90 J. Chem. Eng. Data 1989, 34, 90–91

Excess Volumes of *n*-Aliphatic Acids (C_2, C_3, and C_4) with 1,1,1-Trichloroethane and 1,1,2,2-Tetrachloroethane at 30 and 40 °C

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Excess volumes for the binary mixtures of 1,1,1-trichloroethane with acetic, propionic, and butyric acid have been determined at 303.15 and 313.15 K. Excess volumes for mixtures of 1,1,2,2-tetrachloroethane with the aforementioned acids at 303.15 and 313.15 K have also been measured. The excess function is positive for the mixtures of trichloroethane with acids at both temperatures. The excess volume is also positive for the mixtures of 1,1,2,2-tetrachloroethane with acetic acid. However, it becomes negative at both the temperatures in the mixtures of propionic and butyric acids. The results suggest that structure-breaking effect is dominant in four mixtures and structure-making effect becomes dominant in the remaining two mixtures.

Introduction

We report here new experimental data for excess volumes of six binary mixtures. The mixtures included 1,1,1-trichloroethane and 1,1,2,2-tetrachloroethane as common components. The noncommon components were a homologous series of aliphatic acids. These were acetic acid, propionic acid, and butyric acid. Excess volumes of the six binary mixtures were measured at 303.15 and 313.15 K. The experimental results were analyzed in terms of depolymerization of associated acids by the chloroalkane and also possible interaction between the molecules of the acids and of the two alkanes. The data also have been used to understand the trend between the excess volume and the temperature.

Experimental Section

Excess volumes were measured directly 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 with 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 fitted with a ground glass stopper. The excess volumes 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*).

Table I. Densities of Pure Components at 303.15 K

component	density, g/cm³ lit. (*3*)	density, g/cm³ present study
1,1,1-trichloroethane	1.320 96	1.320 89
1,1,2,2-tetrachloroethane	1.578 60	1.578 66
acetic acid	1.038 02	1.038 08
propionic acid	0.982 60	0.982 52
butyric acid	0.947 97	0.947 82

Table II. Excess Volumes at 303.15 and 313.15 K

mole fractn (x)	V^E	mole fractn (x)	V^E	mole fractn (x)	V^E
		1,1,1-Trichloroethane + Acetic Acid			
		303.15 K			
0.1265	0.374	0.4439	0.573	0.7228	0.549
0.2319	0.507	0.5512	0.576	0.8032	0.490
0.3261	0.554	0.6308	0.571	0.8941	0.344
		313.15 K			
0.1074	0.409	0.4266	0.702	0.6942	0.643
0.1964	0.585	0.4916	0.705	0.7612	0.592
0.2874	0.669	0.5864	0.683	0.8219	0.517
		1,1,1-Trichloroethane + Propionic Acid			
		303.15 K			
0.1649	0.224	0.4831	0.281	0.6901	0.262
0.2543	0.260	0.5681	0.276	0.7861	0.244
0.3904	0.274	0.6031	0.271	0.8532	0.210
		313.15 K			
0.1251	0.149	0.4167	0.282	0.6933	0.247
0.2508	0.234	0.5299	0.283	0.7812	0.206
0.3241	0.263	0.6107	0.271	0.8532	0.156
		1,1,1-Trichloroethane + Butyric Acid			
		303.15 K			
0.1624	0.040	0.4751	0.090	0.7512	0.061
0.2531	0.059	0.5632	0.090	0.8261	0.044
0.3861	0.084	0.6478	0.080	0.8932	0.027
		313.15 K			
0.1751	0.118	0.4521	0.163	0.7561	0.149
0.2650	0.140	0.5721	0.166	0.8340	0.130
0.3468	0.154	0.6862	0.163	0.8958	0.097
		1,1,2,2-Tetrachloroethane + Acetic Acid			
		303.15 K			
0.1462	0.146	0.4105	0.205	0.7486	0.189
0.2309	0.179	0.5206	0.208	0.8032	0.171
0.3286	0.193	0.6739	0.198	0.8862	0.128
		313.15 K			
0.1423	0.168	0.4926	0.217	0.7511	0.198
0.2312	0.205	0.5589	0.214	0.8318	0.170
0.3639	0.218	0.6973	0.205	0.8814	0.140
		1,1,2,2-Tetrachloroethane + Propionic Acid			
		303.15 K			
0.1096	−0.077	0.4458	−0.122	0.6592	−0.105
0.1759	−0.100	0.5034	−0.124	0.7511	−0.094
0.3840	−0.119	0.5945	−0.115	0.8510	−0.074
		313.15 K			
0.1322	−0.068	0.4811	−0.133	0.7618	−0.094
0.2713	−0.090	0.5627	−0.104	0.8439	−0.079
0.3626	−0.106	0.6945	−0.103	0.8823	−0.069
		1,1,2,2-Tetrachloroethane + Butyric Acid			
		303.15 K			
0.1056	−0.062	0.4465	−0.130	0.7220	−0.120
0.1921	−0.090	0.5241	−0.138	0.8150	−0.098
0.3850	−0.127	0.6463	−0.133	0.8752	−0.081
		313.15 K			
0.1293	−0.059	0.4466	−0.123	0.7314	−0.094
0.2094	−0.083	0.5942	−0.122	0.8011	−0.076
0.3627	−0.114	0.6571	−0.110	0.8830	−0.050

