Effect of Barrier Height Uncertainty

As noted above, we have assumed that in a large secondary or tertiary free radical, the rotational barrier height decreases to one-half the height of the barrier in the parent alkane, rather than to two-thirds, as assumed in refs 4 and 5. In the case of a 3300 cal/mol barrier, the difference amounts to a difference in S_{298} in the radical of 0.3 cal/(mol K). The differences in Cp between 298 and 1500 K are between 0.3 and 0.05 cal/(mol K) for almost any value of the partition function and almost any parent alkane barrier between 3 and 5 kcal/mol—the range of most experimental values. In Table XII are listed Cp corrections should the barrier height be either two-thirds or one-third of the parent alkane barrier height, rather than one-half the value, as we have assumed. Corrections are also shown for the unlikely case that rotation is free ($V = 0$). These latter figures give an indication of the maximum possible errors in the assigned values. The differences in any equilibrium constants involving the radicals (including Kf, the equilibrium constants for formation from the elements) over the same temperature range are 10–20%—not significant, compared to other probable uncertainties.

References and Notes

(1) Chase, M. W., Jr.; et al. *JANAF Thermochemical Tables*, 3rd ed.; *J. Phys. Chem. Ref. Data* **1985,** *14* (Suppl. 1).
(2) Cohen, N.; Benson, S. W. The Thermochemistry of Alkanes and Cycloalkanes. In *The Chemistry of Alkanes and Cycloalkanes*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1992.
(3) Purnell, J. H.; Quinn, C. P. *J. Chem. Soc.* **1964,** 4049.
(4) O'Neal, H. E.; Benson, S. W. *Int. J. Chem. Kinet.* **1969,** *1,* 221.
(5) O'Neal, H. E.; Benson, S. W. Thermochemistry of Free Radicals. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; pp 275–359.
(6) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.
(7) Stull, D. R.; Westrum, D. R., Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Krieger: Malabar, FL, 1987.
(8) Alberty, R. A.; Gehrig, C. A. *J. Phys. Chem. Ref. Data* **1984,** *13,* 1173.
(9) Pacansky, J.; Dupuis, M. *J. Am. Chem. Soc.* **1982,** *104,* 415.
(10) Pacansky, J.; Schrader, B. *J. Chem. Phys.* **1983,** *78,* 1033.
(11) Chen, Y.; Rauk, A.; Tschuikow-Roux, E. *J. Chem. Phys.* **1990,** *93,* 1187.
(12) Pacansky, J.; Horne, D. E.; Gardini, G. P.; Bargon, J. *J. Phys. Chem.* **1977,** *81,* 2149.
(13) Pacansky, J.; Gutierrez, A. *J. Phys. Chem.* **1983,** *87,* 3074.
(14) Pacansky, J.; Coufal, H. *J. Chem. Phys.* **1980,** *72,* 3298.
(15) Pacansky, J.; Brown, D. W.; Chang, J. S. *J. Phys. Chem.* **1981,** *85,* 2562.
(16) Schrader, B.; Pacansky, J.; Pfeiffer, U. *J. Phys. Chem.* **1984,** *88,* 4069.
(17) Pacansky, J.; Chang, J. S. *J. Chem. Phys.* **1981,** *74,* 5539.
(18) Pacansky, J.; Coufal, H. *J. Chem. Phys.* **1980,** *72,* 5287.
(19) Wong, M. W.; Baker, J.; Nobes, R. H.; Radom, L. *J. Am. Chem. Soc.* **1987,** *109,* 2245.
(20) Pacansky, J.; Dupuis, M. *J. Chem. Phys.* **1979,** *71,* 2095.
(21) Pacansky, J.; Yoshimine, M. *J. Phys. Chem.* **1987,** *91,* 1024.
(22) Chen, Y.; Rauk, A.; Tschuikow-Roux, E. *J. Phys. Chem.* **1990,** *94,* 2775.
(23) Chen, Y.; Rauk, A.; Tschuikow-Roux, E. *J. Phys. Chem.* **1990,** *94,* 6250.
(24) Pacansky, J.; Schubert, W. *J. Chem. Phys.* **1982,** *76,* 1459.
(25) Pacansky, J.; Yoshimine, M. *J. Phys. Chem.* **1986,** *90,* 1980.
(26) Krusic, P.; Meakin, P.; Jesson, J. *J. Phys. Chem.* **1971,** *75,* 3438.
(27) Adrian, F. J.; Cochran, E. L.; Bowers, V. A. *J. Chem. Phys.* **1973,** *59,* 3946.
(28) Tsang, W. *J. Phys. Chem. Ref. Data* **1988,** *17,* 887.
(29) Pitzer, K. S.; Brewer, L.; Lewis, G. N.; Randall, M. *Thermodynamics*, 2nd ed.; McGraw-Hill: New York, 1961; Chapter 27.
(30) Gutman, D. *Acc. Chem. Res.* **1990,** *23,* 375.
(31) Seetula, J. A.; Russell, J. J.; Gutman, D. *J. Am. Chem. Soc.* **1990,** *112,* 1347.
(32) Nicovich, J. M.; van Dijk, C. A.; Kreutter, K. D.; Wine, P. H. *J. Phys. Chem.* **1991,** *95,* 9890.
(33) Seakins, P. W.; Pilling, M. J. *J. Phys. Chem.* **1991,** *95,* 9874.
(34) Tsang, W.; Hampson, R. F. *J. Phys. Chem. Ref. Data* **1986,** *15,* 1087.
(35) Tsang, W. *J. Phys. Chem. Ref. Data* **1990,** *19,* 1.

