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Atmospheric
Chemistry
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Discussions

Interactive comment on “A new atmospheric aerosol phase equilibrium model (UHAERO): organic systems” *by* N. R. Amundson et al.

N. R. Amundson et al.

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We thank the referees for their helpful comments. We indicate below our responses to these comments.

Anonymous Referee #1

1) Importance of organics (at least the ones present in this study) on inorganic species deliquescence RH?

To further illustrate the effect of organics on inorganic deliquescence behavior, Fig. 10 shows deliquescence curves for the system $(NH_4)_2SO_4$/H_2SO_4/NH_4NO_3/ HNO_3/H_2O at 298.15 K for various (X, Y) compositions. The relative water content (defined as the ratio $\frac{b_{\mathrm{H_2O}}}{\sum_{i=1}^{n_i} b_{\mathrm{INORG}_i}}$) is depicted with changing relative humidity when (0) (solid red curve) the system is pure inorganic, or the system also includes two organic species with organic/inorganic mixing ratio $\alpha = 0.2$: (1) (dashed green curve) 1-hexacosanol ($\mathrm{ORG_1}$) and pinic acid ($\mathrm{ORG_2}$) with $f_{\mathrm{ORG_1}}$=0.5 and $f_{\mathrm{ORG_2}}$=0.5; (2) (dashed magenta curve) adipic acid ($\mathrm{ORG_1}$) and glutaraldehyde ($\mathrm{ORG_2}$) with $f_{\mathrm{ORG_1}}$=0.15 and $f_{\mathrm{ORG_2}}$=0.85; (3) (dashed blue curve) pinonic acid ($\mathrm{ORG_1}$) and nonacosane ($\mathrm{ORG_2}$) with $f_{\mathrm{ORG_1}}$=0.5 and $f_{\mathrm{ORG_2}}$=0.5; (4) (dashed cyan curve) 2-hydroxy-glutaric acid ($\mathrm{ORG_1}$) and palmitic acid ($\mathrm{ORG_2}$) with $f_{\mathrm{ORG_1}}$=0.5 and $f_{\mathrm{ORG_2}}$=0.5. These curves represent the relative water content on the vertical cuts at X=0.6 in Figs. 7–9.

