TABLE III: Summary of Dimerization Constants (20-25 °C) of the Secondary Amides as a Function of Solvent

solvent	dielectric constant ^a	<i>K</i> , M ⁻¹		
		cis lactams	NMA	
CCl ₄ C ₆ H ₆ CHCl ₃ dioxane H ₂ O	2.23 2.28 4.70 2.21 78.5	100-15020-45b1-30.4d0.014f	$24 \\ 6.1^{c} \\ 2.7-2.8 \\ 0.5^{e} \\ 0.005^{e}$	

^a Reference 33. ^b References 8, 21, 26, and 28. ^c Reference 29. ^d Reference 4. ^e Reference 11. ^f Reference 3.

two opposing influences on the position of the equilibrium. Considering the geometries of the cis vs. trans secondary amide dimers (cyclic vs. open-chain) and their respective dipole moments, NMA dimers would be expected to be much more prone to stabilization by solvation (e.g., by hydrogen bonding of terminal carbonyl groups with CHCl₃) than would be so for the closed dimers of the lactams. which have no polar terminal groups. Granted, solvation of the monomers is a major process inhibiting the dimerization reaction of both amide classes and resulting therefore in lower dimerization constants. Nonetheless, a change from a less to a more solvating solvent is expected, at the same time then, to exert an opposing favorable effect on displacement of the dimerization equilibrium toward formation of dimer much more so in the case of NMA than would be so for the cis lactams. The greater likelihood of partial nullification of the inhibitory effect of monomer solvation by solvent stabilization of the dimer product in the former case but the operation primarily of the inhibiting solvent effect in the latter compounds might therefore be expected to lead to convergence of the values of K_{dimer} for the two classes of secondary amides as the possibility of solute-solvent interaction increases, as is observed in the present study.

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The consistency of the above argument and the role which the mechanism of solvation plays on the magnitude of the dimerization constants can be seen from a comparison of the K's for the cis lactams vs. NMA as a function of a range of solvents. The first three rows of Table III illustrate the relationship between solvent polarity. magnitude of K, and solvent leveling effect proposed. The data in the table, however, also indicate that the chemical nature of the solvent plays a more important role than does merely dielectric constant in influencing the extent of self-association of the secondary amides. For example, despite the near-equality of the dielectric constants of CCL. $C_6\dot{H}_6$, and dioxane, K_{dimer} decreases dramatically according to solvent in that order. The extrapolar effects operative here and responsible for the observed order must include specific solvation of the amide grouping via the electrondonating properties of the π -electron system in the case of benzene^{17,28,28} and via the proton-accepting properties of the ether oxygen atoms in the case of dioxane.⁴ Clearly, the latter hydrogen-bonding effect is a dominant influence based on the magnitude of the change in K occurring relative to CCl₄ solution. In this regard it is instructive to note that, based on the successive order-of-magnitude difference in the K's measured in the three hydrogenbonding solvents compared in Table III, the order of solvating ability toward the secondary amide grouping is proton donor < proton acceptor < amphiprotic. This suggests that the acidic properties of the N-H group exert a greater driving force in involving the amide grouping in hydrogen-bonded interactions than does the basicity of the carbonyl group. As expected, if both sites are "neutralized" (H_2O) , amide self-association becomes minimal.

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Limitations of the Pseudophase Model of Micellar Catalysis. The Dehydrochlorination of 1,1,1-Trichloro-2,2-bis(p-chlorophenyl)ethane and Some of Its Derivatives

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The dehydrochlorination of 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane (DDT), 1,1-dichloro-2,2-bis(pchlorophenyl)ethane (DDD), and 1-chloro-2,2-bis(p-chlorophenyl)ethane (DDM) with hydroxide ion was studied in the presence of hexadecyltrimethylammonium bromide (CTAB) micelles at 25.0 °C. The experimental results indicate that there is good agreement between the experimental results and theoretical models of micellar catalysis for (OH) in the range of 10^{-3} - 10^{-2} M. For (OH) values higher than 10^{-2} M, the pseudophase model fails and there is a significant deviation between the theoretically calculated and observed values of the pseudo-first-order rate constant. The experimental results can be explained by considering an additional reaction pathway across the micellar boundary, in which hydroxide ion in the aqueous phase reacts directly with the organic substrate in the micelle. This additional reaction pathway is probably of a phase transfer catalysis type.

