Proton Magnetic Resonance Investigations of Nonionic Polyoxyethylene Nonylphenol Surfactant Aggregates in Nonpolar Solvents [1]

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^{1}H n.m.r. chemical shifts of polyoxyethylene(1.5) nonylphenol (Igepal CO–210); polyoxyethylene (4) nonylphenol (Igepal CO–430); polyoxyethylene(5) nonylphenol (Igepal CO–520); polyoxyethylene(6) nonylphenol (Igepal CO–530); polyoxyethylene(9) nonylphenol (Igepal CO–630); polyoxyethylene(10-11) nonylphenol (Igepal CO–710); and polyoxyethylene(15) nonylphenol (Igepal CO–730) in CDCl$_3$ and those of Igepal CO–530 in CH$_2$Cl$_2$, CCl$_4$, C$_6$H$_6$ and C$_6$D$_{12}$ have been determined as functions of the stoichiometric surfactant concentration. The data are best fitted in terms of a monomer $\overset{K_2}{\rightleftharpoons}$ dimer $\overset{K_3}{\rightleftharpoons}$ trimer ... $\overset{K_i}{\rightleftharpoons}$ *i*-mer type association, assuming $K_1 = K_2 = K_3 \ldots = K_i$. Based on this model percentages of dimers, trimers and of higher aggregates have been calculated at several stoichiometric surfactant concentrations. Percentages of monomers decrease at the expense of predominantly dimers and of small amounts of trimers and higher aggregates with increasing concentrations of surfactant. In CDCl$_3$ the association is most prominent for Igepal CO–710. Aggregation is considerably more pronounced in C$_6$H$_6$ and C$_6$D$_{12}$ than in CDCl$_3$, CH$_2$Cl$_2$ or CCl$_4$. Addition of water hinders the dimerization. Structures of the aggregates are discussed.

The observed rate enhancements of inorganic and organic reactions by surfactant aggregates in nonpolar solvents [2-8] have prompted our structural investigations of alkylammonium carboxylates in nonaqueous solvents.[9-11] Chemical shifts of the magnetically discrete surfactant protons have been determined at different stoichiometric surfactant concentrations, C_D, in CDCl$_3$, CH$_2$Cl$_2$, C$_6$H$_5$Cl, C$_6$H$_6$ and DMAC.[9-11] The data have been rationalized by assuming that the monomeric surfactants are in equilibrium with the reversed micelles. In spite of the apparent internal consistency of the aggregation parameters obtained for alkylammonium carboxylates in nonpolar solvents several facts could not be readily reconciled with the proposed monomer $\rightleftharpoons$ n-mer association model. Particularly disconcerting has been the observation of only small aggregates, with $n = 3$-7, and the dependence of the aggregation numbers on experimental conditions. For aggregates containing such few monomers plots of the ^{1}H n.m.r. chemical shifts against surfactant concentration are expected to be curvilinear rather than two straight lines with an intersection. These contradictions are circumvented if the association of surfactants are assumed to be sequential. Indeed Muller has demonstrated that the observed concentration dependence of the ^{1}H n.m.r. chemical shifts for alkylammonium carboxylates in benzene [9-11] fits equally well either a single or a multiple equilibrium model.[12]

Since nonionic polyoxyethylenes also affect the rates of reactions in nonaqueous solvents [3, 8] we have investigated their ^{1}H n.m.r. behaviour in CDCl$_3$, C$_6$H$_6$, CH$_2$Cl$_2$, C$_6$D$_{12}$ and CCl$_4$. The chemical shifts of the magnetically discrete sufractant protons, as a function of the stoichiometric surfactant concentration, have been treated in terms of multiple equilibrium models.

