
01 Jan 1987

Fourier Transform NMR Self-diffusion Studies Of A Nonaqueous Microemulsion System

K. P. Das

A. Ceglie

B. Lindman

Stig Friberg

Missouri University of Science and Technology, stic30kan@gmail.com

Follow this and additional works at: https://scholarsmine.mst.edu/chem_facwork

 Part of the [Chemistry Commons](#)

Recommended Citation

K. P. Das et al., "Fourier Transform NMR Self-diffusion Studies Of A Nonaqueous Microemulsion System," *Journal of Colloid And Interface Science*, vol. 116, no. 2, pp. 390 - 400, Elsevier, Jan 1987.

The definitive version is available at [https://doi.org/10.1016/0021-9797\(87\)90135-4](https://doi.org/10.1016/0021-9797(87)90135-4)

This Article - Journal is brought to you for free and open access by Scholars' Mine. It has been accepted for inclusion in Chemistry Faculty Research & Creative Works by an authorized administrator of Scholars' Mine. This work is protected by U. S. Copyright Law. Unauthorized use including reproduction for redistribution requires the permission of the copyright holder. For more information, please contact scholarsmine@mst.edu.

Fourier Transform NMR Self-Diffusion Studies of a Nonaqueous Microemulsion System

K. P. DAS*,¹ A. CEGLIE*,² B. LINDMAN,* AND S. E. FRIBERG†

*Physical Chemistry 1, Chemical Center, University of Lund, P.O. Box 124, S-221 00 Lund, Sweden, and

†Department of Chemistry, University of Missouri, Rolla, Missouri 65401

Received February 21, 1986; accepted June 11, 1986

Self-diffusion coefficients of the components of the microemulsion system glycerol/hexanol/sodium dodecyl sulfate (SDS) were determined in the presence and absence of an oil, *p*-xylene, and the results were compared with those from corresponding aqueous systems (i.e., glycerol replaced by water). In the aqueous system, the water in the hexanol rich isotropic liquid showed a diffusion coefficient less than 10% of that of free water, while that of hexanol was roughly 80% of that of free hexanol; such restricted motion of the water is consistent with the presence of water as discrete droplets. Partial substitution of *p*-xylene for hexanol did not affect the diffusion coefficient of water appreciably. In the nonaqueous three-component system, the diffusion coefficients of glycerol, SDS, and hexanol all decreased in concert as the glycerol content increased; e.g., that of hexanol goes from $1.75 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ to $2.7 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ as the glycerol content ranges from 10 to 80%. The diffusion coefficient of glycerol was always greater than that of neat glycerol by a factor of 5 to 45. As the diffusion coefficients of all components were within a factor of 2, the idea of segregating one or more components into disconnected domains is not supported. There is no support for glycerol droplets but these microemulsions appear to be structureless.

© 1987 Academic Press, Inc.

INTRODUCTION

In recent years much interest has been focused on microemulsion systems. Microemulsions cover a wide range of surfactant systems containing hydrophilic and hydrophobic components and their definition has been limited to thermodynamically stable optically isotropic systems (1). They are interesting from the structural point of view and a number of studies have examined this aspect (2–8). In general in an extended microemulsion region, two distinctly different structural types are found at the extreme composition regions which lack a hydrophilic component and are rich in a hydrophobic one or vice versa. The situation represents a rather com-

plete confinement of either of these two components in a closed domain. The intermediate region however does not show complete confinement characteristics but exhibits intermediate behavior between the two extremes. Several models exist to explain these structures (9–16) but the overall picture is still far from clear. The present knowledge of microemulsion structure has been reviewed recently (17, 18). All this information comes from studies which have invariably been done by using water as the only hydrophilic component. This is primarily because the solution behavior of surfactants has been studied extensively in the aqueous medium.

Studies of surfactant behavior in nonaqueous media are not new although the number of such studies is limited (19). Micelle formation in nonaqueous media such as amides (20), dimethyl sulfoxides (20), and glycols (21, 22) was reported earlier. Some low melting salt-melts have also been tried as the micelle

¹ Permanent address: Department of Chemistry, Vidyasagar College, 39 Shankar Ghosh Lane, Calcutta 700 006, India.

² Permanent address: Dipartimento di Chimica, Università degli Studi di Bari, Via Amendola 173, 70126 Bari, Italy.

forming media by Evans and his co-workers (23) and they reported the hydrophobic bonding behavior of surfactants in such systems (24). These studies raised the possibility of replacing water with some other hydrophilic substances in microemulsions. Very recently some nonaqueous microemulsion systems have been reported independently by Fletcher *et al.* (25), Friberg and Podzimek (26), Friberg and Wohn (27), and Rico and Lattes (28, 29). While Friberg and Fletcher replaced water by glycerol, Rico and Lattes introduced formamide in place of water and indicated the usefulness of such nonaqueous microemulsions as reaction media. Some of these microemulsions are found to be birefringent but their thermodynamic stability has been questioned (27). These nonaqueous microemulsions have been suggested to have the same microscopic structure as the aqueous microemulsions (28, 29). However, this assumption is based on the similarity of phase regions between aqueous and glycerol or formamide systems and they have been suggested recently to be initial and simple solutions with critical behavior (30). This means that the degree of parallelism between aqueous and nonaqueous microemulsions from a structural point of view is yet a matter of speculation as no work is reported to date on the structural behavior in these kinds of nonaqueous systems.

With this in mind we found a study of self-diffusion coefficient measurements to be useful in order to explore the microscopic structure of these systems. We found this method appealing because of the relevance of self-diffusion measurements in directly reflecting the structural properties of microemulsions, a fact which has been established in a number of recent articles (2, 3, 31, 32) and reviews (18, 33). In the present paper we report self-diffusion studies of the nonaqueous microemulsion system glycerol/hexanol/sodium dodecyl sulfate (SDS) with and without the presence of an oil, *p*-xylene. Measurements have also been carried out on the analogous aqueous system water/hexanol/SDS and the results have been compared.

