SOLUBILITY OF NITROGEN IN CLEAN FIRE EXTINGUISHING AGENTS AT HIGH PRESSURE

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ABSTRACT

Isothermal solubilities of nitrogen in clean fire extinguishing agents, such as bromotrifluoromethane (Halon-1301), bromochlorodifluoromethane (Halon-1211), 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea), and trifluoroiodomethane (FIC-13I1) were measured in a circulation-type equilibrium apparatus. The temperature range was (293.2 to 313.2) K and the pressure range was (30 to 100) bar. The experimental data were well correlated with the Peng-Robinson equation of state using the Wong and Sandler mixing rules, and the relevant parameters are presented.

INTRODUCTION

Bromotrifluoromethane (halon-1301) and bromochlorodifluoromethane (halon -1211) have been used as a clean, non-toxic and effective fire extinguishing agents for a long time. But these compounds are being phased out because of their ozone-depletion potential. 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea) and trifluoroiodomethane (CF_3I) are known to be the promising replacement agents of halon-1301 and halon-1211.

The solubility 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 pressurize the vessel plays a major role in the determination of the final pressure of the vessel because if the amount of pressurization gas is significant, a dangerously high pressure may result when the vessel is exposed to elevated temperatures (Yang et al., 1993). Very few experimental data (Yang et al., 1993, 1995), however, have been previously reported in the literature.

In this work, we measured the solubility for the binary systems nitrogen + halon-1301, nitrogen + halon-1211, nitrogen + HFC-227ea, and nitrogen + CF_3I in the temperature range of (293.2 to 313.2) K and pressure range of (30 to 100) bar. The experimental data were correlated with the

Peng-Robinson equation of state (1976) using the Wong and Sandler mixing rules (1992).

EXPERIMENT

Chemicals

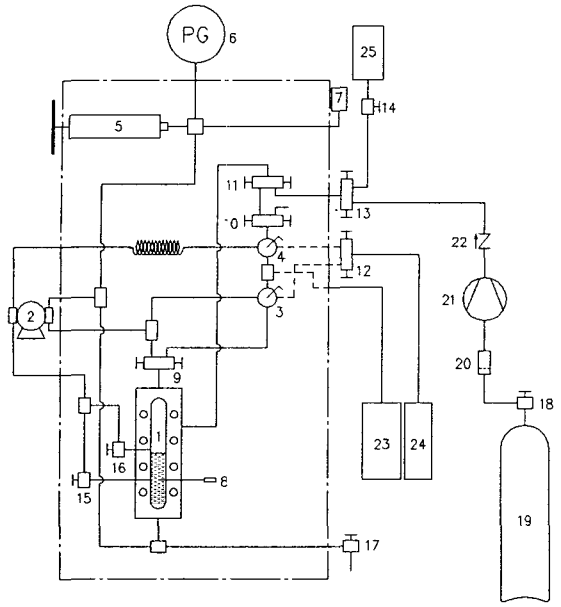
The purities of the chemicals used in this work were guaranteed by the manufacturers as shown in Table 1. They were used without any further purification.

Table 1. Suppliers and Purities of the Chemicals used

Component	Supplier	*Purity/* (mass %)
Nitrogen (N_2)	Shin-Yang Chemical Co., Korea	> 99.9
Bromotrifluoromethane (Halon-1301)	Hanju Chemical Co., Korea	> 99.9
Bromochlorodifluoromethane (Halon-1211)	Hanju Chemical Co., Korea	> 99.5
1,1,1,2,3,3,3 -Heptafluoropropane (HFC-227ea)	Great Lakes Chemical Co., USA	> 99.9
Trifluoroiodomethane (CF_3I)	Pacific Sci. Co., USA	> 99.9

Experimental Apparatus

The experimental approach for the solubility measurements in the present work adopted a circulation type apparatus in which both vapor and liquid phases were continuously recirculated. The experimental apparatus are shown in Figure 1. The system consists of five major parts: an equilibrium cell, duplex circulation pump, hand pump, vapor and liquid sampling valves, and a temperature-controlled air bath. The 80 cm^3 volume of equilibrium cell (Penberthy-Houdaile Co.) was equipped with dual glass windows for visual observation of the phases at equilibrium. The temperatures in the cell were measured by a K-type thermocouple (OMEGA Co.), and a digital indicator (OMEGA model DP41-TC) which was calibrated by KRISS (Korea Res. Inst. of Standards and Sci.) with an uncertainty of ±0.1 K. The hand pump (HIP model 62-6-10) was equipped to manually adjust the system pressure to the desired pressure within ±0.01 bar. The pressure in the cell was measured by a Heise pressure gauge (Model CMM 104637) which was calibrated by a dead weight gauge (NAGANO KEIKI PD12) with an uncertainty of the pressure measurement is to be within ±0.01 bar. Dual head circulation pump (Milton Roy Co.) was used to circulate the liquid at one head and the vapor at the other. A temperature control system was equipped to maintain the system temperature constant within ±0.1 K. Except for the duplex circulation pump, all the equilibrium apparatus was located in a temperature-controlled air bath.



