Table VIII. Model Parameters for the Three Binary Systems

	anisaldehyde (1)/ methyl anisate (2)	anisaldehyde (1)/ anisyl alcohol (2)	methyl anisate (1)/ anisyl alcohol (2)
	Wilson Model		
$(\lambda_{12} - \lambda_{11})/R$	231.36	-176.12	20.917
$(\lambda_{21} - \lambda_{22})/R$	-185.82	338.09	109.43
	NRTL Model (α = 0.3)		
$(g_{12} - g_{22})/R$	-184.56	418.94	46.737
$(g_{21} - g_{11})/R$	236.78	-261.18	81.498
	UNIQUAC Model		
$(u_{12} - u_{22})/R$	-110.87	221.97	60.092
$(u_{21} - u_{11})/R$	134.92	-159.12	-28.104

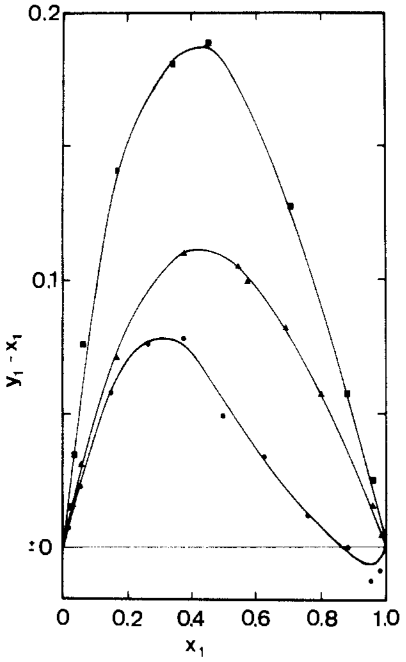

Figure 1. Vapor-liquid equilibria of the three binary systems. Plots of $y_1 - x_1$ vs. x_1: (▲) anisaldehyde (1)/methyl anisate (2), (■) anisaldehyde (1)/anisyl alcohol (2), (●) methyl anisate (1)/anisyl alcohol (2). Equilibrium curves are calculated by using the UNIQUAC model.

the difference $y_1 - x_1$ is plotted against x_1.

The azeotropic data at 2 kPa for the methyl anisate/anisyl alcohol system are 136.3 °C at a mole fraction of 0.892 of methyl anisate.

Acknowledgment

We express our grateful thanks to Dr. F. Caesar for his kind help in obtaining the gas-chromatographic data.

Glossary

A, B, C	parameters of the Antoine equation
p	total pressure, kPa
p_i°	vapor pressure of pure component i, kPa
q	area parameter
R	gas constant
r	volume parameter
t	temperature, °C
v	molar volume, cm^3/mol
x_i	liquid-phase mole fraction of component i
y_i	vapor-phase mole fraction of component i
g_{ij}, u_{ij}, λ_{ij}	interaction parameter between components i and j
α	nonrandomness parameter
γ_i	activity coefficient of component i

Registry No. Anisaldehyde, 123-11-5; methyl anisate, 121-98-2; anisyl alcohol, 105-13-5.

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Received for review March 5, 1984. Accepted June 19, 1984.

Solubilities of Methoxy-1-tetralone and Methyl Nitrobenzoate Isomers and Their Mixtures in Supercritical Carbon Dioxide

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Solubilities in supercritical carbon dioxide at 308 K over a pressure range of 80–280 bar were measured for two sets of isomers: methoxy-1-tetralone and methyl nitrobenzoate. Solubilities of binary mixtures of two isomers within each isomer group in supercritical carbon dioxide were also measured at 308 K and 110 bar. The data show solubility trends within an isomer group, and the influence of solute composition and condensed-phase behavior on the mixture solubilities.

Introduction

Extractions with supercritical fluids as a solvent have received wide attention recently. The major advantages of using supercritical fluids are that the solvent capacities can be controlled by the system pressure and temperature and that the viscosities are lower than conventional liquid solvents. Carbon dioxide is a preferred supercritical solvent, since it is nontoxic, nonflammable, environmentally acceptable, and relatively inexpensive. Its low critical temperature (304 K) is especially suitable for thermally labile materials. Supercritical carbon dioxide extraction has been commercially applied to caffeine removal from green coffee beans (*1*), and bitter-component recovery from hops (*2*). Other applications have been described in several review articles (*3*–*7*).