EXPERIMENTAL ASPECTS

Materials

Glycerol (>99.5%), hexanol (99%), and *p*-xylene (98.5%) were obtained from BDH, England, and used without further purification. SDS used was a specially pure biochemical grade also from BDH, England. The heavy water used for preparing aqueous samples for self-diffusion measurements was 99.7% $^2\text{H}_2\text{O}$ from Ciba-Geigy, Switzerland.

Samples were prepared in the isotropic regions of the phase diagrams by weighing the components into glass ampoules which were then flame sealed. To ensure equilibrium all samples were left for 7 days before any measurement was performed. All solutions were examined under crossed polaroid to ascertain optical isotropy.

Self-diffusion coefficient measurements were carried out by Stilbs' Fourier transform NMR pulsed gradient spin echo method (34) on a Jeol FX-60 FT NMR instrument equipped with a home-built field gradient unit. Spin echo proton NMR spectra were used in the diffusion studies at an NMR frequency of 60 MHz. The details of this method were reported earlier (2, 18, 34). The probe temperature was adjusted to within $\pm 0.5^\circ\text{C}$ which was measured by a calibrated copper-constantan thermocouple. For the purpose of field-frequency lock, samples were taken in sealed capillary tubes of 2.5 mm outer diameter which were fitted coaxially within standard 5-mm NMR tubes containing D_2O . This arrangement was not necessary for aqueous samples as internal D_2O could be used for the lock purpose. This however did not permit us to carry out measurements at very low heavy water content. The intensity of NMR signals was taken directly from the computer printout. Usually a good signal-to-noise ratio was obtained with one accumulation but in a few cases a number of transients were accumulated to improve signal-to-noise ratio, especially when the glycerol contents were high. For each sample at least 10–12 different values of the duration of the field gradient (δ) in the range

5–99 ms were applied and for each value of δ , at least three intensity (I) values were taken for averaging. The intensity data were fitted to the equation

$$I_i = A \exp[-GD_i\delta^2(\Delta - \delta/3)]. \quad [1]$$

Here G is a constant, D_i is the self-diffusion coefficient of the i th component, Δ is a time parameter denoting the time between the 90 and 180° pulses and was kept fixed at 140 ms, and A is a parameter which was varied to give the best fit to the data. The constant G was normally determined every day of the experiment by a separate calibration experiment in which D₂O was used. The self-diffusion coefficient of trace HDO in D₂O at the experimental temperature was known from the literature (35).

An NMR spectrum of a typical four-component glycerol/hexanol/*p*-xylene/SDS system is shown in Fig. 1. Both the normal NMR spectrum and the spin echo spectrum are shown. The signal assignments were done by comparing the normal NMR spectrum and the spin echo spectrum with the spectra of the different components in their neat liquids or in their simple solution. For example, the main -CH₂ peak of hexanol, but not of SDS, practically disappears in the spin echo spectrum and hence the observed -CH₂ peak in this four-component system can be attributed with good approximation to SDS only. Similarly, the -CH₃ peak of SDS (measured in D₂O solution) has a very low intensity in the spin echo spectrum, whereas the -CH₃ of hexanol gives a sharp peak. This attenuation effect arises from the transverse relaxation of the respective protons and also from the chosen NMR parameters. Particularly important is the value of Δ ; the value of Δ used in the present work has been chosen based on Stilbs' work (36). The other hexanol and glycerol peaks were assigned in discussion analogous to the one given above. Thus, although in the normal NMR spectrum, peaks other than that from *p*-xylene are composite peaks, the spin echo spectrum fortunately becomes much simpler as each peak can be attributed to one component.

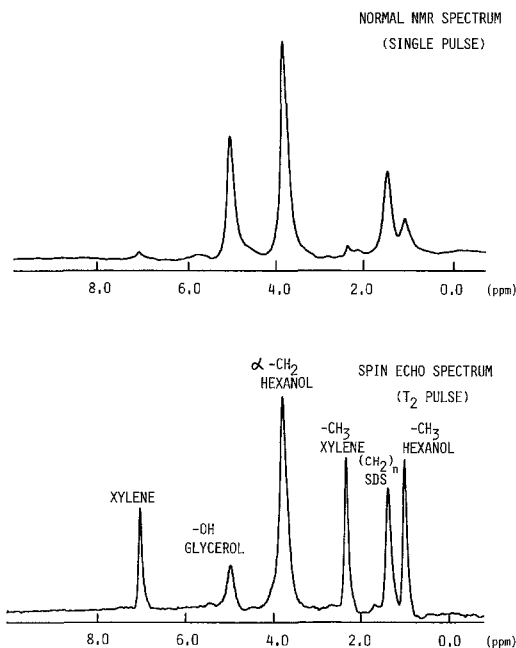


FIG. 1. A typical ¹H NMR spectrum of a sample glycerol/hexanol/*p*-xylene/SDS system at 45°C. Both spectra are from nonspinning samples with one accumulation in each case. In the spin echo spectrum of this four-component system at 25°C there is no glycerol peak due to the reasons discussed in the text.

This attribution was checked again by noting the decay of each of the signal intensities with the duration of the applied field gradient. The individual intensities fit quite nicely to single exponentials according to Eq. [1] (see Fig. 2). The diffusions of *p*-xylene or hexanol calculated from two different peaks agree very well (within 3%).

All self-diffusion coefficient calculations were done by using a UNIVAC (Sperry 1100 OS) computer with a nonlinear least-squares fitting procedure via a Monte Carlo simulation. The details of the calculation subroutine and error analysis used in the present study can be found in Refs. (34, 37–39). In calculating water and glycerol self-diffusion coefficients, the exchange of water and glycerol hydrogens has been taken into account as was done earlier (2). This correction is however quite small and often insignificant.

