

CALORIMETRIC INVESTIGATION OF WATER/LECITHIN/CYCLOHEXANE MICROEMULSIONS

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Abstract

The enthalpies of dilution of water/lecithin/cyclohexane microemulsion-gels at various R values ($R=[\text{water}]/[\text{lecithin}]$) and molar enthalpies of solution of water in lecithin/cyclohexane at a fixed lecithin concentration were determined calorimetrically at 25°C. Through a description of the process of dilution of water/lecithin/cyclohexane microemulsion-gels as one involving mainly the scission of lecithin reversed micelles in to smaller ones, the concentration dependence of the enthalpy was rationalized. Surprisingly, in order to account for the dilution enthalpies, it was not necessary to hypothesize a thermal effect arising from the breakage of the micellar network present in the microemulsion-gels. This result indicates that the building-up of the micellar network mainly arises from topological entanglements and steric hindrances among the lecithin reversed micelles. Attribution of the molar enthalpy of solution of water essentially to the thermal effect arising from the intermicellar aggregation process induced by the water addition allowed a rough estimation of the scission energy (the energy necessary to break an Avogadro's number of micelles) and of the micellar aggregation number.

Keywords: calorimetry, lecithin reversed micelles, microemulsion-gels

Introduction

Lecithin is a diacyl phosphatidylcholine mixture that occurs widely in biological systems (microorganisms, biological membranes, animal tissues and organs). The presence of distinct polar and nonpolar regions confers on lecithin molecules the typical behavior of surfactants, i.e. a marked ability to form in water molecular aggregates (micelles, bilayers and vesicles) characterized by a

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quite ordered molecular arrangement. All these aggregates have been extensively studied as models for biological membranes [1].

Far less attention, on the other hand, has been devoted to the aggregational behavior of lecithin in apolar solvents. Only recently, there has been growing interest in the study of static and dynamic properties of water/lecithin/organic solvent microemulsions, as a consequence of the discovery of two well-distinct processes: i) an intermicellar aggregation process responsible for a unidimensional increase in the size of water/lecithin reverse micelles, leading to the formation of very long and flexible cylindrical reversed micelles, and ii) a micelle-micelle interaction between these very long reversed micelles, responsible for the formation of an entangled transient network similar to that found in semi-dilute polymer solutions [2]. Both these processes can be induced simply by changing certain external parameters of the system, i.e. the lecithin volume fraction (Φ), the molar ratio R ($R=[\text{water}]/[\text{lecithin}]$) or temperature [3].

It is interesting that, when the mean length of the reversed micelles and their concentration reach threshold values and an extended infinite dynamic network of entangled micelles has been established, the static viscosity of the system reaches very high values (up to 10^6 cP) and the system appears macroscopically gel-like. Several investigations have shown that this extended network arises mainly for topological reasons and that only a small fraction of the lecithin molecules are involved at the entanglement sites, i.e. the micellar network is a three-dimensional grid with large mesh size [4–6].

In order to analyze the behavior of water/lecithin/organic solvent microemulsion-gels, remarkable success has been achieved with the simple model proposed by Cates [7, 8] for living polymers, i.e. linear chain polymers which can break or recombine along the chain, reversibly. This model is based on two main assumptions: (i) a chain can break with equal probability per unit length at all points in the chain, and (ii) two chains can combine at a rate proportional to the product of their concentrations. According to the Cates model, the lecithin volume fraction dependence of hyperacoustic parameters and also results from quasi-elastic incoherent neutron scattering experiments could be consistently rationalized by using an exponential micelle size distribution with a mean length proportional to $\Phi^{1/2}$ [4, 9, 10].

With the aim of investigating the energetics of the intermicellar aggregation process and at the same time of making a further test of the Cates model, we have selected calorimetry as a well-established probe. In this report we present and analyze the results of calorimetric experiments relating to the dilution of water/lecithin/cyclohexane microemulsion-gels at various R values ($R=5.1, 10.1$ and 15.3) and to the solubilization of water in a lecithin/cyclohexane solution at a fixed lecithin volume fraction ($\Phi=0.135$).

