

Intermicellar Material Exchange and Droplet Clustering in AOT Reverse Micellar Systems. A Pulse Radiolysis Study of (SCN)₂^{•−} Radical Anion Spectra and Decay

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The recombination of (SCN)₂^{•−} radical anions has been used as an indicator reaction to study material exchange between reverse micelles of AOT in different hydrocarbons. The (SCN)₂^{•−} radical anions were radiolytically produced in the reaction of OH[•] radicals with thiocyanate anions contained in the water droplets. The obtained data, both spectral and kinetic, are discussed in terms of interdroplet and intercluster reactant exchange. The average number of droplets per cluster seems to be significantly greater for AOT reverse micelles in *n*-heptane than in isooctane.

Introduction

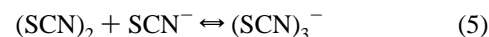
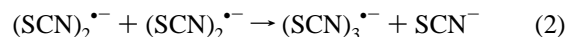
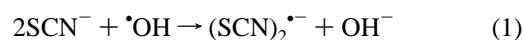
Reverse micelles or microemulsions are ternary and sometimes (when cosurfactant is added) quaternary systems. The external shell of reverse micelles is made up of the hydrocarbon chains of amphiphilic surfactants, while the polar or charged headgroups are directed toward the interior of the aggregate. Such surfactants are able to entrap water to form so-called "water pools" or "water droplets" (radii of about 1.5–10 nm) in hydrocarbon solvent. The molar ratio of water to surfactant, usually denoted as *w*₀, is called the hydration ratio and is primarily responsible for the size of the aggregate.^{1–3} Anionic AOT, sodium bis(ethylhexyl)sulfosuccinate is the most widely used surfactant in the studies of reverse micelles. It has been shown that AOT reverse micelles attract themselves to form clusters at sufficiently high concentration.^{4–8} The individual character of droplets is retained within such clusters.⁹ Very recently Goto et al.¹⁰ have confirmed by visual observations that clusters occur before percolation does.

Although microemulsions are extensively investigated and thus well-known systems, there still exist a number of controversies. Inspection of literature shows that the values of the rate constant, *k*_{ex}, of material exchange in reverse micellar or microemulsion systems range from 1.4 × 10⁷ (Fletcher et al.¹¹) at 25 °C in *n*-heptane as an oil up to 6.9 × 10⁹ M^{−1} s^{−1} (Lang et al.¹²) at 45 °C in *n*-decane as an oil. It seems that the value obtained for *k*_{ex} depends strongly on the experimental conditions (e.g. temperature, *w*₀, oil phase). Sometimes, however, the indicator reaction chosen to probe the material exchange seems to play some role. Almgren's group obtained a first-order rate constant for the exchange on the order of 2 × 10⁵ s^{−1} using feroin or NO₂[−] as excited species quenchers and 2 × 10⁶ s^{−1} with J[−] as a quencher.^{5,14} Different mechanisms for the material exchange between droplets are proposed. One is fusion/fission with temporary merging of micelles which needs the opening of the micellar walls. It has been shown to be rather slow (*k*_{ex} ≅ 10⁷ M^{−1} s^{−1}).¹¹ Much faster exchange might be due to the transport via water channels formed rapidly between colliding micelles or between micelles within a cluster.^{4,13,14}

For several years we have studied such systems by means of pulse radiolysis technique.^{15–17} In this work we have applied the decay of the (SCN)₂^{•−} radical anion to study intermicellar

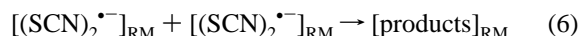
material exchange in AOT (sodium bis[2-ethylhexyl] sulfosuccinate), oil, and water reverse micelles.

