Pressure-Volume-Temperature Behavior of Binary Mixtures of Hydrogen Fluoride with HCFC-22, HFC-32 and HFC-134a

Howard L. Wilson and W. Vincent Wilding

Department of Chemical Engineering, Brigham Young University, Provo, UT, USA

Abstract

Vapor phase pressure-volume-temperature (P-V-T) measurements have been performed for binary mixtures of hydrogen fluoride(HF) with three different alternative refrigerants. A total of 62 mixtures were tested at temperatures ranging from 283.15 K to 343.15 K. Pressures ranged from 100 to 1400 kPa and HF concentrations varied from about 0.2 to 0.9 mole fraction HF. Several data were also obtained for the system HF/Nitrogen at 323.15 K. Data have been compared to a model based on a monomer-hexamer chemical association model and the Soave equation of state. The deviation of the model from the experimental compressibility data averaged 1.5 percent.

Keywords: Experimental Data, Pressure-Volume-Temperature, Hydrogen Fluoride, Refrigerants, Monomer, Hexamer

Presented at the National Institute of Standards and Technology's Thirteenth Symposium on Thermophysical Properties, June 24, 1997 at Boulder, CO, USA.

1. Introduction

Hydrogen fluoride (HF) is used as a reactant in the production of alternative refrigerants such as hydrochlorofluorocarbons (HCFC's) and hydrofluorocarbons (HFC's). Phase equilibrium data are required for the design of economical separation systems for refrigerant purification. One commonly used method to obtain phase equilibrium data is the pressure-temperature-liquid composition (PTx) method. The isothermal PTx method requires measurement of total pressure of mixtures of known composition at constant temperature. Mixture pressure data is correlated with nonidealities in the liquid phase represented by an activity coefficient equation and nonidealities in the vapor phase represented by an equation of state.

The PTx method is advantageous for systems involving hazardous materials because the method does not require sample analysis and therefore, the handling of hazardous materials is kept to a minimum. This makes the PTx method a prime candidate for systems involving HF. However, HF is highly polar and self-associates in the vapor phase to form hydrogen bonded oligomers such as dimer, trimer, tetramer, etc. The formation of these various oligomers makes the vapor phase very nonideal relative to an ideal gas. These vapor phase nonidealities require accurate treatment to make the PTx method viable for systems containing hydrogen fluoride.

To test and improve the PTx method for systems involving HF, vapor P-V-T measurements have been performed for the systems HF/chlorodifluoromethane (HCFC-22), HF/difluoromethane (HFC-32) and HF/1,1,1,2-tetrafluoroethane (HFC-134a). These refrigerants were chosen because of their role as replacements for ozone depleting

chlorofluorocarbons. Measurements were performed in a 6.25 liter stainless steel cell at temperatures from 283.15 K to 343.15 K and pressures of 100 to 1400 kPa. The mixture compressibilities obtained from the P-V-T data were compared to values calculated from the monomer-hexamer model of Wilson et al.[1] and found to agree within 1.5 percent.

2. Experimental Method

A schematic of the apparatus used for experimental vapor-phase P-V-T measurements is shown in Figure 1. The primary components of the apparatus are the pressure cell, the constant temperature bath, the temperature controller and the pressure transducer. The pressure cell is constructed of stainless steel and has a volume of approximately 6.25 liters. The cell is equipped with lines and valves to allow charging, evacuation and pressure measurement. The cell has a removable top that is sealed with a compressed Teflon packing. The cell contents are stirred by a magnetically driven Teflon coated stir bar.

Materials were charged to the cell under their own vapor pressure from stainless steel sample cylinders. After given time to equilibrate at the bath temperature, the pressure was recorded. Additional materials were then added to the cell incrementally and the next pressure was recorded. After the completion of a run the contents of the cell were sent to a scrubbing system containing NaOH to remove the hydrogen fluoride.

