Henry's Law Constant Measurements of CCl_2F_2, $CHClF_2$, CH_2F_2, C_2ClF_5, C_2HF_5, CH_2FCF_3, and CH_3CHF_2 in Methanol, Ethanol, and 2-Propanol

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Isothermal vapor−liquid equilibria for 21 fluorocarbon + alcohol systems ranging from 283 to 313 K at atmospheric pressure were measured. The solubility of fluorocarbons into alcohols decreases with increase in temperature and is on the order of a thousand times greater than that of water. The solubility of fluorocarbons derived from ethane in methanol increases as the number of hydrogen atoms in a molecule increases. From the experimental data, Henry's law constants of dichlorodifluoromethane (CCl_2F_2, CFC12), chlorodifluoromethane ($CHClF_2$, HCFC22), difluoromethane (CH_2F_2, HFC32), chloropentafluoroethane (C_2ClF_5, CFC115), pentafluoroethane (C_2HF_5, HFC125), 1,1,1,2- tetrafluoroethane (CH_2FCF_3, HFC134a), and 1,1-difluoroethane (CH_3CHF_2, HFC152a) in methanol, ethanol, and 2-propanol were obtained. The values were correlated as a function of temperature with the Valentiner equation.

Introduction

Chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) containing chlorine were widely used by many industries since 1926 because of the low toxicity and chemical stability. However, their production has been or will be prohibited soon because they are considered to deplete the ozone layer. One of the authors proposed a photodecomposition process which removes chlorine atoms from chlorinated compounds such as CFCs or HCFCs dissolved in an alcohol (Sato et al., 1998; Nishiumi and Sato, 1999). To design a photochemical reactor, we need the solubility of CFC or HCFC in alcohol.

This work was undertaken to provide the Henry's constant data from isothermal vapor−liquid equilibrium measurements for fluorocarbon + alcohol systems ranging from 283 to 313 K at atmospheric pressure.

Experimental Section

Purity of Materials. Daikin Industries, Ltd., supplied CFC12, HCFC22, CFC115, HFC125, HFC134a, and HFC152a with purities over 99.8%, and Showa Denko provided HFC32 with purity over 99.9%. Methanol, ethanol (99.8%), and 2-propanol (99.5%) were purchased from Wako Pure Chemicals, Ltd. They were used without further purification.

Calibration. Samples were analyzed with a Shimadzu Corporation Model GC-8A gas chromatograph, through a gas sampling six-port valve for a gas-phase sample and a microsyringe for a liquid-phase one. Using 1 and 2 mL gas sampling loops whose exact volumes were measured by weighing mercury-filled loops, the exact volume of the gas sampling section was determined from their gas chromatogram areas. From the volume, pressure, and temperature of a gas sampling section under ideal gas conditions, the moles of CFCs and HCFCs and the small amount of alcohol in the gas were determined, which lead to a straight-line calibration through an origin. The moles of methanol, ethanol, and 2-propanol liquid samples were determined by mass or volume scale of a microsyringe. For 2-propanol, the results from both the gas sampling valve and microsyringe methods agreed well, as shown in Figure 1. The maximum deviation was 3% in a liquid phase and 1% in a vapor phase. The overall average deviation was 1.4% in a liquid phase and 0.3% in a vapor phase.

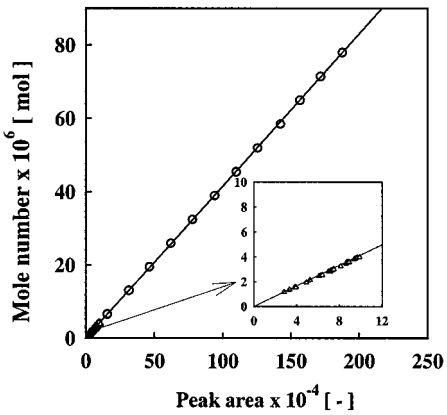

Figure 1. Calibration curves of 2-propanol: O, volumetric method for liquid-phase sample; △, pressure method for gas-phase sample; —, calibration.