Experimental

Materials and apparatus

Soybean lecithin was obtained from Lucas Meyer (Epicuron 200). Before use, the lecithin was stored under high vacuum at low temperature ($<0^{\circ}\text{C}$). Cyclohexane for HPLC (Fluka) was used as received. Water was deionized and bidistilled. Samples for calorimetric experiments were prepared by mass. Lecithin volume fractions (Φ) were calculated by using density data previously reported [4, 9].

The calorimetric measurements were carried out at 25°C with an LKB Thermal Activity Monitor (TAM) equipped with a mix-flow cylinder (LKB 2277–204) and a perfusion cell (LKB 2277–402) and connected to a personal computer (PC/286, Commodore) via an RS–232–C interface. The following procedure was used. A known amount (about 2.6 cm^3) of a solution of lecithin in cyclohexane at $\Phi=0.135$ for the enthalpy of solution experiments (S experiments), or in cyclohexane for the dilution experiments (D experiments), was placed in the sample compartment of the perfusion cell. Then, the cell was introduced in to the calorimeter and, after thermal equilibration, small amounts of water (for S experiments) or of a microemulsion-gel at $\Phi_i=0.123$ (for D experiments) were added into the sample compartment by an injection cannula connected to a Hamilton syringe. The calorimetric signal, appropriately amplified, was transferred into the computer and used to calculate the thermal effect (estimated uncertainty about 0.5%).

Results and discussion

The experimental enthalpies (Q) involved in the process of dilution of water/lecithin/cyclohexane micremulsion-gels (see scheme in Fig. 1) are reported in Table 1.

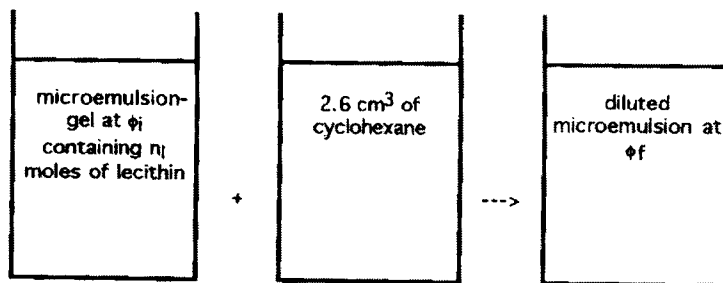


Fig. 1 Scheme of the process of dilution of water/lecithin/cyclohexane micremulsions (Φ_i and Φ_f indicate the volume fraction of lecithin before and after the dilution process, respectively)

Table 1 Experimental enthalpies of dilution (Q) of microemulsion-gels at $\Phi_i=0.123$ as a function of final lecithin volume fraction (Φ_f) and of lecithin mole number (n_l) at various R values

$n_l 10^6/\text{mol}$	$\Phi_f 10^3$	$R=5.1$	$R=10.1$	$R=15.3$
		$Q 10^2/\text{J}$	$Q 10^2/\text{J}$	$Q 10^2/\text{J}$
1.6	0.482	5.70	15.2	15.2
3.2	0.964	6.37	16.6	16.1
6.4	1.93	7.35	18.0	16.8
9.6	2.89	8.20	19.0	17.5
12.8	3.86	8.90	20.0	18.0
16.0	4.82		20.8	18.5
19.2	5.79	9.98		
22.4	6.76			19.2
25.6	7.72	10.70		
28.8	8.69			19.8

The Q values can be regarded as the sum of two contributions [11]:

- i) the enthalpy (Q_d) relating to the dilution of the micellar solution;
- ii) the enthalpy (Q_s) due to the re-equilibration process between the water inside the micelles and the water in the bulk cyclohexane. It must be stressed that, since the processes of dilution of the microemulsions refer to the same quantity of pure cyclohexane, Q_s is a constant quantity at each R [11, 12].

To describe the Q_d term arising from the process of dilution of water/lecithin/cyclohexane microemulsion-gels, we postulate that this represents the enthalpy change associated with the breakage of the lecithin micelles into smaller ones as a consequence of the micellar concentration decrease. Moreover, according to the Cates model and by treating the water/lecithin micelles as living polymers, we assume that the mean length L of water/lecithin micelles is proportional to the lecithin volume fraction Φ [7, 8]:

$$L \propto \Phi^{1/2} \quad (1)$$

When an aggregate of length L_i breaks in N_p points along the chain, it gives N_p+1 aggregates of mean length L_f , and thus

