the same feed composition but at different solvent flow rates, confirming that equilibrium was attained in the column.

Feed/solvent pinching would not occur at S/F ratios above a minimum value. The minimum S/F ratio for each system was determined experimentally and is given in Table II. The minimum ratio is approximately equal to the inverse of the distribution coefficient m, defined as

$$m = Y_e/X_f$$

where Y_e = alcohol loading in the exiting solvent phase and X_f = alcohol loading in the feed.

The measured distribution coefficients compared quite well with previously published values. Average percent differences from the literature of 5.5% and 8.4% were obtained for the SC/E/W (*9*) and SC/I/W (*11*) systems, respectively. The experimental uncertainty in the distribution coefficient values was ±2%.

Finally, it is interesting to compare the distribution coefficients for the SC/I/W system at 40 °C and 102.0 atm to those for the NC/I/W system at 25 °C and 81.6 atm. Values in Table II indicate that the alcohol loadings in the supercritical CO_2 phase are only 20% more than in near-critical CO_2.

Conclusions

A novel technique was developed to measure equilibrium information for liquid mixtures and high-pressure solvents. The phase equilibria for near-critical and supercritical CO_2/alcohol/water systems were measured by using this method, and the data compared favorably with previously reported values. For experiments with 2-propanol solute, it was observed that the solute loading in supercritical CO_2 was only slightly larger than its loading in near critical carbon dioxide. This implies that a commercial alcohol/water separation unit could be run as efficiently with near-critical carbon dioxide as with supercritical carbon dioxide, but for less cost due to the lower pressures involved.

Registry No. CO_2, 124-38-9; ethanol, 64-17-5; 2-propanol, 67-63-0.

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Excess Volumes of the System Benzene + 1,1,2-Trichloroethylene at 283.15 and 313.15 K

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Excess volumes were measured for the benzene + 1,1,2-trichloroethylene system at 283.15 and 313.15 K and atmospheric pressure. The excess volumes were positive, decreasing with temperature, and exhibited maxima at approximately 59.1 mol % benzene. Data have been correlated by generalized equations.

This article reports the excess volume measurements for (x)benzene + (1 − x)1,1,2-trichloroethylene at 283.15 and 313.15 K. Also reported are the empirical equations fitted to the results obtained at each temperature.

Experimental Methods

The excess volumes were measured directly by means of a Kumaran and McGlashan type continuous dilution dilatometer with a back-pressure device (*1*). The temperature of the water bath containing the dilatometer was kept constant to within ±0.001 K with a Tamson Model TCV 70 bath and associated cooler. Values of temperature were measured with an NBS calibrated thermometer to ±0.05 K. The operational technique has been described elsewhere) (*2*).

Table I. Experimental Densities at Various Temperatures and Refractive Indices at 293.15 K and Comparison with Literature Values

	density, kg/m³		refract. index
	283.15 K	313.15 K	293.15 K
	Experimental		
benzene	890.23	858.37	1.50067
trichloroethylene	1483.44	1431.78	1.44705
	Literature		
benzene	889.5[b]	857.7[b]	1.5011[c]
trichloroethylene	1482[a]	1430[a]	1.4773[c]

[a] Reference *3*. [b] Reference *4*. [c] Reference *5*.

An attempt was made to further purify the benzene (Aldrich purity >99.9%) and trichloroethylene (Aldrich purity >99%) by means of simple distillation with the first and last 20% of the distillate being discarded. Precision refractometry indicated that the purity of each product was not enhanced by this process, and hence, they were used as received. The reagents were

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Table II. Data Comparison for the Benzene + Cyclohexane System at 298.15 K

	std devn, $cm^3\ mol^{-1}$	max V^E, $cm^3\ mol^{-1}$	V^E at $x = 5$, $cm^3\ mol^{-1}$
this work	0.00275	0.6529	0.6523
Handa and Benson			
comparison 1	0.00157	0.6511	0.6509
comparison 2	0.00161	0.6520	0.6518
range of other works	0.00003–0.0050	0.6315–0.6555	0.6312–0.6552