The temperature controller was manufactured by Bayley Instrument and kept the bath temperature within ±0.02 K of the desired temperature. The cell temperature was measured using a calibrated platinum resistance temperature detector (RTD) from Omega

and a Keithley 199/1992 digital multimeter. Cell temperature is estimated to be accurate to within ±0.1 K. The mass of the materials was measured by weight to within ±0.005 grams. Loss of material from connections to the cell was kept to a minimum by using 1/16 inch valves from High Pressure Equipment. The dead volume of the connecting fittings was approximately 0.06 cc. This results is a loss of material on the order of .001 to .002 grams per charge. The effect of errors in mass in the cell on the measured density is estimated to be ±0.1 percent. Pressures were measured with a Paroscientific Digiquartz pressure transducer. The major uncertainties in pressure measurement are due to the liquid head in the line to the transducer which could add an error of ±0.2 percent at 500 kPa rising to ±0.5 percent at 200 kPa. The cell volume as a function of temperature and pressure was determined from hydrostatic measurements using water as the working fluid. A Ruska hand pump was used to vary the pressure. The cell volume is estimated to be accurate within ±0.05 percent.

The hydrogen fluoride was electronic grade obtained from Matheson Gas Products and had a purity from lot analysis of 99.99%. The HCFC-22 and HFC-134a were obtained from DuPont and had purities by gas chromatography of 99+ percent. The HFC-32 was obtained from Solvay and also had a purity from analysis of 99+ percent. Other than degassing, the materials were used as received. The HF was drawn from the vapor phase to exclude possible water contamination which tends to stay in the liquid phase. The overall accuracy of the measured densities is estimated to be ±0.3 percent at 500 kPa and ±0.6 percent at 200 kPa.

3. Results

Experimental results are given in Tables 1-3 for the systems HF/HCFC-22, HF/HFC-32 and HF/HFC-134a. Given in the tables are the temperature, pressure, mixture composition and the compressibility, $Z_{measured}$, determined at the experimental condition. Also given are predicted compressibilities, Z_{model}, and percent deviation between the model and the experimental values. The Soave equation of state[2] was used to calculate fugacities and a chemical equilibrium model was used to represent the association of HF monomer to form HF hexamer. This method is discussed below. Critical constants used in the equation of state and the chemical association model are given in Table 5.

A plot of percent deviation between the monomer-hexamer model and the measured value of the compressibility versus mole fraction HF is shown in Figure 2. The average deviation is 1.5 percent, with higher deviations present at the extremes of the composition range. At high mole fractions of HF, there is a high degree of association and the monomer-hexamer model does not represent the data well. This appears to be due to the formation of oligomers larger than hexamer at the higher pressures. At low concentrations of HF, the inability of the model to predict the compressibilities is probably due to neglecting the formation of smaller oligomers such as dimer, trimer and tetramer. An overall bias is also visible in the figures. The model, using the chemical association constants from Long et al.[3] as a basis, tends to underestimate the vapor density. This overall bias could be partially corrected by modifying the values for the chemical association constant. This tends to improve the data at high HF concentrations, while doing little for the data at low HF concentration.

PVT properties of four mixtures of nitrogen with HF were also measured and are reported in Table 4. The model shows deviations from these data of similar magnitude to the deviations from the other mixture data.

Four data points on pure HF were measured as listed in the data tables. Figure 3 shows the data of Wilson et al.[4] at 323.15 K and 343.15 K with our data at the same temperatures. The figure also shows compressibilities from both the monomer-hexamer model[1] and the monomer-dimer-hexamer model[4] along the same isotherms. The monomer-hexamer association model with the Soave EOS gives an average absolute deviation of 3.1 percent for these points. From the figure it is evident that the monomer-hexamer model is in error at both low and high pressures. The temperature dependance is also off at 343.15 K. These four pure HF data were compared to interpolated values of the data of Wilson et al.[4] shown in the figure and found to agree with an average deviation of 0.8 percent.

During the experimental program, four P-V-T points were also measured for pure HCFC-22. These data show an average deviation from the Soave equation of state of 0.4 percent with the error increasing as pressure increases.