Apparatus and Procedure. An equilibrium cell in a thermostatic water bath was used for the measurement of vapor−liquid equilibria, as shown in Figure 2. The temperature uncertainty was ±0.1 K using a platinum resistance temperature sensor. Pressure was maintained at atmospheric pressure. The gases were blown into an alcohol solvent to dissolve and agitate the solution through a ball filter. Vapor-phase gas was drawn with a 2.5 mL warmed syringe containing 0.5 mL of helium gas to prevent alcohol condensation. A liquid sample was taken with a 10 μL microsyringe. The samples were injected into a gas chromatograph with a TCD detector to determine a vapor- or

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10.1021/je000346p CCC: $20.00
Published on Web 04/06/2001

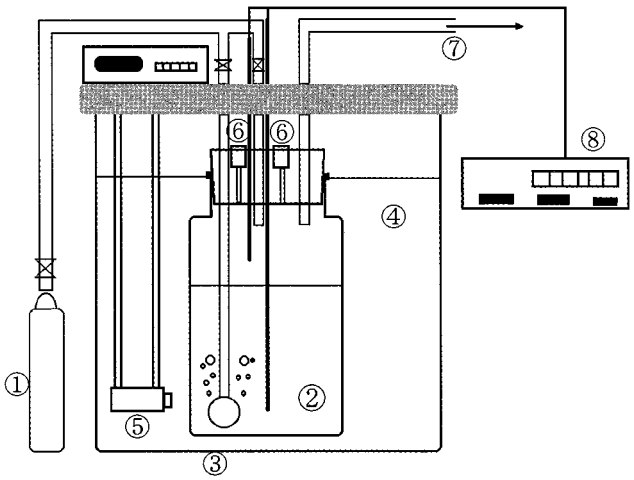

Figure 2. Experimental apparatus: ①, (H)CFC cylinder; ②, equilibrium cell; ③, ball filter; ④, water bath; ⑤, agitator; ⑥, sampling septum for microsyringe; ⑦, open to air; ⑧, thermometer.

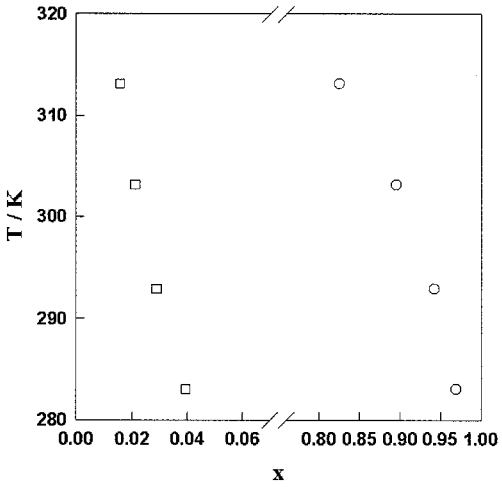

Figure 3. VLE for the system (x)chloropentafluoroethane (HFC125) + (1 − x)2-propanol: ○, vapor phase; □, liquid phase.

liquid-phase composition. Three repeated measurements were made.

Results

Vapor−Liquid Equilibria. Table 1 shows experimental data on vapor−liquid equilibria for the binary systems of alcohols (methanol, ethanol, and 2-propanol) + fluorocarbons (CFC12, HCFC22, HFC32, CFC115, HFC125, HFC134a, and HFC152a) ranging from 283 to 313 K at atmospheric pressure. The uncertainties of composition are estimated to be <2.0% for a liquid phase and <0.5% for a vapor phase. Some of the results are shown in Figure 3. It shows that a few mole percent of fluorocarbons dissolves in alcohols. Taking into consideration that the solubility of CFC115 (C_2ClF_5) and CFC12 (CCl_2F_2) in water is 7.07 × 10^{-6} and 4.22 × 10^{-5} in mole fraction, respectively (JCME, 1988), the solubility of fluorocarbons in alcohols is about a thousand times greater than that of water.

