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Use of the ASPEN Plus Process Simulator in Modeling Systems Containing Hydrofluoric Acid[1]

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Nonideal association in the vapor phase of HF poses a challenge in modeling. In this paper, a hybrid HF equation in the ASPEN Plus process simulation software and an equation of Anderko and co-workers are compared. Lencka and Anderko used a general framework to combine a simple association model with a cubic equation. This formulation helps to represent the phase behaviors of HF and halocarbon mixtures, especially for systems containing two liquid phases.

KEY WORDS: ASPEN Plus process simulator; CFC-113a; dichlorodifluoromethane; equation of state; HCFC-22; HFC-134a; heat capacity; hydrofluoric acid; 1,1,1,2-tetrafluoroethane; 1,1,1-trichloro-2,2,2-trifluoroethane; vapor phase association; VLE.

1. INTRODUCTION

Hydrofluoric acid has the unique property of associating in the vapor phase below about 140° C, which leads to many anomalous properties of HF below that temperature. Research has been carried out to model HF in the vapor phase starting from the initial work of Hildebrand and his co-workers [1,2]. They treated the system as a mixture of a monomer and a hexamer that gave results strikingly close to real behavior. However, it has been found that the vapor phase is not so simple; there is a distribution of associated species in the vapor phase of HF. The distribution is highly temperature dependent, which the Hildebrand equation does not take into

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account. This association in the vapor phase ceases to exist above a temperature of 130° C. There has been a lot of research since then to represent better the association in the vapor phase for HF. Lencka and Anderko [3] have provided a model of HF that combines the chemical theory of association with a cubic equation of state and has been shown to represent thermodynamic properties of HF and its mixtures with fluorocarbons very well. In this paper we compare the two models in the ASPEN Plus process simulation software and showed the perspective of using one or the other model for this system.

2. MODELS

Hildebrand's original formulation used a mixture of two species, the $(HF)_6$ hexamer of HF and the HF monomer, to estimate the properties of HF below 130° C. His theory, despite its simplicity, was very successful in predicting the anomalous behavior of HF at lower temperatures. This can be used to calculate the molecular weight distribution, partial pressure, and liquid molar volume of HF. ASPEN Plus uses a modified form of Hildebrand's formulation of a mixture of a monomer and a hexamer to describe the vapor phase [4]. In the ASPEN Plus formulation, the temperature-dependent hexamerization equilibrium constant is fitted to the experimentally determined association factors. This is, however, found not to be the best model to use for mixtures of systems containing HF and some fluorocarbons.

For both HF and mixtures of HF and fluorocarbons, Lencka and Anderko [3] proposed a model which combines an equation of state model and a cubic equation such as a Peng–Robinson equation with an additional part which incorporates chemical association of HF. A preferable form of the equation for chemical association contains a sum of equilibrium constants accounting for successive degrees of association of HF.

In the Lencka and Anderko formulation, the compressibility factor Z is written

$$Z = Z^{(ch)} + Z^{(ph)} - 1 \tag{1}$$

Here $Z^{(ph)}$ and $Z^{(ch)}$ stand for the physical and chemical parts of the compressibility factor, respectively. $Z^{(ph)}$ is the physical part given by a cubic equation such as the Peng–Robinson equation [5] as shown in Eq. (2), and $Z^{(ch)}$ is the part which represents the association of HF in the vapor phase.

$$Z^{(ph)} = \frac{v}{v-b} - \frac{a(T)\, v}{RT[(v(v+b)+b(v-b)]} \tag{2}$$

Here $a(T)$ is the temperature-dependent molar attraction constant and b is the excluded volume parameter in the Peng–Robinson equation. For most compounds parameters a and b can be estimated from T_c, P_c, and ω, where ω is the acentric factor of the compounds [5]. For mixtures the following mixing rules are used to calculate parameters a and b for the mixture:

$$\begin{aligned} a_{ij} &= \sum x_i x_j \sqrt{a_i a_j}\,(1-k_{ij}) \\ b_{ij} &= \sum x_i b_i (1-l_{ij}) \end{aligned} \tag{3}$$

where k_{ij} and l_{ij} are the binary interaction parameters.