EXPERIMENTAL

Polyoxyethylene(1.5) nonylphenol (Igepal CO–210), polyoxyethylene(4) nonylphenol (Igepal CO–430), polyoxyethylene(5) monylphenol (Igepal CO–520), polyoxyethylene(6) nonylphenol (Igepal CO–530), polyoxyethylene(9) nonylphenol (Igepal CO–630), polyoxyethylene(10-11) nonylphenol (Igepal CO–710) and polyoxyethylene(15) nonylphenol (Igepal CO–730), were used as received from General Anilin and Film Corporation. These surfactants are not completely homodispersed; the number of predominant ethylene oxide units in the surfactants are indicated by the CO-number. Reagent grade deuterochloroform (Merck, 99.8 % D.), methylene chloride, (Fisher Scientific), carbon tetrachloride (Fisher Scientific), deuterocyclohexane (Merck 99.5 % D.) and benzene (Fisher Scientific) were dried by and stored over Linde Type 4A molecular sieve. Since solubilized water significantly affects the results, special care was taken to exclude moisture during the preparation of stock solutions. The water content of the organic solvents was determined, and monitored for each set of experiments by gas–liquid–partition chromatography. A Hewlett–Packard 7620A gas chromatograph, equipped with a three feet long one-eighth inch i.d. stainless steel Porapak Q (Waters Associates) column, was used. The temperature of the column was maintained isothermally at 100 °C, that of the injection block and the detector at 200 °C; helium was used as a carrier and its flow rate was 45 cm^3 min^{-1}.

The ^{1}H nuclear magnetic resonance spectra were obtained on a modified Varian Associates HA–100 spectrometer with a Hewlett–Packard Model 200 ABR audio oscillator and frequency counter. All spectra were determined at ambient probe temperature (~ 34 °C) on freshly prepared solutions in the organic solvents and were measured relative to neat tetramethylsilane (TMS) contained in a Wilmad 520-2 internal coaxial capillary tube. A downfield chemical shift difference of 47.5 Hz (at 100 MHz) was observed for the chloroform signal (10 % v/v in CCl$_4$) between " external " neat TMS in the coaxial tube and " internal " 10 volume % TMS in the same solution. Chemical shifts were obtained from spectra recorded at 500 or 1000 Hz sweep widths and are given on the δ scale in p.p.m. ($\delta_{TMS} = 0$ p.p.m.) relative to the " external " TMS. Individual measurements are accurate to ± 0.002 p.p.m. The resonance frequency of the discernible solvent protons relative to the standard exhibited a negligible shift over the surfactant concentration ranges employed and consequently bulk susceptibility corrections were not applied. However, they are predictably small and would not affect the obtained results appreciably.

Curve fitting of the experimental data to the appropriate equations was carried out on an IBM 360 computer.

## RESULTS AND DISCUSSION

PROTON N.M.R. SPECTRA

^{1}H n.m.r. chemical shifts of polyoxyethylene(6) nonylphenol in CH$_2$Cl$_2$, CCl$_4$, C$_6$H$_6$ and C$_6$D$_{12}$ are given in table 1, while table 2 lists the chemical shifts of polyoxyethylene(x) nonylphenols in CDCl$_3$. Resonance frequencies of the magnetically discrete surfactant protons in solution, just as in the case of alkylammonium carboxylates,[9-11] consist of simple weight-averaged resonances for protons in the monomeric and aggregate forms of the polyoxyethylene nonylphenols. Aggregation, therefore, is rapid on the n.m.r. time scale. Spectra of Igepal CO–(210, 430, 520, 530, 630, 710 and 730) in CDCl$_3$, and that of Igepal CO–530 in CH$_2$Cl$_2$ and CCl$_4$ show similar features. Fig. 1 illustrates a typical ^{1}H n.m.r. spectra. Resonances due to the aromatic protons (F) are at 7.0-8.0 p.p.m., those to the ethylene oxide units (C, D and E) are at 4.0-5.0 p.p.m. and those to the methylene groups of the alkyl chain (A and B) are at 1.5-2.0 p.p.m. (see fig. 1). These assignments are based on considerations of electron shielding effects [13, 14] and on available data for neat p-tert-octylphenoxy(polyethoxy)ethanols, Triton X-100, Triton X-102 and Triton X-305, and alkylpolyoxyethyleneglycol monoethers.[15] The protons on the aromatic ring show a well-resolved doublet centred at 7.342 p.p.m. and a partially resolved

