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Oil-in-Water Microemulsions as Reaction Media

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Fluorescent spectral shifts suggest that oil-in-water microemulsions of cetyltrimethylammonium bromide (CTABr), an alcohol, and a hydrocarbon have polarities, as measured by Kosower's Z scale, similar to those of cationic micelles, and consistently the rates of decarboxylation of 6-nitrobenzisoxazole-3-carboxylate ion are similar in the two sets of aggregates. The spontaneous, water-catalyzed hydrolysis of bis(4-nitrophenyl) carbonate is only slightly slower in the microemulsion than in water, suggesting that water penetrates the microemulsion droplet.

Microemulsions are transparent dispersions of an oil in water (o/w) or water in oil (w/o) in the presence of a surfactant (detergent) and a cosurfactant.[1] In an o/w system the submicroscopic droplets are believed to have oil at their center and are stabilized by a layer of surfactant and cosurfactant. The cosurfactant is typically an alcohol or amine and the surfactant may be ionic or nonionic. Formation of detergentless microemulsions has been reported.[2]

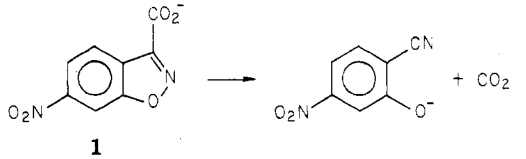
The o/w microemulsions have similarities to normal micelles in water, and w/o microemulsions should be similar to the inverse micelles in apolar solvents. Reactions in micelles have been studied extensively, and large effects on rate and equilibrium constants are often observed,[3] but, although the physical chemistry of microemulsions is well-studied, there are few rate studies.[2,4,5]

Mackay and his co-workers examined dephosphorylation in o/w microemulsions and found that the alcohol cosurfactant is an effective nucleophile at high pH,[5] and reactions of halonitroarenes in similar microemulsions generate ethers and, in some systems, Meisenheimer complexes.[6] These results show that alkoxide is more reactive than hydroxide ion in the microemulsion droplets.

The aim of our work was to obtain evidence regarding the polarities of o/w microemulsion droplets and the availabilities of water in them, and we used the probes which have been applied to aqueous micelles.

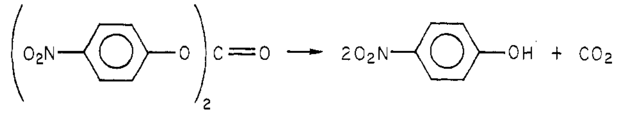
Shifts in charge transfer and fluorescence spectra have been used to estimate the polarities of micellar surfaces, and it was concluded that effective dielectric constants are ~50,[7] and that Z values are ~85,[8] suggesting that micellar surfaces have polarities between those of water and ethanol. We used fluorescence shifts[8,9] to estimate Z values for o/w microemulsions.

Decarboxylation of 6-nitrobenzisoxazole-3-carboxylate (1) is a useful indicator of polarity of reaction medium, and the rate increases as water is replaced by less polar solvents.[10] The reaction is effectively catalyzed by cationic and zwitterionic micelles in water,[11] by cyclodextrins,[12] and by synthetic polymers.[13] The effects can be ascribed to a beneficial effect of decreased hydrogen bonding to the carboxylate ion in 1 and, in some cases, to a favorable interaction between cationic head groups and the transition state.



1

The bimolecular (water-catalyzed) hydrolysis of bis(4-nitrophenyl) carbonate (2) has been used to probe the nature of ionic micelles in water.[14] The rate of this hydrolysis decreases with decreasing water content of aqueous dioxane but is only slightly lower in cationic micelles than in water,[15,16] suggesting that reaction occurs in a water-rich environment. Similar relatively small micellar effects have been observed for rate and equilibrium constants of other reactions of water with organic substrates.[17-19]



2

The effect of microemulsions on hydrolysis of 2 should therefore give evidence for the availability of water in o/w microemulsion droplets, whereas rate constants of decarboxylation of 1, and fluorescence spectral shifts, should not be so directly dependent on water activity, and these indicators should be located at the surface of the droplet.