Pseudophase Ion-Exchange Model Applied to Kinetics in Aqueous Micelles under Extreme Conditions: A Simple Modification

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The dehydrochlorination of 1,1-diphenyl-2,2,2-trichloroethane (DTE) with hydroxide ion was studied in the presence of hexadecyltrimethylammonium hydroxide (CTAOH) micelles at 25.0 °C, under conditions where the pseudophase ion-exchange model (PPIE) normally fails (high sodium hydroxide and salt concentrations). A simple modification of the model, which includes the variable degree of dissociation concept and the contribution of the counterion in the aqueous phase to the interfacial counterion concentration, allows the application of the PPIE model to all ranges of concentrations in the presence and absence of added salts.

Introduction

The pseudophase ion-exchange (PPIE) formalism effectively describes most of the observed effects in bimolecular reactions of uni- and bivalent ions with organic substrates in ionic micellar solutions.[1-5] The fact that PPIE ignores details of micelle structure allows the application of its basic mathematic formalism to synthetic vesicles,[6] reversed micelles,[7] microemulsions,[8] and ionenes.[9]

The reported "failures" of the PPIE model, in particular with highly hydrophilic reactive counterion surfactants such as CTA-OH,[10-14] were initially rationalized in terms of an additional rate contribution across the micelle–water boundary.[11,15] Other approaches used include (i) the assumption that counterion binding obeys a micelle surface potential independent, mass action law[15,16]

and (ii) spherical cell models, in which local counterion concentrations are calculated by solving nonlinear Poisson–Boltzmann equations and treating the size of CTAOH micelles as an adjustable parameter.[17-19] More recently,[20] it was demonstrated that the apparent breakdown of PPIE, in the case of reactive counterion surfactants, is due not to fundamental defects of the model but to the inadequacy of the assumption that the degree of micellar dissociation, α, is independent of the salt and detergent concentration. Indeed, good agreement is obtained between observed rate constants and the PPIE model when experimentally determined values of α (obtained from straightforward conductivity measurements) are employed for the simulation of the dehydrochlorination of DDT and DDD in CTAOH and for the fluoride
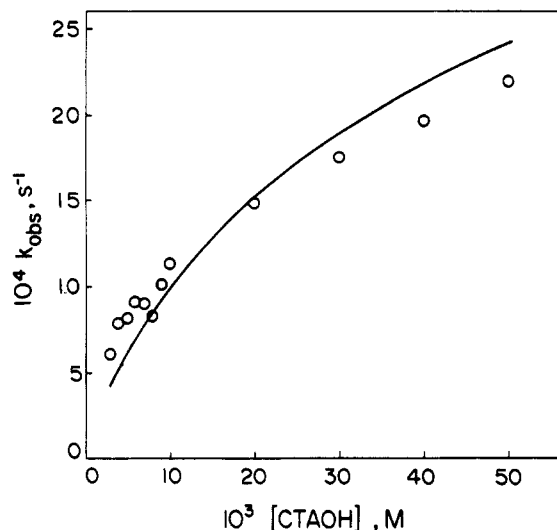
Figure 1. Plot of pseudo-first-order rate constant (k_{obs}) against [CTAOH] for the dehydrochlorination of DTE in the absence of KOH at 25.00 ± 0.01 °C.