4. Chemical Association Model

The monomer-hexamer model used in the data reduction was the same one used by Wilson et al.[1], which is a slight modification of the method developed by Gillespie et al.[5]. This model is based on the HF association model of Simons and Hildebrand[6]. Simons and Hildebrand assumed only one HF oligomer (hexamer) was formed in the vapor

phase according to the following equation.

$$6\,HF \rightleftharpoons (HF)_6$$

This association can be represented with an equilibrium constant based on pressure.

$$K_P = \frac{P_{Hexamer}}{(P_{Monomer})^6}$$

The total pressure of HF is then equal to the sum of the partial pressures of HF species:

$$P_{HF} = P_{monomer} + K_P\,(P_{Monomer})^6$$

Long et al.[3] found that a monomer-hexamer model could fit their P-V-T data adequately so neglected other smaller and larger oligomers. They determined that $\log K_p = 8910./T - 43.65$ where K_p has units of $torr^{-5}$ and temperature is in Kelvin. To improve accuracy in correlating HF vapor P-V-T data, other authors have included additional oligomers in their models as more data have become available A few examples are the monomer-trimer-hexamer model of Bekerdite et al.[7], the monomer-dimer-hexamer model of Wilson et al.[4] and the monomer-dimer-hexamer-octamer model of Schotte.[8] Several models considering a continuous distribution of oligomers have also been developed by Bekerdite et al.[7], Łencka and Anderko[9] and Anderko and Prauznitz[10].

For this work we have used the modifications to Long's monomer-hexamer model proposed by Gillespie et al.[5] and Wilson et al.[1] They propose an equilibrium constant based on fugacities rather than pressures:

$$K_f = \frac{f_{Hexamer}}{(f_{Monomer})^6} = \frac{\phi_{Hexamer}\ P_{Hexamer}}{(\phi_{Monomer})^6\ (P_{Monomer})^6}$$

At low pressure K_f is equivalent to K_p because the fugacity coefficients approach unity. Long and coworkers[3] determined their parameters at relatively low pressures so their K_p is probably close to K_f.

An iterative procedure was used to determine the predicted compressibilities reported in the tables. Initially the partial fugacity coefficients, ϕ_i, are set to unity and an estimate is made of the partial pressure of HF, P_{HF}. The following equation, for the partial pressure of the monomer, $P_{Monomer}$, was then solved using a Newton-Raphson technique.

$$P_{HF} = P_{Monomer} + K_f \frac{(P_{Monomer})^6 (\phi_{Monomer})^6}{\phi_{Hexamer}}$$

The moles of HF monomer and hexamer, n_i, were then found from

$$n_i = \frac{P_i}{P_{Monomer} + P_{Hexamer}} (n_{Monomer} + n_{Hexamer})$$

where

$$n_{Monomer} + n_{Hexamer} = \frac{P_{Monomer} + P_{Hexamer}}{P_{Monomer} + 6\,P_{Hexamer}} (n_{HF})_{Bulk}$$

The apparent number of moles of HF in the cell $(n_{HF})_{Bulk}$ is the mass of HF charged to the cell divided by 20.006, the molecular weight of HF monomer. The 'true' number of moles of HF in the cell, $(n_{Monomer} + n_{Hexamer})$, is less than the apparent number of moles because of

the formation of the hexamer.

With a value for the true number of moles of each species in the cell, an estimate of the true vapor mole fractions, y_i, was calculated from

$$y_i = \frac{n_i}{n_{Monomer} + n_{Hexamer} + n_{Refrigerant}}$$

From the new vapor mole fractions, the partial pressures, P_i, and the partial pressure of HF were recalculated.

$$P_i = y_i \, P_{Measured}$$

$$P_{HF} = P_{Monomer} + P_{Hexamer}$$

Once a new partial pressure of HF was determined, the entire procedure was repeated. The program completes the calculations for several iterations until the y_i have converged.

