Quantitative Treatment of Bromide Ion Nucleophilicity in a Microemulsion

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The reaction of *p*-bromophenacylmethyl picryl ether with bromide ion was followed in a microemulsion of cetyltrimethylammonium bromide (CTABr), n-octane, and n-butyl or tert-amyl alcohol. The second-order rate constants in the microemulsion droplets were estimated from the concentration of Br⁻ in the droplets determined electrochemically. These rate constants are insensitive to the composition of the microemulsion, are similar to those in CTABr micelles in water and in aqueous n-butyl, n-hexyl, and tert-amyl alcohol, and are slightly higher than those estimated for the reaction in water. They are smaller than rate constants in the water-alcohol mixtures of relatively low water content.

Microemulsions are transparent dispersions which typically contain water, an oil, a surfactant, and a cosurfactant, which is typically an alcohol with an alkyl group of C_4 to C_{8} .^{1,2} Two types are recognized; in the so-called oil-inwater (O/W) microemulsions, the oil is believed to be at the center of the droplet and is surrounded by surfactant and cosurfactant, whereas water is at the droplet center in the water-in-oil (W/O) microemulsions. Microemulsions have been reported in some systems even in the absence of surfactant.^{3,4}

Microemulsions are similar in some respects to micelles, and O/W microemulsions can be regarded as analogues to normal micelles and the terms W/O microemulsions and reverse micelles are synonymous.³ These submicroscopic droplets can take up solutes and provide an environment different from that of bulk solvent, and the properties of the droplets have been compared with those of bulk solvents by estimating their polarity, as given by dielectric constant or Z value, for example.^{5,6} The surfaces of micelles and O/W microemulsion droplets appear to be slightly less polar than water.

Another important question is that of the availability of water at the micellar or droplet surface. The surfaces of normal micelles are extensively hydrated,⁷ and the water molecules are not much less reactive than in bulk water.⁷⁻¹⁰ This appears to be true also for O/W microemulsion droplets.⁶

Microemulsion droplets and micelles can provide reaction media distinct from that of water,^{4,5a,6,11-13} and microemulsions have the distinct advantage as reaction media

that they can solubilize relatively high concentrations of reactants, whereas micelles generally have much less capacity. Micelles speed bimolecular reactions largely by bringing both reactants together in a small volume,¹⁴⁻¹⁷ and microemulsion droplets could act in the same way. However, with both systems we must also consider the properties of the droplets as reaction media.

A major problem in treating second-order rate constants in such pseudophases as micelles and microemulsions is the estimation of reagent concentrations in the pseudophase. This problem has been partially solved for micelles, and typically second-order rate constants in micellar pseudophases are similar to those in water.¹⁴⁻¹⁸ There is less evidence on microemulsions.^{12,13} If the incorporation of ionic reagents in microemulsions is governed by the surface potential of the droplet it would appear that, as in micelles, second-order rate constants are not very different from those in water.¹² However, the surface potential of micellar and microemulsion droplets is often derived from assumed estimates of counterion binding, so direct measurement of ion binding to the droplets is needed.

Ion binding to micelles can be measured directly, usually electrochemically,¹⁹⁻²¹ and, for mixtures of ions the binding can be treated in terms of interionic competition for the ionic head groups of the micelle.²² Another, and conceptually simpler, approach is to use a reactive-counterion micelle, in which the counterion is the only reactant.^{23,24} In these systems the concentration of reactive ion in the micellar pseudophase can be estimated from the extent of charge neutralization of the micellar head groups, and, where this approach has been used, second-order rate constants in the micellar and aqueous pseudophases have

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not been very different, except for reactions involving hydrogen ions.

We planned a similar approach to the study of an ionic reaction in an O/W microemulsion containing cetyltrimethylammonium bromide (CTABr). The reaction was the $S_N 2$ attack of Br⁻ upon *p*-bromophenacylmethyl picryl ether (1).



For reaction in aqueous quaternary ammonium bromides the first-order rate constants, k_{ψ} , increase to constant values as 1 becomes incorporated into the micelle,^{24,25} which is consistent with the micelle being saturated with Br⁻, i.e., β is constant (β is the fraction of micellar head groups neutralized by Br⁻ and $\alpha = 1 - \beta$).

