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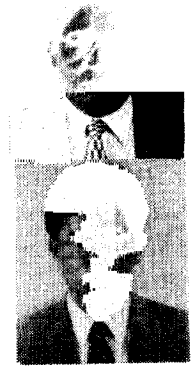
總 說

계면활성제 용액의 미셀형성에 있어 FT-PGSE의 응용



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Application of FT-PGSE for Micelle Formation of Surfactant Solution

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요 약 : 계면활성제는 수용액에서 미셀을 형성함에 있어서 자기확산이 분자 운동과 상변화에 대하여 자세한 정보를 제공하고 공업적으로 응용할 수 있는 기술이 점차 증가하고 있다. 계면활성제가 미셀을 형성함에 있어 자기확산 정도는 화학구조의 변화성과 상호 결합 및 회합현상에 매우 민감한 것은 사실이다. 특히 계면활성제 용액의 넓은 범위의 분자 시스템과 콜로이드 상태의 변화성은 다양한 물리, 화학적 성질에 기여됨이 많다. 더욱이 미셀 형성에서 자기확산 계수는 분자 치환에 직간접적으로 상호관계가 있어 NMR 분광학에서 스핀 이완속도의 해석과 분자의 재배열, 스핀 이완에 대한 모델선정 등에 많은 관심을 갖는다. 그중 미셀형성에 있어서 자기확산에 대한 측정 방법중 가장 많이 이용되고 있는 Fourier Transform Pulsed Gradient Spin Echo(FT-PGSE) 측정법은 계면활성제의 미셀 형성에 대한 상변화성 및 물리, 화학적 성질을 다루는데 새로운 도구로 제공되고 있다. 이는 이 계통의 기술적 측정방법에 있어서 적절한 개선과 새로운 응용분야를 확장하는데 있어서 많은 가능성을 갖고있다. 그리하여 이들에 대한 역사적 배경과 기초적인 이론을 가지고 미셀 형성에 있어 자기확산에 대한 개념을 말하고 그에 대한 응용성을 계통적으로 설명하고자 한다.

1. Introduction

The interest in studies of diffusional processes in solution and in the solid state has grown rapidly during the past few years. This is in part due to an increased number of available techniques for the purpose and the realization that self diffusion data provide uniquely detailed and easily interpreted information on molecular organization and phase structure. Self diffusion rates are quite sensitive to structural changes and to binding and association phenomena, in particular for colloidal or macromolecular systems in solution. As an additional benefit, experimental self diffusion coefficients need to further interpretation: there values are directly related to lateral molecular displacement in the laboratory frame. From an NMR-spectroscopic point of view, one should note that the interpretation of spin relaxation rates, on the other hand, relies on model framework for molecular reorientation and spin relaxation.

A general trend in the description of matter

in recent decades is to turn to computer simulation of structure and dynamics, for example in terms of Monte Carlo and molecular dynamics method. It is straightforward and natural to evaluate self diffusion coefficients from the latter type of simulations and the comparison between predictions of theory and experimental results thus becomes particularly meaningful.

The traditional way to measure self diffusion coefficients is through radioactive tracer techniques: self diffusion coefficients are also frequently called tracer diffusion coefficients in the literature. Tracer method, at their best, are still the most accurate techniques for the purpose. For anything but simple liquids, they require difficult synthetic work and measurement periods that may be of the order of days or weeks for a single component. A further disadvantage of the technique is the inherent system perturbation by isotope substitution. As will be demonstrated in the present review, NMR techniques can provide individual multicomponent self diffusion coefficients with good precision in a few minutes, without the need for isotopic labelling.

Self diffusion measurements by NMR have been utilized in numerous studies ever since the discovery of spin echoes by Hahn[1]. In that pioneering study, several effects on spin echoes were discovered and correctly interpreted, one of which was the diffusional effect on echo amplitudes in an inhomogeneous magnetic field. In its basic form, the (SE) technique for measuring diffusion entails monitoring of spin echo amplitudes obtained in the presence of a linear gradient in the Bo-field. The SE experiment was significantly improved in the mid-sixties in the form of the pulsed field gradient spin echo(PGSE) technique. The basic idea was evidently put forward in a paper by McCall et al.[2] and the methodology, first experiments and the detailed analysis were later presented by Stejskal and Tanner[3(a,b)]. Several modifications to the PGSE technique were later suggested and tested and the technique has been heavily utilized for investigation of molecular transport in matter during more than three decades.

