

Project Title: Evaluation of Phase Coexistence and Heat Effects for Hydrogen Fluoride Mixtures using a Novel Equation of State

Date: August 2002 – August 2003

Total Funds Requested: \$25,939

Faculty Member(s): D.P. Visco, Jr.

Project Description:

In the production of hydrofluorocarbons (HFC's) and hydrofluorochlorocarbons (HCFC's), hydrogen fluoride (HF) provides the fluorine ion source. Accordingly, design of heat exchange and separation equipment for the multi-component mixtures that exit the reactor, especially during the process analysis phase, require robust models to predict the thermodynamic properties (partitioning coefficient, heat of vaporization, heat capacity, etc.) of these mixtures.

Development and evaluation of models for HF-mixtures are hampered by two specific problems. First, HF is a caustic and toxic substance. A spill of concentrated HF to skin of 2% of the total body area is fatal. Thus, it is not surprising that experimental data for HF, both as a pure component and in mixtures, are quite limited. This lack of data inhibits parameterization and testing of models. The second problem is that HF associates substantially in all phases, including the vapor-phase (even at very low pressures).

Thus, any model that attempts to describe HF (and HF-mixtures) must specifically include a term that accounts for this important attractive force.

For equations of state (EOS) developed for HF, only pressures and/or phase densities have been

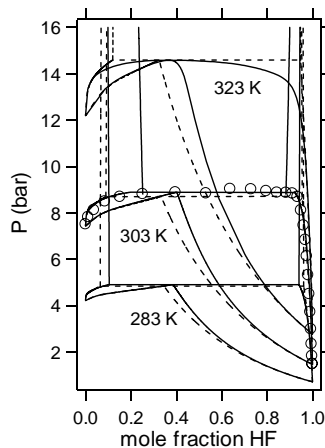


Figure 1: Pxy diagram for HF-R12 system. Expt. data is shown as empty circles. The solid lines are predictions using the van der Waal mixing rule while the dashed lines are using the Wong-Sandler mixing rule.

used during the parameterization process.^[1] Unfortunately, if one uses an EOS parameterized in this fashion, derivative properties (heat of vaporization, heat capacity, etc.) need not be adequately represented by these parameters.^[2, 3] Recently, a work by the PI has shown that a successful EOS for HF^[4] in the prediction/correlation of densities and vapor pressure does, in fact, perform poorly for the heat effects. The PI has modified this EOS to produce a robust model for both phase densities, vapor pressures and heat effects.^[5]

The next step in this research is to determine if this modified model can correlate/predict the phase coexistence properties of HF-mixtures. Preliminary results to this end are encouraging. However, more systems need to be evaluated as well as a more thorough comparison of the effects of mixing rules on the predicted system properties. (ie: one mixing rule will show a liquid-liquid phase splitting while another mixing rule will show a totally

miscible liquid phase – see Figure 1). Additionally, and often neglected, the heat effects of these mixtures need to be determined and, when available, compared to experimental information. It is only at the conclusion of this part of the study can we confidently state that a successful, robust model for HF-mixtures has been developed.

1 Galindo, A., P.J. Whitehead, G. Jackson, and A.N. Burgess. "Predicting the Phase Equilibria of Mixtures of Hydrogen Fluoride with Water, Difluoromethane and (Hfc-32), and 1,1,1,2-Tetrafluoroethane (Hfc-134a) Using a Simplified Saft Approach." *J. Phys. Chem. B* 101, no. 11 (1997): 2082-91.

2 Visco, D.P., Jr., E. Juwono, and D.A. Kofke. "Heat Effects of Hydrogen Fluoride from Two Thermodynamic Models." *Int. J. Thermophysics* 19 (1998): 1111.

3 Visco, D.P., D.A. Kofke, and R.R. Singh. "Thermal Properties of Hydrogen Fluoride from an Eos + Association Model." *AIChE J.* 43 (1997): 2381.

4 Lencka, M., and A. Anderko. "Modeling Phase Equilibria in Mixtures Containing Hydrogen Fluoride and Halocarbons." *AIChE J.* 39 (1993): 533.

5 Visco, D. P., and D. A. Kofke. "Improved Thermodynamic Equation of State for Hydrogen Fluoride." *Ind. Eng. Chem. Res.* 38, no. 10 (1999): 4125-29.

Alignment with Center Focus:

This project falls squarely under the “Pervasive Simulation & Modeling” focus area of the Center for Manufacturing Research (CMR) as it is, at its base, a project on modeling the solution properties of systems that include hydrogen fluoride. In a smaller way, this project can be considered under the “Next Generation Materials and Manufacturing Processes” focus area of the CMR as well. This later focus area includes the phrase “...simulation of material phenomena”. In this proposal we predict two important solution phenomena, namely azeotropy and miscibility gaps. Knowledge of when (ie: what states) systems exhibit this behavior is very important when it becomes necessary to separate these systems.

Unfortunately this work does not compliment existing research from other PI’s within the CMR. However, discussion is underway between Dr. Richard Booth and the PI of this project involving the prediction of properties for HFC’s – these substances are important in this current research as well as the work on blowing agent diffusion in Polyurethane foams that is performed by Dr. Booth.

Potential Payoff

The potential payoff in a variety of areas is large for this work.

Industrial/Govt. Contacts

- Contacted Atofina (Dr. S.G. Schon) in April 2002 about utilizing the modified model to predict azeotropes of multi-component HF mixtures. Discussion is pending.
- Contacted Dr. Lawal at Texas Tech in April 2002 about opportunities that exist to provide this model for use by BP-Amoco. Discussion is pending.
- Contacted by Dr. B. Davison (ORNL) in April 2002 about experimental measurement capabilities to verify/validate predictions of the model. Discussion is pending.
- Will contact Process Simulation companies in mid-April about opportunities to provide the code for the modified model into their software.
- Will contact various smaller hydrofluorocarbon producers depending on the outcome of the contacts above.

External Sponsorship

- Depending on the interest of the companies contacted above, the NSF-GOALI program may be very useful. Such a submission would be made during the Summer/early-Fall of 2002.

Dissemination of Research

- Presentation at 2003 Spring AIChE Meeting
- Presentation at 2003 Annual AIChE Meeting
- Presentation/Posters at other such events (eg: TTU Chapter of Sigma Xi presentation, poster at 2002 ASEE Summer School, etc.)
- One paper in *Industrial and Engineering Chemistry Research* on the phase coexistence properties of HF-mixtures via this model (to be submitted during 2002).
- One paper in either *Industrial and Engineering Chemistry Research* or *Journal of Physical Chemistry B* on the heat effects of HF-mixtures via this modified model (to be submitted during 2003).

Previous Support from the CMR in the Last Five Years

None

Requested Budget from CMR:

	Fall 2002	Spring 2003	Summer 2003
Release Time	1976	1976	0
1/4 month	1544	1544	0
benefits	432	432	0
Summer Pay	0	0	0
R & D Engr. Support	0	0	0
Tech Support	0	0	0
Secretarial Support	0	0	0
Hourly Student	0	0	0
MS Students	0	0	0
PhD Students	6000	6000	2400
Travel	0	1250	1250
Supplies	2221	2221	645
books	250	250	0
GSF	1971	1971	645
Equipment Usage	0	0	0
Equipment Purchase	0	0	0
	10197	11447	4295

Total Funds Requested 25939

Matching Commitments from the Department:

\$1,000 for travel.

Approvals and/or Comments of the Department Chair: