In a new report on Science Advances, T. Voisin and a research team in the Scientific Research National Center and the Institute of Technology and Energy Management in France, proposed a new solvent system. The hydrothermal molten salt (HyMoS) system, is composed of a molten salt in pressurized water and is able to change the solubility of inorganics in supercritical water. The scientists used sodium hydroxide (NaOH); a low melting temperature salt, and showed the ability to precipitate it at a temperature above its melting point, to instantly form HyMoS. The molten salt could then dissolve a large amount of inorganic salt including sodium sulfate (Na₂SO₄). The solvent system opens a new path in diverse fields including materials synthesis, biomass conversion, green chemistry, recycling, catalysis and sustainable manufacture. The work offers opportunities beyond hydrothermal dynamics to investigate the chemistry and insights of innovative salt precipitation.

Supercritical water is often known as a "magic" solvent, due to its ability to dissolve oil. This property has widened the potential applications for SCW in materials synthesis, recycling or biomass conversion. However, as the polarity of SCW breaks down, the solubility of the inorganic compounds drop. The challenge can be resolved by identifying good co-solvent candidates with great dissolution capacity for inorganic compounds alongside high thermal stability, to overcome the limits of SCW. Molten salts are an attractive possibility due to their high density and important dissolution capacities. Molten salts are highly diverse and used abundantly for decades as nitrate salts, carbonates, hydroxides or eutectic mixtures to dissolve inorganic materials. In this work, Voisin et al. proposed to generate molten salt within SCW to overcome the limits of SCW alone. They composed the hydrothermal molten salt (HyMoS) with a salt of interest alongside SCW, for high-temperature hydrothermal applications.

For HyMoS formation, the team injected a homogenous electrolyte water/salt solution under pressure and heated it up for the salt to precipitate. Since the temperature of precipitation was higher than the melting temperature, fusion of the salt
instantly followed precipitation, to form HyMoS. The scientists noted the evolution and movement of a molten NaOH droplet in SCW within a sapphire capillary. When they cooled down the system, they could recover the initial homogeneous electrolyte water/salt solution, since the mechanism was completely reversible. Voisin et al. selected the NaOH salt for its high thermal stability and low melting temperature (318°C) and high capacity to dissolve inorganic salts.

The team used an experimental setup, detailed elsewhere, to measure the solubility values and study the behavior of sodium hydroxide in SCW. They explored the difference in density and viscosity between the two components to measure the solubility of the compound under SCW conditions. The two-step mechanism of solid precipitation was fast, and no solid particles were observed in the sapphire capillary equipment fitted with a conventional charge-coupled device camera at 50 frames per second. The results demonstrated the feasibility of creating a dense co-solvent flowing alongside SCW. The team then focused on the capacity of NaOH to dissolve other inorganic salts under SCW conditions.

To highlight the capacity for NaOH-based HyMoS to dissolve a solid salt in SCW, the team proposed a different experimental protocol. During the experiment, they first injected an aqueous solution of the inorganic salt sodium sulfate (Na₂SO₄) into the system at a given temperature to deposit the solid salt on the reactant wall. Since Voisin et al. knew the solubility of Na₂SO₄, they checked if precipitation occurred in the system during continuous measurements of conductivity. The scientists calculated the concentration of sodium sulfate in the sodium hydroxide solution. Although the increasing temperature in the setup had little influence on the inorganic salt sodium sulfate, the initial concentration of the molten salt sodium hydroxide was a major influence on its rate of dissolution. Quite logically therefore as the concentration of sodium hydroxide increased, its corresponding molten phase also increased in the setup, causing higher dissolution rates of inorganic salts deposited in the reactor to ensure continuous flow.

Validation of the dissolution of the deposited Na₂SO₄ solid salt by the NaOH HyMoS in SCW in continuous flow. (A) Raw conductance (in red) and temperature (in
blue) signals obtained from the experimental setup, showing the different steps of the protocol. Green zone represents the Na$_2$SO$_4$ precipitation and salt deposition step into the reactor, and blue zone represents the injection of NaOH solution to dissolve the deposited salt. (B) Scheme illustrating the first step of the experiment consisting in salt deposition by precipitation. (C) Scheme illustrating the second step of the experiment, with precipitation/melting of NaOH and the dissolution of the previously deposited Na$_2$SO$_4$. (D) Na$_2$SO$_4$ ICP concentration results according to the temperature, for different times during the dissolution by NaOH. Comparison between the measures and the normal solubility of Na$_2$SO$_4$ in SCW. (E) Evolution of the Na$_2$SO$_4$ mass fraction in the NaOH molten phase with time, for two different NaOH feed concentrations. Credit: Science Advances, doi: 10.1126/sciadv.aaz7770

In this way, T. Voisin and colleagues observed molten salt in SCW to address the existing challenges with supercritical fluid-based technologies. Using a stable molten hydroxide salt such as sodium hydroxide they generated an in situ solvent to dissolve a large quantity of the sodium sulfate solid salt. The scientists demonstrated the first application of HyMoS and bypassed salt deposition and obstruction in the reactors to develop continuous flow processes. The technique is cost-effective, since basic salts such as NaOH used in the experiments are relatively cheap materials, when compared with complex ionic liquids. The capacity to generate a dense solvent with a simple and cheap system also has an impact on hydrothermal systems. Molten salts are, however, limited relative to processability for continuous systems due to the high temperature and high viscosity required in batch systems. The diphasic HyMoS system is composed of SCW and a molten salt, and the setup can be explored as a new type of hydrothermal water/salt emulsion to effectively dissolve a variety of different salts.


Conductance of Dilute LiCl, NaCl, NaBr, and CsBr Solutions in Supercritical Water Using a Flow Conductance Cell: https://pubs.acs.org/doi/abs/10.1021/jp970197q

Miroslaw S. Gruszkiewicz and Robert H. Wood, 1997, ACS publications


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