$Z^{(\mathrm{ch})}$ is given by the ratio n_T/n_0, where n_T is the number of moles of all species in the associated mixture and n_0 is the total number of moles in the absence of association. Lencka and Anderko showed that $Z^{(\mathrm{ch})}$ depends on the dimensionless quantity $q = RKT/v$, where R is the gas constant, K is the equilibrium constant for dimerization, T is the absolute temperature, and v is the molar volume. $Z^{(\mathrm{ch})}$ for HF is derived by Lencka and Anderko [3] in the following form as a ratio of polynomials and the constants a_k's are also given in that reference:

$$Z^{(\mathrm{ch})}_{\mathrm{pure}} = F(q) = \frac{1+\sum_{k=1}^{8} a_k q^k}{(1+q)^8} \tag{4}$$

$Z^{(\mathrm{ch})}$ for mixtures containing an associating component A and a non-associating component can be written

$$Z^{(\mathrm{ch})} = x_A F(RTKx_A/v) + \sum_{k=1}^{r} x_k \tag{5}$$

Here x is the apparent mole fraction and F is the same algebraic function as in Eq. (4). For detailed derivation of the equation and its assumptions, readers are referred to the paper by Lencka and Anderko [3].

3. RESULTS

To investigate the behavior of HF and its application to mixtures, we look at properties of HF and its mixtures with various fluorocarbons. Specifically, mixtures of HF with CFC-113, HCFC-22, and HFC-134a are chosen to test the models. Our need was to apply the models to process improvements of manufacturing HF and also to process design and developments of various fluorocarbons that use HF in the manufacturing processes. ASPEN Plus was our preferred process modeling software to use these models.

First, we looked at the thermodynamic properties of pure HF. The HF association occurs below 130° C, and the anomalous behavior of the HF heat of vaporization is shown in Fig. 1. In ASPEN, a correlation equation is used for the heat of vaporization for HF. This equation predicts the experimental heat of vaporization very well. Since the heat of vaporization is not evaluated for HF from the equation of state, the selected equation of state has no effect on the anomaly of the heat of vaporization. The anomaly results from the chemical bonding of HF monomers. As HF forms oligomers, it releases energy, thereby reducing the heat required for vaporization.

Next, we looked at the heat capacity of HF. The heat capacity at constant pressure C_p also shows anomalous behavior well below the critical point. C_p data at 15.5 kPa are from Franck and Meyer [6]. This anomaly in heat capacity is again due to the formation of oligomers. It is observed that Lencka and Anderko's equation predicts higher heat capacity values than those obtained by the ASPEN plus formulation as shown in Fig. 2.

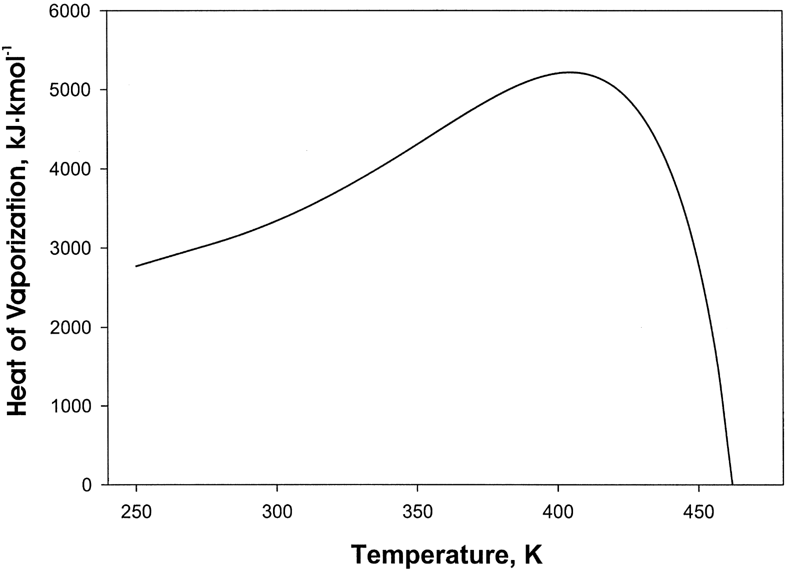

Fig. 1. HF heat of vaporization from ASPEN Plus process simulation software.