doublet, centred at 7.720 p.p.m. Resonance frequencies due to the ethylene oxides consist of a large unresolved signal (C) and two smaller multiplets (D and E) which, with the exception in benzene, are at lower field than those due to C. Integration of these chemical shifts for neat Igepal CO–530 establishes the number of protons to be 2, 2 and 20 for E, D and C respectively. The lower field resonance frequencies (E and D) are assigned to the protons nearest to the aromatic nucleus, and those at higher field (C) correspond to the main ethoxy units. These assignments are based on the expected magnetic anisotropy effect of the aromatic nucleus and are substantiated by measurements on Triton X surfactants.[15] Integration of the areas under the resonance signals due to the alkyl chain as well as their chemical shifts establish the unresolved multiplets at higher field to be A and those at lower field to be B (fig. 1).

TABLE 1.—^{1}H N.M.R. CHEMICAL SHIFTS OF POLYOXYETHYLENE(6) NONYLPHENOL

solvent		0.10	0.20	0.30	[Igepal CO–530]/mol dm^{-3} 0.40	0.50	0.60	0.70	0.80
CH$_2$Cl$_2$	δ_B	1.782	1.778	1.771	1.765	1.765	1.765	1.749	1.745
	δ_C	4.108	4.102	4.096	1.089	4.084	4.079	4.069	4.063
	δ_D								
	δ_E								
	δ_F	7.368	7.364	7.358	7.352	7.352	7.347	7.336	7.332
CCl$_4$	δ_A	1.284				1.277			
	δ_C	4.012	4.004	4.000	3.994	3.993	3.985	3.985	3.976
	δ_D	4.204				4.196			
	δ_E	4.482				4.472			
C$_6$H$_6$ ^{a}	δ_B	1.039	1.043	1.046	1.045	1.047	1.050	1.054	1.057
	δ_C	3.266	3.270	3.274	3.276	3.279	3.282	3.282	3.287
	δ_D	3.151	3.156	3.162	3.165	3.172	3.177	3.181	3.184
	δ_E	3.207	3.213	3.218	3.222	3.226	3.230	3.231	3.237
C$_6$D$_{12}$ ^{a}	δ_A				0.977	0.974	0.974		0.972
	δ_B		1.446	1.448	1.447	1.448	1.449		1.448
	δ_C	3.725	3.726	3.727	3.727	3.728	3.728		3.730
	δ_D		3.921	3.923	3.923	3.928	3.928		3.930
	δ_E		4.190	4.196	4.195	4.197	4.197		4.199
	δ_F	6.962	6.970	6.971	6.972	6.977	6.976		6.978

^{a} surfactant concentrations are a factor of ten smaller than those indicated
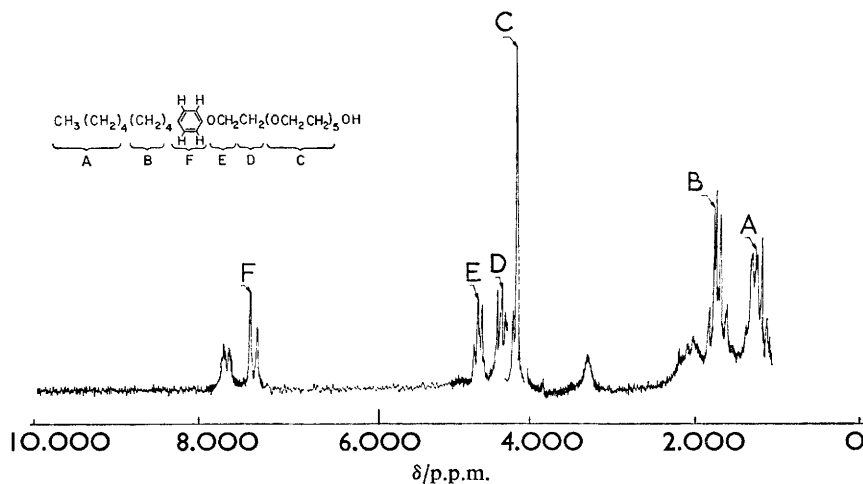
FIG. 1.—^{1}H n.m.r. spectra of 0.3 mol dm^{-3} Igepal CO–530 in CDCl$_3$.