Apart from the pioneering work mentioned so far, a number of review articles on the basic methodology have appeared[4~8]. The most complete discussion so far is that of Reeves[9], which gives a literature survey of the methodological developments up to the early seventies. Very knowledgeable presentations of the practical aspects of 'large-gradient PGSE' along with an outline of the underlying theory were presented quite recently by Hrovat and Wade in two paper[10(a,b)] and by Fukushima and Roeder in their unique NMR textbook approach[11]. In combination with Reeves review, these three presentations cover most methodological developments of time-domain SE and PGSE techniques. The basic techniques will therefore not be covered in too much detail here.

The physico-chemical applications of normal, single component, self diffusion measurements are also well established: excellent reviews by Callaghan on the use of NMR based diffusion data for probing liquid state molecular organization[12] and by von Meerwall on the subject of investigating molecular transport in polymeric systems[13] have been published recently. Self diffusion studies on solid have been reviewed by Gordon and Strange[14] and by Stokes[15]. Studies on plastic crystals have been reviewed by Britcher and Strange[16], and mesophase structure of menbrane liquid by Lindblom[17], colloidal systems by Stejskal [18] and microemulsions by Lindman and Stilbs [19]. The utilization of NMR techniques for studies of ionic diffusion in solid electrolytes has also been summarized recently[20].

One should also note the overlap in methodology between PGSE and NMR imaging techniques. Some recent reviews and monographs in the later field contain much reference material which is also useful in the present context[21,22], for example chapters on gradient coil design, diffusional effects on NMR images[23] and the best available review so far on NMR measurements of flow

[24].

SE and PGSE methods in their original form are unresolved techniques in the frequency domain: in the SE technique, the frequency resolution is intrinsically worse than normal because of the intentionally poor Bo homogeneity. In the common implementation of the PGSE technique, frequency resolution is hampered through characteristics of the traditional instrumental design, which involve field homogeneities at the sample location that are not of 'high-resolution magnitude', and rather primitive techniques for the actual registration on the spin echo.

In the time domain, one find that unless isotopic labelling is made of all but one component, one cannot distinguish between individual contribution to the multiexponential echo decay of SE or PGSE experiments on multicomponent systems unless rather restrictive criteria are fulfilled with regard to relations between individual diffusion rates and tranverse(T_2) spin relaxation rates. AS an example, it is quite easy to study(rapid) solvent and (slow) polymer diffusion separately in a polymer solution, through straightforward selection of the appropriate PGSE pulse parameters. Boss et al. have used a technique where the PGSE experiment is preceded by an inversion pulse of selected decay, so as to null the contribution of one of the two components in a mixture[25]. In most multicomponent self diffusion studies this approach will fail, since NMR bands from the same molecule have different spin relaxation rates. An extension of this experiment varies both the inversion recovery and PGSE time delays. In the FT mode one can then achieve a simultaneous determination of T_1 and D in a single experiment.

The concept of frequency resolved FT-PGSE was evidently first put forward by Bold et al. in their classic paper on spin relaxation measurements in the pulsed Fourier transform mode and the technique(FT-PGSE) was first tested by James and McDonald on the system water- dimethylsulphoxide[26].

The present review will, after a brief introduction to the general subject and the older literature in the field, focus on the methodology needed to perform accurate, quantitative, frequency resolved, diffusion measurements of the type illustrated in Fig. 1, and on the recent physico-chemical applications of such multicomponent self diffusion measurements. The utilization of the combined information in multicomponent self diffusion data and the selective measurement of individual self diffusion coefficients in complex systems are new tools in chemistry.

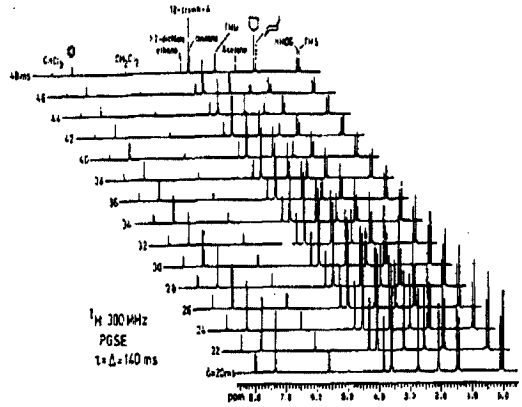

Fig. 1. Diffusional effects on the Fourier transformed 300MHz absorption mode ^{1}H-PGSE echo singnal from a 12-component solvent mixture. The signal amplitudes are shown as a function of the duration of the 0.64×10^{-4} T/cm field gradient pulsed.(the previous record, 8 component was set in Ref. 82). From left to right an evaluation of the experiment leads to D- value(10^{-9} m^2/s) of 2.76, 3.10, 3.25, 2.84, 1.99, 2.69, 2.30, 3.35, 3.07, 2.78, 2.10, and 2.65: all determined with 1% accuracy.

For obvious reason, high resolution FT-PGSE applications almost exclusively concern liquid system. References will be included on the merit of : (a) basic theoretical or methodological interest for FT-PGSE techniques, (b) basic theoretical or methodological interest

for multicomponent self diffusion studies, (c) actual experimental utilization of multicomponent self diffusion data, as obtained by frequency resolved FT-PGSE techniques.

Reference to applications of traditional time domain PGSE or SE techniques will not be included unless one or more of the above criteria are met. Emphasis will be on NMR methodology, also in the context of applications. The physico-chemical aspects of the applications will only be briefly touched upon.

2. Diffusion

When a liquid system is heated, the energy added increase the internal kinetic energy, leading to overall increased rates of molecular and particle motion. Apart from macroscopic convection and convection-like phenomena one usually considers motional partitioning into internal molecular motions, and overall reorientation and translation diffusion of molecules and aggregates.

The theory of diffusion and molecular transport in solution is highly developed and extensive. There exist several excellent monographs on diffusion processes, to which the reader is referred for a more complete presentation[27~28].

2-1. Self diffusion

Self diffusion is the net result of the thermal motion induced random walk process experienced by particles or molecules in solution. In an isotropic homogeneous system the conditional probability $P(\gamma_o, \gamma, t)$ of finding a molecule, initially at a position γ_o, at a position γ after a time t is equal to

$$P(\gamma_o, \gamma, t) = (4\pi Dt)^{-3/2} \exp\{-(\gamma - \gamma_o)^2/4Dt\} \quad (1)$$

The radial distribution function of molecules with regard to their original positions in an infinitely large system with regard to an arbitrary reference time is thus a Gaussian one, increasingly growing in width as time increase. The single parameter D, the self diffusion coefficient characterizes this radial distribution completely.

The situation differs for obvious reasons under certain circumstances. Statistical considerations must be taken into account if the system has very few particles or if the observation time is short. Different manifestation of restricted diffusion are often significant in micro- and macro-heterogeneous systems and anisotropic diffusion rates are a characteristic feature of many liquid crystalline systems.

In an isotropic system, without thermal or concentration gradients, the average molecule/particle displacement in all three direction is zero: the mean square displacement is non-zero, however, and is given by the Einstein relation:

$$(\gamma^2) = 6Dt. \quad (2)$$

In these equations the regular brackets symbolize a time average. There are as many self diffusion coefficients in a system as there are distinct components during the time of observation. For NaCl in water there are, in principle four, one each for Na^+, Cl^-, hydrogen and OH^-. Although H_2O is a distinct species, the later two self diffusion coefficients in principle differ because of water autoionization. The actual values for proton and OH^- self diffusion are almost the same, however. Proton migration mechanisms in water have been throughly discussed in two papers by Halle and Karlstrom[29].

Typical self diffusion coefficients in liquid systems at room temperature range from about 10^{-9} m^2/s, to 10^{-1} m^2/s. With regard to the actual magnitudes of displacement, the figure 10^{-9} m^2/s corresponds to a root mean square displacement during one second in the three-dimensional space of 7.7×10^{-5} m. For a 100 times smaller self diffusion coefficients is consequently 10 times smaller. Within a given phase boundary, self diffusion coefficients are not dramatically for example, is approximately

3% per degree at 25 ℃, a rather typical value.

Formally, the magnitude of the diffusion coefficient is given by

$$D = K_B T/f, \quad (3)$$

where T represents the absolute temperature, K_B Boltzman's constant and f the so-called frictional factor. For a sphere of radius γ in a continuous medium of viscosity η, f is given by the Stokes equation:

$$f = 6\pi\eta\gamma \quad (4)$$

which, when combined with eqn. (3), lead to the familiar Stokes-Einstein relation:

$$D = K_B T/6\pi\eta\gamma \quad (5)$$

For other geometries, and when the diffusing particle is of similar size to the solvent molecules, more complex theories and equations describe f[27,28]. A representative collection of typical self diffusion coefficients is given in Table 1.

2-2. Mutual diffusion

In a non-equilibrium two-component system: for example, solvent/solute layered upon pure solvent, the mutual diffusion coefficients characterizes the relaxation of concentration gradients in the system according to Fick's Law

$$J = -D'(dC/dx) \quad (6)$$

where dC/dx represents the solute concen-

Table 1. Some Representative Self-Diffusion Coefficients($10^{-9}m^2s^{-1}$) at Infinite Dilution at 25℃

Gases	Oxygen in air	18000
solids	Helium in pyrex	4×10^{-6}
Aqueous solution	Oxygen	2.1
	Benzoic acid	1.0
	Sucrose	0.52
	Haemoglobin	0.069
	Typical surfactant micelle	0.01-0.05
	Li^+	1.03
	Na^+	1.33
	Cl^-	2.03
	I^-	2.05
	$Acetate^-$	1.09
Organic solution	Benzene in ethanol	1.81
	Cyclohexane in benzene	2.09
Polymer system	Polystyrene($M=10^5$) in CCl_4	0.05
	n-octane in *cis*-polyisoprene	0.06

Data taken from Refs [27] and [13].

tration gradient. D' the mutual diffusion coefficient and J the flow of solute molecules per unit cross section area. The net molecular motion, of course, originates from the same thermal motion that causes self diffusion. Eventually the once sharp boundary becomes blurred and the concentration difference disappears and a single homogeneous solution remains.

