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Discussions

Interactive comment on "An analytical solution to calculate bulk mole fractions for any number of components in aerosol droplets after considering partitioning to a surface layer" *by* D. Topping

Anonymous Referee #2

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Surface active species have high tendency to partition to solution surface, which has an effect on bulk solution concentrations. Recent calculations have shown that this may be important for aerosol growth and cloud droplet activation. Further calculations are definitely needed, but the numerical partitioning calculations are too slow for large scale applications. Current manuscript describes an analytical equation for calculating bulk solution mole fractions even in the case of multi-component surfactant solutions. Therefore, I recommend this paper for publication after a few corrections.

General comments

In general, it would be very useful to derive the equations for the "any number of

components"-case. Currently it is not clear how the calculations are made in the case of multi-component mixtures. Also, some additional approximations, which are not justified in the current manuscript, are needed for the multi-component case.

Optionally, predictions from the analytical equations could be compared with those from a numerical model, where approximations are not needed. This update is optional, because suitable numerical models may not be directly available for multi-component solutions. Of course, it is possible to develop such a model, but the numerical solution is not that simple.

Specific Comments

The derivation of the analytical solution (Sect. 2) begins with a rather lengthy (about three pages) review of surface tension models. I agree that it is important to show that the surface tension model (Eq. 6) is really working, but otherwise this part of the text could be condensed. It looks like Eqs 5 and 6 are needed in the derivation of the analytical solution, so what is the reason for showing Eqs 4 (single solute case of Eq. 6), 7 and 8 (the same as Eq. 6)? Is Eq. 5 valid for the multi-component case? If yes, what approximations are needed for this?

There could be more discussion about validity and usability of Eq. 6. For example, what about the effect of common ions? Added sodium chloride increases surface tension of pure water, but it decreases surface tension of aqueous SDS solution (e.g. Li et al., 1998). Equation 6 is based on solute activities, but activity coefficients are rarely used in surface tension parametrization. In addition, concentration scales other than mole fractions are commonly used. Does this mean that most published surface tension parameters are not directly valid for the analytical equation?

It is recommended that Eq. 9 (page 1095) is derived for the multi-component case. Then e.g. the effect of common ions should be explained. For example, Raatikainen and Laaksonen (2010) have derived different analytical equations for mixtures with and without common ions, and they have also shown that the common ion effect is important for surfactant partitioning.

The justification for getting rid of the activity coefficients (page 1096) is not very clear. First of all, zero water surface excess and chemical equilibrium (line 2) does not mean that activity coefficients in Eq. 8 can be set to unity. The justification for Eq. 12 is either the ideal solution approximation or that the surface tension parametrization is based on concentrations instead of activities. However, the ideal solution approximation is needed for Eq. 17.

The usage and meaning of the dotted surface tension parameters (page 1097, line 2) is not clear. Concentration dependent activity coefficients can not be taken into account by these dots, so why these are used? What is the relation between parameters with and without dots (based on Eqs 19 and 20 they should be equal)? This should be explained at least in the example in the beginning of Sect. 3.

Technical corrections

In general, paragraphs and sections are quite long. Readability of the manuscript could be improved by increasing the number of paragraphs and/or subsections. The other technical corrections are listed below.

Page 1090, lines 13–16: Computational efficiency of the analytical solution is ... *less* than a similar iterative approach?

Page 1090, line 23: RH *is*, ν_w *is*, σ_{ws} *is*, r_{drop} *is*

Page 1090, line 24: The unit of ν_w should be m^3 mol^{-1}

Page 1091, line 2: Reference Topping et al. (2007) is missing

Page 1091, line 15: Maybe "... and n_i^b *and* n_i^s *are* the bulk ..."

Page 1091, line 24: Why there is reference to Eq. 2?

Page 1091, line 24: Something missing from "systems two solutes"

Page 1091, line 26: Reference Sorjamaa and Laaksonen (2006) is missing

Page 1092, line 1: If there is just one organic component, "binary organic systems in water" could be "binary organic/water systems". Also, "ternary mixed inorganic/organic systems in water" could be "ternary inorganic/organic/water systems"

Page 1093, line 8: Reference Topping et al. (2005b) is missing or it should be referenced as Topping et al. (2005)

Page 1093, line 10: Maybe "surface area" instead of "cross sectional area"?

Page 1093, line 14: Eq. 2 is not the Gibbs adsorption equation (equation instead of Eq.). Also, it looks like Eq. 5 is not based on Eq. 4, so the origin of Eq. 5 should be clarified. I assume that Eq. 5 is based on Eq. 3; then chemical potentials (μ_i) should be defined.

Page 1093, line 18: "Sjorjamaa" should be "Sorjamaa"

Page 1094, line 11: Check the style of references Fainerman and Miller (2001) and Fainerman et al. (2001)

Page 1095, line 12: Eq. 2 does not describe surface tensions

Page 1095, line 16: Something missing from "it would in a binary"

Page 1095, Eq. 9: There are different notations (super and subscripts; capital and lower case letters) in the manuscript, e.g. n_i^s and n_{is}. Consistent notations should be used through the manuscript.

Page 1097, Eq. 20: Wrong sign, and different notation for the dotted K_i

Page 1098, line 5: (1-x_{iB}) missing from the first term

Page 1098, Eq. 27: $-4ac$ should be in the square root term

Page 1099, Eq. 29: Wrong value and unit

Page 1099, line 13: Unit of Γ_i (should it be $\Gamma_i^{wo'}$ or are these equal?) is missing

Page 1099, line 18: The latter bulk mole fraction is not correct

Page 1103, line 23: “Inluence” should be “Influence”

References

Li, Z., Williams, A. L., and Rood, M. J.: Influence of soluble surfactant properties on the activation of aerosol particles containing inorganic solute, J. Atmos. Sci., 55, 1859–1866, 1998.

Raatikainen, T. and Laaksonen, A.: A simplified treatment of surfactant effects on cloud drop activation, Geosci. Model Dev. Discuss., 3, 1139–1159, 2010.

Interactive comment on Geosci. Model Dev. Discuss., 3, 1089, 2010.