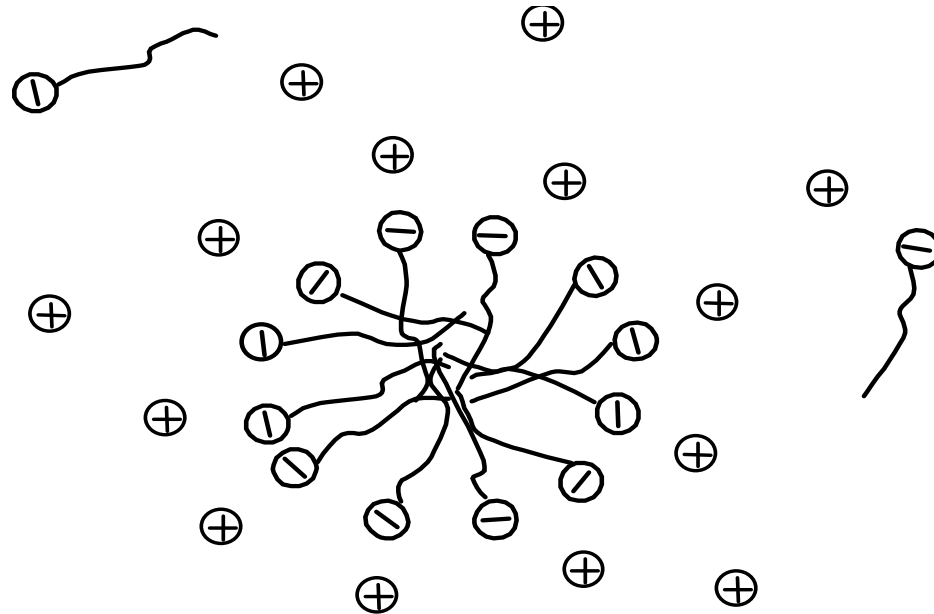


MICELLES OF COLLOIDAL SURFACTANTS



Investigations of surfactant micelles using indicators

1. Acid-base indicators
2. Solvatochromic indicators
3. Fluorescent indicators

Acid-base indicators as molecular probes

Hartley 's rules

THE EFFECT OF LONG-CHAIN SALTS ON INDICATORS: THE VALENCE-TYPE OF INDICATORS AND THE PROTEIN ERROR.

BY G. S. HARTLEY.

Received 8th March, 1934.

The pH range of color transition of indicators, bound to cationic micelles, shifts toward the acidic region, and in the case of anionic surfactants the effect is reverse

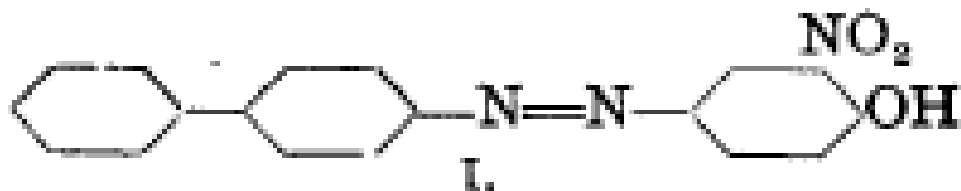
Acid-base indicators as molecular probes

A next pioneering work by Hartley

IONIC CONCENTRATIONS AT INTERFACES.

BY G. S. HARTLEY AND J. W. ROE.

Received 7th August, 1939.



(Application of an acid-base indicator readily attached to surfactant micelles)

What does it mean?

$$(P_K)_s = P_K - \zeta/60$$

$$(pH)_s = (pH)_b + \zeta/60$$

Current state of the problem

Pure Appl. Chem., Vol. 80, No. 7, pp. 1459–1510, 2008.

doi:10.1351/pac200880071459

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Protolytic equilibrium in lyophilic nanosized dispersions: Differentiating influence of the pseudophase and salt effects*

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Abstract: The so-called apparent ionization constants of various versatile organized solutions are analyzed. Aqueous micelles and related lyophilic colloidal systems display a strong acidic strength of indicators located in the dispersed pseudophase. The change of pK_a on going from water to the given system. This confirms the differentiating influence of the dispersed pseudophase on acid–base properties of dissolved reagents to be rather significant. The differentiating phenomenon is the main reason for limiting the model of acid–base interactions, and is the principal hindrance in the study of interfacial electrical potentials of ionic micelles by means of potentiometry. The influence of supporting electrolytes on the acid–base indicators in the Stern region of ionic micelles, can be conventionally divided into two kinds, namely, general and specific effects. While the first type adds up to screening of the surface charges, the second consists in micellar transitions caused by hydrophobic counterions.

Keywords: protolytic equilibrium; lyophilic dispersions; differentiating influence; salt effects.

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Chapter 1

ACID-BASE EQUILIBRIUM IN AQUEOUS MICELLAR SOLUTIONS OF SURFACTANTS

*Nikolay O. Mchedlov-Petrosyan**, *Natalya A. Vodolazka*

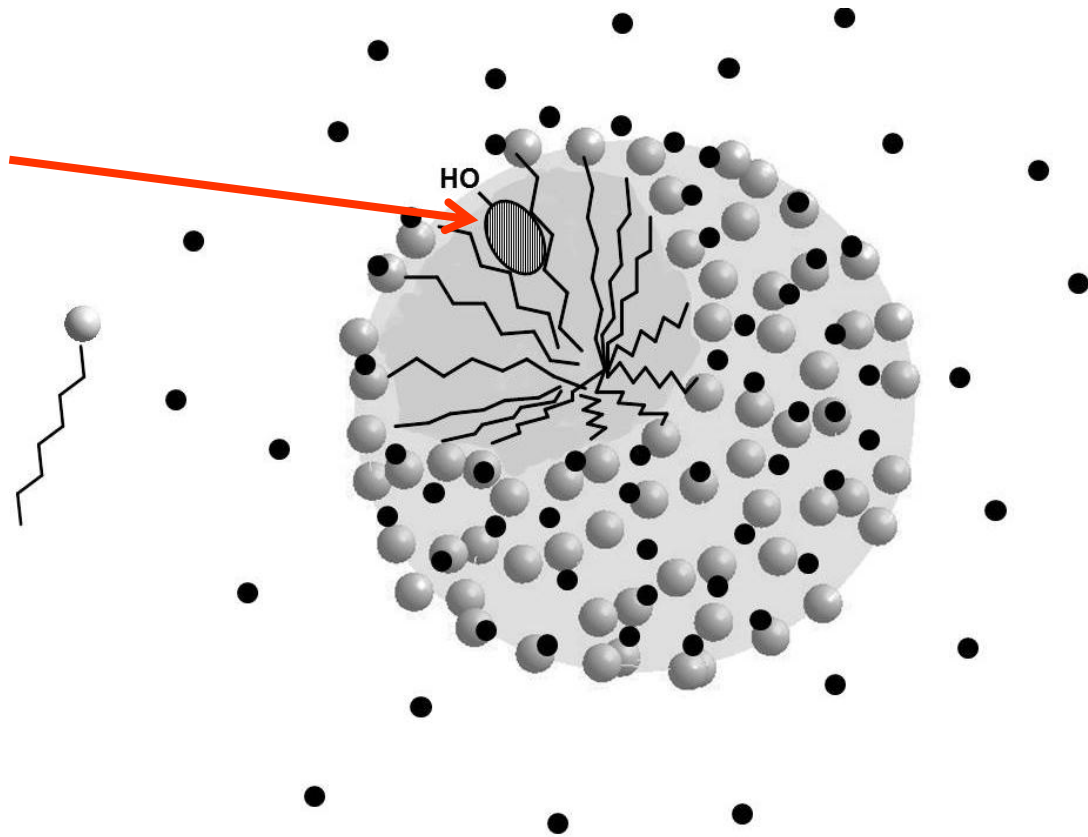
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ABSTRACT

Molecular probes: Acid-base indicators fixed in micelles

$$pK_a^{\text{app}} = \text{pH}_w + \log \frac{[\text{HA}]_m}{[\text{A}]_m}$$



The ionic micelle with an acid-base indicator molecule; grey and black circles depict the **head groups** and **counter-ions**, respectively.

Dissociation constant of an acid in solution



Omitting the ionic charges for the sake of simplicity:

Thermodynamic dissociation constant $\longrightarrow K_a = a_{\text{H}^+} \frac{a_{\text{A}}}{a_{\text{HA}}}$; a_i are activities

“Mixed“ dissociation constant $\longrightarrow K_a^* = a_{\text{H}^+} \frac{[\text{A}]}{[\text{HA}]}$; $[i]$ are equilibrium concentrations

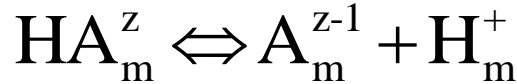
Index of the dissociation constant, $\text{p}K_a^* = -\log K_a^*$

$\text{p}K_a^* = \text{pH} + \log \frac{[\text{HA}]}{[\text{A}]}$ \leftarrow Determined via spectrophotometry, or fluorometry, ESR., etc.

\downarrow
Determined using a glass electrode in a cell with liquid junction

Acid-base indicators under conditions of complete binding

Now let us consider an **indicator involved into the micellar pseudophase**



$$K_a^m = a_{\text{H}^+}^m \frac{a_{\text{A}}^m}{a_{\text{HA}}^m}; \quad a_i^m \text{ are activities in the micellar pseudophase}$$

Partition between two phases: Equilibrium conditions

$$\mu_i^w = \mu_i^m \quad (\text{for non-electrolytes})$$

$$\tilde{\mu}_i^w = \tilde{\mu}_i^m \quad (\text{for ionic compounds})$$


$$\mu_i^{0w} + RT \ln a_i^w = \mu_i^{0m} + RT \ln a_i^m + z_i \Psi F$$

$$\frac{a_i^m}{a_i^w} = \exp \frac{\mu_i^{0w} - \mu_i^{0m} - z_i \Psi F}{RT}$$

$$\frac{a_i^m}{a_i^w} = \exp \frac{\mu_i^{0w} - \mu_i^{0m} - z_i \Psi F}{RT}$$

$$\frac{a_i^m}{a_i^w} = P_i = \exp \frac{\mu_i^{0w} - \mu_i^{0m}}{RT} \exp \frac{-z_i \Psi F}{RT}$$

$$\frac{a_i^m}{a_i^w} = P_i = \gamma_i^{-1} \exp \frac{-z_i \Psi F}{RT}$$

Activity coefficients of transfer of “i”
from water to micellar pseudophase  $\gamma_i = \frac{\mu_i^{0m} - \mu_i^{0w}}{RT}$

The pH values on the charged micellar surface

$$\frac{a_{\text{H}^+}^{\text{m}}}{a_{\text{H}^+}^{\text{w}}} = \gamma_{\text{H}^+}^{-1} \exp \frac{-1 \times \Psi F}{RT}$$

$$\text{pH}_{\text{m}} = \text{pH}_{\text{w}} + \frac{\Psi F}{2.303RT} + \log \gamma_{\text{H}^+}$$

$$\frac{\Psi F}{2.303RT} = \frac{\Psi}{59.16}$$

(Ψ in mV;