The structure of the microemulsion droplets has been studied by quasi-elastic light scattering for the CTABr-octane-n-BuOH microemulsions used in some of the present work.[20]

Experimental Section

Materials. Purification of most of the materials has

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TABLE I: Z Values of CTABr Micelles[a]

[NaBr], M	[NaOTos], M	$10^{-3}\bar{\nu}_{max}$, cm^{-1}	Z
		20.75[b,c]	85.5
		20.84	85.0
		20.85[d]	85.0
0.022		20.91	84.5
0.050		20.99	83.5
0.10		21.00	83.5
0.16		21.01	83.5
0.20		21.06	83.0
0.33		21.03	83.5
	0.020	20.99	83.5
	0.035	21.03	83.5
	0.050	21.05	83.0
	0.20	21.12	82.0
	0.30	20.96	84.0

[a] 3×10^{-2} M CTABr unless otherwise specified. [b] 1.5×10^{-3} M CTABr. [c] 1.5×10^{-2} M CTABr. [d] 6.3×10^{-2} M CTABr.

TABLE II: Z Values in Microemulsions[a]

n-BuOH, %	NaBr, wt %	$10^{-3}\bar{\nu}_{max}$, cm^{-1}	Z
20		20.88	84.5
15		20.87	84.5
10		20.82	85.0
14	0.3	20.88	84.5
10	0.3	20.88	84.5
10	0.4	20.95	84.0
5	0.7	20.92	84.5
5	1.0	20.83	85.0
5	1.6	20.88	84.5

[a] Composition of the microemulsions was 2:1:1 (by weight) *n*-BuOH/CTABr/octane.

TABLE III: Decarboxylation in *n*-Butyl Alcohol Microemulsions

type[a]	*n*-BuOH, %	hydrocarbon	NaBr, wt %	NaOTos, wt %	$10^4 k_\psi$, s^{-1}
1	2.6	n-C_8H_{18}		0.8	2.53
1	2.6	n-C_8H_{18}		1.2	2.48
1	4.5	n-C_8H_{18}	1.0		1.58
1	4.7	n-C_8H_{18}	0.5		1.42
1	5.0	n-C_8H_{18}		0.7	1.38
1	8.1	C_6H_6			1.20
1	9.4	n-C_6H_{14}			0.92
1	9.5	n-C_8H_{18}		0.4	0.89
1	19.0	n-C_6H_{14}			0.59
1	23.5	n-C_8H_{18}			0.85
2	2.7	C_6H_6			1.60
3	1.8	C_6H_6			1.86

[a] Types 1–3 are 2:1:1, 1:1:1, and 0.5:1:1 (by weight). BuOH/CTABr/hydrocarbon, respectively.

TABLE IV: Decarboxylation in Cyclohexanol Microemulsions[a]

composition[b]	$C_6H_{11}OH$, wt %	hydrocarbon	$10^4 k_\psi$, s^{-1}
1:3:2	0.96	C_6H_6	2.35
1:2:2	1.2	C_6H_6	2.70
1:1:1	1.3	C_6H_6	1.87
2:1:1	2.3	C_6H_6	1.49
1:1:1	2.5	C_6H_6	1.57
2:2:1	2.6	C_6H_6	1.55
1:1:1	3.4	$C_6H_5CH_3$	1.59
3:1:5:1	15.4	β-pinene	1.60
3:2:1	20.7	C_6H_6	1.73
4:3:1[c]	21.0	C_6H_6	1.66
1:1:1[d]	1.7	C_6H_6	1.26

[a] Unless otherwise specified. [b] Alcohol/CTABr/hydrocarbon, except where specified. [c] Cetylpyridinium chloride. [d] Isoamyl alcohol.

been described.[11] The fluorescent indicator, 1-anilinonaphthalene-8-sulfonic acid (1,8-ANS), was used as its magnesium salt, which was prepared from the sodium salt and was purified by using Norit followed by five recrystallizations from hot water. Only one spot was formed by TLC on Al_2O_3 and silica gel plates. Bis(4-nitrophenyl) carbonate (2) was prepared and purified by standard methods, mp 139–141 °C (lit.[14] 139–141 °C).

Kinetics. Decarboxylation of 1 was followed spectrophotometrically at 410 nm in the presence of 2.5×10^{-3}–4×10^{-3} M Et_3N.[11] Hydrolysis of bis(4-nitrophenyl) carbonate was followed spectrophotometrically at 310 nm in the presence of 3×10^{-3} M HCl.

