of the R 12 + R 22 system shown in a previous publication (*2*). The maximum pressure difference between dew and bubble points at a given temperature is about 0.72 MPa for the mixture of 30 wt % R 22 + 70 wt % R 114 at 376 K. The critical locus is convex with a maximum pressure corresponding to a critical pressure of the mixture of around 75 wt % R 22 + 25 wt % R 114. This trend of the critical locus is in contrast to that for the R 12 + R 22 system (*8*) for which the pressure decreases with increasing temperature. There is a similar difference concerning the composition dependence in the shape of the coexistence-state surface in the critical region. The surface for the R 22 + R 114 system is shaped like a ridge, while that for the R 12 + R 22 system is shaped like a saddle as shown in a previous publication (*8*).

Acknowledgment

We are greatly indebted to Du Pont-Mitsui Fluorochemicals Co., Ltd., Tokyo, for kindly furnishing the samples of R 22 and R 114. We are also grateful to the National Research Laboratory of Metrology, Ibaraki, Japan, for their calibration of the thermometer. S. Wada, H. Hasegawa, and K. Hatano have provided valuable assistance in the experiments.

Glossary

B_{11}	second virial coefficient for R 22, cm^3/mol
B_{22}	second virial coefficient for R 114, cm^3/mol
B_{12}	interaction virial coefficient, cm^3/mol
CP	critical point
P	pressure, MPa
P_{calcd}	pressure value calculated by Wilson–Hules equation of state (*4*), MPa
P_{exptl}	pressure value of experimental data, MPa
T	temperature, K
w_1	mass fraction of R 22
x_1	mole fraction of R 22
ρ	density, kg/m^3

Registry No. Freon 22, 75-45-6; Freon 114, 76-14-2.

Literature Cited

(1) Takaishi, Y.; Uematsu, M.; Watanabe, K. *Bull. Jpn. Soc. Mech. Eng.* **1982**, *25*, 944.
(2) Takaishi, Y.; Kagawa, N.; Uematsu, M.; Watanabe, K. *Proc. Symp. Thermophys. Prop., 8th* **1982**, *2*, 387.
(3) Martin, J. J. *J. Chem. Eng. Data* **1960**, *5*, 334.
(4) Wilson, D. P.; Hules, K. P. *Proc. Symp. Thermophys. Prop., 8th* **1982**, *2*, 361.
(5) Bottomley, G. A.; Nairn, D. B. *Aust. J. Chem.* **1977**, *30*, 1645.
(6) Kagawa, N.; Takaishi, Y.; Uematsu, M.; Watanabe, K. *Nippon Kikai Gakkai Ronbunshu, B Hen* **1983**, *49-448*, 2811.
(7) Morsy, T. E. *J. Chem. Eng. Data* **1970**, *15*, 256.
(8) Higashi, Y.; Okazaki, S.; Takaishi, Y.; Uematsu, M.; Watanabe, K. *J. Chem. Eng. Data* **1984**, *29*, 31.

Received for review September 6, 1983. Revised manuscript received April 30, 1984. Accepted June 19, 1984.

Excess Volumes of Nitrobenzene with Alkyl-Substituted Chloroethanes at 303.15 and 313.15 K

K. Dayananda Reddy and M. V. Prabhakara Rao*
Chemical Laboratories, Sri Venkateswara University, Tirupati—517 502, India

Excess volumes of nonelectrolyte solutions of nitrobenzene with 1,2-dichloroethane, 1,1,1-trichloroethane, and 1,1,2,2-tetrachloroethane were measured at 303.15 and 313.15 K by using a dilatometer and are reported in this paper.

Introduction

In view of their probable value in the systematic analysis of the behavior of substances, experimental excess volumes of nitrobenzene with 1,2-dichloroethane, 1,1,1-trichloroethane, and 1,1,2,2-tetrachloroethane have been undertaken and are reported in this paper. These measurements were made as part of a continuing project on the thermodynamic and physical properties of nonelectrolyte solutions (*1–4*).