Introduction

The role of micelles in the enhancement of the rate of reactions in organic and inorganic chemistry is well-known and has been thoroughly reviewed in the literature.¹⁻¹⁰ In

the last few years, significant progress has been made in the quantitative treatment of the dependence of the rate

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of a particular reaction on the concentration of surfactant. $^{\hat{9},11-21}$ It is generally agreed that micellar catalytic effects in bimolecular reactions are observed only when there is a favorable partition of the substrate and the reactant between the aqueous and micellar phases. Thus, the rate increase and/or decrease observed is explained in terms of changes in concentration and rate constant in the two pseudophases.

The equations used in the kinetic treatment of the rate-surfactant profile in bimolecular reactions (A + B \rightarrow products) are derived from eq 1. The terms k_{2w} and k_{2m}

$$rate = k_{2w}(A)_w(B)_w + k_{2m}(A)_m(B)_m$$
(1)

are the second-order rate constants in the aqueous and micellar phases, and the subscripts w and m refer to incorporation of the reactants in water and micelles, respectively. Indeed, eq 1 is consistent with a phase separation model, where the reaction occurs in the aqueous phase (first term in eq 1) or in both phases.

This treatment appeared to be satisfactory until recently, when Bunton, Romsted, and Savelli²² reported a system in which a partial failure of the pseudophase model occurs. Indeed, in the reactions of 2,4-dinitrochlorobenzene and 2,4-dinitrochloronaphthalene with hydroxide ion in the presence of *p*-octyloxybenzyltrimethylammonium hydroxide, an additional reaction pathway was found. The authors postulated a reaction across the interfacial boundary between micellar bound organic substrate and ionic reactant in the aqueous pseudophase.

Considering that the report of Bunton and co-workers is a major breakthrough in micellar catalysis, we decided to investigate further this subject. Particularly, we were interested in analyzing the possible existence of this additional pathway in reactions catalyzed by hexadecyltrimethylammonium bromide (CTAB).

The reactions chosen for this purpose were the dehydrochlorination of 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane (DDT), 1,1-dichloro-2,2-bis(p-chlorophenyl)ethane (DDD), and 1-chloro-2,2-bis(p-chloro-

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phenyl)ethane (DDM) with hydroxide ion, according to eq 2. The reason for choosing these particular reactions was



that their mechanisms are well understood and that DDT, DDD, and DDM are sparingly soluble in water.²³ Accordingly, they have a very high octanol/water²⁴ partition coefficient. Thus, these systems obviate the possibility of the pathway in the aqueous phase being important, as to obscure the reactions across the interfacial boundary.

Our results support the report of Bunton, Romsted, and Savelli²² and give further evidence for this third reaction pathway as a normal component in micellar catalysis.

Experimental Section

The compounds 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane (DDT) and 1,1-dichloro-2,2-bis(p-chlorophenyl)ethane (DDD) were purchased from Aldrich Chemical Co., and their purity was found to be satisfactory by thin-layer-chromatographic, UV, and IR analyses. The compound 1-chloro-2,2-bis(p-chlorophenyl)ethane (DDM) was prepared by a slight modification of a previously described procedure²⁵ and crystallized several times from ethanol, mp 51-51.5 °C (lit.²⁵ mp 51-51.5 °C). The observed NMR spectra (A₂B₂ aromatic protons multiplet centered at 7.19 ppm, doublet at 3.95 ppm, and triplet at 4.25 ppm, integration 8:2:1) was identical with that reported elsewhere.26

Purification of hexadecyltrimethylammonium bromide (CTAB) has been described.^{1,2} All other materials used were of the best available grade. Aqueous solutions were prepared in distilled water, and the concentration of hydroxide ion was determined by titration.

Rates of dehydrochlorination of DDT, DDD, and DDM were determined following (Shimadzu UV-210-A spectrophotometer) the appearance of 1,1-dichloro-2,2-bis(pchlorophenyl)ethylene (DDE) at 260 nm, 1-chloro-2,2bis(p-chlorophenyl)ethylene (DDMU) at 257 nm, and 1,1-bis(p-chlorophenyl)ethylene (DDNU) at 252 nm, respectively.