Solubility. Hildebrand showed the following relation

$$\Delta S_1 = (s_1 - s_1^\circ) = R\left(\frac{\partial \ln x_1}{\partial \ln T}\right)_{\mathrm{sat},T} \qquad (1)$$

where x_1 is the solubility of a solute gas in the liquid at T, s_1 is the partial molar entropy of a solute, and s_1^0 is the entropy of a pure solute. Table 1 shows that the solubility of fluorocarbons in alcohols decreases with temperature. So, ΔS_1 is expected to be negative. Figure 4 shows that experimental results can be expressed by eq 1. From the slopes, we obtained the values of ΔS_1 given in Table 2 together with calculated solubility values at 303 K.

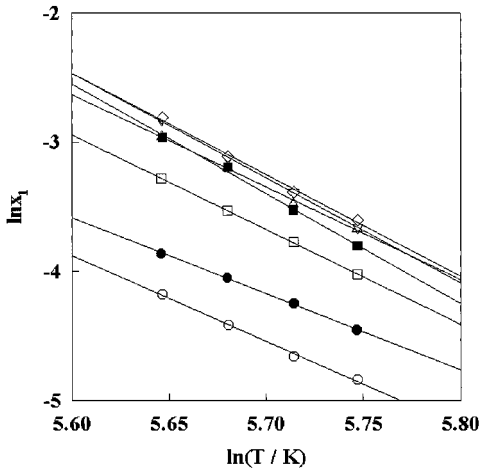

Figure 4. Effect of temperature on solubility of hydrofluorocarbons in 2-propanol: ◇, dichlorodifluoromethane (CFC12); ●, chlorodifluoromethane (HCFC22); ■, difluoromethane (HFC32); ○, chloropentafluoroethane (CFC115); □, pentafluoroethane (HFC125); △, 1,1,1,2-tetrafluoroethane (HFC134a); ▽, 1,1-difluoroethane (HFC152a); —, Valentiner equation.

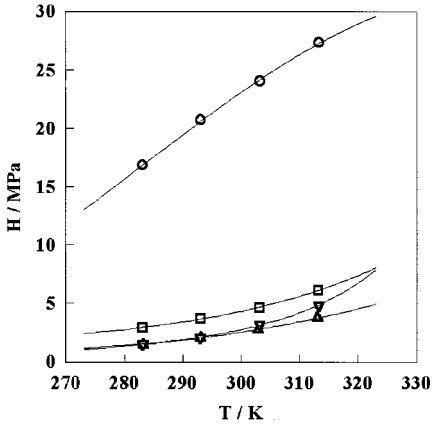

Figure 5. Henry's law constants (H) of chloropentafluoroethane (CFC115), pentafluoroethane (HFC125), 1,1,1,2-tetrafluoroethane (HFC134a), and 1,1-difluoroethane (HFC152a) in methanol: ○, chloropentafluoroethane (CFC115); □, pentafluoroethane (HFC125); ▽, 1,1,1,2-tetrafluoroethane (HFC134a); △, 1,1-difluoroethane (HFC152a); —, Valentiner equation.

Henry's Law Constants. The Henry's law constant at atmospheric pressure is indicated by the following simplified relation

$$H_{12} = 0.1013\frac{y_1}{x_1} \qquad (2)$$

where H_{12} is the Henry's law constant in MPa, x_1 and y_1 are the solute mole fractions in the liquid and vapor phases, respectively, and the subscripts 1 and 2 mean solute and solvent, respectively. The Henry's law constants listed in Table 1 have uncertainties of 2.5% determined from the composition measurement reproducibility.

All the values of Henry's law constants listed in Table 1 increase with temperature. The temperature dependence

