

WATER COMPRESSIBILITY IN CONFINED SPACES

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Abstract - In order to explore the compressibility of water sequestered in droplets surrounded by surfactant molecular films (reverse micelles), we custom-built a high-precision velocimeter. The apparatus comprises two ultrasonic small-sized cells, electronic generators and a computer-controlled digital scope. We carried out a systematic study of the stability and reproducibility of the experimental set-up which yields an accuracy of 10^{-5} . The ultrasound velocity, the apparent volume, and compressibility of encapsulated water were determined in charged and uncharged molecular films as a function of water concentration. We observed a close relationship between the measured parameters of encapsulated water, the chemical nature of the surfactant molecular film and the number of water molecules in interaction. The values obtained are higher than that reported for bulk water and are assigned to the surfactant-water interactions arising between the head groups and water molecules.

INTRODUCTION

It is common wisdom that water plays a fundamental role in the formation and in the structure of organized molecular assemblies such as lamellae, vesicles and micelles [1]. In the present work, we have used high precision density and sound velocity experiments, to characterize further water-surfactant surface interactions and to obtain additional insights on the peculiar properties of water within interfaces in such microassemblies. In this regard, water-in-oil reverse micelles, which have been described as water microdroplets of variable size, stabilized by a monolayer of surfactant and dispersed in nonmiscible apolar solvents, are of particular interest. They are able to solubilize substantial amounts of water and to interact with biopolymers hosted in the water pool of the optically transparent microemulsion [2,3]. Ultrasonic measurements of small liquid volumes require a high precision instrumentation. An experimental set-up, based on frequency measurements, has been described previously by

Sarvazyan et al. [4]. In our laboratory, we developed a difference ultrasound precision velocimeter and we carried out measurements of water sequestered in reverse micelles, using ionic and nonionic surfactants at increasing water concentration. We show a close relation between the apparent compressibility of encapsulated water and the chemical nature of the surfactant used in reverse micelles.

EXPERIMENTAL SECTION

Volumetric measurements

The densities ρ of solutions, at various solute concentration C , were determined at 25.00°C using the vibrating tube Anton Paar DMA 58 digital density meter, with a precision of $\pm 0.510^{-5}$. The apparent specific volume ϕV was determined according to [5]:

$$\phi V = \frac{1}{\rho_0} - \left(\frac{\rho - \rho_0}{\rho_0 C} \right) \quad (1)$$

where ρ_0 is either the density of the solvent, or of the mixed solvents (isooctane-AOT or decane- $C_{12}E_4$), and ρ is the density of the solution respectively.

Compressibility Measurements

Ultrasound velocity measurements were performed on a custom-built apparatus (Fig. 1.). It measures the difference in velocity between two small (3 ml) identical cells enclosed in a single metal bloc and thermostated at $25.00 \pm 0.01^\circ\text{C}$. One of them is filled with the solvent, (reference cell), while the second, (measuring cell), contains the solute in the same solvent. A 10 MHz sine signal is gated by short pulses (400 ns). The issued signal drives simultaneously the emitting transducers (ceramic) of both cells and the output signals are captured by a digital scope. The apparatus is automated using a PC equipped with an IEEE interface. We have developed a method based upon the determination of the propagation time between the emitted and the

received pulse. The distance between the transducers was determined by a calibration of the system [6]. Under these conditions, the uncertainty of the time measurements is around 0.1 ns.

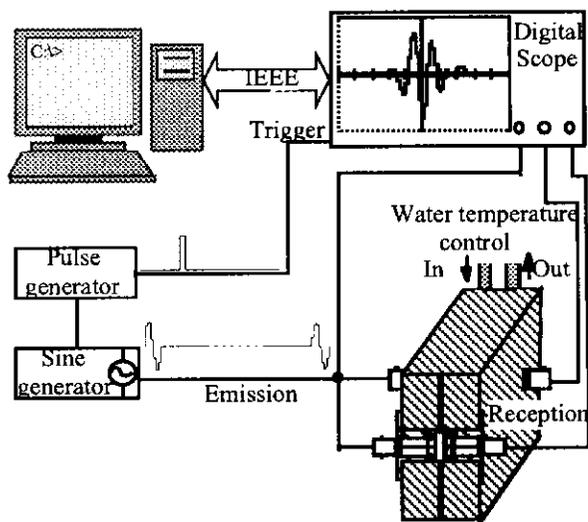


Fig. 1. Ultrasound velocity experimental set up.

A systematic study of the stability and the reproducibility of the measurements showed a velocity accuracy better than $\pm 10^{-5}$. Each volumetric or ultrasonic measurement was repeated from three to five times, averaged and used to calculate ϕK_s and ϕV .

