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Comment

Interactive comment on “Calibration and measurement uncertainties of a continuous-flow cloud condensation nuclei counter (DMT-CCNC): CCN activation of ammonium sulfate and sodium chloride aerosol particles in theory and experiment” by D. Rose et al.

S. Clegg

s.clegg@uea.ac.uk

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Regarding the Comment of Topping, and the Response of Rose and co-workers:

The comment and response concern the relative accuracies of the numerous equations used to represent the water activity/concentration relationships of aqueous NaCl and (NH₄)₂SO₄ solutions. Several have been used in the work of Rose et al., and in their comment Topping et al. recommend the use of the Aerosol Inorganics Model (AIM)

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(Wexler and Clegg, 2002) which is based upon a much larger set of data than any of the parameterizations considered by Rose et al.

Near the end of their response, Rose et al. state:

“In view of these results, it is not clear to us that the AIM can indeed be regarded as an entirely accurate source for the water activity in the systems investigated in this study. As already pointed out in our discussion paper, we see a need for further evaluation and experimental confirmation of preferred data sets and parameterizations/models for the activity of water in dilute aqueous solutions of ammonium sulfate and sodium chloride.”

There is no need for such uncertainty or, in our opinion, any additional study of dilute aqueous solutions of these two salts. Rose et al. should be aware that aqueous NaCl solutions of up to 6 mol kg⁻¹ concentration (saturation with respect to the solid NaCl) have long been used as a reference standard for the vapour pressure of water. See Archer (1992) for a critical evaluation of the data. That is to say, the relationship between NaCl molality and water activity is known very accurately, and probably better than for most other salts. For example, for an uncertainty of about 0.003 in the osmotic coefficient of aqueous NaCl at 25 °C, which is typical of many well-studied electrolyte solutions, the corresponding uncertainty in water activity is given for various concentrations in the following list in the order: (molality, water activity, osmotic coefficient, uncertainty in the water activity).

([0.01, 0.999651, 0.9680, 0.000001]), ([0.02, 0.999310, 0.9582, 0.000002]), ([0.05, 0.998302, 0.9434, 0.000005]), (0.10, 0.99665, 0.9322, 0.00001), (0.20, 0.99337, 0.9235, 0.00002), (0.50, 0.98353, 0.9218, 0.00005), (1.0, 0.96680, 0.9372, 0.0001), (2.0, 0.9314, 0.9869, 0.0002), (4.0, 0.8512, 1.1178, 0.0004) (6.0, 0.7600, 1.2695, 0.0005).

The osmotic coefficients and water activities above were calculated using Archer's fitted Pitzer model. The uncertainties (the last entry for each group of values) are all very

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small. Square brackets indicate that for these very dilute solutions the values of osmotic and activity coefficients are usually obtained using equations which incorporate a Debye-Hückel term to give an accurate extrapolation of properties to infinite dilution. This is true of both the Pitzer molality-based equations (the “OS” model of Rose et al. in their section 3.3) and the Pitzer-Simonson-Clegg model used in AIM.

While the properties of aqueous $(\text{NH}_4)_2\text{SO}_4$ have been less comprehensively measured, its water activity/concentration relationship is still known with a high degree of accuracy below about 6 mol kg^{-1} concentration and close to room temperature - see Clegg et al. (1995, 1996) for critical evaluations of the available data, and for the fitted model equation that is used within AIM. The uncertainties in water activity are likely to be similar to those given in the table above. The available electrodynamic balance data (from 3 different sources, see Figure 15 of Clegg et al. 1995) show some significant differences, but these measurements for highly concentrated solution droplets are not relevant to the present discussion.

Regarding the AIM model: some accuracy in the representation of water activity at low to moderate concentrations has been sacrificed in order to achieve a satisfactory fit over a very wide range. This is shown in Figure 9 of Clegg et al. (1998) for the fit for aqueous NaCl used in AIM, including a comparison with reference osmotic coefficients from Archer. However, the loss is small and less than the differences between the various equations discussed by Rose et al.

We have supplied Fortran codes to Rose et al. that employ a combination of models to yield, essentially exactly, the reference values of water activities and solute activity coefficients of solutions of the two salts at 25 degrees Centigrade. These should facilitate their comparisons and enable them to make more definitive statements in their manuscript.

Simon L. Clegg and Anthony S. Wexler, UC Davis, 17 August 2007.

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