Table 1. Experimental Vapor−Liquid Equilibrium Data

T/K	x_1	y_1	Henry's law constant, *H*/MPa
Dichlorodifluoroethane (CFC12) + Methanol			
283.28	0.0280	0.9273	3.35
293.04	0.0200	0.8608	4.36
303.21	0.0140	0.7762	5.61
313.19	0.0093	0.6372	6.9
Dichlorodifluoroethane (CFC12) + Ethanol			
283.43	0.0482	0.9650	2.02
293.11	0.0356	0.9456	2.69
302.98	0.0261	0.9014	3.50
313.29	0.0191	0.8237	4.36
Dichlorodifluoroethane (CFC12) + 2-Propanol			
283.36	0.0600	0.9826	1.65
293.11	0.0445	0.9620	2.18
303.16	0.0338	0.9358	2.80
313.39	0.0273	0.8637	3.20
Cholordifluoromethane (HCFC22) + Methanol			
283.22	0.0856	0.9326	1.10
292.99	0.0609	0.8757	1.45
303.08	0.0401	0.7792	1.96
313.47	0.0267	0.6478	2.45
Chlorodifluoromethane (HCFC22) + Ethanol			
283.36	0.0690	0.9581	1.40
292.96	0.0551	0.9201	1.69
303.08	0.0381	0.8602	2.28
313.47	0.0274	0.7615	2.82
Chlorodifluoromethane (HCFC22) + 2-Propanol			
283.33	0.0516	0.9618	1.88
293.05	0.0410	0.9226	2.27
303.14	0.0295	0.865	2.97
313.25	0.0223	0.7634	3.46
Difluoromethnae (HFC32) + Methanol			
283.14	0.0261	0.931	3.61
292.91	0.0169	0.8754	4.52
303.22	0.0148	0.7833	5.34
313.06	0.0099	0.6551	6.7
Difluoromethane (HFC32) + Ethanol			
283.17	0.0278	0.9735	3.54
292.96	0.0214	0.9518	4.50
303.81	0.0174	0.9099	5.30
312.95	0.0134	0.8448	6.40
Difluoromethane (HFC32) + 2-Propanol			
283.16	0.0210	0.9745	4.60
292.99	0.0174	0.9544	5.55
303.25	0.0143	0.9232	6.54
313.18	0.0116	0.8656	7.58
Chloropentafluoroethane (CFC115) + Methanol			
283.3	0.0056	0.9369	16
293.06	0.0043	0.8793	20
303.29	0.0033	0.7899	24
313.38	0.0024	0.6449	27
Chloropentafluoroethane (CFC115) + Ethanol			
283.05	0.0107	0.9721	9.2
292.96	0.0083	0.9453	11
303.04	0.0064	0.9002	14
313.44	0.0051	0.8281	16
Chloropentafluoroethane (CFC115) + 2-Propanol			
283.34	0.0153	0.9836	6.50
293.13	0.0121	0.9636	8.04
303.27	0.0095	0.9282	9.8
313.3	0.0079	0.8616	11
Pentafluoroethane (HFC125) + Methanol			
283.07	0.0318	0.9235	2.94
293.05	0.0238	0.8695	3.69
303.14	0.0169	0.7797	4.66
313.18	0.0107	0.6466	6.12
Pentafluoroethane (HFC125) + Ethanol			
283.02	0.0394	0.9697	2.49
292.94	0.0289	0.9429	3.30
303.15	0.0212	0.8961	4.29
313.11	0.0157	0.8258	5.31
Pentafluoroethane (HFC125) + 2-Propanol			
283.16	0.0376	0.9747	2.62
292.99	0.0293	0.9556	3.30
303.17	0.0230	0.9223	4.05
313.26	0.0179	0.8602	4.87
1,1,1,2- Tetrafluoroethane (HFC134a) + Methanol			
283.26	0.0629	0.9309	1.49
293.04	0.0426	0.8761	2.08
302.93	0.0287	0.7822	2.75
313.08	0.0176	0.6546	3.77
1,1,1,2- Tetrafluoroethane (HFC134a) + Ethanol			
283.17	0.0579	0.9702	1.69
293.03	0.0440	0.9444	2.17
303.09	0.0330	0.9003	2.76
313.13	0.0246	0.8230	3.39
1,1,1,2- Tetrafluoroethane (HFC134a) + 2-Propanol			
283.25	0.0518	0.9799	1.91
293.08	0.0408	0.9603	2.38
303.1	0.0308	0.9205	3.02
313.25	0.0255	0.8617	3.42
1,1- Difluoroethane (HFC152a) + Methanol			
283.18	0.0603	0.9279	1.55
293.02	0.0420	0.8733	2.10
303.17	0.0261	0.8176	3.17
313.29	0.0146	0.7002	4.87
1,1- Difluoroethane (HFC152a) + Ethanol			
283.18	0.0611	0.9708	1.61
292.94	0.0465	0.9460	2.06
303	0.0348	0.8976	2.61
313.1	0.0253	0.8228	3.29
1,1- Difluoroethane (HFC152a) + 2-Propanol			
283.18	0.0590	0.9758	1.67
293.06	0.0438	0.9565	2.21
293.06	0.0438	0.9565	2.21
303.15	0.0338	0.9269	2.78
313.3	0.0258	0.8614	3.38