CHEMICAL SHIFTS AS A FUNCTION OF CONCENTRATION

[1]H n.m.r. chemical shifts of polyoxyethylene nonylphenols as functions of their stoichiometric concentrations, C_D, are given in tables 1 and 2. It is seen that increasing the stoichiometric surfactant concentrations results in upfield shifts of the magnetically discrete protons in $CDCl_3$, CH_2Cl_2 and CCl_4. In benzene, surfactant proton resonances shift, however, to lower magnetic field strength as a consequence of shielding by the high electron density solvent. Chemical shifts of alkylammonium carboxylate protons behave analogously.[10-11] Magnitudes of given chemical shifts in the ranges of polyoxyethylene nonylphenol concentrations investigated are considerably smaller than those observed for the cationic surfactants.[10-11]

Values of the monomeric chemical shifts of the magnetically discrete surfactant protons, δ_m, are easily obtained from linear extrapolations of δ-values, determined at low surfactant concentrations, to $C_D = 0$. The error in these extrapolations and hence in δ_m is expected to be small. Values of the micellar shifts of the magnetically discrete protons, δ_M, are, however, more difficult to evaluate. At high surfactant concentrations, if $[S_1]$ remains essentially constant for moderate changes of C_D, δ becomes a linear function of $1/C_D$ approaching δ_M at $1/C_D = 0$. However, plots of δ against $1/C_D$ are not strictly linear, particularly when small aggregates are present.[16]

Additionally viscosity effects at high surfactant concentrations introduce errors in the chemical shift measurements. Consequently, chemical shift determinations were limited to 0.8 mol dm^{-3} stoichiometric surfactants. δ_M values were obtained from the intercepts of the best computer fit of the data in terms of second degree polynomials.[17] Values for δ_m and δ_M are given in table 3.

Values for δ_m and δ_M could not be correlated with any microscopic solvent polarity parameters. Values of δ_m and δ_M are in the order $CDCl_3 > CH_2Cl_2 > CCl_4$ conceivably reflecting that structural changes of these aggregates do not follow solvent polarities in a straightforward manner. Significantly, however, for all the protons observed, solvent effects are greater for δ_m than for δ_M. For the monomeric surfactants, as expected, the most pronounced solvent effects are on protons associated with the ethylene oxide units. Proton donation and hydrogen bonding clearly predominate at the hydrophilic polyoxyethylenes. Interactions between the solvent and monomeric surfactants are overcome by association between surfactants with the resultant partial exclusion of solvent molecules.

Interaction of the solvent with monomeric polyoxyethylene nonylphenols can also be assessed from δ_m values of the magnetically discrete protons as functions of the ethylene oxide chain lengths, X, (table 3). The observed slopes of δ_m against X in $CDCl_3$ (not shown) are in the order of E > D > C > F > A which indicates that increasing the chain length of the surfactant, more ethylene oxide units become available for solvent interaction. Addition of water to Igepal CO–630 in $CDCl_3$ manifests in increased values of $\delta_M - \delta_m$ for all protons (table 3). More significantly, the effect of water on $\delta_M - \delta_m$ is most pronounced on the main ethylene oxide protons (C). It is likely, therefore, that water interacts strongly with the ethylene oxide units of the surfactants, presumably by hydrogen bonding.

