

Vapor–Liquid Equilibria for the 1,1,1,2-Tetrafluoroethane + *m*-Cresol and + *p*-Cresol and 1,1,1,2-Tetrafluoroethane + *m*-Cresol + *p*-Cresol Systems

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Compositions in vapor and liquid phases for the binary systems 1,1,1,2-tetrafluoroethane (HFC-134a) + *m*-cresol and HFC-134a + *p*-cresol were measured by a dual recirculation technique over a pressure range from (0.3 to 2.4) MPa at (343.2, 363.2, and 383.2) K. Vapor–liquid equilibrium was also measured over the same temperature and pressure ranges for the ternary system HFC-134a + *m*-cresol + *p*-cresol with three different ratios of *m*-cresol to *p*-cresol in the liquid phase.

Introduction

Cresol isomers are in large demand for manufacturing antioxidants, phenolic resins, plasticizers, and inhibitors (Lone et al., 1992). Owing to their close boiling points, it is difficult to separate *p*- and *m*-cresols from their mixture by distillation. When the crystallization and adsorption techniques are used, some disadvantages exist, such as the existence of a highly viscous fluid at low temperatures and the requirement of a large amount of desorbent (Tasaka et al., 1977). Because of these disadvantages, use of 1,1,1,2-tetrafluoroethane (HFC-134a) as a solvent to separate *m*- and *p*-cresols may be an alternative separation method. HFC-134a was chosen as a solvent on the following basis: (1) it is a currently environmentally acceptable chemical; (2) it can be easily recovered after separation because of its low boiling point (247 K); (3) the operation pressure may be lower than the frequently used supercritical carbon dioxide; (4) it is a polar compound. To determine if HFC-134a is a good solvent, phase equilibrium data for HFC-134a and cresol isomers are needed.

In this study, vapor–liquid equilibrium data for the binary systems HFC-134a + *m*-cresol and HFC-134a + *p*-cresol and for the ternary system of HFC-134a + *m*-cresol + *p*-cresol over the pressure range from (0.3 to 2.4) MPa at (343.2, 363.2, and 383.2) K are reported. The Peng–Robinson equation of state (Peng and Robinson, 1976) was used to correlate the composition data in the vapor and liquid phases.

Experimental Section

The experimental apparatus of the dual-recirculation operation used for the VLE measurements is illustrated in Figure 1. The entire apparatus was constructed with 0.63-cm o.d. stainless steel 316 tubing except the equilibrium cell. *m*- and *p*-cresol isomers were purchased from Janssen Co. with a claimed purity of 99+%. Both chemicals were used without further purification. The equilibrium cell, having a diameter of 6.0 cm and a volume of 700 mL, was filled with 100–300 mL of *m*- or *p*-cresol or the mixture of *m*- and *p*-cresols. A magnetic stirring bar was

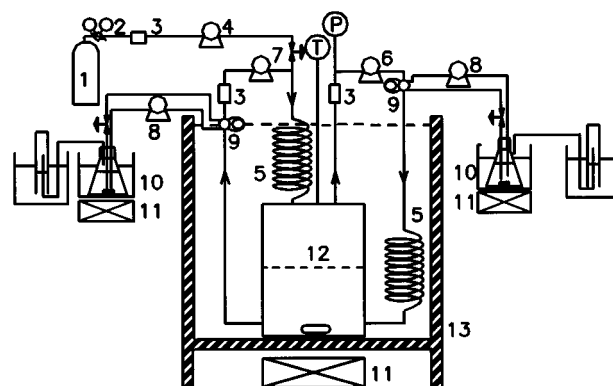


Figure 1. Schematic diagram of apparatus: (1) HFC-134a cylinder; (2) pressure regulator; (3) filter; (4) metering pump; (5) coil; (6) gas recirculation pump; (7) liquid recirculation pump; (8) peristaltic pump; (9) sampling valve; (10) cold trap; (11) stirrer; (12) equilibrium cell; (13) constant-temperature bath; (P) pressure gauge; (T) temperature indicator.

placed in the cell to provide agitation. The equilibrium cell was immersed in a constant-temperature bath (Yihdern Co.) whose temperature could be controlled to within ± 0.5 K. The actual pressure was monitored by a pressure gauge (Druck Inc.) that had an accuracy of ± 0.003 MPa.