In a two-component system there is only one mutual diffusion coefficient. Depending on the composition, it may approach ether of the self diffusion coefficients of the components. In an infinitely dilute 'two component' solution the mutual diffusion coefficient is equal to the self diffusion coefficient of the solute and not directly related to that of the solvent. At intermediate concentration ranges, the distinction between mutual and self diffusion coefficients is important[27~28].

With regard to self diffusion in the NaCl/water example just given, one should also note that although individual chloride ions diffuse about 50% faster than individual sodium ions in water, their net transport rates must equal those of the sodium ions to preserve electroneutrality when relaxing a concentration gradient: the overall chloride ion transport is thus to some extent rate determined by the parallel transport of chloride ions.

The formalism for describing mutual diffusion and self diffusion in ideal associated systems has been discussed by Hall in a recent paper[30].

2-3. Multicomponent diffusion in non-equilibrium system

This is, of course, the most common situation in nature. The formal treatment of multicomponent diffusion is made in the framework of irreversible thermodynamics, and the reader is referred to Refs 27 for an introduction to the subject. In general, there are $(n-1)^2$ different diffusion coefficients characterizing the relative fluxes of species in an n-component mixture. These multicomponent diffusion coefficient are difficult to measure or interpret physically unlike the multicomponent self diffusion coefficient measured by FT-NMR techniques. Experimental values exist to any appreciable extent only for rather simple three-component systems[27].

The quantitative treatment of non-equilibrium multicomponent diffusion in heterogeneous or partly organized systems is even more complex than that of homogeneous solution in phases[31].

3. Applications of FT-PGSE

3-1. Isotropic system

3-1-1. Miscellaneous application of FT-PGSE spectroscopy

(1) Analytical utilization: 'Size-resolved NMR'. As evident from the discussion in T_2 and J-modulation effects, J-modulation and other T_2-related effects combine into a single term, which depends only on the 90°-180° rf pulse interval. This is true for each part of the bandshape in absorption -mode FT-PGSE since individual absorption bandshapes are additive at each point. Furthermore, each atom in a given molecule has the same self diffusion coefficient. It is therefore possible to separate and assign signals from different components in a complex mixture by FT-PGSE spectroscopy, based on their common diffusion-related echo attenuation[32].

(2) Solvent signal suppression: It is evident that signal contributions from low-molecular weight solvents can be completely suppressed in FT-PGSE experiments, by extending the diffusion period to a suitable length: for example a 99% H_2O proton signal($D=2.3\times10^{-9}$ m^2/s at 25℃) is completely nulled with a gradient of 10 mT/m, $\tau=\Delta=140$ msec and $\delta=70$ msec. Under the same conditions, most of the signal of components with a value of five times lower 'survive'. In biological applications, where the T_2 values are often quite short, one may have to utilize stronger gradients and shorter rf pulse intervals than those given in the example. If one is content with

spin echo spectra on non-spinning samples this technique outperforms by far all other approaches to solvent signal suppression. The stimulated echo varient of FT-PGSE has less amplitude distortion effects and is probably a better technique in this particular application.

J-modulation effects essentially disappear in the limit of zero interval between the 180 ° pulses of the CPMG spin echo experiment. The successful application of the narrow pulse interval CPMG technique for water signal suppression in the particular case of exchange broadened(T_2)water signals was described recently by Rabenstein et. al[33]. The ultimate choice would probably be an has the most easily suppressed signal in FT-PGSE experiments.

3-1-2. Diffusion in simple liquid mixture

Diffusion in simple liquid is a matter of much fundamental theoretical interest. SE investigations on binary solutions were reported as early as 1967 by McCall and Douglass[34]. FT-PGSE techniques can provide the same information, without the need for deuteriation or component masking, even on 12-component solutions(c.f. Fig. 1). A more detailed approach to the problem was taken in an investigation of 1,1,2,2,-tetrabromoethan and solvent diffusion in solutions in alkylbenzenes($C_{0\sim14}$) [35], a study that had been essentially impossible with any other method than FT-PGSE.

The original papers by James and McDonald[26] and Kida and Ueidara[36] should also be mentioned in the present Subsection. An FT-PGSE investigation of carbohydrate diffusion in water also noteworthy[37].