Experimental Section

The excess volumes have been determined at 303.15 and 313.15 K by using a single composition per loading type dilatometer described by Rao and Naidu (*5*). The excess volumes are accurate to ±0.003 cm^3 mol^{-1}. The dilatometer was standardized with a cyclohexane–benzene system at 298.15 K. The measured excess volumes for the standard system are in good agreement with the earlier values reported (*6*).

***Purification of Materials*.** Nitrobenzene (BDH) was dried over anhydrous calcium chloride for 2 days and the dried sample was distilled by using a 1-m fractionating column under reduced pressure. 1,2-Dichloroethane (BDH) was washed with a dilute solution of potassium hydroxide and then with water. It was dried over phosphorus pentoxide and distilled in a fractionating column. The fraction of the second distillation was collected and stored in an amber-colored bottle.

1,1,1-Trichloroethane (Koch-light Laboratories) was washed with concentrated sulfuric acid and then with 10% sodium chloride solution. It was dried over calcium chloride and distilled in a fractionating column. The middle fraction was collected and stored.

During the distillation 0.5 g of phenol was added as a stabilizer.

1,1,2,2-Tetrachloroethane (BDH) was stirred with concentrated sulfuric acid at 80 °C for 10 min. The discolored acid was removed and again 25 mL of the acid was added. The liquid was then washed with water, dried over potassium carbonate, and distilled under vacuum.

During the distillation about 0.5 g of phenol was added as a stabilizer.

The purity of the compounds was checked by densities, refractive indices, and boiling points. The densities were measured with a bicapillary pyconometer. The densities are accurate to 5 parts in 10^5. The refractive indices were measured with an Abbe refractometer which gave an accuracy of ±0.0002.

The boiling points were measured with a Swietoslawaki type ebulliometer which gave an accuracy of ±0.1 °C. The measured values are presented in Table I along with the literature values (*7*, *8*).

Table I. Boiling Points, Refractive Indices, and Densities of the Pure Compounds at 303.15 K

compd	bp/K present work	bp/K lit. (*7*)	ρ^a/(g cm^{-3}) present work	ρ^a/(g cm^{-3}) lit. (*7*)	n^b present work	n^b lit. (*8*)
nitrobenzene	483.55	483.81	1.193 38	1.193 41	1.5525	1.5524
1,2-dichloroethane	356.75	356.65	1.238 25	1.238 47	1.4395	1.4393
1,1,1-trichloroethane	347.35	347.25	1.330 1	1.331 4^c	1.4360	1.4359
1,1,2,2-tetrachloroethane	419.35	419.35	1.586 4	1.587 6^c	1.4910	1.4910

^{a} Density. ^{b} Refractive index. ^{c} 298.15 K.