The microemulsion problem therefore involves estimation of the concentration of Br^- in the droplet and measurement of the reaction rate under conditions in which 1 is fully bound to the droplet. It is necessary to suppress reaction of OH^- with 1 by keeping the pH of the solution low.²⁵ We also compared our rate constants in the microemulsion with those in alcohol-water mixtures in the absence of surfactant.

Experimental Section

Kinetics. The formation of picrate ion from 1 was followed spectrophotometrically at 355 nm, using (1.5-2.5) $\times 10^{-5}$ M substrate and $(1-3) \times 10^{-5}$ M HClO₄ or H₂SO₄ to suppress reaction with OH^{-.24,25} The rate measurements were at 25.0 °C and the first-order rate constants, k_{ψ} , are in reciprocal seconds.

EMF Measurements. Initially we used Lazar 1S-146 bromide or chloride ion electrodes with a DJ-146 double junction reference electrode. However, after some time the bromide ion electrode gave irreproducible responses, and we replaced it with an AgBr electrode made electrochemically from Ag wire. The results obtained with this electrode agreed with those obtained with a new 1S-146 electrode. Electrodes were calibrated, and recalibrated, with 10⁻⁴-0.3 M solutions of NaBr or NaCl. Plots of emf against log [Br⁻] or log [Cl⁻] were linear with a slope of 59 mV up to ca. 0.03 M, and the slope was lower at higher salt concentrations. We did not apply an activity coefficient correction to our data but relied on the calibration curve. The response of the electrode was affected by added alcohols, and the electrode was calibrated for each mixed solvent. The value of $\alpha = 1 - \beta$ was calculated from the concentration of halide ion in the aqueous pseudophase, estimated electrochemically.¹⁹⁻²¹

Binding of tert-Amyl Alcohol to CTABr Micelles. Wyn-Jones and co-workers have estimated the binding constants of *n*-butyl and *n*-hexyl alcohol to CTABr micelles by solubility measurements,²⁶ and we followed their general method for tert-amyl alcohol at 25.0 °C.

TABLE I: Reaction of 1 with Et_4NBr in the Absence of Surfactant^a

x _{ROH}	[Et₄N Br], M	$10^{3}k_{\psi},\ { m s}^{-1}$	$10^{3}k_{\psi}/[\mathrm{Br}^{-}], M^{-1} \mathrm{s}^{-1}$
0.873 ^b	0.045	1.57	34.9
0.740^{b}	0.046	0.547	11.9
0.640^{b}	0.047	0.247	5.25
0.645^{c}	0.090	0.460	5.09
0.219 ^c	0.090	0.048	0.53
0.0 99 ^c	0.090	0.028	0.31
^a At 25.0 °C.	^b t-C,H,,OH.	^c t-C₄H _o OI	ł.

TABLE II: Reaction of 1 with Br^{-} in Microemulsions and Micelles^{*a*}

	CT.	ABr	ROH		oc- tane.	H.O	10 ⁴ k
run	%	М	%	М	%	%	s ⁻¹
1		0.010				100	8.8
2	0.36	0.010	3.7	0.50		96.0	1.50
3	0.36	0.010	7.4	1.00		92.2	0.22
4	2.60	0.071				97.4	12.7
5	3.34	0.092	0.90	0.12		95.8	9.0
6	3.33	0.091	3.35	0.45		93.3	4.48
7	3.33	0.091	6.66	0.90		90.0	1.94
8	3.33	0.091	0.85^{b}	0.084		95.8	7.80
9	3.32	0.091	3.33 ^c	0.38		93.3	6.49
10	4.99	0.14	10.0	1.35	5.0	80.0	1.71
11	9.18	0.25	18.4	2.48	9.2	63.3	1.45
12	9.97	0.27	20.0 <i>°</i>	2.27	10.0	60.0	3.01
13	13.3	0.37	13.4^{c}	1.52	13.3	59.9	6.06
14	13.7	0.38	27.4^{c}	3.11	13.7	45.0	3.28

^a At 25.0 °C with *n*-BuOH, unless specified. The percentages are by weight. ^b n-C₆H₁₃OH. ^c t-C₅H₁₁OH.