$T = 298.15 \text{ K}$)

glass electrode (H^+) | H^+ in water | 1 M KCl | AgCl | Ag

(cell with liquid junction)

$$K_a^w = a_{H^+}^w \frac{a_A^w}{a_{HA}^w}; \quad \text{in water}$$

$$K_a^m = a_{H^+}^m \frac{a_A^m}{a_{HA}^m}; \quad \text{in the micellar pseudophase}$$

$$\frac{K_a^w}{K_a^m} = \frac{a_{H^+}^w}{a_{H^+}^m} \frac{a_A^w}{a_A^m} \frac{a_{HA}^m}{a_{HA}^w} = P_{H^+}^{-1} \times P_A^{-1} \times P_{HA} =$$

$$\gamma_{H^+} \times \gamma_A \times \gamma_{HA}^{-1} \times \exp \frac{-\Psi F(1-1+0)}{RT} = \gamma_{H^+} \times \gamma_A \times \gamma_{HA}^{-1}$$

$$pK_a^m - pK_a^w = \log \gamma_{H^+} + \log \gamma_A - \log \gamma_{HA}$$

$\Psi - ?$

Hence, in this equation the electrical potential is absent

The concept of the “apparent” dissociation constant

$$pK_a^{\text{app}} = \text{pH}_w + \log \frac{[\text{HB}^z]_t}{[\text{B}^{z-1}]_t} \quad \text{“t” means “total”}$$

If the indicator is fixed in the micellar pseudophase:

$$pK_a^{\text{app}} = \text{pH}_w + \log \frac{[\text{HA}]_m}{[\text{A}]_m} \quad \text{“m” means “in micelles”}$$

$$\frac{K_a^w}{K_a^{\text{app}}} = \frac{a_A^w}{a_A^m} \frac{a_{\text{HA}}^m}{a_{\text{HA}}^w} = P_A^{-1} \times P_{\text{HA}} = \gamma_A \times \gamma_{\text{HA}}^{-1} \times \exp \frac{-\Psi F (z_{\text{HA}} - z_A)}{RT}$$

$$pK_a^{\text{app}} = pK_a^w + \log \frac{\gamma_A}{\gamma_{\text{HA}}} - \frac{\Psi F}{2.303RT}$$

$\Psi - !$

Now, the equations in the paper by Hartley and Roe (1940) are understandable

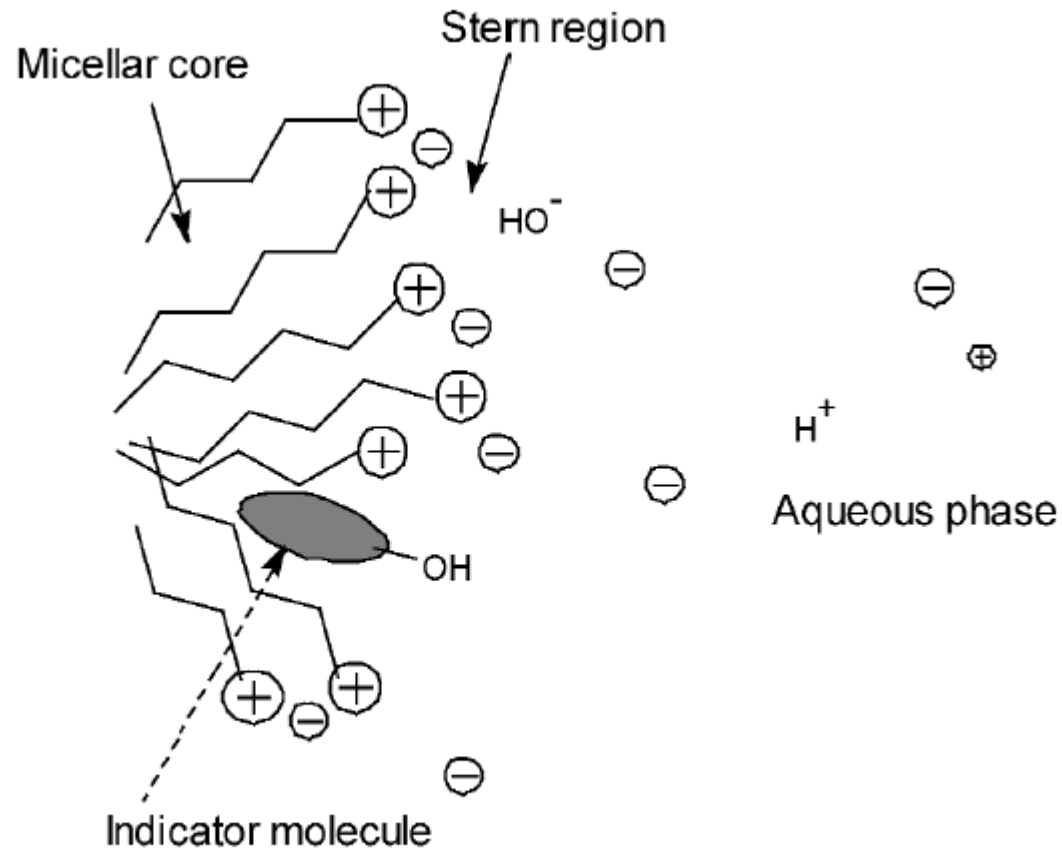
$$(p_{\mathbf{H}})_s = (p_{\mathbf{H}})_b + \zeta/60 \qquad \text{pH}_m = \text{pH}_w + \frac{\Psi F}{2.303RT} + \log \gamma_{\mathbf{H}^+}$$

$$(P_{\mathbf{K}})_s = P_{\mathbf{K}} - \zeta/60 \qquad \text{p}K_a^{\text{app}} = \text{p}K_a^w + \log \frac{\gamma_A}{\gamma_{\text{HA}}} - \frac{\Psi F}{2.303RT}$$