Despite the successful application of supercritical fluids to some commercial processes, the understanding of associated phenomena is limited. One potentially useful application of supercritical fluid extraction is for the isolation and purification of pharmaceuticals. These compounds, whether synthetic or derived from natural sources, are often complex and thermally labile. Although Stahl and others (*8*) have demonstrated that these molecules can be extracted, no extensive data base has been reported. These data are essential for the design of a commercial-scale extraction system.

This study was designed to reveal solubility behavior in supercritical carbon dioxide and to gather information for isomer separation. Two model isomer systems, methoxy-1-tetralones and methyl nitrobenzoates, were investigated. These isomers are similar to some pharmaceuticals in their structures and functional groups. Solubilities of pure compounds as a function of pressure were obtained, effects of the mixture composition which are important in separations were studied, and phase changes under extraction conditions were observed.

Experimental Section

A schematic diagram of a flow type apparatus used to obtain the experimental data is shown in Figure 1 (*9*, *10*). Liquid carbon dioxide from a warmed cylinder equipped with a full-length eductor tube is pumped to the desired pressure with a Milton Roy ConstaMetric III pump. The system pressure is monitored by a Heise pressure transmitter (715T and 715R) and controlled by a back-pressure regulator which allows excess liquid to recirculate back to the pump suction side. Fluctuations in pressure due to pumping are less than 1% of the operation pressure over the entire pressure range.

The extractor is a $^3/_4$ in. o.d. × 12 in. 316ss, medium-pressure tubing. The solute is packed into the tubing in several short sections separated with glass wool. For mixtures, the solutes are melted, mixed, cooled to room temperature, and then pulverized before packing into the extractor. Before flowing into the extractor, the carbon dioxide is preheated to the desired temperature. The preheater and the extractor are submerged in a water bath where the temperature is maintained within 0.1 K of the set point. For observation of phase behavior, the extractor is replaced with a Jerguson gage (Model 17T40) with a sight glass.

After saturation, the supercritical solvent saturated with solutes is expanded to atmospheric pressure through a heated metering valve (Whitey SS-31RS4). The flow rate is regulated by the metering valve. Solvent flow rates used in this study range from 0.02 to 0.03 standard m^3/h. Within this range, the flow rate has a negligible effect on the experimental results. A similar negligible flow rate effect was reported elsewhere (*9*). The solutes separate from gaseous carbon dioxide and accumulate in the Pyrex U-tube separator. The solute-free gas is vented through a rotameter and then a dry test meter where, respectively, the instantaneous and accumulated gas flow rates are monitored. The U-tube is packed with glass wool to prevent entrainment. Separation of solute and gas is completed in one U-tube as evidenced from the fact that nothing is collected in the second U-tube in series.

Pure-component solubilities were calculated from the weight of the collected solute and the accumulated gas flow. The solubility of the supercritical solvent in the condensed phase was not measured. For mixtures, the compositions of the extracts were analyzed by HPLC (Hewlett-Packard 1082B). The compositions of the condensed phase, and thus the fluid phase, inside the extractor changed somewhat as the extraction proceeded. Due to experimental difficulty, these changes were not monitored. However, since less than 5% of the total extractor loading was extracted in each experiment, these composition changes could only add as much as 1.5% of uncertainty to the final results which are averaged over the extracting period.

Table I. Experimental Mole Fractions of Naphthalene in Supercritical Carbon Dioxide at 318 and 328 K

T = 318 K		T = 328 K	
P, bar	y	P, bar	y
83	0.0009	112	0.0058
103	0.0089	138	0.0223
139	0.0198	172	0.0323
172	0.0223	276	0.0546
207	0.0243		
276	0.0252		

Table II. Sources, Purities, and Melting Points of the Substances

substance	source	purity, wt %	mp, K
carbon dioxide	Matheson	99.99	
naphthalene	Eastman	NA[a]	353–354
5-methoxy-1-tetralone	Aldrich	98	357–361.5
6-methoxy-1-tetralone	Aldrich	99	350–351
7-methoxy-1-tetralone	Aldrich	99	334–335
methyl *o*-nitrobenzoate	Aldrich	99	260
methyl *m*-nitrobenzoate	Aldrich	NA[a]	351–353
methyl *p*-nitrobenzoate	Aldrich	99	367–369

[a] NA: not available.

