

Crystallization and the role of solvent structure dynamics

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Precipitation of barium sulfate in aqueous solutions of different background electrolytes (KCl, NaCl, LiCl, NaBr or NaF) was investigated at two different supersaturation (Ω) and ionic strength (IS) conditions in order to assess the effect of solution composition on kinetics. The mean crystal size, crystal size distribution and heat of precipitation of barium sulfate were shown to vary at constant thermodynamic driving force (Ω) and constant IS depending on background salt present in solution. With increasing IS the relative inversion in the effect of respective electrolytes on the characteristics of the precipitate and on reaction enthalpy was observed.

Our findings are interpreted from the perspective of the influence of background electrolyte on water of solvation and bulk solvent structure dynamics and imply that salt specific effects on kinetics of new solid-liquid interface formation result from differences in dehydration rates of barite building units. Such an approach is in agreement with the hypothesis that the kinetic barrier for barite nucleation depends on the frequency of water exchange that determines mobility of ions in solution and the probability of effective contact of ions in their “dehydrated state” – the starting point for phase transition. In the electrolyte solution the relative switchover between long range electrostatic interactions and short range hydration forces gives rise to the observation that increasing IS causes inversion in the influence of background ions on reaction rates and resulting precipitate characteristics. Furthermore our results support the idea that the kinetic barriers for nucleation and for growth of an ionic crystal from aqueous solution are different and suggest that this can result in increasing particle size with supersaturation.

Interfacial processes in multicomponent electrolyte solution cannot be properly described by bulk solution properties such as saturation state, surface tension and ionic strength: characteristics of the specific background ions responsible for solvation forces and ion distribution in solution must be taken into account.

Manganese and molybdenum: Biogeochemical tracers for dynamics of benthic-pelagic coupling in temperate tidal systems

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Dynamics of the redox-sensitive trace metals manganese and molybdenum and their response to biological activity are investigated in the open water column and shallow pore waters of the German Wadden Sea (North Sea). Two systems, one from the southern and one from the eastern part of the German Bight are compared.

Mn shows strong tidal and seasonal variations with water column values generally increasing towards low tide and summer. However, distinct fluctuations were observed for Mn during summer months caused by Mn pool sizes and microbial activity in the surface sediments. Non-conservative behaviour of Mo has been observed in the open water column of both study areas. After breakdown of summer algae blooms Mo shows distinct depletions to more than 50% of the usual seawater level. The release of organic matter during breakdown of algae blooms causes formation of Mo and Mn enriched aggregates, which are incorporated into the sediment after deposition. Elevated microbial activity and a shift in redox-conditions lead again to release of both metals. Both study areas show similar Mo and Mn dynamics suggesting that this may be a common behaviour in the North Sea tidal areas.