The temperature for the kinetic runs was maintained at 25.0 \pm 0.1 °C by using a water-jacketed cell compartment. Individual pseudo-first-order rate constants, $k_{\psi m}$, were obtained from linear plots of $\ln (A_{\infty} - A_t)$ vs. time. All of these plots were linear for at least 90% of the reaction, and the correlation coefficients were greater than 0.99.

Results and Discussion

The dehydrochlorination reaction of DDT, DDD, and DDM with hydroxide ion in aqueous solutions of CTAB

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TABLE I: Pseudo-First-Order Rate Constants for the Reaction of DDT with Base at Different Surfactant Concentration at 25.0 °C

		$k_{\psi m}, s^{-1}$				
10²(KOH), M	10 ³ (CTAB), M	6.00	10.0	30.0	100	
0.10		7.70 × 10 ⁻⁴	6.90 × 10 ⁻⁴	3.00 × 10 ⁻⁴	1.15×10^{-4}	
0.16		1.19×10^{-3}	1.21×10^{-3}	5.90 × 10⁻⁴	1.75 × 10⁻⁴	
0.24		1.71×10^{-3}	1.64×10^{-3}	9.00 × 10 ⁻⁴	2.93 × 10 ⁻⁴	
0.32		2.46×10^{-3}				
0.40			$3.20 imes 10^{-3}$	1.40×10^{-3}	5.64×10^{-4}	
0.43		3.80 × 10⁻³				
0.60		4.56×10^{-3}	4.24×10^{-3}	2.00×10^{-3}	9.18 × 10⁻⁴	
0.80		5.78 × 10 ⁻³		2.50×10^{-3}	9.96×10^{-4}	
0.98		7.67×10^{-3}				
1.00			6.05×10^{-3}	3.20×10^{-3}	1.00×10^{-3}	
1.24			7.35×10^{-3}	3.90×10^{-3}	1.72×10^{-3}	
1.60		1.19×10^{-2}				
1.86			1.01×10^{-2}	6.20×10^{-3}	2.68×10^{-3}	
2.48		1.65×10^{-2}	1.25×10^{-2}	7.20×10^{-3}	3.35×10^{-3}	
3.10		1.36 × 10 ⁻²				
3.72		2.43×10^{-2}	$1.73 imes 10^{-2}$	1.11×10^{-2}	5.30×10^{-3}	
5.58		3.12×10^{-2}				
6.20			2.23×10^{-2}	$1.52 imes 10^{-2}$	9.01×10^{-3}	
6.58			$2.51 imes 10^{-2}$	1.71×10^{-2}		
7.44		$3.93 imes 10^{-2}$	$2.92 imes 10^{-2}$	1.81×10^{-2}		
9.30		$4.39 imes 10^{-2}$		2.14×10^{-2}	1.40×10^{-2}	
11.20		$5.22 imes 10^{-2}$	$4.75 imes 10^{-2}$	$2.32 imes 10^{-2}$		
14.90		6.24×10^{-2}	$5.23 imes 10^{-2}$	2.75×10^{-2}	2.05×10^{-2}	
18.60		6.77×10^{-2}				
22.30		$7.03 imes 10^{-2}$	$6.42 imes 10^{-2}$	3.65×10^{-2}	2.91 × 10 ⁻²	
26.00		8.06×10^{-2}	6.41×10^{-2}	3.88×10^{-2}		
29.80		$8.53 imes 10^{-2}$				
33.50		9.42×10^{-2}	$7.13 imes 10^{-2}$	$5.05 imes 10^{-2}$	$4.16 imes 10^{-2}$	
37.20		1.00×10^{-2}	$7.45 imes 10^{-2}$	$5.58 imes 10^{-2}$		
40.90		1.09×10^{-2}				
63 20					7.57×10^{-2}	

can be considered as a bimolecular reaction between an uncharged substrate and a univalent ion of charge opposite to the surfactant. Since the concentration of hydroxide ion in the micellar phase is dependent upon the concentrations of bromide ion and surfactant, any quantitative treatment of the reaction rate will have to consider ionexchange phenomena occurring on the micellar surface. The model proposed by Quina and Chaimovich¹⁸ that can be reduced to eq 3 has been used for this purpose.

