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THE EFFECT OF EMULSION FORMATION ON NMR SPECTRA

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Emulsions

Emulsion formation is widespread in foods.

In the present study the emulsion forming compounds are members of the ubiquitous class of phthalates. From a practical point of view they are very useful as the density is changing with the chain length of the esters.

Another good reason for using phthalates is that the magnetic susceptibility is very similar to that of e.g. fatty acids (see later).

Figure 1 shows the ^1H spectrum of neat diethylphthalate (DEP).

Figure 2 shows the ^1H spectrum of diethylphthalate in water after sonification. Why do we see two sets of signals?

In the lower spectrum the concentration is the highest.



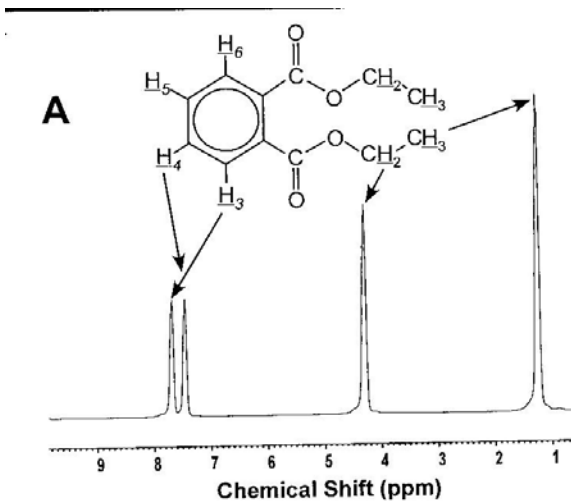


Figure 1

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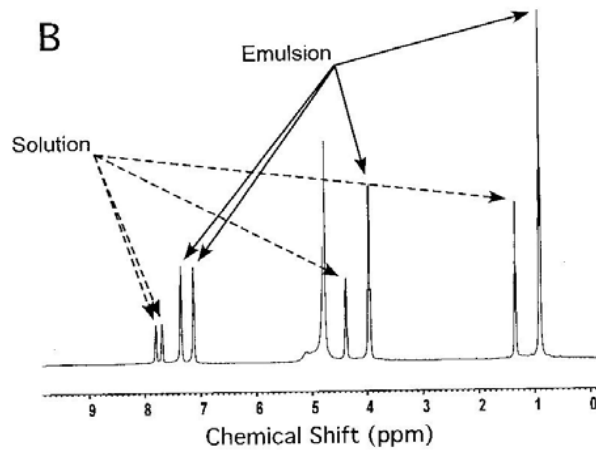
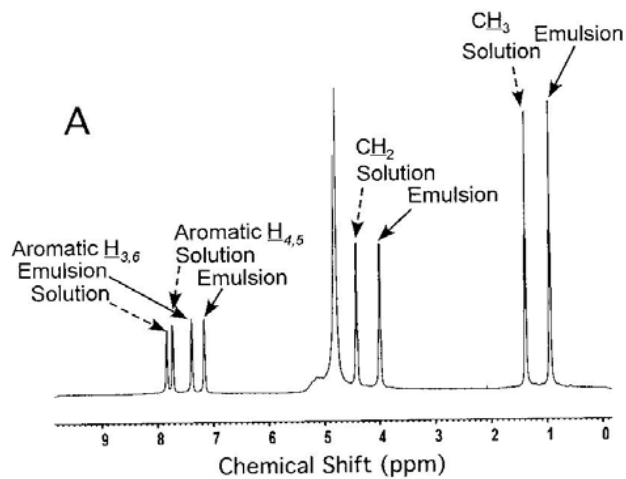