This seems to be one of the weaknesses of the Lencka and Anderko equation. Further improvements to the model are needed to represent the HF equation better. The ASPEN Plus formulation represents the heat capacity better than Lencka and Anderko's equation as shown in Fig. 3. Various approaches, e.g., Visco et al. [7, 8], are also used to modify and improve the Lencka and Anderko equation, and they have made significant progress to improve the fit to C_p.

To study the effect of the equation of state on HF/fluorocarbon mixtures we chose three fluorocarbons, CFC-113a, HCFC-22, and HFC-134a. The reason for choosing these three is to look at three kinds of molecules; they all form azeotropes with HF. One is a CFC which forms two liquid phases with HF, the second is an HCFC that is miscible at room temperature, and the final one is a new-generation non-ozone depleting refrigeration compound, HFC-134a, which has no chlorine in it and is also miscible with HF. The sources of VLE data are as follows; HF and CFC-113a VLE measurements are from Knapp et al. [9], HF and HCFC-22 data are from Wilson et al. [10], and HF and HFC-134a data are from Lee et al. [11]. VLE data and their comparisons to the calculated values for these mixtures are shown in Figs. 4–7. It is interesting to note that the VLE for HF and all

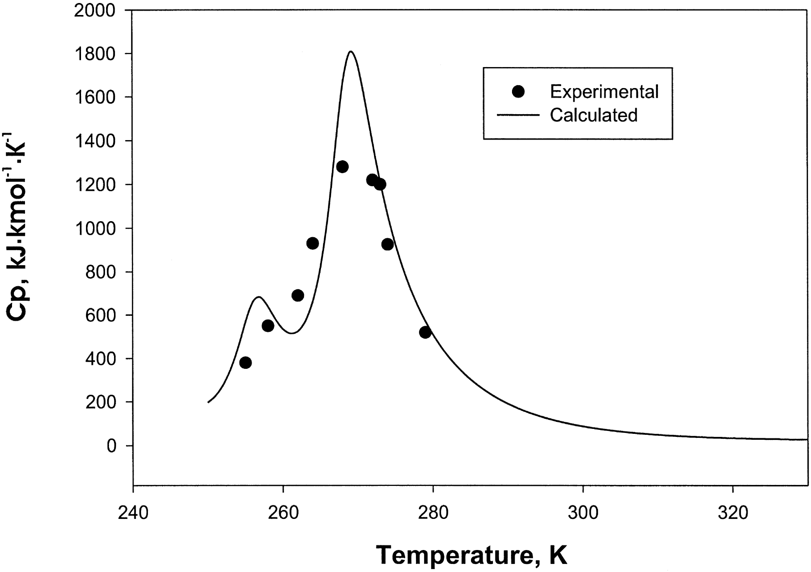

Fig. 2. Vapor C_p of HF: comparison of experimental data of Franck and Meyer [6] with values calculated using the Lencka and Anderko equation [3].