1	Equilibrium Cell	14-18	Two way Valve
2	Duplex High Pressure Pump	19	N_2 Cylinder
3	Gas Sampling Valve	20	Line Filter
4	Liquid Sampling Valve	21	Compressor
5	Pressure Generator	22	Check Valve
6	Pressure Gauge	23	Gas Chromatographe
7	Rupture Disc	24	He Gas
8	Thermocouple	25	Liquid Reservoir
9 - 13	Three way valve		

Figure 1 Experimental Apparatus for the Measurement of Solubility of Nitrogen in Clean Fire Extinguishing Agents

Experimental Procedure

Each experiment was started by evacuating the apparatus. A certain amount of clean fire extinguishing agent was supplied to the equilibrium cell. By controlling the temperature of the air bath, the temperature of the entire system was maintained constant. After the desired temperature was attained, a proper amount of nitrogen was introduced into the cell from a charging cylinder until the system pressure was to be around the desired pressure. Both vapor and liquid phases were allowed to circulate for about an hour to ensure equilibrium. During circulation, the system pressure was adjusted minutely to the desired equilibrium pressure using the hand pump. After equilibrium was attained, vapor and liquid samples were then taken from the recycling lines by use of the vapor and liquid sampling valves (Rheodyne, Model 7413). The loop volume of vapor sampling valve was 5 μL and that of liquid sampling valve was 1 μL. They were directly injected into the gas chromatograph (HP-5890 series II) equipped with TCD and column packed with Porapak Q which is connected on-line to both vapor and liquid sampling valves.

We measured the solubilities at least three times to obtain reliable values. Average deviations of the equilibrium concentration were ±0.001 (mole fraction) for both liquid and vapor phases.

RESULTS AND DISCUSSION

The solubilities of nitrogen in halon-1301, halon-1211, HFC-227ea, and CF_3I, obtained by this these experiments, are shown in Figure 2, 3, 4 and 5 respectively. Experiments for all systems except nitrogen + halon-1301 were performed in the temperature range of (293.2 to 313.2) K and pressure range of (30 to 100) bar. For nitrogen + halon-1301 system, experiments were performed below 92 bar at 303.2 K and 77 bar at 313.2 K, due to the critical points of the system.

The solubility data were correlated with the Peng-Robinson equation of state (Peng and Robinson, 1976). The Peng-Robinson equation of state is expressed as follows:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \tag{1}$$

$$a = (0.457235R^2T_c^2 / P_c)\alpha(T) \tag{2}$$

$$b = 0.077796RT_c / P_c \tag{3}$$

$$\alpha(T) = \left[1+\kappa(1-T_r^{0.5})\right]^2 \tag{4}$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{5}$$

where the parameter a is a function of temperature; b is constant; κ is a constant characteristic of each substance; ω is the acentric factor; P is pressure; P_C is the critical pressure; T is absolute temperature; T_C is the critical temperature; T_r is the reduced temperature; and v is molar volume.

In this work, we used the Wong-Sandler mixing rule (Wong and Sandler, 1992) 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

$$b_m = \frac{\sum_i \sum_j x_i x_j (b - a/RT)_{ij}}{(1 - A_\infty^E / CRT - \sum_i x_i a_i / RTb_i)} \tag{6}$$

$$(b - a/RT)_{ij} = \frac{1}{2}\left[(b - a/RT)_i + (b - a/RT)_j\right](1 - k_{ij}) \tag{7}$$

$$\frac{a_m}{b_m} = \sum_i x_i \frac{a_i}{b_i} + \frac{A_\infty^E}{C} \tag{8}$$

where C is a numerical constant equal to $\ln(\sqrt{2}-1)/\sqrt{2}$ for the Peng-Robinson equation (1976)