3-1-3. Diffusion in solvent-polymer system

Solute/solvent Interaction: The subject of diffusion in polymer solutions has been reviewed recently by von Meerwall[13], and also by Callaghan[12]. Low gradient FT-PGSE techniques almost always fail for the investigation of polymer diffusion(because of short T_2, slow diffusion). An exception is the polymer poly(ethyleneoxide)(PEO), which is unusually flexible in solution and has long proton spin relaxation times.

We have successfully investigated non-aqueous and aqueous PEO solutions with the purpose of testing the existence of the suggested anomalous structure of PEO in aqueous solution[38]. FT-PGSE techniques also cope easily with otherwise difficult experimental problem of investigating the diffusion of polymer 'A' in a solution of polymer 'B'[39]. The good precision of the measurements allowed combined studies to be made on self diffusion(FT-PGSE), mutual diffusion(quasi-elastic light scattering, QELS) and sedimentation(ultracentrifugation), for the purpose of studying experimentally the theoretically different frictional coefficient for the three processes[40]. Dextran diffusion(a linear polysaccaride) in aqueous solution could also be studied in a similar way, except that elevated temperatures had to be used[41]. A combined QELS and FT-PGSE study made possible definite statements on the origin of the so-called 'slow-mode' tails in the observed autocorrelation function in QELS on concentrated solutions[42].

The experimental investigation of solvent diffusion in polymer solutions by low gradient FT-PGSE techniques is, on the other hand, trivially simple[43~44].

3-1-4. Solute diffusion in gel

The self diffusion of small to medium sized molecules in serum albumin solutions and gels[94], in cellulose gels[45~46] has been investigated by FT-PGSE NMR. Such experiments have the advantage that permeant diffusion rates can be determined selectively to quite low concentrations even in the presence of a huge water peak. In addition, the signal from the gel framework is completely absent with relatively long rf pulse intervals used(100 ms).

3-1-5. Counterion diffusion in polyelectrolyte systems in solution

(1) Polymeric polyelectrolytes(counterion bi-

nding): Ion binding and counterion transport processes in polyelectrolyte solutions is a field of much current interest and has attracted much experimental, theoretical and computational effort. Counterion diffusion rates are easily related to concepts such as ion binding and also to the numerical results of computer simulation experiments on polyelectrolyte solutions. Much interest has also been focused on the relations between counterion size and type and ion binding. The low gradient FT-PGSE technique is a good method for studying the relatively rapid counterion diffusion found experimentally(counterion diffusion rates are seldom less than 25% of those of corresponding simple salt solutions), and is easily applicable to all organic counterions(FT-PGSE), and several inorganic counterions with 'favourable' PGSE characteristics($^{19}F^-$, $^{35}ClO_4^-$, $^7Li^+$, $^{133}Cs^+$, $^{113}Cd^{2+}$, $^9Be^{2+}$). In many cases, the lower concentration limit is in the submillimolar range, so that total concentration range of four decades may then be accessible for study, which is a highly relevant factor in investigation of the present type. The applications and physco-chemical aspects are discussed in greater depth in Refs. [47~51].

(2) Ionic surfactant aggregates(counterion binding): The problems and experimental conditions for these systems are very much the same as in the previous Subsection. Since these are self aggregates systems, one can conveniently monitor the whole aggregation process through multicomponent self diffusion studies, thus providing a detailed picture of the aggregation conditions of each constituent(i) down to millimolar or submillimolar concentrations in water[52]. The analysis of the aggregation process is based on the two-site micelle/free model, such that

$$D^i_{obs} = p^i_{micelllar} D_{micelle} + (1 - p^i_{micellar}) D^i_{free} \qquad (7)$$

which is known as Lindman's first law: $0 < p < 1$. The micellar diffusion coefficient can be determined from the time average self diffusion coefficient of a completely solubilized hydrophobic solubilizate, or through iterative computer fitting of the surfactant ion self diffusion rate as a function of concentration.

The binding of organic counterions is easy to study with the FT-PGSE technique[53,54], studies of competitive ion binding in the presence of several counterions pose no problems whatsoever. There are no alternative methods for the latter purpose.

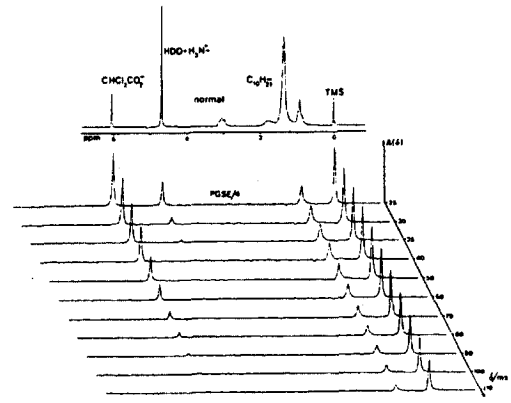

Fig. 2. An FT-PGSE experiment on a micellar decylammonium dichloroacetate solution in heavy water at 40℃[53].

