A Simple Pulse Sequence to Exclude Falsification of NMR Self-diffusion Results by Multi-Phase Relaxation

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The existence of various phases with large differences in the nuclear magnetic relaxation times within one sample may lead to substantial ambiguities in self-diffusion measurements by the conventional NMR pulsed-field gradient method, which may be excluded by the proposed pulse sequence.

With the advent of the pulsed field gradient method,[1] NMR spectroscopy has become a most versatile tool for studying diffusion phenomena in heterogeneous systems.[2-4] In this technique, the self-diffusion coefficient is determined from an analysis of the attentuation of the NMR signal (the 'spin echo') dependent on the width and/or intensity of the applied magnetic field gradient pulses. While investigating heterogeneous or, in general, multi-phase systems, however, one must be aware of the fact, that the contribution of the various phases to the spin echo is controlled by their nuclear magnetic relaxation properties. Thus, with increasing observation times the contribution of the phases with the largest relaxation times will become more and more dominant leading to a dependence of the apparent self-diffusion coefficient on the observation time. Such a behaviour is well-known from the investigation of polymer melts or solutions with broad molar mass distributions,[5-7] and may be generally encountered in non-uniform systems.[1] While investigating samples containing a small amount of molecules with extremely large relaxation times, this effect may even lead to completely erroneous
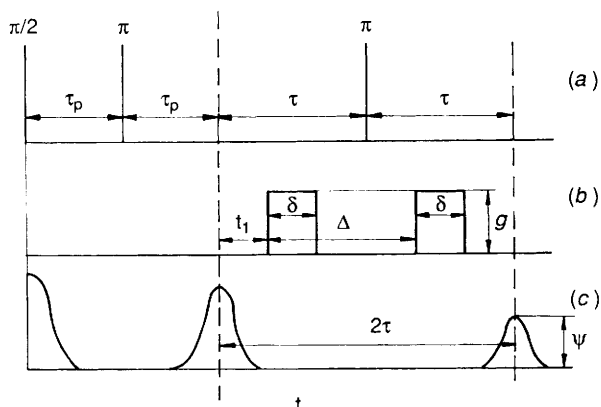
Fig. 1 RF pulses (*a*), magnetic field gradient pulses (*b*) and observed NMR signals (*c*) in a modified NMR pulsed field gradient sequence. The dependence of the spin-echo intensity on the applied pulsed field gradient sequence is determined for different spacings τ_p between the preparatory RF pulses. The disturbing influence of multi-phase relaxation can only be excluded if the observed spin-echo attention ψ (δ, g, Δ) is independent of τ_p

Fig. 2 Spin-echo attenuation in dependence on the field gradient intensity g for self-diffusion measurements with the pulse sequence of Fig. 1 (with $t_1 \approx 0$ and $\Delta = \tau$) for n-hexane (2*a*), ethylene glycol (2*b*) and a sample containing both liquids in separate tubes in a ratio 1:100 (2*c*). The interval τ_p between the RF pulses of the preparatory sequence was 0 (○), 1 (□), 4 (◇), 10 (△), 20 (▽) and 30 (+) ms, respectively

results. For sufficiently large observation times it is the diffusivity of these molecules rather than that of the bulk phase that is obtained in the NMR self-diffusion experiments. Such a situation may occur in diffusion studies with microporous adsorbent crystallites (zeolites[8]), in which instead of the intracrystalline diffusivity a formal analysis of the observed echo attentuation would yield the diffusivity of a small amount of extracrystalline molecules.[9,10]

It is true that any dependence of the self-diffusion coefficients on the observation time may serve as a first indication of the influence of multiphase relaxation. However, the evidence of such experiments is limited, since a time dependence of the self-diffusion coefficient may also be brought about by structural effects such as restricted or multiphase diffusion.[2] Moreover, any change in the observation time (*i.e.* in the separation between the two magnetic field gradient pulses) implies the risk that an incomplete adjustment of the gradient pulses and/or an interference of the tailings of the gradient pulses with the RF pulses or the NMR signal may lead to differences in the spin echo attenuation with increasing gradient intensities or widths (and, correspondingly, to the, thus, determined self-diffusion coefficients) that are not due to multiphase relaxation. Therefore, an experimental technique is needed that allows a variation of the influence of relaxation on the observed NMR signal without any change in the field gradient sequence. In this way any change in the spin-echo attenuation may be unambiguously attributed to the influence of relaxation.

A straightforward possibility for carrying out such experiments is provided by the pulse sequence presented in Fig. 1. It may be considered to be a conventional primary spin-echo pulsed field gradient experiment, in which instead of the starting $\pi/2$ pulse one has applied a preparatory spin-echo sequence. Evidently, the function of the second half of the spin-echo brought about by the 'preparatory' sequence is completely equivalent to that of the free induction decay following the $\pi/2$ pulse in the original version of the pulsed field gradient experiment. However, in contrast to this original experiment, by varying the spacing τ_p between the preparatory RF pulses, the proposed sequence allows a variation of the influence of relaxation on the observed NMR signal without the necessity for any change of the pulsed field gradient sequence, *i.e.* of the magnetic field gradient pulses with respect to each other as well as to the last RF pulse and
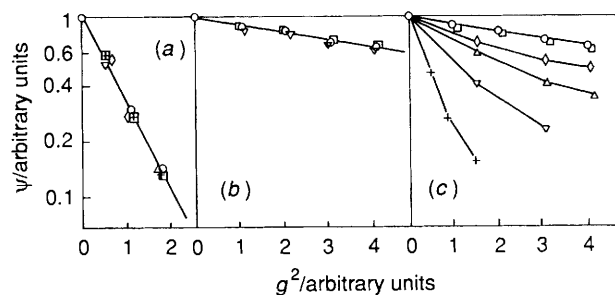
the spin echo. This procedure may be carried out with both the primary and the stimulated spin-echo sequences,[2] in which, in principle, as a preparatory sequence either a primary or a stimulated spin sequence may, likewise, be applied.

The mode of operation of the proposed sequence has been tested by measuring two liquids (n-hexane and ethylene glycol), at first separately, and then simultaneously in a sample composed of two glass tubes containing these two liquids. In order to make the effect as pronounced as possible, the transverse nuclear magnetic relaxation time of ethylene glycol has been reduced, by dissolving manganese chloride, to a value of about 4 ms, in contrast to $\gtrsim$ 500 ms for n-hexane. The ratio of the signal intensities of the pure, separated samples of n-hexane and ethylene glycol was *ca.* 1:100.

Figs. 2*a* and *b* show that for the separated liquids the echo attenuation due to the applied field gradient intensities is in fact independent of the preparatory pulse sequence. An analysis of the slope of the ln ψ *vs.* g^2 representation would yield, therefore, true self-diffusion coefficients. In contrast to this result, the composed sample (Fig. 2*c*) shows a strong dependence of the observed slopes on the separation τ_p of the preparatory pulses. In particular, for small values of τ_p an analysis of the spin-echo attenuation would yield the diffusivity of ethylene glycol, since under these conditions the major contribution to the NMR signal is in fact brought about by ethylene glycol. For large preparation times, however, the main contribution to the observed NMR signal is due to the n-hexane molecules, so that it is their diffusivity that is determined in the pulsed field gradient experiments.

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