results suggest that the molecules of *n*-hexane get interstitially accommodated between the aggregates of self-associated chloroalkane, as the size of hexane molecules is small, resulting in no loss of self-association of chloroalkane. An intercomparison between the algebraic values of the four mixtures shows that V^E becomes more positive with increase in chain length. This may be ascribed to the increase in the loss of self-association of chloroalkanes and the decrease in the interstitial accommodation of alkanes with increase in the size of molecules. Finally, the results point out that there is no regular trend between excess volume and temperature in the four mixtures.

Registry No. 1,1,2,2-Tetrachloroethane, 79-34-5; *n*-hexane, 110-54-3; *n*-heptane, 142-82-5; *n*-octane, 111-65-9; *n*-nonane, 111-84-2.

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Vapor–Liquid Equilibria for the Ternary System 2-Propanol–Chloroform–Benzene at 50 °C

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Isothermal *P*–*x*–*y* data for the binary system 2-propanol–chloroform and the ternary system 2-propanol–chloroform–benzene at 50 °C are reported. Experimental data are reduced with the UNIQUAC associated solution theory with good accuracy.

Vapor–liquid equilibrium (VLE) measurements were made for the 2-propanol–chloroform and 2-propanol–chloroform–benzene systems at 50 °C. VLE data for the two constituent binaries at 50 °C have been reported: 2-propanol–benzene (*1*); chloroform–benzene (*2*). The apparatus for experimental work is a Boublik vapor-recirculating still described by Ohta et al. (*3*).

All first-grade chemicals supplied were purified for VLE measurements. 2-Propanol was distilled in a 1-m glass column packed with McMahon packing after being dried over anhydrous copper sulfate. Chloroform was washed with concentrated sulfuric acid, dilute sodium hydroxide, and distilled water. It was dried over calcined sodium carbonate and fractionally distilled in an atmosphere of nitrogen. Benzene was recrystallized 3 times. Vapor and liquid sample compositions were analyzed by a Shimadzu (GC-7A) gas chromatograph combined with a Shimadzu (ITG-2A) digital integrator. Measured variables have the following errors: composition, 0.002 mole fraction; pressure, 13.3 Pa; temperature, 0.05 K.

Results and Data Analysis

Table I shows pure-component vapor pressures obtained in this work, pure liquid molar volumes calculated from the modified Rackett equation (*4*), second virial coefficients estimated from the generalized method of Hayden and O'Connell (*5*), and pure-component structure constants calculated by the method of Vera et al. (*6*). These values were used in calculating the liquid-phase activity coefficients from experimental VLE data and data analysis. Tables II and III give experimental VLE data for binary and ternary mixtures.

Table I. Properties Used in Data Analysis

	2-propanol (1)–chloroform (2)	2-propanol (1)–benzene (3)	chloroform (2)–benzene (3)
P_i^s, kPa	23.931	23.931	69.181
P_j^s, kPa	69.181	36.210	36.210
v_i^L, cm^3/mol	81	81	83
v_j^L, cm^3/mol	83	92	92
B_{ii}, cm^3/mol	-1619	-1619	-958
B_{jj}, cm^3/mol	-958	-1205	-1205
B_{ij}, cm^3/mol	-815	-808	-1126
r_i	2.23	2.23	2.30
r_j	2.30	2.56	2.56
q_i	1.98	1.98	2.04
q_j	2.04	2.05	2.05

Table II. Vapor-Liquid Equilibrium Data for the System 2-Propanol (1)-Chloroform (2) at 50 °C

x_1	y_1	P, kPa	γ_1	γ_2	ϕ_1	ϕ_2
0.047	0.043	69.088	2.625	1.003	0.981	0.976
0.061	0.053	68.874	2.484	1.004	0.981	0.976
0.164	0.105	67.861	1.800	1.051	0.979	0.976
0.230	0.135	66.288	1.611	1.078	0.978	0.977
0.377	0.188	62.395	1.288	1.180	0.977	0.979
0.411	0.199	61.248	1.227	1.209	0.977	0.979
0.511	0.243	57.889	1.139	1.303	0.977	0.981
0.620	0.306	52.756	1.078	1.404	0.977	0.983
0.713	0.383	47.263	1.052	1.485	0.978	0.986
0.824	0.508	39.757	1.017	1.631	0.980	0.990
0.901	0.658	33.077	1.005	1.684	0.982	0.993

The liquid-phase activity coefficients were derived from eq 1

$$\gamma_i = \phi_i y_i P / \{\phi_i^s x_i P_i^s \exp[v_i^L(P - P_i^s)/RT]\} \qquad (1)$$

where the fugacity coefficients, ϕ_i and ϕ_i^s, were calculated from the volume-explicit virial equation truncated after the second term.