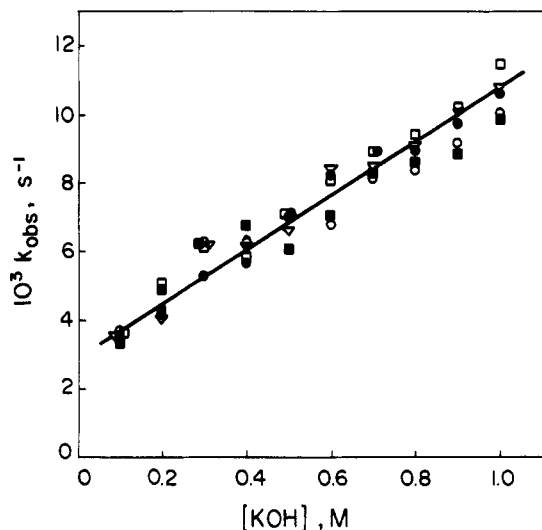**Figure 2.** Plot of pseudo-first-order rate constant (k_{obs}) against [KOH] at [CTAOH]: 0.005 (o), 0.010 (■), 0.030 (●), 0.04 (▽), and 0.05 M (□) at 25.00 ± 0.01 °C.

ion catalyzed hydrolysis of p-nitrophenyl diphenyl phosphate in CTAF.

The failure of the PPIE model observed for cationic micelles at high hydroxide ion concentration,[11] for anionic micelles at high hydrogen ion concentration,[21] and for both cationic and anionic micelles at high salt concentration[18-21] still remains to be rationalized and mathematically treated.

The inability of any theory to fit experimental rate or equilibrium data stems from the unsuitability of the analytical expression used to calculate the reactive ion concentration at the micellar surface. The two-step function, which is at the very basis of the PPIE model, does not include any contribution from the ionic concentration in the aqueous phase. Clearly, this simplification works well when the concentration of reactive ion is low, say below 10^{-2} M; however, the failure of the PPIE model at high concentration of any salt with a reactive ion is intrinsically related to this oversimplification. Recently, Romsted successfully treated counterion effects on the acid-catalyzed hydrolyzed of a hydrophobic ketal in cationic micelles at high salt concentration by using Quina's suggestion that the interfacial counterion concentration is equal to an initial effective counterion concentration plus the counterion in the aqueous pseudophase.[22]

The present results demonstrate that good agreement between experimental data and the PPIE model is obtained by using an appropriate analytical expression for the hydroxide ion concentration (including the contribution of hydroxide ion in the aqueous phase and taking into account activity corrections), in the dehydrochlorination reaction of 1,1-diphenyl-2,2,2-trichloroethane under experimental conditions where the normal PPIE equations fail.

Experimental Section

Hexadecyltrimethylammonium hydroxide (CTAOH) was purified by previously described procedures.[23] In all experiments CO_2-free water was used and manipulations of CTAOH were carried out under a N_2 atmosphere. The kinetic and physicochemical (conductivity and surface tension versus concentration) behavior of CTAOH were found to be identical with that of a sample of the same detergent prepared by the method reported by Bunton et al.[22] The compound 1,1-diphenyl-2,2,2-trichloroethane (DTE) was prepared according to a previously described procedure,[5] mp 64–65 °C, lit. mp 65 °C,[24] and its purity was found to be satisfactory by thin-layer chromatography, UV, and IR analysis. All other chemicals used were the best available grade.

