148o Incorporating Cross-Association in Aqueous Hydrogen Fluoride Mixtures

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A complete understanding of the phase behavior of aqueous hydrogen fluoride (HF) is important for several industries. However, the caustic nature of HF and the non-ideal interactions with water have limited the development of experimental studies as well as robust thermodynamic models. Previous studies have failed to provide a reasonable description of this mixture, in that the complex association interactions between these compounds were not adequately modeled. We explore these interactions in order to deliver a new model developed on the basis of association patterns. The pure components are modeled with no considerations for association and then the association interactions are subsequently included through simple patterns (1-2, 1-6, 1-2-6 etc) that allow formations of different kind of physically meaningful oligomers. The models are then extended to the binary mixture. During this extension, the mixture is first considered to be self associating with no considerations for cross association. The phase co-existence properties for this mixture are correlated using different self association patterns for the pure components. Finally, the cross association is included via different association schemes. By different schemes, we mean that the cross association is considered to be same as well as different from the self association pattern. In order to explore meaningful cross association patterns, molecular level studies will be performed using semi empirical methods. These molecular level studies are specifically directed towards gaining information on association patterns in this mixture using energy considerations to eliminate poor-performing cross-associates. The cross association equilibrium constants will also be dealt in two different ways, as an adjustable parameter as well as a function of the self association equilibrium constants. The significance of these association patterns are studied based on the predictive ability of the model. A complete association pattern for both water as well as the HF along with the cross association scheme will be proposed based on the results obtained.