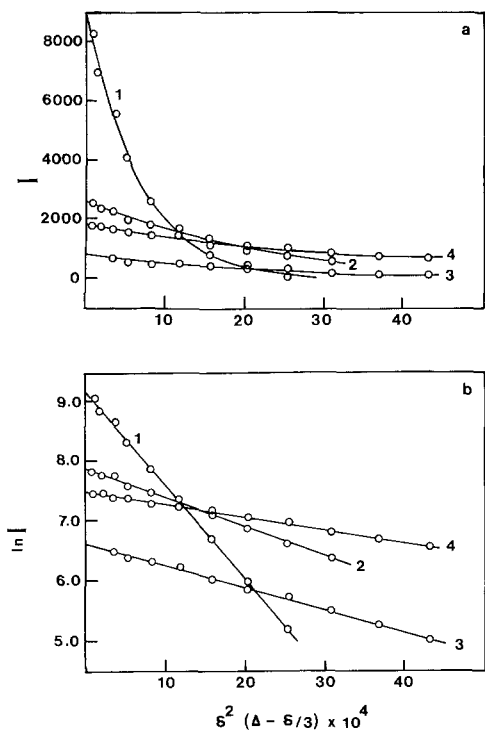


FIG. 2. A plot of intensity (I) as a function of $\delta^2 (\Delta - \delta/3)$ in (a) linear and (b) semilog scale. Lines represent best exponential (a) or linear (b) fit through the experimental points. 1, *p*-xylene; 2, glycerol; 3, hexanol; and 4, SDS. Intensities of *p*-xylene and hexanol are taken from their respective $-\text{CH}_3$ peaks. Temperature of the experiment is 45°C.

RESULTS AND DISCUSSION

The isotropic region of the three-component nonaqueous microemulsion system containing glycerol, hexanol, and SDS is shown in Fig. 3 (30). The isotropic region is connected to the hexanol and glycerol corners and is far from the SDS corner. The maximum surfactant concentration in the isotropic region is about 22 wt%. The addition of an oil like *n*-decane decreases the isotropic area and causes a detachment of the region from the glycerol corner; the region moves further away from this corner as the ratio between hexanol and *n*-decane is decreased (see Fig. 4). Figure 3 can be compared with Fig. 5 where the regions for the analogous aqueous system (glycerol replaced by water) have been shown. Two op-

tically isotropic regions, one small along the water-surfactant line and another well separated from this extending from the hexanol corner, can be identified. This type of phase behavior is typical in three-component water/alcohol/surfactant systems (40) and the two regions are generally known as water rich, L_1 , and water poor, L_2 , regions. Liquid crystals are encountered in the intermediate regions (40). The maximum water content in the L_2 phase of the present system is about 40 wt%. All phase diagrams and sample compositions indicated in Figs. 3, 4, and 5 are on a weight percentage basis.

Self-diffusion coefficient measurements have been done on the isotropic region of Fig. 3 and on the L_2 region of Fig. 5. The sample compositions are indicated in the figures. For comparison, the composition of the aqueous samples was chosen at a small ratio between SDS and water in order not to be far from the composition of the samples of the nonaqueous system. The results are presented in Fig. 6. Self-diffusion coefficients of all the components of the nonaqueous system are found to decrease with an increase in the weight percentage of glycerol, the trends being nearly parallel to each other. At a low concentration of glycerol (about 20% or less) the self-diffusion coefficients of all the components are quite high. The glycerol self-diffusion coefficient is

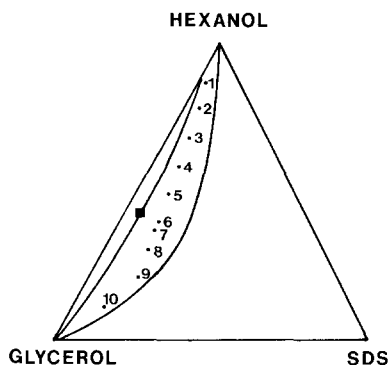


FIG. 3. The phase diagram showing the isotropic microemulsion region in the three-component nonaqueous system (30). (■) Indicates the critical point. All compositions are expressed in weight percentage.