The relative specific sound velocity increment [u], is defined as [7]

$$[u] = \frac{u - u_0}{u_0 C} \quad (2)$$

where u and u_0 are the sound velocities in the solution and in the solvent respectively, and C is the specific concentration of the solute in kg.m^{-3} . The apparent specific adiabatic compressibility was calculated using the values of [u] in conjunction with the measured apparent specific volume ϕV .

$$\phi K_s = \frac{1}{\rho_0 \cdot u_0^2} \left(2\phi V - 2[u] - \frac{1}{\rho_0} \right) \quad (3)$$

RESULTS

Throughout this work, organic solutions of the surfactants were used as a mixed solvent [8], while water, on a weight basis (in kg.m^{-3}), was considered as the solute. The variation of ϕV , [u] and ϕK_s , as a function of water concentration, is illustrated in Figs 2, 3 and 4 for the anionic surfactant sodium 2-(bis ethylhexyl) sulfosuccinate (AOT) reverse micelles in isooctane and for the nonionic surfactant, tetraethylene glycol monododecyl ether ($C_{12}E_4$) reverse micelles in decane. The difference between

the curve profiles obtained for each surfactant is striking.

If we turn to the plot of ϕV vs. water concentration, (Fig. 2A), in AOT reverse micelles we observe that the overall variation of the volume $\Delta\phi V$ is of the order of $3.5 \cdot 10^{-5} \text{ m}^3.\text{kg}^{-1}$. A detailed analysis reveals that the curve can be divided into three segments. The first part extends until a water concentration of 5 kg.m^{-3} . The second extends to about 25 kg.m^{-3} with the midpoint around 13 kg.m^{-3} . The final part of the curve is a plateau. Fig. 2B illustrates the variation of ϕV with increasing water concentration for $C_{12}E_4$ reverse micelles. For the nonionic surfactant the overall variation is higher and corresponds to $8 \cdot 10^{-5} \text{ m}^3.\text{kg}^{-1}$.

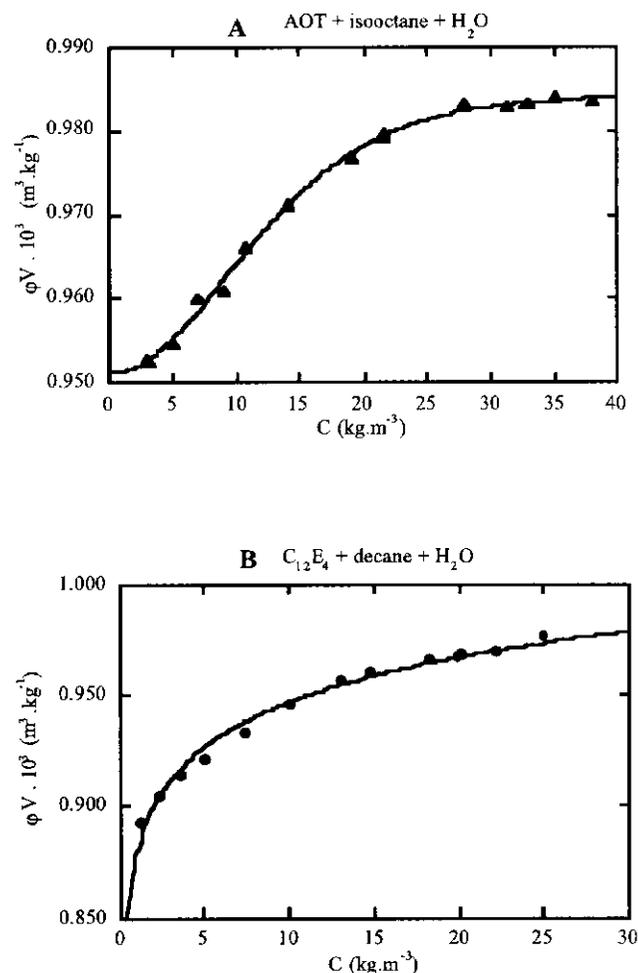


Fig. 2. Apparent specific volume of water ϕV , as a function of water concentration in ionic (A) and nonionic (B) surfactant reverse micelles. The molarity of surfactant solutions is 0.1 mole.dm^{-3} in isooctane and decane respectively.