HFC-134a with a purity of 99.95+% (Daikin Co.) was compressed by a metering pump (LDC Analytical, NSI-33R) and was allowed to fill the whole system. When the temperature and pressure reached the desired values, the liquid cresol and the HFC-134a gas in the equilibrium cell were recirculated by two metering pumps (Thermo Separation Products, model 396). In each run, the pressure could be maintained to within ± 0.02 MPa of the desired value. After a certain period of operation, the liquid and gas samples were collected by two six-port sampling valves located in the liquid and gas recirculation loops. The loop volumes of the sampling valves were 5 mL and 20 mL for the liquid and gas loops, respectively. The collected liquid and gas samples were expanded across an expansion valve that was wrapped with a heating tape. The condensed liquid portion was collected in a cold trap containing 200 mL of isopropyl alcohol. The cold trap was surrounded by a mixture of liquid nitrogen and ethanol at about 253 K.

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Table 1. Comparison of Vapor–Liquid Equilibrium Data for the System CO₂ + Toluene

P/MPa	T/K	x _{CO₂}		y _{CO₂}	
		this work	Ng–Robinson	this work	Ng–Robinson
1.40	352.6	0.077	0.0765	0.963	0.963
3.08	352.6	0.172	0.172	0.978	0.978
5.72	352.6	0.328	0.328	0.981	0.981

Table 2. Vapor–Liquid Equilibrium Data for the System HFC-134a (1) + *m*-Cresol (2), and + *p*-Cresol (3)

HFC-134a (1) + <i>m</i> -cresol (2)			HFC-134a (1) + <i>p</i> -cresol (3)		
P/MPa	x ₁	y ₂	P/MPa	x ₁	y ₃
T = 343.2 K			T = 343.2 K		
0.38	0.026	0.205	0.32	0.020	0.248
0.55	0.038	0.198	0.55	0.041	0.199
0.71	0.054	0.195	0.77	0.073	0.173
0.90	0.080	0.193	0.92	0.099	0.166
1.12	0.121	0.190	1.17	0.141	0.157
1.30	0.169	0.191	1.32	0.197	0.150
T = 363.2 K			T = 363.2 K		
0.44	0.021	0.217	0.39	0.015	0.269
0.66	0.034	0.210	0.57	0.030	0.245
0.97	0.066	0.205	1.00	0.070	0.197
1.21	0.093	0.199	1.31	0.119	0.161
1.54	0.127	0.192	1.62	0.179	0.150
1.69	0.158	0.192	1.90	0.238	0.151
T = 383.2 K			T = 383.2 K		
0.51	0.017	0.230	0.54	0.020	0.280
0.91	0.036	0.221	0.88	0.041	0.242
1.19	0.058	0.217	1.25	0.077	0.217
1.71	0.094	0.207	1.83	0.129	0.184
2.10	0.137	0.198	2.17	0.170	0.166
2.30	0.160	0.197	2.38	0.210	0.158

The isopropyl alcohol in the cold trap was also pumped to the sampling loops to remove the liquid retained. Liquid samples of 2 μ L were sent to a flame ionization detector gas chromatograph (Varian 3400CX) for composition analysis. The amount of the expanded HFC-134a in each sampling loop was determined by measuring the volume displaced in a column that was filled with water. To eliminate possible measurement error, water in the column and isopropyl alcohol in the cold trap were saturated with HFC-134a first. The composition in the liquid and gas phases at each temperature and pressure could then be determined from the measured amounts of condensed solute and HFC-134a in the sampling loops. At least three measurements (the first sample was taken after 5 h) were carried out to see if the compositions in the liquid and gas phases reached a stable value. The deviation in compositions among these measurements was observed to be less than $\pm 3.0\%$.