With better approximations of the true vapor mole fractions, partial fugacity coefficients from the Soave EOS are then calculated, again using a Newton-Raphson convergence method. The Soave EOS requires critical constants and the acentric factor for each species. Estimates of these constants for HF monomer and hexamer have been made by Wilson et al.[1] and are listed in Table 5. With new partial fugacity coefficients the calculations are repeated starting from the beginning. Once the y_i and fugacity coefficients have converged, the apparent compressibility is calculated using

$$Z_{Model} = \frac{PV}{RT} \frac{(P_{Monomer} + P_{Hexamer} + P_{Refrigerant})}{(P_{Monomer} + 6\,P_{Hexamer} + P_{Refrigerant})}$$

where V is the molar volume calculated from the equation of state.

5. Conclusion

The monomer-hexamer association model based on fugacities represents the experimental data fairly well over the ranges studied. This is encouraging because the PTx method for systems involving HF often depends on this or similar models to represent the vapor phase nonidealities. These data show some of the weaknesses of the monomer-hexamer model. The monomer-hexamer model is not able to predict to a high degree of accuracy the properties of the pure HF, which contributes significant errors to the mixture predictions. Switching to other more complex chemical species models, such as a monomer-dimer-hexamer-octamer model, should allow better vapor compressibility prediction.

One of the future developments of this research is to include in the equation of state interaction terms between the various species in the vapor phase. In these calculations the Soave binary interaction terms, k_{ij}, were not included. From the correlation of the data, it is apparent that the monomer-hexamer model needs to be improved before the adequacy of the mixing rules and the values of the specific interaction k_{ij}'s can be determined. With improved models, a comparison of the mixture properties with the model will show whether additional mixture parameters, such as the Soave k_{ij} are needed.

List of Symbols

f_i	partial fugacity of component i
ϕ_i	partial fugacity coefficient of component i
k_{ij}	binary interaction term in Soave equation
K_p	association constant based on pressure
K_f	association constant based on fugacity
n_i	number of moles of component i
P	pressure/kPa
R	Universal Gas Constant
T	temperature/K
V	molar volume, liters/mol
y_i	vapor mole fraction of component i
Z	compressibility

Acknowledgments

We express thanks to Dr. Fran Nordmeyer and the Department of Chemistry at Brigham Young University for generously providing laboratory facilities for these measurements.

References

[1] Wilson, L. C., W. V. Wilding and G. M. Wilson, *Experimental Results from the Design Institute for Physical Property Data: Phase Equilibria and Pure Component Properties Part II*, AIChE Symposium Series, No. 271, **85** (1989).

[2] Soave, G., *Chem. Eng. Sci*., **27**, 1197 (1972).

[3] Long, R. W., J. H. Hildebrand and W. E. Morrell, *J. Am. Chem. Soc.*, **65**, 182-187 (1943).

[4] Wilson, L. C., W. V. Wilding and G. M. Wilson, "Vapor PVT and Vapor Pressure of Hydrogen Fluoride", Paper presented at the 12th Symposium on Thermophysical Properties, National Institute of Standards and Technology, Boulder, CO, USA, June 20, 1994.

[5] Gillespie, P. C., J. R. Cunningham and G. M. Wilson, *AIChE Symposium Series*, No. 244, **81**, 41-48 (1985).

[6] Simons, J. And J. H. Hildebrand, *J. Am. Chem. Soc.*, **46**, 2183-2191 (1924).

[7] Beckerdite, J. M., D. R. Powell and E. T. Adams, Jr., *J. Chem. Eng. Data*, **28**, 287-293 (1983).

[8] Schotte, W., *Ind. Chem. Process Des. Dev.*, **19**, 432-439 (1980).

[9] Łencka, M. and A. Anderko, "Modeling Phase Equilibria in Mixtures Containing Hydrogen Fluoride and Halocarbons", *AIChE J.*, **39**, 533-538 (1993).

[10] Anderko, A. and J. M. Prausnitz, *Fluid Phase Equilibria*, **95**, 59-71 (1994).

[11] Daubert, T. E. and R. P. Danner, *Physical and Thermodynamic Properties of Pure Chemicals: Data Compilation*, Hemisphere, New York (1991).

