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ORIGINAL CONTRIBUTION

P.C. Schulz
M.E.G. de Ferreira
G.L. Sierra

Evaporation rate from aerosol OT-water-*n*-heptane inverse micellar systems

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Dr. P.C. Schulz (✉)
M.E.G. de Ferreira · G.L. Sierra
Dept. de Quimica e Ing. Quimica
Universidad Nacional de Sur
Avda. Alem 1253
8000 Bahia Blanca, Argentina

Abstract The evaporation rate of aerosol OT-water-*n*-heptane inverse micellar systems was studied. The evaporation behavior of solutions was strongly affected when compared with pure heptane. The changes are related to the structure of the micelles and the properties of the water molecules dissolved in the micelles. The initial rate of evaporation reaches a maximum when the surfactant head groups are hydrated with three water molecules, a minimum when the first hydration shell of Na^+ ions is completed, and then rises and stabilizes until the second hydration shell is completed. The presence of free water when the ratio water molecules to surfactant molecules exceeds 12 produces a new rise of the initial evaporation rate, which is always higher than that of pure *n*-heptane.

Key words Surfactants – evaporation – inverse micelles – microemulsions – aerosol OT

Introduction

Inverse micellar systems have been extensively investigated for structure and dynamics and their main characteristics are well known by now [1–9].

One aspect that has not received the attention it deserves from an application point of view is the relation of evaporation rate on structure, which is essential for many applications, including motor fuels, cosmetic and pharmaceutical applications.

As far as we are aware, no research has been published on the evaporation rate from inverse micellar systems. Recent static measurements on inverse four-component microemulsions [10] showed that there is a significant influence on the evaporation of the microemulsion structure.

To avoid complications on interpretation arising from a system having too many components, in this work we used a well-known inverse micellar system: aerosol OT (AOT)-water-*n*-heptane.

Experimental

Materials

AOT (Fluka, purity > 98%) was purified by a literature method [11]: *n*-heptane (Carlo Erba, p.a.) was used without purification. Water was deionized, double-distilled.

Solutions

Solutions were prepared in the zone of existence of inverse micelles given by the literature [12]. Water was added to the appropriate amount of AOT and left 3 h in a volumetric flask. Then the samples were made up to the desired volume with *n*-heptane. All solutions were 2.27 wt.% (0.1588 g/mL) in disperse material (AOT + water). Solutions were made with the relation R = moles of water/moles of AOT = 0, 3, 6, 10, 12 and 14.

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Measurements

The evaporation rate measurements were performed in a CAHN 1000 electrobalance, operating in a register range of 100 mg and an output potential of 10 mV.

The pressure was 101.325 kPa. The samples were measured at 293.2 and 311.2 K, thermostatted at ± 0.1 K with water circulation. Known volumes of the solutions were poured into pyrex cylindrical containers with a 2.9 cm internal diameter. To avoid secondary Archimedes effects, a compensator container was hung on the other arm of the electrobalance.

The thermocouple (Fe-constantan) was in contact with the solution through a thin glass sheath.

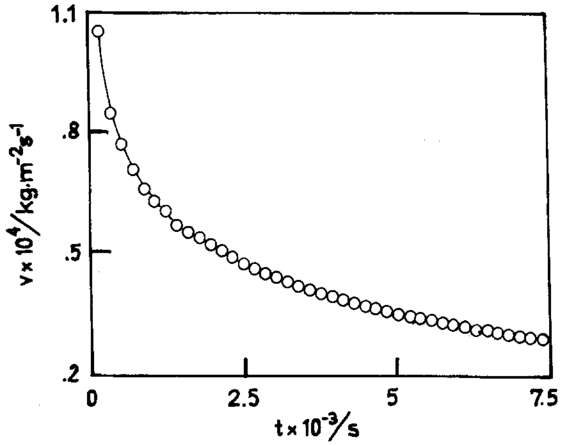

Fig. 1 Loss of weight (v) of the solution with $R = 0$ at 293.2 K with the time

Results

Figure 1 shows the loss of weight (in kg per square meter and second) of the solution with $R = 0$ at 293.2 K with the time. The other systems gave similar curves, following parabolic equations with the general form:

$$v = v_0 - Kt^{1/2}, \tag{1}$$

where v and v_0 are the rate of evaporation at the time t and the initial evaporation, measured in lost mass per square meter and second. The values of v_0 and K were found by the least-squares linear regression method using Eq. (1) and the experimental data, and they are summarised in Table 1. The correlation coefficients were between − 0.9637 and − 0.9994. Table 1 also shows the micellar aggregation numbers (n) taken from literature.