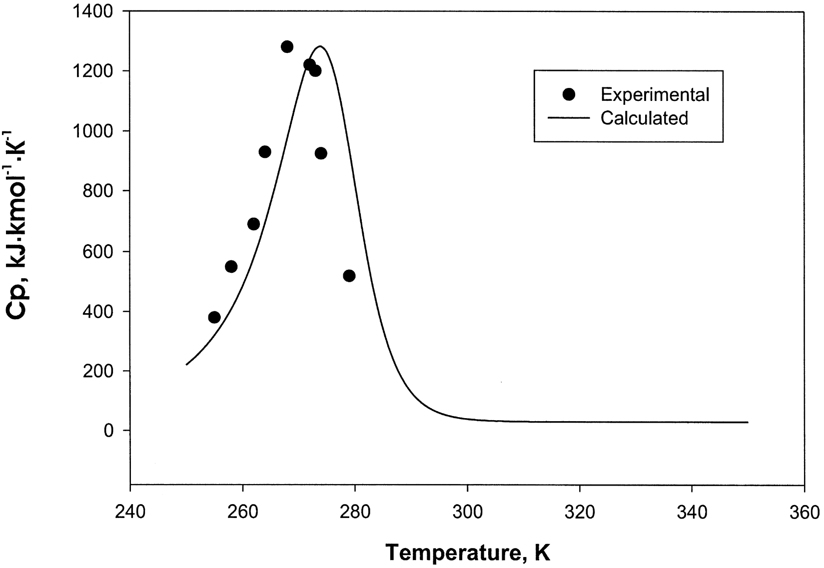

Fig. 3. Vapor C_p of HF: comparison of experimental data of Franck and Meyer [6] with values calculated using the ASPEN Plus model [4].

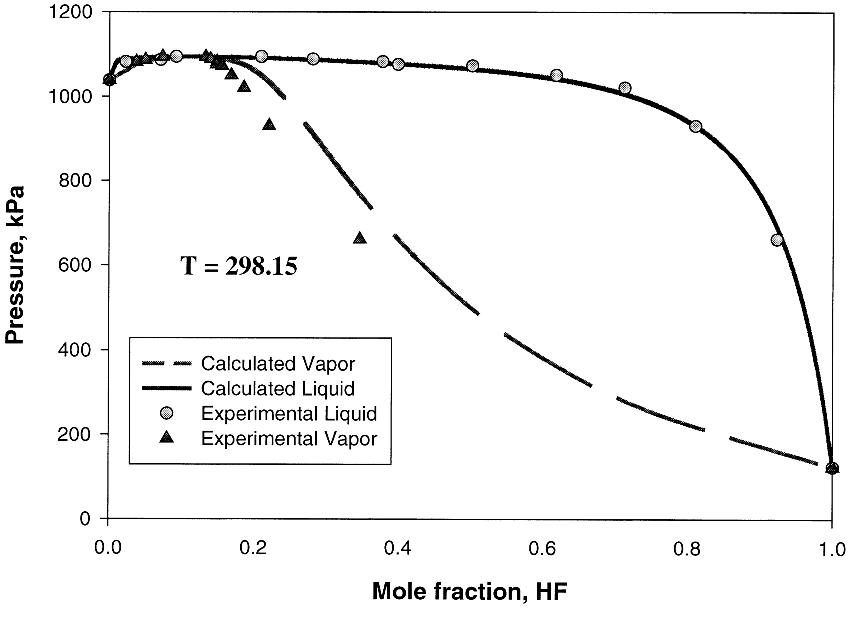

Fig. 4. Comparison of *P–xy* data on HF/HCFC-22 [10] at 298.15 K with values calculated using the Lencka and Anderko [3] equation.

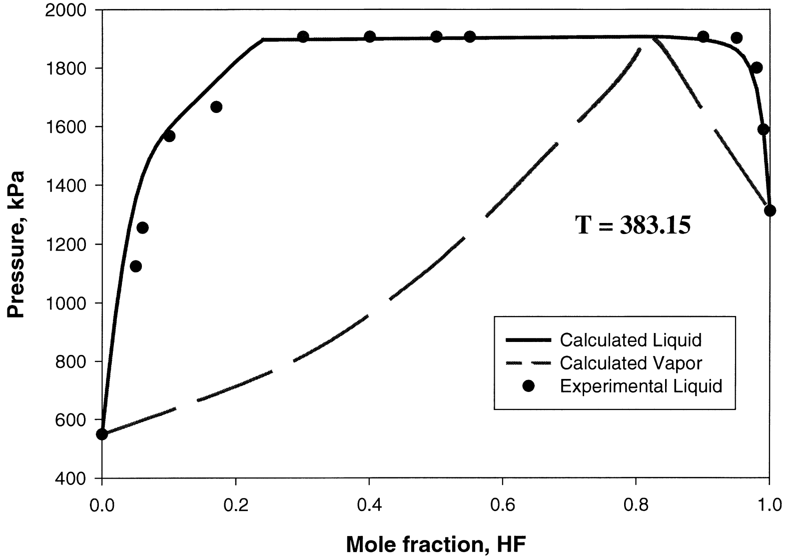

Fig. 5. Comparison of *P–xy* data on HF/HCFC-113a [9] at 383.15 K with values calculated using the Lencka and Anderko [3] equation.