[12] Piao, C.-C., M. Noguchi, H. Sato and K, Watanabe, *ASHRAE Transactions*, **100**, 358-366 (1994).

Table 1

PVT Measurements for the system Hydrogen Fluoride/HCFC-22

T/K	P/kPa	y HF	$Z_{measured}$	Z_{model}	% Dev
303.15	285.50	0.7230	0.5009	0.5096	1.75
303.15	426.68	0.5692	0.5893	0.5948	0.94
303.15	647.13	0.4203	0.6601	0.6650	0.73
303.15	881.60	0.3220	0.6889	0.6965	1.10
303.15	1126.12	0.2500	0.6832	0.7055	3.27
323.15	151.97	0.0000	0.9812	0.9839	0.28
323.15	283.35	0.0000	0.9663	0.9697	0.35
323.15	555.09	0.0000	0.9344	0.9392	0.51
323.15	679.97	0.0000	0.9191	0.9246	0.60
323.15	184.74	0.5668	0.9130	0.9409	3.06
323.15	209.23	0.7827	0.7542	0.7538	-0.06
323.15	308.51	0.5707	0.8109	0.8099	-0.12
323.15	939.15	0.5306	0.5828	0.6004	3.02
323.15	1330.16	0.4001	0.6226	0.6380	2.48
323.15	56.85	1.0000	0.9694	0.9922	2.35
323.15	200.45	1.0000	0.5156	0.5112	-0.86
323.15	263.00	0.8578	0.5803	0.5769	-0.59
323.15	369.86	0.6881	0.6546	0.6509	-0.58
323.15	489.65	0.5602	0.7055	0.7022	-0.48
323.15	585.98	0.4856	0.7320	0.7288	-0.44
323.15	771.01	0.3837	0.7610	0.7587	-0.30
323.15	1067.37	0.2818	0.7738	0.7736	-0.03
343.15	356.43	1.0000	0.5857	0.6048	3.26
343.15	455.62	0.8554	0.6405	0.6524	1.86
343.15	599.79	0.7037	0.6937	0.7011	1.08
343.15	795.24	0.5635	0.7364	0.7412	0.64
343.15	1025.66	0.4521	0.7622	0.7656	0.45
343.15	1316.67	0.3573	0.7731	0.7761	0.39

Table 2

PVT Measurements for the system Hydrogen Fluoride/HFC-32

T/K	P/kPa	y HF	$Z_{measured}$	Z_{model}	% Dev
283.15	115.84	0.7101	0.5279	0.5271	-0.15
283.15	208.87	0.4918	0.6592	0.6614	0.34
283.15	369.22	0.3165	0.7499	0.7583	1.12
283.15	587.29	0.2079	0.7838	0.8025	2.39
303.15	177.11	0.8256	0.4866	0.4924	1.20
303.15	242.16	0.6960	0.5609	0.5661	0.92
303.15	322.45	0.5811	0.6236	0.6294	0.92
303.15	430.56	0.4732	0.6781	0.6856	1.10
303.15	550.28	0.3903	0.7149	0.7249	1.39
303.15	748.49	0.2993	0.7455	0.7607	2.03
323.15	280.45	0.8757	0.5280	0.5331	0.96
323.15	346.82	0.7743	0.5774	0.5825	0.88
323.15	446.12	0.6583	0.6314	0.6373	0.93
323.15	569.06	0.5531	0.6767	0.6843	1.12
323.15	756.24	0.4417	0.7182	0.7291	1.52
323.15	1021.61	0.3394	0.7456	0.7618	2.17