In solutions with $R > 0$, two evaporable species exist: water and heptane. Ueda and Schelly [13] measured the vapor pressure of water in equilibrium with inverse micelles of AOT in cyclohexane and isooctane, and their results are possibly valid to the system with heptane. We calculated the value of water vapor pressure relative to that of pure water, $P_w/P_{w,0}$ in the systems with $R > 0$, on the basis of the Ueda and Schelly results; the values are shown in Table 1. The evolution of n and $P_w/P_{w,0}$ with R is

Table 1 Values of the paramethers of Eq. (1), micellar aggregation number (n) and $P_w/P_{w,0}$

Solution	$T = 298.2\,K$		$T = 310.2\,K$			
	v_0 kg·m^{-2}s^{-1} ×10^5	K kg·m^{-2}s$^{-3/2}$ ×10^7	v_0 kg·m^{-2}s^{-1} ×10^5	K kg·m^{-2}s$^{-3/2}$ ×10^7	n	$P_w/P_{w,0}$
water	1.000 ± .028	1.634 ± .09	4.973 ± .020	1.001 ± .076	–	1
heptane	3.684 ± 0.80	2.72 ± .24	22.49 ± .15	14.16 ± .42	–	0
$R = 0$	11.36 ± .16	15.58 ± .54	24.495 ± .030	10.991 ± .082	18.6^{a,d} 23^{b,d}	0
$R = 3$	12.36 ± .43	19.2 ± 1.4	25.91 ± .11	13.45 ± .34	30.7^{a,d}	.59^c
$R = 6$	5.27 ± .27	3.787 ± .074	16.68 ± .13	7.19 ± .40	57.9^{a,d}	.88^c
$R = 10$	7.528 ± .079	8.01 ± .22	22.70 ± .14	14.83 ± .42	114.3^{a,d}	.985^c
$R = 12$	7.741 ± .055	8.44 ± .15	24.55 ± .38	14.70 ± .13	142.9^{a,d}	1^c
$R = 14$	11.30 ± .29	16.2 ± 1.1	26.113 ± .038	13.81 ± .13	171.4^{a,d}	1^c

[a] from ref. [24], [b] from ref. [17], [c] from ref. [13], [d] cylindrical, from ref. [15], [e] spherical, from ref. [21].