Rates of dehydrochlorination of DTE were determined by following (Shimadzu UV 210 A spectrophotometer) the appearance of 1,1-diphenyl-2,2-dichloroethylene at 260 nm; in all cases the substrate concentration was 2.00×10^{-5} M. The temperature for the kinetic runs was maintained at 25.00 ± 0.01 °C

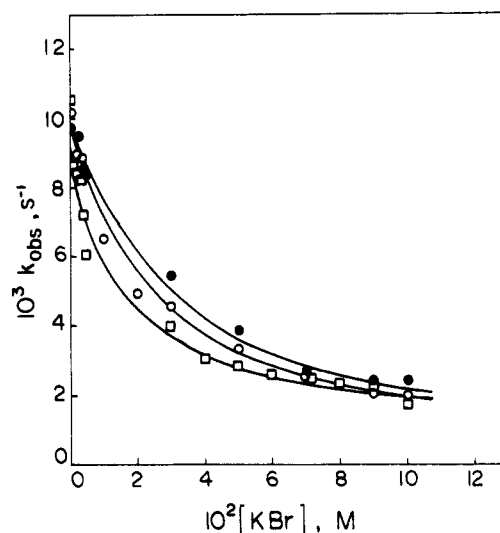**Figure 3.** Plot of pseudo-first-order rate constant (k_{obs}) as a function of [KBr] at [KOH] = 1.0 M and [CTAOH]: 0.005 (□), 0.010 (o), and 0.025 M (●) at 25.00 ± 0.01 °C.

by using a water-jacketed cell compartment. Individual first-order rate constants, k_{obs}, were obtained from linear plots of ln (A_∞ – A_t) vs time. All plots were linear for at least 90% of reaction, and correlation coefficients were greater than 0.99.
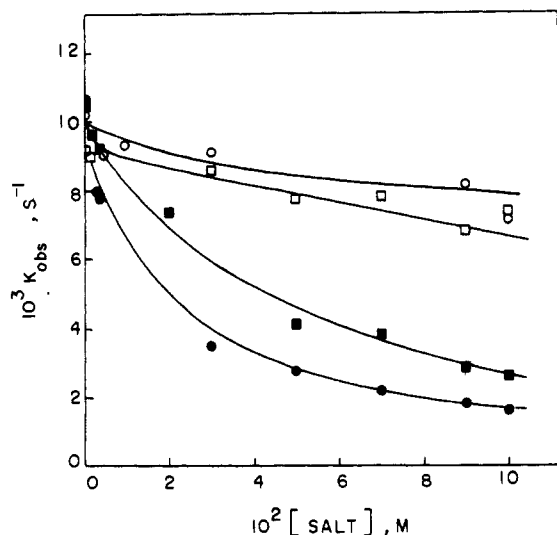
Results

Figure 1 shows the first-order rate constants for the dehydrochlorination of DTE (eq 1). In aqueous solutions of CTAOH

$$(C_6H_5)_2CH\text{-}CCl_3 + HO^- \rightarrow (C_6H_5)_2C{=}CCl_2 + H_2O + Cl^- \quad (1)$$

the observed first-order rate constant increases smoothly as a function of surfactant concentration. Figure 2 illustrates results obtained for the same reaction at five different detergent concentrations, in the range 0.005–0.050 M, as a function of added KOH. In all cases the rate constant increased linearly with hydroxide ion concentration.

Figure 3 shows the inhibition of the dehydrochlorination caused by addition of KBr to 0.005, 0.010, and 0.025 M solutions of CTAOH in the presence of 1.0 M KOH. As expected, in terms of ion exchange at the micelle surface, a marked decrease of the rate constant is observed.

Similar results are obtained by addition of KCl, KNO_3, KF, and CH_3COOK to 5×10^{-3} M CTAOH in the presence of 1.0 M KOH (Figure 4). Qualitatively, the inhibition follows the

Figure 4. Plot of pseudo-first-order rate constant (k_{obs}) as a function of: KCl (■), KNO$_3$ (●), KF (O), and CH$_3$COOK (□) at [CTAOH] = 0.005 M and [KOH] = 1.0 M at 25.00 ± 0.01 °C.

expected order,[25] i.e., $NO_3^- > Cl^- > CH_3COO^- > F^-$.

Discussion

The results shown in Figures 1–4 were obtained under conditions where the original PPIE formalism does not work, i.e., the highly hydrophilic reactive counterion surfactant CTAOH (Figure 1), the additional complication of a high concentration of added NaOH (Figure 2), and high concentrations of nonreactive salts (Figures 3 and 4).