Table 2. Entropy and Solubility of Fluorocarbons in 2-Propanol (303 K, 101 kPa)

compound	$(s_1 - s_1^0)$ [J mol^{-1} K^{-1}]	x_1
dichlorodifluoromethane (CFC12)	−65.299	0.0348
chlorodifluoromethane (HCFC22)	−70.620	0.0298
difluoromethane (HFC32)	−48.782	0.0142
chloropentafluoroethane (CFC115)	−55.154	0.0097
pentafluoroethane (HFC125)	−60.856	0.0229
1,1,1,2-tetrafluoroethane (HFC134a)	−59.651	0.0318
1,1-difluoroethane (HFC152a)	−67.603	0.0338

was correlated with the Valentiner equation (Hildebrand and Scott, 1962)

$$\ln H = a + b/T + c \ln T \qquad (3)$$

The extended scale-particle theory (Li and Mather, 1994) is successfully used to correlate the Henry's law constant data, but we use the Valentiner equation here. The values of the above coefficients are shown in Table 3. The solubility of (hydro)fluorocarbons derived from ethane not only in methanol as shown in Figure 5 but also in ethanol and 2-propanol increases as the number of hydrogen atoms in a molecule increases, although those from methane have no such tendency, as shown in Figure 6.

Because the Cl atom is larger than F and H atoms, the structures of CFC115 (C_2ClF_5) and CFC12 (CCl_2F_2) like 2-propanol (CH_3COHCH_3) more than that of methanol (CH_3OH). CFC115 in Figure 7 and CFC12 are more soluble in 2-propanol than in methanol; however, HCFC22 in Figure 8 and HFC32 are on the contrary and have small effects for HFC125, HFC134a, and HFC152a. So, we could not find a solvent structure effect on the solubility of fluorocarbons in alcohols.

Conclusion

Vapor−liquid equilibria were measured for 21 fluorocarbon + alcohol systems ranging from 283 to 313 K at atmospheric pressure. Negative values of ΔS_1 were ob-

Table 3. Valentiner Constants[a] of Fluorocarbon + Alcohol Systems Ranging from 283 to 313 K

compound	*a*	*b*	*c*
In Methanol			
dichlorodifluoromethane (CFC12)	92.516	−5869.633	−12.501
chlorodifluoromethane (HCFC22)	81.923	−5659.544	−10.953
difluoromethane (HFC32)	−70.077	1663.16	11.6
chloropentafluoroethane (CFC115)	191.746	−9595.128	−27.461
pentafluoroethane (HFC125)	−215.617	7822.205	33.489
1,1,1,2- tetrafluoroethane (HFC134a)	−29.597	−960.938	5.915
1,1- difluoroethane (HFC152a)	−487.045	18819.437	74.57
In Ethanol			
dichlorodifluoromethane (CFC12)	138.314	−8045.409	−19.342
chlorodifluoromethane (HCFC22)	−106.536	2971.915	17.068
difluoromethane (HFC32)	106.501	−6132.004	−14.802
chloropentafluoroethane (CFC115)	208.356	−10591.234	−29.885
pentafluoroethane (HFC125)	110.72	−6763.19	−15.218
1,1,1,2- tetrafluoroethane (HFC134a)	56.848	−4238.572	−7.324
1,1- difluoroethane (HFC152a)	−18.866	−925.958	4.005
In 2-Propanol			
dichlorodifluoromethane (CFC12)	374.242	−18287.97	−54.758
chlorodifluoromethane (HCFC22)	46.617	−3613.24	−5.886
difluoromethane (HFC32)	3.88	−1292.48	0.396
chloropentafluoroethane (CFC115)	231.832	−11573.794	−33.491
pentafluoroethane (HFC125)	73.392	−4754.616	−9.854
1,1,1,2- tetrafluoroethane (HFC134a)	227.428	−11566.178	−32.933
1,1- difluoroethane (HFC152a)	174.993	−9500.782	−24.96

[a] $\ln(H/\mathrm{MPa}) = a + b(K/T) + c\ln(T/\mathrm{K})$.