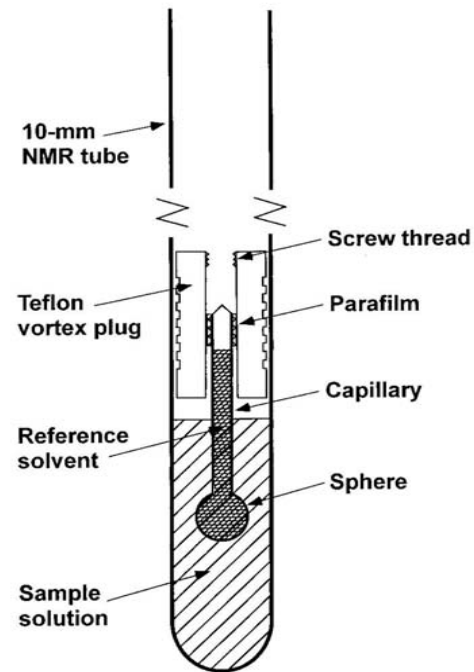
Figure 2

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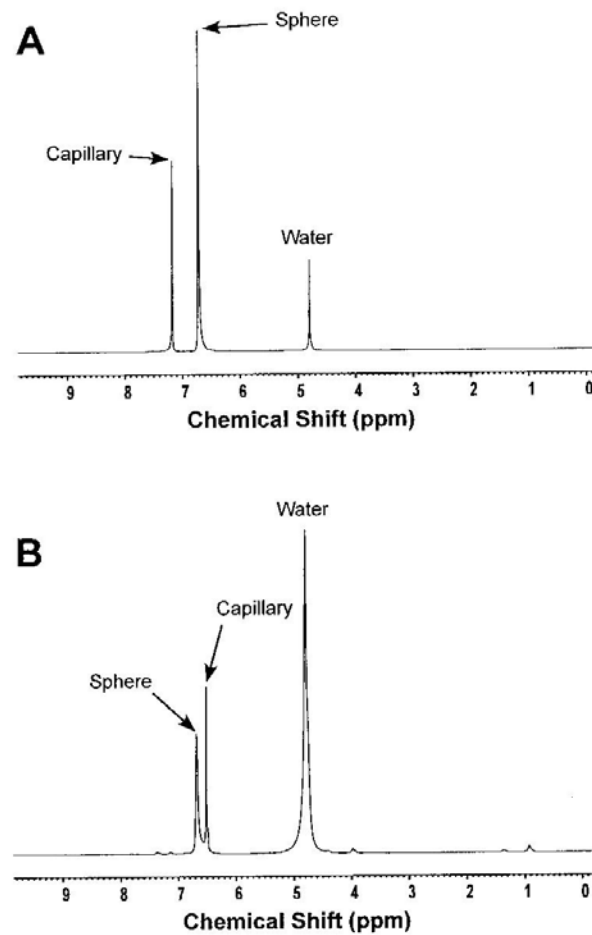
An emulsion is a solution with non-dissolved compounds in small spheres (droplets). The Frei-Bernstein experiment (See Fig. 3 for the experimental setup) shows that we get two sets of signals, one from the benzene in the bulb and one from the benzene of the stem. The use of a bulb and stem corresponds to the emulsion spheres and the solution (cylindrical).

Figure 3.



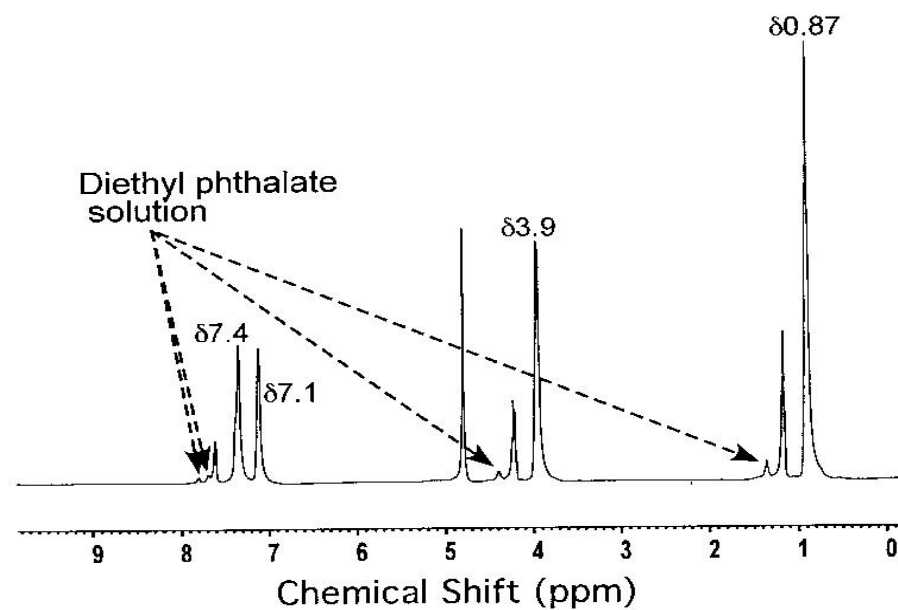
Frei-Bernstein set up with benzene in the bulb and stem and heavy water in the NMR tube. A. Heavy water. B. Heavy water with iron dextran.

Figure 4.



Figur 5 illustrate how signals from droplets and from bulb coincides (marked with number). DEP is both in the bulb and stem and in the NMR tube.

Fig. 5.