The last equation is used for determination of Ψ

Examining of surfactant micelles using indicators

The concept of the apparent dissociation constant

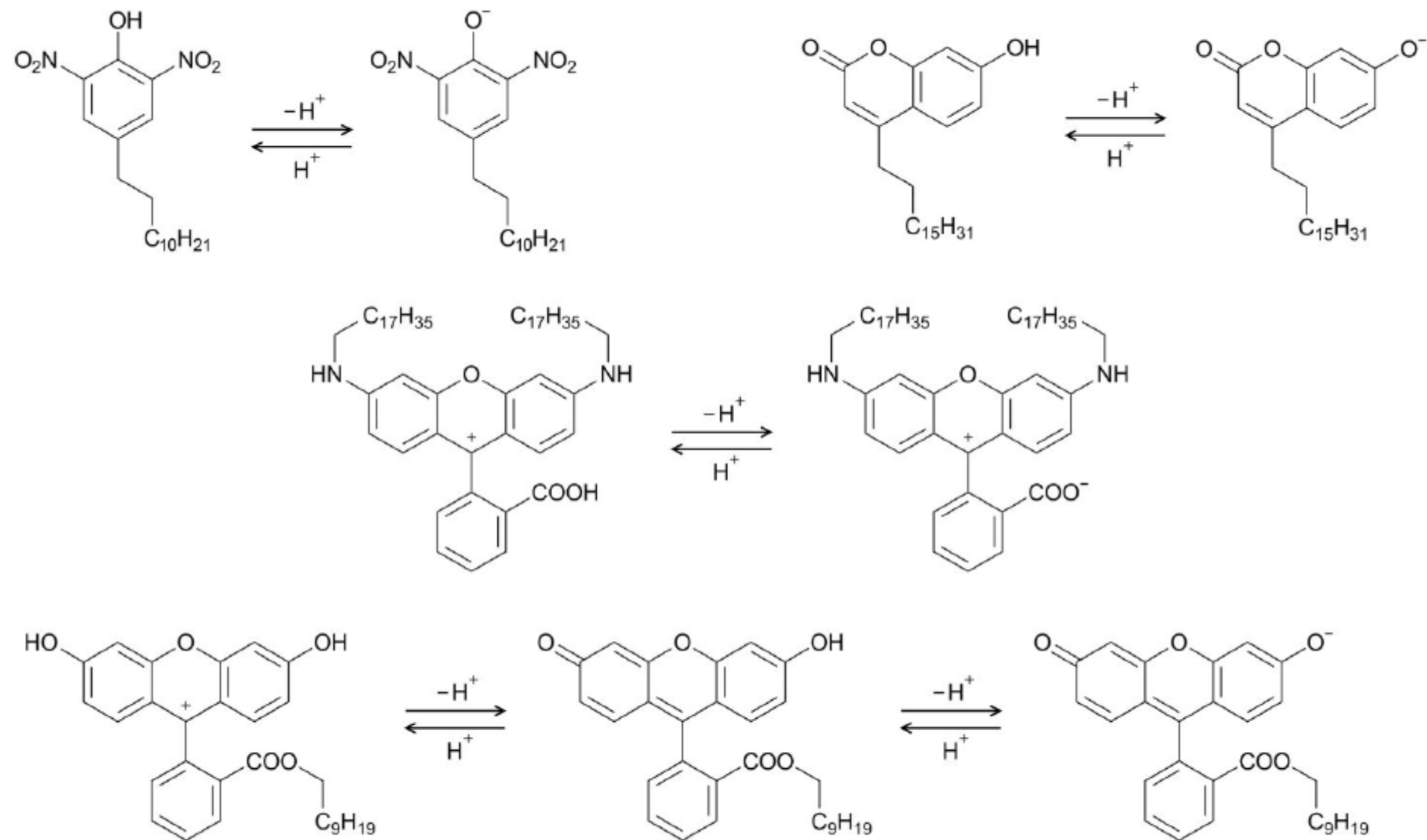


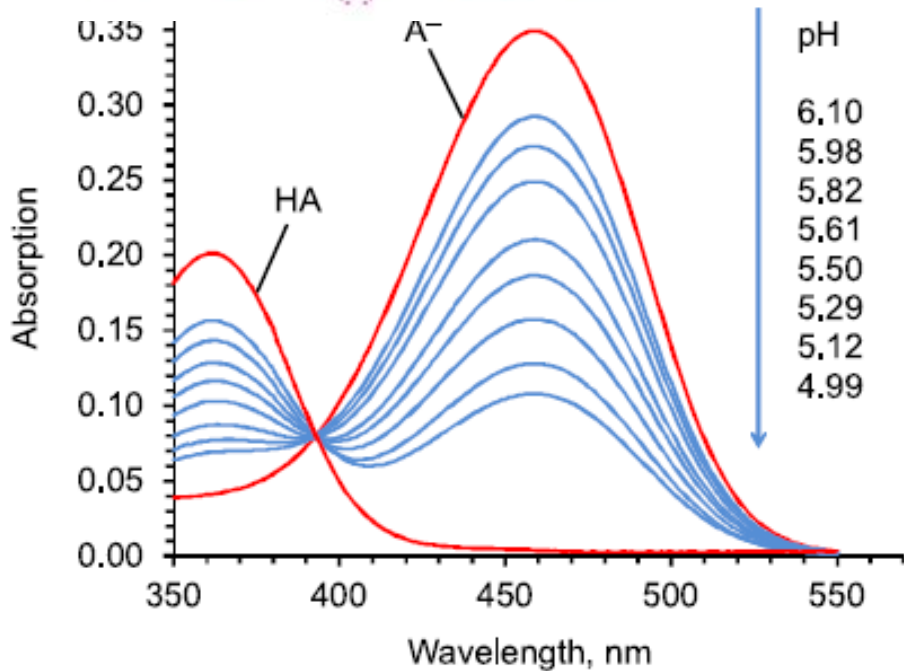
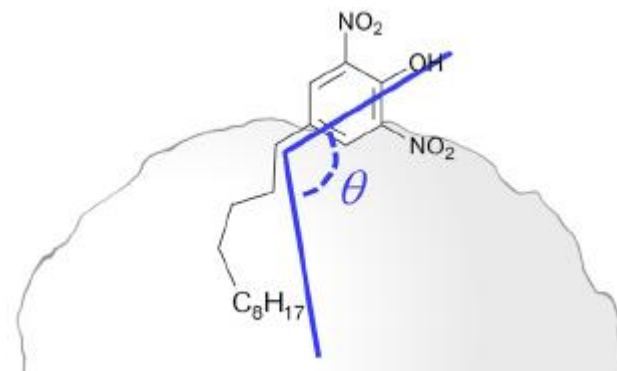
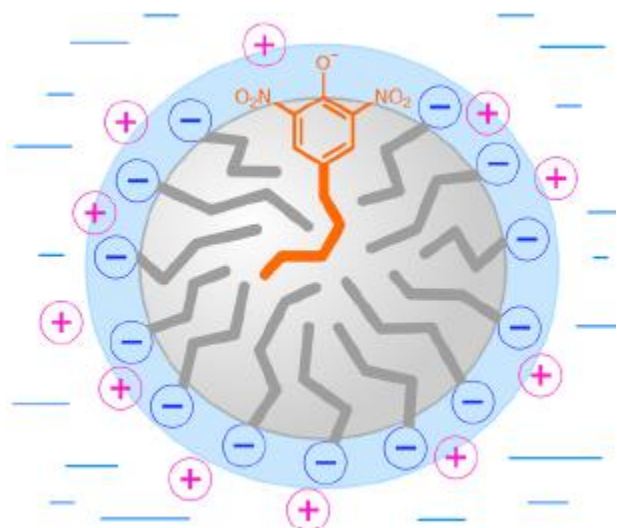
A schematic picture of a fragment of a cationic micelle with an embedded indicator.

Most important conditions

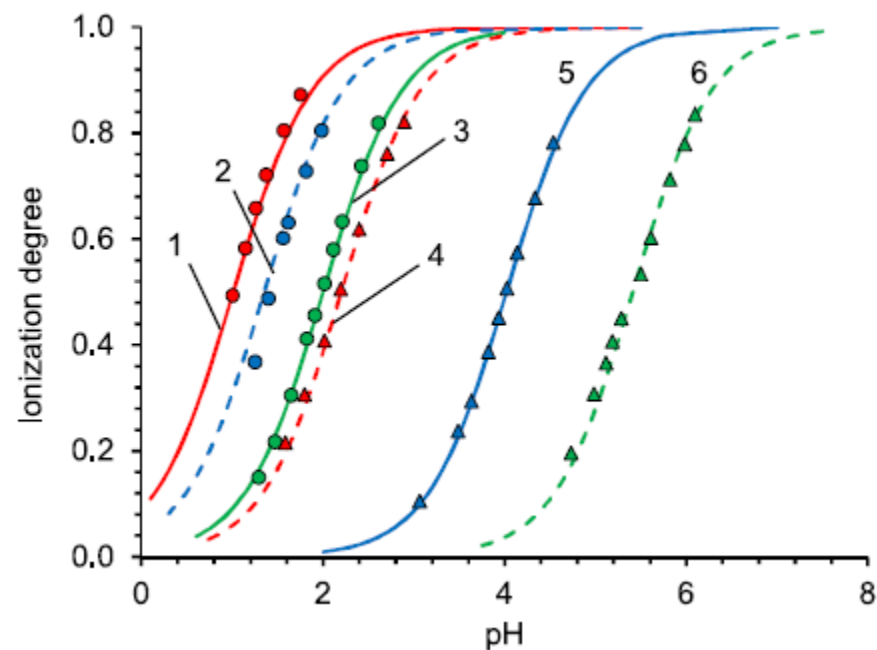
- 1) The micellar pseudophase occupies only a small part of the total volume (about **1 % or even lower**).
- 2) The number of micelles is not less than the number of indicator molecules; *i.e.*, there is **no more than one indicator molecule per micelle**.
- 3) The above equation is valid for an indicator **completely bound** to the pseudophase. Normally, this is ensured by “attaching” a long hydrophobic hydrocarbon tail.

Some representative acid-base long-tailed indicators





SDS micelles, 0.10 M NaCl



CPC (1); CTAB (2,4); CDAPS (3); TX-100 (5); SDS (6); 0.10 M NaCl (1-3, 5,6) and 4 M KCl (4)

Hartley 's rules

$$pK_a^{\text{app}} = pK_a^{\text{w}} + \log \frac{\gamma_A}{\gamma_{\text{HA}}} - \frac{\Psi F}{2.303RT}$$

Not taken into account in
earlier works

Medium effects:



$$pK_a^{\text{app}} - pK_a^{\text{w}} = \log \frac{\gamma_A}{\gamma_{\text{HA}}} - \frac{\Psi F}{2.303RT}$$

In cationic surfactant micelles

$$\Delta pK_a = pK_a^{\text{app}} - pK_a^{\text{w}}$$

Table 3. The indices of the apparent ionization constants in CTAB micellar solution, at low bulk Br⁻ concentrations; 20–25 °C

Indicator dye	Charge type	Br ⁻	pK _a ^{app,c}	ΔpK _a ^{app,c}
Bromophenol blue, pK _{a,2} ^a	HB ⁻ /B ²⁻	0.011	2.26	-1.94
Bromocresol green, pK _{a,2} ^a	HB ⁻ /B ²⁻	0.011	3.47	-1.43
Bromothymol blue, pK _{a,2} ^a	HB ⁻ /B ²⁻	0.011	6.59	-0.71
Thymol blue, pK _{a,2} ^a	HB ⁻ /B ²⁻	0.011	8.90	-0.30
Fluorescein, pK _{a,2} ^b	HB ⁻ /B ²⁻	0.030	5.81	-0.99
HHC, pK _{a,1} ^c	HB ⁰ /B ⁻	0.014	6.48	-1.49
2-Nitro-4- <i>n</i> -nonylphenol, pK _{a,1} ^d	HB ⁰ /B ⁻	< 0.01	5.86	-1.61
Di-(4-nitrophenyl)cyanomethane, pK _{a,1} ^e	HB ⁰ /B ⁻	< 0.01	5.75	-4.60
Fluorescein, pK _{a,1} ^b	H ₂ B ⁰ /HB ⁻	0.030	4.48	+0.03
Fluorescein, pK _{a,1} ^{COOH b,f}	H ₂ B ⁰ /HB ⁻	0.030	3.10	-0.39
4-Octadecyloxy-1-naphthoic acid, pK _{a,1} ^g	HB ⁰ /B ⁻	0.014	4.20	+0.10
Tetradecanoic acid, pK _{a,1} ^h	HB ⁰ /B ⁻	< 0.01	5.34	+0.54
<i>N,N</i> -Di- <i>n</i> -octadecylrhodamine, pK _{a,0} ⁱ	HB ⁺ /B [±]	0.019	2.24	-1.00
Standard Reichardt dye, pK _{a,0} ^j	HB ⁺ /B [±]	0.014	7.22	-1.41
1-Hexadecyl-6-hydroxyquinoline, pK _{a,0} ^k	HB ⁺ /B [±]	0.014	6.32	-0.83
<i>N-n</i> -Dodecylanilinium, pK _{a,0} ^l	HB ⁺ /B ⁰	< 0.01	1.65	-3.1

In anionic surfactant micelles

$$\Delta pK_a = pK_a^{\text{app}} - pK_a^{\text{w}}$$

Table 5. The indices of the apparent ionization constants in SDS micellar solution, 25 °C or room temperature

Indicator dye	Charge type	$pK_a^{\text{app,c}}$	$\Delta pK_a^{\text{app,c}}$
HHC ^a	HB ⁰ /B ⁻	11.48	3.51
2-Nitro-4- <i>n</i> -nonylphenol ^b	HB ⁰ /B ⁻	10.05	2.58
4-Octadecyloxy-1-naphthoic acid ^c	HB ⁰ /B ⁻	8.10	4.0
Tetradecanoic acid ^d	HB ⁰ /B ⁻	8.45	3.65
Rhodamine B, $I = 0.015 \text{ M}^e$	HB ⁺ /B [±]	5.70	2.48
<i>N,N'</i> -Di- <i>n</i> -octadecylrhodamine, $I = 0.02 \text{ M}^f$	HB ⁺ /B [±]	5.52	2.28
Standard Reichardt dye ^g	HB ⁺ /B [±]	10.72	2.09
1-Hexadecyl-6-hydroxyquinoline ^h	HB ⁺ /B [±]	9.84	2.69
Acridinium ^l	HB ⁺ /B ⁰	7.01	1.75
Neutral red cation ^l	HB ⁺ /B ⁰	9.17	2.67
<i>N-n</i> -Dodecylanilinium ^j	HB ⁺ /B ⁰	7.35	2.6
1-Methyl-2-phenylbenzimidazolium ^k	HB ⁺ /B ⁰	7.8	2.4
CS1 ^{l,m}	HB ⁺ /B ^{0m}	10.10	1.58
CS2 ^l	HB ⁺ /B ⁰	8.17	2.09
4-Hecadecyl-7-dimethylaminocoumarin cation ⁿ	HB ⁺ /B ⁰	3.55	1.2
Hexamethoxy red, $I = 0.01 \text{ M}$	B ⁺ /BOH ⁰	5.89	2.79
Methyl yellow cation, $I = 0.01 \text{ M}$	HB ⁺ /B ⁰	5.28	2.03

In non-ionic surfactant micelles

$$\Delta pK_a = pK_a^{\text{app}} - pK_a^{\text{w}}$$

Table 2. The indices of the apparent ionization constants in brij 35 micellar solution, 25°C or room temperature ^a

Indicator dye	Charge type	$pK_a^{\text{app,c}}$	$\Delta pK_a^{\text{app,c}}$
Bromophenol blue, $pK_{a,2}$	$\text{HB}^-/\text{B}^{2-}$	5.10	0.90
Bromothymol blue, $pK_{a,2}$	$\text{HB}^-/\text{B}^{2-}$	9.19	1.89
Phenol red, $pK_{a,2}$	$\text{HB}^-/\text{B}^{2-}$	8.73	0.73
2-Nitro-4- <i>n</i> -nonylphenol, $pK_{a,1}$ ^b	HB^0/B^-	8.52	1.05
4-Octadecyloxy-1-naphthoic acid, $pK_{a,1}$ ^c	HB^0/B^-	6.60	2.50
Tetradecanoic acid, $pK_{a,1}$ ^d	HB^0/B^-	6.36	1.56
Rhodamine B, $pK_{a,0}$	HB^+/B^\pm	4.08	0.86
<i>N,N'</i> -Di- <i>n</i> -octadecylrhodamine, $pK_{a,0}$	HB^+/B^\pm	4.12	0.88
Acridinium, $pK_{a,0}$ ^e	HB^+/B^0	3.69	-1.39
Neutral red cation, $pK_{a,0}$ ^e	HB^+/B^0	5.64	-0.86
Hexamethoxy red, $pK_{a,0}$	B^+/BOH^0	2.10	-1.00
Methyl yellow cation, $pK_{a,0}$	HB^+/B^0	1.12	-2.13