Table 3

PVT Measurements for the system Hydrogen Fluoride/HFC-134a

T/K	P/kPa	y HF	$Z_{measured}$	Z_{model}	% Dev
303.15	212.05	0.8577	0.4073	0.4188	2.83
303.15	285.79	0.7435	0.4758	0.4860	2.14
303.15	366.53	0.6452	0.5295	0.5409	2.14
303.15	489.80	0.5303	0.5816	0.5993	3.04
323.15	305.90	0.7851	0.6086	0.6043	-0.72
323.15	531.87	0.5239	0.7062	0.7071	0.12
323.15	722.44	0.4027	0.7374	0.7399	0.34
323.15	980.54	0.2985	0.7418	0.7506	1.19
323.15	1239.94	0.2295	0.7212	0.7384	2.38
323.15	254.68	0.8176	0.6422	0.6341	-1.26
323.15	334.88	0.6733	0.6954	0.6899	-0.79
323.15	424.99	0.5592	0.7330	0.7296	-0.46
323.15	552.94	0.4471	0.7625	0.7621	-0.06
323.15	764.89	0.3299	0.7782	0.7826	0.56
323.15	1087.85	0.2268	0.7612	0.7742	1.71
323.15	1368.42	0.1687	0.7121	0.7465	4.83
343.15	434.23	1.0000	0.4610	0.4885	5.98
343.15	491.32	0.9401	0.4903	0.5123	4.48
343.15	572.95	0.8642	0.5256	0.5433	3.36
343.15	651.76	0.8001	0.5536	0.5690	2.78
343.15	723.46	0.7487	0.5750	0.5888	2.40
343.15	857.70	0.6654	0.6059	0.6188	2.13

Table 4
PVT Measurements for the system Hydrogen Fluoride/Nitrogen

T/K	P/kPa	y HF	$Z_{measured}$	Z_{model}	% Dev
323.15	301.37	0.8908	0.4880	0.4957	1.59
323.15	352.08	0.8222	0.5262	0.5338	1.45
323.15	422.03	0.7421	0.5693	0.5793	1.76
323.15	572.23	0.6119	0.6365	0.6534	2.67

Table 5
Constants used in data reduction

Compound	T_c/K	P_c/kPa	Acentric Factor	Molecular Weight	Reference
HCFC-22	369.3	4971.	0.2192	86.468	[11]
HFC-32	531.6	5830.	0.2727	52.024	[11]
HFC-134a	374.27	4063.5	0.3266	102.032	[12]
Nitrogen	126.10	3394.4	0.0403	28.014	[11]
HF monomer	307.6	8308.65	0.06	20.006	[4]
HF hexamer	471.2	4053.	0.2353	120.036	[4]

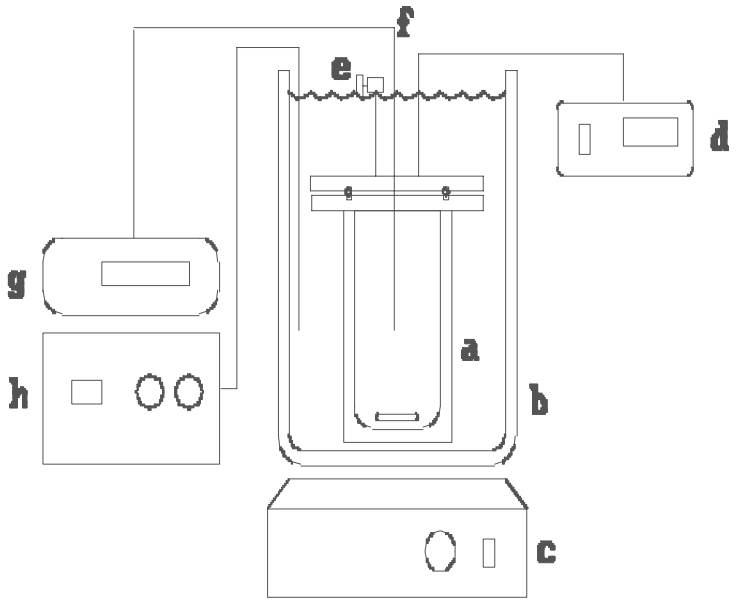

Figure 1. Schematic of experimental apparatus with (a) pressure cell, (b) water bath, (c)magnetic stirrer, (d) pressure transducer, (e) addition line and valve, (f) platinum resistance temperature detector, (g) digital multimeter, (h)temperature controller.

