청정소화약제내에서 질소의 용해도 측정

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Solubility of nitrogen in clean fire extinguishing agents at high pressure

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Introduction

Bromotrifluoromethane (halon-1301) and bromochlorodifluoromethane(halon-1211) have been widely used as a clean fire extinguishing agents due to their outstanding properties. However, production and use of halon are currently being phased out under international agreements Montreal Protocol because of global environmental concerns and HFCs have been considered as promising candidates for the replacement of halon since their ozone depletion potentials are low. The vapor-liquid equilibrium data for the systems nitrogen + clean fire extinguishing agents are essential because nitrogen is used as a pressurization gas to shorten the discharging time of the agents. This information is important because it will provide safety guidelines for the pressure vessels. The amount of nitrogen needed to pressurization gas is significant, a dangerously high pressure may result when the vessel is exposed to elevated temperature [1]. Very few experimental data [1,2] however, have been previously reported in the literature.

In this work, we choose HFCs such as HFC-22, HFC-125, and HFC-134a for clean fire extinguishing agents and nitrogen as a pressurization gas for a proper jet velocity of these. Phase equilibria for binary mixtures of nitrogen + HFC-22, nitrogen + HFC-125, and nitrogen + HFC-134a were measured in the temperature range from 283.15 K to 303.15 K. For equilibrium measurement, we used a circulation type apparatus in which both vapor and liquid phases were continuously recirculated. The experimental result was correlated with the Peng-Robinson equation of state [3] with Wong-Sandler mixing rules [4]. The calculated values from equation of state have shown satisfactory results in comparison with the experimental data.

Theory

The VLE experimental data were correlated with the Peng-Robinson-Stryjek-Vera (PRSV) equation of state. The Peng-Robinson (PR) equation of state expressed as follows.

The Peng-Robinson-Stryjek-Vera (PRSV) equation of state

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)}$$

$$a(T)=\left(0.457235\frac{R^2T_C{}^2}{P_C}\right)\alpha(T)$$

$$b=0.077796\frac{RT_C}{P_C}$$

$$\alpha(T)=\left[1+\kappa\left(1-\sqrt{T/T_C}\right)\right]^2$$

$$\kappa_0=0.378893+1.4897153\omega-0.1713184\omega^2+0.0196554\omega^3$$

where the parameter a is a function of temperature, b is constant, is a constant characteristic of each substance, is the acentric factor, P(MPa) is pressure, Pc(MPa) is the critical pressure, T(K) is absolute temperature, Tc(K) is the critical temperature, Tr is the reduced temperature, and v is molar volume. The Wong-Sandler mixing rule (Wong and Sandler, 1992) was used in this work to obtain equation of state parameters for a mixture from those of the pure components. This mixing rule for a cubic equation of state can be written as

$$b_m=\frac{\Sigma\Sigma x_i x_j(b-a/RT)}{(1-A^E_\infty/CRT-\Sigma x_i a_i/RTb_i)}$$

$$(b-a/RT)_{ij}=\frac{1}{2}\left[(b-a/RT)_i+(b-a/RT)_j\right](1-k_{ij})$$

$$\frac{a_m}{b_m}=\Sigma x_i\frac{a_i}{b_i}+\frac{A^E_\infty}{C}$$

and where C is a numerical constant equal to $\ln(\sqrt{2}-1)/\sqrt{2}$ for the Peng-Robinson equation used in this work. Also, A^E_∞ is an excess Helmholtz free energy model at infinite pressure which can be equated to a low-pressure excess Gibbs free energy model; in this study we use the NRTL model given by

$$\frac{A^E_\infty}{RT}=\Sigma x_i\frac{\Sigma x_i G_{ij}\tau_{ji}}{\Sigma x_k G_{ki}}$$

$$G_{ji}=exp(-\alpha_{ji}\tau_{ji})\,\text{and}\,\tau_{ij}=A_{ij}/(RT)$$

where G_{ij} is the local composition factor for the NRTL model, τ_{ij} is the NRTL model binary interaction parameter, $A_{ij}=(g_{ij}-g_{jj})$ and g_{ij} is an interaction energy parameter of the *i-j*, *ij* is a non-randomness parameter and R is the universal gas constant (8.314 $JK^{-1}mol^{-1}$). The critical properties (T_c, P_c) and acentric factors of nitrogen, HFC-22, HFC-125, and HFC-134a used to calculate the parameters for the Peng-Robinson equation of state are given in Table 1. We have set the non-randomness parameter α_{12} equal to 0.3 for all the binary mixtures studied here. The Marquardt algorithm was applied to obtain the parameters with the following objective function.

$$objectivefunction=\frac{1}{N}\Sigma\left[\left(\frac{P_{j,exp}-P_{j,cal}}{P_{j,exp}}\right)\times 100\right]^2$$