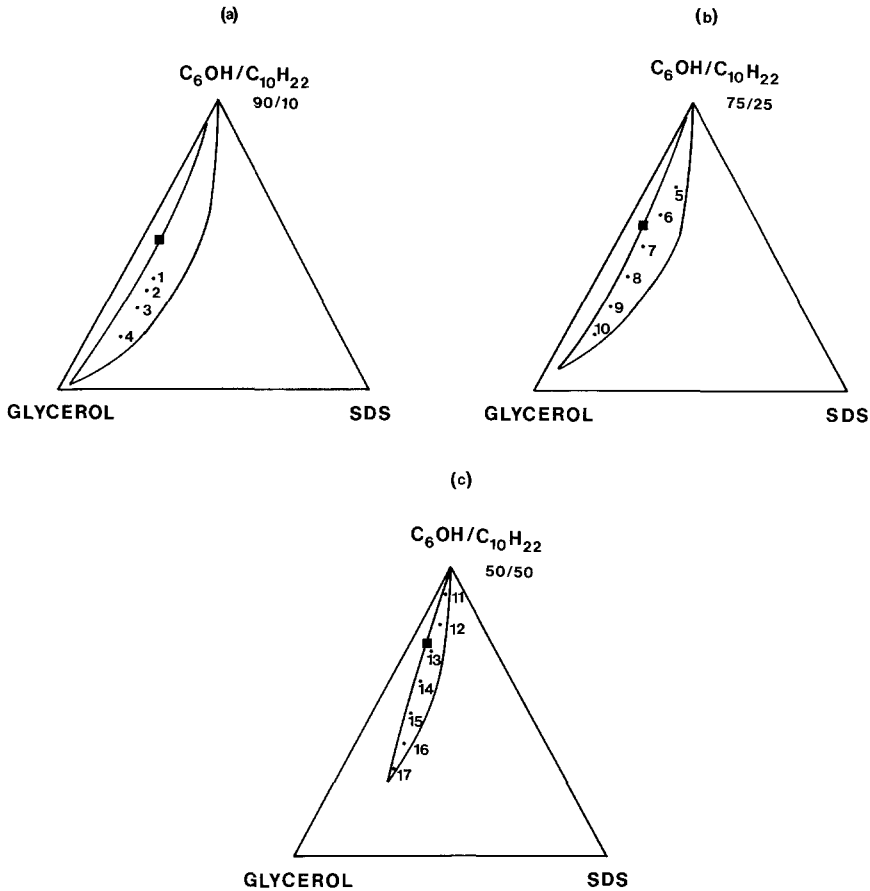


FIG. 4. The pseudoternary phase diagram showing the isotropic region for the system glycerol/hexanol/*n*-decane/SDS (30). Different ratios between alcohol and decane are shown in the figure. (■) Indicates the critical point. Compositions indicated in the figure by numbers are of samples prepared with *p*-xylene in place of *n*-decane for self-diffusion measurements.

about 35–40 times higher than that of pure glycerol, while the hexanol self-diffusion coefficient is almost of the same order of magnitude as that of pure hexanol (see Table I). Even for the surfactant, the self-diffusion coefficient is of the order $10^{-10} \text{ m}^2 \text{ s}^{-1}$ in these regions, which is typically about five times greater than that in normal aggregate form (33). This indicates the absence of a well-defined aggregate or that any such aggregate must have a limited spatial extension. Even at a higher glycerol content where the microemulsion must be glycerol continuous, as the isotropic region is connected to the glycerol corner, the self-diffusion coefficient of glycerol is always higher

than that of pure glycerol. This rules out the possibility of any confinement of glycerol. In addition in Fig. 6, it can be observed that the glycerol diffusion coefficient falls below the surfactant diffusion coefficient above 30% content of glycerol.

The following discussion also serves as a qualitative test for the presence of glycerol droplets.

Within glycerol droplets, the diffusion coefficient of glycerol molecules is assumed to be of the same level as the diffusion coefficient in pure glycerol and the net self-diffusion coefficient observed is approximated as the diffusion coefficient of the droplets only. The ap-

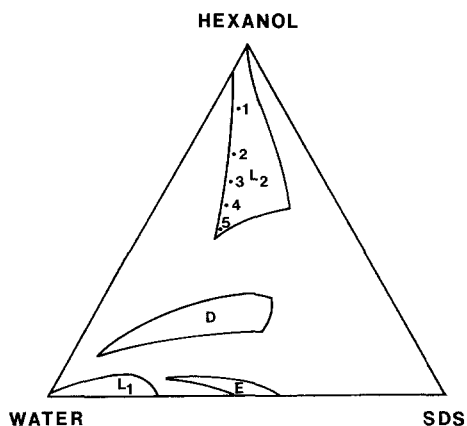


FIG. 5. The phase diagram showing regions (30) for the isotropic and liquid crystalline phases in the three-component water/hexanol/SDS system. L_1 and L_2 are isotropic, D is a lamellar, and E is a hexagonal liquid crystalline phase(s).

parent radius r_{app} of the equivalent sphere of the droplet is calculated using the Stokes-Einstein equation

$$D_{droplet}^0 = \frac{kT}{6\pi\eta r_{app}}, \quad [2]$$

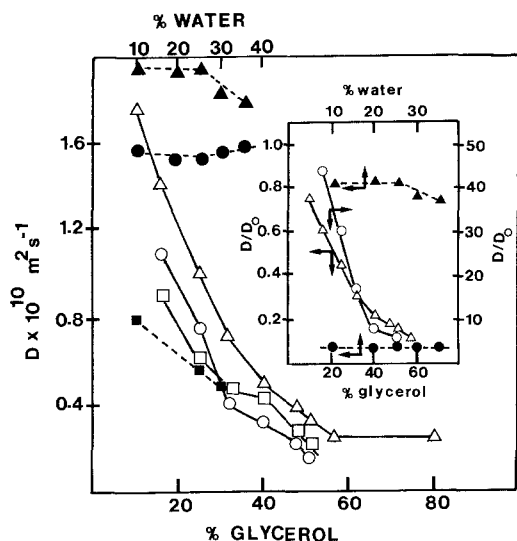


FIG. 6. Self-diffusion coefficient data of the three-component aqueous (filled symbols) and nonaqueous (open symbols) systems as a function of composition. Circles are for glycerol and water, triangles are for hexanol, and squares are for SDS. Inset shows the variation of D/D_0 with composition.

where the symbols have the usual meaning. $D_{droplet}^0$ in this equation refers to the self-diffusion coefficient at infinite dilution of hard spheres. The retardation of droplet diffusion due to hard sphere droplet-droplet interactions is (41)

$$D_{droplet} = D_{droplet}^0(1 - \alpha\phi), \quad [3]$$

where $\alpha = 1.73$ in the presence of hydrodynamic interactions and ϕ represents the volume fraction of particles. Volume fraction was calculated from the sample composition assuming the density of surfactant to be equal to 1.0. Combining Eq. [2] and [3] one can estimate r_{app} provided η is known. To a good approximation, the viscosity of the medium can be taken to be that of hexanol saturated with glycerol. The viscosity of glycerol-saturated hexanol was measured at 25°C in an Ostwald's viscometer. Using this value of η (0.07 poise) the estimated droplet radius was found to be always less than 1.0 nm. Systems in which droplets are well established and which contain a large volume of dispersed phase are known to have much bigger droplets (31, 42). For instance, Zulauf and Eicke (42) reported water droplets of radii in the range 5–15 nm from light-scattering measurements in the L_2 solution of the system water/isoocctane/AOT (sodium di(2-ethylhexyl) sulfosuccinate). Stilbs and Lindman (31) reported hydrodynamic radii to vary in the range 8–25 nm in a water/*p*-xylene/AOT system from the self-diffusion coefficient measurements. Our