Determination of the electrostatic surface potential of micelles

$$pK_a^{\text{app}} = pK_a^{\text{w}} + \log \frac{\gamma_A}{\gamma_{\text{HA}}} - \frac{\Psi F}{2.303RT}$$

$$pK_a^{\text{app}} = pK_a^{\text{i}} - \frac{\Psi F}{2.303RT}$$

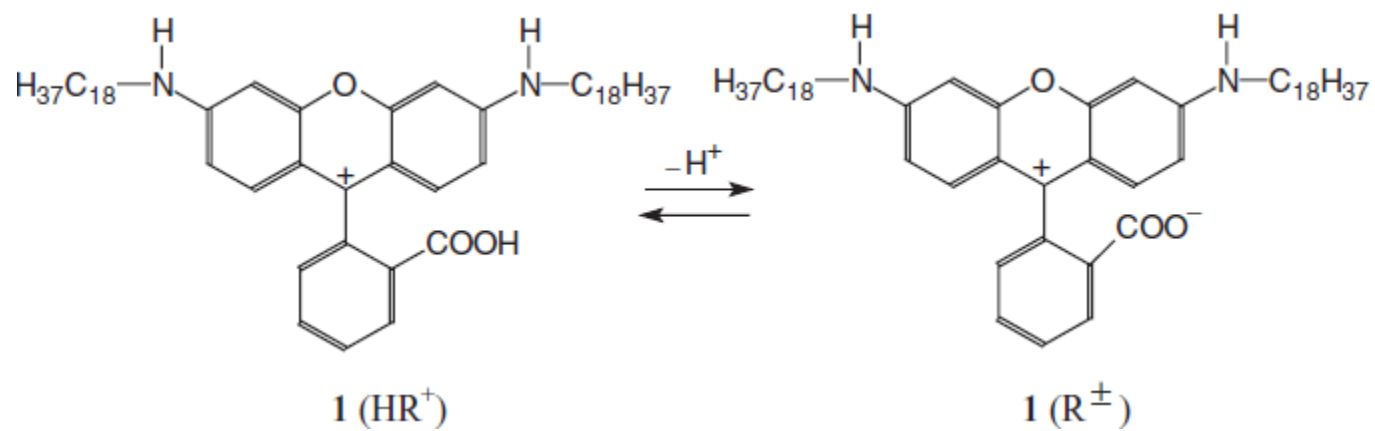
Index of the intrinsic
dissociation constant



$$pK_a^{\text{i}} = pK_a^{\text{w}} + \log \frac{\gamma_A}{\gamma_{\text{HA}}}$$

$$\Psi = \frac{2.303RT}{F} (pK_a^{\text{i}} - pK_a^{\text{app}}) = \underline{59.16 (pK_a^{\text{i}} - pK_a^{\text{app}})}, \text{mV}$$

Most popular approach is equating the intrinsic constant **in ionic micelles** to the apparent constant **in non-ionic micelles**.



$\text{p}K_a^i = 4.21$

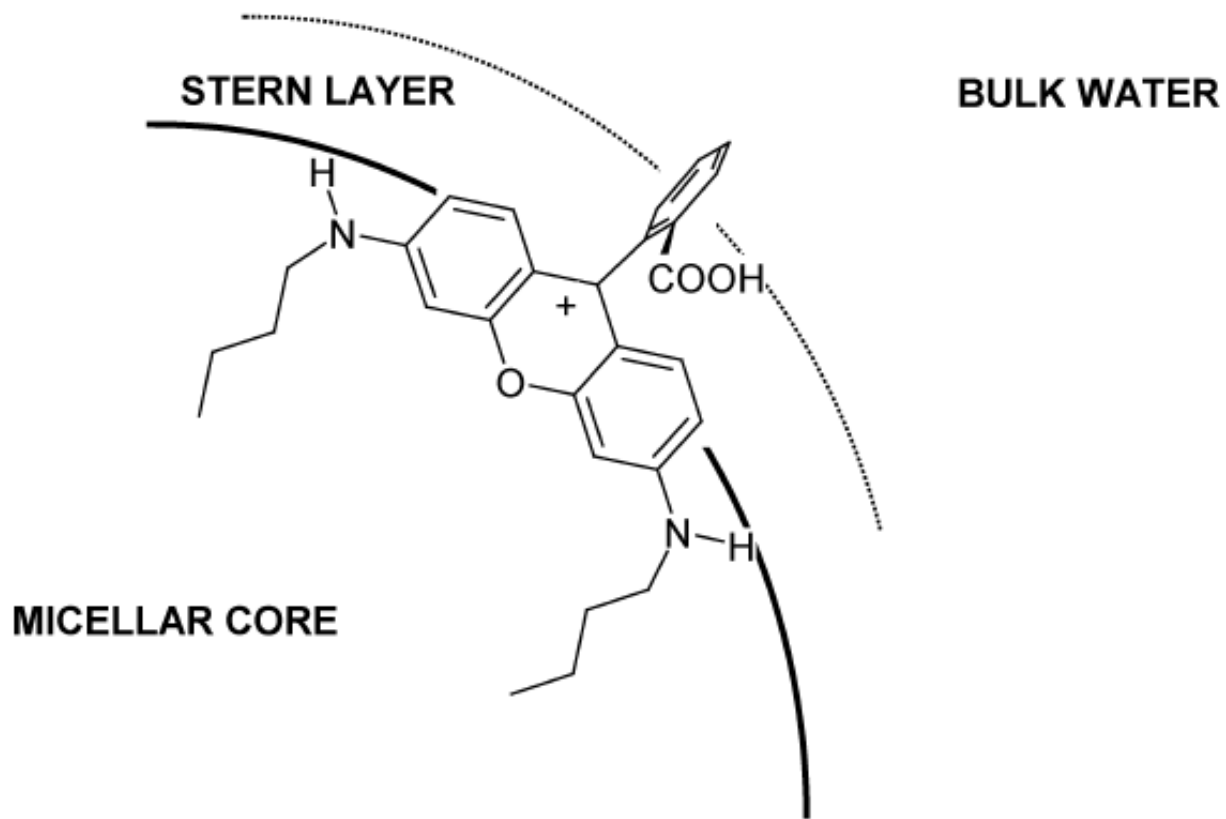


Table 2. Evaluation of the Ψ values of micelles using the pK_a^a values of DODR

Surfactant ^a	Bulk counterion concentration, M ^b	Ψ , mV obtained with DODR $\pm(7-11)$ mV
$n\text{-C}_{18}\text{H}_{37}\text{N}(\text{CH}_3)_3^+\text{Cl}^-$	0.053	+124
$n\text{-C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3^+\text{Br}^-$	0.019 ^c	+118
$n\text{-C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3^+\text{Br}^-$	0.053	+102
$n\text{-C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3^+\text{Br}^-$	0.053 ^c	+100
$n\text{-C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3^+\text{Br}^-$	0.403 ^c	+54
$n\text{-C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3^+\text{Br}^-$	4.00 ^d	+17
$n\text{-C}_{16}\text{H}_{33}\text{N}^+(\text{CH}_3)_2(\text{CH}_2)_3\text{SO}_3^-$	0.05	+37
$n\text{-C}_{16}\text{H}_{33}\text{OSO}_3^- \text{Na}^+$	0.052	-74
$n\text{-C}_{12}\text{H}_{25}\text{OSO}_3^- \text{Na}^+$	0.020 ^e	-76
$n\text{-C}_{12}\text{H}_{25}\text{OSO}_3^- \text{Na}^+$	0.054	-58
$n\text{-C}_{12}\text{H}_{25}\text{OSO}_3^- \text{Na}^+$	0.077	-49
$n\text{-C}_{12}\text{H}_{25}\text{OSO}_3^- \text{Na}^+$	0.203	-27
$n\text{-C}_{12}\text{H}_{25}\text{OSO}_3^- \text{Na}^+$	0.303	-14
$n\text{-C}_{12}\text{H}_{25}\text{OSO}_3^- \text{Na}^+$	0.403	-11

^aThe C_S and T values are as indicated in Table 1.

^b Created by the buffer system and NaCl; the contribution of surfactant counterions is also taken into account.

^c HBr + KBr.

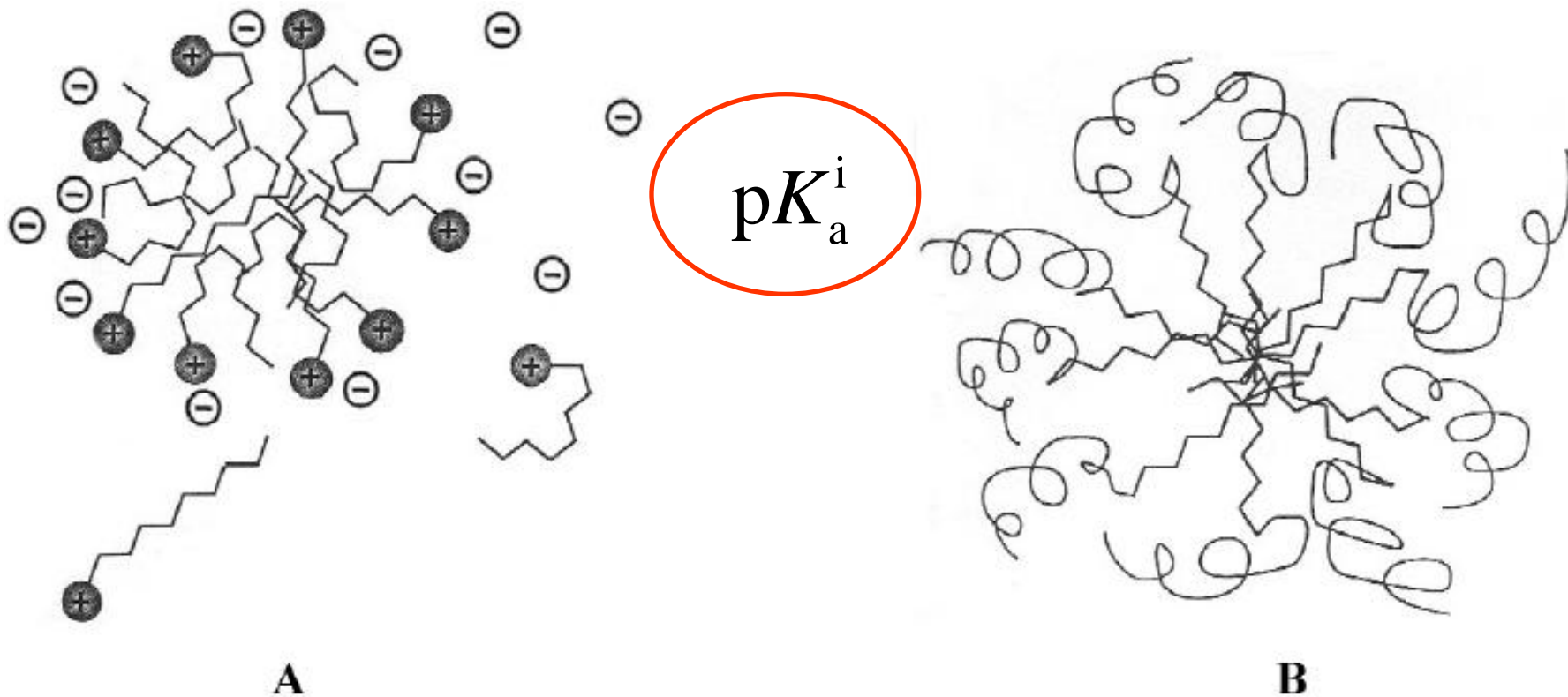
^d KCl.