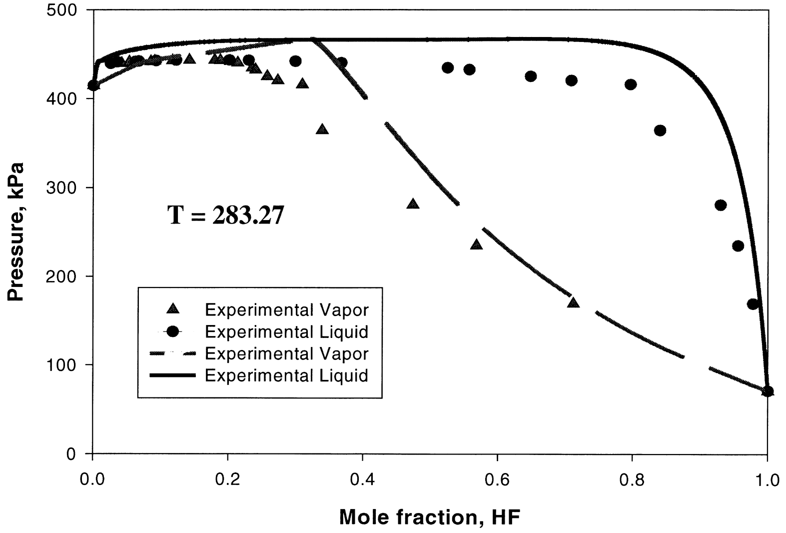

Fig. 6. Comparison of *P–xy* data on HF/HCFC-134a [11] at 283.27 K with values calculated using the Lencka and Anderko [3] equation without any binary interaction.

three of the compounds can be represented quite well by the assumption of chemical association in the manner in which Lencka and Anderko [3] have postulated, without using any binary interaction parameter. In that sense the Lencka and Anderko equation is a good predictive tool for binary mixtures of HF and fluorocarbons. The ASPEN Plus internal equation based on the mixture of a monomer and a hexamer is inadequate to represent the binary mixtures, especially where the mixture forms two liquid phases.

The Lencka and Anderko equation seems to do very well for HF mixtures with a CFC or an HCFC without the use of any binary interaction parameter. For an HFC, the Lencka and Anderko equation did not work very well as a predictive model. Binary interaction parameters helped to fit the data much better. Here the k_{ij} and l_{ij} parameters in Eq. (3) were fitted and values of -0.05 and 0.06, respectively, were obtained and represented the data much better as shown in Fig. 7. We also used various activity coefficient models with the ASPEN Plus formulation that improved the fit somewhat, but the Lencka and Anderko equation is still found to represent the mixture data better. HF and HCFC-22 data from Wilson et al. [10] are also compared to calculations from the ASPEN Plus internal