$$k_{\psi m} = \frac{\left[\frac{k_{2m}}{\bar{V}}K_{s}K_{OH/Br}\frac{(Br)_{m}}{(Br)_{w}} + k_{2}^{0}\right](OH)_{T}}{(1 + K_{s}C_{D})(1 + K_{OH/Br}(Br)_{m}/(Br)_{w})}$$
(3)

Equation 3^{18} describes the theoretical dependence of the observed pseudo-first-order rate constant, $k_{\psi m}$, as a function of the total concentration of hydroxide ion, (OH)_T.

The term k_{2m} is the second-order rate constant in the micellar phase, \vec{V} is the effective volume per mole of micellized detergent, K_s represents the binding constant for the substrate, $K_{OH/Br}$ represents the ion-exchange constant, k_2^{0} is the second-order rate constant in the aqueous phase, C_D represents the concentration of micellized detergent, and the subscripts m and w in the concentration terms refer to incorporation of the reagents in the micellar and aqueous phases, respectively.

In order to test the validity of eq 3 in a quantitative way, we measured the dependence of $k_{\rm ym}$ on the total hydroxide ion concentration. Table I contains the pseudo-first-order rate constants for the reaction of DDT with hydroxide ion as a function of surfactant and hydroxide ion concentrations.

As can be observed, for any given concentration of base there is a decrease in the value of $k_{\psi m}$ with increasing surfactant concentration. This behavior is normally found in CTAB-catalyzed bimolecular reactions.^{1,3,9} However, at constant surfactant concentration, the increase in $k_{\psi m}$ is not linearly dependent on the total hydroxide ion added to the system. An identical behavior was observed by using DDD and DDM as substrates (Table II).

Considering that the solubility of DDT in water at 25.0 °C is of the order of 0.2–1.2 ppb and that in the presence of 6.0×10^{-3} M CTAB a concentration of 1.0×10^{-5} M DDT can be easily solubilized, the K_s value in eq 3 can be estimated from (DDT)_m/(DDT)_w = 1 + K_sC_D to be higher than 5.0×10^5 M⁻¹. Accordingly, eq 3 can be simplified to a more convenient expression, since $K_sC_D \gg 1$ and the molar fraction of organic substrate in the aqueous phase approaches zero (eq 4).

$$k_{\psi \mathrm{m}} = \frac{k_{\mathrm{2m}}}{C_{\mathrm{D}}\bar{V}}(\mathrm{OH})_{\mathrm{T}} \frac{K_{\mathrm{OH/Br}}(\mathrm{Br})_{\mathrm{m}}/(\mathrm{Br})_{\mathrm{w}}}{1 + K_{\mathrm{OH/Br}}(\mathrm{Br})_{\mathrm{m}}/(\mathrm{Br})_{\mathrm{w}}}$$
(4)

The broken lines in Figure 1A-F show the result of the treatment of the experimental data with eq 4. Values of 0.08 for $K_{\text{OH/Br}}$ and 0.37 for \bar{V} were used. The concentration of bromide ion in the micellar and aqueous phases was calculated according to Quina and Chaimovich,¹⁸ using a value of 0.2 for the degree of ionization, α .

As can be seen, for (OD) between 10^{-3} and 10^{-2} M there is a good agreement between the experimental data and the theoretical line calculated by means of eq 4 for all cases. However, at (OH) values higher than 10^{-2} M a significant deviation from the theoretically calculated result is observed, the increase in $k_{\forall m}$ being greater than predicted by the ion-exchange theory. The values of k_{2m} that were obtained for the best fit of the experimental data are given in Table III. A small but consistent increase in k_{2m} is observed with increase in surfactant concentration. This fact also indicates a lack of validity of the ion-exchange model of Quina and Chaimovich¹⁸ in the pH range studied, since k_{2m} should be independent of surfactant concentration.

