Characterization of micellar systems for removal by MEUF of refractory organic from contaminated groundwater

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Introduction

One of the severe problems challenging management of aquifers, is their contamination by small molecular weight organic compounds. Rehabilitation of or recovery from such aquifers requires developing techniques for removing the contaminants either in-situ or by pump and treat schemes. One of the methods that has been extensively studied is micellar enhanced ultrafiltration (MEUF) [1-2]. There are a number of aquifers in Israel that are challenged by this problem and may be amenable to treatment by MEUF. Tribromo-neopentyl alcohol (TBNPA), a biorefractory compound, was found at relatively high levels in groundwater samples in a number of test wells in the Negev. The present study examined the feasibility of removing it by MEUF, based on an evaluation of its distribution coefficient between the micellar and aqueous phases:

$$K = \frac{O_m}{S_m O_w}$$, in units of M^{-1}

where O refers to organic solubilizate and S refers to surfactant molar concentrations relative to the aqueous solution volume. The subscripts m and w refer to the micellar and aqueous phases respectively.

Experimental

The distribution coefficients were determined by two separate methods: micellar enhanced ultrafiltration using centrifuge tubes [3] equipped with regenerated cellulose membrane of 10 kDa MWCO (Amicon Centriprep YM membranes in 10 ml centrifuge tubes) and by solid phase matrix extraction (SPME) [4] (Carbowax 30 μm, Supelco). In the MEUF experiments, the permeate contained only monomeric surfactactant at a concentration S_w and non-solubilized organic in the aqueous phase at a concentration O_w. The concentration of the monomeric surfactant S_w should be that of the critical micelle concentration (cmc). If the surfactant has a low cmc which is the case for the nonionic surfactants used in this work, then $S_m \sim S_{tot}$.

Analyses of the organic solubilizate in the permeate were determined by GC. Sample preparation was carried out by solid phase matrix extraction (SPME) and electron capture was used as the detection method.

Samples of 10 g/L of Brij 58 ($C_{16}EO_{20}$), 10 g/L of Brij 58 in the presence of 100 mg/L TBNPA, and 1 g/L of Brij 58 in presence of 100 mg/L of TBNPA concentrated 10 fold by centrifugal UF were studied by Cryo-TEM to determine effect of high solubilizate loading on micelle size and shape.

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Results

The distribution coefficient for the most effective surfactant (Brij 58) was ~450-500 M^{-1} and was fairly constant over a wide range of loadings (mole fraction of TBNPA in micelle from 0.07-0.45) using centrifugal UF. It was also found that the distribution coefficient was only slightly reduced by the presence of 1% NaCl. On the other hand the distribution coefficients determined by SPME were about 33% lower. This is most likely explained by the high concentration polarization of micelles in the centrifugal UF leading to a more effective retention of the TBNPA. Therefore the values obtained by SPME are to be considered closer to the true distribution coefficient for TBNPA in Brij 58 micelles.

Cryo-TEM shows that the Brij 58 micelle size (5-7 nm in absence of TBNPA) were not affected by TBNPA when prepared by solution, but interestingly became less uniform with the appearance of some micelles with much larger diameters (>15 nm) after centrifugal UF with TBNPA. (see Figure 1). Apparently hydrynamic stresses at the membrane surface promote coalescence of some of the micelles.

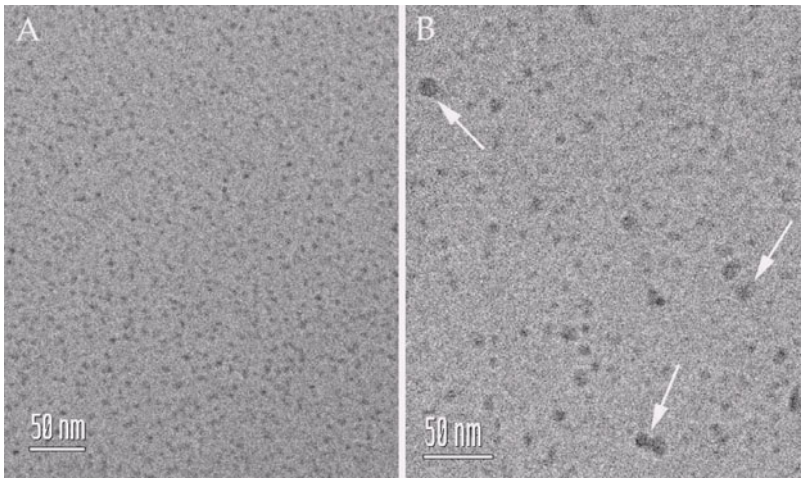

Figure 1. Cryo-TEM images of Brij 58 micellar solution: (A) a 10 g/L aqueous solution; (B) a 1 g/L Brij 58 aqueous solution, swollen with 100 mg/L TBNPA, then concentrated x10 by centrifugal ultrafiltration. Arrows point to larger swollen micelles

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References

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