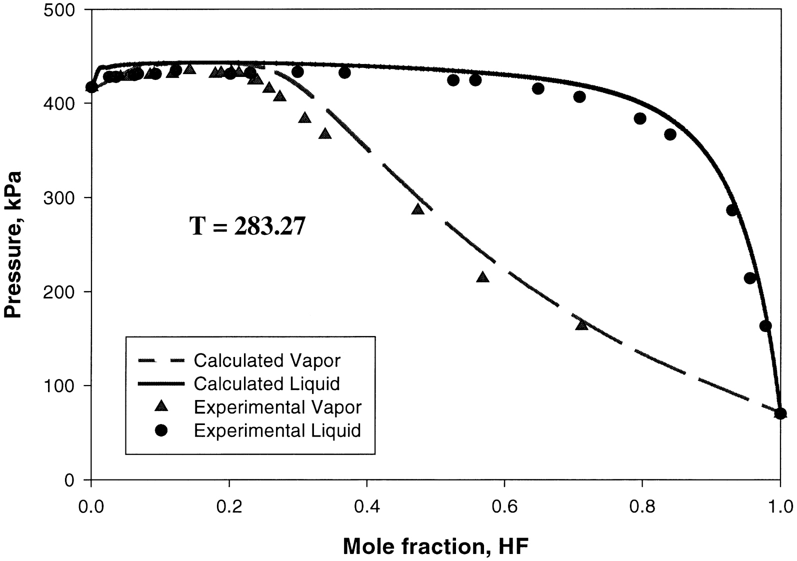

Fig. 7. Comparison of *P–xy* data on HF/HCFC-134a [11] at 283.27 K with values calculated using the Lencka and Anderko [3] equation with binary interaction.

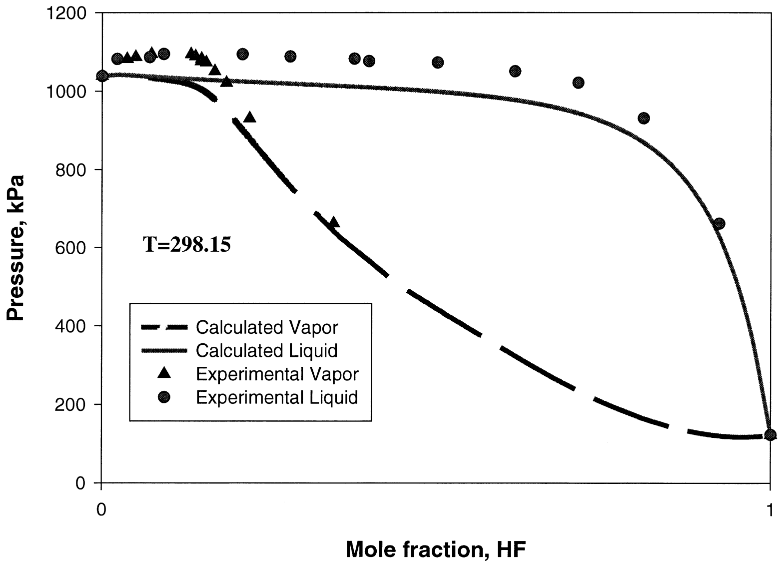

Fig. 8. Comparison of *P–xy* data on HF/HCFC-22 [10] at 298.15 K with values calculated using the ASPEN Plus internal equation.

equation using the WILSON-HF option set from ASPEN. The comparison is shown in Fig. 8. The ASPEN Plus internal equation is found inadequate to represent HF/HCFC-22 VLE data.

4. CONCLUSION

In this paper we have looked into models for the thermodynamic properties of HF and its mixtures and used these in the ASPEN Plus process simulation software for process design and optimization. Although the HF equation formulation used in ASPEN has merits because of its simplicity, it is found to be clearly inadequate for representing mixture properties. The Lencka and Anderko equation uses chemical association to represent the vapor-phase association of HF and represents both pure HF and mixture properties remarkably well even without the use a binary interaction parameter. In other words, the Lencka and Anderko equation can be used as a predictive equation. Results are shown for mixtures of HF with CFC-113a, with HCFC-22, and with HFC-134a (Figs. 4–7). CFC-113a and HCFC-22 binaries with HF are very well represented by the equation, while the HFC-134a binary with HF is not predicted as well, especially the azeotropic composition. The use of binary interaction parameters in the Lencka and Anderko formulation improves the fit to the azeotropic composition. This points to some of the characteristics of the physical nature of VLE for these mixtures of HF and various fluorocarbons. A definite recommendation can be made to use the Lencka and Anderko equation in process simulation to represent both pure HF and its mixtures with fluorocarbons.

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