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Reactivity and formulation in microemulsions*

Microemulsions are dispersions of oil in water (O/W) or water in oil (W/O) containing large volumes of the "dispersed" phase (high phase volumes ; e.g. 20–80 %) and relatively large amounts of emulsifier (e.g. 5–50 %). They are characterized by low viscosity, are transparent or slightly translucent, and possess high mechanical (and usually thermodynamic) stability. The emulsifier commonly consists of an ionic or nonionic surfactant and, frequently, a cosurfactant. Although medium chain length alcohols are most often used as cosurfactants, other polar substances have been employed. The phase maps of these systems vary considerably, but many microemulsions have fairly wide compositional ranges of existence. The internal microstructure of all known systems in all parts of their phase diagrams is not completely resolved, but generally consists of microdroplets (aggregates) at low phase volumes and some types of "bicontinuous" region at intermediate phase volumes. Waterless systems are also known which employ polar solvents such as formamide or glycerol in place of the aqueous phase.

The macroscopic physical properties of microemulsions, including their ability to dissolve large amounts of both oil and water soluble solutes coupled with their large internal interfacial area (e.g. 100 m²/g) make them useful media for carrying out chemical reactions of all types (thermal, photo, and electrochemical), with applications to synthesis, decontamination, electrochemical cells, solar energy conversion, drug delivery, and other products of commercial interest. This paper will survey various types of reactions which have been studied in microemulsions, and will focus on a model nucleophilic displacement reaction as a probe of the relationship between formulation (composition and cosurfactant) and reactivity.

Introduction

Microemulsion have attracted a great deal of attention in recent years, stemming from investigations of their potential use for tertiary oil recovery. This interest has arisen because of their fundamentally intriguing properties [1-3] as well as their practical applications to areas such as flavor, pesticide, cleaning oil and wax emulsions, cutting oils, blood substitutes, drug delivery and separations [4-7], as well as solar energy conversion, synthesis, preparation of colloidal catalysts and others [8-10].

There have been many definitions of microemulsions proposed, since there has not been universal agreement on just what constitutes such a system. Therefore, for the purpose of this discussion, a microemulsion will be defined as a clear or translucent, mechanically stable, isotropic fluid of relatively low viscosity which forms spontaneously when two immiscible liquids and one or more amphiphilic components (emulsifier) are mixed. The two immiscible liquids are usually water and an oil, although "waterless" systems in which ethylene glycol, formamide or glycerol replaces the aqueous phase are known [11]. The emulsifier is most frequently a mixture of a surfactant and cosurfactant such as a long chain alcohol, although a number of other polar solvents such as amines and sulfones have been employed [12]. Although the microscopic structure of these microemulsions

have not been fully elucidated, there is general agreement that at least three general structural regimes exist ; nanodroplets of oil in water (O/W) or water in oil (W/O), and a "bicontinuous" region.

Although current definitions generally refer to microemulsions as thermodynamically stable, a number of systems exist in the literature which are called microemulsions and are demonstrably only kinetically stable [13, 14]. Although most systems studied and reported in the literature appear to be thermodynamically stable, they have frequently not been exhaustively examined for this purpose. In any event, they are very definitely mechanically stable, and generally require the input of little or no energy to form, although most are at least gently stirred to speed mixing. Finally, it may be noted that other components may be added in order to achieve the desired phase behavior, and are generally counted as components rather than solutes. Salts such as sodium chloride are frequently used for this purpose.

As the title of this paper implies, the principal interest of the author is in the use of microemulsions as media in which to carry out reactions for many of the applications mentioned above. For this purpose, the great utility of microemulsions is that they can dissolve large quantities of both oil and water soluble solutes, and are generally stable over fairly wide temperature, compositional and pH ranges. In addition, they possess a large internal oil-water interfacial area, on the order of 100 m²/g, at which reaction between oil and water soluble reagents can take place.

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In this paper a number of representative reactions will be surveyed in order to illustrate the properties of the microemulsions which affect the results. No attempt has been made to give a comprehensive review, and most of the systems discussed are from the author's laboratory. The factors linking reactivity patterns for a particular class of reactions with the formulation of the microemulsion in terms of the choice of surfactant and cosurfactant will be discussed.

Properties

Phase Maps

A basic microemulsion system consisting of oil (O), water (W), and a single-component emulsifier (E), can be represented by an isothermal and isobaric triangular phase diagram [15]. In general, however, a triangular slice through a multi-component phase diagram is employed. This is referred to as a phase map, and is illustrated schematically in figure 1. A few typical types of microemulsion regions are illustrated. It should be emphasized that other isotropic and liquid crystalline phases may be present, and that not all of the one phase region contains micellar or microemulsion aggregates. In particular, regions near the E-O axis normally are either molecular dispersions or contain only very small pre-micellar clusters.

