Excess Volumes of 2-Alkoxyethanols with Trichloroethylene and Tetrachloroethylene

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Excess volumes of binary liquid mixtures of trichloroethylene and tetrachloroethylene with 2-methoxyethanol, 2-ethoxyethanol, and 2-butoxyethanol have been measured at 303.15 and 313.15 K with a dilatometer. Excess volumes are positive over the entire range of composition for the systems trichloroethylene + 2-methoxyethanol and tetrachloroethylene + 2-methoxyethanol, + 2-ethoxyethanol, and + 2-butoxyethanol and change sign from negative to positive for the remaining two systems, trichloroethylene + 2-ethoxyethanol and + 2-butoxyethanol.

Introduction

As a continuation of our earlier work (*1*), we report in this paper molar excess volumes V^E for trichloroethylene and tetrachloroethylene with 2-methoxyethanol, 2-ethoxyethanol, and 2-butoxyethanol at 303.15 and 313.15 K. No literature results are available for these mixtures.

Experimental Section

Apparatus and Procedure. Excess volumes were measured by a single composition per loading type of dilatometer described by Rao and Naidu (*2*). The dilatometer was made of two bulbs of different capacities connected through a U-tube. Mercury in the U-tube separated the liquids in the two bulbs. 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 the aforementioned type were used to cover the entire range of composition. The composition of each mixture was determined from the measured mass of each component with an accuracy of x = 0.0002. All masses were corrected for

Table I. Densities ρ of Pure Components at 298.15 K

	ρ/(gm cm^{-3})	
component	present work	literature (*3*)
trichloroethylene	1.451 34[a]	1.451 40[a]
tetrachloroethylene	1.606 36[a]	1.606 40[a]
2-methoxyethanol	0.960 18	0.960 24
2-ethoxyethanol	0.925 15	0.925 20
2-butoxyethanol	0.896 21	0.896 25

[a] Density at 303.15 K.

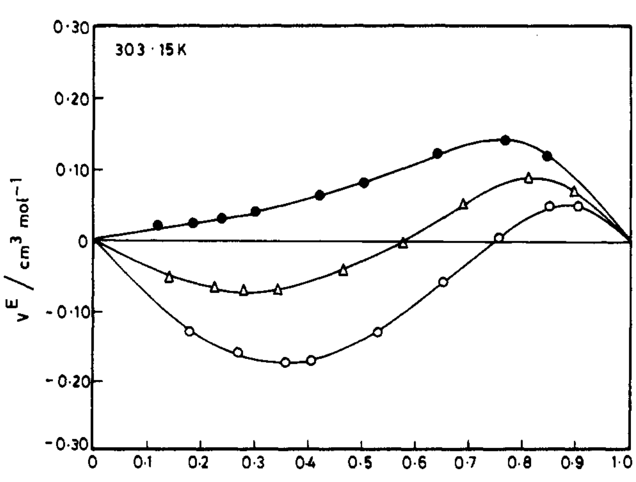

Figure 1. Excess volumes (V^E) for trichloroethylene (1) + 2-methoxyethanol (2) (●), + 2-ethoxyethanol (2) (△), and + 2-butoxyethanol (2) (○) at 303.15 K.

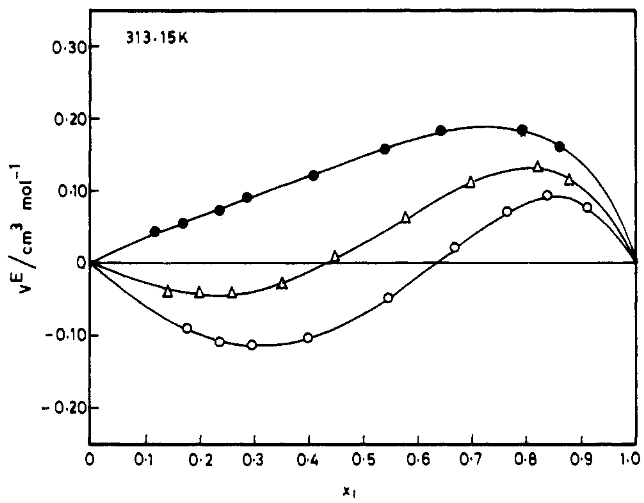

Figure 2. Excess volumes (V^E) for trichloroethylene (1) + 2-methoxyethanol (2) (●), + 2-ethoxyethanol (2) (△), and + 2-butoxyethanol (2) (○) at 313.15 K.

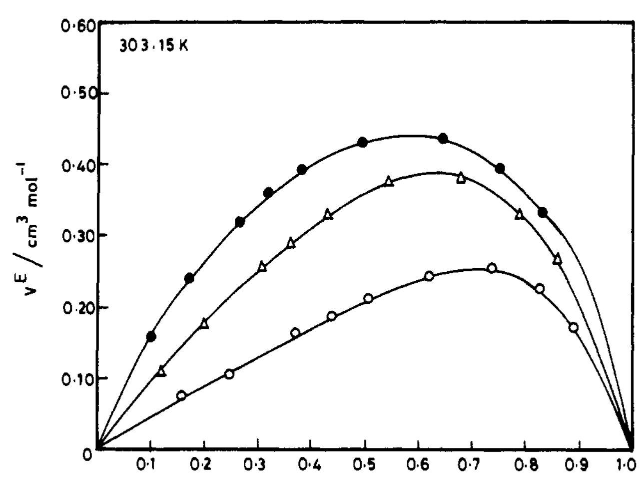

Figure 3. Excess volumes (V^E) for tetrachloroethylene (1) + 2-methoxyethanol (2) (●), + 2-ethoxyethanol (2) (△), and + 2-butoxyethanol (2) (○) at 303.15 K.