Table 1. Properties of the Pure Components (data source: REFPROP 6.01 [7])

component	chemical formular	M.W.	Tc/K	P_c/MPa	V_c(cm^3/mol)	Z_c	ω
nirogen	N_2	28.01	126.21	3.390	0.900	0.290	0.0390
HFC-22	$CHClF_2$	86.47	369.30	4.990	169.00	0.274	0.2208
HFC-125	C_2HF_5	120.03	339.33	3.629	21.099	0.270	0.3035
HFC-134a	CF_3CH_2F	102.03	374.21	4.059	199.316	0.260	0.3268

Data source : REFPROP(V. 6.01) [7]

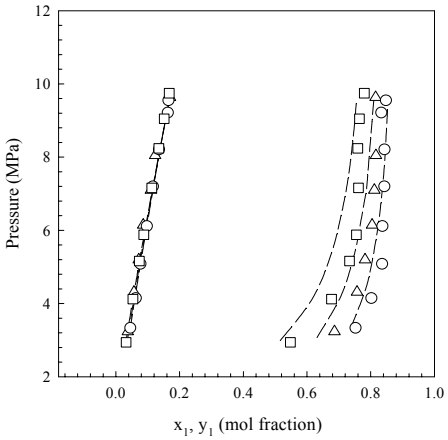

Figure 1. Pxy diagram of N_2/HFC-22; (○) 283.15K, (△) 293.15K, (□) 303.15K.

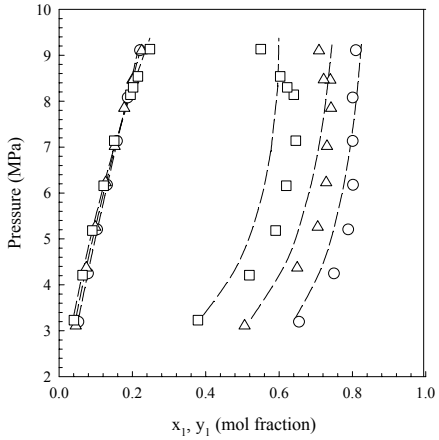

Figure 2. Pxy diagram of N_2/HFC-125; (○) 283.15K, (△) 293.15K, (□) 303.15K.

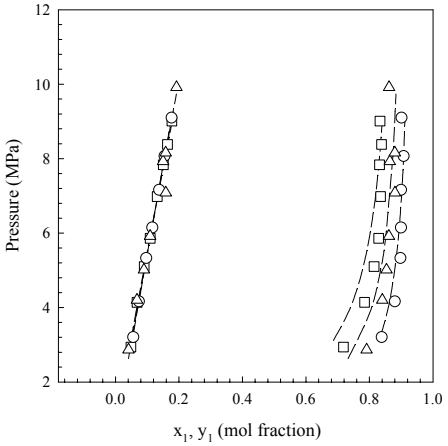

Figure 3. Pxy diagram of N_2/HFC-134a; (○) 283.15K, (△) 293.15K, (□) 303.15K.

Table 2. Interaction Parameters, NRTL parameters, and Average Deviations of P and y by PR equation of state

T/K	Interaction parameters	NRTL parameter		Deviation	
		τ_{12}[kJ/mol]	τ_{21}[kJ/mol]	δP^a	δy^b
		N_2 (1) + HFC-22 (2)			
283.15				0.0140	0.0147
293.15	0.6905	1.9487	-1.0125	0.0506	0.0379
303.15				0.0164	0.0417
		N_2 (1) + HFC-125 (2)			
283.15				0.0090	0.0213
293.15	0.8750	2.6733	-1.3255	0.0111	0.0271
303.15				0.0125	0.0385
		N_2 (1) + HFC-134a (2)			
283.15				0.0075	0.0073
293.15	0.7948	1.8335	-1.0674	0.0487	0.0022
303.15				0.0108	0.0193

[a] $\triangle x = |x_{exp} - x_{cal}|$, [b] $|\triangle P/P|(\%) = |(P_{exp} - P_{cal})|/P_{exp}| \times 100$

Results and Discussion

Vapor liquid equilibria of these mixtures were measured in the range of 3.0 MPa~10.0 MPa for a proper jet velocity of clean fire extinguishing agents (HFC-22, HFC-125, and HFC-134a) + nitrogen(pressurization gas) mixtures. The experimental data for isothermal vapor liquid equilibria (VLE) for the binary systems of nitrogen/HFC-22, nitrogen/HFC-125, and nitrogen/HFC-134a at 283.15K, 293.15 K and 303.15 K are shown in Figure 1,2, and 3. In these Figures, the comparison of measured and calculated values with PR equations of state was represented. The interaction parameters by this equation are listed in Table 2. Our experimental data have shown relatively good agreements with the calculated values using the PR equations of state. Azeotropic behavior has not been found in any of these mixtures.

Conclusion

We measured vapor-liquid equilibria for binary systems of nitrogen + HFC-22, nitrogen + HFC-125, and nitrogen + HFC-134a. The PR equation of state has given satisfactory results in comparison with the experimental data. An azeotropic composition was not found in any case.

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