ANALYSIS IN TERMS OF INDEFINITE SELF-ASSOCIATION

Aggregation of surfactants in nonpolar solvents has been analysed in terms of two types of indefinite self-association. In Type I (indefinite self-association), the presence of all associating species and the equality of all equilibrium constants (*i.e.*, $K_2 = K_3 = K_4 \ldots = K_i$) are assumed. In Type II (indefinite self-association) equilibrium constants for the formation of higher aggregates than dimers are assumed

TABLE 2.—^{1}H N.M.R. CHEMICAL SHIFTS OF POLYOXYETHYLENE(S) NONYLPHENOLS IN $CDCl_3$

[surfactant]/mol dm⁻³

surfactant		0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50	0.60	0.70	0.75	0.80
Igepal CO–430	δ_A	1.351	1.350		1.345				1.336				1.322		
	δ_B	1.806	1.807		1.802		1.796		1.792		1.784	1.782	1.775		1.762
	δ_C	4.187	4.192		4.180		4.172		4.167		4.153	4.146	4.134		4.125
	δ_D	4.363	4.367		4.360		4.345		4.336		4.328	4.325	4.316		4.313
	δ_E	4.641	4.655		4.647		4.640		4.625		4.617	4.617	4.605		4.602
	δ_F	7.400	7.401		7.397		7.392		7.387		7.376	7.374	7.365		7.359
Igepal CO–520	δ_A		1.351		1.354		1.350		1.339						
	δ_B		1.806		1.800		1.796		1.792		1.788			1.772	
	δ_C		4.188		4.177		4.173		4.162		4.157			4.131	
	δ_D		4.363		4.358		4.351		4.344		4.335			4.312	
	δ_E		4.650		4.645		4.636		4.630		4.620			4.600	
	δ_F		7.401		7.394		7.390		7.387		7.381			7.361	
Igepal CO–530	δ_A	1.363					1.342								1.306
	δ_B	1.808	1.805		1.804		1.794		1.798		1.785	1.775			1.762
	δ_C	4.193	4.190		4.182		4.170		4.161		4.150	4.140			4.117
	δ_D	4.367					4.350								4.302
	δ_E	4.654					4.365								4.587
	δ_F	7.400	7.399		7.391		7.384		7.377		7.373	7.364			7.351
Igepal CO–630	δ_A			1.350	1.356		1.335		1.350		1.322		1.305		
	δ_B	1.796	1.809	1.797	1.789		1.788		1.802		1.766		1.754		
	δ_C	4.173	4.182	4.173	4.168		4.162		4.168		4.134		4.105		
	δ_D	4.352	4.367	4.353	4.346		4.340		4.349						
	δ_E	4.637	4.655	4.639	4.634		4.625		4.632		4.615		4.579		
	δ_F	7.385	7.405	7.395	7.386		7.385		7.389		7.357		7.341		
Igepal CO–630+ 0.15 mol dm⁻³ H_2O	δ_A		1.359						1.333		1.317		1.309		1.297
	δ_B		1.807		1.805		1.800		1.791		1.777	1.776	1.764		1.752
	δ_C		4.178		4.173		4.164		4.152		4.140	4.139	4.126		4.100
	δ_D		4.362						4.342				4.304		
	δ_E		4.656						4.630				4.597		
	δ_F		7.402		7.398		7.389		7.381		7.366	7.364	7.356		7.338

TABLE 2 (cont.)

Igepal CO–710

δ_A	1.337								1.323	1.321
δ_B	1.800	1.795	1.794	1.792	1.789	1.787	1.783	1.777	1.779	1.775
δ_C	4.169	4.166	4.164	4.156	4.153	4.151	4.148	4.145	4.140	4.136
δ_D	4.346								4.331	4.314
δ_E	4.633								4.619	4.605
δ_F	7.390	7.386	7.384	7.381	7.379	7.376	7.373	7.367	7.366	7.362

Igepal CO–730

δ_A	1.350						1.328	1.315
δ_B	1.797	1.796	1.793	1.791	1.784	1.781	1.773	1.769
δ_C	4.164	4.164	4.165	4.155	4.146	4.141	4.135	4.121
δ_D	4.378						4.331	
δ_E	4.641						4.621	4.596
δ_F	7.387	7.388	7.383	7.380	7.370	7.366	7.359	7.352