The pie charts below each panel in Fig. 10 show, at the RH-values of 10, 20, 30, 40, 50, 60, 70, the contents of two organics ($\mathrm{ORG_1}$ and $\mathrm{ORG_2}$) and water (H_2O) in each liquid phase, represented counterclockwise by three adjacent sectors that are colored in red, yellow and blue, respectively. The size of a sector is proportional to the corresponding quantity, whose value for case (1) in Fig. 10a, for example, is given by: at RH $= 10\%$, $(y_1, y_2) = (5.8\%, 94.2\%)$ with $\mathbf{x}_1^o = (.042, .815, .143)$ and $\mathbf{x}_2^o = (.493, .446, .061)$; at RH $= 20\%$, $(y_1, y_2) = (20.7\%, 79.3\%)$ with $\mathbf{x}_1^o = (.023, .675, .302)$ and $\mathbf{x}_2^o = (.528, .358, .114)$; at RH $= 30\%$, $(y_1, y_2) = (37.1\%, 62.9\%)$ with $\mathbf{x}_1^o = (.008, .511, .481)$ and $\mathbf{x}_2^o = (.571, .275, .154)$; at RH $= 40\%$, $(y_1, y_2, y_3) = (33.0\%, 35.4\%, 31.6\%)$ with $\mathbf{x}_1^o = (.002, .372, .626)$, $\mathbf{x}_2^o = (10^{-12}, .003, .997)$ and $\mathbf{x}_3^o = (.609, .219, .172)$; at RH $= 50\%$, $(y_1, y_2, y_3) = (24.7\%, 51.5\%, 23.8\%)$ with $\mathbf{x}_1^o = (.002, .372, .626)$, $\mathbf{x}_2^o = (10^{-12}, .003, .997)$ and $\mathbf{x}_3^o = (.609, .219, .172)$; at RH $= 60\%$, $(y_1, y_2, y_3) = (16.1\%, 68.1\%, 15.8\%)$ with $\mathbf{x}_1^o = (.002, .372, .626)$, $\mathbf{x}_2^o = (10^{-12}, .003, .997)$ and $\mathbf{x}_3^o = (.609, .219, .172)$; at RH $= 70\%$, $(y_1, y_2, y_3) = (9.4\%, 81.1\%, 9.5\%)$ with $\mathbf{x}_1^o = (.002, .372, .626)$, $\mathbf{x}_2^o = (10^{-12}, .003, .997)$ and $\mathbf{x}_3^o = (.609, .219, .172)$. Here, y_α denotes the total number (fraction) of moles in phase α and $\mathbf{x}_\alpha^o = (x^{o\alpha}_{\mathrm{ORG_1}}, x^{o\alpha}_{\mathrm{ORG_2}}, x^{o\alpha}_{\mathrm{H_2O}})$ denotes the (partial) mole fraction vector (of the two organics and water) for phase α with $\alpha = 1$, 2, or 3. Thus, the contents of two organics ($\mathrm{ORG_1}$ and $\mathrm{ORG_2}$) and water (H_2O) in phase α, for $\alpha = 1$, 2, or 3, are given by $y_\alpha x^{o\alpha}_{\mathrm{ORG_1}}$, $y_\alpha x^{o\alpha}_{\mathrm{ORG_2}}$ and $y_\alpha x^{o\alpha}_{\mathrm{H_2O}}$, respectively. Note that at RH $> 36.5\%$ for case (1) in Fig. 10a, the mixture is partitioned into three equilibrium liquid-phases: two organic phases of compositions $\mathbf{x}_1^o$ and $\mathbf{x}_3^o$ and an aqueous phase of composition $\mathbf{x}_2^o$, thus the system has a maximum number of liquid phases permissible by the Gibbs phase rule; as RH increases, the compositions of the three liquid-phases $\mathbf{x}_1^o$, $\mathbf{x}_2^o$ and $\mathbf{x}_3^o$ stay the same, the total numbers of moles in the two organic phases y_1 and y_3 decrease, whereas the total number of moles in the aqueous phase y_2 increases. It should be noted that sectors of small quantity are not visible in the present scale.