A specific example is shown in figure 2 for potassium linoleate/1-alkanol/hexadecane/water systems [16]. Although 1-butanol is used as a cosurfactant in many systems which form microemulsions, the clear, fluid, single phase region here does not contain any aggregates of sufficient size to be distinguishable from a molecular dispersion as evidenced by quasi-elastic light scattering (QLS). Sizeable correlation lengths are obtained from all single phase regions of the 1-pentanol and 1-hexanol systems,

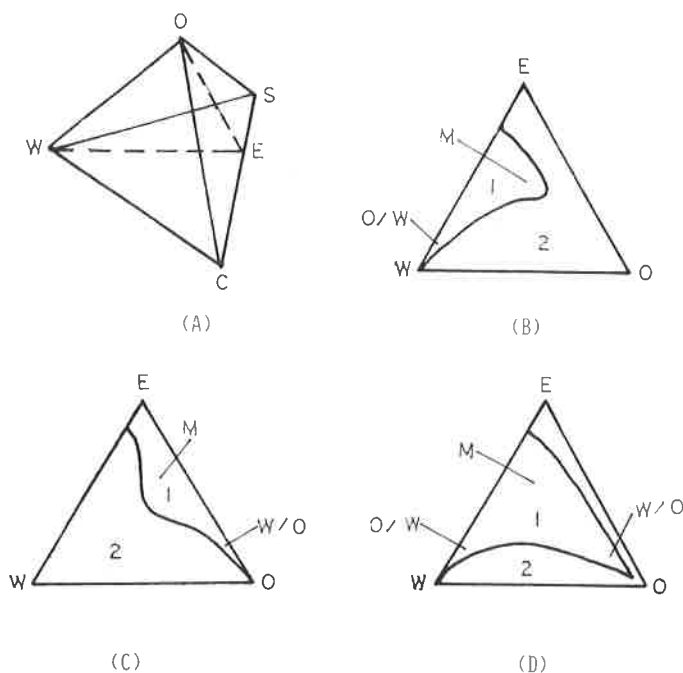


FIGURE 1. - Schematic of four component microemulsion phase diagram (A), where W, O, S, and C are water, oil, surfactant and cosurfactant, respectively. A given ratio of S and C is designated as the emulsifier (E). Figures (B), (C) and (D) are representative phase maps of a WEO slice through the quaternary phase diagram. The symbols O/W, W/O and M refer to oil in water, water in oil, and middle or bicontinuous phases (vide text). The numbers 1 and 2 refer to one and two (or more) phase regions.

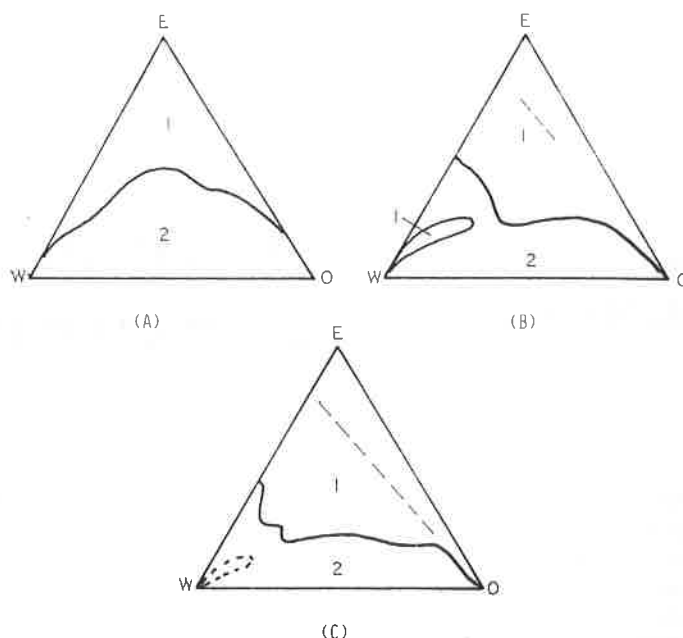


FIGURE 2. - Phase maps of water (W), hexadecane (O), emulsifier (E) systems, where E is a 1:6 mole ratio of potassium linoleate and (A) 1-butanol, (B) 1-pentanol and (C) 1-hexanol. The numbers 1 and 2 refer to single and two (multi) phase regions (vide text).

except for the areas between the dashed line and the E-O axis. These areas yield a flat QLS correlation curve, as does a solution.