Table III. Excess Molar Volumes at Various Temperatures for (x)Benzene + (1 − x)Trichloroethylene

x	V^E, $cm^3\ mol^{-1}$	δV^E, $cm^3\ mol^{-1}$	x	V^E, $cm^3\ mol^{-1}$	δV^E, $cm^3\ mol^{-1}$
		283.15 K			
0.0195	0.0091	0.0004	0.4879	0.2494	−0.0010
0.0593	0.0386	0.0021	0.5159	0.2563	0.0003
0.0909	0.0674	0.0028	0.5340	0.2624	0.0036
0.1221	0.0890	0.0047	0.5591	0.2665	0.0049
0.1604	0.1062	0.0068	0.6404	0.2622	0.0015
0.2003	0.1320	0.0052	0.6692	0.2516	−0.0048
0.2357	0.1537	0.0031	0.7059	0.2384	−0.0090
0.2656	0.1677	0.0095	0.7514	0.2253	−0.0053
0.3007	0.1837	0.0076	0.7853	0.1964	−0.0172
0.3350	0.1992	−0.0007	0.8422	0.1678	−0.0081
0.3729	0.2138	−0.0040	0.8969	0.1247	−0.0029
0.4264	0.2325	−0.0007	0.9441	0.0799	0.0045
0.4459	0.2375	−0.0019	0.9691	0.0463	0.0027
0.4671	0.2413	−0.0040			
		313.15 K			
0.0399	0.0368	0.0047	0.5124	0.2114	−0.0038
0.0796	0.0430	−0.0134	0.5133	0.2138	−0.0015
0.1219	0.0797	0.0022	0.5293	0.2145	−0.0029
0.1524	0.0894	−0.0018	0.5345	0.2174	−0.0005
0.1812	0.1043	0.0009	0.5594	0.2171	−0.0027
0.2187	0.1208	0.0019	0.5874	0.2215	0.0009
0.2647	0.1401	0.0024	0.6130	0.2192	−0.0006
0.3193	0.1684	0.0089	0.6335	0.2123	−0.0059
0.3397	0.1720	0.0051	0.6557	0.2173	0.0016
0.3654	0.1794	0.0027	0.6791	0.2116	−0.0003
0.3907	0.1908	0.0054	0.7082	0.2082	0.0026
0.3924	0.1890	0.0030	0.7388	0.1971	0.0000
0.4143	0.1918	−0.0011	0.7652	0.1931	0.0047
0.4186	0.1969	0.0027	0.7925	0.1825	0.0048
0.4422	0.1925	−0.0083	0.8237	0.1650	0.0019
0.4461	0.2036	0.0018	0.8423	0.1518	−0.0014
0.4604	0.2026	−0.0028	0.8690	0.1353	−0.0015
0.4676	0.2039	−0.0031	0.8905	0.1199	−0.0017
0.4791	0.2049	−0.0046	0.9184	0.0989	0.0004
0.4935	0.2125	0.0003	0.9515	0.0648	−0.0004
0.4938	0.2115	−0.0008	0.9697	0.0434	0.0002

also heated prior to loading the dilatometer to prevent degassing problems. The observed densities and refractive indices of benzene and trichloroethylene at each of the temperatures employed are given in Table I along with the published values (*3–5*) for comparison.

In an effort to measure the accuracy of the equipment and experimental technique used in this investigation, the test system, benzene + cyclohexane at 298.15 K, was studied first. There were 96 data points used in this work in an effort to accurately describe this system. Handa and Benson went to great lengths to document the test system parameters in their work (*6*). Table II is a comparison of the test system data. As indicated by this table, the accuracy of the apparatus and experimental procedure used in this investigation is well within acceptable limits.