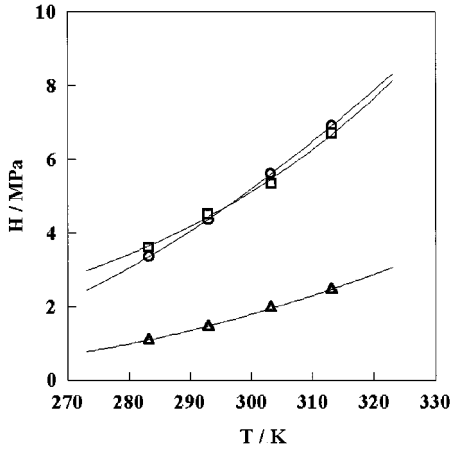

Figure 6. Henry's law constants (*H*) of dichlorodifluoromethane (CFC12), chlorodifluoromethane (HCFC22), and difluoromethane (HFC32) in methanol: ○, dichlorodifluoromethane (CFC12); △, chlorodifluoromethane (HCFC22); □, difluoromethane (HFC32); —, Valentiner equation.

tained, since the solubility of fluorocarbons in alcohols decreases with an increase in temperature. The solubility of fluorocarbons in alcohols is about a thousand times greater than their solubility in water. From the experimental data, Henry's law constants of CFC12, HCFC22, HFC32, CFC115, HFC125, HFC134a, and HFC152a in methanol, ethanol, and 2-propanol were obtained. The values were correlated as a function of temperature with the Valentiner equation. The solubility of (hydro)fluorocarbons derived from ethane not only in methanol but also in ethanol and 2-propanol increases as the number of hydrogen atoms in a molecule increases.

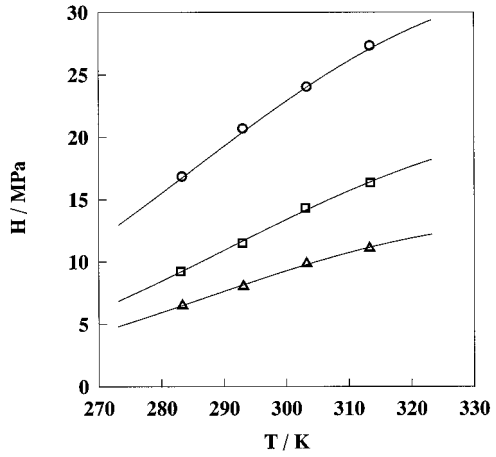

Figure 7. Henry's law constants (*H*) of chloropentafluoroethane (CFC115) in alcohols: ○, methanol; □, ethanol; △, 2-propanol; —, Valentiner equation.

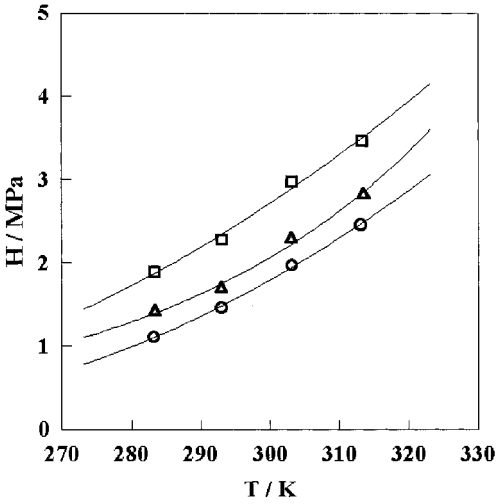

Figure 8. Henry's law constants (*H*) of chlorodifluoromethane (HCFC22) in alcohols: ○, methanol; □, ethanol; △, 2-propanol; —, Valentiner equation.

Acknowledgment

The authors wish to thank Mr. Takafumi Kanaya, who assisted with the experiments.

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Received for review October 25, 2000. Accepted February 13, 2001.

JE000346P