It is known that in aqueous solution thiocyanate anion efficiently scavenges OH[•] radicals forming dithiocyanate radical anions according to the simplified scheme¹⁸



The (SCN)₂^{•−} radical anion shows intense absorption peaking at 480 nm with an extinction coefficient $\epsilon \cong 7600 \text{ M}^{-1} \text{ cm}^{-1}$ and thus is easy to follow spectrophotometrically.¹⁹

(SCN)₂^{•−} decays mainly in reaction 2 with a second-order rate constant in water on the order of (2–3) × 10⁹ M^{−1} s^{−1}, slightly dependent on ionic strength.¹⁸ This reaction is fast enough to be used as an indicator reaction to determine interdroplet exchange rates.^{11,20} The formation of this radical anion in reaction 1 is, however, much faster so that it does not interfere with its decay.¹⁸ It is expected that (SCN)₂^{•−}, being negatively charged, is located exclusively in water pools, and its decay in reverse micellar systems should be controlled by the material exchange process according to the scheme



where the subscript RM denotes species entrapped within water droplets.

First we show that (SCN)₂^{•−} radical anions do form in irradiated AOT reverse micelles containing KSCN in proportion to the water content (ranging in our experiments from 1.8 to 18 vol %). This leads to an average occupancy number well below unity. Therefore the intradroplet recombination of these radical anions should be unlikely. Then we discuss the decay of dithiocyanate anion radicals in terms of interdroplet and intercluster material exchange.

Experimental Section

AOT, sodium bis(ethylhexyl) sulfosuccinate (SIGMA), was dried under vacuum over P₂O₅. *n*-Heptane and isooctane (Fluka,

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TABLE 1: Some Relevant Parameters of the AOT Reverse Micellar System in *n*-Heptane

[AOT] ^a (M)	w_0 [water]/[AOT]	[RM] ^b (mM)	water content (vol, %)	water pool radius, ^c (nm)
0.05	20	0.185	1.8	3.50
0.10	20	0.370	3.6	3.50
0.20	20	0.740	7.2	3.50
0.40	20	1.480	14.4	3.50
0.50	20	1.850	18.0	3.50
0.10	10	1.000	1.8	1.75
0.10	20	0.370	3.6	3.50
0.10	40	0.150	7.2	7.00
0.10	50	0.125	9.0	8.75

^a Refers to the volume of oil phase. ^b [RM] = average concentration of reverse micelles calculated using aggregation numbers taken from Lang et al.¹² ^c Calculated using the formula $r_{WP} = 1.5 \times w_0^{1,2,23}$

TABLE 2: Probability, $P(j \geq 2)$, That at Least Two KSCN Molecules Occupy One Droplet as Calculated Assuming Poissonian Distribution; 0.1 M AOT in *n*-heptane, $w_0 = 20$

	[KSCN], M			
	0.01	0.025	0.05	0.1
$P(j \geq 2)$	0.254	0.698	0.953	0.999

puriss) were used as received. Decalin cis-trans (Fluka, purum) was passed through a 1.5 m column of freshly activated silica gel. KSCN (POCh, Poland) was used as received. Water from MilliQ Plus (Millipore) was used throughout.

The pulse radiolysis system at the Institute of Applied Radiation Chemistry has been described elsewhere.^{21,22} Pulses of electrons of 1 μ s from LINAC delivering doses of ca. 240 Gy were utilized.

AOT reverse micelles of desired composition were prepared as follows. The appropriate amounts of water or KSCN solution in water were added into alkane AOT stock solution of desired concentration (usually 0.05–0.5 M). The samples were saturated with N₂O to remove electrons formed in the oil phase upon irradiation. All measurements were carried out at temperature 24 ± 1 °C, i.e., below percolation threshold for all hydrocarbons investigated.

KSCN concentrations are given with respect to water and AOT concentrations with respect to oil phase. The ratio $w_0 = [\text{H}_2\text{O}]/[\text{AOT}]$ does not include very small amounts of water introduced into a system with AOT. Our estimations show that these amounts are well below $w_0 = 1$.

Table 1 includes some useful numbers characterizing the investigated reverse micellar solutions.

Results and Discussion

Absorption Spectra and Yield of (SCN)₂^{•−} Radical Anions.

Assuming Poissonian distribution of KSCN among water droplets,²³ the probability, $P(j \geq 2)$, that two or more thiocyanate molecules occupy one droplet has been calculated. The resulting values for a typical droplet concentration of 3.7×10^{-4} M (aggregation number for 0.1 M AOT in *n*-heptane at $w_0 = 20$ is 270)¹² and different KSCN concentrations in water are given in Table 2. Note that even for [KSCN] = 0.01 M the occupancy of droplets by thiocyanate molecules is high enough for (SCN)₂^{•−} radical anions to be produced in some droplets.

Indeed the characteristic absorption spectra observed after irradiation of reverse micellar systems containing KSCN confirm that radical anions are formed. Figure 1 shows absorption spectra observed after pulse irradiation of AOT reverse micelles at different w_0 and different KSCN concentrations. A well-known spectrum of (SCN)₂^{•−} radical anions, very much the same as observed in bulk water, is seen. The absorbance increases

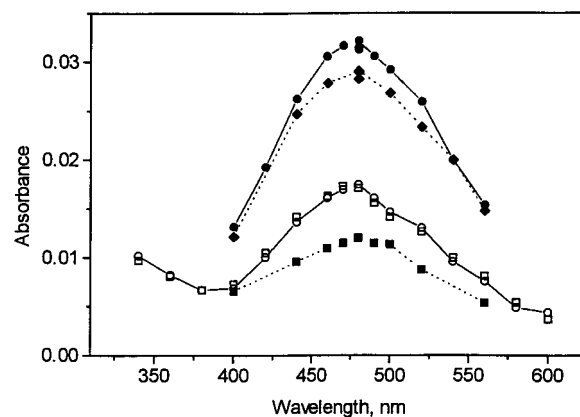


Figure 1. Absorption spectra taken after pulse irradiation of 0.1 M AOT reverse micelles containing 0.025 M KSCN (solid points) or 0.1 M KSCN (hollow squares) at different w_0 : (■) or (□) — $w_0 = 20$, (◆) — $w_0 = 40$, (●) or (○) — $w_0 = 50$.

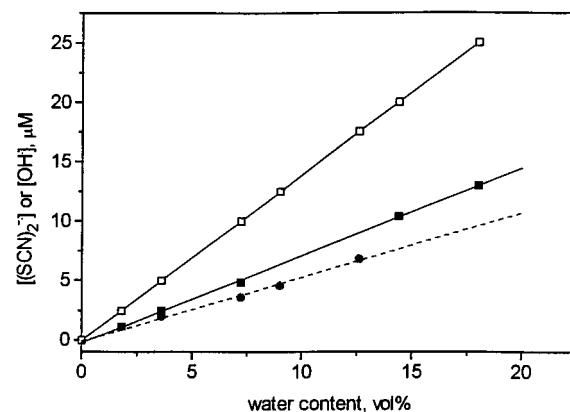


Figure 2. Measured overall concentration of (SCN)₂^{•−} radical anions vs water content in the system for 0.025 M KSCN (●) and for 0.1 M KSCN (■). The yield of OH• radicals in N₂O-saturated solution as calculated from water content is also shown (□).

with increasing w_0 for samples containing 0.025 M KSCN (concentration refers to water) but does not change on going from $w_0 = 20$ to $w_0 = 50$ for samples containing 0.1 M KSCN.

It should be noted here that we observed phase separation in the systems where the concentration of KSCN in water was 0.1 M or higher and w_0 exceeded 20 for [AOT] = 0.1 M. The upper reverse micellar phase was taken for measurements, and the above results show that its properties refer to those of the system at $w_0 = 20$ even if the nominal w_0 value is higher. The excess water forms a lower phase. This corroborates with published data on reduced water uptake by reverse micelles containing electrolytes.²⁴ The whole confirms that pulse radiolysis is a sensitive technique for the study of reverse micellar systems.

We also observed the spectrum of Br₂^{•−} ($\lambda_{\text{max}} = 360$ nm) after irradiation of reverse micelles containing Br[−] (data not shown). However, to obtain an undisturbed spectrum of this species, a correction for the absorption of alkyl radicals was needed, and hence this system was not studied in detail.

Figure 2 shows the initial yield of (SCN)₂^{•−} radical anions (extinction coefficient equal to 7600 M^{−1} cm^{−1} as in bulk water has been assumed)¹⁹ as a function of water content in the system. The latter was changed either by variation of AOT concentration at constant w_0 or by changing w_0 at constant [AOT] (cf. Table 1). The yield of •OH radicals expected from the water content is also shown for comparison. The radiation yield of •OH radicals in water saturated with N₂O is 6.¹⁹ It is seen that this gives the concentration of (SCN)₂^{•−} radical anions about 2-fold

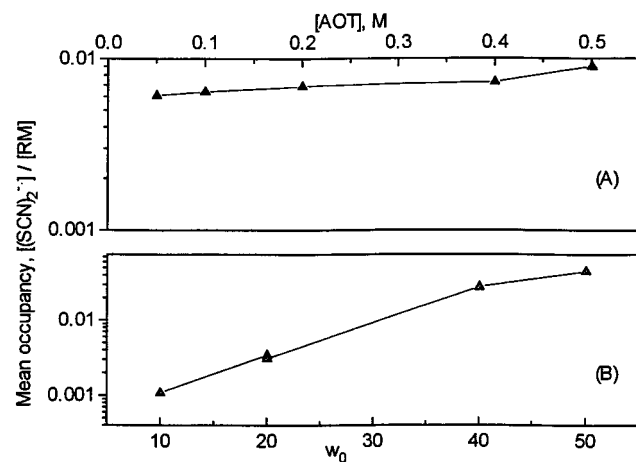


Figure 3. Mean occupancy of droplets by $(\text{SCN})_2^{\bullet-}$ radical anions as calculated from measured overall concentration of radical anions vs $[\text{AOT}]$ (A) and vs w_0 (B). $[\text{RM}]$ taken from Table 1.

higher than observed by us experimentally (Figure 2). The probable reason for this discrepancy is the competition between thiocyanate and AOT toward $\bullet\text{OH}$ radicals as well as toward SCN^\bullet radicals within water pools of reverse micelles. Both competitions would lead to lowering the observed yield of $(\text{SCN})_2^{\bullet-}$ radical anions.

A good linearity observed for both KSCN concentrations shown in Figure 2 allows the conclusion that the competition mentioned above influences the yield of $(\text{SCN})_2^{\bullet-}$ radical anions in proportion to the system composition. Moreover the ratio of the yield of $(\text{SCN})_2^{\bullet-}$ at $[\text{KSCN}] = 0.025 \text{ M}$ to that at $[\text{KSCN}] = 0.1 \text{ M}$ equals the ratio of $P(j \geq 2)$ for these two thiocyanate concentrations. This is nice evidence for a Poissonian distribution of the solute among droplets.

Figure 3 shows the mean occupancy of droplets with $(\text{SCN})_2^{\bullet-}$ radical anions as a function of $[\text{AOT}]$ and w_0 . It is seen that varying AOT concentration does not significantly influence the mean occupancy, while changing w_0 from 10 to 40 increases the mean occupancy by over 2 orders of magnitude. This allows observations of the influence of droplet concentration or of mean occupancy on $(\text{SCN})_2^{\bullet-}$ decay rate. Note the very low values of mean occupancy of droplets by $(\text{SCN})_2^{\bullet-}$ radical anions, implicating that the number of droplets containing two or more radical anions is close to zero.

Decay of $(\text{SCN})_2^{\bullet-}$ Radical Anions. The decay of $(\text{SCN})_2^{\bullet-}$ radical anions in reverse micellar systems appears complex under all conditions studied. A spike is followed by a slower decay, as shown for example in Figure 4A. The decay curve can be fairly well approximated with two parallel, second-order reactions (solid line in Figure 4A) according to the expression:

$$A = A_1/(1 + A_1 2k_1 t/\epsilon) + A_2/(1 + A_2 2k_{\text{ex}} t/\epsilon) + A_n \quad (7)$$

where A is the total absorbance, A_1 the amplitude of the fast decaying component, k_1 the rate constant of the fast decay, A_2 the amplitude of the slow decaying component, k_{ex} the rate constant of the exchange process, ϵ the extinction coefficient of the $(\text{SCN})_2^{\bullet-}$ radical anion, and A_n the infinity level ($=0$ within experimental error). For the long time scale observations (milliseconds), where the fast part of the decay was completed ($A_1 = 0$), we used only the second and third summand in the expression (7) and observed again very good fit (solid line in Figure 4B).

From the spectral analysis we know that observed spectra decay uniformly over the whole spectral range (400–600 nm), implying that we follow solely one species, i.e., the $(\text{SCN})_2^{\bullet-}$

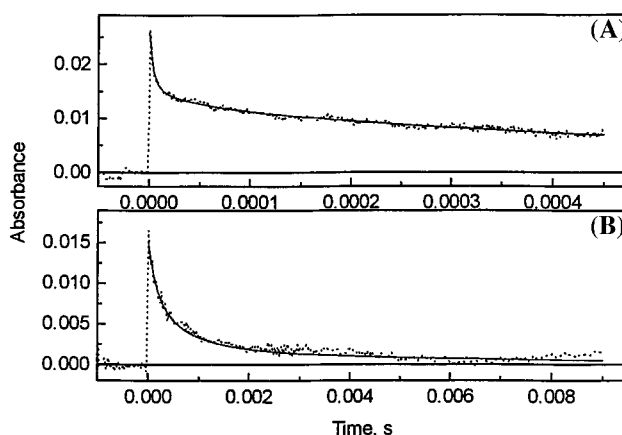


Figure 4. Typical decay curve observed at 480 nm after irradiation of the AOT reverse micellar system containing KSCN: (A) short time scale and (B) long time scale. Solid lines show the fit with eq 7; see text for details.

TABLE 3: Amplitude Ratio, A_1/A_2 , at Different w_0 for Different Hydrocarbons (See Text for Details)

	A_1/A_2		
	$w_0 = 20$	$w_0 = 40$	$w_0 = 50$
<i>n</i> -heptane	0.82	1.20	1.33
isooctane	1.05	1.37	
Decalin	1.24		

radical anion. The rate constant estimated from the fast part of the decay (spike) is higher than $10^{11} \text{ M}^{-1} \text{ s}^{-1}$ and exceeds by far the diffusion-controlled rate constant, k_D , of droplet encounters calculated from the Smoluchowski and Einstein–Stokes relationships:

$$k_D = 8RT/\eta \quad (8)$$

where R is the gas constant, T is the absolute temperature, and η is the solvent viscosity. For *n*-heptane at 25°C η is 3.86 cP^{25} and k_D calculated from eq 8 is $1.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. Thus the fast part of the decay should be ascribed to the reactions taking place within droplets. As the process appears to be second order, the reaction of $(\text{SCN})_2^{\bullet-}$ radical anions with AOT molecules, being in large excess, has to be excluded. One may consider reaction with radicals formed on AOT molecules upon irradiation. It is observed that the A_1/A_2 ratio increases on increasing the w_0 parameter as well as on changing hydrocarbon (Table 3). Indeed both effects would be expected for the reaction with AOT radicals for the following reasons: first, because larger micelles (higher w_0) contain more AOT molecules; second, because our observations in the UV range suggest that with Decalin as an oil phase more radicals are formed upon irradiation, probably due to different structure of the AOT interface.²⁶

The slow part of the decay is most likely connected with reaction 6. The curve approaches zero level, as seen from Figure 4B, which means that any product giving absorption at this wavelength is formed. As the mean occupancy of the droplets by $(\text{SCN})_2^{\bullet-}$ radical anions is very low, the only way for the two species to meet is interdroplet material exchange represented by process (6). The values of the rate constant, k_{ex} , of this process are determined from the best fit as shown in Figure 4.