Table II. Excess Volumes, V^E (cm^3 mol^{-1}) of Nitrobenzene with Chloroethanes

$x_A{}^a$	V^E	ΔV^E	$x_A{}^a$	V^E	ΔV^E
Nitrobenzene + 1,2-Dichloroethane 303.15 K			Nitrobenzene + 1,1,2,2-Tetrachloroethane 303.15 K		
0.1462	0.000	-0.001	0.1168	-0.060	-0.003
0.2163	0.000	0.000	0.1971	-0.089	-0.001
0.3564	0.000	0.006	0.3125	-0.115	0.005
0.4517	-0.010	+0.001	0.4046	-0.126	0.005
0.5306	-0.017	-0.002	0.5232	-0.128	0.000
0.6519	-0.020	-0.001	0.6285	-0.113	-0.002
0.7891	-0.016	+0.002	0.7618	-0.074	-0.001
0.8534	-0.010	0.005	0.8314	-0.052	-0.002
313.15 K			313.15 K		
0.1422	-0.016	-0.001	0.1097	-0.052	0.002
0.2633	-0.025	0.000	0.2014	-0.100	-0.005
0.3527	-0.030	-0.001	0.3026	-0.133	0.003
0.4278	-0.033	-0.002	0.4465	-0.149	-0.001
0.5024	-0.032	0.000	0.5253	-0.142	0.002
0.5761	-0.030	-0.001	0.6387	-0.118	0.003
0.6510	-0.025	0.001	0.7061	-0.096	0.004
0.7325	-0.020	0.000	0.8225	-0.060	0.003
0.8496	-0.012	-0.001			
Nitrobenzene + 1,1,1-Trichloroethane 303.15 K					
0.1037	-0.230	0.003			
0.1785	-0.351	0.000			
0.3969	-0.521	-0.004			
0.4253	-0.525	-0.002			
0.5312	-0.521	-0.002			
0.6646	-0.460	-0.002			
0.7634	-0.376	-0.002			
0.8526	-0.265	0.000			
313.15 K					
0.1041	-0.270	0.000			
0.1525	-0.372	-0.002			
0.2531	-0.524	-0.002			
0.3928	-0.622	0.004			
0.4606	-0.630	0.001			
0.5524	-0.600	0.002			
0.6952	-0.475	0.005			
0.7849	-0.360	0.003			
0.8172	-0.319	-0.004			
0.8734	-0.225	-0.001			

^{a} Mole fraction of nitrobenzene.

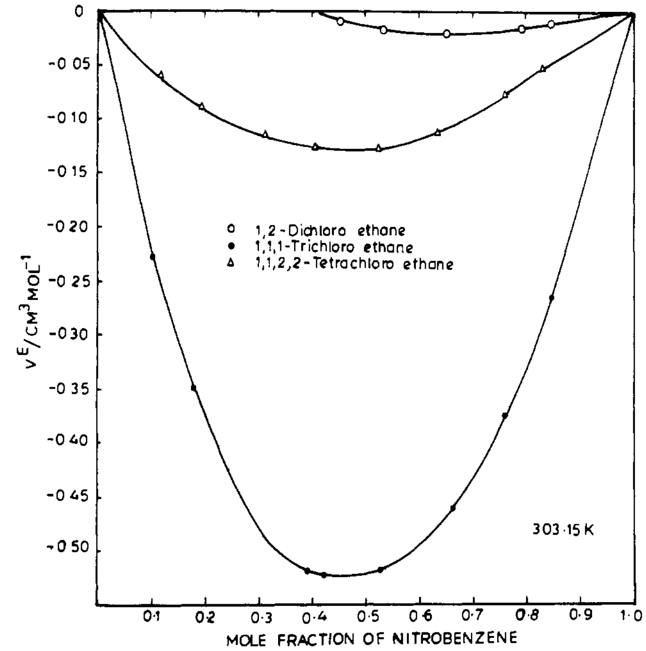

Figure 1. Excess volume-composition curves for nitrobenzene + chloroethanes at 303.15 K.

