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Report:

Spatial confinement of binary liquid mixtures close to the critical point leads to the emergence of a critical force - the so-called critical Casimir force [1]. However, the question how to simultaneously describe electrostatic and critical Casimir forces still remains unsolved [2]. Recent experimental [3] and theoretical work [4] suggests a coupling between ion distributions and concentration fluctuations in critical binary mixtures, but in order to verify this hypothesis, it is of utmost importance to directly measure interfacial ion profiles in critical solvents.

In order to address this question, we have probed interfacial ion distributions at the hydrophobic liquid-gas interface of a critical binary mixture consisting of water and 2,6-lutidine by simultaneous grazing-incidence x-ray fluorescence (GIXF) and x-ray reflectivity (XRR) measurements. The experiment was carried out for different concentrations of KCl in the range 10-100 mM and for temperatures below the critical temperature for demixing, $T_C = 304$ K. Data from aqueous KCl was also collected for reference. The experiment was carried out using an incident x-ray energy of 8 keV.

In Fig. 1 we present room-temperature GIXF data as a function of incident angle obtained at the liquid-gas interface of two different liquids, the water-2,6-lutidine mixture and water, with 100 mM added KCl. The data exhibit two notable features:

First, the fluorescence signals measured from the water-2,6-lutidine mixture below the critical angle of total reflection are a factor of 1.5 - 2 smaller than those measured from water. This can be qualitatively understood in terms of wetting preferences of the hydrophobic liquid-gas interfaces. Second, and more surprisingly, the anion and cation interfacial profiles are indistinguishable for the water-2,6-lutidine mixture. Quantitative analysis within classical density-functional theory [5] is in progress, in order to explain the observations in Fig. 1 as well as the temperature- and concentrationdependent data.

References:

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Fig. 1: Normalized K^+ (solid line) and Cl^- (dashed line) GIXF data obtained from the water-2,6-lutidine mixture and water (the latter vertically offset by a factor of ten). The ion concentrations are 100 mM and the data are collected at 297 K.