Figure 5A shows the influence of AOT concentration on k_{ex} . Clearly two regions can be appointed in the *n*-heptane system. For $[\text{AOT}] < 0.2 \text{ M}$ the rate constant is on the order of $0.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, while for $[\text{AOT}] \geq 0.2 \text{ M}$ the k_{ex} drops down 3- to 4-fold to $(0.2\text{--}0.3) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Note that this effect cannot be due to the change in the mean occupancy, as the latter

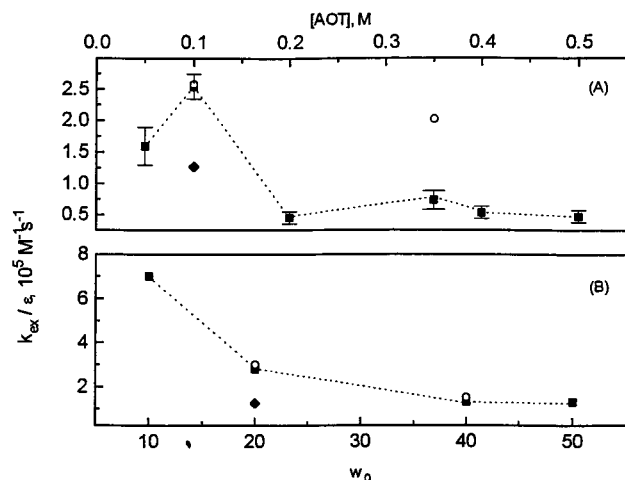


Figure 5. Apparent k_{ex} as a function of AOT concentration at constant $w_0 = 20$ (A) and as a function of w_0 at constant $[AOT] = 0.1$ (B): (■) — *n*-heptane; (○) — isooctane; (◆) Decalin. The error bars, given as an example for one set of data, represent standard deviations from multiple measurements. Bulk water value for the extinction coefficient of the $(\text{SCN})_2^{\bullet-}$ radical anion is $7600 \text{ M}^{-1} \text{ cm}^{-1}$.¹⁹

remains nearly constant while changing $[AOT]$ (cf. Figure 3A). The latter value compares with that given by Mays et al.,^{6,7} Lang et al.,¹² or the Pileni group²⁷ for the same system below percolation threshold.

We postulate that at low AOT concentrations the exchange between individual droplets and at higher AOT concentrations between clusters is observed. In the former case the distance between reactants at the time of collision equals more or less the sum of the radii of two colliding micelles, and a double interface is to be overcome. In the latter case the situation is more complex. An intracluster exchange should be ruled out as the mean occupancy of clusters by $(\text{SCN})_2^{\bullet-}$ radical ions is below 0.1, even for clusters consisting of 10–20 droplets (cf. Figure 3). When two clusters encounter each other, the average distance between two reactants and the number of walls to be overcome depend on the number of droplets in a cluster. An increase of both factors would decrease the rate constant of the exchange. The ratio of the rate constants for interdroplet and for intercluster exchange found for AOT micelles in heptane is around 3 (cf. Figure 5). Johannsson et al. found an average number of droplets per cluster for AOT reverse micelles in dodecane to be 8.4.⁵ Simple geometrical considerations made under assumption that the reactant, $(\text{SCN})_2^{\bullet-}$, is located randomly within the cluster show that 7–9 droplets per cluster is enough to increase the average distance and number of walls between reactants by a factor of 3. It seems clusters in the reverse micellar system AOT/oil/water with heptane as an oil phase consist of a similar number of droplets as in dodecane.

The fact that we observe two discrete k_{ex} values, instead of a monotonic decrease of k_{ex} values with increasing AOT concentration, might suggest that clustering becomes significant above a certain critical surfactant concentration. To derive more convincing conclusions, a detailed study of temperature dependence is needed. In our case, for AOT reverse micelles in *n*-heptane at $w_0 = 20$ the above suggested critical concentration falls in the range between 0.1 and 0.2 M. Note that Manabe et al. have found 0.12 M AOT in dodecane at $w_0 \approx 5$ to be a critical composition above which coagulation of micelles occurs.²⁸