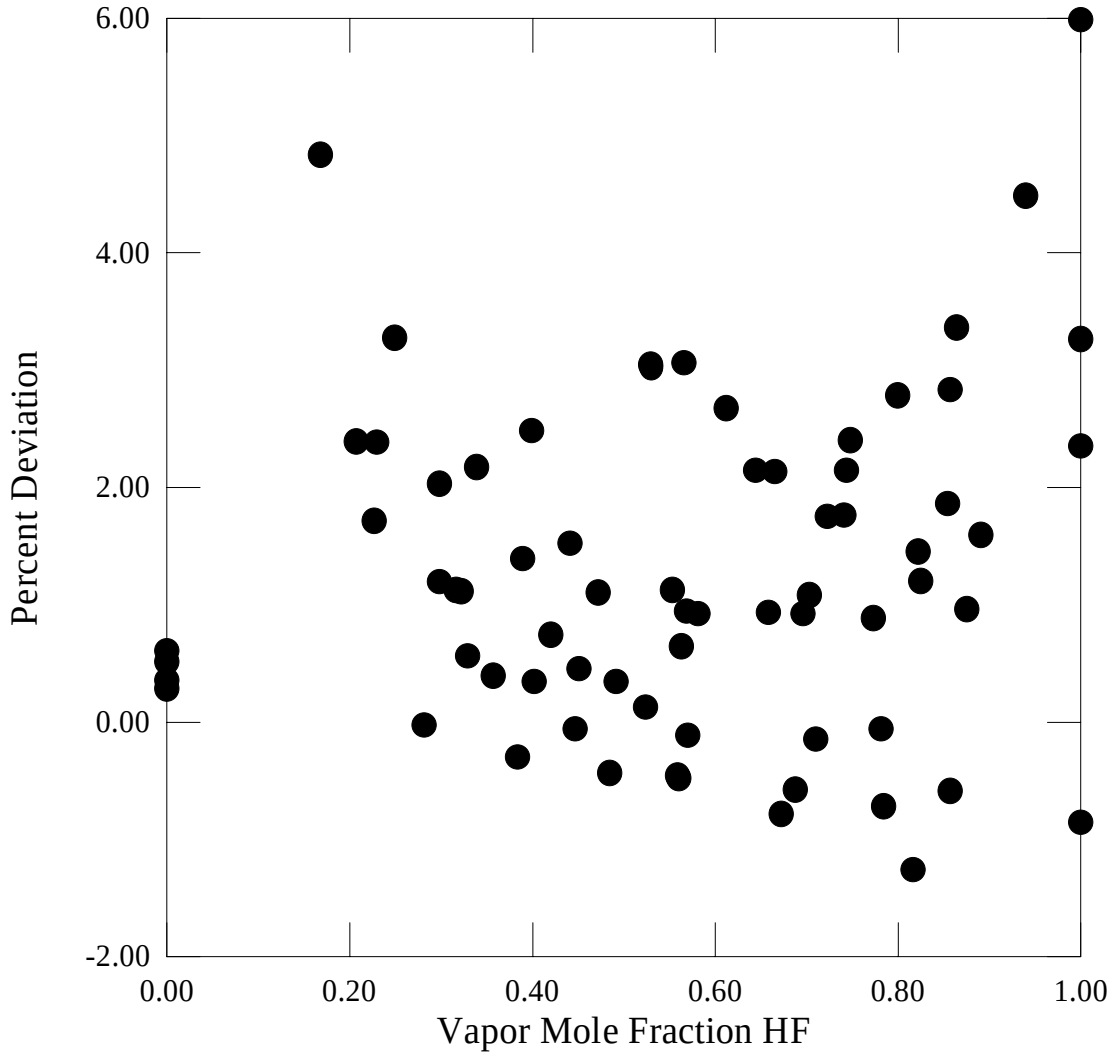

Figure 2. Percent deviation between the monomer-hexamer model and the experimentally determined compressibility versus mole fraction hydrogen fluoride.

