



The Mobility of Organic Contaminants in Hydrated Clays at Elevated Pressures and Temperatures

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The interlayer pores of swelling clays provide an ideal environment in which to study confined fluids, and are the site of many important hydrological and petrological processes. Swelling clays, such as vermiculites, are layered minerals, widespread in soils and sedimentary rocks and are an important sink/source of many toxic organic chemicals. Knowledge of diffusion of organics through clay-rich materials is therefore highly relevant to environmental issues. Experimental studies of solvation structure in aqueous systems show that charged groups can co-ordinate the surrounding water molecules quite strongly, but there is less certainty about the effect of polar and apolar groups. There is currently interest in bulk water-alcohol systems since these are known to aggregate at the nanometer scale. Our hypothesis is that the property of the interlayer fluids in clays arises from the very subtle balance of forces between the interactions of water, cations, clay and organic species. Quasi Elastic Neutron Scattering (QENS) has been used to probe the dynamics of fluids trapped inside clays and reveal the first detailed picture of confined methanol, phenol and glycol in aqueous solution. The picture that emerges is that these model contaminant molecules are surprisingly mobile. Successive QENS broadening for methanol in Na-Vermiculite over 150-330K was measured. The progressive broadening of the energy signal was accompanied by decrease in amplitude with rise in temperature. This is indicative of an overall increase in rotational and translational freedom. Methanol exhibits a Fickian diffusion mechanism as an unconfined fluid, characterised by a linear dependence of broadening of the energy signal with the scattering vector. Inside Na-Vermiculite clay however, the

same fluid produces a signal broadening that becomes non-linear indicating a jump activated motion to be present. Glycol and phenol are also of fundamental interest, the former as a clay-swelling inhibitor of relevance to the petroleum industry, the latter as an aromatic hydrogen-bonder, soluble in water and of major environmental importance. Rotational modes are distinguished from translational motions by an independence of the signal broadening on the scattering vector. Aqueous solutions of ethylene glycol revealed translational motion of the interlayer glycol molecules down to 325K, whilst the rotational motion persisted down to below 100K. Above 325K however, an increased residence time of the solution in clay in comparison to the free fluid is observed. In comparison, the diffusion coefficient of pure ethylene glycol at 325K reveals much slower dynamics, by almost a factor of three. In both the bulk aqueous phenol and confined systems, translational motion down to 290K is observed, the residence times for the clay system consistently higher for the clay samples in comparison to the bulk phenol solution again suggesting a favoured interaction of the fluid with the clay surface.