The first-order rate constants, k_ψ, at 25.0 °C are in units of s^{-1}. Hydrolysis of bis(4-nitrophenyl) carbonate was followed in microemulsions based on *tert*-amyl alcohol. However, *tert*-amyl alcohol is only sparingly soluble in water, so for the comparison reactions in the absence of microemulsions we used mixtures of H_2O and *tert*-butyl alcohol or *tert*-amyl alcohol. (We could not obtain stable microemulsions of octane, *t*-BuOH, and H_2O, but they formed readily with *t*-AmOH.) Hydrogen chloride (3×10^{-3} M) was used to suppress reaction with hydroxide ion.

Fluorescence Spectra. A Perkin-Elmer MPF-3 fluorescence spectrophotometer was used. The excitation wavelength was 380 nm and [1,8-ANS] = 2×10^{-5} M. The fluorescence maxima, $\bar{\nu}_{max}$ (cm^{-1}), vary smoothly with Z for a series of solvents (Table S1; see paragraph at end of text regarding supplementary material).

Results

We tabulate our results in terms of concentration of the components of the microemulsion expressed as weight percent rather than as molarity or mole fraction. In view of the importance of packing of the components in the microemulsion droplet, weight percent (or volume percent) is probably a more realistic measure of concentration than mole fraction (cf. ref 4 and 5). However, in all of our systems, alcohol and hydrocarbon are in molar excess over surfactant.

Fluorescence Spectra in Microemulsions. Values of $\bar{\nu}_{max}$ for various microemulsions are given in Tables I and II. They are insensitive to composition and added NaBr, and Z[21] is in the range 84–85.5; our value of Z for CTABr agrees with an earlier value.[8] The values are very similar to that in CTABr micelles,[8] except that here added salt slightly decreases Z (Table I). This salt effect may be due to a small decrease of water content at the micellar surface, because added anions may reduce interhead group repulsions and so allow the surfactants to come closer in the micelle and therefore expel water from it.[22] The polarity of a microemulsion droplet, as measured by Z, is much higher than that of *n*-BuOH[9,21] (Tables II and S1).

Decarboxylation in Microemulsions. The first-order rate constants, k_ψ, of decarboxylation in microemulsions (Tables III and IV) are similar to those in micellized CTABr,[11] where $k_\psi \approx 3 \times 10^{-4}\ s^{-1}$.

Large changes in the microemulsion composition and addition of salts have relatively small effects upon the rate constants of decarboxylation (Tables III and IV). In particular changes in the hydrocarbon or alcohol have no simple effect upon reaction rate. This pattern of behavior

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[22] See ref 14 and 23 for discussion of water penetration into micelles, and see ref 24 for other views.

TABLE V: Hydrolysis of Bis(4-nitrophenyl) Carbonate in *tert*-Amyl Alcohol Microemulsions[a]

CTABr, wt %	*t*-AmOH, wt %	$10^4 k_\psi$, s^{-1}
10.0	20.0	1.31
10.0	20.0	1.15[b]
13.3	13.3	1.39

[a] 1:1 (w/w) *n*-octane/CTABr. [b] 0.5 wt % NaBr.

TABLE VI: Hydrolysis of Bis(4-nitrophenyl) Carbonate in Alcohol-Water

t-BuOH, wt %	*t*-AmOH, wt %	$10^4 k_\psi$, s^{-1}	*t*-BuOH, wt %	*t*-AmOH wt %	$10^4 k_\psi$, s^{-1}
		4.50[a]	60.0		1.80
	8.0	3.8	90.0		1.00
17.0		3.05		90.0	0.94
37.0		2.21	100		0.073
40.0		1.95[b]			

[a] Reference 16. [b] 0.6 M Et_4NBr.

is very similar to that observed with micelles where micellar catalysis is modestly affected by added salts and by changes in surfactant.[11] This decarboxylation is very sensitive to small changes in the reaction environment.[10]

The value of k_ψ in water is ca. 3×10^{-6} s^{-1} at 25 °C[11] so that the rate enhancements by the microemulsions are by factors of between 20 and 90 (Tables III and IV) and are similar to those found by Kemp and Paul[10] at 30 °C on changing the solvent from water to MeOH (a factor of ca. 30) or EtOH (a factor of ca. 125).