Mixtures were shaken for several hours to ensure complete equilibration, and at the solubility limit it was assumed that the concentration of *tert*-amyl alcohol in the aqueous pseudophase was constant, and gives $[ROH_w]$. The binding constant, K, is given by

 $K = [\mathrm{ROH}_{\mathrm{W}}] / [\mathrm{ROH}_{\mathrm{M}}] ([\mathrm{CTABr}] + [\mathrm{ROH}_{\mathrm{M}}]) \} (1)$

Equation 1 can be rearranged in terms of the total concentration of *tert*-amyl alcohol $[ROH_T]$, so that

$$[\mathrm{ROH}_{\mathrm{T}}] = \frac{[\mathrm{ROH}_{\mathrm{W}}]K[\mathrm{CTABr}]}{(1 - [\mathrm{ROH}_{\mathrm{W}}]K)} + [\mathrm{ROH}_{\mathrm{W}}] \qquad (2)$$

where W and M denote aqueous and micellar pseudophases and $[ROH_w]$ is given by the solubility in water.

Equation 2 predicts that solubility in a micellar solution, [ROH_T], should vary linearly with [CTABr]. We observed such a linear plot with a positive deviation above 0.08 M CTABr. The data below this concentration give K = 0.77 M^{-1} , which is consistent with values of 1.0 and 10.2 M^{-1} for *n*-butyl and *n*-hexyl alcohol, respectively, because *tert*-amyl alcohol is slightly more soluble in water than *n*-butyl alcohol.²⁷

Results

Reactions in the Absence of Surfactant. The reaction of Et_4NBr with 1 was followed in aqueous *tert*-butyl or *tert*-amyl alcohol. This salt was chosen because it is soluble in alcohols and quaternary ammonium bromide ion pairs less than LiBr.²⁸ The reaction is speeded by addition of alcohol (Table I), as expected,²⁹ and the rate constants

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TABLE III: Binding of Bromide Ion to Microemulsion Droplets^a

	CTABr: ROH:	[ROH], M									
R	$C_{8}H_{18}^{b}$	0.95	1.05	1.15	1.4	1.8	1.95	2.2	2.4	2.6	2.85
$\frac{n \cdot C_4 H_9}{n \cdot C_4 H_9}$ $t \cdot C_5 H_{11}$	$1:1:1 \\ 1:2:1 \\ 1:1:1$	0.28	0.26 0.22	$\begin{array}{c} 0.24\\ 0.24\end{array}$	$0.21 \\ 0.27 \\ 0.32$	$\begin{array}{c} 0.20\\ 0.24\end{array}$	0.23	0.22		<u>- y 44 , , </u>	
$t - C_{5}^{3} H_{11}^{11}$	$1\!:\!2\!:\!1$						0.33	0.32	0.30	0.30	0.28

^{*a*} Values of α . ^{*b*} By weight.



Figure 1. Reaction in CTABr plus alcohols (Δ , *n*-butyl alcohol; \blacktriangle , *tert*-amyl alcohol; \ast , *n*-hexyl alcohol) and in microemulsions of, O, *n*-butyl alcohol and \bigcirc , *tert*-amyl alcohol.

are similar in solutions containing the same mole fraction, x_{ROH} , of either alcohol. There is a reasonably good linear relation between log $k_{\psi}/[\text{Br}^-]$ and x_{ROH} , and extrapolation to pure water gives a second-order rate constant of 0.16 $\times 10^{-3}$ M⁻¹ s⁻¹.

Reactions in Micelles and Microemulsions. Our aim was to compare reactions in micelles and microemulsions, and Table II gives results of experiments in O/W microemulsions of octane, CTABr, and n-butyl or tert-amyl alcohol, and in micellar solutions containing alcohols. In both systems reaction is slowed by addition of alcohol, and qualitatively k_{ψ} decreases steadily as the mole ratio of alcohol to CTABr increases. The variation of k_{ψ} with mole ratio is similar for micelles and microemulsions and is not very sensitive to the nature of the alcohol. The first-order rate constants qualitatively follow [ROH]/[CTABr] except for the runs in aqueous CTABr (Figure 1), where the solution contains no alcohol. There is no obvious difference in the behavior of micelles and microemulsions, and the alcohol could retard reaction by reducing binding of Brto the micellar microemulsion aggregate.^{19,20}

