Excess Volumes of Binary Mixtures of 1,2,4-Trichlorobenzene with 1-Alkanols

Tirumala S. Vijayalakshmi and Pulligundla R. Naidu*

Department of Chemistry, Sri Venkateswara University, Tirupati 517 502, India

Excess molar volumes, V^E, for binary mixtures of 1,2,4-trichlorobenzene with 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol have been measured at 303.15 K. V^E is negative in mixtures rich in alcohols and positive in those rich in 1,2,4-trichlorobenzene.

Introduction

This work forms part of a program to determine molar excess volumes V^E for a number of binary mixtures which include a chlorinated benzene as a common component and a homologous series of 1-alkanols as noncommon components (*1*). An earlier communication (*2*) included V^E for binary mixtures of 1,2-dichlorobenzene with 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol.

New experimental V^E data for mixtures of 1,2,4-trichlorobenzene, measured at 303.15 K, with the five alcohols are included here. The study was taken up to understand the influence of a third chloro group on molecular interactions.

Experimental Section

Excess volumes were measured as described previously (*2*) by using the dilatometer designed by Rao and Naidu (*3*). Measurements were made employing a thermostatic bath controlled to ±0.01 K. Values of V^E were accurate to ±0.003 cm^3 mol^{-1}.

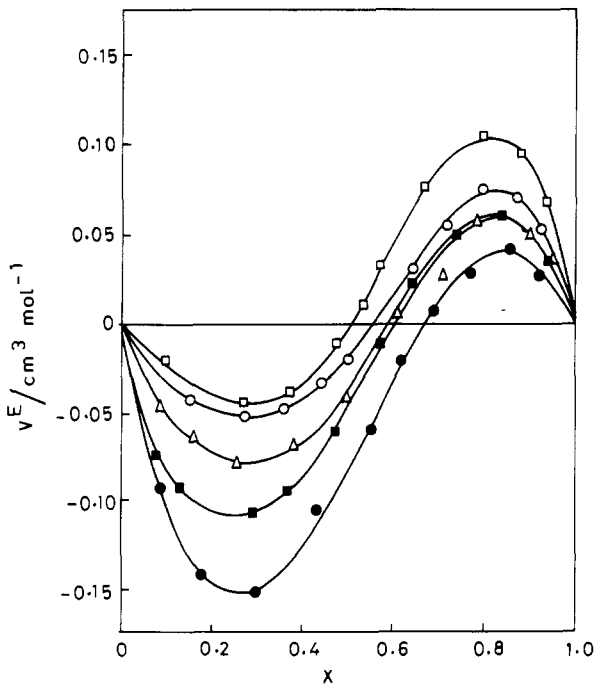

Figure 1. Molar excess volumes, V^E, at 303.15 K plotted against x, the mole fraction of 1,2,4-trichlorobenzene, for the mixtures of 1,2,4-trichlorobenzene with (●) 1-butanol, (■) 1-pentanol, (△) 1-hexanol, (○) 1-heptanol, and (□) 1-octanol.

Table I. Densities ρ of Pure Liquid Components at 303.15 K

component	ρ/(g cm^{-3}) present work	ρ/(g cm^{-3}) lit.
1,2,4-trichlorobenzene	1.44212	1.44215 (*6*)
1-butanol	0.80206	0.8022 (*7*)
1-pentanol	0.80760	0.8079 (*7*)
1-hexanol	0.81205	0.8121 (*7*)
1-heptanol	0.81572	0.8148 (*7*)
1-octanol	0.82188	0.8184 (*7*)

Table II. Molar Excess Volumes of 1,2,4-Trichlorobenzene + 1-Alkanols at 303.15 K as a Function of the Mole Fraction x of 1,2,4-Trichlorobenzene, Coefficients a, b, and c, Equation 1, and Standard Deviations σ, Equation 2