Results and Discussion

To ensure the applicability of the present apparatus and the recirculation operation, the vapor–liquid equilibrium data for the system carbon dioxide + toluene was first measured over the pressures range from (1.4 to 5.7) MPa at 352.6 K. The measured VLE data, shown in Table 1, were found to agree well with those reported by Ng and Robinson (1978) with an average deviation of less than $\pm 2.0\%$.

The experimental vapor–liquid equilibrium data for the binary systems HFC-134a + *m*-cresol and HFC-134a + *p*-cresol at the temperatures of (343.2, 363.2, and 383.2) K are tabulated in Table 2 and represented graphically in Figures 2 and 3. The reproducibility was also performed in this study. It was found that the data could be

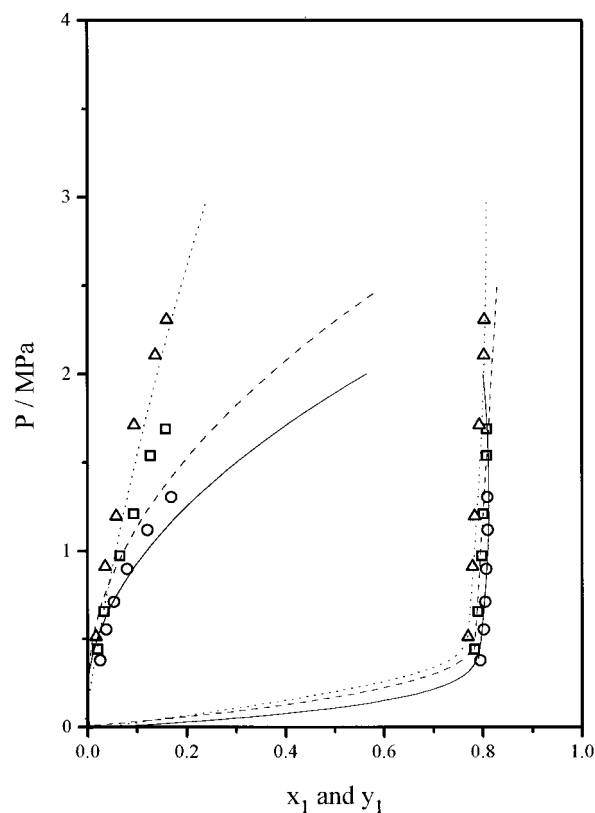


Figure 2. Comparison between the predicted and the experimental data for the system HFC-134a (1) + *m*-cresol (2): experimental data at (○) 343.2 K, (□) 363.2 K, (△) 383.2 K; calculated by Peng–Robinson EOS at (—) 343.2 K, (---) 363.2 K, (···) 383.2 K.