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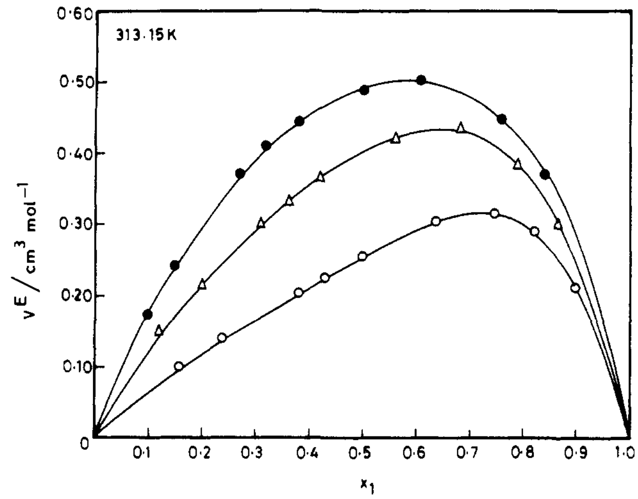

Figure 4. Excess volumes (V^E) for tetrachloroethylene (1) + 2-methoxyethanol (2) (●), + 2-ethoxyethanol (2) (△), and + 2-butoxyethanol (2) (○) at 313.15 K.

Table II. Experimental Excess Molar Volumes V^E as a Function of x_1, Coefficients a_i for Equation 1, and Standard Deviations $\sigma(V^E)$ (cm^3 mol^{-1})

303.15 K		313.15 K	
x_1	V^E/(cm^3 mol^{-1})	x_1	V^E/(cm^3 mol^{-1})
Trichloroethylene (1) + 2-Methoxyethanol (2)			
0.1165	0.018	0.1231	0.042
0.1852	0.025	0.1697	0.055
0.2415	0.032	0.2365	0.073
0.2950	0.040	0.2927	0.090
0.4151	0.065	0.4075	0.120
0.5054	0.083	0.5398	0.155
0.6416	0.120	0.6515	0.181
0.7732	0.139	0.7889	0.183
0.8462	0.123	0.8573	0.158
a_0 = 0.3378		a_0 = 0.5831	
a_1 = 0.5602		a_1 = 0.6146	
a_2 = 0.4616		a_2 = 0.4984	
$\sigma(V^E)$ = 0.002		$\sigma(V^E)$ = 0.003	
Trichloroethylene (1) + 2-Ethoxyethanol (2)			
0.1369	−0.052	0.1432	−0.040
0.2218	−0.065	0.1969	−0.042
0.2826	−0.072	0.2617	−0.041
0.3406	−0.070	0.3495	−0.028
0.4703	−0.039	0.4536	0.008
0.5745	−0.001	0.5832	0.061
0.6895	0.049	0.6955	0.108
0.8093	0.086	0.8219	0.128
0.8913	0.070	0.8796	0.115
a_0 = −0.1121		a_0 = 0.0987	
a_1 = 0.7524		a_1 = 0.9089	
a_2 = 0.4356		a_2 = 0.4825	
$\sigma(V^E)$ = 0.003		$\sigma(V^E)$ = 0.003	
Trichloroethylene (1) + 2-Butoxyethanol (2)			
0.1841	−0.128	0.1762	−0.091
0.2721	−0.162	0.2432	−0.109
0.3602	−0.175	0.3027	−0.115
0.4090	−0.173	0.4000	−0.105
0.5339	−0.133	0.5467	−0.049
0.6545	−0.060	0.6708	0.022
0.7588	0.005	0.7656	0.068
0.8526	0.045	0.8432	0.089
0.9047	0.049	0.9105	0.081
a_0 = −0.5899		a_0 = −0.2978	
a_1 = 0.8440		a_1 = 0.9444	
a_2 = 0.7114		a_2 = 0.7192	
$\sigma(V^E)$ = 0.002		$\sigma(V^E)$ = 0.004	

buoyancy. Measurements were made at 303.15 and 313.15 K by employing a thermostatic bath maintained constant to

Table III. Experimental Excess Molar Volumes V^E as a Function of x_1, Coefficients a_i for Equation 1, and Standard Deviations $\sigma(V^E)$ (cm^3 mol^{-1})