TABLE I

Self-diffusion Coefficients of Each of the Microemulsion Components in Its Own Neat Liquid at 25°C

Component (pure)	D ($10^{-9} \text{ m}^2 \text{ s}^{-1}$)	Information source
Glycerol	0.0025	Ref. (51)
<i>p</i> -Xylene	2.17	Ref. (2)
<i>n</i> -Hexanol	0.23	Ref. (32)
Heavy water (trace HDO in D_2O)	1.90	Ref. (35)

estimated maximum hydrodynamic radius (1.0 nm) is indeed too small in comparison to this and since this hydrodynamic radius would also include the length of the surfactant molecule, we can safely argue that there is negligible droplet formation. It could be mentioned here that a standard calculation based on a geometric consideration and a head group area of the surfactant molecule (43, 44), assuming all the surfactant molecules to be present at the interface, does not support the existence of glycerol droplets. The radius of the inner core (excluding the surfactant chain) so calculated is larger in orders of magnitude than the observed hydrodynamic radius. Another consideration taking into account the variation of viscosity of the microemulsions with composition in the Stokes–Einstein equation also speaks against the droplet proposition.

The results of the analogous aqueous system are also presented in Fig. 6. One finds that while the surfactant diffusion coefficient is lower than that in a nonaqueous system, the hexanol diffusion coefficient is higher. The water diffusion coefficient is practically constant. Comparison of the data of the aqueous and nonaqueous systems becomes interesting when the variation with composition of the ratio between the self-diffusion coefficients of the component in a microemulsion and those in pure liquid (relative diffusion D/D_0) is examined. This is shown in the inset of Fig. 6. Notable differences can be observed. In the nonaqueous system, D/D_0 for both glycerol and hexanol decreases sharply with an increase in glycerol content but in the aqueous system, water shows a constant value of D/D_0 and hexanol shows a slow decrease. The value of D/D_0 for hexanol lies in the range 0.82–0.74 in the aqueous system and 0.76–0.11 in the nonaqueous system. For water, the relative diffusion coefficient lies constant at 0.08 while for glycerol it varies from 44 to 6 in the range of composition studied. The decrease in the water diffusion coefficient by more than one order of magnitude and the high relative diffusion coefficient of hexanol clearly indicate

the confinement of water in droplets in an alcohol continuum. This situation is clearly far from the one in the corresponding nonaqueous system.

From Fig. 6 it can be seen that the water self-diffusion coefficient is higher than the surfactant diffusion coefficient, indicating that not all water molecules are confined to the aggregates. Instead, there are some free water molecules also. The amount of water bound to the aggregates may be calculated from diffusion data by applying a two-site model (45). In such a model the observed diffusion coefficient of water is considered to be a weighted average of the diffusion coefficient of free and bound water according to

$$D_{\text{obs}} = p_f D_f + p_b D_b, \quad [4]$$

where p_f and p_b represent free and bound fractions of water and D_f and D_b represent the diffusion coefficients of the free and bound water, respectively. Since the presence of the aggregate creates an obstruction for the free water, D_f is lower than the D_0 of water (45, 46). D_f in Eq. [4] can, however, be replaced by the D_0 of water together with an “obstruction factor” A . Equation [4] then becomes

$$D_{\text{obs}} = (1 - p_b) A D_0 + p_b D_b. \quad [5]$$

An estimation of bound water fraction (p_b) from the diffusion data, assuming $A = 0.8$ and surfactant diffusion to be equal to aggregate diffusion, shows that about 94% of water is bound in the aggregate.

In view of some published work on similar aqueous systems, it can be relevant at this point to compare our results with the published ones. Fabre *et al.* (47) reported self-diffusion measurements in the L_2 region of the system water/decanol/sodium octanoate. The relative diffusion of decanol was found to be close to 0.8 which is nearly the same as that for hexanol in our present system. D/D_0 of water was found to be around 0.02 as compared to 0.08 in our case. The amount of water in the intermicellar solution was estimated to be slightly less than 4%, which corresponded

roughly to the solubility limit of water in decanol. Our estimate of 6% water by weight in the continuous phase is also close to the solubility limit of water in hexanol, vide Fig. 5. Fabre *et al.* (47) also reported the D/D_0 of surfactant taking D_0 , the reference molecular diffusion of surfactant, to be that in water at infinite dilution. Over the entire L_2 region, D/D_0 of octanoate was found to be roughly constant around 0.1. If we do the same thing for SDS in our water/hexanol/SDS system, taking D_0 of SDS to be $6.1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ at infinite dilution in water (48), D/D_0 is found to vary in the range 0.13–0.08 indicating its restricted translational motion. Thus the structure of this three-component aqueous system with hexanol is not much different from that with decanol. Similar systems with lower alcohols like pentanol or butanol are, however, much less structured.