Associated water

As stated above, most microemulsions appear to be a thermodynamically stable single phase. They are therefore not emulsions, which are two phase systems. Nonetheless, it is convenient to employ emulsion nomenclature when discussing the internal or microstructure (more properly nanostructure) of microemulsions. Thus, the phase volume (ϕ) in an O/W system refers to the volume fraction occupied by the "oil" droplets. If the cosurfactant solubility in water is low, this would normally consist of the oil, surfactant and cosurfactant, and is designated as the compositional phase volume (ϕ_{comp}). It is calculated by equation (1), where w is the weight fraction water and g is the specific gravity of the microemulsion at that composition.

$$\phi_{\text{comp}} = 1 - wg \quad (1)$$

Similar phase volumes can be defined for W/O and bicontinuous systems. However, not all the water present in a given microemulsion is "free" or bulk water. Part of the water is "bound" water which is associated in some fashion with the "oil" phase. This associated water may consist of primary and secondary water of hydration of the surfactant and cosurfactant as well as some water solubilized in the oil/cosurfactant core. Dielectric dispersion measurements have shown that a significant fraction of water is bound [17].

For example, in microemulsions containing nonionic polyoxyethylene surfactant and alcohol cosurfactant, the bound water averages 2-4 moles of water per mole of ethylene oxide or alcohol hydroxyl group. This has the effect of increasing the effective "oil" phase volume as shown in Table I [18]. Typically, for example, at 60 % water one third is bound or associated. Thus, for $\phi_{\text{comp}} = 0.4$, $\phi' = 0.6$. This bound water has the same static dielectric constant as bulk water, but is motionally restricted. In effect, its viscosity is about six times that of free water. Thus transport properties such as diffusion and ionic conductivity

TABLE I. - *Effective phase volumes*^a.

Comp	Tween 60 ^b	Brij 96 ^b	SCS ^b	CTAB ^b
0.20	–	0.39	0.35	0.34
0.40	0.60	0.61	0.67	0.52
0.60	0.79	0.80	0.80	0.74
0.80	0.94	–	–	0.86

^a Data from ref. [18].

^b Systems employed are Tween 60/1-pentanol/hexadecane ; Brij 96/1-butanol/hexadecane ; sodium cetyl sulfate (SCS)/1-pentanol/heavy mineral oil (Nujol) ; cetyl trimethylammonium bromide (CTAB)/1-butanol/hexadecane. Compositions are given in ref. [18].

are decreased but thermal conductivity remains unaffected. This increased obstruction effect can be quantitatively predicted. For example, the measured conductivity in a microemulsion (σ) may be related to the conductivity in water (σ_0) by equation (2).

$$\sigma/\sigma_0 = (1 - \phi)^{1.5} \quad (2)$$

It may also be noted that this effective phase volume determines the compositional boundary beyond which droplets cannot exist. The phase volume for randomly close-packed spheres is 0.64, which for O/W microemulsions correspond to a water content of about 60 % rather than the lower compositional value of 36 %.

Effect on electrodes

Potentiometric measurements using specific ion electrodes are made in emulsions, most frequently to determine pH or the effective concentration of an added salt. Great caution, however, must be exercised in making such measurements in microemulsions. In the absence of medium effects on the electrode, saturated solutions of a sparingly soluble salt in two different solvents should give identical electrode potentials since they have the same activity. This is clearly not the case, as shown in *Table II*. Since the solubility of a given salt would in general be different in water and microemulsion, salts of different solubility were employed to insure that the salt concentration was not affecting the results. Saturated solutions of BaF₂, PbF₂, and CaF₂ in water are 12, 3.3, and 0.34 mM, respectively. In general, the results are independent of salt concentration of PbF₂, and CaF₂, but begin to deviate for BaF₂ at lower water content. As expected, the difference between water and microemulsion decreases as water content increases. While these data can be used to correct readings in microemulsions so that an aqueous calibration curve can

TABLE II. - *Fluoride ion electrode measurements in a nonionic microemulsion*^a.

wt. % H ₂ O ^b	BaF ₂ ^c	PbF ₂ ^c	CaF ₂ ^c
20	108	119	121
30	85	93	90
40	60	66	64
50	41	45	44
60	24	29	27
70	17	18	18
80	10	11	10

^a Tween 40/1-pentanol/Nujol [19].

^b Water dilutions of an initial composition 93.3 % E, 6.7 % O.