303.15 K		313.15 K	
x_1	V^E/(cm^3 mol^{-1})	x_1	V^E/(cm^3 mol^{-1})
Tetrachloroethylene (1) + 2-Methoxyethanol (2)			
0.1009	0.157	0.1017	0.175
0.1730	0.238	0.1509	0.242
0.2662	0.320	0.2699	0.367
0.3206	0.357	0.3225	0.405
0.3790	0.389	0.3789	0.441
0.4945	0.428	0.5047	0.492
0.6467	0.435	0.6084	0.504
0.7527	0.395	0.7615	0.447
0.8339	0.326	0.8354	0.368
a_0 = 1.7222		a_0 = 1.9721	
a_1 = 0.4928		a_1 = 0.5875	
a_2 = 0.6381		a_2 = 0.6691	
$\sigma(V^E)$ = 0.003		$\sigma(V^E)$ = 0.003	
Tetrachloroethylene (1) + 2-Ethoxyethanol (2)			
0.1206	0.114	0.1233	0.152
0.2005	0.180	0.1979	0.215
0.3117	0.255	0.3106	0.301
0.3624	0.295	0.3568	0.330
0.4301	0.331	0.4192	0.365
0.5414	0.375	0.5559	0.421
0.6785	0.385	0.6760	0.435
0.7885	0.335	0.7931	0.385
0.8630	0.266	0.8689	0.305
a_0 = 1.4426		a_0 = 1.6049	
a_1 = 0.7859		a_1 = 0.8496	
a_2 = 0.4078		a_2 = 0.7747	
$\sigma(V^E)$ = 0.003		$\sigma(V^E)$ = 0.003	
Tetrachloroethylene (1) + 2-Butoxyethanol (2)			
0.1632	0.075	0.1572	0.102
0.2445	0.104	0.2375	0.138
0.3728	0.163	0.3810	0.196
0.4436	0.185	0.4324	0.218
0.5084	0.208	0.4989	0.250
0.6173	0.243	0.6338	0.302
0.7411	0.254	0.7448	0.315
0.8330	0.225	0.8215	0.286
0.8910	0.173	0.9007	0.210
a_0 = 0.8279		a_0 = 0.9937	
a_1 = 0.7846		a_1 = 0.9328	
a_2 = 0.5604		a_2 = 0.9100	
$\sigma(V^E)$ = 0.004		$\sigma(V^E)$ = 0.002	

within 0.01 K. Values of V^E were reproducible to ±0.003 cm^3 mol^{-1}.

Materials. Trichloroethylene (BDH), tetrachloroethylene (BDH), 2-methoxyethanol (E. Merck), 2-ethoxyethanol (E. Merck), and 2-butoxyethanol (E. Merck) were purified by the standard methods described by Riddick and Bunger (*3*). The purities of the chemicals were checked by comparing the densities measured with a bicapillary pycnometer (*4*) with literature data (*3*) (Table I). The density values were reproducible to 2 parts in 10^5. The purity of the liquids was further confirmed in terms of gas–liquid chromatography single sharp peaks.

Results and Discussion

The excess volume results for trichloroethylene + 2-methoxyethanol, + 2-ethoxyethanol, and + 2-butoxyethanol and tetrachloroethylene + 2-methoxyethanol, + 2-ethoxyethanol, and + 2-butoxyethanol at 303.15 and 313.15 K are presented as a function of mole fraction in Tables II and III and are graphically presented in Figures 1–4. The experimental V^E_{exp} values were fitted to the equation

$$V^E/(\mathrm{cm^3\ mol^{-1}}) = x_1(1-x_1)\,[a_0 + a_1(2x_1-1) + a_2(2x_1-1)^2] \quad (1)$$

The parameters a_i along with the standard deviations $\sigma(V^E)$

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

where n is the number of experimental points and p the number of parameters a_i, were evaluated by the least-squares technique and are given in Tables II and III.

In general positive excess volumes can be ascribed to breaking of hydrogen bonds in 2-alkoxyethanols by the addition of trichloroethylene and tetrachloroethylene; negative values can be ascribed to complex formation between π-electrons of chloroethenes and oxygen (–O–) in 2-alkoxyethanols. The observed excess volumes result from the above two major effects. The excess volumes are more positive in mixtures of tetrachloroethylene with 2-alkoxyethanols than in mixtures of trichloroethylene at both the temperatures.

Excess volumes are positive for tetrachloroethylene + 2-methoxyethanol, + 2-ethoxyethanol, and + 2-butoxyethanol over the entire range of composition, and the curves are symmetric at both temperatures. For trichloroethylene, the excess volumes are positive for trichloroethylene + 2-methoxyethanol over the entire range of composition, but a change in sign is observed for trichloroethylene + 2-ethoxyethanol and + 2-butoxyethanol at both temperatures.

The algebraic values of V^E of all the binary systems with trichloroethylene and with tetrachloroethylene fall in the order

2-methoxyethanol > 2-ethoxyethanol > 2-butoxyethanol

The comparison of V^E values at 303.15 and 313.15 K reveals that the temperature coefficient dV^E/dT is positive over the entire range of compositions for all the systems.

Literature Cited

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Registry No. Trichloroethylene, 79-01-6; tetrachloroethylene, 127-18-4; 2-methoxyethanol, 109-86-4; 2-ethoxyethanol, 110-80-5; 2-butoxyethanol, 111-76-2.