Comment on "Vapor-Liquid Condensation in Charged Colloidal Suspensions"

Recently Tata, Rajalakshmi, and Arora (TRA) reported a vertical separation of an initially homogeneous, charge stabilized suspension into two regions of different particle densities n_p upon the addition of mixed-bed ion exchange resin (IEX) [1]. They interpreted their findings as a novel *equilibrium* vapor-liquid condensation, contradicting calculations of the equilibrium structure based on potentials of DLVO type, in order to establish evidence for the partly attractive potential suggested by Sogami [2]. Here we will present strong evidence that the conditions reported by TRA are *nonequilibrium* conditions and suggest a different explanation.

We repeated the experiment of TRA under equal and also under slightly altered conditions. Glass vials were filled with salty suspensions of latex spheres (Seradyn Industries, U.S.A.; diameter $d=109$ nm; charge number $Z^*=520$; $n_p=1.2\times10^{18}$ m^{-3}). To each of these 1 g of IEX was added (MB1, Serva, FRG). Two were sealed by Teflon linings pressed onto the glass rim by screw caps. Sample *A* was left to stand upright; sample *B* was de-ionized in an upside down position with IEX next to the sealing. Sample *C* was sealed with a silicone rubber stopper and left to stand upright. There were no further preparational differences.

Vertical gradients in the salt concentration c_s naturally occur when the de-ionization begins. During this early stage n_p next to the IEX roughly doubled and a considerable thinning occurred in the upper parts of all the vials. However, we found no sharp boundaries. This is a strong indication of a transport process driving the particles via gradients in c_s. Calculations using the well-known DLVO based theory for the diffusiophoretic motion of particles [3] are currently in progress.

Over the next few days the n_p distributions became stationary: a small and smooth gradient in sample *A*, a completely homogeneous distribution in sample *B*, and a sharp separation in sample *C*. All these repeatedly reformed after shaking. All samples showed fluidlike order; sample *C*, however, only in the lower region. Photographs of samples *C* and *B* taken after 4 weeks are shown in Fig. 1.

The three vials differed only in their sealing against contamination with airborn CO_2. *Stationary gradients* in c_s will result for samples *A* and *C* because the carbonate ions have to cross the samples before they are caught by the IEX. Silicone has an excellent permeability for CO_2. Thus in sample *C* the supply of HCO_3^- establishes the largest gradient in c_s. Only then is the separation stabilized and the boundary sharpened. We suspect that such a gradient is also present in the samples of TRA, who claimed an averaged residual c_s of 2.4×10^{-6} mol l^{-1}.

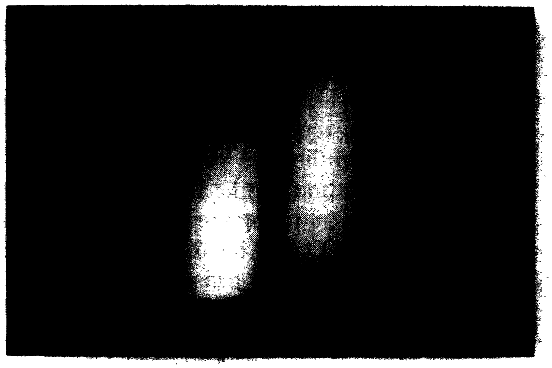

FIG. 1. Samples *B* and *C* after 4 weeks. Note that the final state of the suspension is strongly dependent on the sealing conditions.

The same dependence on sealing procedures was found for lower n_p. We further used an advanced, gradient-free method with *in situ controle* of n_p and c_s [4], where the IEX was well separated from the sample cell. Neither under completely de-ionized conditions nor upon the controlled subsequent addition of salt did we observe separations of the kind reported by TRA. Even when the calculated R_m [1] were much smaller than the mean particle spacing d_{NN}, the samples stayed homogeneous. Thus the *equilibrium* phase behavior was always consistent with DLVO theory [5].

In summary, we are able to reproduce the separation phenomenon reported by TRA only in the presence of a gradient in HCO_3^-. It is absent for gradient-free deionization techniques. We therefore judge the experiments of TRA to be very interesting nonequilibrium experiments, which, however, do not seem to bear an experimental justification for a discussion of the validity of particle pair potentials. We suggested an explanation on the basis of a gradient in c_s rather than on its absolute value.

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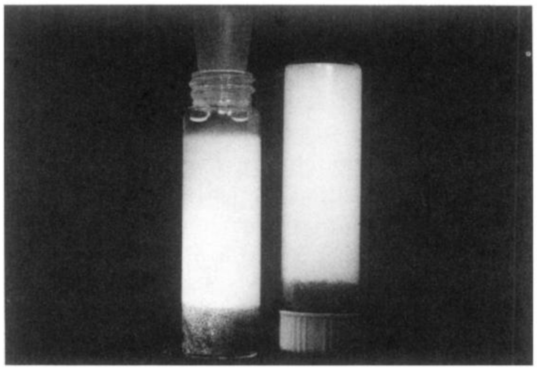

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