Table III. Experimental Mole Fractions of Pure Methoxy-1-tetralone Isomers in Supercritical Carbon Dioxide at 308 K

7-methoxy-1-tetralone		6-methoxy-1-tetralone		5-methoxy-1-tetralone	
P, bar	y	P, bar	y	P, bar	y
85	0.0074	83	0.0013	83	0.0022
111	0.0172	111	0.0035	110	0.0042
138	0.0241	138	0.0052	138	0.0044
179	0.0369	179	0.0068	172	0.0049
219	0.0585	219	0.0100	207	0.0054
276	0.0753	277	0.0120	275	0.0060

Table IV. Experimental Mole Fractions of Pure Methyl Nitrobenzoate Isomers in Supercritical Carbon Dioxide at 308 K

methyl *o*-nitrobenzoate		methyl *m*-nitrobenzoate		methyl *p*-nitrobenzoate	
P, bar	y	P, bar	y	P, bar	y
83	0.0057	83	0.0027	83	0.0012
111	0.0146	111	0.0063	110	0.0048
138	0.0212	200	0.0160	138	0.0070
220	0.0346	277	0.0191	172	0.0094
278	0.0512			207	0.0111
				272	0.0149

A number of experiments were conducted to assure that the system would provide reliable data. Results from the naphthalene–carbon dioxide system are listed in Table I. Figure 2 compares naphthalene solubility data from this study with those reported in the literature (*10*, *11*). Our results agree with those reported data to better than 5%. Solubilities of naphthalene in supercritical carbon dioxide at various temperatures were also reported by other investigators (*12*, *13*).

Sources, purities, and melting points of the substances used in this study are listed in Table II. The chemicals were used without further purification.

Results and Discussion

The solubilities of pure methoxy-1-tetralone isomers and methyl nitrobenzoate isomers in supercritical carbon dioxide at

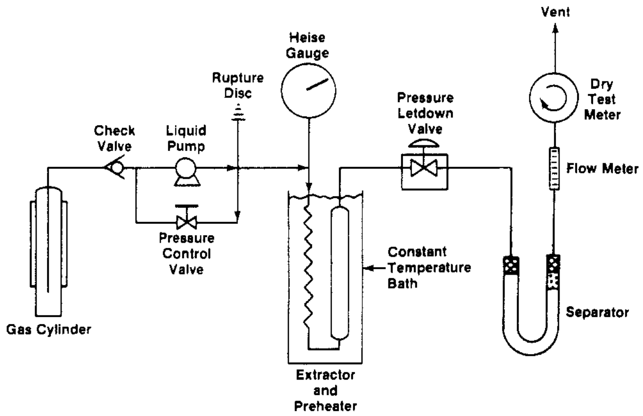

Figure 1. Schematic diagram of the experimental apparatus for measuring solubilities.

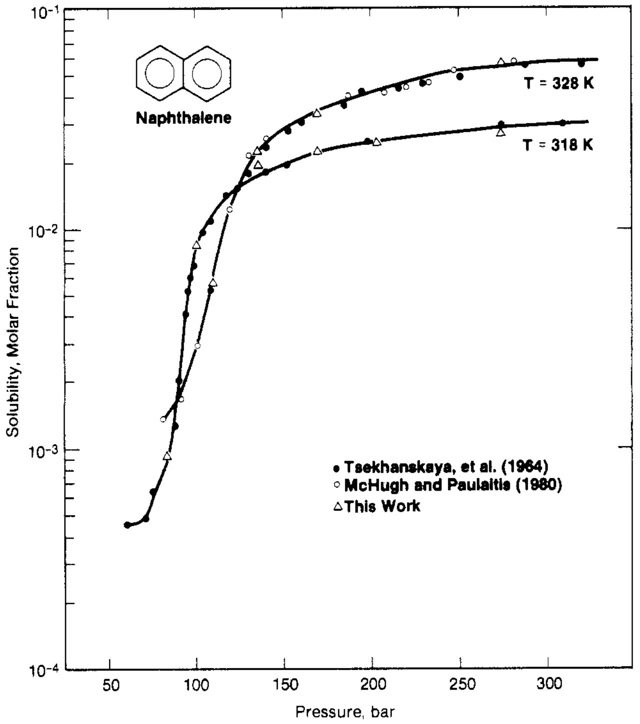

Figure 2. Experimental solubilities for pure naphthalene in supercritical carbon dioxide at 318 and 328 K.