$$(N_p + 1)L_f = L_i \quad (2)$$

and consequently

$$N_p = (L_i L_f^{-1} - 1) = (\Phi_i^{1/2} \Phi_f^{-1/2} - 1) \quad (3)$$

where Φ_i and Φ_f are the lecithin volume fractions before and after the dilution process, respectively (Fig. 1). In addition, if it is assumed that the thermal effect (ΔH_M) due to the breakage of one mole of aggregates with a mean length L_i to give N_P+1 moles of aggregates with a mean length L_f is proportional to N_P , then

$$\Delta H_M = EN_p = E(\Phi_i^{1/2}\Phi_f^{-1/2} - 1) \quad (4)$$

where E is the scission energy, i.e. the energy required to break an Avogadro's number of micelles into two pieces. On the other hand, the thermal effect (Q_d) due to the dilution of a microemulsion-gel containing n_1 moles of lecithin is given by

$$Q_d = n_1(E/N_{agg})(\Phi_i^{1/2}\Phi_f^{-1/2} - 1) \quad (5)$$

where N_{agg} is the number of lecithin molecules in a micelle of length L_i . Since it can be expected that N_{agg} is proportional to L_i , it follows that

$$N_{agg} = K_R\Phi_i^{1/2} \quad (6)$$

where K_R is a proportionality constant representing the aggregation number at unitary lecithin concentration. It must be noted that, given the R dependence of the micellar length, K_R should also depend upon R . Introducing Eq. (6) into Eq. (5), the following equation can be obtained:

$$Q_d = n_1(E/K_R)(\Phi_f^{-1/2} - \Phi_i^{-1/2}) \quad (7)$$

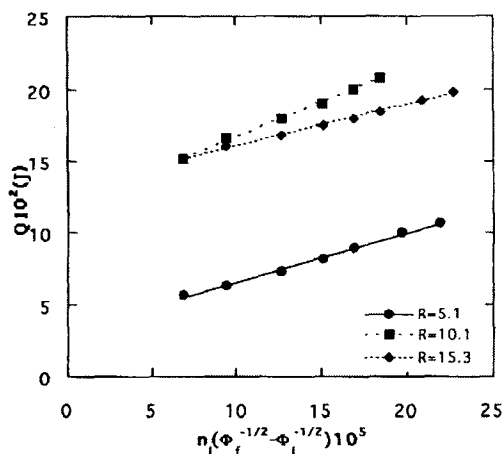


Fig. 2 Heat of dilution (Q) of water/lecithin/cyclohexane microemulsion-gel as a function of $n_1(\Phi_f^{1/2} - \Phi_i^{1/2})$ (see text) at $R=5.1$, $R=10.1$ and $R=15.3$)

It is interesting that Eq. (7) can also be obtained by a more complex treatment which takes into account a distribution of micellar length. However, in the interest of simplicity, we preferred the above-reported derivation. Finally, if one considers that $Q=Q_s+Q_d$, then

$$Q = Q_s = n_l(E/K_R)(\Phi_f^{-1/2} - \Phi_i^{-1/2}) \quad (8)$$

Equation (8) represents the expected relationship between Q and $n_l(\Phi_f^{-1/2}-\Phi_i^{-1/2})$. Figure 2 shows the experimental trends. It can be seen that, according to Eq. (8), quite straight lines are obtained at each R value investigated.

From the intercepts and slopes of the Q vs. $n_l(\Phi_f^{-1/2}-\Phi_i^{-1/2})$ straight lines, the following Q_s (expressed in mJ) and E/K_R (expressed in kJ mol^{-1}) values were obtained: $Q_s=32$ and $E/K_R=0.34$ at $R=5.1$; $Q_s=121$ and $E/K_R=0.47$ at $R=10.1$; and $Q_s=133$ and $E/K_R=0.28$ at $R=15.3$. Since the K_R values are certainly positive numbers, the scission energies are also positive, i.e. the micellar aggregation is an exothermic process and thus energetically favoured. It must be emphasized that, in order to account for the dilution enthalpies, it was implicitly assumed that no thermal effect arises from the breakage of the micellar network present in the microemulsion-gels (negligible chain-chain interactions). The success of this treatment can therefore be taken as confirmation of the previous finding that the building-up of the micellar network arises mainly from topological entanglements and steric hindrances among lecithin reversed micelles [4-6].