Fig. 11 shows deliquescence curves for the system $(NH_4)_2SO_4$(AS)/H_2O at 298.15 K, when (0) (solid red curve) the system is pure inorganic, or the system also includes two organic species with organic/inorganic mixing ratio $\alpha = 0.2$: (1) (dashed green curve) 1-hexacosanol (ORG_1) and pinic acid (ORG_2) with f_{ORG_1}=0.5 and f_{ORG_2}=0.5; (2) (dashed magenta curve) adipic acid (ORG_1) and glutaraldehyde (ORG_2) with f_{ORG_1}=0.15 and f_{ORG_2}=0.85; (3) (dashed blue curve) pinonic acid (ORG_1) and nonacosane (ORG_2) with f_{ORG_1}=0.5 and f_{ORG_2}=0.5; (4) (dashed cyan curve) 2-hydroxyglutaric acid (ORG_1) and palmitic acid (ORG_2) with f_{ORG_1}=0.5 and f_{ORG_2}=0.5. When mixed with the organics (ORG_1 and ORG_2), the deliquescence curves are constructed by: **(a)** calculating the liquid phase equilibria occurring in the system, **(b)** assuming only one liquid phase occurring in the system. The curves in **(a)** represent the relative water content on the vertical cuts at X=1 in Figs. 7a and 8. The pie charts below each panel show, at various water activities: 0.5, 0.6, 0.7, 0.8, 0.9 in **(a)**, or 0.6, 0.9, 1.2, 1.5, 1.8 in **(b)**, the contents of two organics (ORG_1 and ORG_2) and water (H_2O) in each liquid phase, represented counterclockwise by three adjacent sectors that are colored in red, yellow and blue, respectively. The size of a sector is proportional to the corresponding quantity. The deliquescence curve and pie charts for case (2) in Fig. 11a are identical to the deliquescence curve and pie charts for case (2) in Fig. 11b, as the system for case (2) in **(a)** is in a single liquid (water + organics) phase equilibrium, which is the phase assumption used in **(b)**. However, for cases (1), (3) and (4) in **(a)**, the phase pie charts and water uptake are quite different as compared to those in **(b)**, as the system for cases (1), (3) and (4) in **(a)** is in multiple liquid phase equilibrium, whereas the system in **(b)** is assumed to involve only one liquid phase. Note that the curves (1), (3) and (4) and their corresponding pie charts in Fig. 11b are not physical, as they contradict thermodynamic principles: the value of water activity needs to be less than or equal to 1 and needs to be a monotonic increasing function of the water content (a consequence of Gibbs tangent plane criterion). The violation is due to the erroneous assumption of only one liquid phase involved in the system for cases (1), (3) and (4), where the organic contribution to the activity of water $a_w^{(o)}$ can take a value greater than 1. Moreover, a stack of pie charts in Fig. 11b indicates that there are multiple configurations of the liquid phase at a given water activity. At water activity $a_w = 0.9$, for example, the relative water content for case (1), (3), (4) in **(a)** is 6.23, 6.13, 7.02, respectively, compared to the values of 0.108, 0.0275, 4.89 (or 1.90, or 0.443), respectively, for case (1), (3) or (4) in **(b)**. Note that there is a stack of three pie charts at $a_w = 0.9$ for case (4) in **(b)**, representing three different configurations of the liquid phase with the relative water content being 4.89, 1.90, and 0.443, respectively, all of them give RH $= 90\%$, but none of them is physical. Therefore, calculating liquid phase equilibrium is necessary for thermodynamically consistent prediction of inorganic deliquescence behavior in the presence of organic species that are ‘partially miscible’ or ‘immiscible’.

Fig. 12 shows deliquescence relative humidity for the system: **(a)** $(NH_4)_2SO_4$(AS)/H_2O, **(b)** $(NH_4)_3H(SO_4)_2$(LET)/H_2O, at 298.15 K with changing organic/inorganic mixing ratio α (defined in Eq. 12) when the system also includes the two organic species (ORG_1 and ORG_2). A decrease in DRH of AS and LET is observed and the magnitude of the change depends on both the type of organics present in the system and the corresponding organic/inorganic mixing ratio. This is to be expected based on the thermodynamics of mixed aerosols (Tang, 1976). The pie charts below each panel show, at various organic/inorganic mixing ratios (α): 0.1, 0.3, 0.5, 0.7, 0.9, the contents of two organics (ORG_1 and ORG_2) and water (H_2O) in each liquid phase, represented counterclockwise by three adjacent sectors that are colored in red, yellow and blue, respectively. The size of a sector is proportional to the corresponding quantity. As shown in Fig. 11, liquid phase equilibrium calculation is required here to quantify the effect of organics on the deliquescence relative humidity of inorganic salts.

Additional references:

Tang, I. N.: Phase transformation and growth of aerosol particles composed of mixed salts, J. Aerosol Sci., 7, 361–371, 1976.

Additional figures:

Fig. 10: Deliquescence curves for the system $(NH_4)_2SO_4/H_2SO_4/NH_4NO_3/HNO_3/H_2O$ with the ammonium fraction X=0.6 and the sulfate fraction: **(a)** Y=1, **(b)** Y=0.85, at 298.15 K. Relative water content (defined as the ratio $\frac{{}^{b}\mathrm{H_2O}}{\sum_{i=1}^{n_i} b_{\mathrm{INORG}_i}}$) with changing relative humidity when (0) (solid red curve) the system is pure inorganic, or the system also includes two organic species with organic/inorganic mixing ratio $\alpha = 0.2$: (1) (dashed green curve) 1-hexacosanol ($\mathrm{ORG_1}$) and pinic acid ($\mathrm{ORG_2}$) with $f_{\mathrm{ORG_1}}=0.5$ and $f_{\mathrm{ORG_2}}=0.5$; (2) (dashed magenta curve) adipic acid ($\mathrm{ORG_1}$) and glutaraldehyde ($\mathrm{ORG_2}$) with $f_{\mathrm{ORG_1}}=0.15$ and $f_{\mathrm{ORG_2}}=0.85$; (3) (dashed blue curve) pinonic acid ($\mathrm{ORG_1}$) and nonacosane ($\mathrm{ORG_2}$) with $f_{\mathrm{ORG_1}}=0.5$ and $f_{\mathrm{ORG_2}}=0.5$; (4) (dashed cyan curve) 2-hydroxy-glutaric acid ($\mathrm{ORG_1}$) and palmitic acid ($\mathrm{ORG_2}$) with $f_{\mathrm{ORG_1}}=0.5$ and $f_{\mathrm{ORG_2}}=0.5$. These curves represent the relative water content on the vertical cuts at X=0.6 in Figs. 7–9. The pie charts below each panel show, at the RH-values of 10, 20, 30, 40, 50, 60, 70, the contents of two organics ($\mathrm{ORG_1}$ and $\mathrm{ORG_2}$) and water (H_2O) in each liquid phase, represented counterclockwise by three adjacent sectors that are colored in red, yellow and blue, respectively. The size of a sector is proportional to the corresponding quantity.

Fig. 11: Deliquescence curves for the system $(NH_4)_2SO_4$(AS)/H_2O at 298.15 K, constructed by: **(a)** calculating the liquid phase equilibria occurring in the system, **(b)** assuming only one liquid phase occurring in the system. Relative water content vs.

water activity (a_w) when (0) (solid red curve) the system is pure inorganic, or the system also includes two organic species with organic/inorganic mixing ratio $\alpha = 0.2$: (1) (dashed green curve) 1-hexacosanol (ORG_1) and pinic acid (ORG_2) with f_{ORG_1}=0.5 and f_{ORG_2}=0.5; (2) (dashed magenta curve) adipic acid (ORG_1) and glutaraldehyde (ORG_2) with f_{ORG_1}=0.15 and f_{ORG_2}=0.85; (3) (dashed blue curve) pinonic acid (ORG_1) and nonacosane (ORG_2) with f_{ORG_1}=0.5 and f_{ORG_2}=0.5; (4) (dashed cyan curve) 2-hydroxy-glutaric acid (ORG_1) and palmitic acid (ORG_2) with f_{ORG_1}=0.5 and f_{ORG_2}=0.5. The pie charts below each panel show, at various water activities: 0.5, 0.6, 0.7, 0.8, 0.9 in **(a)**, or 0.6, 0.9, 1.2, 1.5, 1.8 in **(b)**, the contents of two organics (ORG_1 and ORG_2) and water (H_2O) in each liquid phase, represented counterclockwise by three adjacent sectors that are colored in red, yellow and blue, respectively. The size of a sector is proportional to the corresponding quantity. A stack of pie charts in **(b)** indicates that there are multiple configurations of the liquid phase at a given water activity.

Fig. 12: Deliquescence relative humidity for the system: **(a)** $(NH_4)_2SO_4$(AS)/H_2O, **(b)** $(NH_4)_3H(SO_4)_2$(LET)/H_2O, at 298.15 K with changing organic/inorganic mixing ratio α (defined in Eq. 12) when the system also includes two organic species: (1) (dashed green curve) 1-hexacosanol (ORG_1) and pinic acid (ORG_2) with f_{ORG_1}=0.5 and f_{ORG_2}=0.5; (2) (dashed magenta curve) adipic acid (ORG_1) and glutaraldehyde (ORG_2) with f_{ORG_1}=0.15 and f_{ORG_2}=0.85; (3) (dashed blue curve) pinonic acid (ORG_1) and nonacosane (ORG_2) with f_{ORG_1}=0.5 and f_{ORG_2}=0.5; (4) (dashed cyan curve) 2-hydroxy-glutaric acid (ORG_1) and palmitic acid (ORG_2) with f_{ORG_1}=0.5 and f_{ORG_2}=0.5. The pie charts below each panel show, at various organic/inorganic mixing ratios (α): 0.1, 0.3, 0.5, 0.7, 0.9, the contents of two organics (ORG_1 and ORG_2) and water (H_2O) in each liquid phase, represented counterclockwise by three adjacent sectors that are colored in red, yellow and blue, respectively. The size of a sector is proportional to the corresponding quantity.