^e Sodium acetate, without NaCl addition.

Indicator, reference	C_s , M	$[\text{Br}_w^-]$, M	Ψ , mV ^a
DODR, this work	0.050	0.019	+118
4-Heptadecyl-7-hydroxycoumarin ^b	0.050	0.014	+117 ^c (+145) ^d
4-Undecyl-7-hydroxycoumarin ^e	0.024	0.007	+148
4-Heptadecyl-7-hydroxycoumarin ^f	0.050	0.014	+139
Reichardt's betaine ^g	0.050	0.014	+141
4-Octadecyloxy-1-naphthoic acid ^c	0.050	0.014	+143
4-Heptadecyl-7-hydroxycoumarin ⁱ	0.050	0.014	+151

Indicator, reference	C_s , M	$[\text{Na}_w^+]$, M	Ψ , mV ^a
DODR, this work	0.050	0.020	-76
Reichardt's betaine ^b	0.050	0.0185	-83
4-Octadecyloxy-1-naphthoic acid ^c	0.050	0.0185	-85 ^d (-93) ^e
4-Heptadecyl-7-hydroxycoumarin ^f	0.050	0.0185	-102 ^d (-105) ^e
4-Undecyl-7-hydroxycoumarin ^g	0.024	0.012	-134
4-Heptadecyl-7-dimethylaminocoumarin ^h	0.024	0.012	-134
<i>n</i> -Decyl eosin ⁱ	0.020	0.012-0.014	-143
<i>n</i> -Decyl eosin ^{ij}	0.010	0.020	-134
4-Heptadecyl-7-hydroxycoumarin ^k	0.020	0.065	-110
4-Heptadecyl-7-hydroxycoumarin ^l	0.020	0.0185	-144
Hexamethoxy red ^m	0.020	0.019	-217
Methyl yellow ^m	0.020	0.019	-230

Difference between the structure of ionic and non-ionic surfactant micelles in water



A schematic sketch of the section of cationic (A) and nonionic (B) surfactant micelles.

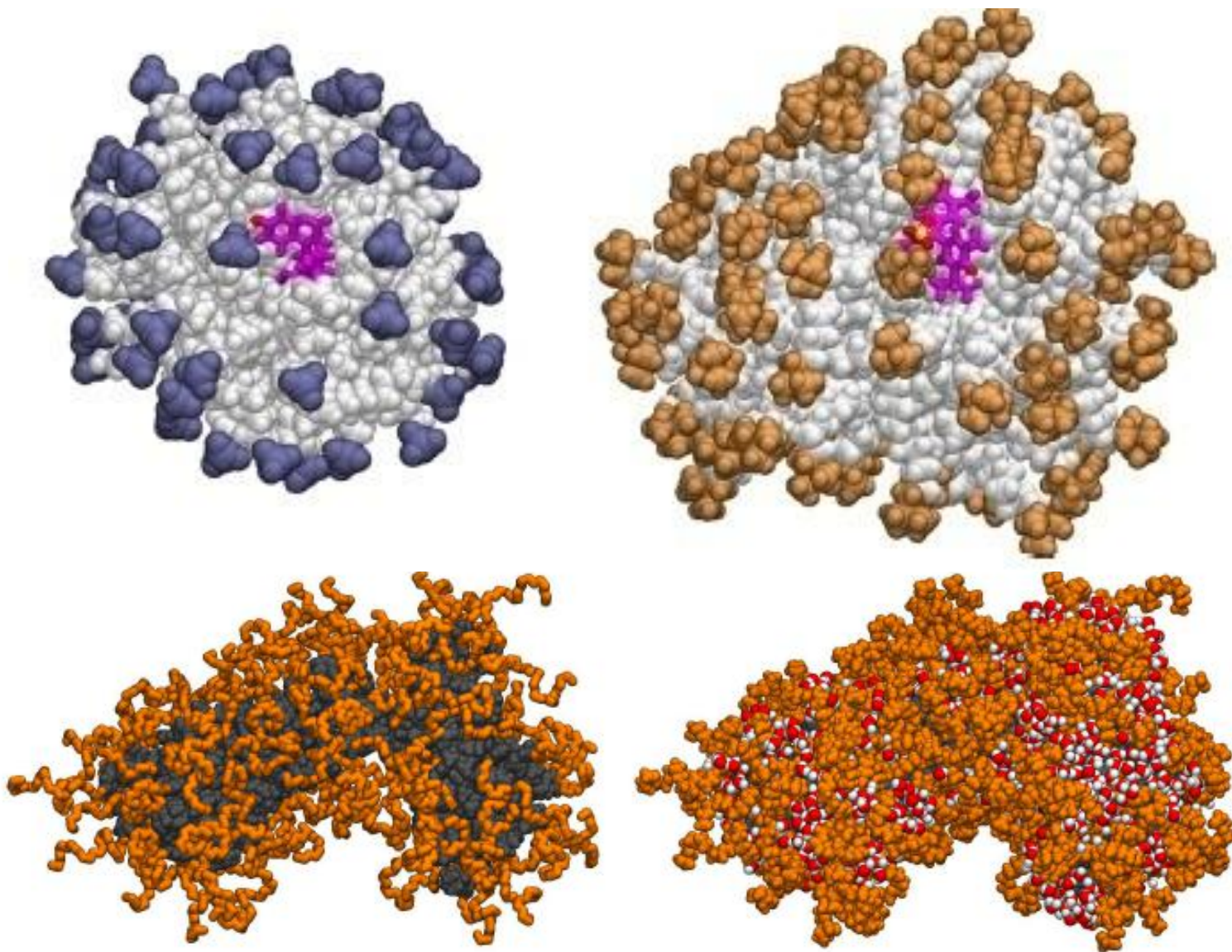


Fig. 2. Equilibrated Triton X-100 micelle. Hydrocarbon core is colored gray, hydrophilic shell is colored orange. On the left image, polyoxyethylene chains are depicted as simplified; on the right image, water molecules within 0.6 nm of hydrocarbon core are shown as well

Independent estimation of the electrostatic surface potential

Ohshima, Healy, White equation for a spherical charged colloidal particle

$$\frac{\alpha}{s_i} - \frac{2\varepsilon\varepsilon_o kRT}{F} \sinh(Y / 2) \left(1 + \frac{2}{kr \cosh^2(Y / 4)} + \frac{8 \ln [\cosh(Y / 4)]}{(kr)^2 \sinh^2(Y / 2)} \right)^{\frac{1}{2}} = 0$$

Here, s_i is the area of the charged head-group, $Y = \Psi F / RT$, F is the Faraday constant, k^{-1} is the Debye length, $\varepsilon_o = 8.854 \times 10^{-12} \text{ F m}^{-1}$, $\varepsilon = 78.5$ at $T = 298.15 \text{ K}$. Actually, α/s_i is the surface charge density.

Problems consist in the values of the parameters: degree of counterions binding, molecular area, micellar size

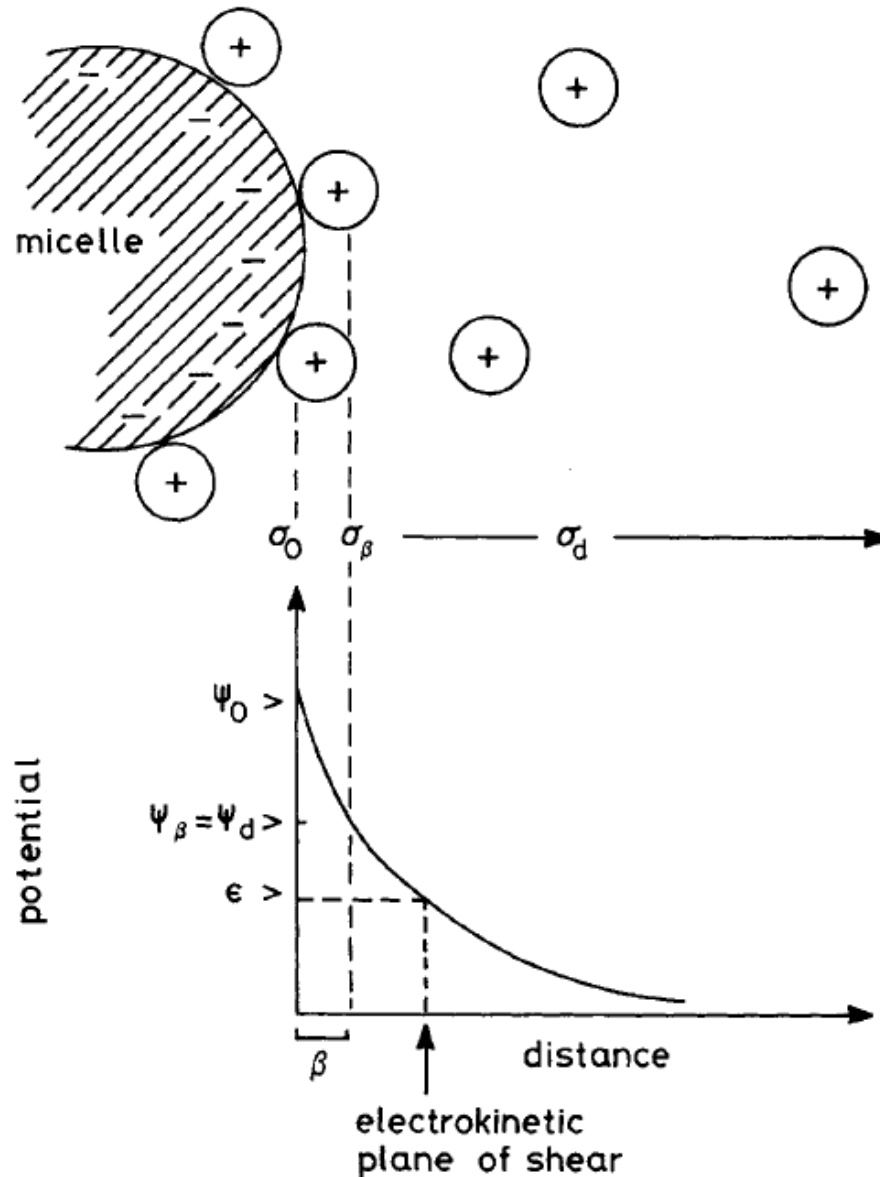
Table 2 The Ψ values of SDS and CTAB, calculated by eq. 9; 25 °C [29j,56].^a

$[\text{Na}_w^+]/M$	r/nm	s_i, nm^2	α	Ψ/mV
SDS micelles				
0.01	1.8	0.500	1	-199
0.008	1.8	0.609	1	-193 ^b
0.01	1.8	0.609	0.55	-148
0.01	1.8	0.609	0.20	-78
0.01	1.8	0.660	0.30	-100
0.01	2.0	0.900	0.20	-59
0.05	1.8	0.609	1	-147
0.05	1.8	0.609	0.55	-111
0.05	1.8	0.609	0.30	-75
0.05	1.8	0.384	0.55	-140
0.05	1.8	0.384	0.20	-78
0.05	2.0	0.600	0.20	-57
0.05	1.8	0.459	0.20	-68
0.05	1.8	0.506	0.20	-63
0.05	1.8	0.663	0.20	-50
0.05	1.8	0.660	0.35	-79
CTAB micelles				
0.053	2.56	0.474	0.27	+88
0.019	2.56	0.474	0.27	+110
0.019	2.56	0.675	0.27	+87
0.005	2.56	0.474	0.19	+101
0.019	3.5	0.474	0.27	+113

^aAs a rule, $c_{\text{surf}} = 0.01$ M.