Table 2 Molar enthalpies of solution of water in a lecithin/cyclohexane solution at $\Phi=0.135$ as a function of R

R	$-\Delta H_w/\text{kJ mol}^{-1}$
0.81	7.25
1.61	4.81
2.42	3.76
4.03	2.60
5.65	1.95
7.27	1.65
10.51	1.22
12.13	1.08
15.37	0.91

Let us now consider that data relating to the water solubilization in the lecithin/cyclohexane system. The molar enthalpies of solution (ΔH_w) of water in lecithin/cyclohexane solutions as a function of R are summarized in Table 2.

Before an analysis of the observed trend, it must be considered that, on addition of water to lecithin/cyclohexane solutions, a fraction of the water will be solubilized in the bulk solvent in order to maintain the water partition equilibrium between the lecithin reversed micelles and the bulk organic solvent [11, 12]. As a consequence, an enthalpic contribution to the total thermal effect must be expected. In order to estimate this effect, we utilized the Q_s values obtained from the dilution experiments (see above). With these data, we found that the water solubilization in the bulk cyclohexane affects, quite independently of R , the molar enthalpy of solution of water by about 1%. Therefore, it follows that this effect can be neglected and consequently the observed thermal effects can be attributed to the solubilization of water within the lecithin reversed micelles.

On the other hand, when water is solubilized in the lecithin/cyclohexane system, two thermal effects are involved:

- i) the thermal effect due to interactions between water molecules and the lecithin polar head groups;
- ii) the thermal effect arising from the intermicellar aggregation process induced by the water addition.

As concerns contribution i), it must be pointed out that much smaller molar enthalpies of solution are observed when water is solubilized in analogous systems, but where the intermicellar aggregation process does not occur [13]. Thus, as a rough approximation, we assume that this contribution is negligible with respect to that arising from the intermicellar aggregation process induced by the water addition. Since contribution i) tends to become even smaller on increase of R , this assumption becomes more reasonable as the value of R increases.

As concerns effect ii), let us consider a system at $R=0$ containing N moles of lecithin micelles with a mean aggregation number N_o , such that water addition determines the formation of one mole of micelles with a mean aggregation number $N_{agg}=NN_o$. Under these conditions, the thermal effect accompanying the process would amount to $-(N-1)E$. It follows that the enthalpy change for one mole of lecithin (ΔH_L) is given by

$$\Delta H_L = -\frac{(N-1)E}{NN_o} = -\left(\frac{1}{N_o} - \frac{1}{N_{agg}}\right)E \quad (9)$$

Moreover, combining Eq. (6) and Eq. (9) and considering that $\Delta H_L = \Delta H_w R$, we obtain

$$E = N_o \left(\frac{E}{K_R \Phi^{1/2}} - \Delta H_w R \right) \quad (10)$$

Through Eq. (10) and with use of the previously determined E/K_R values at $R=5.1, 10.1$ and 15.3 and a value of 120 for N_o [3], the following scission energies

were estimated: $E=1420 \text{ kJ mol}^{-1}$ at $R=5.1$, $E=1690 \text{ kJ mol}^{-1}$ at $R=10.1$ and $E=1770 \text{ kJ mol}^{-1}$ at $R=15.3$.

In order to test the reliability of these E values and taking into account that $N_{\text{agg}}=K_R$ when $\Phi_i=1$ (Eq. (6)), we calculated the corresponding aggregation numbers at unit lecithin concentration by combining them with the E/K_R values. The following values were obtained: $N_{\text{agg}}=4200$ at $R=5.1$, $N_{\text{agg}}=3600$ at $R=10.1$, and $N_{\text{agg}}=6300$ at $R=15.3$. These values are of the same order of magnitude as those obtained directly from SANS experiments [10]. It is interesting to note, moreover, that the smallest aggregation number is obtained at $R=10.1$, where the maximum in the static viscosity of the water/lecithin/cyclohexane system is observed [3]. This can be rationalized by hypothesizing that the stability of the micellar network depends not only on the micellar length, but also on their flexibility. In fact, previous investigations have evidenced an R dependence of the micellar flexibility [6].

In conclusion, important parameters of the lecithin reversed micelles were obtained by the calorimetric technique which, we hope, will be useful for further refinement of the Cates model. The theoretical calculation of the R dependence of the scission energy and of the aggregation number remains an open question.

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