The solubility of DTE in water is less than 5.7×10^{-8} M assuming a molar absorptivity of 17 300 M^{-1} cm^{-1} and a minimum detectable value of 0.001 absorbance units, because no absorbance was detected at 235 nm for a saturated solution of DTE in water. The low solubility of DTE is not unexpected since the solubility of 1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethane (DDT) in water[26,27] is ca. 10^{-10} M. This very low solubility of DTE in the aqueous phase allows us to treat the kinetic data using a simple rate expression (eq 2) based in the PPIE model, where $k_{2,m}$

$$k_{obs} = k_{2,m}[\overline{HO^-}]_m \qquad (2)$$

corresponds to the second-order rate constant in the micellar phase and $[\overline{HO^-}]_m$ is the local concentration of hydroxide ion in the micellar phase.

The concentration of hydroxide ion in the micellar phase, was estimated by using the PPIE formalism and assuming that the interfacial counterion concentration corresponds to an effective counterion concentration resulting from micelle formation plus the counterion concentration in the aqueous phase (eq 3),[22] where

$$[\overline{HO^-}]_m = [HO^-]_m/C_d \overline{V} + [HO^-]_w \qquad (3)$$

C_d corresponds to the concentration of micellized surfactant and $\overline{V}$ to the reactive volume in liters/mole of reactive region. This equation is formally different from the commonly used two step function of the pseudophase model, in which the $[HO^-]_w$ term is not considered to contribute to the interfacial counterion concentration. Equation 3 formally attributes the contribution of high concentrations of hydroxide ion added as salt, $[HO^-]_w$, to the local interfacial counterion concentration, to invasion of the micellar surface by added hydroxide ion; similar to the concept of electrolyte invasion in ion exchange resins. The addition of the $[HO^-]_w$ term to eq 3 permits treatment of all the experimental data reported in this paper by means of the PPIE formalism, despite the fact that the data were obtained under conditions where the original PPIE formalism normally fails (see above).

Combining eqs 2 and 3 gives an expression for the observed rate constant (eq 4):

$$k_{obs} = k_{2,m}([HO^-]_m/C_d\overline{V} + [HO^-]_w) \qquad (4)$$

TABLE I: Parameters Used To Fit the Effect of Added Salts on the Observed Rate Constants for Dehydrochlorination of DTE at 25 °C[a]

salt (concn, M)	10^3[CTAOH], M	$10^4 k_{2,m}$, M^{-1} s^{-1}	$K_{OH/X}$
KBr (0–0.10)	5.0	6.80	0.050
KBr (0–0.10)	10.0	6.50	0.050
KBr (0–0.10)	25.0	6.80	0.050
KCl (0–0.10)	5.0	6.50	0.100
KNO$_3$ (0–0.10)	5.0	6.50	0.043
KF (0–0.10)	5.0	6.50	1.020
CH$_3$COOK (0–0.25)	5.0	6.50	0.425

[a] $\overline{V} = 0.18$ L mol^{-1}; $\alpha = 0.02$; [KOH] = 1.0 M.

The data in Figure 1 were fit by using eq 4 and degrees of micellar dissociation, α, obtained from conductivity measurements.[20] The conductivity data were fit with a Langmuir type adsorption isotherm[15,16] (eq 5), and a value of $K_{OH} = 73$ M^{-1}. This

$$K_{OH} = [HO^-]_m/\{[HO^-]_m(C_d - [HO^-]_m)\} \qquad (5)$$

value of K_{OH} was used to obtain α values by extrapolation for concentrations of CTAOH and added hydroxide ion outside the range used in the conductivity measurements.[20] The best fit of the data in Figure 1 was obtained with $k_{2,m} = 6.50 \times 10^{-4}$ M^{-1} s^{-1} and $\overline{V} = 0.180$ L mol^{-1}.

A similar result was obtained when the data in Figure 2, showing values of the observed rate constant for a series of CTAOH concentrations in the range 0.005–0.050 M and variable added KOH (up to 1.0 M) were fit with eq 4. Indeed, all the data sets, could be fitted with the values of $\overline{V}$ and $k_{2,m}$ cited above within 5% error limits. The first part of the rate constant–[KOH] profile, up to 0.2 M KOH, is described primarily by the first term in eq 4, but the second term becomes predominant at higher KOH concentrations.