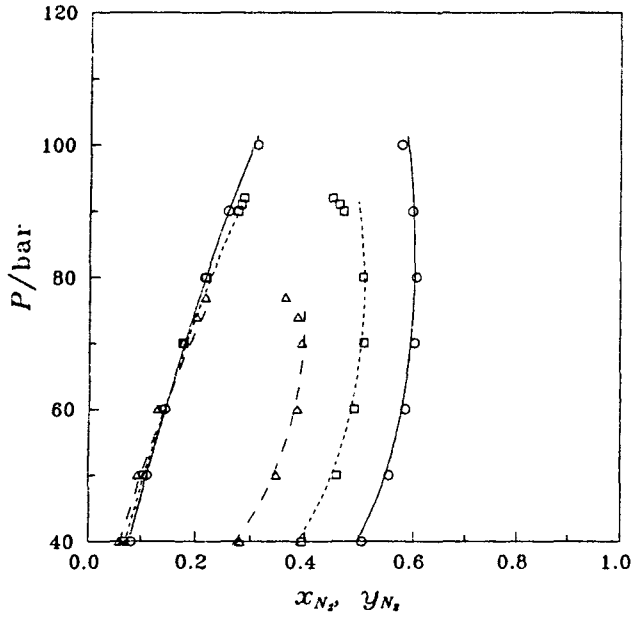


Figure 2. Pressure-Composition Diagram for the Nitrogen + Halon-1301 System
(O 293.2 K, □ 303.2 K, Δ 313.2 K)

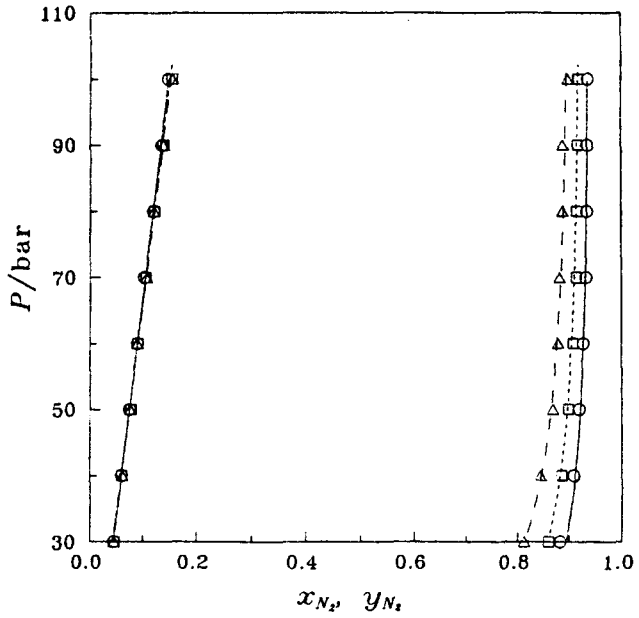


Figure 3. Pressure-Composition Diagram for the Nitrogen +Halon-1211 System
(O 293.2 K, □ 303.2 K, Δ 313.2 K)

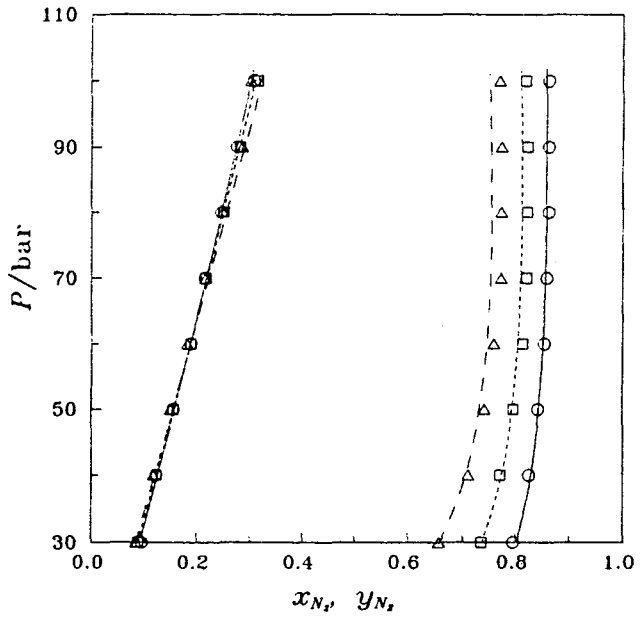


Figure 4. Pressure-Composition Diagram for the Nitrogen + HFC-227ea System
(O 293.2 K, □ 303.2 K, Δ 313.2 K)

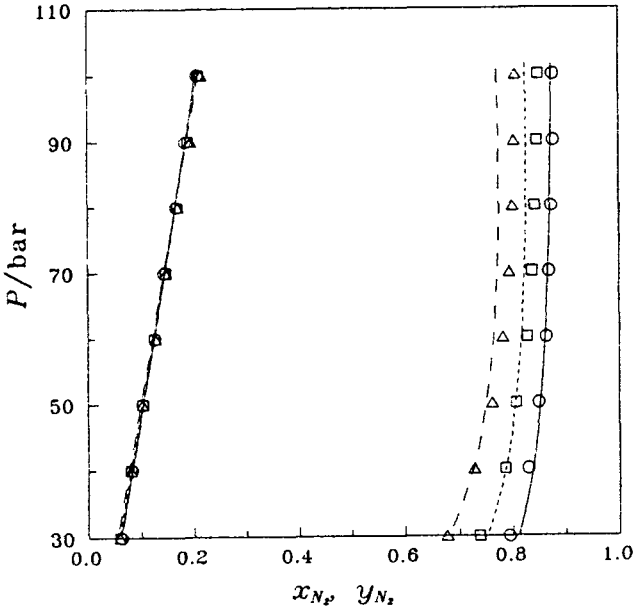


Figure 5. Pressure-Composition Diagram for the Nitrogen +CF_3I System
(O 293.2 K, □ 303.2 K, Δ 313.2 K)