Hydrolysis of Bis(4-Nitrophenyl) Carbonate. The microemulsions slow hydrolysis (Tables V and VI), and inhibition is slightly larger than in cationic micelles. (For substrate fully bound to CTABr, the rate constants, relative to those in water, are 0.6[16] and 0.5[14] at 25 and 50 °C, respectively, and with sodium lauryl sulfate it is 0.1 at 25 °C.)[16]

The rate constants are insensitive to the composition of the microemulsion and are similar to that in 80:20 (w/w) *t*-BuOH/H_2O (Tables V and VI). There are small negative salt effects in both microemulsions and *t*-BuOH–H_2O. (We could not use a wide range of *tert*-amyl alcohol–water mixtures because of the limited miscibility of these solvents.)

Discussion

Comparison of Micelles and Microemulsions. The fluorescence spectral shifts, or the *Z* values (Tables I and II), suggest that micelles and microemulsions have very similar polarities, based on an indicator which should be located near the surface of the aggregate. As noted by Cordes and Gitler, micelles (and proteins) have surface polarities intermediate between those of water and ethanol.[8] These general conclusions are consistent with those based on rate constants of decarboxylation in micelles and microemulsions (Tables III and IV and ref 11).

The slightly greater inhibition of the hydrolysis of bis(4-nitrophenyl) carbonate by microemulsions, as compared with cationic micelles (Tables V and VI), is understandable because the microemulsion droplets should contain large amounts of *tert*-amyl alcohol, whereas water is the only solvent available to penetrate the aqueous micelle.

The various probes may measure different properties of a solvent or aggregate, especially in micelles or microemulsions where solutes have considerable mobility and migrate rapidly between various regions of the aggregate and between it and bulk solvent. For example, a substrate may reside mostly in one region of a droplet but react in another, so that the estimated polarity depends on the rate of movement and of the sensing process, which may be rapid, as in fluorescence, or relatively slow, as in decarboxylation or hydrolysis. In addition, rates of decarboxylation are not related in any simple way to water activity or solvent parameters such as *Z* or E_t.[10] They are very dependent on the hydrogen-binding ability of the medium, and the kinetic solvent effects parallel those on nucleophilicity of the azide ion.

In principle, both fluorescence shifts and rate constants of unimolecular decarboxylation should depend on the polarity of the environment, but the availability of water should be of greater importance in bimolecular, water-catalyzed reactions. The similarity of rate and equilibrium constants of water addition in water and ionic micelles suggests that water activities are not very different in the two media,[14,18,19,23] and this generalization also seems to be correct for o/w microemulsions. Despite differences between these various probes of structure of the aggregates, they all lead to the conclusion that ionic reactions in both micelles and o/w microemulsions occur in an environment whose polarity is lower than that of water, but in which water is available and reactive. At the same time the alcohol in a microemulsion is itself very reactive, as alkoxide ion, at high pH[5,6] so that it appears that the outer region of a microemulsion droplet contains both water and the alcohol cosurfactant and the greater reactivity of alkoxide over hydroxide ion in microemulsions simply reflects the different nucleophilicities of these ions.[25,26]

It does not seem possible to relate directly, in a realistic way, the medium properties of the microemulsion droplet to those of a given mixed solvent. For example, the fluorescence shifts, and *Z*, in a microemulsion are similar to those in 5:95 (v/v) *n*-BuOH/H_2O, although *Z* values are insensitive to solvent composition between 5% and 90% *n*-BuOH (Table S1), but the rates of decarboxylation of **1** in microemulsions are probably similar to those in MeOH or EtOH, and the rates of hydrolyses of **2** in *tert*-amyl alcohol microemulsions are similar to those in a solvent containing relatively little water (Tables V and VI). In part, this behavior stems from the fact that parameters such as *Z* change very sharply at the ends of the water–organic solvent composition scale and slowly in the middle of that scale (cf. Tables S1 and VI and ref 9 and 21). In addition, the various indicators probably probe the properties of different regions of a microemulsion droplet or micelle; e.g., the anions **1** and 1,8-ANS should be close to the cationic head groups, whereas bis(4-nitrophenyl) carbonate could be deeper in the aggregate (cf. ref 7 and 14). So far as we can judge from our spectroscopic and kinetic probes, there are no major changes in the structures of the droplets in the range of concentration used in this work.

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Supplementary Material Available: Table S1 shows solvent effects on fluorescence spectral shifts (1 page). Ordering information is given on any current masthead page.

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