0021-9568/89/1734-0090$01.50/0

Table III. Standard Deviation (V^E) and Values of Constants in Eq 1

	a_0	a_1	a_2	$\sigma(V^E)$
	303.15 K			
1,1,1-trichloroethane + acetic acid	2.2965	0.0758	2.0587	0.001
1,1,1-trichloroethane + propionic acid	1.0925	−0.0184	1.1635	0.004
1,1,1-trichloroethane + butyric acid	0.3614	0.0102	−0.1432	0.001
1,1,2,2-tetrachloroethane + acetic acid	0.8158	0.0166	0.7129	0.003
1,1,2,2-tetrachloroethane + propionic acid	−0.4753	0.1056	−0.3651	0.003
1,1,2,2-tetrachloroethane + butyric acid	−0.5341	−0.0579	−0.2549	0.002
	313.15 K			
1,1,1-trichloroethane + acetic acid	2.7943	−0.2155	2.1209	0.002
1,1,1-trichloroethane + propionic acid	1.1398	−0.0618	0.3073	0.001
1,1,1-trichloroethane + butyric acid	0.6536	0.0806	0.5061	0.001
1,1,2,2-tetrachloroethane + acetic acid	0.8609	−0.0615	0.9013	0.001
1,1,2,2-tetrachloroethane + propionic acid	−0.4310	−0.0365	0.3228	0.005
1,1,2,2-tetrachloroethane + butyric acid	−0.4899	0.0169	0.0226	0.002

1,1,2,2-Tetrachloroethane 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 over potassium carbonate, and finally fractionated.

1,1,1-Trichloroethane was washed with concentrated hydrochloric acid, then with 10% sodium chloride solution, dried over calcium chloride, and finally distilled twice. The middle sample of the second distillation was collected.

Acetic acid (BDH) was mixed with a calculated amount of acetic anhydride and refluxed for about 10 h. It was then distilled by using a fractionating column. Propionic acid (BDH) was dried over anhydrous sodium sulfate for 2 days and the dried sample was distilled in a fractionating column. These products were distilled again over potassium permanganate. *n*-Butyric acid (E. Merck) was dried over anhydrous sodium sulfate for 2 days and the dried sample was distilled in a fractionating column.

The purity of the samples was determined by comparing the measured densities of the compounds with those reported in the literature (*3*). Densities were determined with a bicapillary type pycnometer which offered an accuracy of 2 parts in 10^5. The measured densities and those reported in literature are given in Table I.

Results

Experimentally determined excess volumes at 303.15 and 313.15 K are given in Table II. The dependence of excess volume as a function of composition may be expressed by an empirical equation of the form

$$V^E\ (\mathrm{cm^3\ mol^{-1}}) = x(1-x)[a_0 + a_1(2x-1) + a_2(2x-1)^2] \qquad (1)$$

where a_0, a_1, and a_2 are adjustable parameters and x is the mole fraction of 1,1,1-trichloroethane or 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 $\sigma(V^E)$.

Discussion

The results included in Table II show that excess volumes for mixtures of trichloroethane with the three acids, (i.e., acetic, propionic, and *n*-butyric acids) are positive over the whole range of compositions at both temperatures. V^E values for mixtures of acetic acid with tetrachloroethane are also positive over the whole range of compositions. However, V^E values become negative for the mixtures of propionic acid butyric acid with tetrachloroethane. These excess volumes may be ascribed to the following factors: (i) breakup of hydrogen bonds in the self-associated carboxylic acid and loss of dipolar association between the molecules of polar carboxylic acids; (ii) interstitial accommodation of halogenated alkanes in hydrogen-bonded acid aggregates and weak hydrogen-bonding (Cl···H---O) interaction between unlike molecules. While factor 1 contributes to expansion of volume, factor 2 leads to contraction of volume. The results presented here suggest that the first factor is dominant in mixtures of the three acids with trichloroethane, and also in mixtures of acetic acid with 1,1,2,2-tetrachloroethane. However, factor 2 becomes dominant in mixtures of the 1,1,2,2-tetrachloroethane with the remaining two acids.

Excess volumes measured at 303.15 and 313.15 K show that the temperature coefficient is positive over the whole range of compositions in mixtures of 1,1,1-trichloroethane with acetic acid and butyric acid. However, in the case of propionic acid the coefficient is negative. The coefficient is negative in mixtures rich in alkane and is positive in mixtures rich in acid. A similar trend between excess volumes and temperatures exists in mixtures of 1,1,2,2-tetrachloroethane with the three acids.

Registry No. 1,1,1-Trichloroethane, 71-55-6; 1,1,2,2-tetrachloroethane, 79-34-5; acetic acid, 64-19-7; propionic acid, 79-09-4; butyric acid, 107-92-6.

Literature Cited

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Received for review March 5, 1987. Accepted March 28, 1988.