Results and Discussion

Table IV. Curve-Fitting Data for the Benzene + Trichloroethylene System

	283.15 K	313.15 K
A_0	1.01210	0.85322
A_1	−0.40853	−0.33270
A_2	0.06809	−0.05935
A_3	0.0	0.00858
A_4	0.0	0.46777
s, $cm^3\ mol^{-1}$	0.00603	0.00412

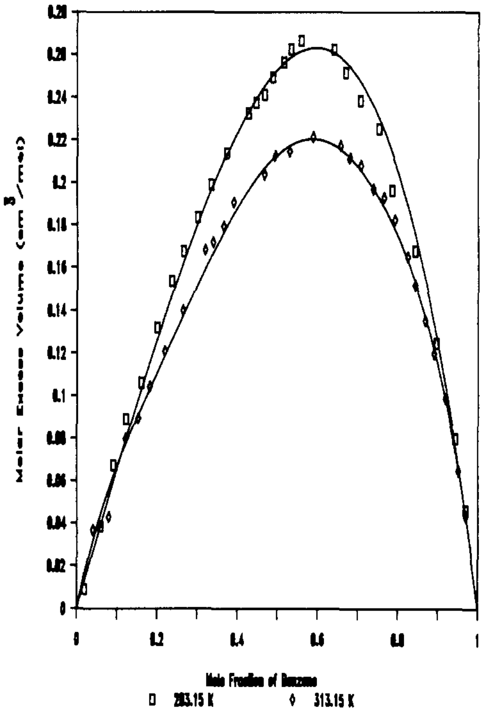

Figure 1. Fitted V^E curves and experimental points for benzene + trichloroethylene at (□) 283.15 and (◇) 313.15 K.

Table III lists the excess molar volumes V^E calculated from measurements made with the dilatometer on the system benzene + trichloroethylene. There were 27 data points collected at 283.15 K and 42 at 313.15 K. For each temperature, equations of the form

$$V^E(\mathrm{cm^3\ mol^{-1}}) = x(1-x)\sum_{k=0}^{\leq 4} A_k(1-2x)^k \quad (1)$$

were fitted to the experimental results. The deviations, δV^E, of the measured values from the correlations are also shown in Table III. The parameters A_k and the standard deviations (s) of the fit are listed in Table IV. The number of parameters utilized was determined by sequentially fitting the data with larger numbers of parameters until either the optimum standard deviation was determined or five constants were used. Figure 1 shows the fitted V^E curves together with the experimental points. For graphical clarity, only 28 points are shown for 313.15 K in Figure 1.

In all cases V^E is positive and the curves are skewed to the right. The maximum occurs at a value of approximately 59.1 mol % benzene. The excess volumes decrease with increasing temperature. For example, at the maximum point, V^E(283.15 K) was 0.2632 $cm^3\ mol^{-1}$ while V^E(313.15 K) was 0.2205 $cm^3\ mol^{-1}$.

Martin, Rodriguez, and Villena (*7*) report measured densities (to 0.001 g/cm^3) of benzene + trichloroethylene at various temperatures. Excess volume data calculated from these measurements also exhibit slightly skewed uniformly positive curves decreasing with increasing temperatures. Location of the maximum is difficult to locate precisely since only four points are available for each temperature. Values of the excess volume calculated from the densities are several times larger than those reported in the present study. Errors in their measured densities of less than $^1/_2$ of 1% would, however, bring the two sets of data into agreement. Much larger errors in the direct measurement of the volumes, as in the case of dilatometric measurements, can be tolerated without making such significant variations.

These results allow us to draw a qualitative conclusion concerning the dependence of excess molar entropy S^E on pressure. According to Maxwell's equation

$$(\partial S^E/\partial P)_T = -(\partial V^E/\partial T)_P \qquad (2)$$

and from the previous discussion, we get a positive derivative $(\partial S^E/\partial P)_T$, and the deviation from ideal behavior thus increases with pressure.