^bClose to the $\Psi = -195$ mV value reported in ref. [29d].

Another way: measurements of the electrokinetic potential



$$\zeta < \Psi$$

(Hartland, Grieser, White)

Electrokinetic potential, or zeta-potential.

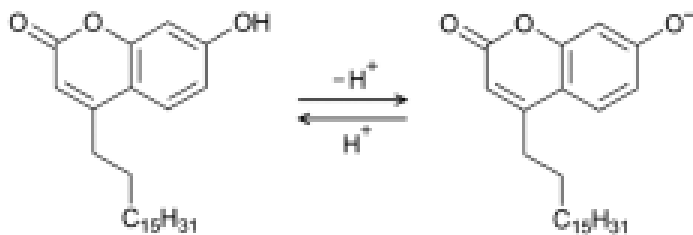
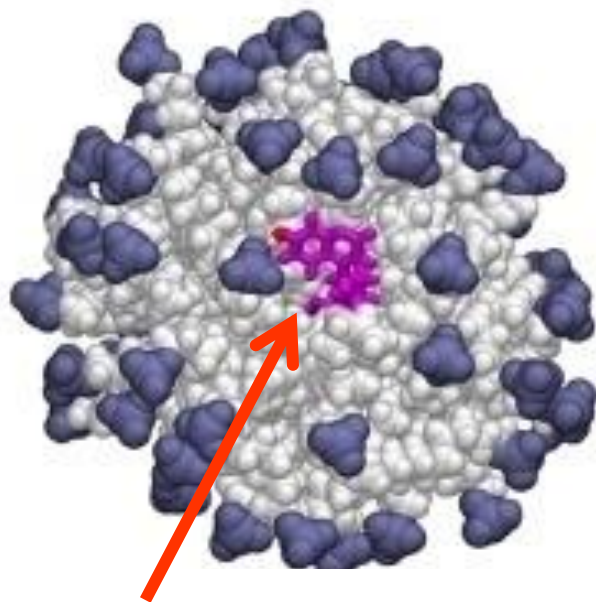
$$\zeta = u_e \frac{3\eta}{2\epsilon_r \epsilon_0} \times \frac{1}{f}$$

The f function is described by the approximate equation by Ohshima

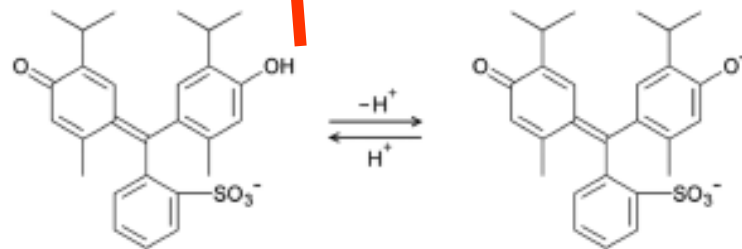
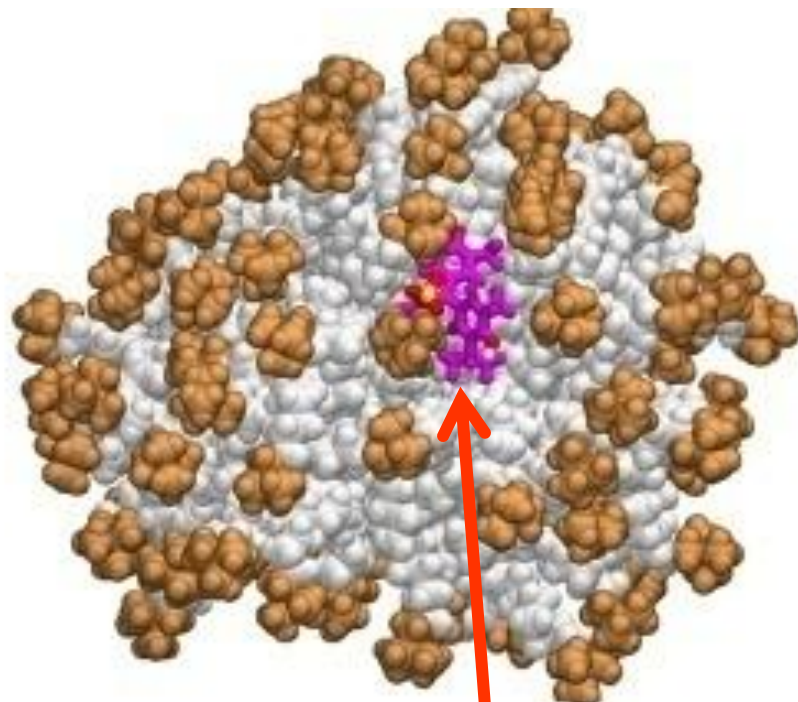
$$f = 1 + 0.5 \left[1 + \frac{2.5}{\kappa r (1 + 2 \exp(-\kappa r))} \right]^{-3}$$