It might be of interest to look into the cause of the anomalously high relative self-diffusion value of glycerol in the microemulsion. Pure glycerol is a highly nonideal liquid, greatly associated in pure form through hydrogen bonding, forming an extensive network-type structure. This makes it highly viscous (about 10^3 times more viscous than water at 25°C) and consequently it has a very low self-diffusion coefficient (see Table I). But in a microemulsion state, this hydrogen-bonded network may be disrupted to a great extent causing the molecules to diffuse faster than in the pure liquid as has earlier been observed for some medium chain alcohols in a microemulsion state (2). Another factor is the lower viscosity of a microemulsion compared to that of the pure liquid; a comparison with the self-diffusion of glycerol in other media may be of interest. Figure 7 shows the self-diffusion coefficient of glycerol in heavy water. The diffusion coefficients are of the order $10^{-10} \text{ m}^2 \text{ s}^{-1}$ and fall steadily with an increase in glycerol content. This fall in diffusion coefficient correlates with the increase in viscosity of the medium, and the self-diffusion coefficient varies linearly with the inverse of viscosity (see Fig. 7) ac-

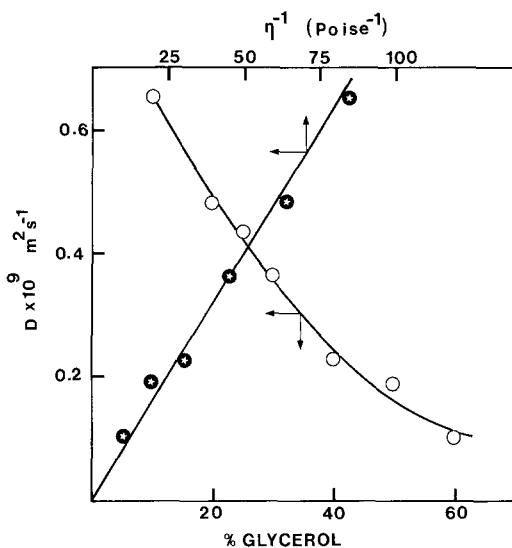


FIG. 7. Plot of self-diffusion coefficient of glycerol dissolved in heavy water against weight percentage of glycerol and inverse viscosity of the solution.

ording to the Stokes–Einstein equation [2]. The viscosity data used for this plot were taken from literature (50). r_{app} calculated from the slope of this straight line is 0.28 nm, which is a reasonable measure of the equivalent size of the glycerol molecule. Hence, the decrease in the self-diffusion coefficients of all the components in the microemulsion with an increase in glycerol content can for a structureless situation be understood due to an increased viscosity.

In the region of high glycerol content, the self-diffusion coefficient of hexanol remained higher than that of glycerol. This makes the possibility of hexanol droplets in this part of the solubility region unlikely.

The picture that emerges from the above discussion is that while water is almost completely confined to the surfactant aggregate, the diffusion coefficient data for the nonaqueous systems do not point to any appreciable confinement of any component to disconnected domains. Or, in other words, while the results support the concept of dispersed long-life aggregates in the aqueous system, the non-

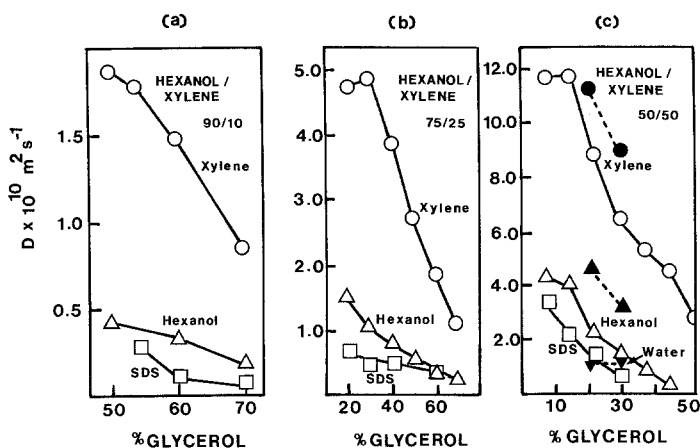


FIG. 8. Self-diffusion coefficient data in the nonaqueous system with *p*-xylene at different ratios between hexanol and *p*-xylene. In (c) are also shown the data for the analogous aqueous system (filled symbols).

aqueous system is less structured and closely resembles a normal solution.

Self-diffusion coefficient measurements of the four-component microemulsion system with *n*-decane as oil proved to be difficult because of the complex nature of the NMR spectrum arising from the overlap of the decane signals with hexanol and SDS signals. Hence, measurements were made by replacing *n*-decane with *p*-xylene, an oil which produces signals well separated from the aliphatic signals. Although the isotropic regions with decane and *p*-xylene may not be exactly the same, the sample compositions shown in Fig. 4 are all within the isotropic range.

The results of the self-diffusion experiments with the *p*-xylene-containing systems are presented in Figs. 8 and 9. Unfortunately, due to the disappearance of the glycerol peak in the spin echo spectra at 25°C, information about the glycerol diffusion coefficient could not be gained. The general features of the data can be summarized as follows: (1) $D_{\text{xylene}} > D_{\text{hexanol}} > D_{\text{SDS}}$ at the different ratios between hexanol and *p*-xylene; (2) all the self-diffusion coefficients decrease with an increase in glycerol content; and (3) as the ratio between hexanol and *p*-xylene decreases, the self-diffusion coefficients of all the components increase. Surfactant diffusion coefficients at a 50/50

ratio between alcohol and *p*-xylene, especially at low contents of glycerol, clearly indicate the absence of any important organization; any aggregates present must be small. In general the enhanced self-diffusion coefficient of all the components may at least be due in part to some decrease in the viscosity of the microemulsion with an increased *p*-xylene content

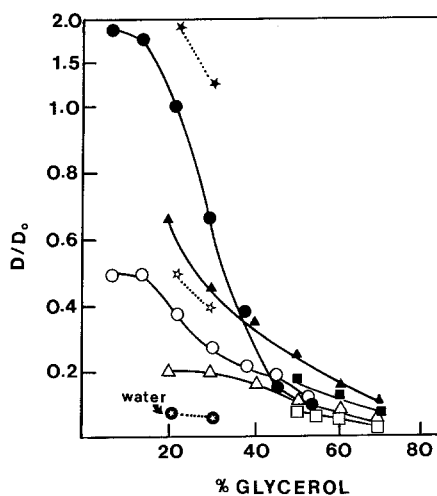


FIG. 9. Values of D/D_0 for the data shown in Fig. 8. Circles represent 50/50, triangles 75/25, and squares 90/10 ratio between hexanol and *p*-xylene. Filled symbols are for hexanol and open symbols are for *p*-xylene. Dotted lines show the data for the aqueous system.