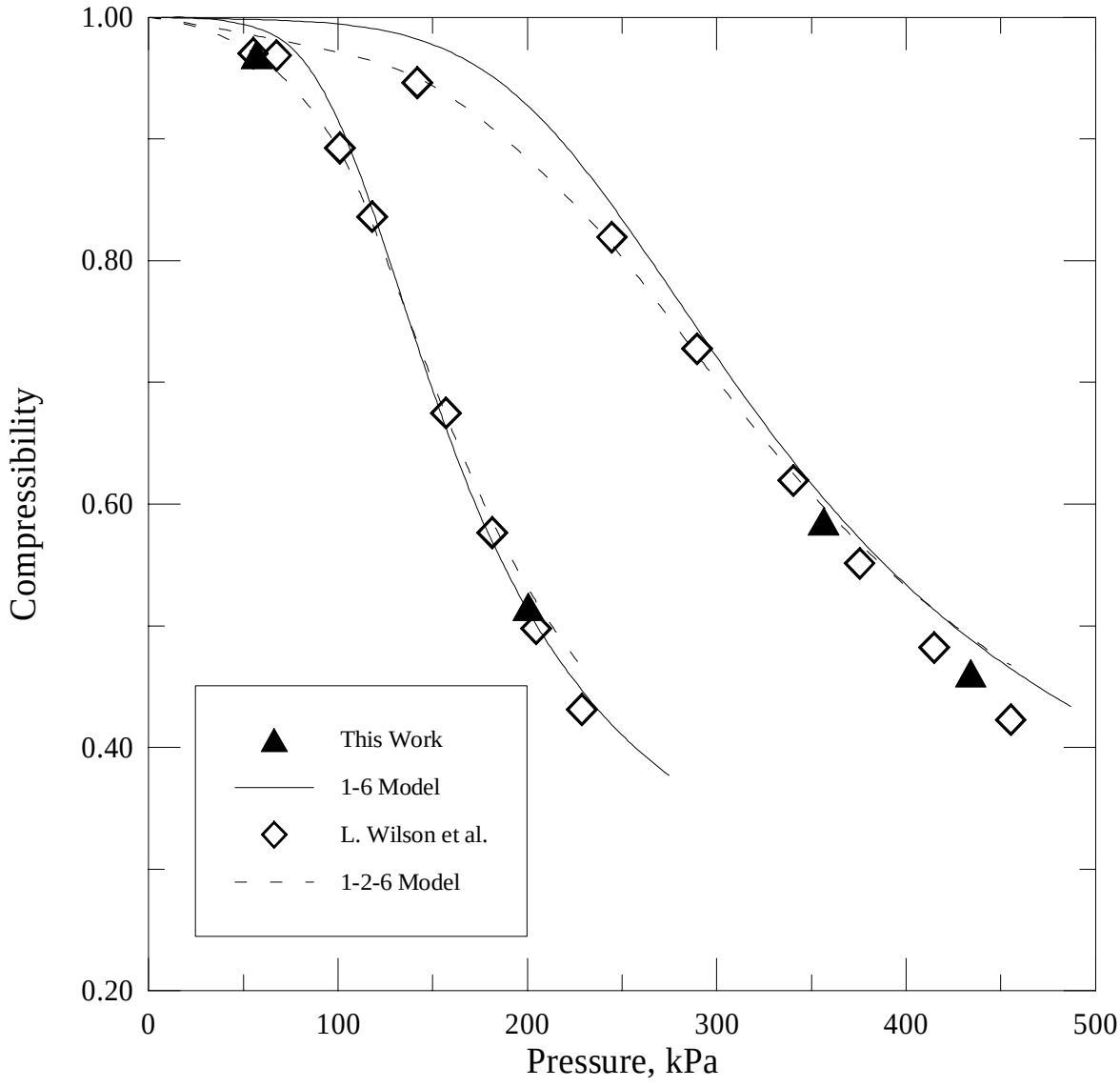

Figure 3. Compressibility of pure hydrogen fluoride at 323.15 K and 343.15 K from this work and the work of Wilson et al.[4] Monomer-hexamer model from [1] and monomer-dimer-hexamer model from [4].