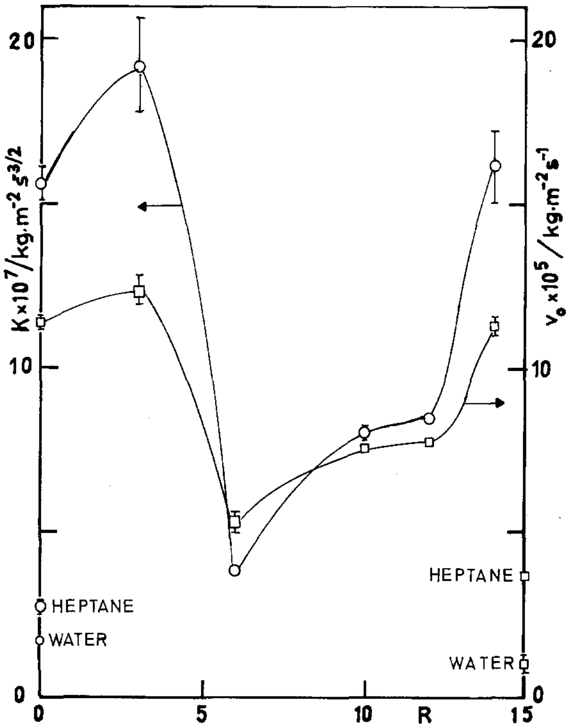

Fig. 2 Values of v_0 (□) and K (0) at 298.2 K as a function of R

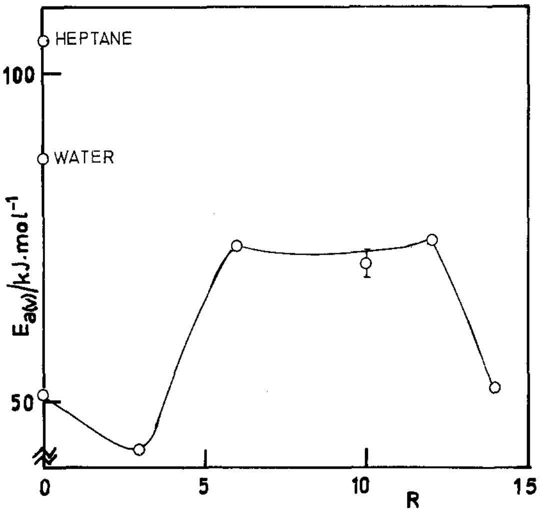

Fig. 3 Activation energy of v_0 as a function of R

correlated with the evaporation rate in the discussion section.

Figure 2 shows the values of v_0 and K at 298.2 K as a function of R. A similar plot is obtained at 310.2 K.

By suppossing that the initial process of evaporation depends on temperature by an Arrhenius equation, from v_0 values at 298.2 and 310.2 K, the activation energies ($E_{a(v0)}$) have been obtained and plotted in Fig. 3.

Discussion

The initial rate of evaporation (v_0)

The only hindrance for the initial rate of evaporation v_0 is the reluctance of the molecules of the evaporating substances (water and *n*-heptane) to leave the surface in the initial state of equilibrium, which is related to the evaporation enthalpy [14].

The examination of v_0 at $R = 0$ and 298.2 K indicates that the initial evaporation of the heptane molecules in the solution is easier than that of pure heptane. The v_0 activation energy of the solution is higher than that of heptane, thus, the rise of temperature will make the solution value of v_0 approach that of pure *n*-heptane.

With $R = 3$, an increase is seen in v_0 and $E_{a(v_0)}$. These values fall to a minimum when $R = 6$, showing that the evaporation of molecules is more difficult than in the preceding (and following) solutions. The increment of R produces a monotonic rise of v_0 and a constant value of $E_{a(v_0)}$, up to $R = 12$, when a break occurs with a sharp increase of v_0 and a fall of $E_{a(v_0)}$ at $R = 14$. These changes may be correlated with structural changes in the solution.

When water is added, it locates in the inner part of the micelles, because the mutual solubility of water and *n*-heptane is extremely low.

Goto et al. [15] measured the enthalpy of transference of water from the inner pool of AOT inverse micelles in isooctane to the gas state, and they found that it has a minimum between $R \approx 0$ and $R \approx 3$, with $\Delta H^0_{tr} =$ 40.8 KJ/mol at the minimum, and a plateau at larger R values, with $\Delta H^{\circ}_{tr} = 43.9$ KJ/mol, close to the evaporation enthalpy of 44.24 KJ/mol at 293 K.

The first three water molecules per AOT molecule added to the anhydrous micelle form the hydration of the sulfonate group and are located between this group and the Na^+ ion, being shared by both ion and head group [16]. The increase in v_0 may be due to a slight increment in the vapor pressure caused by the contribution of water. The activation energy falls due to the mutual repulsion of water and heptane molecules at the surface, caused by the hydrophobic effect. This phenomenon is assisted by the low value of ΔH^0_{tr}.

The three water molecules per AOT molecule added from $R = 3$ to $R = 6$ complete the first hydration shell of the Na^+ ion, and are not shared with the sulfonate group [16]. The properties of these six water molecules are very different from that of pure water [16, 17]. There is no free water [18].