TABLE II

Self-Diffusion^a Coefficients of Nonaqueous Microemulsion Components of Samples Indicated in Fig. 4b at 45 and 25°C

Sample No.	% Glycerol by weight	D_{glycerol} 45°C	D_{hexanol}		D_{xylene}		D_{SDS}	
			45°C	25°C	45°C	25°C	45°C	25°C
5	19.8	1.86 ± 0.14	2.45 ± 0.11	1.52 ± 0.12	7.97 ± 0.11	4.74 ± 0.57	1.08 ± 0.05	0.68 ± 0.04
6	29.3	1.25 ± 0.08	1.72 ± 0.12	1.07 ± 0.02	7.14 ± 0.10	4.87 ± 0.09	0.66 ± 0.09	0.48 ± 0.03
7	40.2	—	—	0.80 ± 0.02	—	3.87 ± 0.07	—	0.51 ± 0.03
8	49.9	0.56 ± 0.02	1.28 ± 0.08	0.57 ± 0.01	4.37 ± 0.06	2.73 ± 0.12	0.55 ± 0.02	0.51 ± 0.04
9	60.2	0.45 ± 0.02	0.62 ± 0.04	0.36 ± 0.03	2.72 ± 0.13	1.87 ± 0.02	0.46 ± 0.06	0.38 ± 0.38
10	69.0	0.30 ± 0.03	0.45 ± 0.06	0.25 ± 0.03	1.68 ± 0.04	1.09 ± 0.06	0.27 ± 0.03	—

^a All D values are in 10^{-10} m² sec⁻¹ units.

when compared at a constant percentage of glycerol.

In order to get an idea about the self-diffusion coefficient of glycerol in these systems containing *p*-xylene, a few measurements were also taken at an elevated temperature of 45°C. The disappearance of the glycerol peak in the spin echo spectra is due to the short transverse relaxation time of glycerol. By accelerating molecular motions by raising the temperature to 45°C, the peak of glycerol in the spin echo spectra was developed. A typical set of data corresponding to the same composition as shown in Fig. 4b is presented in Table II together with the data of 25°C for comparison. There is roughly a twofold increase in the self-diffusion coefficients of the components hexanol, *p*-xylene, and SDS at 45°C. If the same factor is also assumed for glycerol, the self-diffusion coefficients are still very high compared to pure glycerol. Table II shows that at a high glycerol content, the surfactant diffusion coefficient becomes almost equal to the glycerol diffusion coefficient at 45°C. But an estimation of droplet radius, r_{app} , with Eqs. [2] and [3], taking the viscosity of the medium (hexanol + *p*-xylene, 3:1 by weight) at 45°C to be 0.025 poise, gives a maximum value of r_{app} as 1.5 nm, again inclusive of the surfactant molecules. Thus, a droplet of glycerol is unlikely. So we can say that these four-component nonaqueous microemulsions are similar in structure to the three-component ones.

Due to a different phase diagram for the analogous aqueous system in the presence of *p*-xylene, it is not possible to compare the self-diffusion coefficients of four-component aqueous and nonaqueous systems at the same or even nearly the same compositions. It was however possible to prepare two aqueous microemulsions having similar compositions as those of samples 12 and 13 in Fig. 4c, replacing glycerol by heavy water. The results are included in Fig. 8c and Fig. 9. Although values for only two samples are presented, the results clearly indicate the almost complete confinement of water to the aggregates.

Summarizing our results, it can be said that the L₂ phase of the hexanol/water/SDS system is hexanol continuous and water discontinuous with water confined to the inside of the surfactant aggregates. Conversely, the nonaqueous glycerol/hexanol/SDS system does not show any pronounced confinement characteristics but more closely resembles a structureless simple solution. The same conclusion also holds for the four-component systems with added *p*-xylene.

ACKNOWLEDGMENTS

We are grateful to J. O. Carnali and U. Olsson for their kind help with the NMR instrument and for many helpful discussions. This work was supported by grants from the Swedish Board of Technical Development (K. P. Das and B. Lindman), The National Council of Researches, C. N. R. Italy (A. Ceglie) and from the U.S. Department of Energy, Office of Basic Sciences (S. E. Friberg). We are

thankful to one of the referees for making helpful comments.