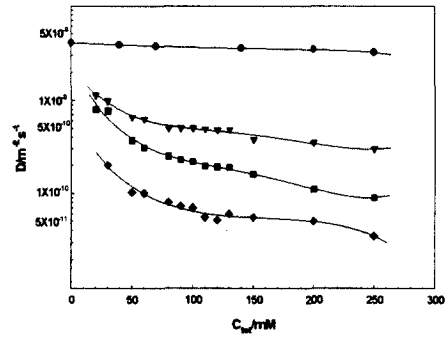

Fig. 3. The diffusion coefficients of the constituents as a function of concentration [53].
● : HDO, ▼ : $CHCl_2COO^-$,
■ : $C_{10}H_{21}NO_3^+$, ◆ : TMS

The problem of ion transport (rather than aggregation and binding) in concentrated micellar solution is of current theoretical interest. Experimentally (and theoretically), traces of

divalent counterions($^9Be^{2+}$) and monovalent counterions($^7Li^+$ of litium dodecylsulphate) in a mono valent surfactant solution exhibit quite different transport conditions, as monitored by FT-PGSE[55].

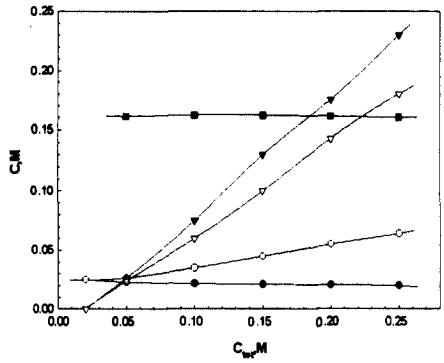

Fig. 4. An analysis of the data in terms of a two-site micellarly bound/free model: β denotes the degree of ion binding [53].
●: C^+_{free}, ○: C^-_{free}, ▼: C^+_{mic}, ▽: C^-_{mic}, ■: β

3-1-6. Diffusion in binary surfactant/water systems(surfactant aggregation): The micellization process, and subsequent changes in micelle shape can be studied by measuring self-diffusion coefficient by the FT-PGSE method. Multicomponent self-diffusion data,(in particular when combined with laser light scattering and sedimentation measurements[56]) provide a detailed picture of the aggregation processes of nonionc surfactant systems[57].

3-1-7. Diffusion in ternary surfactant/water systems

Solubilization (the incorporation of a highly hydrophobic third component into the micellar pseudophase of surfactant /water solution) is a process of considerable technical and theoretical interest. Multi-component self-diffusion data on the micellar solution provide a new and direct method[58,59] for the quantification of the partitioning of solubilizate between the aqueous and micellar pseudophases, according to the simple relation:

$$D^s_{obs} = p^s_{micellar} D_{micelle} + (1 - p^s_{imicellar}) D^s_{free} \quad (8)$$

where $p_{micellar}$ is the degree of solubilization ($0<p<1$)and all other parameters are accessible experimentally by FT-PGSE technique. D^s_{free} is measured in a separate experiment on a solution of the solubilizate in water[58~64]. The same technique is easily adaptable for investigations of solubilization into vesicular membranes.[65]

Mixed micellization, which is the partial partitioning of two or more micellizable surfactants into the same micelle, can also be studied by FT-PGSE along the same lines [66,67].

3-1-8. Diffusion in microemulsions

The structure of 'microemulsions'(isotropic surfactant systems, simultaneously containing large amounts of water and hydrocarbon, and often also co-surfactant: commonly a medium -chain alcohol) has been a subject of considerable controversy during the last decades. Are they at all 'emulsion-like' or are they just normal liquids with 'partly aggregated' constituents?

The idea is to utilize the combined information on the self-diffusion of the individual constituents: of the microemulsion.

(1) In a micellar (or 'oil-in-water') system, water diffusion is rapid, while that of surfactant and solubilized hydrocarbon is slow

(2) In an inverted micellar system, the hydrocarbon diffusion rate is high, while those of water and surfactant remain slow.

(3) In a 'structureless' system, all constituents diffuse rapidly.

(4) In a bi-continuous system, the constituents confined to the structural framework diffuse slowly, while all other constituents diffuse rapidly.

