

In-situ observations of liquid-liquid immiscibility in the system $\text{MgSO}_4\text{-H}_2\text{O}$ (D_2O)

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Liquid-liquid immiscibility has been documented in aqueous UO_2SO_4 solutions at temperatures up to 468 °C [1]. Recently, we reported our observations on the liquid-liquid phase separation in vapor-saturated aqueous MgSO_4 solutions at temperatures up to 350 °C [2]. Under these conditions, we observed that MgSO_4 -rich droplets were separated from the original aqueous MgSO_4 solutions during heating, and these two coexisting liquid phases homogenized during cooling. It has been found that the phase separation temperature decreases from 304.5 °C to 259.5 °C as MgSO_4 concentration increases from 1.19 % to 19.36%. The newly discovered liquid-liquid phase separation in MgSO_4 solutions was characterized by a lower critical solution temperature phenomenon, which was considered to be a macro-scale chemical property of polymeric mixtures.

To further characterize the properties of the immiscible fluids in the system $\text{MgSO}_4\text{-H}_2\text{O}$, we documented in-situ Raman spectroscopic investigations and observed a distinctly new $\nu_1(\text{SO}_4^{2-})$ mode at $\sim 1020\text{ cm}^{-1}$ in the MgSO_4 -rich droplets; the new $\nu_1(\text{SO}_4^{2-})$ mode was predicted to be present in MgSO_4 polymer(s) in aqueous solutions. As mentioned above, both the phase behavior and relevant Raman spectra indicate the existence of polymer(s) in MgSO_4 solutions.

We compared the new $\nu_1(\text{SO}_4^{2-})$ mode with that of MgSO_4 -rich droplets in the system $\text{D}_2\text{O-MgSO}_4$. We found that there was also an $\nu_1(\text{SO}_4^{2-})$ mode at $\sim 1020\text{ cm}^{-1}$. This observation suggests that the polymer(s) in aqueous MgSO_4 solutions is not bonded through H_2O and is probably contact ion pair chain(s), although the exact structure of the polymer(s) is still unknown. In addition, we investigated the hydrogen-bonds in the immiscible fluids. We found that the MgSO_4 -rich fluids has higher potential for the preservation of hydrogen bonds compared with that in the MgSO_4 -poor fluid at the same temperature. This can be ascribed to the formation of hydrogen bonds between SO_4^{2-} and water molecules because the probability of collision of H_2O with SO_4^{2-} in MgSO_4 -rich fluid is higher than that in the MgSO_4 -poor fluid.

[1] Marshall *et al.* (1962) *J. Inorg. Nucl. Chem.* **24**, 889-897.

[2] Wang *et al.* (2013) *Geochim. Cosmochim. Acta* **103**, 1-10.

The distribution of DBT and DBF in Mesoproterozoic (1.36 Ga) sediments

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Previous studies of polycyclic aromatic hydrocarbons considered dibenzofuran (DBF) and dibenzothiophene (DBT) to be derived from phenolic compounds of lignin from woody plants, thus their occurrence was attributed to terrestrial organic matter input^[1]. However, in our recent works in North China Craton, high contents of DBF and DBT were both detected in the Mesoproterozoic (1.36 Ga) low mature mudstones and shales. No matter how high of the total organic carbon contents in the shales, the distribution of DBF and DBT were more likely to be controlled by the paleoredox conditions (Figure 1). DBT had a peak abundance in the anoxic zone, while DBF was enriched in the oxic minimum zone, the transition zone from oxic to anoxic. When the redox conditions changed to oxic, a dramatic decrease was happened in the abundances of DBF and DBT. Thus, we speculated that the abundance and distribution of DBT and DBF in ancient sediments may be controlled by the dynamic sulfic-oxic conditions.

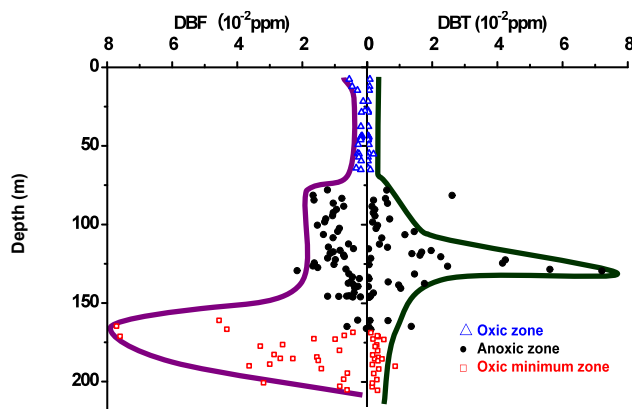


Figure 1: The distribution of DBF and DBT in Mesoproterozoic low mature mudstones and shales.

[1] Fenton *et al.* (2007) *EPSL* **262**, 230-239.