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Interactive comment on “Effects of molecular weight and temperature on liquid–liquid phase separation in particles containing organic species and ammonium sulfate” *by* Y. You and A. K. Bertram

Anonymous Referee #2

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General comments:

The authors present experimental data focusing on liquid-liquid phase separation (LLPS) in aqueous solution droplets for a set of organics mixed with ammonium sulfate. Specifically, they look at the effect of molecular mass of the organic compound and temperature on the onset relative humidity (SRH) of LLPS. The find negligible influences for both parameters for the systems they studied. The paper is well written and the conclusions are clearly supported by the experimental data.

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However, what is missing is a discussion why there is reason to believe that the two parameters studied (molecular mass and temperature) should influence LLPS at all.

The last paragraph before the conclusion section seems to indicate that the authors think of kinetic limitations to LLPS. The argument being that higher molecular mass organics exhibit high viscosity at lower temperature and hence diffusion may kinetically inhibit LLPS on atmospherically relevant timescales. Of course, if this is the argument the authors have in mind, they should look for a system with high molecular mass but even more important low SRH, because viscosity (and diffusivity) depends strongly on water content in the droplet. From their previous studies (You et al., 2013) a system with low water content at the onset of LLPS is α,4-dihydroxy-3-methoxybenzeneacetic acid mixed with ammonium bisulfate (SRH = 38 %). It is not quite clear to me why they choose the systems they studied (specifically, the type of salt and the specific OIR).

And how about thermodynamic reasons for an influence of molecular mass and/or temperature on LLPS? Why I do not see any immediate reason for molecular mass influencing miscibility of ternary mixtures of organic, water and salt, temperature could be a very significant parameter. It is well known that binary aqueous organics exhibiting a miscibility gap show an upper critical solution point which is the highest temperature at which two phases coexist because of the temperature dependence of the entropy of mixing. (This point may be not accessible experimentally because its temperature is higher than the boiling temperature of the mixture.) Some aqueous systems show in addition a lower critical solution temperature, because of the temperature dependence of the hydrogen bonding network of the organic compound in water. To be specific, for example polypropylene glycol (425) - one of the systems studied in the paper – show a lower critical solution temperature of about 50°C (Malcom and Rowlinson, 1957), i.e. it is miscible at room temperature at any ratio with water, while at higher temperatures two phases coexist in equilibrium. The results reported in the manuscript indicate that at an organic to inorganic ratio (OIR) of 2 (as chosen by the authors) the miscibility gap is extended very significantly to lower temperatures. Here the authors could have studied the system at higher OIR ratios and still observe LLPS if it occurred because the volume ratio of the two phases would be significant at intermediate RH even for low salt concentrations. Does a lower critical solution temperature still exist for small to moderate salt concentrations? Of course, this would mean a strong dependence on SRH with temperature as well.

The authors may argue that high OIR is not atmospherically relevant, but extending (or at least discussing) the more basic physical chemistry aspects would make it more interesting and relevant at least in my view.

Minor comments:

In the introduction you state that the occurrence of LLPS is not a strong function of the type of the inorganic salt. However, in You et al. (2013) you show that the type of salt becomes significant for an O:C ratio between 0.5 and 0.8 which may be quite significant in an atmospheric context.

In section 2.1 you state that the RH sensor was calibrated using the deliquescence humidity of ammonium sulfate. It is not absolutely clear to me, but I assume the sensor is at room temperature? Does your calibration mean that you use one calibration point only? Could you please describe your calibration and your estimate of RH accuracy in more detail?

Of the twelve systems which show LLPS, most of those exhibiting a significant trend in temperature show a decrease in SRH with decreasing temperature. Could you please comment on this? It may be expected if there would be a closed loop miscibility gap of which you probe the lower temperature part?

References:

Malcom and Rowlinson, “THE THERMODYNAMIC PROPERTIES OF AQUEOUS SOLUTIONS OF POLYETHYLENE GLYCOL, POLYPROPYLENE GLYCOL AND DIOXANE”, Trans. Faraday Soc. 53, 921 (1957).

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You et al., “Liquid–liquid phase separation in particles containing organics mixed with ammonium sulfate, ammonium bisulfate, ammonium nitrate or sodium chloride”, Atmos. Chem. Phys., 13, 11723, (2013).

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 23341, 2014.