The variation of $[u]$ vs. water concentration, is illustrated in Fig. 3. In experiments carried out with AOT reverse micelles (Fig. 3A), we observe a sharp drop in the relative specific sound velocity increment, reaching a minimum of $-0.25 \cdot 10^{-3} \text{ m}^3 \cdot \text{kg}^{-1}$ for a concentration of water in the $3\text{-}4 \text{ kg} \cdot \text{m}^{-3}$ range. Then $[u]$ increases rapidly until a water concentration of $15 \text{ kg} \cdot \text{m}^{-3}$. In the final part of the curve, $[u]$ returns smoothly to the initial experimental value around $-0.13 \cdot 10^{-3} \text{ m}^3 \cdot \text{kg}^{-1}$. For C_{12}E_4 reverse micelles (Fig. 3B), we observe an initial drop of $[u]$ until a value of $-0.16 \cdot 10^{-3} \text{ m}^3 \cdot \text{kg}^{-1}$, and then a slow and steady increase. The sharp minimum seen in Fig. 3A is absent, but the final values obtained at the highest water concentration are similar for both surfactants.

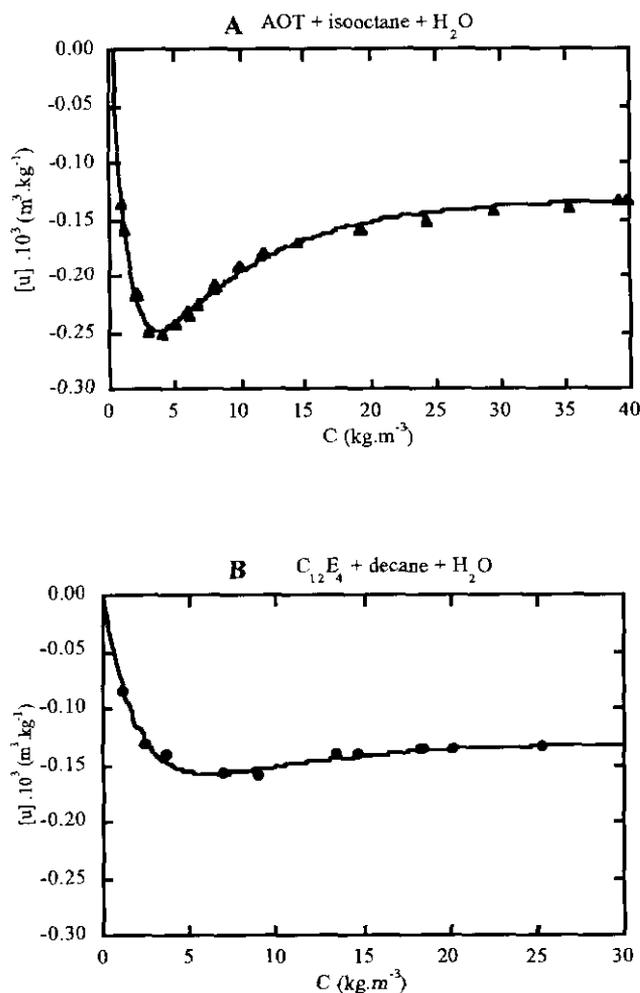


Fig. 3. Relative velocity increment $[u]$ as a function of water concentration in ionic (A) and nonionic (B) surfactant reverse micelles. Same experimental conditions as in Fig. 2.

The curves of ϕK_S , vs. water concentration, are displayed in Fig. 4. For AOT, curve 4A looks like a mirror image of curve 3A, indicating that in this case, the velocity is the predominant factor of the observed phenomenon. The compressibility maximum $120 \cdot 10^{-14} \text{ Pa}^{-1} \cdot \text{m}^3 \cdot \text{kg}^{-1}$, is attained for a water concentration in the $3\text{-}4 \text{ kg} \cdot \text{m}^{-3}$ range, the plateau region corresponding to a value of $100 \cdot 10^{-14} \text{ Pa}^{-1} \cdot \text{m}^3 \cdot \text{kg}^{-1}$. It is obvious that the picture emerging for the nonionic surfactant, (Fig. 4B) is quite different : the value of ϕK_S grows from about $50 \cdot 10^{-14} \text{ Pa}^{-1} \cdot \text{m}^3 \cdot \text{kg}^{-1}$, up to a plateau located around $75 \cdot 10^{-14} \text{ Pa}^{-1} \cdot \text{m}^3 \cdot \text{kg}^{-1}$, which is reached for a water concentration of $7 \text{ kg} \cdot \text{m}^{-3}$.