Glossary

A_k	curve-fitting parameters
P	pressure
S^E	excess entropy
T	temperature
V^E	excess volume
δV^E	deviation of measured excess volumes from correlation
x	mole fraction benzene

Registry No. Benzene, 71-43-2; trichloroethylene, 79-01-6.

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Thermodynamic Properties of Some Organic Compounds with Tetrachloroterephthaloyl Oligomers by Gas Chromatography

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Specific retention volumes of 30 solutes in three stationary phases, *O*,*O*″-1,3-propanediyl *O*′,*O*‴-di-*n*-propyl bis(tetrachloroterephthalate) at 130, 140, and 150 °C, *O*,*O*″-1,3-propanediyl *O*′,*O*‴-di-*n*-butyl bis(tetrachloroterephthalate) at 110, 122, and 130 °C, and a propyl–trimer mixture at 110 and 130 °C, were determined by gas chromatography. Activity coefficients at infinite dilution and excess partial molar thermodynamic properties are reported at 130 °C. Relative retentions and selectivities for three series of meta and para isomers in the aforementioned liquid phases are discussed. Also, the variation of specific retention volume and activity coefficient with the liquid-phase molecular weight of a group of tetrachloroterephthalate esters is described.

Introduction

It has been shown in a previous work (*1*) that tetrachloroterephthalate esters are suitable as a stationary liquid phase in gas chromatography. The wide range of temperatures over which they can be used, the possibility of making derivative compounds taking the tetrachloroterephthaloyl nucleus as the basic unit (*2*, *3*), and their selectivity for the separation of aromatic isomers are some of the major features that make them a good choice for a liquid phase in gas chromatography.

Data of thermodynamic properties at 100 and 110 °C have been reported already (*1*) for four tetrachloroterephthalate esters (TCTP) (di-*n*-propyl–, di-*n*-butyl–, di-*n*-amyl–, and di-*n*-octyl–TCTP) with aromatic compounds as solvents.

To further explore the behavior of TCTP esters as liquid phases in chromatography, a study of thermodynamic properties of 30 solutes in higher molecular weight TCTP esters is reported in this work. The synthesis of the esters used as stationary phases has been reported (*2*). These include the compounds *O*,*O*″-1,3-propanediyl *O*′,*O*‴-di-*n*-propyl bis(tetrachloroterephthalate) (1,3-propanediyl$(PrTCTP)_2$), *O*,*O*″-1,3-propanediyl *O*′,*O*‴-di-*n*-butyl bis(tetrachloroterephthalate) (1,3-propanediyl$(BuTCTP)_2$), and bis(3-((4-(propoxycarbonyl)-2,3,5,6-tetrachlorobenzoyl)oxy)propyl) tetrachloroterephthalate. This last compound was not used in its pure form as the liquid phase because of its high melting point but was mixed with 1,3-propanediyl$(PrTCTP)_2$ in 59.6 wt % of this TCTP ester. This mixture will be referred to throughout this work as Pr–trimer mixture.

Experimental Section

The gas chromatograph used for this study is a modified Perkin-Elmer Model 800 gas chromatograph equipped with a thermal conductivity detector. Its modifications were described in a previous work (*1*). The column temperature could be controlled to ±0.02 °C and was measured with a precision thermometer inserted into the center of the oven.

The columns with 1,3-propanediyl$(PrTCTP)_2$ and Pr–trimer mixture were made of stainless steel tubing, 0.64 cm × 1.4 m, the liquid phases being supported on 60-80 mesh Gas Chrom RZ from Applied Science Laboratory, Inc. The amount of liquid phase in both columns was 15%. The column with 1,3-propanediyl$(BuTCTP)_2$ was prepared in the same way but was made of 0.48 cm × 2.40 m tubing and the amount of liquid phase was 8% of the dried coated support. The packed columns were conditioned under a gentle flow of helium for about 18 h at 100 °C.

Commercial solutes were used without any further purification, and mixtures containing between four and eight solutes were injected depending on the individual retention times of the

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