Very pronounced changes occur at this time in the solution. Almost all AOT molecules in the system are inside the micelles, which are strongly favored by the presence of water, whereas at smaller R values some AOT molecules were dissolved in a monomeric form [19]. Micelles undergo a structural change from rodlike to spherical shape [20, 21], which reduces their influence on the properties of heptane. The value of v_0 (0.000053 kg.m^{-2}s^{-1}) is almost equal to the sum of that of pure n-heptane and 0.88 ($= P_w/P_{w,0}$) times that of pure water ($0.000037 + 0.88 \times 0.000010 = 0.000046$). The energy associated with the initial evaporation rate is somewhat larger, probably due to the increase in the ΔH°_{tr} value. This may indicate that the structural change of micelles favors their retention of water. Notice that until the second hydration shell is completed ($R = 12$), $E_{a(v_0)}$ is constant.

There is a gradual change in the characteristics of water in excess of $R = 6$ [16, 18]; it is weakly associated to the micellar interface, whose association becomes weaker as R becomes larger. This produces a gradual rise of v_0, because the molecules of water become less retained by the micelles.

There is some evidence that the water in excess of $R > 12$ behaves similarly to bulk water [16]. However, this similarity is not totally in agreement with pure water, because of the high concentration of Na^+ ions in the water pool. The polarity increases with water addition, but even with high R values, it remains below that of pure water [17]. Simultaneously, the microviscosity of the water core diminishes when R increases [17]. These phenomena cause the rise of v_0, because the extra-water molecules can evade the aqueous pool more easily. The activation energy diminishes, indicating that free water is easier to evaporate.

In conclusion, the initial rate of evaporation depends strongly on the nature of the interactions between water molecules and the AOT micellar surface. The "freer" the water molecules, the easier the initial evaporation. This correlates with other properties found in the literature, such as vapor pressure, polarity and transference enthalpy.

The variation in time of the evaporation rate (K)

The variation in time of the evaporation rate (K) is related to the rate of diffusion of molecules with sufficient energy to evaporate, from the bulk to the surface, where the initial evaporation created a deficit of energetic molecules [14].

The examination of the K value of $R = 0$ and 298.2 K indicates that the reposition of evaporable molecules from bulk of surface is slower in the solution than in pure heptane.

With $R = 3$, an increase is seen in K, which falls to a minimum when $R = 6$, showing that the reposition of evaporating molecules to the surface from the bulk is easier. The increment of R produces a monotonic rise of K up to $R = 12$, when a break occurs with a sharp increase at $R = 14$. These changes may be correlated with structural changes in the solution.

The reduction of K at $R = 0$ may be due to the viscosity increment of the medium, caused by the rigid, anisometric micelles of anhydrous AOT [17, 20]. This may affect the diffusion coefficient of both micelles and solvent molecules.

When water is added, it locates in the inner part of the micelles, because of the extremely low mutual solubility of water and n-heptane. Constantino et al. [22, 23] found that in the system under study, water is carried by diffusion mainly by the inverse micelles, even against its own concentration gradient. Therefore, the increase of K at $R = 3$ may be due to the contribution of the water molecules, which must diffuse from the bulk to the surface inside of the anisometric micelles.

When $R > 3$ micelles undergo a structural change from rodlike to spherical shape, which reduces their influence on the properties of heptane and its diffusion coefficient [21]. Therefore, there is a reduction of K because spherical micelles can diffuse more easily and affect the viscosity of the solution less than the anisometric ones.

When $R > 6$ the micelles become larger and less concentrated (in micelles/volume unit) and both factors negatively affect the – diffusion of micelles from the bulk to the surface, so the value of K increases. When $R > 12$ there is an increase in K, because the increase in size and decrease in concentration of micelles reduces its diffusion rate from bulk to surface.

In conclusion, the easy reposition of molecules from bulk to surface with enough energy to evaporate depends on the size and shape of micelles, factors affecting the diffusion coefficients of both heptane and micelles.

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