Excess Volumes of 1,1,2,2-Tetrachloroethane or Tetrachloroethene + 2-Chlorotoluene, + 3-Chlorotoluene, and + 4-Chlorotoluene at 303.15 and 313.15 K

B. Busa Goud, P. Venkatesu, and M. V. Prabhakara Rao*

Department of Chemistry, Sri Venkateswara University, Tirupati-517 502, Andhra Pradesh, India

Excess volumes, V^E, have been determined for 1,1,2,2-tetrachloroethane or tetrachloroethene + 2-chlorotoluene, + 3-chlorotoluene, and + 4-chlorotoluene at 303.15 and 313.15 K. The V^E values are found to be positive for 1,1,2,2-tetrachloroethane + 2-chlorotoluene, + 3-chlorotoluene, and + 4-chlorotoluene at both temperatures and are negative for tetrachloroethene + 2-chlorotoluene, + 3-chlorotoluene, and + 4-chlorotoluene at both temperatures except for tetrachloroethene + 3-chlorotoluene which shows positive V^E values at 303.15 K.

Introduction

This paper forms part of our program on the measurement of thermodynamic properties of nonelectrolyte solutions (Venkatesu and Rao, 1994; Ramadevi and Rao, 1995). In this work we report excess volumes of 1,1,2,2-tetrachloroethane and tetrachloroethene with 2-, 3-, and 4-chlorotoluenes at 303.15 K and 313.15 K.

Experimental Procedure

Apparatus. The dilatometer used for measuring excess volumes in the present experiment is similar to that described by Rao and Naidu (1974). The mixing cell contains two bulbs of differing capacities that are connected through a U-tube containing mercury to separate the components. One end of the first bulb is fitted with a capillary tube, and the other end of the second bulb is closed with a ground glass stopper. Five dilatometers with differing capacities were used to cover the entire composition range. The composition of each mixture was determined by mass. The dilatometers were kept in a thermostat controlled to ±0.01 K. The excess volumes are accurate to ±0.003 $cm^3·mol^{-1}$. The dilatometers were standardized against measurements for the cyclohexane + benzene system at 298.15 K. The measured V^E for the standard system were in good agreement with earlier values reported by Wieczorek and Zywocinski (1983).

Materials. All the chemicals used were of analytical grade. 1,1,2,2-Tetrachloroethane was purified by the method described by Reddy et al. (1984). Tetrachloroethene was dried over anhydrous sodium sulfate and fractionally distilled. Isomeric chlorotoluenes were washed successively with 30 mL of 10% sodium hydroxide solution and equal volume of concentrated sulfuric acid and water, dried with anhydrous calcium chloride, decanted, and distilled on asbestos-centered gauze (Vogel, 1978). The purities of the sample were checked by comparing the measured densities of the components with those reported in the literature (Riddick and Bunger, 1970; Timmermans, 1962). Densities were determined with a bicapillary type pycnometer, of capacity 12 mL, which offers an accuracy of 2 parts in 10^5. The measured densities and those reported in the literature are listed in Table 1.

Table 1. Densities (ρ) of Pure Components at 303.15 K

component	ρ/(g·cm⁻³) exptl	ρ/(g·cm⁻³) lit.
1,1,2,2-tetrachloroethane	1.578 59	1.578 60
tetrachloroethene	1.606 37	1.606 40
2-chlorotoluene	1.072 76	1.072 79
3-chlorotoluene	1.072 19[a]	1.072 20[a]
4-chlorotoluene	1.069 68[a]	1.069 70[a]

[a] At 293.15 K.

Table 2. Excess Volumes (V^E) for the Binary Mixtures of 1,1,2,2-Tetrachloroethane (1) and Isomeric Chlorotoluenes (2)

303.15 K x_1	303.15 K $V^E/(cm^3·mol^{-1})$	313.15 K x_1	313.15 K $V^E/(cm^3·mol^{-1})$
1,1,2,2-Tetrachloroethane (1) + 2-Chlorotoluene (2)			
0.1222	0.051	0.1087	0.055
0.1993	0.087	0.2011	0.089
0.3215	0.121	0.2632	0.115
0.4133	0.134	0.3821	0.140
0.5321	0.141	0.4906	0.143
0.6315	0.130	0.6431	0.133
0.7531	0.104	0.7032	0.124
0.8571	0.070	0.7602	0.105
0.9143	0.045	0.8761	0.065
1,1,2,2-Tetrachloroethane (1) + 3-Chlorotoluene (2)			
0.1221	0.092	0.0993	0.086
0.1995	0.140	0.1924	0.150
0.3242	0.195	0.2915	0.199
0.4412	0.223	0.3981	0.235
0.5585	0.230	0.5050	0.250
0.6325	0.220	0.5813	0.245
0.7400	0.181	0.6813	0.215
0.8678	0.103	0.7660	0.181
0.9152	0.072	0.8841	0.101
1,1,2,2-Tetrachloroethane (1) + 4-Chlorotoluene (2)			
0.1152	0.055	0.1020	0.051
0.2004	0.087	0.2032	0.091
0.3312	0.121	0.2836	0.120
0.4081	0.132	0.3722	0.138
0.4931	0.133	0.4741	0.150
0.5391	0.132	0.5386	0.145
0.6354	0.119	0.6585	0.129
0.7448	0.087	0.7577	0.103
0.8636	0.049	0.8829	0.059

* To whom correspondence should be addressed.