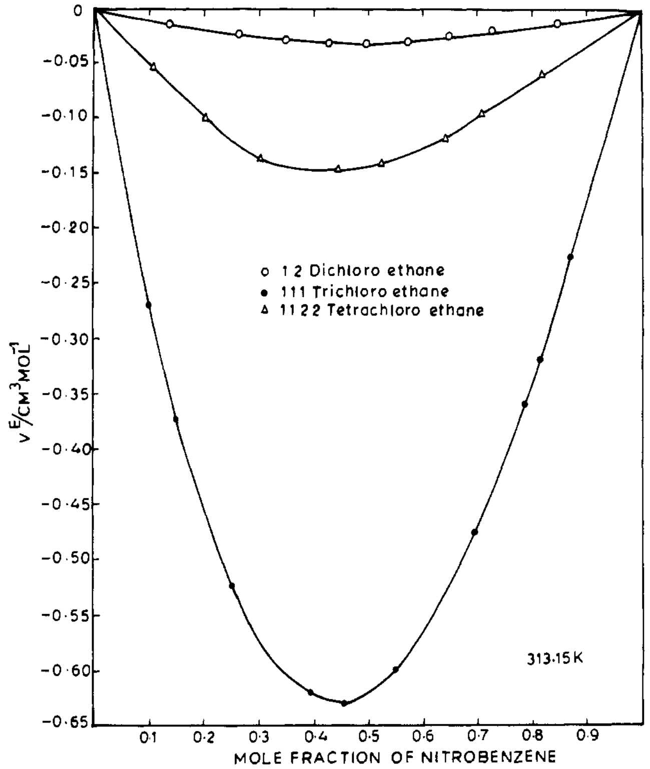

Figure 2. Excess volume-composition curves for nitrobenzene + chloroethanes at 313.15 K.

Results and Discussion

The excess volume data at 303.15 and 313.15 K for all three binary liquid mixtures are presented in Table II and the graphs are represented in Figures 1 and 2. The excess volumes, V^E, are negative over the entire range of composition in all the binary liquid mixtures, except in the system of nitrobenzene with 1,2-dichloroethane at 303.15 K. Here, up to 0.35 mole fraction of nitrobenzene, the excess volume is zero. The negative excess volumes for the above mixtures fall in the following order for both temperatures of interest:

nitrobenzene + 1,2-dichloroethane > nitrobenzene + 1,1,2,2-tetrachloroethane > nitrobenzene + 1,1,1-trichloroethane

The excess volume-composition curves are symmetric over the entire range of composition in all the binary mixtures. The measured values show a maximum value around 0.5 mole fraction of nitrobenzene at both temperatures studied. From the figures we can conclude that the negative excess volumes increase when temperature increases. For each mixture, the

Table III. Values of the Corresponding Constants in Eq 1 and Standard Deviation, σ, for All Six Binary Mixtures

T/K	a_0[a]	a_1[a]	a_2[a]	σ[a]
Nitrobenzene + 1,2-Dichloroethane				
303.15	−0.0554	−0.0978	−0.0004	0.003
313.15	−0.1261	−0.0285	0.0325	0.001
Nitrobenzene + 1,1,1-Trichloroethane				
303.15	−2.0968	0.2374	−0.3635	0.002
313.15	−2.4991	0.5716	0.0674	0.003
Nitrobenzene + 1,1,2,2-Tetrachloroethane				
303.15	−0.5235	0.1492	0.1447	0.003
313.15	−0.5863	0.1525	0.2363	0.003

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

excess quantities were fitted by the method of least squares by using the polynomial form

$$V^E = x_A(1 - x_A) \sum_{n=0} a_i(2x_A - 1)^i \qquad (1)$$

The coefficients a_i and the corresponding standard deviations are given in Table III. The solid curves in Figures 1 and 2, which give plots of V^E vs. mole fraction x_A, were calculated by using these coefficients. The measured V^E data at 303.15 and 313.15 K for nitrobenzene with chloroethanes are presented by the points in Figures 1 and 2.

Acknowledgment

K.D.R. is thankful to University authorities for providing the necessary facilities.

Registry No. Nitrobenzene, 98-95-3; 1,2-dichloroethane, 107-06-2; 1,1,1-trichloroethane, 71-55-6; 1,1,2,2-tetrachloroethane, 79-34-5.