The form of the PPIE model developed by Quina and Chaimovich was applied[2] to calculate the local concentration of hydroxide ion in the micellar phase, for the experiments in the presence of salt and 1.0 M KOH. Because the KOH concentration is rather high, eq 5 predicts that α is approximately constant and in the range of 0.02. Table I contains low-exchange constants and $k_{2,m}$ values obtained by fitting of the experimental data in Figures 3 and 4 with eq 4. In all cases the theoretical curves (solid lines) agree reasonably well with the experimental data using essentially a single $k_{2,m}$ value, within 5%, and ion-exchange constants ($K_{OH/X}$) which are in good agreement with values reported in the literature.[25]

In conclusion, we believe that by using the appropriate degree of micellar dissociation, α, and eq 3 to calculate local counterion concentration in the micellar phase, we can extend the application of the PPIE model to concentrated salt solutions and to reactive counterion micelles in the presence of high concentrations of added KOH. Thus, the modified PPIE model, including the variable α concept and eq 3 as the appropriate analytical expression to calculate the reactive counterion concentration, can be applied in practically all cases.

References and Notes

(1) Fendler, J. H. *Membrane Mimetic Chemistry*; Wiley: New York, 1982.
(2) Quina, F. H.; Chaimovich, H. *J. Phys. Chem.* **1979**, *83*, 1844.
(3) Berezin, I. V.; Martinek, K.; Yatsimirski, A. K. *Russ. Chem. Rev. (Engl. Transl.)* **1973**, *43*, 487.
(4) Romsted, L. S. In *Surfactants in Solution*; Mittal, K. L., Lindman, B., Eds.; Plenum: New York, 1984; p 1015.
(5) Bunton, C. A. *Catal. Rev.-Sci. Eng.* **1979**, *20*, 1.
(6) Cuccovia, I. M.; Quina, F. H.; Chaimovich, H. *Tetrahedron* **1982**, *38*, 917.
(7) El Seoud, O. A.; Chinelatto, A. M. *Colloid Interface Sci.* **1983**, *95*, 163.

(8) Pereira, R. R.; Zanette, D.; Nome, F. *J. Phys. Chem.* **1990**, *94*, 356.

(9) Soldi, V.; Erismann, N.; Quina, F. H. *J. Am. Chem. Soc.* **1988**, *110*, 5137.

(10) Bunton, C. A.; Romsted, L. S.; Savelli, G. *J. Am. Chem. Soc.* **1979**, *101*, 1253.

(11) Nome, F.; Rubira, A. F.; Ionescu, L. G. *J. Phys. Chem.* **1982**, *86*, 1881.

(12) Stadler, E.; Zanette, D.; Rezende, M. C.; Nome, F. *J. Phys. Chem.* **1984**, *88*, 1892.

(13) Bunton, C. A.; Romsted, L. S. In *Solution Behavior of Surfactants: Theoretical and Applied Aspects*; Mittal, K. L., Fendler, E. J., Eds.; Plenum: New York, 1982; p 975.

(14) Broxton, T. J.; Sango, D. B. *Aust. J. Chem.* **1983**, *36*, 711.

(15) Rodenas, E.; Vera, S. *J. Phys. Chem.* **1985**, *89*, 513.

(16) Vera, S.; Rodenas, E. *J. Phys. Chem.* **1986**, *90*, 3414.

(17) Franm, J.; Diekmann, S. In *Surfactants in Solution*; Mittal, K. L., Lindman, B., Eds.; Plenum: New York, 1984.

(18) Bunton, C. A.; Moffatt, J. R. *J. Phys. Chem.* **1986**, *90*, 538.

(19) Ortega, F.; Rodenas, E. *J. Phys. Chem.* **1987**, *91*, 837.

(20) Neves, M. F. S.; Zanette, D.; Quina, F.; Moretti, M. T.; Nome, F. *J. Phys. Chem.* **1989**, *93*, 1502.

(21) Gonsalves, M.; Probst, S.; Rezende, M. C.; Nome, F.; Zucco, C.; Zanette, D. *J. Phys. Chem.* **1985**, *89*, 1127.

(22) He, Z. M.; Loughlin, J. A.; Romsted, L. S. *Bol. Soc. Chil. Quim.* **1990**, *35*, 43.

(23) Bunton, C. A.; Gan, L. H.; Moffatt, J. R.; Romsted, L. S.; Savelli, G. *J. Phys. Chem.* **1981**, *85*, 1148.