- - - - -

Third approach: Molecular dynamics simulation



In sodium *n*-dodecylsulfate
micelle

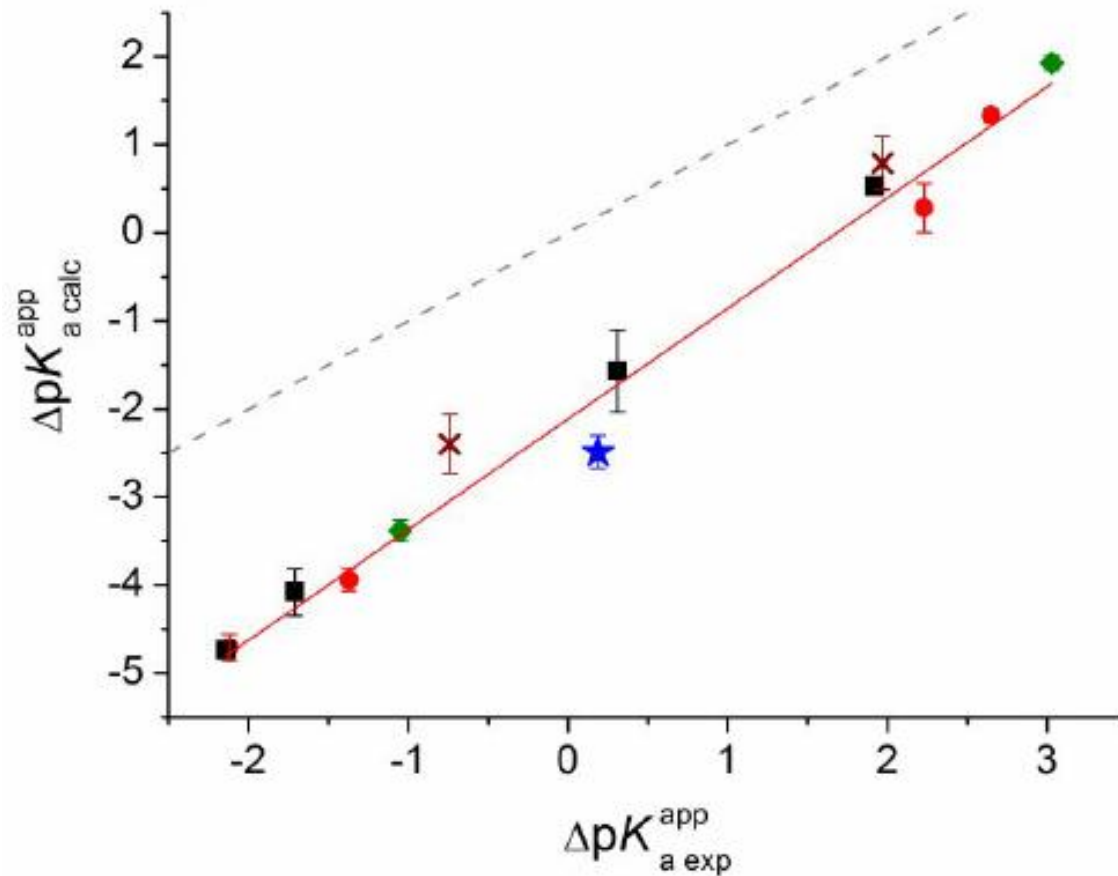


In cetyltrimethylammonium
bromide micelle

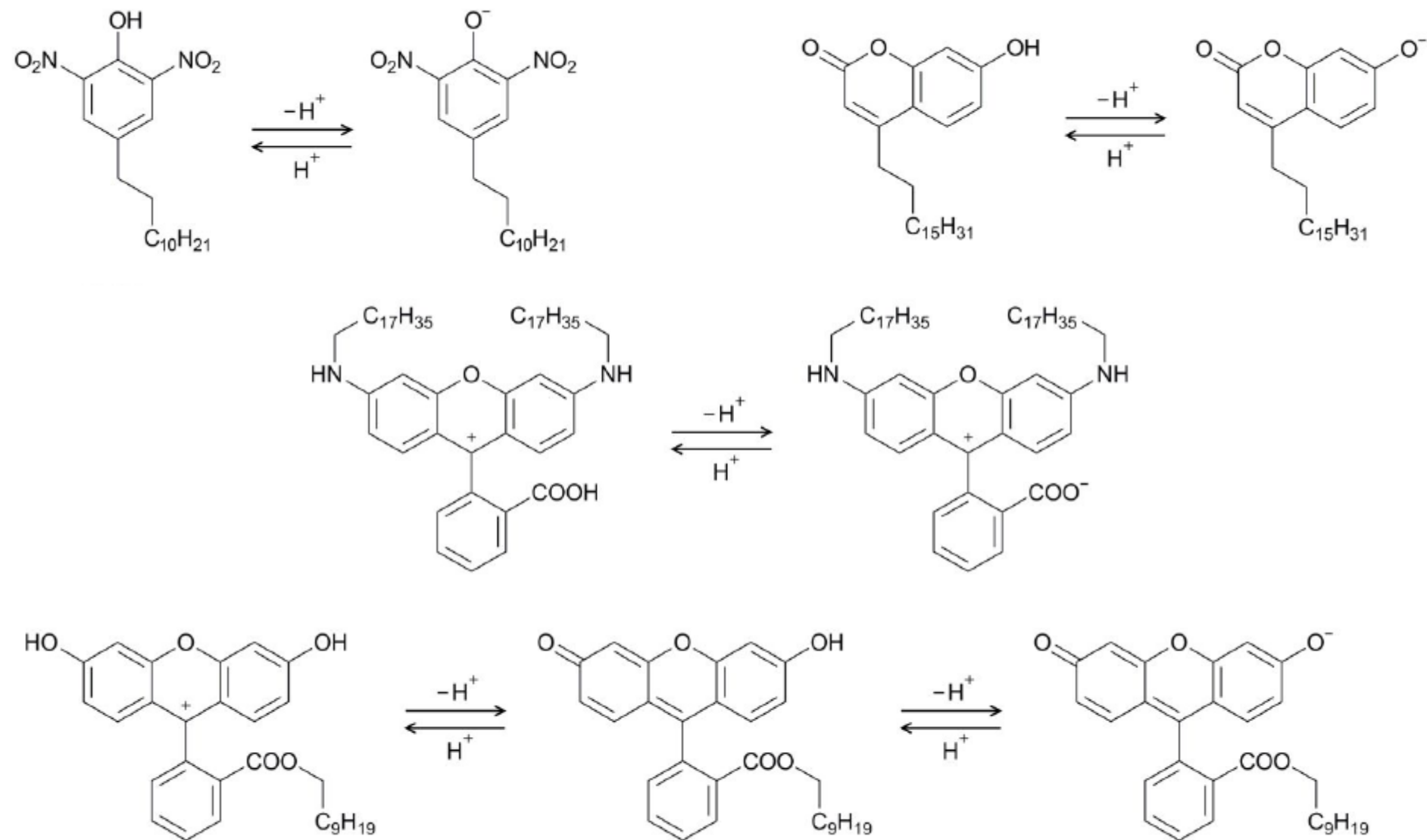
(Farafonov, 2020)

Theoretical calculation *via* MD simulations

$$\Delta pK_a^{\text{app}} = pK_a^{\text{app}} - pK_a^{\text{w}}$$



Some representative acid-base long-tailed indicators

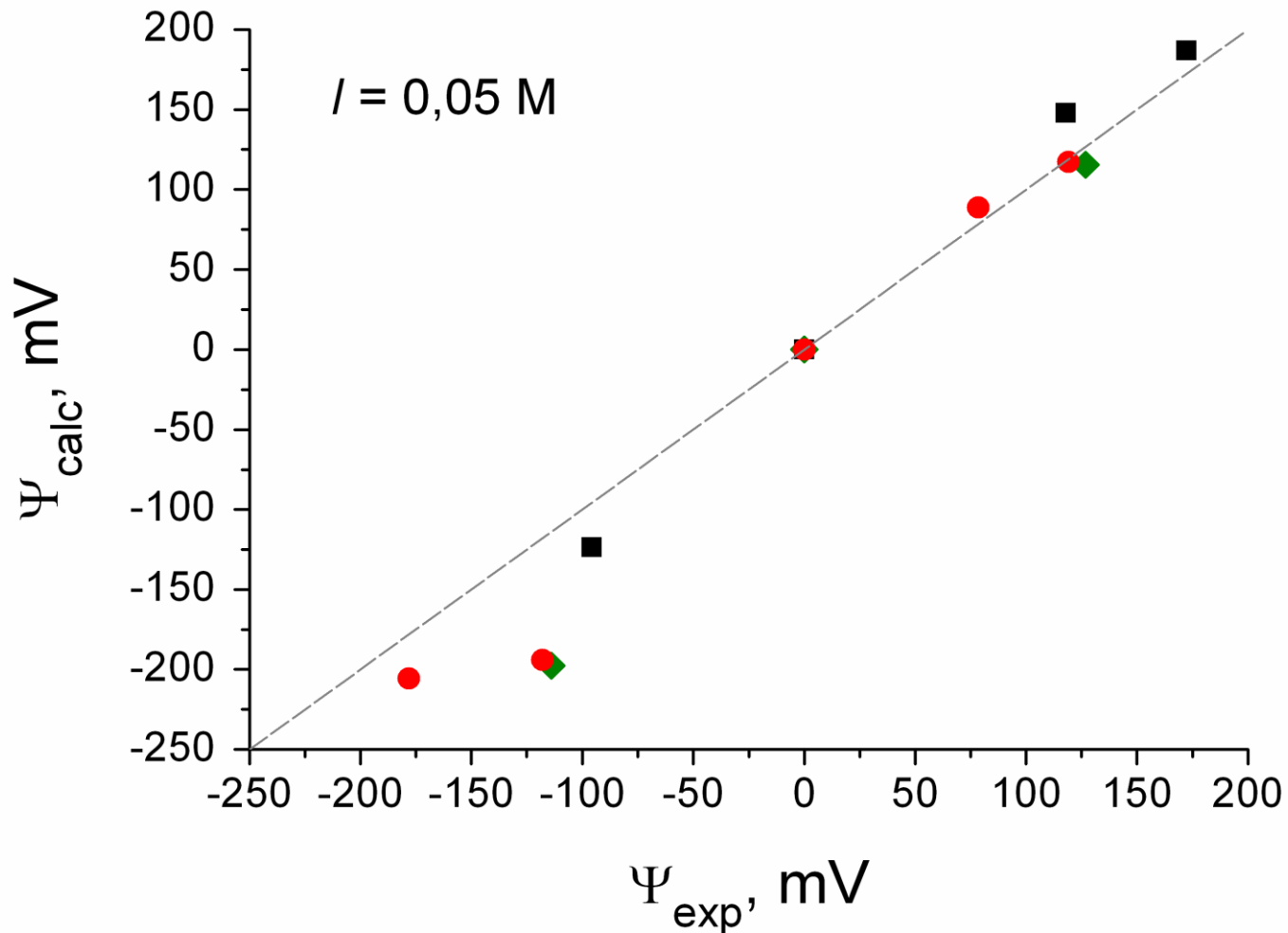


Experimental and calculated values of Ψ in ionic micelles, bulk ionic strength 0.05 M

INDICATORS	Ψ_{exp} , mV	Ψ_{calc} , mV	Difference, mV
SDS, anionic surfactant			
<i>n</i> -Dodecyldinitrophenol	-95.6	-123.6	-28
<i>n</i> -Decylfluorescein (I)	-178.2	-205.7	-28
<i>n</i> -Decylfluorescein (II)	-118.0	-194.0	-76
<i>n</i> -Heptadecylcoumarin	-113.9	-197.8	-84
CTAB, cationic surfactant			
<i>n</i> -Dodecyldinitrophenol	+172.3	+186.9	15
<i>n</i> -Decylfluorescein (I)	+78.5	+88.7	11
<i>n</i> -Decylfluorescein (II)	+119.2	+117.3	-2
<i>n</i> -Heptadecylcoumarin	+126.9	+115.4	-12
CDAPS, zwitterionic surfactant			
<i>n</i> -Dodecyldinitrophenol	+118.0	+147.7	30

Theoretical calculation *via* MD simulations

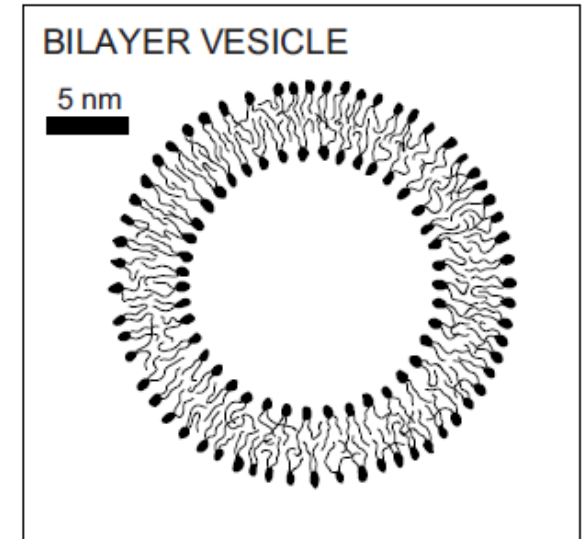
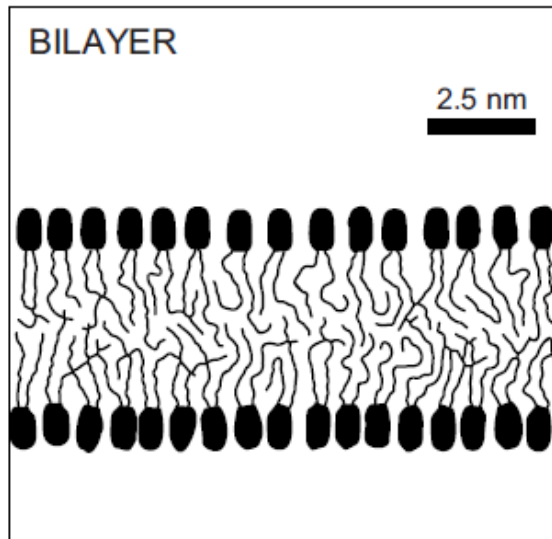
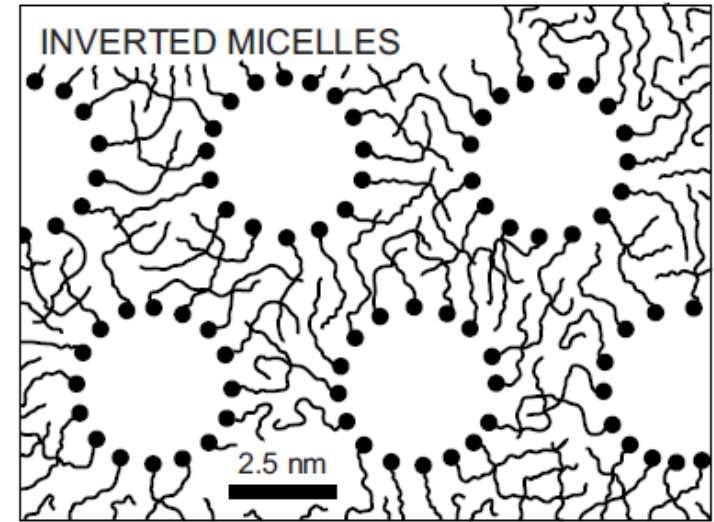
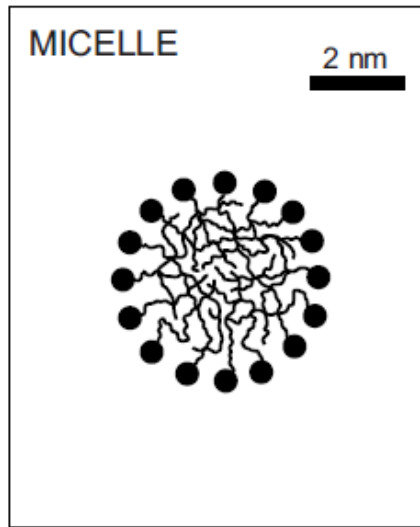
$$\Psi = 59.16(\text{p}K_a^i - \text{p}K_a^{\text{app}}), \text{mV}$$