^c Potential difference (mV) between saturated salt solutions in water and microemulsion [20].

be used, the cumulative error (in mV) will be on the order of a 30 % uncertainty in concentration. This is illustrated by the use of fluoride ion electrode measurements to determine phase volume, as shown in *Table III*. The phase volume (ϕ) was determined by using 0.01 M sodium fluoride in water as the aqueous component, correcting the electrode readings using the saturated salt values in *Table II*, and then determining the corrected fluoride ion concentration (F⁻) from an aqueous calibration curve. The value of ϕ is then given by equation (3).

$$(F^-) = 0.01 / (1 - \phi) \quad (3)$$

TABLE III. - *Phase volumes from fluoride ion electrode measurements in microemulsions*^a.

Comp ^b	Uncorr. ^c	Corr. ^c
0.20	0.00	0.10
0.30	0.01	0.31
0.40	0.02	0.53
0.50	0.08	0.70
0.60	0.19	0.78
0.70	0.36	0.89
0.80	0.57	1.16

^a ref. [20].

^b Tween 40/1-pentanol/Nujol (see *Table II*).

^c values given are (1- ϕ) from eqn. (3).

The uncorrected values are also shown for comparison. The values of ϕ determined in this fashion should be in the range $\phi_{\text{comp}} \leq \phi \leq \phi'$. Therefore, while specific ion electrodes can be used to determined analytical concentrations in a microemulsion using a calibration curve in that medium, the readings are too inaccurate to permit their use in phase volume determinations.

Structural probes

Electroactive probes of diffusion

The use of oil and water soluble electroactive species, principally aqueous and organic ions, as diffusional probes in microemulsions has been examined [21]. The overall results of a number of studies are shown schematically in *figure 3*. The diffusion coefficient (D) of aqueous ions which are not bound in either ionic or nonionic microemulsions, behave as predicted by equation (2). They can therefore be used to obtain effective phase volumes. Surfactant-like probes or aqueous ions which are electrostatically bound yield radii (r) via the Einstein equation (4) which have relatively constant values of D and correlate well with values obtained by other methods (*Table IV*).

$$D = kT / 6 \pi \eta r \quad (4)$$

In equation (4), k, T and η are the Boltzman constant, absolute temperature, and continuous phase viscosity, respectively. The surfactant-like probes in nonionic microemulsions yield values of D which decrease with increasing water content, and obey the equations governing percolative behavior [22]. Thus, nonionic O/W droplets undergo "sticky" collisions since there is no electrostatic barrier to retard collisional exchange.

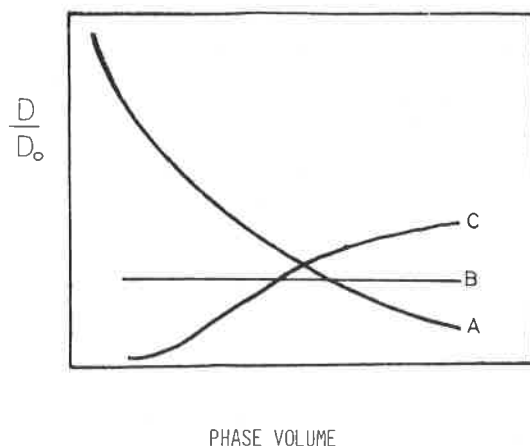


FIGURE 3. - Schematic plot of the ratio of the polarographic diffusion coefficient (D) of an electroactive probe in microemulsion to its value in water vs. phase volume (decreasing water content). Curve A is for a free aqueous ion in ionic or nonionic systems. Curve B is for an interfacially-bound species in an ionic system. Curve C is for a surfactant-like probe in a nonionic system.

TABLE IV. - Comparison of O/W microemulsion droplet diameters^a from electrochemical and other methods.

System (% H ₂ O) ^{b,c}	EC	Other (method)
SCS/PeOH/MO (60)	117	100 (X-ray)
(66)	132	153 (QLS)
SDS/PeOH/DD (70)	82	80 (FC)
(79)	74	74 (FC)
CTAB/BuOH/Oct. (90)		
% NaBr 1.3	204	204
1.5	361	294 (QLS)
1.6	427	427
1.7	587	587

^a Diameter in angstroms. The methods are electrochemical (EC), low angle X-ray (X-ray), quasi-elastic light scattering (QLS), and fluorescence quenching (FC).

^b The surfactants, cosurfactants and oils are sodium cetyl sulfate (SCS), sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB), 1-butanol (BuOH), 1-pentanol (PeOH), heavy mineral oil (MO), dodecane (DD), and octane (Oct).

^c For compositions and data, see ref. [21].