Binding of Bromide Ion. Addition of n-butyl or tertamyl alcohol to aqueous CTABr increases α , especially in dilute CTABr. The determination, using a specific ion electrode, is inherently insensitive and subject to error because of interactions between surfactant and electrode, but our values of $\alpha \approx 0.2$ in aqueous CTABr agree with Larsen's value of 0.2 in 0.05 and 0.1 M CTABr,¹⁹ and Zana's value of 0.16 at just above the cmc.²⁰ Other values in the literature range from 0.12 to 0.35,²² and a value of 0.22 has recently been estimated with quasi-elastic light scattering.³⁰

Addition of *n*-butyl and *tert*-amyl alcohol in aqueous CTABr sharply increases α (Figures 2 and 3), especially in dilute CTABr with *n*-butyl alcohol. The effect of *n*-butyl alcohol is qualitatively similar to that reported by Zana and co-workers for ca. 10^{-3} M CTABr.²⁰ Unexpectedly, *n*-hexyl alcohol did not increase α (Figure 3), although





Figure 2. Effect of *n*-butyl alcohol upon α of CTABr: \bullet , 0.01, O, 0.07; \blacktriangle , 0.1; Δ , 0.2 M CTABr.



Figure 3. Effect of alcohols upon α of 0.1 M CTABr; O, *n*-butyl alcohol; \bullet , *tert*-amyl alcohol; Δ , *n*-hexyl alcohol.

we could not go beyond 0.15 M *n*-hexyl alcohol. This observation agrees with Larsen's finding that *n*-hexyl alcohol did not affect α in CTABr–NaBr.^{19,31}

Cetyltrimethylammonium chloride (CTACl) behaves similarly to CTABr, in that added *n*-butyl alcohol increases α , estimated by using a specific chloride ion electrode. The increase is greatest with the most dilute CTACl, and α increases with decreasing [CTACl] (Figure S1, supplementary material). These observations are consistent with Cl⁻ being more hydrophilic than Br⁻ and therefore bound less tightly to a cationic micelle.³³

Values of α for microemulsions are not very dependent upon the concentration of alcohol, provided that the ratio of alcohol to CTABr is kept constant (Table III). They are in the range 0.2–0.3 and are consistent with values of α in the more concentrated solutions of CTABr in aqueous

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TABLE IV: Estimation of Second-Order Rate Constants in Micelles and Microemulsions

run ^a	$10^{4}k_{\psi}$,	β	R	$10^4 k_{ m M}, { m s}^{-1}$	$V_{m'}, M^{-1}$	$10^4 k_{2'}, M^{-1} s^{-1}$	$V_{m}^{''}, M^{-1}$	$\frac{10^4 k_{2^{''}}}{M^{-1} s^{-1}}$
1	8.8	0.76	1	11.6	0.18	2.09	0.36	4 18
2	1.50	0.52	0.51	5.6	0.13	0.73	0.22	1.23
3	0.22	0.13	0.095	17.8	0.10	1.78	0.10	1.78
4	12.7	0.87	1	14.6	0.18	2.63	0.36	5.26
5	9.0	0.83	0.80	13.5	0.16	2.16	0.31	4.19
6	4.48	0.75	0.61	9.8	0.14	1.37	0.25	2.45
7	1.94	0.62	0.33	9.5	0.11	1.05	0.17	1.62
8	7.80	0.87	0.65	13.8	0.15	2.12	0.27	3.73
9	6.49	0.78	0.73	7.3	0.16	2.17	0.29	2.12
10	1.71	0.73	0.20	11.7	0.096	1.12	0.13	1.52
11	1.45	0.80	0.13	13.9	0.088	1.22	0.11	1.53
12	3.01	0.67	0.18	25.0	0.10	2.62	0.14	3.50
13	6.06	0.74	0.35	23.2	0.12	2.81	0.18	2.32
14	3.28	0.73	0.16	28.1	0.12	2.90	0.13	3.65

^a From Table II.

alcohol (Figures 2 and 3). These observations suggest that the presence of *n*-octane in microemulsion droplets has little effect on the binding of Br⁻ at the surface. Values of α tend to decrease with increasing alcohol concentration, and α is slightly larger when the microemulsion contains *tert*-amyl alcohol as compared with *n*-butyl alcohol.