Table V. Experimental Mole Fractions of 6-Methoxy-1-tetralone and 7-Methoxy-1-tetralone Mixtures in Supercritical Carbon Dioxide at 308 K and 110 bar

condensed phase x_6:x_7	fluid phase y_6	y_7	phases present
0:100	0	0.0172	S-L-F
10:90	0.0008	0.0124	L-F
30:70	0.0024	0.0090	L-F
50:50	0.0042	0.0060	L-F
65:35	0.0050	0.0036	S-L-F
70:30	0.0047	0.0028	S-L-F
70:30	0.0051	0.0031	S-L-F
80:20	0.0046	0.0030	S-F
90:10	0.0048	0.0024	S-F
100:0	0.0035	0	S-F

Table VI. Experimental Mole Fractions of 7-Methoxy-1-tetralone and 5-Methoxy-1-tetralone Mixtures in Supercritical Carbon Dioxide at 308 K and 110 bar

condensed phase x_7:x_5	fluid phase y_7	y_5	phases present
0:100	0	0.0042	S-F
30:70	0.0046	0.0061	S-L-F
70:30	0.0090	0.0028	L-F
100:0	0.0172	0	S-L-F

Table VII. Experimental Mole Fractions of Methyl *o*-Nitrobenzoate and Methyl *m*-Nitrobenzoate Mixtures in Supercritical Carbon Dioxide at 308 K and 110 bar

condensed phase x_o:x_m	fluid phase y_o	y_m	phases present
0:100	0	0.0063	S-F
30:70	0.0042	0.0102	S-L-F
70:30	0.0108	0.0051	L-F
100:0	0.0146	0	L-F

Table VIII. Experimental Mole Fractions of Methyl *o*-Nitrobenzoate and Methyl *p*-Nitrobenzoate Mixtures in Supercritical Carbon Dioxide at 308 K and 110 bar

condensed phase x_o:x_p	fluid phase y_o	y_p	phases present
0:100	0	0.0048	S-F
30:70	0.0072	0.0143	S-L-F
70:30	0.0110	0.0069	L-F
100:0	0.0146	0	L-F

308 K and different pressures are listed in Tables III and IV, respectively. These equilibrium solubilities are also plotted in Figures 3 and 4. Methyl *o*-nitrobenzoate is liquid at room temperatures and pressures, while 7-methoxy-1-tetralone is solid under ambient conditions but liquid under carbon dioxide pressure (melting point: 305 K at 75 bar). The other pure solutes are solids under ambient or extraction conditions. Figure 3 shows that, for the methoxy-1-tetralones at high pressure, the 7-position isomer has the highest solubility, followed by the 6-position isomer and then by the 5-position isomer. At pressures lower than 125 bar, the 5-position isomer has a higher solubility than the 6-position isomer. For the methyl nitrobenzoates, the ortho isomer has the highest solubility, followed by the meta isomer and then by the para isomers, as shown in Figure 4. Solubilities of several other isomers in supercritical carbon dioxide were reported by Stahl et al. (*8*). Their qualitative results are consistent with this observation that the closer the functional groups of an isomer, the higher the solubility of this isomer in supercritical carbon dioxide.

The solubility differences within an isomer group can be explained qualitatively by the melting point effect. For ideal solutions, the solubility of a solid solute in a liquid solvent can be expressed as (*14*)

$$\ln (1/y) = (\Delta h^f/RT)(1 - T/T_M) \tag{1}$$

where y is the solubility of a solute in a solvent at the system temperature T, T_M the melting point, Δh^f the heat of fusion of the solute, and R the gas constant. Equation 1 can be used to describe qualitatively the relative solute solubilities in supercritical fluids. At constant temperature T, T/T_M's are smaller for higher melting points, T_M's; thus, from eq 1 the solubilities, y's, are smaller. Furthermore, the heat of fusion for isomers generally increases with the melting point; this phenomenon makes the solubilities of the isomers even more dependent on their melting temperatures.