Fluorescent probes of aggregation number and dynamics

The aggregation number of the nanodroplets as well as the binding and dynamics of various solutes, can be determined by means of both static and time resolved quenching of fluorescent probes [23, 24]. The aggregation numbers of a number of microemulsion systems have been examined by this method, including many at this laboratory [25]. All have been systems of high water content, generally > 70 % water and most frequently 90 % water. Aggregation numbers have been measured which range from about 100-500 surfactant molecules per droplet. These include systems composed of cationic and some anionic surfactants, toluene, hexadecane or dodecane as the oil, and a wide variety of cosurfactants including medium chain length alcohols, formamides, and pyrrolidinones. One system which gave an aggregation number of 153 at 90 % water yielded a single expo-

ponential decay at 80 % water. This behavior would be expected if either the aggregates were very large or if there were exchange of fluorescer or quencher between aggregates on a time scale short compared with the fluorescent decay time. Systematic studies are being initiated to examine these effects. In the majority of the above measurements the aggregation number was constant over time. However, in a few cases, the aggregation number did vary with time, although no visible changes occurred in the clear, fluid microemulsion. For example, over a four day period, a CTAB/formamide toluene/90 % water system increased in aggregation number from 133 to 285, while a CTAB/cyclohexylpyrrolidinone/t-butyl toluene/90 % water system decreased from 409 to 141. The latter is indicative of slow microscopic approaches to equilibrium, while the former may be indicative of kinetic stability.

A limited study of the dynamics of methyl viologen, a mobile, water soluble dicationic quencher, was carried out in a SDS (6.65 %)/1-pentanol, (3.2 %) dodecane (0.94 %)/0.1 M NaCl (89.21 %) microemulsion system [26]. The aggregation number of the droplet was determined to be 99, while the binding constant of viologen to the anionic interface was $3.7 \times 10^3 \text{ M}^{-1}$. This corresponds to about 90 % of the viologen bound to the aggregate. The rate constant of $7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for binding indicates diffusion control, while the exit rate constant was $1.8 \times 10^6 \text{ s}^{-1}$. This corresponds to an exit time of about 0.5 μs . These values are in line with those expected based on previous studies [27], and reinforce the idea that microemulsions are generally flexible and dynamic, resembling more closely surfactant micelles rather than vesicles or bilayers.

Reactions

As mentioned in the introduction, the principal focus of the author's work and interest lies in the use of microemulsions as reaction media. In this section a few representative types of reactions will be surveyed which illustrate the important structural, and thus formulation, aspects of microemulsions which affect the course and rates of the reactions. The great utility of microemulsions as solvents for chemical reactions lies in their ability to solubilize polar and non-polar substances and to compartmentalize and concentrate reagents.

Alkylation

A color reaction for the detection of alkylating agents such as alkyl halides (RX) provides a good example of the microemulsion properties which can be utilized for reaction control. The oil

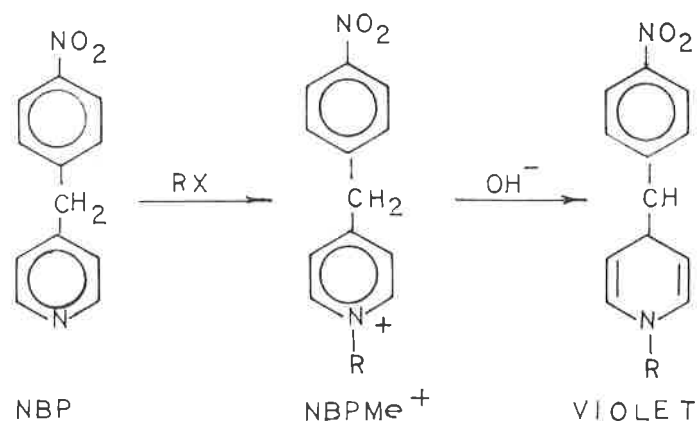


FIGURE 4. - Scheme for the reaction of *p*-nitrobenzylpyridine (NBP) with alkylhalide (RX) and hydroxide ion to form a violet product.