Although there is considerable uncertainty in some of the values of α this is not a major problem in treating the kinetic data, because the comparisons depend upon the amount of Br⁻ in the aggregate which is given by $\beta = 1 - \alpha$.

Discussion

Analysis of the Kinetic Data. For reactions in normal micelles the rate constants depend on the reactant concentrations and the rate constant at the surface.^{14-18,22,23} We assume that this behavior also applies to microemulsions,¹³ and that because 1 is very hydrophobic, and almost insoluble in water, it will be fully incorporated in the micelle or microemulsion droplets.

The first rate-order rate constant is then given by¹⁶

$$k_{\psi} = k_{\mathrm{M}}[\mathrm{Br}_{\mathrm{M}}] / ([\mathrm{CTABr}] + [\mathrm{ROH}_{\mathrm{M}}])$$
(3)

where the quantities in square brackets are molarities in terms of total solution volume and the subscript M denotes the micellar or microemulsion pseudophase. The second-order rate constant in the droplet, $k_{\rm M}$, is defined in terms of the mole ratio of Br⁻ to CTABr + ROH, and we assume that we can neglect the amount of CTABr in the aqueous pseudophase, because we work well above the critical micelle concentration.³⁴ Equation 3 can be written as

$$k_{\psi} = k_{\rm M} \beta R \tag{4}$$

where $\beta = [Br_M]/[CTABr]$, and $R = [CTABr]/([CTABr] + [ROH_M])$.

The estimated values of $k_{\rm M}$ are given in Table IV. They are calculated from values of $\beta = 1 - \alpha$ from Figures 2 and 3 and the values of R estimated by solubility. We assume that the values of R, determined for micelles, can also be applied to microemulsions, which will not be correct if alcohol is taken up by the hydrocarbon in the microemulsion droplet. Values of $k_{\rm M}$ are not very different, although they depend upon the composition of the reaction mixture. However, second-order rate constants are generally written in terms of moles of reactant per unit volume of the reaction medium, and we can convert values of $k_{\rm M}$, s⁻¹, into the usual form of second-order rate constants whose dimensions are ${\rm M}^{-1}~{\rm s}^{-1}$ by estimating the volume element of reaction.¹⁶

There is a problem in defining this volume element in both aqueous micelles and in microemulsions. In aqueous micelles we can define it as the volume of the micellar Stern layer, or of the micelle itself, and these volumes differ by a factor of approximately two.^{14-18,22} For the microemulsions, and the micelles in the presence of alcohol, we make two alternative assumptions.¹³ In one we assume that reaction occurs in a region consisting of half the volume of the surfactant, and that of the bound alcohol. The molar volume of this element, $V_{\rm m}'$, is given by

$$V_{\rm m}' = \frac{R}{2} \frac{\rm MW_{\rm CTABr}}{1000} + (1-R) \frac{\rm MW_{\rm ROH}}{1000}$$
(5)

where MW denotes molecular weight and unit density is assumed for all components. (Our calculations are insensitive to small density changes.)

In the second assumption we write the volume element, $V_{\rm m}''$, in terms of the total volumes of surfactant and bound alcohol:

$$V_{\rm m}'' = R \, \frac{\rm MW_{\rm CTABr}}{1000} + (1 - R) \frac{\rm MW_{\rm ROH}}{1000}$$
 (6)

The corresponding second-order rate constants, k_{2}' and k_{2}'' , are given by

$$k_{2}' = k_{\rm M} V_{\rm m}' \qquad k_{2}'' = k_{\rm M} V_{\rm m}''$$
 (7a,b)

The values of $k_{2'}$ and $k_{2''}$ are in Table IV. The values of $k_{2'}$ are somewhat less sensitive to changes in composition than those of $k_{2''}$, but both sets of values are similar in magnitude. Our values of k_{ψ} differ by a factor of ca. 60 (Table II), whereas variations of $k_{2'}$ (or $k_{2''}$) are much smaller, suggesting that in both alcohol-containing micelles (runs 1–9) and microemulsions (runs 10–14) the observed rate enhancements depend largely upon the concentration of both reactants in the micelle or microemulsion droplets, and we see no obvious differences between the two systems.

