148i Thermodynamic Expression of Electrolyte Solution

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The vapor-liquid equilibrium (VLE) of a mixture containing both volatile components and dissolved salt behave quite differently from a mixture composed of volatile components alone. When a salt is added to a volatile component system, the composition of the vapor phase will change, as well as the temperature or pressure. This change, called the salt effect on VLE, requires that these types of mixtures be processed in entirely different ways. This is because the structure of the salt-containing liquid solution is entirely different from that of the no-salt solution. We developed a model that can express such a system thermodynamically. This model, the solvation model, can express the salt effect fully in terms of change of vapor phase composition and total vapor pressure. Another approach is the local composition model, which is designed for non-electrolyte liquid solutions with adjustable parameters. A third model, the activity coefficient model (ACM), extends the local composition model to deal with salt-containing systems. By the addition of "electrolyte terms," the ACM is applied also to salt-containing systems to determine the salt effect on VLE. Though the ACM models have found common use, they have some drawbacks or deficiencies. They do not represent the system realistically. Superficially their results are adequate, but the margin of error is significantly larger. Furthermore, they are hard to apply to multi-component systems. The extended version of the ACM approach modifies a non-salt system model to handle a salt system. But without corrective data fitting, such a hybrid model cannot yield as much accuracy as a method designed specifically for salt systems. Results obtained using the extended ACM model can yield markedly greater error compared to the solvation model. In some cases this could cause a significant difference in performance or cost. Both the original and the extended ACM possess curve fitting capability to express activity coefficients of volatile components in liquid solutions containing dissolved salt. However, the original ACM, in itself, without the extension, is capable of representing the activity coefficients; it does this by treating the salt as a third component. But since it is based on the local composition model, which was developed for non-electrolyte solutions, the original ACM should not be applied to electrolyte solutions, in which electrolytes and solvent molecules are strongly associated. This combination of disparate models also may not yield a high level of consistency in terms of thermodynamics. In our solvation model, our approach is to simply assume that there are two types of molecules in the solution containing dissolved salt. The first type is composed of a solvate and a combination of salt and volatile components; the second consists of only non-solvated free volatile components. The second type can contribute to VLE whose liquid compositions differ as to the number of molecules solvated with salt, while the first cannot contribute to VLE at all, because of the non-volatility of salt and solvates. Using this simple assumption, our model affords, compared to the extended ACM, a more versatile method for correlating and predicting VLE for electrolyte solutions, yet with superior accuracy. Once solvation numbers between each of the volatile components and salt are determined, the salt effect on VLE can be calculated for both binary and multi-component solvents. The solvation numbers can be obtained from data on either the lowering of vapor pressure or the raising of the boiling point of either pure or binary solvents with salt systems. The effect of salt on VLE can be predicted from the solvation numbers using the data of a pure solvent and salt system. Moreover, our model expresses the salt effect more meaningfully, yet without resorting to undue complexity. To fully express a binary system, the ACM (NRTL) requires three parameters. With salt added, it needs six more, for a total of nine. In contrast, our model requires two for the binary system, and only two more parameters need be added for the salt, for a total of four, to fully express the same system. As a result, our model offers more consistency than the NRTL model in expressing the salt effect. A further notable advantage of our model is that the visual interpretation of our parameters reflects more realistically the actual chemical structure of the liquid solution, making it easier to comprehend. Our first model, the preferential solvation model, was presented at the American Chemical Society meeting in 1975. The model is widely referred to as “Ohe's model” by researchers. In 1996, we made our own modifications to our preferential solvation model to develop the solvation model, in which all of the volatile components are solvated by the dissolved salt. We made oral presentations of this model at the AIChE spring meetings in 2004 and 2005. Also, the modified method was published in the Journal of Fluid Phase Equilibria in 1998 and 2002. In conclusion, in predicting the salt effect precisely, models should be used that, constructed specifically for handling electrolyte systems, can yield highly consistent and accurate results in a direct and uncomplicated manner. Our model has three major advantages. It can explain and demonstrate thermodynamically the mechanism of the salt effect on VLE. It can predict the salt effect realistically, requiring only the vapor-pressure-lowering data of an individual pure solvent mixed that is mixed with a salt. For calculation, it needs only the solvation numbers of the individual pure solvents mixed with that salt. Use of such a model contributes to a clearer and fuller comprehension of electrolyte systems. This, in turn, will ensure more efficient performance of unit operations.