Tables V and VI list the solubilities of methoxy-1-tetralone mixtures in carbon dioxide at 308 K and 110 bar, and Tables VII and VIII the solubilities of methyl nitrobenzoate mixtures at the same conditions. Note that the condensed phase may contain solids and/or liquid. The composition of the condensed phases shown in the tables is the composition excluding carbon dioxide. The data from 7-methoxy-1-tetralone and 6-methoxy-1-tetralone in carbon dioxide as a function of condensed-phase compositin are also plotted in Figure 5. As the figure shows, the solubility of 7-methoxy-1-tetralone in the ternary system

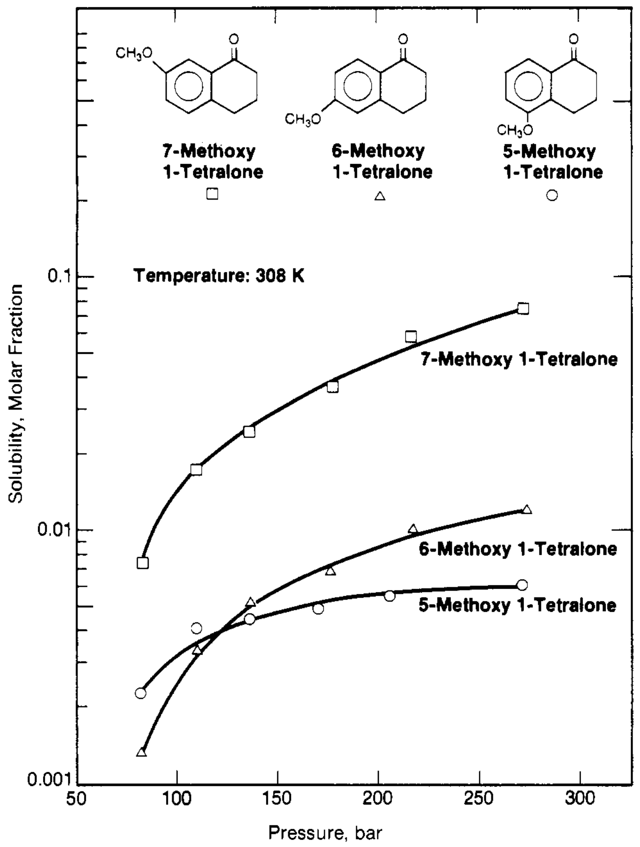

Figure 3. Experimental solubilities for three pure methoxy-1-tetralone isomers in supercritical carbon dioxide at 308 K.

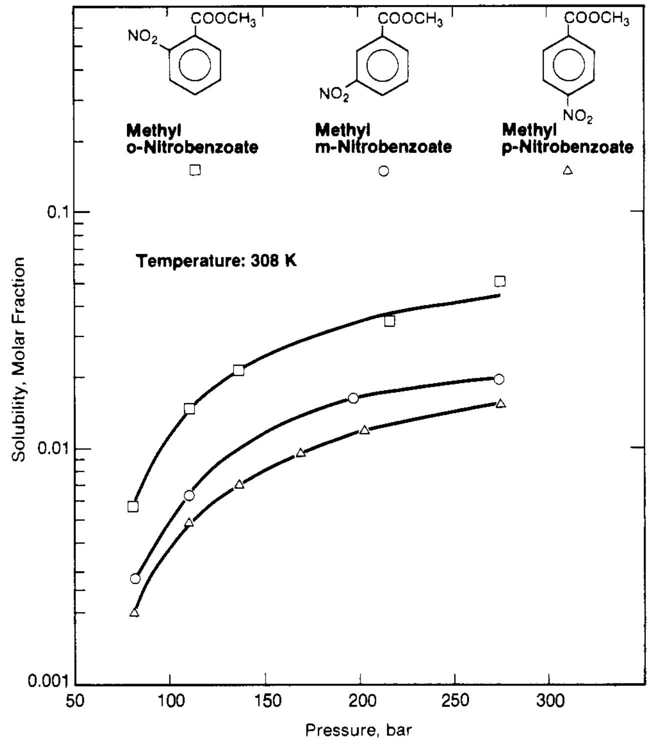

Figure 4. Experimental solubilities for three pure methyl nitrobenzoate isomers in supercritical carbon dioxide at 308 K.