Literature Cited

(1) Rao, M. V. P.; Naidu, P. R. *J. Chem. Thermodyn.* **1976**, *8*, 96.
(2) Rao, M. V. P.; Naidu, P. R. *Can. J. Chem.* **1976**, *54*, 2280.
(3) Reddy, S. S.; Reddy, K. D.; Rao, M. V. P. *J. Chem. Eng. Data* **1982**, *27*, 173.
(4) Karunakar, J.; Reddy, K. D.; Rao, M. V. P. *J. Chem. Eng. Data* **1982**, *27*, 346.
(5) Rao, M. V. P.; Naidu, P. R. *Can. J. Chem.* **1974**, *52*, 788.
(6) Storkey, D. J.; Sallak, H. M.; Smith, B. D. *J. Chem. Thermodn.* **1973**, *5*, 741.
(7) Timmermans, J. "Physico-Chemical Constants of Pure Organic Compounds"; Elsevier: New York, 1965.
(8) Dreisbach, R. R. "Physical Properties of Chemical Compounds"; American Chemical Society: Washington, DC, 1955 and 1957.

Received for review September 23, 1983. Revised manuscript received April 23, 1984. Accepted May 18, 1984.

Viscosities and Activation Energies of Viscous Flow of the Ternary Mixtures of *n*-Hexane, Toluene, Chlorobenzene, and 1-Hexanol

Ramesh P. Singh* and Chandreshwar P. Sinha[†]
Department of Chemistry, Bhagalpur College of Engineering, Bhagalpur, India

Mixture viscosities and the densities of the ternary mixtures of *n*-hexane, toluene, chlorobenzene, and 1-hexanol were measured at 30, 40, 50, and 60 °C over the complete composition range. The experimental viscosity–composition–temperature data were compared with those calculated from an equation based on the significant liquid structure theory. Activation enthalpies and entropies for viscous flow have been obtained and their variations with composition have also been discussed.

Introduction

Considering the usefulness of the predictions of mixture viscosities with the help of pure-component data as input, our earlier work (*1*) on the binary mixtures of *n*-hexane with toluene, chlorobenzene, and 1-hexanol was extended to ternary mixtures. In this paper, we report the viscosities and activation energies of viscous flow of the title ternaries at different temperatures and include the comparison of the experimental data with those predicted by an equation based on significant liquid structure theory (SLS) using only pure-component parameters.

Experimental Section

Materials. *n*-Hexane, toluene, and chlorobenzene were BDH (India) chemicals, procured from Glaxo Laboratories (India) Ltd., Bombay, while 1-hexanol was a BDH (England) chemical, procured from BDH Chemicals Ltd., Poole, England. These chemicals were further purified by fractional distillation and drying. Experimentally determined densities, viscosities, and refractive indices of these liquids checked within allowed limits with the corresponding literature values (Table I).

The water used for checking the instruments and calibrating the pycnometers for density measurements was redistilled and deionized till it showed an electrical conductivity of <7.0 × 10^{-7} mho cm^{-1}. Before calibration, the dissolved air was expelled from the water used.

Experimental Measurements. Ternary liquid mixtures were prepared by weight in a chemical balance with an accuracy of 0.0001 g, using certified weights. The procedure remained the same as that followed in the case of binary mixtures (*1*, *2*), and, knowing the component weights, we calculated the exact compositions. The experimental determinations were carried out by using required volumes of the same stock solution. Ostwald viscometers used for viscosity measurements were thoroughly cleansed, dried, and calibrated in each case. Errors due to alignment and loading of viscometers were minimized by taking proper precautionary measures such that the viscometer limbs coincided with the vertical within 0.5° and the standard deviations for time of flow were well within 0.1%. The experimental procedure adopted for viscosity measurements was the same as that described elsewhere (*3*).

Densities were determined pycnometrically (*3*) by using distilled conductivity-grade water with 0.997 07 as its density at 25 °C for calibration. The pycnometer used in the experiments was of weld type (volume, 25 mL; and capillary diameter, <1 × 10^{-4} m).

In each case, viscosity and density measurements using the same stock solution were carried out in a Toshniwal GL-15 precision thermostat allowing sufficient time for attaining thermal equilibrium and minimizing evaporation. Bath temperatures

---

[†] Present address: Department of Chemistry, Ananda Chandra College, Jalpaiguri 735101, West Bengal, India.