Investigations along these lines were started with cumbersome radioactive tracer and traditional PGSE techniques in the late seventies by Lindman et al. The FT-PGSE technique,

of course, is the ideal method in this case: there are usually no problems whatsoever to monitor simultaneously the self-diffusion of say water, hydrocarbon, co-surfactant alcohol and surfactant in a matter of minutes per sample. We[68,69~74], and later also other groups[75~78], have made several studies along these lines. The work has been summarized in overviews and review papers. According to our findings, microemulsion 'structure' can span all extremes, depending on composition and constituent chain length.

3-1-9 Diffusion-based monitoring of miscellaneous aggregation processes in aqueous solution.

We have studied the binding of various substrates to cyclodextrins in aqueous solution through FT-PGSE-techniques[79], with essentially the same approach as that in the solubilization studies just mentioned. Mononucleotide aggregation[80,81] and ion binding to nucleotide aggregates[82] have also been monitored successfully. All these studies are analogous to those on surfactant systems, but the approach is not quite as powerful here: the binding had only a small effects on the time-averaged diffusion coefficients the cyclodextrin and nucleotide aggregate diffusion is not as slow as that of micelles.

3-2 Restricted and Anisotropic Diffusion in Heterogeneous Systems

3-2-1. Solute diffusion in liquid crystals and emulsions-phase structure.

Diffusion rates of small molecules in heterogeneous systems provide information on the phase structure and may have significant interest in their own right. Some thermotropic and lyotropic liquid crystals align in a magnetic field, or at least keep their macroscopic alignment long enough to allow NMR PGSE measurements to be made. Depending on the situation, one can measure the anisotropy of diffusion in the mesophase by merely rotating the sample tube through any chosen angle, or to utilize two different field gradient coils(for example one in the x-direction and one in the z-direction in an iron magnet geometry) on a static sample. It is also possible to rotate a quadrupole gradient coil in the main field in order to change the gradient direction[83,84]. Moseley et al[85,86] have utilized the two-coil approach in their elegant FT-PGSE studies on permeants such as methane and chloroform in various mesophases (Fig. 5).

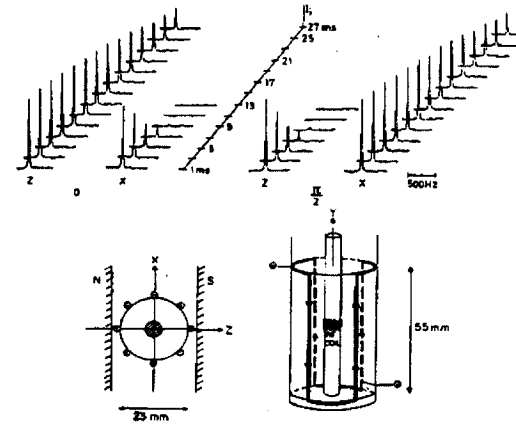

Fig. 5. Diffusion experiments on methane in the smectic B phase of p-butylbenzyliden-n-hexylaniline(40.6) at 26.8℃. The methane diffusional echo attenuation is shown as a function of field gradient duration and direction(z and x magnetic axes). The intergradient pulse interval was 90.9 ms and the gradient strength was of the order of 8×10^{-1} T/cm. FT spectra are based on four accumulated spectra and 5 Hz artificial line broadening. The coil design is outlined in the lower part of the figure[92]

Callaghan and soderman[87] and later Blum et al[88] investigated the echo decay from water in (macroscopically randomly oriented) lamellar and smectic lyotropic mesophases in terms of different models for phase structure and domain size. Callaghan et al. have presented an interesting FT-PGSE study of fat and water diffusion in cheese (Fig. 6)

They discuss the results in terms of different models for water and fat confinement in polydisperse emulsion domains.

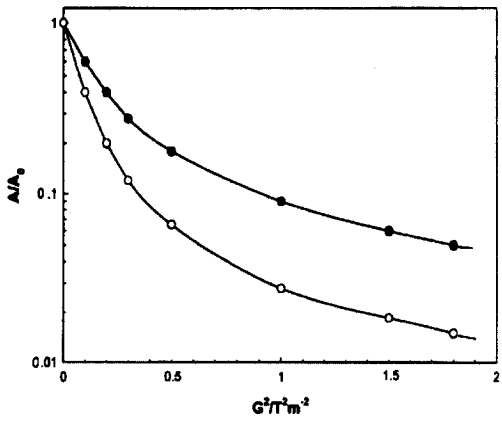

Fig. 6. A medium-resolution proton NMR spectrum of Swiss chesese (●:'water' and ○:'fat', respectively) and the results of PGSE experiments on the fat emulsion droplets at two different PGSE pulse parameter settings. The solid curves are fits to a model of restricted diffusion in spherical cavities(about 5000 nanometers in diameter)[93].