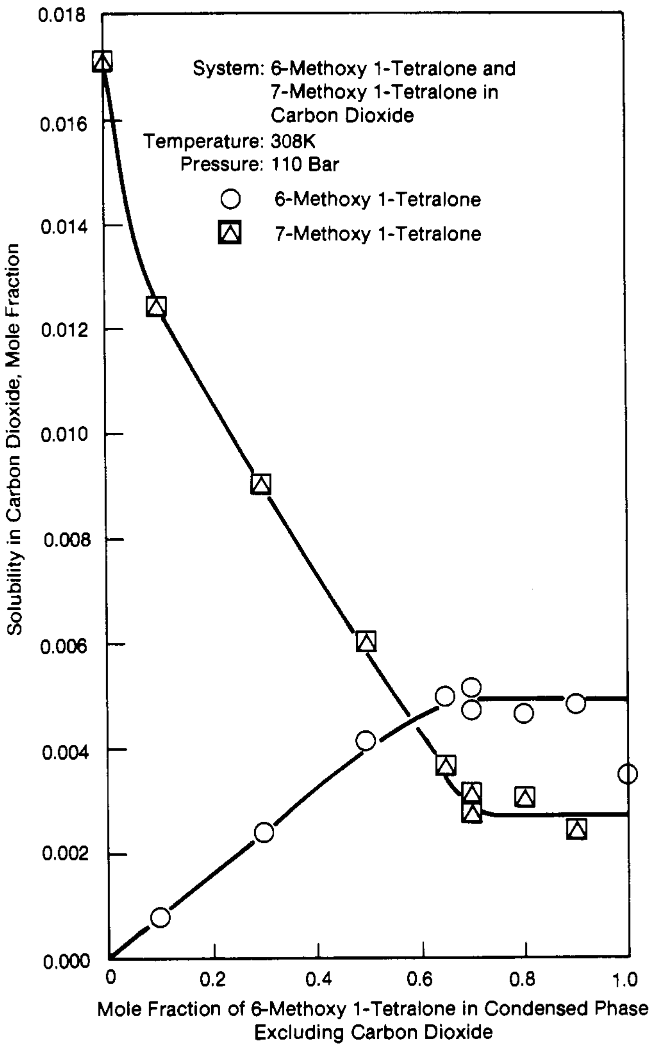

Figure 5. Experimental solubilities for 7-methyl-1-tetralone and 6-methoxy-1-tetralone mixture in supercritical carbon dioxide at 308 K and 110 bar.

decreases rapidly as its composition in the mixture initially decreases from the pure component. At a condensed-phase mole fraction of 0.35 the solubility of 7-methoxy-1-tetralone levels off before further decreases with composition. This change in solubility could be tied to a phase change. Referring to Table V, the condensed phase rich in 7-methoxy-1-tetralone is liquid. However, at a composition of 65:35, the 6-methoxy-1-tetralone-rich region, solid phase begins to form. The solid is primarily composed of 6-methoxy-1-tetralone, and the liquid composition remains constant (65:35). It follows that the solubility of 7-methoxy-1-tetralone in carbon dioxide is relatively constant over this concentration range. On the other hand, the solubility of 6-methoxy-1-tetralone is enhanced by the addition of the second solute at low concentration. The solubility enhancement by the third component was also reported by several investigators (*13*, *15*, *16*). As the concentration of 7-methoxy-1-tetralone increases, the solid phase disappears, and the solubility decreases with composition. Similar solubility behaviors are also observed in other mixture systems with supercritical carbon dioxide: 7-methoxy-1-tetralone and 5-methoxy-1-tetralone (Table VI), methyl *o*-nitrobenzoate and methyl *m*-nitrobenzoate (Table VII), and methyl *o*-nitrobenzoate and methyl *p*-nitrobenzoate Table VIII).

The above facts reveal that if the solute mixture is liquid under extraction conditions, the solubility of an individual component decreases with the addition of the second solute. This is attributed to the Raoult's law effect and is similar to binary liquid–vapor equilibria in which the vapor pressure of a component is reduced by increasing the fraction of the second component. However, if the solid phase of a component is also present in the liquid mixture, then the solubility of this solute can be greatly enhanced. This is attributed to the solvent modification effect. Additional experiments are currently under way to further reveal phase behaviors of these isomer systems.