TABLE II: Pseudo-First-Order Rate Constants for the Reaction of DDD with Base in the Presence of 6.0×10^{-3} M CTAB at 25.0 °C

$k_{\psi m}, s^{-1}$			$k_{\psi m}, s^{-1}$		
10²(KOH), M	DDD	DDM	10°(KOH), M	DDD	DDM
0.16	1.15×10^{-4}		7.44	3.69×10^{-3}	
0.24	1.63×10^{-4}		9.92		3.35×10^{-4}
0.32	$2.30 imes 10^{-4}$	$2.20 imes10^{-5}$	11.2	$5.46 imes 10^{-3}$	
0.40	2.72×10^{-4}		14.9	7.06×10^{-3}	5.36×10^{-4}
0.48	$3.47 imes 10^{-4}$		18.6	7.15×10^{-3}	5.94 × 10 ⁻⁴
0.50		3.60 × 10 ⁻⁵	20.1		6.79×10^{-4}
0.62	4.38×10^{-4}		22.3	$8.72 imes 10^{-3}$	
0.70		$4.92 imes 10^{-3}$	26.0	9.42×10^{-3}	7.75×10^{-4}
0.80	$6.08 imes 10^{-4}$		29.8	9.55×10^{-3}	
0.98	6.66×10^{-4}	6.80×10^{-5}	33.5	1.16×10^{-2}	
1.55		1.11×10^{-4}	37.2	1.04×10^{-2}	9.14×10^{-4}
1.60	$1.07 imes 10^{-3}$		40.9	1.31×10^{-2}	
1.89	$1.34 imes 10^{-3}$		47.0	1.37×10^{-2}	9.95×10^{-4}
2.48	1.71×10^{-3}	1.56 X 10 ⁻⁴	58.8		1.21×10^{-3}
3.10	$2.13 imes 10^{-3}$		70.6		1.44×10^{-3}
3.72	2.42×10^{-3}	$2.12 imes10^{-4}$	82.3		1.51×10^{-3}
4.96	3.00×10^{-3}		94.1		1.78×10^{-3}
6.20	3.56×10^{-3}	2.97 × 10⁻⁴			



Figure 1. Plot of the logarithm of the observed pseudo-first-order rate constant vs. the logarithm of the total hydroxide ion concentration for the dehydrochlorination of DDT at 25.0 °C at CTAB concentrations of (a) 6×10^{-3} , (b) 10×10^{-3} , (c) 30×10^{-3} , and (d) 100×10^{-3} M and for the dehydrochlorination of DDD (e) and DDM (f) at a CTAB concentration of 6×10^{-3} M.

Several other models proposed in the literature¹¹⁻¹⁷ were used to try to explain our experimental data and the same trends were observed. This is really not surprising, since all of them essentially involve a partitioning of the substrate and the reactant between the aqueous and micellar phases and correspond in principle to ion-exchange phenomena that are in the final analysis dependent on a limited number of sites. Otherwise, the system becomes a thermodynamically open one and the assumptions about partition coefficients are no longer valid.

A possible way to explain the discrepancy between the experimental results and the theoretical models so far

 TABLE III:
 Kinetic Parameters Obtained with the

 Theoretical Treatment of the Data
 Item (Content of the Data)

sub- strate	(CTAB), M	$k_{2m}^{a}, M^{-1} s^{-1}$	${{k_{2m}, }^{b}} {{M^{ - 1} {{s^{ - 1}}}}}$	${k_{2}}{m/w}, {b_{1}}{M^{-1}}{s^{-1}}$
DDT	6.0×10^{-3}	1.30×10^{-2}	1.30×10^{-2}	2.20×10^{-1}
DDT	1.0×10^{-2}	$1.57 imes 10^{-2}$	1.40×10^{-2}	$1.33 imes 10^{-1}$
DDT	$3.0 imes 10^{-2}$	1.80×10^{-2}	1.40×10^{-2}	$7.84 imes 10^{-2}$
DDT	1.0×10^{-1}	1.95×10^{-2}	1.40×10^{-2}	$7.80 imes 10^{-2}$
DDD	6.0×10^{-3}	1.10×10^{-3}	4.00×10^{-4}	5.00×10^{-2}
DDM	6.0×10^{-3}	1.20×10^{-4}	1.00×10^{-4}	$2.40 imes10^{-3}$

^a Obtained from fitting of the data with eq 4. ^b Obtained from fitting of the data with eq 5.

$$k_{\psi m} = \frac{k_{2m} (OH)_{T} K_{OH/Br} (Br)_{m} / (Br)_{w}}{C_{D} \bar{V} [1 + K_{OH/Br} (Br)_{m} / (Br)_{w}]} + k_{2m/w} (OH)_{T}$$
(5)

ond-order rate constant for the reaction pathway at the micellar-water interface.