NMR spectra of quadrupolar nuclei in anisotropic environments exhibit quadrupolar splittings. Callaghan et al. analyzed echo decay relations for the pulsed-gradient modification of the 'solid echo sequence' (which differ from the normal Stejskal-Tanner relation) and applied the technique for investigations on the anisotropy of water diffusion un single-crystal samples of potassium palmitate in D_2O.

3-2-2. Monitoring of transport through cell membranes

A very powerful and selective technique for the monitoring of influx of various substrates into living cells was described some years ago by Brown at el[89,90]. It is basically a field gradient SE technique as applied to a case of restricted diffusion. The field gradient in question is one that arises near the outer cell surface as a result of different magnetic susceptibilities inside and outside the cell(Fig. 7). In the cases of spherical geometries there will be no field gradients inside the cells, unless there are internal susceptibility differences. By artificial means, such as the addition of paramagnetic ions to the extracellular solution, the internal/external susceptibility difference can be enhanced. The field gradient magnitude will be proportional to Bo in the case of naturally occurring susceptibility-related gradient and thus it is highly advantageous to use larger magnetic field in these particular experiments: there is also a gain in sensitivity and spectral dispersion. With appropriate field gradient and SE pulse parameters, the signal from the extracellular solution will be completely absent in the SE spectra. The influx into the cells is then monitored simply by recording spectra at different time intervals and measuring the increasing amplitude of the substrate peak(Fig. 8). This experiment is adaptable to any supercon NMR spectrometer

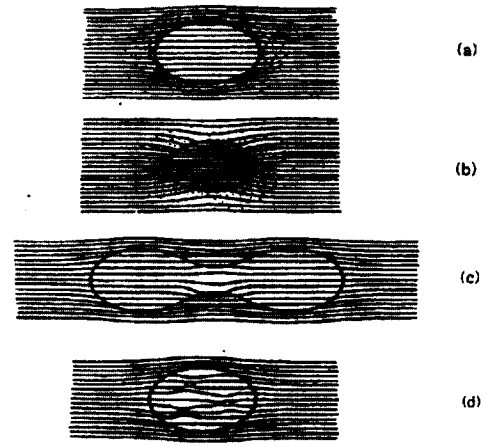

Fig. 7. Illustration of the effects of differences in magnetic susceptibility on the lines of magnetic flux in different geometries.
(a): $\chi_{in} < \chi_{out}$, (b): $\chi_{out} < \chi_{in}$,
(c): representations of lines of flux in the erythrocyte,
(d): representations of the field within a cell containing vesicles of different susceptibilities[89]

that can achieve the pulse programming for a normal Hahn echo with data collection starting at the echo peak, followed by normal Fourier transformation. For practical reasons, the influx kinetics must be reasonably slow(with a half-life of at least a few minutes). The cells die unless the solutions are oxygenated: the periodic oxygenation(which also suppresses sedimentation of the cells to the bottom of the tube) causes secondary problems because of bubbles in the sample, flow effect on SE signal, and so on.

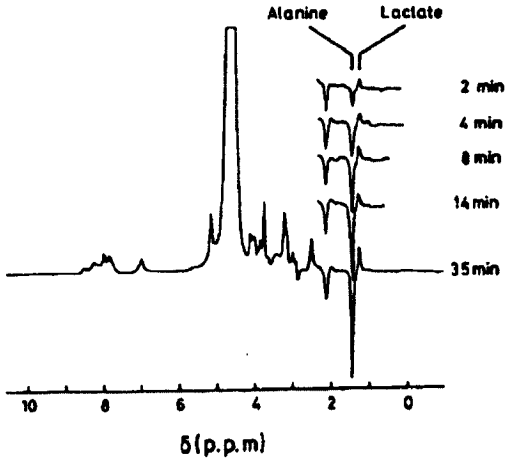

Fig. 8. Proton spin echo spectra(τ =60ms, 270 MHz) obtained during an alanine influx experiment into human erythrocytes[89].

Andrasko[91] has studied the influx of Li^+ ions into erythrocytes a ^7Li PGSE experiment in a similar way. With appropriate PGSE pulse parameters it is possible to suppress the signal from the extracellular solution completely. One then proceeds along the lines just mentioned. We have successfully tested Andrasko's approach on organic substrates using low gradient proton based FT-PGSE techniques at 100 and 300 MHz.

4. Conclusion

It is evident that Fourier transform PGSE techniques provide a new and very powerful tool for the investigation of a large spectrum of physico-chemical problem. When properly applied, the techniques have good accuracy and they are uniquely selective when applied to multicomponent systems. There is still a great potential for methodological refinements of this technique and for extending the application into many new areas of chemistry. It much be said that NMR self diffusion measurements seem to be almost completely overlooked by people who use classic radioactive tracer diffusion techniques.

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