Acknowledgment

We gratefully acknowledge Smith Kline & French Laboratories for their permission to publish this work.

Glossary

F	fluid phase
Δh^f	heat of fusion
L	liquid phase
P	pressure, bar
R	gas constant
S	solid phase
T	temperature, K
x	condensed-phase mole fraction
y	fluid-phase mole fraction

Subscripts

M	melting point
m	methyl *m*-nitrobenzoate
o	methyl *o*-nitrobenzoate
p	methyl *p*-nitrobenzoate
5	5-methoxy-1-tetralone
6	6-methoxy-1-tetralone
7	7-methoxy-1-tetralone

Registry No. Carbon dioxide, 124-38-9; naphthalene, 91-20-3; 5-methoxy-1-tetralone, 33892-75-0; 6-methoxy-1-tetralone, 1078-19-9; 7-methoxy-1-tetralone, 6836-19-7; methyl *o*-nitrobenzoate, 606-27-9; methyl *m*-nitrobenzoate, 618-95-1; methyl *p*-nitrobenzoate, 619-50-1.

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Excess Volumes of Binary Mixtures of 1,1,2,2-Tetrachloroethane with *n*-Alkanes (C_6–C_9)

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Excess volumes for binary mixtures of 1,1,2,2-tetrachloroethane with *n*-hexane, *n*-heptane, *n*-octane, and *n*-nonane have been determined at 303.15 and 313.15 K. V^E is negative over the whole range of composition in the mixtures of 1,1,2,2-tetrachloroethane with *n*-hexane and the function is positive over the whole range of composition in the remaining mixtures. The results have been ascribed to interstitial accommodation of *n*-hexane between the aggregates of self-associated chloroalkane and the structure-breaking effects of *n*-heptane, *n*-octane, and *n*-nonane. The results also have been used to show that increase in chain length of the alkane leads to an increase in the algebraic values of the excess function.

Introduction

The present work forms a part of the program to measure excess volumes and isentropic compressibilities for several binary mixtures (*1-9*) containing chloroalkanes as a common component. The work was taken up to gain insight into the nature and degree of interaction between like and unlike molecules. The binary mixtures studied in the present work include 1,1,2,2-tetrachloroethane + *n*-hexane, + *n*-heptane, + *n*-octane, and + *n*-nonane at 303.15 and 313.15 K.

Experimental Section

Excess volumes were measured by using a single composition per loading type dilatometer described by Rao and Naidu (*10*). The mixing cell contained two bulbs of different capacities that were connected through a U-tube having mercury to separate the two compartments. One end of the first bulb was fitted with a capillary outlet and the opposite end of the second bulb was closed with a ground-glass stopper. Four dilatometers of this type were used to cover the whole range of composition. The composition of each mixture was determined directly by weighing. All weights were corrected for buoyancy. Measurements were made by using a thermostatic bath controlled to within ±0.01 K. The excess volumes were reproducible to ±0.003 $cm^3\ mol^{-1}$.

Table I. Densities, ρ, of Pure Liquids at 303.15 K

	$\rho/(g\ cm^{-3})$	
component	present work	lit.
1,1,2,2-tetrachloroethane	1.578 51	1.578 60
n-hexane	0.650 64	0.650 70
n-heptane	0.675 30	0.675 38
n-octane	0.694 59	0.694 50
n-nonane	0.709 98	0.709 99

Purification of Materials. 1,1,2,2-Tetrachloroethane (Riedel) was purified by the method described earlier (*7*). *n*-Hexane and *n*-heptane supplied by BDH (England) and *n*-octane and *n*-nonane supplied by Veb (West Germany) were purified by the methods described by Reddick and Bunger (*11*). *n*-Hexane was shaken several times with concentrated sulfuric acid, then with a 0.1 N solution of potassium permanganate in 10% sulfuric acid, and finally with a 0.1 N solution of permanganate in 10% sodium hydroxide. The sample was washed with water, dried over sodium wire, and fractionally distilled. *n*-Heptane was shaken twice with concentrated sulfuric acid and washed with

0021-9568/85/1730-0078$01.50/0