The dependence of k_{ex} on w_0 at $[AOT] = 0.1 \text{ M}$, i.e. in the region where clustering is negligible, shown in Figure 5B can be explained in the same way as above, i.e., in terms of the change of the distance the reactants have to overcome on droplet

encounter. This distance increases with droplet radius, which is proportional to w_0 .^{1–3,23} Indeed a nearly 2-fold decrease of k_{ex} is observed on going from $w_0 = 10$ to $w_0 = 20$ and again a 2-fold decrease on going further up to $w_0 = 40$. A similar drop of k_{ex} with increasing w_0 was observed by Genkin et al. in AOT reverse micelles in heptane and octane.²⁹ The authors have chosen the reaction of disproportionation of 2-antraquinone-sulfonate radical anions as an indicator reaction. It is worth noting that electrical conductivity decreases in a similar way with increasing w_0 at constant volume fraction of the micellar phase.^{30,31} It is suggested this might be due to the increasing hydration of AOT headgroups which, in turn, hinders hopping of AOT anions, and in consequence the formation of water channels is also hindered.^{30,31} Our values for k_{ex} are lower than the diffusion limit by a factor of 10–60. They are, however, too high for the process controlled by merging of droplets, as the latter is reported to proceed with a rate constant of the order on $10^7 \text{ M}^{-1} \text{ s}^{-1}$.^{11,20} It may be thus suggested that the transport of $(\text{SCN})_2^{\bullet-}$ radical ions might be discussed in terms of the motion of these radical anions through water channels, as it is postulated to explain conductivity of microemulsions.^{4,13}

Influence of the Oil Phase. Data obtained for the AOT reverse micellar system in isooctane or Decalin are included in Figure 5A,B besides those for *n*-heptane. Increasing AOT concentration in isooctane from 0.1 M up to 0.35 M decreases k_{ex} by only ~20%, i.e., much less than in *n*-heptane. On the other hand the dependence of k_{ex} on w_0 follows the same pattern as in *n*-heptane. The possible explanation may be quite straightforward. The tendency to form clusters of droplets is different for different hydrocarbons. Johannsson et al.⁵ have reported clusters consisting of 8 or 9 droplets in dodecane and of only 2 or 3 droplets in isooctane. Our results also suggest that clusters of droplets are much smaller in isooctane than in *n*-heptane. It has been shown that properties of reverse micelles depend on the oil phase. The hydrocarbon may influence either the orientation and packing of nonpolar tails of AOT molecules^{26,32,33} (see also below) or charge fluctuations claimed to be responsible for gaining a net charge by reverse micelles.^{34–36} Both effects correlate with intermicellar attractive interactions.

It is worth noting that k_{ex} determined in the AOT reverse micellar system in Decalin is 2-fold lower than in the other two hydrocarbons investigated for the same system composition. This can hardly be explained by the difference in diffusion coefficients. The possible rationalization is as follows, again in terms of the distance and number of walls to be overcome. Decalin, being a double ring hydrocarbon, cannot penetrate the space between the hydrocarbon tails of AOT molecules at the interface. Thus staggering of AOT molecules in the interface is possible,^{26,32} and hence material exchange, whatever its mechanism, becomes more difficult as the “wall” is thicker.

Conclusions

The utilization of pulse radiolysis technique allowed us to work at very low average occupancies of droplets/clusters by the reactant. Therefore we were able to measure the second-order rate constants of material exchange, and the values found by us in the AOT/*n*-heptane system at $w_0 = 20$ are $0.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for $[AOT] = 0.1 \text{ M}$ (interdroplet process) and $(0.2–0.3) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for $[AOT] \geq 0.2 \text{ M}$ (intercluster process).

The number of droplets per cluster in the AOT reverse micellar system in *n*-heptane appears higher (possibly 7–9) than in isooctane (possibly 3 or 4).

The AOT reverse micelles in Decalin seem to have less permeable structure (at least for $(\text{SCN})_2^{\bullet-}$) than in other hydrocarbons studied, which is connected with the influence of this hydrocarbon on the structure of the interface.

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