TABLE 3.—CHEMICAL SHIFTS OF THE MONOMERIC (δ_M) AND MICELLAR (δ_m) PROTONS OF POLYOXYETHYLENE(x) NONYLPHENOLS

solvent	surfactant	A		B		C		D		E		F	
		δ_m	δ_M	δ_m	δ_M	δ_m	δ_M	δ_m	δ_M	δ_m	δ_M	δ_m	δ_M
$CDCl_3$	Igepal CO–430 ($x = 4$)	1.354	1.310	1.811	1.709	4.203	4.045	4.376	4.267	4.664	4.545	7.406	7.310
	Igepal CO–520 ($x = 5$)	1.354		1.808	1.743	4.195	4.063	4.370	4.241	4.660	4.536	7.403	7.306
	Igepal CO–530 ($x = 6$)	1.367		1.811	1.715	4.199	4.019	4.370		4.657		7.404	7.277
	Igepal CO–630 ($x = 9$)	1.359	1.163	1.799	1.618	4.183	3.925	4.354		4.638	4.401	7.391	7.217
	Igepal CO–630 ($x = 9$)+ 0.15 mol dm⁻³ H_2O	1.366	1.268	1.813	1.421	4.186	3.934	4.370		4.660		7.404	7.248
	Igepal CO–710 ($x = 10$-11)	1.340		1.801	1.773	4.182	4.067	4.350		4.636		7.392	7.326
	Igepal CO–730 ($x = 15$)	1.350		1.801	1.739	4.171	4.014			4.643		7.391	7.302
CH_2Cl_2	Igepal CO–530 ($x = 6$)			1.787	1.719	4.113	3.964					7.373	7.251
CCl_4	Igepal CO–530 ($x = 6$)	1.286		1.707		4.012	3.926	4.201		4.485		7.217	
C_6H_6	Igepal CO–530 ($x = 6$)					3.262	3.357	3.146	3.277	3.201	3.269		
C_6D_{12}	Igepal CO–530 ($x = 6$)	0.970	0.967	1.445	1.448	3.724	3.748	3.919	3.954	4.190	4.230	6.968	7.025

to be equal but odd species are presumed to be absent. Chemical shift data obtained in the present work were analysed according to both Type I and Type II indefinite self-associations.

In Type I (indefinite self-association) curve fitting of the observed ^{1}H n.m.r. chemical shifts, δ, at different stoichiometric surfactant concentrations affords a " best value " for K_i by the use of eqn (1) :[12]

$$\delta = \delta_M + \left(\frac{1+2K_iC_D-\sqrt{1+4K_iC_D}}{2K_i^2C_D^2}\right)(\delta_m-\delta_M).$$ (1)

The obtained " best value " for K_i leads in turn to the estimation of the concentrations of the monomer [eqn (2)] and of the aggregates [eqn (3)]

$$[S_1] = \frac{1+2K_iC_D-\sqrt{1+4K_iC_D}}{2K_i^2C_D}$$ (2)

$$[S_i] = K_i^{i-1}[S_1]^i.$$ (3)

From the calculated S_i values, percentages of various individual aggregate concentrations can be obtained by means of eqn (4)

$$\% i[S_i] = \frac{i[S_i]}{\sum_{i=1}^{\infty} i[S_i]} \times 100$$ (4)

where

$$\sum_{i=1}^{\infty} i[S_i] = [S_1]+\sum_{i=2}^{\infty} i[S_i] = C_D.$$ (5)

Chemical shifts of the polyoxyethylene protons of the surfactants, proton C (tables 1 and 2) and the corresponding δ_m and δ_M (table 3) were utilized for the calculation of the required parameters for Igepal CO–430, CO–520, CO–530, CO–630, CO–710 and CO–730 in CDCl$_3$, for Igepal CO–630 in CDCl$_3$ in the presence of 0.15 mol dm^{-3} cosolubilized water, and for Igepal CO–530 in CH$_2$Cl$_2$, CCl$_4$, C$_6$H$_6$ and C$_6$D$_{12}$. Table 4 presents typical results. Distributions of individual species for the other surfactants are analogous.[1]