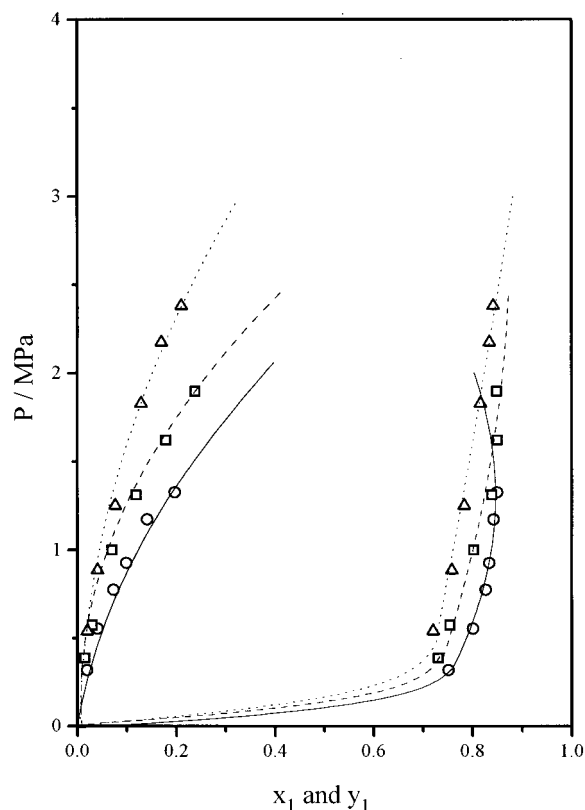


Figure 3. Comparison between the predicted and the experimental data for the system HFC-134a (1) + *p*-cresol (2): experimental data at (○) 343.2 K, (□) 363.2 K, (△) 383.2 K; calculated by Peng–Robinson EOS at (—) 343.2 K, (---) 363.2 K, (···) 383.2 K.

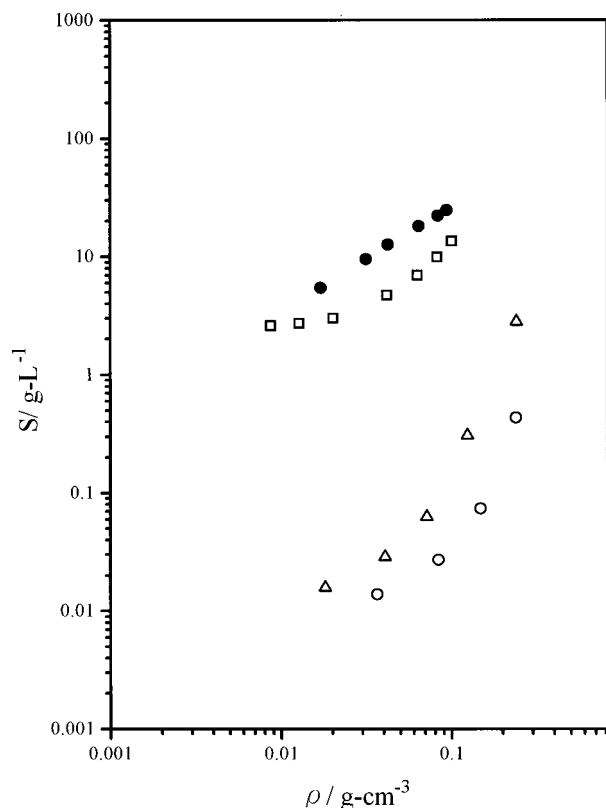


Figure 4. Comparison of solubility S of m -cresol in different solvents: (○) CO_2 + m -cresol at 318.2 K, 2–24 MPa (Lee and Chao, 1988); (□) methane + m -cresol at 462.3 K, 2–25 MPa (Chao et al., 1980); (△) ethane + m -cresol at 328.3 K, 1.5–8 MPa (Lee and Chao, 1988); (●) HFC-134a + m -cresol at 383.2 K, 0.5–2.3 MPa (this work).

Table 3. Critical Properties of Pure Species

	acentric factor	T_c/K	P_c/MPa
HFC-134a ^a	0.325	374.2	4.06
m -cresol ^b	0.454	705.8	4.56
p -cresol ^b	0.505	704.6	5.15

^a Tillner-Roth and Baehr (1994). ^b Reid et al. (1988).

reproduced with a deviation of less than $\pm 2.0\%$. Figure 4 shows that HFC-134a could extract more m -cresol than the frequently used supercritical fluids, such as carbon dioxide, ethane, and methane, at moderate temperatures and pressures.