(24) Forrest, J.; Stephenson, O.; Waters, W. A. *J. Chem. Soc.* **1946**, 333.

(25) Nascimento, M. G.; Miranda, S. F.; Nome, F. *J. Phys. Chem.* **1986**, *90*, 3366.

(26) Rezende, M. C.; Rubira, A. F.; Franco, C.; Nome, F. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1075.

(27) Bowman, M. C.; Acree, F.; Cobert, M. K. *J. Agric. Food Chem.* **1960**, *8*, 406.

Microcalorimetric Investigation of the Solubilization of Water in Reversed Micelles and Water-in-Oil Microemulsions

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Microcalorimetry has been used to study the solubilization of water in reversed micelles and water-in-oil (w/o) microemulsions. The systems were based on Aerosol OT (AOT) and two isomerically pure sodium alkylarenesulfonates as surfactants. The solubilization of water can be described in terms of hydration of the head group (ca. three H_2O molecules per AOT), swelling of the water droplet, and phase separation. All steps are endothermic, indicating that a gain in entropy is the driving force for solubilization. Above 60 °C the hydration energy for AOT is strongly affected by temperature. The swelling of alkylarenesulfonate w/o microemulsions droplets in *n*-heptane is more endothermic than that of AOT w/o microemulsion droplets in *n*-heptane, indicating a significant influence of surfactant structure.

Introduction

In apolar solvents surfactants such as sodium bis(2-ethylhexyl)sulfosuccinate (Aerosol OT, AOT) form aggregates, which are able to solubilize large quantities of water in oil.[1-3] These systems are often referred to as reversed micelles if the number of water molecules per surfactant molecule (W) is smaller than 12 and as water-in-oil microemulsions[4] if W is larger than 12.

W/o microemulsions have a variety of possible and actual applications in fields such as biotechnology, separation processes, and preparation of microparticles.[2,5-10] Physicochemical properties of reversed micelles and w/o microemulsions have been investigated using several physical techniques. Emphasis has been placed, in particular, on the role of water, and most of the results have been interpreted in terms of the model of Zinsli,[11] in which it is assumed that in a w/o microemulsion droplet two types of water exist: (i) water molecules bound to the head groups in the oil-water interface and (ii) free water, which behaves as bulk water. Fluorescence,[11-14] IR and Raman,[15,16] NMR,[17-22] ESR,[22] and DSC measurements[22,23] indicate that the physicochemical properties of AOT reversed micelles change strongly with water content if W is smaller than 6-10. For larger values of W, the behavior of the water is similar to that of bulk water. Light scattering and neutron scattering show that an increase in aggregate growth rate is observed at $W > 12$, which is indicative of the transition of reversed micelles to w/o microemulsions.[24,25] It appears that in this region the micellar size depends linearly on W.[3,24-26] Recently, it has been shown by Maitra and co-workers that, on the basis

of IR measurements, it is better to distinguish three types of water molecules. Besides the bound water molecules and the free water molecules, 1-2 water molecules can be trapped between the head groups, having no hydrogen bond interaction with their surroundings.[16,27] If the water content of the system is increased still further, a phase boundary is passed.[28,29] The exact location of the boundary and the phase types formed, i.e., a w/o microemulsion with water or two microemulsions, depends on the oil and the temperature.[28,29]

Although water-induced alterations in the structure of reversed micelles and w/o microemulsions have been studied in detail,[1-4,11-26] not much is known about the heat effects associated with these alterations. Thus, insight into the strength of various interactions in these systems is almost lacking. As far as the authors know, there have been only three investigations (all based on AOT) in which the heat effects associated with the solubilization of water in these systems have been measured.[30-32] References 30 and 31 show that the solubilization of water is endothermic, so driven by a gain in entropy. By applying a model to interpret the calorimetric data, D'Aprano et al. calculated that the solubilization of the first water molecules is associated with an endothermic heat effect of ca. 750 J/mol H_2O and that approximately six water molecules per surfactant molecule are bound to the interface.[31]

Here we report our microcalorimetric measurements on AOT-based reversed micelles and w/o microemulsions from 25 to 80 °C. The measurements were performed by titrating small quantities of water or w/o microemulsions into a solution of reversed micelles or w/o microemulsions. As a result, the heat effects associated with head group hydration and alterations in