TABLE 4.—DISTRIBUTION OF MONOMERS ($i = 1$) AND OF AGGREGATES
($i = 2, 3, 4, \ldots$) IN IGEPAL CO–530 IN CDCl$_3$ ^{a}

i	% $i[S_i]$ in [Igepal CO–520]/mol dm^{-3}					
	0.10	0.20	0.30	0.40	0.50	0.75
1	91.9	85.4	79.2	75.2	70.8	67.7
2	7.6	13.0	17.4	20.0	22.5	24.0
3	0.5	1.5	2.9	4.0	5.3	6.4
4		0.2	0.4	0.7	1.1	1.5
5			0.1	0.1	0.2	0.3
6					0.1	0.1

^{a} Calculated by using eqn (4) as described in the text. Based on the chemical shifts of the ethylene oxide protons, proton C. $K_i = 0.40$ dm^3 mol^{-1}.

Monomers and dimers are the predominant species. Trimers and higher aggregates are present in only small percentages. Several trends emerge from the distributions of the aggregates. Percentages of monomers decrease at the expense of dimers and of higher aggregates as the stoichiometric concentration of the surfactant increases. This behaviour is the main feature of the multiple step equilibrium model. In CDCl$_3$ percentages of dimers increase with increasing polyoxythylene chain lengths

with the exception of Igepal CO–630. Percentages of trimers and of higher aggregates do not vary appreciably among Igepal CO–430, CO–520, CO–530 and CO–630. Formation of higher aggregates is most pronounced, however, for Igepal CO–710, containing 10 ethylene oxide units. Geometrical arrangement of aggregates containing 10 ethylene oxide units is apparently more favourable than that containing 15 such units (in Igepal CO–730). Although no correlation could be found between percentages of aggregates for Igepal CO–530 and the polarities of the bulk organic solvent, association is most prominent in benzene and deuterocyclohexane. Even in 0.08 mol dm^{-3} Igepal CO–530 in benzene, there are 21.9 % dimers, 5.0 % tetramers and 0.20 % pentamers. Conversely, in 0.10 mol dm^{-3} Igepal CO–530 there are only 7.4, 5.5 and 6.2 % dimers, 0.44, 0.24 and 0.31 % trimers and virtually no tetramers in CDCl$_3$, CH$_2$Cl$_2$ and CCl$_4$, respectively.
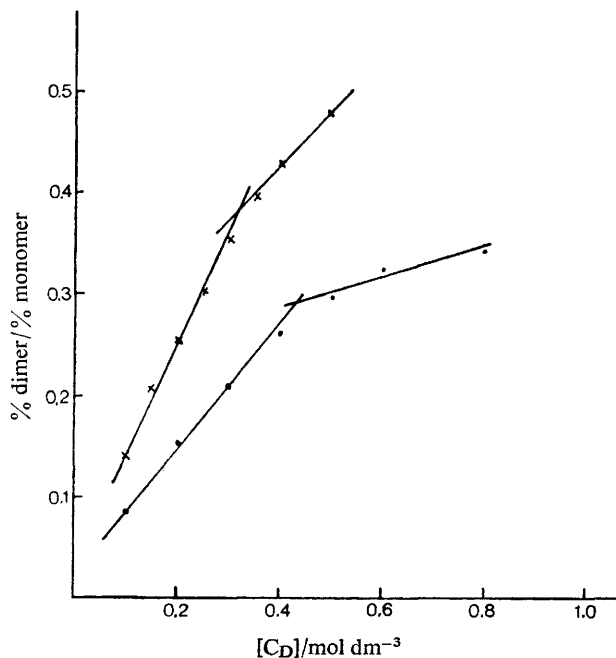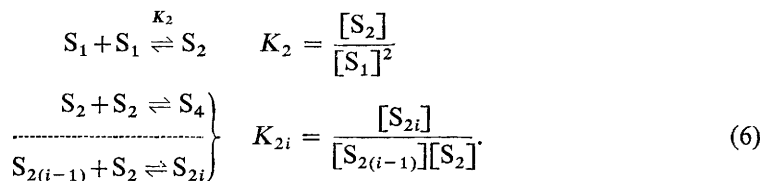

FIG. 2.—Plot of % dimer/% monomer against C_D for Igepal CO–530 (●) and for Igepal CO–710 (×) in CDCl$_3$ using the chemical shifts of proton C.