2) Add a few words in the Conclusions section on the overall practical significance of *the work for secondary aerosol modeling.*

Current atmospheric models for secondary organic aerosol generally assume that two liquid phases exist, one of which is relatively polar (containing mostly water and electrolytes) and the other mostly organic (containing primarily non-electrolytes); see, for example, Pun et al. (2002) and Griffin et al. (2003, 2005). The results in the current work allow one to assess the extent to which this assumption is valid for the particular mixture of compounds simulated in an atmospheric model.

Typographical error (p. 8717)

HR^- and R^{2-} should be anions.

Anonymous Referee #2

1) Discuss estimation of activities using the CSB approach.

The challenge in modeling systems containing water, electrolytes, and organic compounds is twofold. First, there is no generally accepted theoretical model for such mixtures; second, there are insufficient data to constrain a model, as compared, say, to models of electrolyte-water solutions. The models that do exist work only over limited ranges of composition and concentration. The electrolyte-water model that is generally considered as the benchmark is the Aerosol Inorganic Model (AIM) (Clegg et al., 1998 a,b). A general, and widely-used, predictive thermodynamic model for organic liquid mixtures is UNIFAC (Fredenslund et al., 1977), which is based on a group contribution approach. Most thermodynamic models for organic/inorganic/water mixtures use, in some measure, both of these models. The CSB model used in the present work treats organic-water and ion-water interactions separately. Additional terms, which are proportional to ion and organic compound molalities, can be included to describe organic-ion interactions. The ion-water interaction is calculated using AIM, while the organic-water interaction is calculated employing UNIFAC. Interactions between electrolytes and organics are accounted for by additional terms derived from the Pitzer molality-based model. Experimental data are required to determine the mixture parameters; if mixture parameters are available, the Pitzer equations are well validated for solutions at low to moderate concentrations. For the systems studies here, mixture parameters are not available and are set to zero, as in the study of Clegg and Seinfeld (2006a). It is not possible at this point, owing largely to the lack of experimental data, to assess the effect of not including specific electrolyte-organic interactions. It is possible to assess the effect of the different versions of UNIFAC on the predicted liquid-liquid equilibria, and we do so here.

Additional references:

Clegg, S. L., Brimblecombe, P., and Wexler, A.S.: A thermodynamic model of the system H^+-NH_4^+-Na^+-SO_4^{2-}-NO_3^--Cl^--H_2O at 298.15 K, J. Phys. Chem., 102, 2155-2171, 1998a.

Clegg, S. L., Brimblecombe, P., and Wexler, A.S.: A thermodynamic model of the system H^+-NH_4^+-SO_4^{2-}-NO_3^--H_2O at tropospheric temperatures, J. Phys. Chem., 102, 2137- 2154, 1998b.

2) What is the practical effect, on water content and solids formation, if a multi-phase result is assumed only to involve one or two liquid phases?

The effect of assuming only a single liquid phase when the thermodynamics predicts that multiple liquid phases are present is illustrated for the ammonium sulfate/water system in panel (b) of the new Figure 11. In such a case the predicted water activity can exceed unity if the organics are only partially miscible or immiscible in the water phase. In terms of the practical effect, if the goal of the calculation is to produce the deliquescence curves for the system, then this approximation can lead to entirely erroneous results.

3) Figures 7-9 are very complex. It would help greatly if the authors could add some additional information: for example, for points on a section across one or more of the plots, show the content (especially water and organics) in each phase at each selected point.

See new Figures 10 and 12 described in response to Comment (1) from Referee #1.

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