soluble compound *p*-nitrobenzyl pyridine (NBP) reacts with RX and base to produce a violet colored product as shown in *figure 4*. A non-aqueous solvent must be employed to dissolve the NBP and the RX, and then this solution treated with aqueous base, a two-step procedure. The NBP and base cannot be combined as a single reagent because they slowly react to form an interfering blue color. However, use of an anionic microemulsion permits the combination of both reagents in the same solution, as shown in *Table V*. The addition of silver was required to effect the alkylation by methyl iodide. The mechanistic interpretation of the results in *Table V* is as follows : the NBP is solubilized in the oil phase and exposed to only a very low hydroxide ion concentration since OH⁻ is electrostatically repelled by the anionic interface ; added methyl iodide, aided by silver ion which is concentrated at the negative interface, reacts with the NBP to form the *p*-nitrobenzyl-1-methyl pyridinium ion (NBPM^{e+}) ; this ion, being more water soluble, is then accessible to attack by hydroxide to form the final violet product. It is also interesting to note that both silver and hydroxide ions (AgNO₃ and NaOH) were stable in the microemulsion at concentrations which in aqueous solution result in the precipitation of hydrated silver oxide. Therefore, due to the concentration of Ag⁺ and OH⁻ in different regions of the microemulsion, the solubility product of silver hydroxide was never exceeded.

TABLE V. - Alkylation of *p*-nitrobenzylpyridine in microemulsions^a.

System	NBP	OH ⁻	NBPM _e I	CH ₃ I	Ag ⁺	Result
cationic ^b	X	X				blue color
anionic ^c	X	X				no reaction
	X	X		X		no reaction
		X	X			violet color
	X	X			X	no reaction
	X	X		X	X	violet color

^a The X's represent the reagents combined to yield the stated result.

^b CTAB/1-butanol/hexadecane/water (60 %)^d.

^c SCS/1-pentanol/nujol/water (60 %)^d.

^d Compositions described *in ref.* [16].

Photogalvanic cells

Microemulsions have been studied as solvents for the classic iron-thionine system in totally illuminated thin layer cells [28]. A long alkyl chain thionine derivative was found to be more efficient than thionine itself, even in aqueous solution. Compared with water, the power generated was lowest in cationic microemulsion and highest in anionic microemulsion. A significant effect of the anionic systems was to promote an essentially 100 % efficient reduction of thionine by iron (II) due to concentration of reagents at the negative aggregate interface [29]. Another factor which contributed to the increased cell power was the effect of the microemulsion on thionine aggregation. The thionine dye begins to self-associate in water at micromolar concentrations, and aggregated dye is not photoactive. In microemulsion, association does not begin until millimolar dye concentrations. This is on the order of the concentration of nanodroplets. Finally, it may be noted that rhodamine 6G, a highly fluorescent dye which absorbs at higher energy than does thionine, very effectively transfers energy by the Forster mechanism to the thionine in microemulsion and results in a doubling of the solar efficiency of the cell [30]. Although this effect is also observed in aqueous solution, the high efficiency is likely due to the cosolubilization and concentration of the two dyes in the microemulsion interfacial volume.

Nucleophilic displacement

Many studies have been carried out on the effect of both micellar solutions [31] and microemulsions on reactions between oil soluble electrophiles and aqueous nucleophiles, particularly hydroxide. We have conducted a large number of studies of the reactions of phosphate esters with hydroxide and fluoride ; in particular, the reaction of *p*-nitrophenyl diphenyl phosphate with hydroxide ion in cationic microemulsions [32-36]. From the results of all of these studies, the following conclusions may be drawn : there is no effect of ionic strength on the reaction up to added electrolyte concentrations of 0.5 M, a clear indication that the reaction takes place in the microemulsion interphase region or "stern layer" where the effective ionic strength is on the order of 3 M ; the intrinsic rate constants in microemulsions and comparable micelles are essentially the same, the observed rate constant being higher in micelles due to their greater surface potentials ; the principal effect of ionic microemulsions on the rate constant, as opposed to comparable nonionic microemulsions, is due to effective surface potential which may be calculated from the ratio of these two rate constants (*vide infra*) ; the rate constant, corrected for the effect of phase volume on aqueous nucleophile concentration, does not vary with phase volume along a water dilution line for nonionic microemulsions, but increases with increasing water content for cationic microemulsions ; this effect is attributed to the increasing degree of surfactant counterion dissociation, and thus an increasing water content ; the kinetic data have been shown to be consistent with the ion-exchange model [37-38], but a definitive test compared with the effective surface potential model remains to be carried out. It may well be that both models have their range of validity depending upon the average location of the species being attacked by the aqueous nucleophilic ion [38].