At equilibrium, fugacities of each species in vapor and liquid are equal,

$$P y_i \phi_i^V = P x_i \phi_i^L \quad (1)$$

In this work the Peng–Robinson equation of state (Peng and Robinson, 1976) and the two-parameter mixing rules (Occhiogrosso et al., 1986) with the critical properties of HFC-134a and cresol isomers listed in Table 3 were used to calculate fugacity coefficients for cresol and HFC-134a in gas and liquid phases. It is mentioned here that the vapor pressures of cresol isomers and HFC-134a calculated by the present model agreed well with the literature data (Reid et al., 1988; Tillner-Roth and Baehr, 1994). The average differences were about 7.0 and 1.0% for cresol isomers and HFC-134a, respectively. The lines in Figures 2 and 3 represent the calculated compositions for HFC-134a in gas and liquid phases with the interaction parameters $\delta = -0.287$ and $\eta = -0.276$ for the system HFC-134a

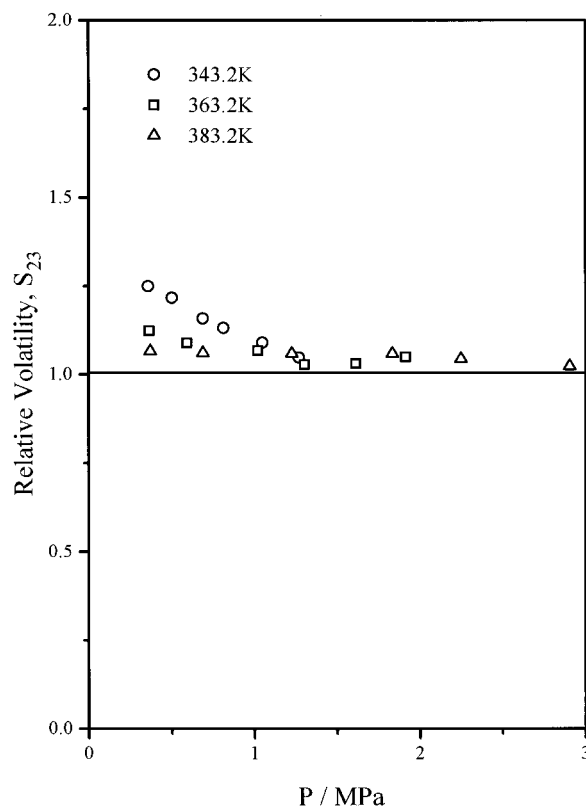


Figure 5. Relative volatility data in the system HFC-134a (1) + m -cresol (2) + p -cresol (3) for the composition ratio of m -cresol to p -cresol at 40.4:59.6 wt %.

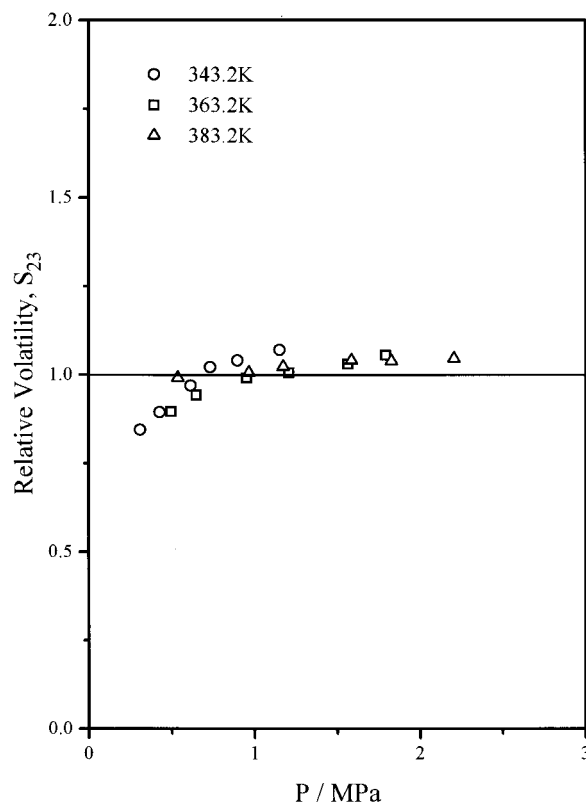


Figure 6. Relative volatility data in the system HFC-134a (1) + m -cresol (2) + p -cresol (3) for the composition ratio of m -cresol to p -cresol at 51.7:48.3 wt %.