In calculating $V_{\rm m}'$ or $V_{\rm m}''$ we neglect the water at the surface of the micelle or microemulsion droplet, even though the surfaces appear to be highly aqueous. This approximation is often made in calculating second-order rate constants in aqueous micelles. One could postulate some extent of hydration of groups at the micellar or droplet surface, which would increase $V_{\rm m}'$ or $V_{\rm m}''$ and therefore k_2' or k_2'' to some arbitrary extent, but the

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TABLE V: Estimation of α by Conductivity^{*a*}

solvent	α		
H ₂ O 0.45 M <i>n</i> -BuOH	$\begin{array}{c} 0.17 \ (0.27) \\ 0.34 \ (0.70) \end{array}$		

 a Values of α calculated by using Evan's treatment. 36 The values in parentheses are calculated from slopes of the conductivity plots. 20

changes would be similar for all the reaction mixtures (cf. ref 35).

Comparison of Rate Constants in Water and Microemulsions. The second-order rate constants, k_2' , are approximately 10⁻⁴ M⁻¹ s⁻¹ (Table IV) and are of the same order of magnitude as the extrapolated value of 1.6×10^{-4} M^{-1} s⁻¹ in water (Table I). Although there are considerable uncertainties in the values of k_2' , they are much smaller than those in alcohol-water mixtures of appreciable alcohol content (Table I), suggesting that reaction occurs in a water-rich environment, even though alcohol is bound to the micelle or droplets. These observations are consistent with others suggesting that the surface of these aggregates, like those of aqueous micelles, are strongly hydrated.^{6,7} Probably our neglect of the water content of the surface is leading to values of $k_{2'}$, or $k_{2''}$, which are too small, but any correction would be smaller than the uncertainties due to the approximations in our treatment, and they do not affect our qualitative conclusions.

The reactivity of water toward bis(4-nitrophenyl)carbonate in microemulsions seems to be insensitive to the composition of the microemulsion and is not very different from that in aqueous micelles.⁶ In addition, the polarities of microemulsion and micellar surfaces are similar and not very sensitive to composition of the microemulsion.^{5,6} However, it is important to note that, at high pH, the alcohol cosurfactant can be a much more effective nucleophile than OH^{-.11,12}

Most of the values of k_2' or k_2'' in Table IV are slightly larger than the second-order rate constant for reaction in water, and, insofar as our neglect of the water content at the droplet surface reduces the calculated rate constant, there may be some rate enhancement at the droplet surface. But the effect is small.

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Appendix

Conductivity. There are breaks in plots of conductivity vs. surfactant concentration at the critical micelle concentration, cmc. Zana and co-workers measured conductivities at just above and below the cmc and estimated α , as the ratio of slopes of the conductivity vs. concentration plots at above and below the cmc.²⁰ In this approach the conductivity of the micelles is assumed to be negligible compared with that of the free counterions and monomeric surfactant. Evans calculated the mobility of the micelles using Stokes Law and obtained³⁶

$$1000S_2 = \frac{(n-m)^2}{n^{4/3}}(1000S_1 - \Lambda_{\rm Br}) + \frac{n-m}{n}\Lambda_{\rm Br} \quad (8)$$

where *m* and *n* are the number of counterions in, and the aggregation number of, the micelle, and $\alpha = m/n$, $\Lambda_{\rm Br}$ is the equivalent conductance of Br⁻, and S_1 and S_2 are the slopes of specific conductance vs. concentration plots below and above the cmc.

Our results using these two methods are in Table V for $(0-1.6) \times 10^{-3}$ M CTABr. The values of α calculated with Evan's equation are similar to those estimated with a specific ion electrode, but differ from those obtained with Zana's method. In estimating α by Evan's method we assumed n = 80 and neglected any effect of 0.45 M *n*-BuOH on it or on $\Lambda_{\rm Br}$; however, small changes in *n* have little effect on α . Because of these uncertainties we did not use the conductivity data in interpreting the kinetics.

Supplementary Material Available: Figure S1, containing values of α for CTACl with added *n*-butyl alcohol (1 page). Ordering information is given on any current masthead page.

⁽³⁵⁾ Halle, B.; Carlström, G. J. Phys. Chem. 1981, 85, 2142.

⁽³⁶⁾ Evans, H. C. J. Chem. Soc. 1956, 579.

⁽³⁷⁾ Lianos, P.; Zana, R. J. Colloid Interface Sci. 1981, 84, 100, and references cited therein.