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 (Wong *et al.*, 1992); in this study we use the NRTL model (Renon and Prausnitz, 1968):

$$\frac{A_{\infty}^{E}}{RT} = \sum_{i} x_i \frac{(\sum_{j} x_j G_{ji} \tau_{ji})}{\sum_{k} x_k G_{ki}} \tag{9}$$

$$G_{ji} = \exp(-\alpha_{ij} \tau_{ji}) \qquad \text{and} \qquad \tau_{ij} = A_{ij} / (RT) \tag{10}$$

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* ; α_{ij} is non-randomness parameter; R is gas constant (8.314 J/K-mol).

The critical properties (T_C, P_C) and acentric factors (ω) of nitrogen, halon-1301, halon-1211, HFC-227ea, and CF_3I used to calculate the parameters for the Peng-Robinson equation of state are given in Table 2. We have set the non-randomness parameter, α_{ij}, equal to 0.3 for all the binary mixtures studied here.

Table 2. Characteristic Properties of the Chemicals

component	T_C(K)	P_C(bar)	ω	data source
Nitrogen	126.26	34.0	0.039	Braker et al. (1976)
Halon-1301	340.15	39.7	0.171	TRC Tables (1996)
Halon-1211	426.9	42.6	0.184	TRC Tables (1996)
HFC-227ea	374.8	29.1	0.357	Robin, M. L. (1994)
CF_3I	395.0	40.4	0.273	Nimitz. J. (1994)

The Marquardt algorithm (1973) was applied to obtain the parameters with the following objective function:

$$\mathbf{obj} = \sum_{j} \left(\frac{P_{j,expt} - P_{j,expt}}{P_{j,expt}} \right)^2 + \sum_{j} (y_{j,expt} - y_{j,calcd})^2 \tag{11}$$

In these calculations the solubilities at 303.2 K and 313.2 K were predicted using the model parameters obtained at 293.2 K. Because the temperature ranges of binary systems studied here were relatively short, k_{ij}, A_{ij} and A_{ji} were fixed with the values obtained at 293.2 K. All the binary parameters of both systems and the average absolute deviations (AAD) between measured and calculated values are listed in Table 3.

The lines in the Fig. 2, 3, 4 and 5 shows calculated values for nitrogen (1) + halon-1301 (2),

nitrogen (1) + halon-1211 (2), nitrogen (1) + HFC-227ea (2), and nitrogen (1) + CF_3I (2) system from 293.2 K to 323.2 K, respectively, while the point shows the experimental data. As shown in these figures and by the low AAD, the calculated values give a good agreement with the experimental data. From these results, the NRTL binary parameters obtained in this work can be used for the prediction of solubilities in the range of temperatures studied. For nitrogen (1) + halon-1301 (2) system, the following critical pressures were observed; about 81 bar at 313.2 K, 96 bar at 303.2 K and 108 bar at 293.2 K, respectively. Other systems exhibited no critical point at these experimental conditions.

Table 3. Values of Binary Parameters and AAD (%) of P and y

System	NRTL parameters[a]			AAD (%)[b]		
	k_{ij}	A_{ji}	A_{ij}	293.2 K	303.2K	313.2K
N_2 + Halon-1301	0.5460	0.9854	0.2996	0.96	1.19	2.92
N_2 + Halon-1211	0.6922	-1.3622	4.6525	0.85	2.44	1.94
N_2 + HFC-227ea	0.5792	-2.7547	8.6937	1.26	0.57	2.70
N_2 + CF_3I	0.4589	-1.6167	12.8562	0.91	1.75	3.29

a Binary parameters for all systems were obtained at 293.2 K and the unit of A_{ij} and A_{ji} is kJ/mol.

b $\text{AAD} = (1/N)\sum_i^N \left[\left| (P_{\text{exptl},i} - P_{\text{calcd},i}) / P_{\text{exptl},i} \right| + \left| (y_{\text{exptl},i} - y_{\text{calcd},i}) \right| \right] \times 100.$

CONCLUSION

1. The solubilities of N_2 are measured in clean fire extinguishing agents, such as Halon-1301, Halon-1211, HFC-227ea and CF_3I.
2. The solubilities of N_2 were well correlated with the Peng-Robinson equation of state using the Wong and Sandler mixing rules, and the relevant parameters are presented.
3. N_2 is much soluble in following order: HFC-227ea , Halon-1301, CF_3I, Halon-1211.

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