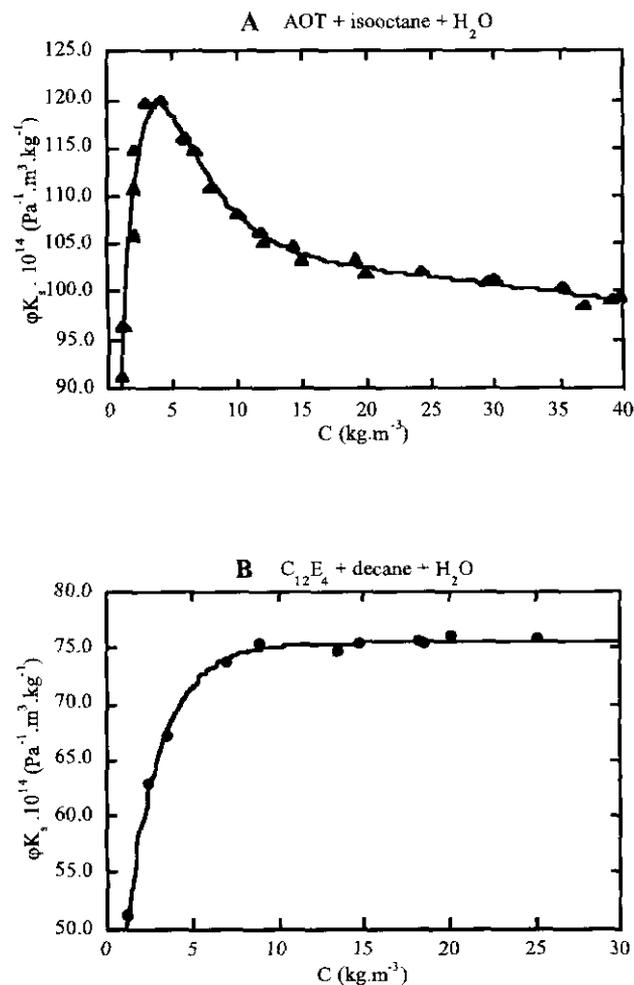


Fig. 4. Apparent specific adiabatic compressibility ϕK_S , as a function of water concentration in ionic (A) and nonionic (B) surfactant reverse micelles. Same experimental conditions as in Fig. 2.

This indicates that here, the factor predominant for the variation of the apparent compressibility is ϕV and not the specific sound velocity increment $[u]$ as observed for AOT reverse micelles.

DISCUSSION

For the ionic surfactant, these results can be examined in the light of previously published studies, in terms of the number of water molecules interacting with the negatively charged sulfonate headgroups of AOT in reverse micelles. Hauser et al. [9] have studied the interaction of water with AOT by ^2H NMR, ESR spin labeling and DSC. Their conclusion was that, although about 3 water molecules are in the tightest interaction, overall, up to 13 water molecules are severely perturbed by one AOT molecule. They also found that all, but the last 6 water molecules, freeze upon cooling AOT reverse micelles to -50°C .

With these results in mind, we can try to interpret our results for AOT: the tight interaction of the first 3 water molecules correlates well with the sharp minimum observed in the relative velocity ultrasound increment $[u]$, for a water concentration of $3\text{-}4\text{ kg}\cdot\text{m}^{-3}$ (Fig. 3A), and with the maximum of the apparent compressibility (Fig. 4A). In the highly non-compressible « dry micelles », the first water molecules which hydrate the surfactant, lead to a very large increase of the micellar compressibility [10]. The midpoint of the volumetric curve can be related to the 6 non-freezing water molecules, evidenced by the above mentioned DSC experiments, and correlates well with the rapid increase in the velocity curve profile. At this stage, the micellar organization proceeds and the compressibility drops. In all the A curves, the final part corresponds to the appearance of unbound water within the water-pool, in increasing amounts. The micelles are now fully constituted and their size grows steadily, paralleled by the slow variation of the plateau region.

The literature concerning the interactions of the nonionic surfactant (C_{12}E_4) reverse micelles with water is rather scarce and sometimes contradictory. From the work of Micali et al. [11], who studied the interactions of polyoxyethylene headgroups with water, it appears that at low surfactant volume fraction, water is only partially bonded and presents a fourfold coordinated environment, analogous to its behavior in confined geometries. In a different set of experiments, Caldararu et al. [12], observed that free water molecules are present in the nonionic reverse micellar water pool, even at the lowest water concentration studied. Their conclusions are in agreement with the continuous variation of our volumetric and compressibility curves, and can account, at least in part, for the different behavior of water in the two surfactant systems reported herein.

CONCLUSIONS

- 1) High-precision volumetric and acoustic measurements can be used to characterize water molecules in confined volumes and at membrane mimetic interfaces.
- 2) From the present work, it is obvious that volumetric and compressibility data obtained for water encased in ionic and nonionic reverse micelles, differ substantially from those reported in for "bulk" water by Kharakoz and Sarvazyan [13].
- 3) At the highest water concentration, the compressibility data obtained with each surfactant reach values of comparable magnitude. This result indicates that, although the surfactant polar head groups perturb the structure of water by different mechanisms, the final compressibility values reflect the compressibility of water in confined spaces.

ACKNOWLEDGMENTS

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