The solid lines in Figure 1A-F represent the result of the analysis of the experimental data by means of eq 5. As can be seen, there is a good correlation between experimental values of $k_{\psi m}$ and values obtained by using the adjusted theoretical model described above. The numerical values of k_{2m} and $k_{2m/w}$ obtained for the best fitting of the experimental data are given in Table III. The second-order rate constant in the micellar phase, k_{2m} , is truly constant within experimental error, a result to be expected. Conversely, $k_{2m/w}$ decreases with an increase in surfactant concentration. However, since the exact nature of $k_{2m/w}$ is unknown, this matter remains to be investigated in detail.

Our results represent the first experimental evidence for the presence of an additional reaction pathway across the micellar-water interface in normal micellar systems, and they fully support the recent proposal of Bunton and his co-workers²² which was based on data obtained with reactive counterion-type micelles.

The additional reaction pathway proposed by Bunton and his collaborators,²² between hydroxide ion in water and the substrate in the micelle, takes place across the interfacial boundary (shear surface) between the Stern and Gouy-Chapman layers of the micelle.²² Conceptually, this interfacial boundary or micellar-water interface, as it has been called, should not be much different from the interface present in systems where phase transfer catalysis is taking place. If such is the case, then a possible explanation of the experimental results could be in terms of an additional reaction pathway that is of the type commonly encountered in phase transfer catalysis.^{26,27} Such a pathway should lead to a linear or exponential increase in $k_{\psi m}$ at high hydroxide concentration. At relatively high OH⁻ concentration, the catalysis observed would be essentially of a phase transfer type and the second term in eq 5, i.e., $k_{2m/w}$ (OH)_T, becomes preponderant until the

process of catalysis is stopped by diffusion barriers due to the formation of gells or liquid crystals.

Additional experimental data in other systems and over a wider range of hydroxide ion is needed in order to understand better the nature of the catalysis involved and the significance of $k_{2m/w}$. However, there appears to be no doubt that the pseudophase model of micellar catalysis fails for dehydrochlorination reactions of DDT, DDD, and DDM at hydroxide concentrations higher than approximately 0.02 M in the presence of micelles of CTAB.

Recent results by Bunton and his associates estimate that the volume of the Stern layer is approximately half the volume of the micelle.²² Clifford and Pethica treated the inner part of the double layer as an approximately 5-Å thick concentrated solution.²⁸

On the other hand, Aniansson²⁹ has concluded that the protrusion of monomers, as well as the resulting increase in electric potential away from the micellar surface, leads to an increase in the effective size of the micelle. He deduced that, for a micelle with aggregation number of 62, on the average eight monomers with protrude more than 4 Å and three more than 6 Å. The micelles are thus characterized by a relatively large and rough surface area. Aniansson²⁹ has also concluded that, for the case of monolayer interfaces between water solution and air, oil, or hydrophobic solid surfaces, the protrusion would be even larger. A high degree of roughness at the micellar-water interface would of course imply a very large surface area available for catalysis. The presence of certain counterions in solution may increase or decrease the total available surface, and thus the idea of a fixed number of ion-exchange sites loses its meaning in a theoretical treatment.

Preliminary results that we have obtained for the hydrolysis of lithium *p*-nitrophenyl phosphate with CTAB micelles using OH⁻ in the 0.01–5.00 M range³⁰ indicate that for hydroxide ion concentrations above 2 M there is a total breakdown of the pseudophase model and that the pseudo-first-order rate constant, $k_{\rm ym}$, increases almost exponentially as a function of hydroxide ion. We are currently continuing our investigations with several reactions at limit conditions in order to arrive at a more general treatment for micellar catalysis, which would be useful for the whole range of hydroxide ion concentration.

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