Novel cosurfactants

Most of the phosphate ester hydrolysis reaction described above were carried out in microemulsions stabilized by a cationic surfactant, usually CTAB and a medium chain length alcohol such as 1-butanol. While these systems were very useful for basic studies, they lack a number of desirable characteristics for practical applications. While the rate constants are reasonable, we wish to achieve even faster rates. In addition, microemulsion systems with a wider composition range of existence are needed, along with more suitable chemical properties. These chemical properties include resistance to strong oxidants, the ability to penetrate and dissolve polymeric materials, and environmentally acceptable components. While, as mentioned above, other cosurfactant such as amines and sulfones have been employed, all failed to meet one or more of the desired characteristics. We were therefore led to examine new materials which include formamides, pyrrolidinones, and tetraalkylammonium halides, principally Adogen 464 (Sherex Chemical Co.). The latter is tri (octyl-decyl) methyl ammonium chloride [36]. The results of these studies with regard to effect on the rate constant are summarized in *figure 5*. All of these curves are for the reaction of *p*-nitrophenyldiphenyl phosphate with hydroxide, catalyzed by iodosobenzoate, in CTAB or CTAC microemulsions. The same general features described in the section above with regard to a constant value of the phase volume corrected rate constant for nonionic systems and increasing values with increasing water content for cationic systems are observed here as well. As would be expected, the systems with Adogen 464 as cosurfactant yields fast rates since all of a nonionic cosurfactant has been replaced with a cationic one. It is very interesting to note, however, that the more polar dibutyl formamide cosurfactant yields higher rate constants than 1-butanol, and the 1-methyl-2-pyrrolidinone has values comparable to that of Adogen 464. This cannot be a solvent polarity effect, since the rate constant should decrease as the solvent polarity increases. The methyl pyrrolidinone has a large dipole moment

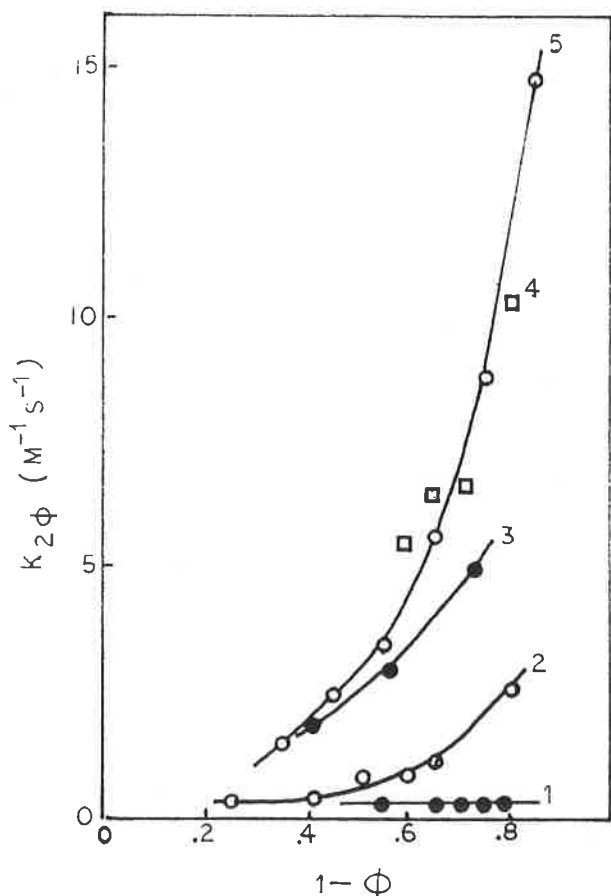


FIGURE 5. - Phase volume corrected rate constant ($k_2\phi$) vs. water content ($1-\phi$) for the IBA catalyzed hydrolysis of *p*-nitrophenyl diphenyl phosphate in microemulsion. Curve 1, Brij 96/BuOH; curve 2, CTAB/BuOH; curve 3, CTAC/DBF; curve 4 (squares), CTAB/MP; curve 5 CTAC/Adogen 464 (vide text).

(4.09 D), and as with dibutyl formamide, the zwitterionic resonance form makes a significant contribution. However, other studies in our laboratory show that these solvents are not taking part directly in the reaction. It therefore seems likely that they are significantly increasing the degree of surfactant counterion dissociation, the pyrrolidinone more than the formamide. It may well be that their miscibility with both oil and water, as well as their polarity, is responsible for this effect. Additional support for this hypothesis is provided by rate constants obtained from a CTAB/toluene microemulsion using a variety of pyrrolidinones, from cyclohexyl to methyl, which generally increased with increasing cosurfactant polarity [39]. It is instructive to compare the values of the effective surface potentials obtained from the rate constants. As mentioned in the preceding section, the non-ionic and ionic second order rate constants (k_2) must either be compared at the same phase volume or the rate constants corrected by multiplying by $(1-\phi)$. These are designated as $k_2\phi$. The effective surface potential (ψ) is then determined by equation (5).

