

Fig. 1: 2D ^1H NMR T_2 - T_2 exchange maps of air bubbles in water recorded with mixing (exchange) times of $\tau = 1$ ms (a) and $\tau = 20$ ms (b).

oil and water in sand, and processes at interfaces such as the liquid-foam interface and the liquid-vapor interface of chloroform.

2. Experimental

The measurements were performed at high field with a 500 MHz Bruker DSX spectrometer and at low field with a 40 MHz Bruker Minispec spectrometer. For the bubble experiment, air bubbles were produced in water with the help of the spectrometer cooling system at medium air flow rate, and for the gas-liquid exchange experiment, a 2 cm high volume of chloroform was contained by a 7 cm high and 0.9 cm inner diameter tube, in the presence of air. In the latter case, the exchange experiment was conducted after a period of 24 h to reach a state of dynamic equilibrium between liquid chloroform and saturated gas. No special preparations were taken for observing exchange in the systems water/shaving-cream, foam and, oil/water in sand. The CPMG pulse sequence with a variable echo number of up to 128 was used to encode the signal amplitude in the indirect dimension. The magnetization decay was recorded in the direct dimension via a CPMG pulse sequence of 400 echoes. The echo time was on the order of ms and the exchange time was changed from 0.1 ms up to 50 ms. To obtain the T_2 - T_2 exchange maps, the 2D time maps were inverted using a fast Laplace algorithm [5, 6] with a fixed value of the regularization parameter α .

3. Results and discussion

The two-dimensional exchange maps of air bubbles in water recorded as a function of mixing time show a diagonal peak associated with the bulk water, and a cross peak associated with the exchange between bubble shell to bulk (Fig. 1). With increasing exchange time, the diagonal and cross-peaks spread over a larger region. Monte-Carlo simulations are being performed to verify the observed decrease of the transverse relaxation time due to molecular

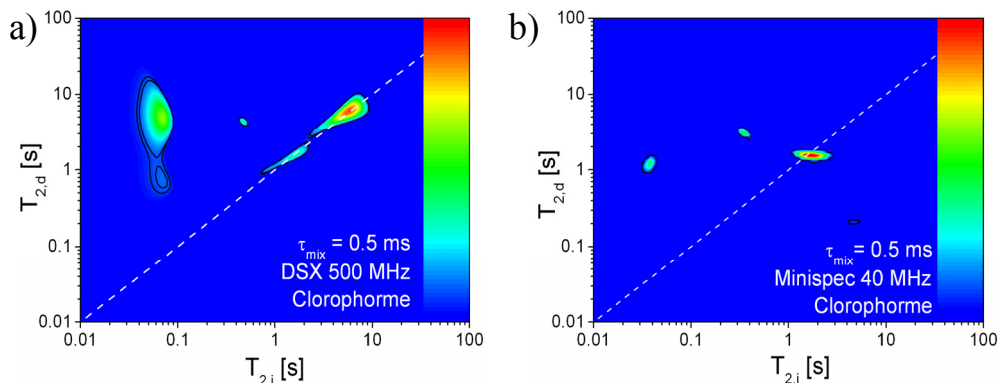


Fig. 2: 2D relaxation exchange maps of liquid chloroform and its vapor recorded at a mixing time of $\tau_{\text{mix}} = 0.5$ ms at a) 500 MHz and b) 40 MHz.

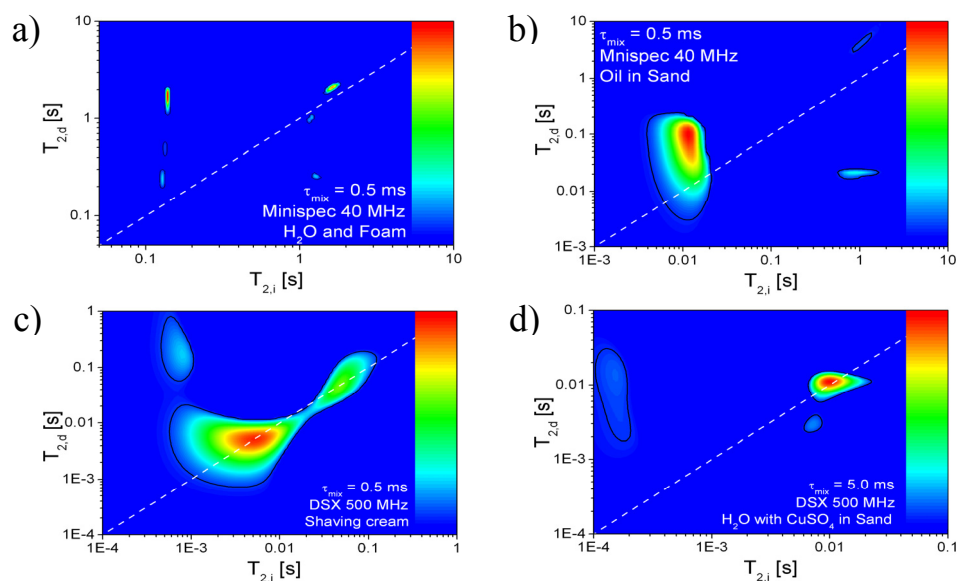


Fig. 3: 2D relaxation exchange maps of a column of a) water and foam; b) oil in sand recorded at low magnetic field; c) water and shaving cream and d) water in sand recorded at high field with $\tau_{\text{exc}} = 0.5$ ms.

exchange and investigate effects of pearling. The lack of the second diagonal peak is a particular feature of these experiments. In this case, the peak corresponding to the bubble shell is missing, which might be explained by the associated small number of molecules.

The resolution of the 2D exchange maps recorded at low field is comparable to that recorded at high fields (see Fig. 2). The chloroform exchange map recorded at high field (Fig. 2a) shows particular features that may be associated with the molecular exchange between three domains from the bulk to a superficial shell/interface and then to the saturated vapor. The experiment performed at low field (Fig. 2b) also shows a cross peak which indicates the reverse process. The expected 2D exchange pattern, with all diagonal and cross peaks is observed for the water/foam system (Fig. 3a). The oil in sand system shows a unidirectional exchange process (Fig. 3b). Another unidirectional process but in the opposite direction is observed for water/shaving-cream which differs from the results for water in sand (Fig. 3d).

3. Conclusions

Transverse relaxation exchange from fast relaxing nuclei in molecules associated with pore surfaces or superficial liquid shells and the more slowly relaxing nuclei associated with molecules in the bulk liquid can be observed as cross-peaks in T_2 - T_2 exchange maps. Our results encourage us to further study 2D Laplace T_2 - T_2 exchange NMR as a tool to investigate the kinetics of molecules in heterogeneous environments. Quantitative interpretation of the T_2 - T_2 exchange maps in the fast exchange limit is possible with the help of numerical simulations.

References

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