Addition of water to CDCl$_3$ solutions of Igepal CO–630 hinders the aggregation. Apparently, water interacts strongly with the ethylene oxide units of the surfactant and aggregation of such hydrated monomers is unfavourable. Other solubilizates enhance appreciably the aggregation of polyoxyethylene nonylphenols. Monomeric hemin, for example, is surrounded by 2100±400 molecules of Igepal CO–530 in benzene.[8] Addition of even 10^{-4} mol dm^{-3} bromophenol blue to 0.10 mol dm^{-3} Igepal CO–530 in benzene results in the formation of appreciably larger aggregates, containing up to 18 monomers. It is interesting to observe that plots of dimers/monomers against stoichiometric surfactant concentrations show a break for each system. These breaks coincide with the onset of rate enhancements.[8] Fig. 2 shows a typical plot. Evidently, the " operational critical micelle concentrations " correspond, at least for the surfactants investigated in the present work, to concentration ranges where the appearance of dimers becomes significant.

In Type II (indefinite self-association) the formation of dimers and only even order oligomers is assumed.[12]

$$S_1 + S_1 \overset{K_2}{\rightleftharpoons} S_2 \qquad K_2 = \frac{[S_2]}{[S_1]^2}$$

$$\left.\begin{array}{c} S_2 + S_2 \rightleftharpoons S_4 \\ \text{--------------------------} \\ S_{2(i-1)} + S_2 \rightleftharpoons S_{2i} \end{array}\right\} \quad K_{2i} = \frac{[S_{2i}]}{[S_{2(i-1)}][S_2]}. \tag{6}$$

If it is further assumed that all values of K_{2i} are identical when $i \geqslant 2$, then the concentration of the surfactant in the aggregated form, $[S_i]$, is calculated from eqn (7):[12]

$$[S_i] = \frac{1}{K_{2i}} \sum_{n=1}^{\infty} 2n(K_2 K_{2i})^n [S_1]^{2n} = \frac{2K_2[S_1]^2}{(1 - K_2 K_{2i}[S_1]^2)^2}. \tag{7}$$

Eqn (7), in essence, affords the use of two association constants, K_2 and K_{2i} compared with one in the Type I (indefinite self-association). The total surfactant concentration, C_D, is given by the sum of $[S_2]$ and $[S_i]$. Concentration of monomers at given C_D are calculated from the chemical shift data, as previously. We have attempted to fit our data to eqn (7) by making refinements in the required parameters as suggested by Muller.[12] None of the surfactant systems, investigated in this work, gave a self consistent fit. Since polyoxyethylene nonylphenols predominantly dimerize in nonpolar solvents, Type I (indefinite self-association) describe their behaviour better than Type II. Aggregation of dodecylamminium propionate in benzene and in cyclohexane is also best described in terms of Type I (indefinite self-association).[18]

CONCLUSION

Chemical shifts of the magnetically discrete polyoxyethylene nonylphenol protons in nonpolar solvents as a function of stoichiometric surfactant concentration are accommodated best in terms of the Type I indefinite self-association in which the association constants for the different aggregates are assumed to be equal. Dimerization is the most predominant; trimers and higher aggregates are formed only in small amounts. Percentages of monomers decrease at the expense of dimers and of higher aggregates with increasing surfactant concentration and with increasing chain length of the ethylene oxide units. Aggregation in benzene and in deuterocyclohexane is more pronounced that that in $CDCl_3$, CH_2Cl_2 and CCl_4. Water hinders the association but other substrates promote the formation of large aggregates. Information obtained in this work is essential for the design and interpretation of reaction kinetics in the presence of polyoxyethylene nonylphenol aggregates in nonpolar solvents.

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