+ m -cresol and $\delta = -0.110$ and $\eta = -0.121$ for the system HFC-134a + p -cresol. From Figures 2 and 3 it can be observed that the agreement is fairly good with an absolute

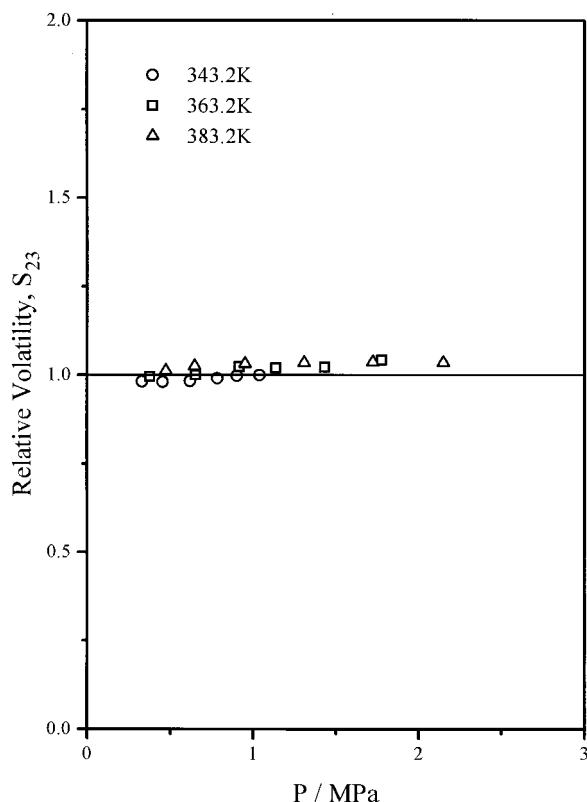


Figure 7. Relative volatility data in the system HFC-134a (1) + *m*-cresol (2) + *p*-cresol (3) for the composition ratio of *m*-cresol to *p*-cresol at 65.3:34.7 wt %.

average deviation of about 13.8% and 7.1% for the systems HFC-134a + *m*-cresol and HFC-134a + *p*-cresol, respectively. It is also noted that the agreement between the calculated and the experimental was not improved when the Soave–Redlich–Kwong equation of state (Soave, 1972) was used.

Vapor–liquid equilibrium for the ternary system HFC-134a + *m*-cresol + *p*-cresol was also measured in this study. Since a commercial mixture of *m*- and *p*-cresols generally has 40–65 wt % of *m*-cresol (Leston, 1981), the liquid mixtures containing the ratios of *m*-cresol to *p*-cresol as 40.4:59.6, 51.7:48.3, and 65.3:34.7 wt % were prepared at the beginning of the experiments. Since the amount of liquid charged to the equilibrium cell was quite large, the ratio of *m*-cresol to *p*-cresol in the liquid phase was observed to be unchanged after each experiment. Figures 5–7 show the relative volatility (S_{23}) at various tempera-

tures and pressures. The relative volatility is defined as

$$S_{23} = \frac{y_2/x_2}{y_3/x_3} \quad (2)$$

where 2 and 3 are denoted as *m*-cresol and *p*-cresol, respectively. Since S_{23} approaches 1.0 at higher pressures, HFC-134a does not exhibit its selectivity toward *m*- or *p*-cresol. Thus HFC-134a is not a good extractant to separate *m*- or *p*-cresol from the mixture, though it could extract more cresol isomers than supercritical carbon dioxide and ethane at relatively lower temperatures and pressures. The compositions in both gas and liquid phases calculated by the Peng–Robinson equation of state combined with the two-parameter mixing rules using the interaction parameters determined from binary systems and assuming the interaction parameter between *m*- and *p*-cresol isomers be zero were found to agree fairly well with the experimental data; the absolute average deviation was 11.0%.

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