0021-9568/95/1740-1211$09.00/0

Table 3. Excess Volumes (V^E) for the Binary Mixtures of Tetrachloroethene (1) with Isomeric Chlorotoluenes (2)

303.15 K		313.15 K	
x_1	V^E/($cm^3 \cdot mol^{-1}$)	x_1	V^E/($cm^3 \cdot mol^{-1}$)
Tetrachloroethene (1) + 2-Chlorotoluene (2)			
0.1252	−0.025	0.1210	−0.015
0.1986	−0.035	0.2016	−0.025
0.3263	−0.051	0.3159	−0.035
0.3946	−0.055	0.3813	−0.041
0.4683	−0.065	0.4544	−0.045
0.5243	−0.065	0.5302	−0.050
0.6357	−0.065	0.6440	−0.045
0.7342	−0.060	0.7683	−0.037
0.8710	−0.041	0.8814	−0.020
Tetrachloroethene (1) + 3-Chlorotoluene (2)			
0.1224	−0.013	0.1217	0.006
0.2040	−0.016	0.2069	0.010
0.2743	−0.020	0.3157	0.015
0.3658	−0.025	0.3745	0.015
0.4545	−0.025	0.4683	0.017
0.5350	−0.029	0.5297	0.021
0.6234	−0.026	0.6338	0.021
0.7588	−0.025	0.7689	0.019
0.8744	−0.015	0.8836	0.016
Tetrachloroethene (1) + 4-Chlorotoluene (2)			
0.1210	−0.035	0.1443	−0.032
0.2077	−0.055	0.2035	−0.048
0.2741	−0.065	0.3209	−0.065
0.3420	−0.075	0.3887	−0.066
0.4526	−0.081	0.4603	−0.071
0.5635	−0.075	0.5859	−0.062
0.6414	−0.066	0.6802	−0.050
0.7612	−0.048	0.7812	−0.035
0.8685	−0.031	0.8761	−0.018

Results and Discussion

The V^E data at 303.15 and 313.15 K for all the mixtures are listed in Tables 2 and 3 and are graphically represented in Figures 1 and 2. The V^E values are fitted by the method of least squares using the polynomial

$$V^E = x_i(1 - x_i)[a_0 + a_1(2x_i - 1) + a_2(2x_i - 1)^2] \quad (1)$$

where x_i is the mole fraction of component i. The values of the coefficients a_0, a_1, and a_2 obtained by the least squares method are included in Table 4 along with the standard deviation $\sigma(V^E)$.

The data included in Table 2 show that the V^E values are positive in the mixtures of 1,1,2,2-tetrachloroethane with 2-chlorotoluene, 3-chlorotoluene, and 4-chlorotoluene at 303.15 and 313.15 K. At both temperatures the algebraic V^E values fall in the order 3-chlorotoluene > 2-chlorotoluene ≃ 4-chlorotoluene. A comparison of V^E at 303.15 and at 313.15 K shows that V^E becomes more positive with an increase in temperature, and the effect is almost the same irrespective of the position of the chlorine atom on the aromatic ring.

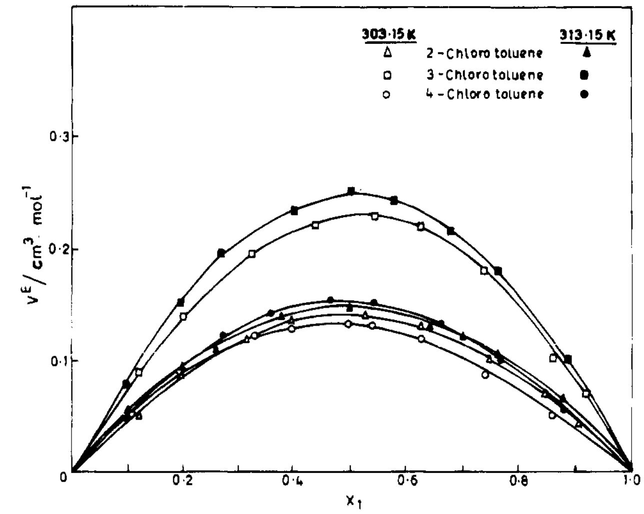

Figure 1. Excess volumes (V^E) for 1,1,2,2-tetrachloroethane (1) + isomeric chlorotoluenes (2).