REFERENCES

- Danielsson, I., and Lindman, B., *Colloids Surf.* **3**, 391 (1981).
- Lindman, B., Stilbs, P., and Moseley, M. E., *J. Colloid Interface Sci.* **83**, 569 (1981).
- Stilbs, P., and Lindman, B., *Prog. Colloid Polym. Sci.* **69**, 39 (1984).
- Kaler, E. W., Bennet, K. E., Davies, H. T., and Scriven, L. E., *J. Chem. Phys.* **79**, 5673 (1983).
- Kaler, E. W., Davies, H. T., and Scriven, L. E., *J. Chem. Phys.* **79**, 5685 (1983).
- Mitchell, D. J., and Ninham, B. W., *J. Chem. Soc. Faraday Trans. II* **77**, 601 (1981).
- Auvray, L., Cotton, J. P., Ober, R., and Taupin, C., *J. Phys. Chem.* **88**, 4586 (1984).
- Lindman, B., Ahlñäs, T., Söderman, O., Walderhaug, H., Rapacki, K., and Stilbs, P., *Faraday Discuss. Chem. Soc.* **76**, 317 (1983).
- Lagues, M., Ober, R., and Taupin, C., *J. Phys. Lett.* **39**, 487 (1978).
- Talmon, Y., and Prager, S., *Nature (London)* **267**, 333 (1977).
- Talmon, Y., and Prager, S., *J. Chem. Phys.* **69**, 517 (1978).
- Shinoda, K., and Saito, H., *J. Colloid Interface Sci.* **26**, 70 (1968).
- Saito, H., and Shinoda, K., *J. Colloid Interface Sci.* **32**, 647 (1970).
- Shinoda, K., *Prog. Colloid Polym. Sci.* **68**, 1 (1983).
- Scriven, L. E., in "Micellization, Solubilization and Microemulsions" (K. L. Mittal, Ed.), Vol. 2, p. 877. Plenum, New York, 1977.
- Friberg, S. E., Lapczynska, I., and Gillberg, G. *J. Colloid Interface Sci.* **56**, 19 (1976).
- Tadros, Th. F., in "Surfactants in Solution" (K. L. Mittal and B. Lindman, Eds.), Vol. 3, p. 1501. Plenum, New York, 1984.
- Lindman, B., and Stilbs, P., in "Microemulsions" (S. E. Friberg and P. Bothorel, Eds.) CRC press, Boca Raton, FL, in press.
- "Solution Behaviour of Surfactants" (K. L. Mittal and E. J. Fendler, Eds.) Vol. 2, Part III, p. 743. Plenum, New York/London, 1982.
- Singh, H. N., Saleem, S. M., Singh, R. P., and Birdi, K. S., *J. Phys. Chem.* **84**, 2191 (1980).
- Ray, R., *J. Amer. Chem. Soc.* **91**, 6511 (1969).
- Ionescu, L. G., and Fung, D. S., *J. Chem. Soc. Faraday Trans. I* **77**, 2907 (1981).
- Evans, D. F., Kaler, E. W., and Benton, W. J., *J. Phys. Chem.* **87**, 533 (1983).
- Evans, D. F., and Chen, S. H., *J. Amer. Chem. Soc.* **103**, 481 (1981).
- Fletcher, P. D. I., Galal, M. F., and Robinson, B. H., *J. Chem. Soc. Faraday Trans. I* **80**, 3307 (1984).
- Friberg, S. E., and Podzimek, M., *Colloid Polym. Sci.* **262**, 252 (1984).
- Friberg, S. E., and Wohn, C. S., *Colloid Polym. Sci.* **263**, 156 (1985).
- Rico, I., and Lattes, A., *Nouv. J. Chim.* **8**, 429 (1984).
- Rico, I., and Lattes, A., *J. Colloid Interface Sci.* **102**, 285 (1984).
- Friberg, S. E., and Liang, Y.-C., *Colloids Surf.*, in press.
- Stilbs, P., and Lindman, B., *J. Colloid Interface Sci.* **99**, 290 (1984).
- Stilbs, P., Rapacki, K., and Lindman, B., *J. Colloid Interface Sci.* **95**, 583 (1984).
- Lindman, B., and Stilbs, P., in "Physics of Amphiphiles Micelles, Vesicles and Microemulsions" (V. Degiorgio and M. Corti, Eds.), North-Holland, Amsterdam, 1984.
- Stilbs, P., "Progress NMR Spectroscopy," **19**, 1 (1987).
- Mills, R., *J. Phys. Chem.* **77**, 685 (1973).
- Stilbs, P., *J. Colloid Interface Sci.* **87**, 385 (1982).
- Stilbs, P., and Moseley, M. E., *J. Magn. Reson.* **31**, 55 (1978).
- Stilbs, P., and Moseley, M. E., *Chem. Scr.* **15**, 176 (1980).
- Chandler, J. P., "Program manual for subroutine STEPIT," program 66, Quantum Chemistry Programme Exchange, Chemistry Department, Indiana University, Bloomington, IN 47401.
- Ekwall, P., in "Advances in Liquid Crystals" (G. H. Brown, Ed.), Vol. 1, p. 1. Academic Press, New York, 1975.
- Ohtsuki, T., and Okano, K., *J. Chem. Phys.* **77**, 1443 (1982).
- Zulauf, M., and Eicke, H.-F., *J. Phys. Chem.* **83**, 480 (1979).
- Sjöblom, J., Rosenquist, K., and Stenius, P., *Colloid Polym. Sci.* **260**, 82 (1982).
- Rosano, H. L., *J. Cosmet. Chem.* **25**, 609 (1974).
- Nilsson, P. G., and Lindman, B., *J. Phys. Chem.* **87**, 4756 (1983); **88**, 4764 (1984).
- Jönsson, B., Wennerström, H., Nilsson, P. G., and Linse, P., *Colloid Polym. Sci.* **264**, 77 (1986).
- Fabre, H., Kamenka, N., and Lindman, B., *J. Phys. Chem.* **85**, 3493 (1981).
- Lindman, B., Puyal, M.-C., Kamenka, N., Rymdén, R., and Stilbs, P., *J. Phys. Chem.* **88**, 5048 (1984).
- Sjöblom, E., Henriksson, U., Stilbs, P., in "Reverse Micelles" (P. L. Luisi and B. E. Straub, Eds.), Plenum, New York, 1984.
- "Handbook of Chemistry and Physics," 42nd ed., Chem. Rubber Pub. Co., Cleveland, 1960.
- Farrar, T. C., and Becker, E. D., "Pulse and Fourier Transform NMR—Introduction to Theory and Methods," p. 103. Academic Press, New York and London, 1971.