The chemical shift difference can be expressed as:

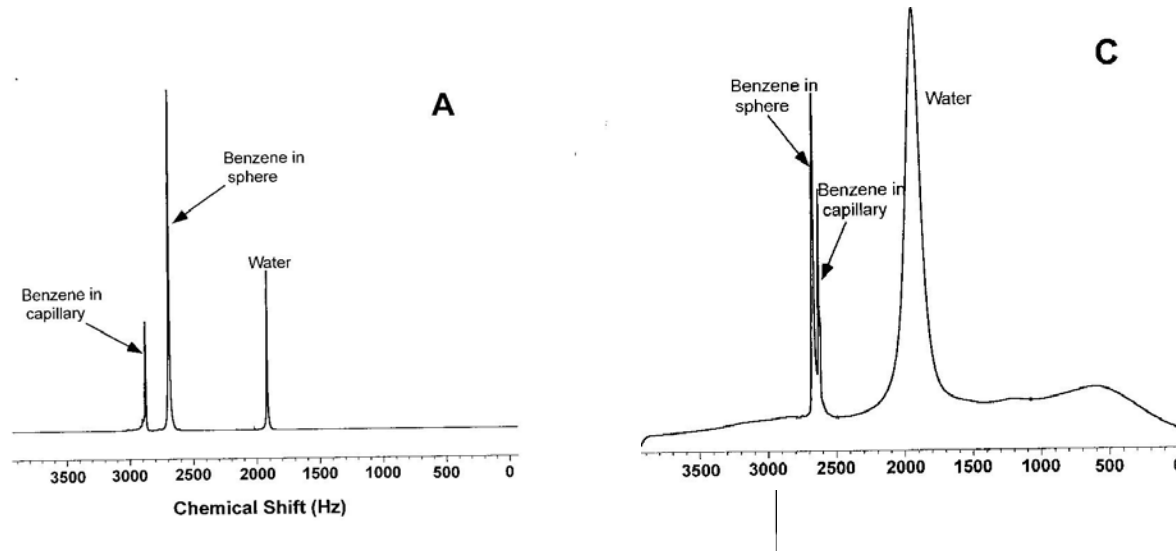
$$\delta_{\text{cyl}}(\text{benzene}) - \delta_{\text{sph}}(\text{benzene}) = (g_{\text{cyl}} - g_{\text{sph}}) [X(\text{benzene}) - X(^2\text{H}_2\text{O})]$$

where δ is the chemical shift (in ppm), the X's denote the magnetic susceptibilities, and the g's are geometric constants that depend on the shape of the compartment. In the particular cases of a cylinder lying parallel to \mathbf{B}_0 , and a sphere, the factors are $-1/3$ and 0, respectively

The effects of paramagnetic materials are also demonstrated in Figure 4B for benzene and in Figure 6.



Figure 6A. In NMR tube oxygenated erythrocytes (Ht=77%).
Figure 6 B. In NMR tube erythrocytes treated with NaNO_2 .
Benzene in bulb and stem.



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Magnetic susceptibilities determined in this study. $\chi(\text{DEP}) -8.31 \times 10^{-6}$
and $\chi(\text{Iron dextran heavy water solution}) -7.20 \times 10^{-6}$

Table 1 Magnetic susceptibilities of substances that are useful for measuring magnetic susceptibilities in biological systems using NMR spectroscopy

Compound name	χ ($-10^6 \times$ SI units; dimensionless) ^a (20 °C)
Acetone	5.78
Benzene	7.68
Carbon tetrachloride	8.68
Dimethyl sulfoxide	8.55
D ₂ O	8.82
Ethanol	7.23
Ethylene glycol	8.77
<i>D</i> -Glucose	10.92 (25 °C)
Glycerol	9.79
H ₂ O	9.04
Mannitol	11.4
Methanol	6.66
Myristic acid	8.31 (60 °C)
Oleic acid	8.31 (18 °C)
Palmitic acid	8.31 (62 °C)
Toluene	7.76



Conclusions.

As seen from the equation, the chemical shift differences between signals from emulsion droplets and the dissolved compound depends on the difference in magnetic susceptibility between the compound and the solvent (in most cases water or heavy water). The latter magnetic susceptibility can be modulated either by co-additions (the magnetic susceptibility of a mixture is equal to the weighted mean of the two components). An effective way of doing this is to add paramagnetic materials as they have positive magnetic susceptibilities in contrast to diamagnetic materials, that have negative ones). It is obvious from Table 1 that the results for e.g. fatty acids will be very similar to those of DEP, but the case of DEP is of course more simple to deal with and use for illustration.



References

More information can be found in:

1. P.W.Kuchel, B.E.Chapman, W.A.Bubbb, P.E.Hansen, C.J.Durant, M.P.Hertzberg, Concepts in Magnetic Resonance **18A**, 56 (2003).
2. C.J.Durant, M.P.Hertzberg, P.W.Kuchel, Concepts in Magnetic Resonance **18A**, 72 (2003).
3. P.E.Hansen, U. Skibsted, C.D. Rae, P.W.Kuchel, Biophys. J. **30**, 69 (2001).
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