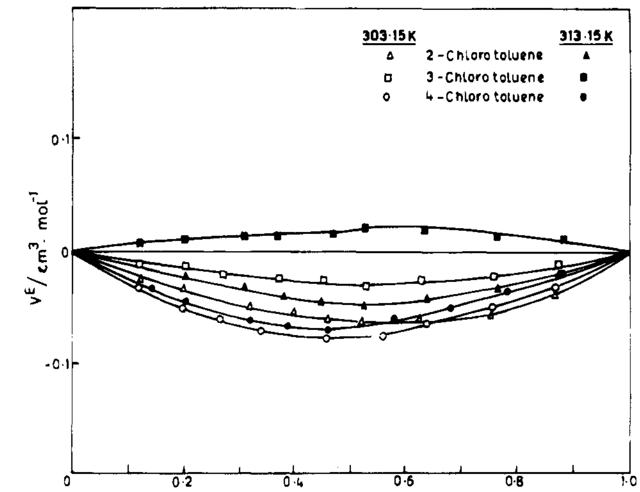

Figure 2. Excess volumes (V^E) for tetrachloroethene (1) + isomeric chlorotoluenes (2).

The measured V^E data are negative in the mixtures of tetrachloroethene with 2-chlorotoluene, 3-chlorotoluene, and 4-chlorotoluene at 303.15 and 313.15 K except for tetrachloroethene with 3-chlorotoluene at 313.15 K, for which very small positive V^E values are observed. The algebraic values of V^E at 303.15 and 313.15 K for the three mixtures are in the order 3-chlorotoluene > 2-chlorotoluene > 4-chlorotoluene. The measured V^E values at 313.15 K are less negative in magnitude than those at 303.15 K for all binary systems, except tetrachloroethene with 3-chlorotoluene which shows positive values of V^E at 313.15 K.

Table 4. Binary Parameters of Eq 1 and Standard Deviation $\sigma(V^E)$ at 303.15 and 313.15 K

system	T/K	a_0/($cm^3 \cdot mol^{-1}$)	a_1/($cm^3 \cdot mol^{-1}$)	a_2/($cm^3 \cdot mol^{-1}$)	$\sigma(V^E)$/($cm^3 \cdot mol^{-1}$)
1,1,2,2-tetrachloroethane (1) + 2-chlorotoluene (2)	303.15	0.5610	0.0426	−0.0430	0.003
	313.15	0.5812	0.0144	−0.0010	0.003
1,1,2,2-tetrachloroethane (1) + 3-chlorotoluene (2)	303.15	0.9239	0.0459	−0.0631	0.003
	313.15	0.9927	0.0234	−0.0328	0.002
1,1,2,2-tetrachloroethane (1) + 4-chlorotoluene (2)	303.15	0.5346	−0.0838	−0.1067	0.001
	313.15	0.5890	−0.0024	−0.0487	0.002
tetrachloroethene (1) + 2-chlorotoluene (2)	303.15	−0.2540	−0.0912	−0.0765	0.002
	313.15	−0.1886	−0.0383	0.0314	0.001
tetrachloroethene (1) + 3-chlorotoluene (2)	303.15	−0.1077	−0.0182	−0.0328	0.002
	313.15	0.0756	0.0556	0.0514	0.002
tetrachloroethene (1) + 4-chlorotoluene (2)	303.15	−0.3128	0.0502	0.0282	0.002
	313.15	−0.2753	0.0709	0.1039	0.002

Literature Cited

Ramadevi, R. S.; Rao, M. V. P. Excess Volumes of Substituted Benzenes with *N,N*-Dimethylformamide. *J. Chem. Eng. Data* **1995**, *40*, 65–67.

Rao, M. V. P.; Naidu, P. R. Excess Volumes of Binary Mixtures of Alcohols in Methylcyclohexane. *Can. J. Chem.* **1974**, *52*, 788–790.

Reddy, K. D.; Iloukhani, H.; Rao, M. V. P. Excess Volumes of Chlorobenzene and Bromobenzene with some Chloroethanes at 303.15 and 313.15 K. *Fluid Phase Equilib.* **1984**, *17*, 123–130.

Riddick, J. A.; Bunger, W. B. *Techniques of Chemistry*, 3rd ed.; Wiley-Interscience: New York, 1970.

Timmermans, J. *Physico-Chemical Constants of pure Organic Compounds*; Elsevier: Amsterdam, 1962.

Venkatesu, P.; Rao, M. V. P. Excess Volumes of Binary Mixtures of Triethylamine with Aromatic Hydrocarbons at 3018.15 K. *Fluid Phase Equilib.* **1994**, *93*, 369–376.

Vogel, A. *Practical Organic Chemistry*, 4th ed.; ELBS Longman Group: Harlow, England, 1978; p 698.

Wiezorek, S. A.; Zywocinski, A. Determination of the Excess Molar Volumes of Cyclohexane + Benzene between 293.15 and 308.15 K by use of Dilatometer. *J. Chem. Thermodyn.* **1983**, *15*, 327–331.

Received for review April 5, 1995. Accepted September 7, 1995.[⊗]

JE950083C

[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1995.