$$k_2 \text{ (ionic)}/k_2 \text{ (nonionic)} = \exp(\psi/kT) \quad (5)$$

The values of ψ obtained from the data in figure 5 are given in Table VI. Although it is certainly not proof of the correctness of the method, it is encouraging to note that the magnitude of the numbers are reasonable. The fact that the same values of ψ are obtained from different nucleophiles would tend to indicate that the effective surface potential model is operative here, unless both hydroxide and iodosobenzoate had similar ion exchange constants. Finally, it may be noted that a few survey studies on the use of double tailed surfactants in place of CTAB, and the use of short-medium chain length tetraalkylammonium chloride

TABLE VI. - Effective surface potentials^a.

System ^b	Nucleophile ^c	0.40 ^d	0.75 ^d
CTAB/BuOH	OH ⁻	38	50
	IBA ⁻	33	52
CTAC/DBF	IBA ⁻	72	83
	IBA ⁻	73	91
CTAB/MP	OH ⁻	81	-
	IBA ⁻	87	97

^a Calculated from equation (5). The nonionic system was Brij 96/BuOH.

^b The microemulsion systems are those shown in figure 5.

^c Using data from the reaction of *p*-nitrophenyldiphenyl phosphate with iodosobenzoate ion (IBA⁻, figure 5) or hydroxide ion (OH⁻).

^d Values of ψ in mV at compositional phase volumes of 0.40 and 0.75. A value of 130 mv was obtained for CTAB micelles.

salts as cosurfactant supplements, have been conducted [40]. The results indicate that while double-tailed surfactants fail to give microemulsions, the tetraalkyl ammonium chlorides do form microemulsions which give rate constants comparable to those with Adogen 464.

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Role of Surfactants and Polymers in Disperse Systems *

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Surfactants and polymers are commonly used in the preparation of disperse systems e.g. suspensions, emulsions and microemulsions, and their subsequent stabilisation. This occurs in many industrial applications of which one may mention paints, dyestuffs, cosmetics, agrochemicals, pharmaceuticals, paper coatings, ceramics and polymer colloids. Surfactants and polymers are used in preparation of solid/liquid dispersions either by condensation or comminution methods. In condensation methods surfactants and polymers control the nucleation and growth of particles. This is particularly the case for the preparation of polymer suspensions by emulsion or dispersion polymerisation. With emulsion polymerisation, surfactants and polymers are used for preparation of monomer emulsions which are then polymerised by addition of an initiator. With dispersion polymerisation, the monomer is dissolved in a solvent to which an initiator and a protective agent is added. The protective agents usually consists of a block or graft copolymer that consists of two main chains : an anchoring chain to the particle surface and a stabilising chain that is well solvated by the medium. In dispersion (comminution) methods a surfactant or polymer is added to facilitate wetting of the powder by the liquid ; breaking of aggregates and agglomerates and comminution of the particles. By adsorption at the particle surface and within cracks, the comminution of particles is facilitated.

Surfactants and polymers also are added for emulsification of oil into water or water into oil. The role of the surfactant and/or polymer is several fold. By adsorption at the liquid-liquid interface, the interfacial tension γ is reduced and hence the energy required for creating a new surface is reduced. On the other hand, by creating an interfacial tension gradient ($d\gamma/dA$), i.e. Gibbs elasticity, film thinning and rupture is reduced, thus reducing coalescence. Finally, the adsorbed surfactant or polymer will provide an energy barrier that reduces close approach of the particles, thus preventing flocculation and coalescence.

Various types of interaction forces may be envisaged when surfactants and polymers are added to dispersions. With ionic surfactants, a double layer is produced which produces strong repulsion on close approach of the particles or droplets. This double layer repulsion counteracts the Van der Waals attraction, thus ensuring colloid stability. With nonionic surfactants and polymers, repulsion occurs as a result of steric interaction between the adsorbed layer. This steric interaction consists of two main contributions : mixing or osmotic and entropic, elastic or volume restriction interaction. As long as the chains are in good solvent conditions, steric repulsion may produce dispersion that approach thermodynamic stability.

Surfactants are also used for preparation of microemulsions. These are clear isotropic thermodynamically stable systems where specific interactions should occur at the interface resulting in ultra-low interfacial tension. In this case, the positive energy of expanding the interface is compensated by the entropy of dispersion and the net free energy of formation of the microemulsion is zero or negative. Both ionic and nonionic surfactants can be used for preparation of microemulsions and in all cases a system has to be chosen that produces

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