x	V^E/(cm^3 mol^{-1})	x	V^E/(cm^3 mol^{-1})	x	V^E/(cm^3 mol^{-1})
1,2,4-Trichlorobenzene + 1-Butanol					
0.0948	−0.093	0.5461	−0.058	0.8607	0.042
0.1770	−0.143	0.6117	−0.019	0.9178	0.027
0.3017	−0.153	0.6910	0.008		
0.4260	−0.106	0.7725	0.028		
a = −0.3080, b = 0.9261, c = −0.0972, σ = 0.005 cm^3 mol^{-1}					
1,2,4-Trichlorobenzene + 1-Pentanol					
0.0834	−0.074	0.4692	−0.060	0.8440	0.060
0.1271	−0.092	0.5773	−0.009	0.9287	0.036
0.2903	−0.107	0.6448	0.022		
0.3722	−0.096	0.7357	0.049		
a = −0.1646, b = 0.8926, c = −0.0515, σ = 0.004 cm^3 mol^{-1}					
1,2,4-Trichlorobenzene + 1-Hexanol					
0.0925	−0.044	0.4989	−0.040	0.9054	0.050
0.1555	−0.063	0.6161	0.008	0.9526	0.036
0.2637	−0.078	0.7106	0.028		
0.3797	−0.067	0.7771	0.059		
a = −0.1711, b = 0.6949, c = 0.3431, σ = 0.006 cm^3 mol^{-1}					
1,2,4-Trichlorobenzene + 1-Heptanol					
0.1475	−0.043	0.5049	−0.021	0.8740	0.072
0.2677	−0.050	0.6537	0.029	0.9248	0.053
0.3584	−0.048	0.7228	0.054		
0.4351	−0.033	0.7965	0.076		
a = −0.1029, b = 0.6949, c = 0.5261, σ = 0.007 cm^3 mol^{-1}					
1,2,4-Trichlorobenzene + 1-Octanol					
0.1034	−0.020	0.5432	0.010	0.8865	0.097
0.2753	−0.044	0.5729	0.032	0.9425	0.068
0.3842	−0.038	0.6675	0.075		
0.4783	−0.011	0.8040	0.105		
a = −0.0185, b = 0.7842, c = 0.6925, σ = 0.005 cm^3 mol^{-1}					

The materials were purified by the methods described in ref 4.

1,2,4-Trichlorobenzene (E. Merck) was purified by repeated fractional distillation and stored in the dark with the vapor phase in contact with anhydrous magnesium perchlorate. The alcohols were purified as before (*2*).

The purities of the samples were checked by GLC and by comparing the densities of the components measured with a bicapillary pycnometer (*5*) with those reported in the literature (*6*, *7*).

0021-9568/92/1737-0368$03.00/0

Results and Discussion

The experimental V^E data are listed in Table II and graphically presented in Figure 1. The data were fitted to the polynomial expression

$$V^E/(\text{cm}^3\ \text{mol}^{-1}) = x(1 - x)[a + b(2x - 1) + c(2x - 1)^2] \quad (1)$$

where a, b, and c are adjustable parameters and x is the mole fraction of 1,2,4-trichlorobenzene. The values of the parameters, computed by the least-squares method, are given in Table II along with the standard deviation, σ:

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

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

The results show that V^E is negative in mixtures rich in alcohols and positive in mixtures rich in 1,2,4-trichlorobenzene. The trend between excess volume and composition is similar to that observed (*2*) for mixtures of 1,2-dichlorobenzene with the five alcohols. However, the V^E values for the mixtures with 1,2,4-trichlorobenzene are algebraically greater than those observed for the mixtures containing 1,2-dichlorobenzene, and the inversion in sign of V^E occurs at lower mole fractions of 1,2,4-trichlorobenzene.

Glossary

a,b,c	constants in eq 1
V^E	molar excess volume, $\text{cm}^3\ \text{mol}^{-1}$
x	mole fraction of 1,2,4-trichlorobenzene
ρ	density, g cm^{-3}
σ	standard deviation, eq 2

Registry No. 1,2,4-Trichlorobenzene, 120-82-1; 1-butanol, 71-36-3; 1-pentanol, 71-41-0; 1-hexanol, 111-27-3; 1-heptanol, 111-70-6; 1-octanol, 111-87-5.

Literature Cited

(1) Dharmaraju, G.; Narayanaswamy, G.; Raman, G. K. *J. Chem. Thermodyn.* **1980**, *12*, 563.
(2) Vijayalakshmi, T. S.; Naidu, P. R. *J. Chem. Eng. Data* **1989**, *34*, 413.
(3) Rao, M. V. P.; Naidu, P. R. *Can. J. Chem.* **1974**, *52*, 788.
(4) Riddick, J. A.; Bunger, W. S. *Techniques of Chemistry*, 3rd ed.; Wiley-Interscience: New York, 1970; Volume II.
(5) Rao, M. V. P. Ph.D. Thesis, Sri Venkateswara University, India, 1974.
(6) Timmermans, J. *Physico-Chemical Constants of Pure Organic Compounds*; Elsevier Publishing Co.: Amsterdam, 1950.
(7) *Thermodynamic Tables-Non-hydrocarbons*; Thermodynamics Research Center, The Texas A&M University System: College Station, TX (loose-leaf data sheets, extant 1968, p d-5000).

Received for review May 18, 1989. Accepted January 30, 1990. T.S.V. is thankful to the University Grant Commission, New Delhi, India, for financial assistance.