Main result: the indicator measurements reflect the electrostatic value in the LOCUS of the molecular probe

$$\Psi = 59.16(\text{p}K_a^i - \text{p}K_a^{\text{app}})$$

The same for related
systems



(From J. N. Israelachvili, Intermolecular and surface forces, 2011)

Salt effects: Influence of the ionic strength of the bulk (aqueous) phase

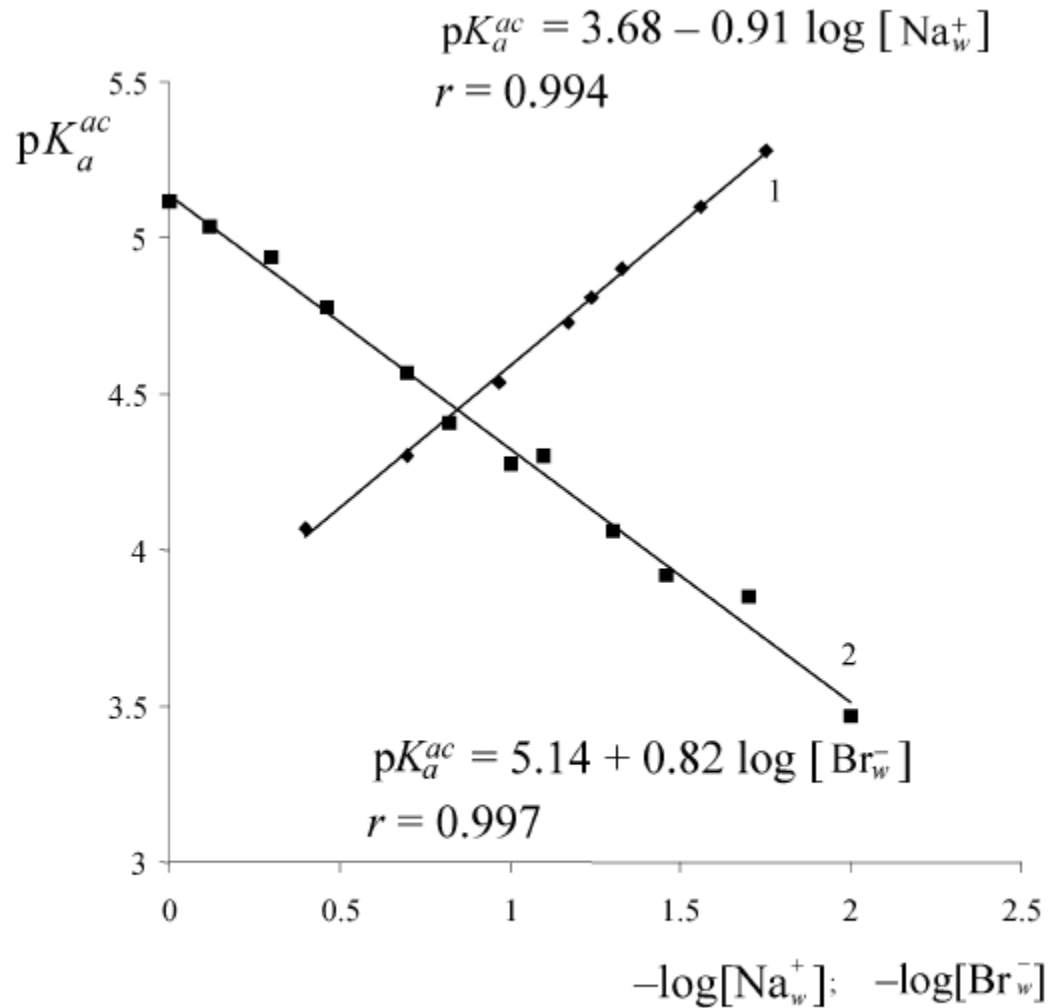


Fig. 3 The dependences of methyl yellow pK_{a0}^{ac} in SDS micelles (1) and bromocresol green pK_{a2}^{ac} in CTAB micelles (2) on logarithm of Na^+ and Br^- bulk concentrations, respectively [1m].

Explanation of the salt effects

$$pK_a^{\text{app}} = pK_a^i - \frac{\Psi F}{2.303RT}$$

Hernst equation $\longrightarrow \Psi = \Psi_0 + \frac{2.303RT}{F} \log a_{\text{Ct}^+}$



Mass action law $\longrightarrow \log a_{\text{Ct}^+} = \frac{1}{n} \log \frac{a_{\text{mic}}}{K} - \frac{m}{n} \log a_{\text{Br}^-}$

$$\textcircled{pK_a^{\text{app}}} = pK_a^i - \left\{ \frac{\Psi_0 F}{2.303RT} + \frac{1}{n} \log \frac{a_{\text{mic}}}{K} \right\} + \textcircled{\beta \log a_{\text{Br}^-}} \quad \frac{m}{n} = \beta;$$

Linear dependence with slope β

$$pK_a^{\text{app}} = pK_a^i - \left\{ \frac{\Psi_0 F}{2.303RT} + \frac{1}{n} \log \frac{a_{\text{mic}}}{K} \right\} + \beta \log a_{\text{Br}^-}$$

For cationic and anionic surfactant micelles, respectively

$$pK_a^{\text{ac}} = B + b \log[X_w^-] = B' + b' \log a_{X_w^-}$$

$$pK_a^{\text{ac}} = B - b \log[M_w^+] = B' - b' \log a_{M_w^+}$$



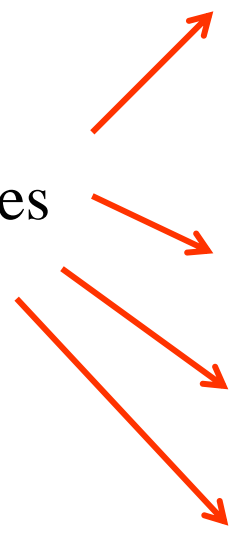
Table I. Literature cmc + [Electrolyte], log cmc, and Ψ_{probe} Results for Micellar Systems Studied^a

system	cmc + [electrolyte], mol dm ⁻³	log cmc	Ψ_{probe}
DTAB/NaBr ^b	0.0148	-1.828	+118
	0.0218	-1.926	+109
	0.0401	-2.081	+96
	0.0718	-2.230	+85
	0.1047	-2.326	+83
	0.3333	-2.620	+58
	0.6667	-2.797	+48
	1.0000	-2.900	+44
	4.0020	-3.377	+18
	DTAC/NaCl ^b	0.0193	-1.712
0.0269		-1.803	+125
0.0456		-1.948	+118
0.0751		-2.085	+109
0.1076		-2.183	+105
0.3333		-2.493	+85
0.6660		-2.683	+75
1.0000		-2.794	+69
4.0000		-3.174	+47
SDS/NaCl ^c		0.008	-2.090
	0.020	-2.393	-125
	0.025	-2.448	-122
	0.065	-2.732	-110
	0.102	-2.857	-95
	0.202	-3.044	-85
	0.302	-3.154	-73
	0.382	-3.219	-72
SDS/NaCl ^d	0.481	-3.281	-67
	0.0081	-2.090	-134
	0.0521	-2.670	-119
	0.1014	-2.857	-101
	0.2009	-3.044	-91
SDS/NaClO ₄ ^e	0.4006	-3.231	-68
	0.0084	-2.073	-130
	0.0153	-2.277	-120
	0.0359	-2.542	-100
SDeS/NaClO ₄ ^e	0.1018	-2.738	-77
	0.0327	-1.485	-95
	0.0393	-1.533	-90
	0.0569	-1.622	-90
	0.1154	-1.812	-79

Healy, Drummond, Grieser,
Murray, 1990

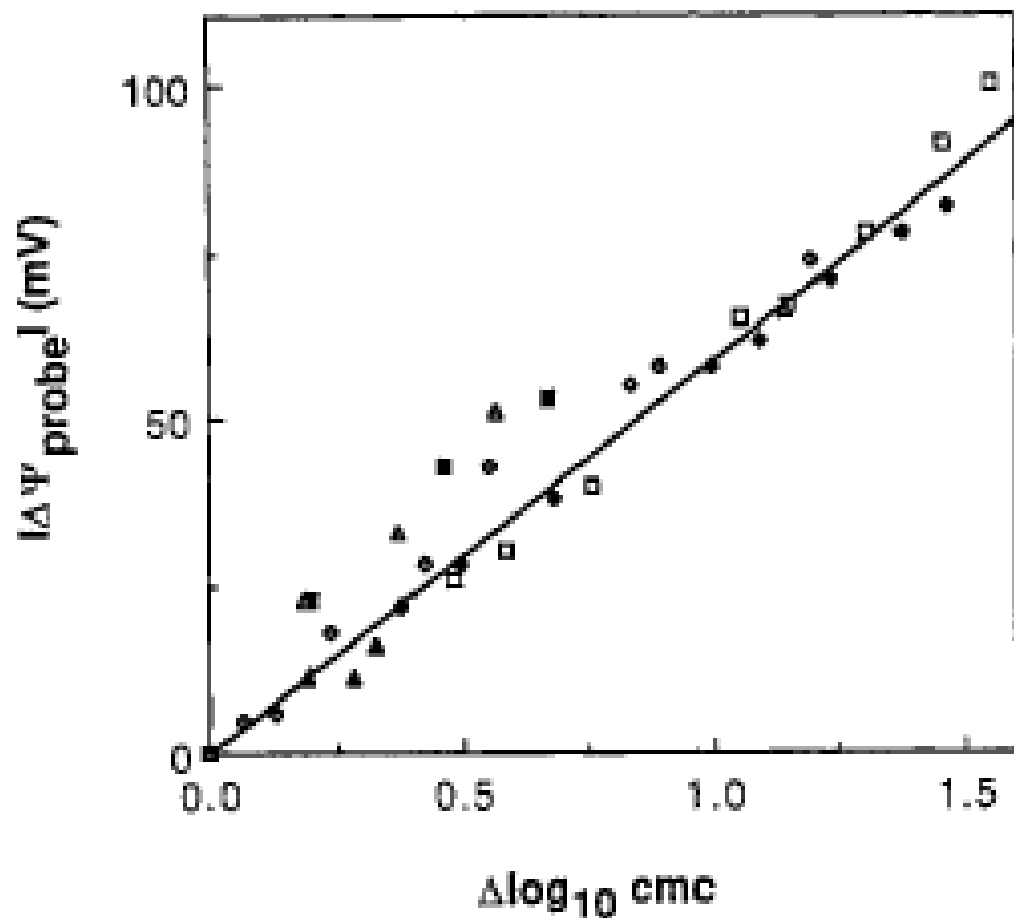
Cationic surfactant micelles

Anionic surfactant micelles



Electrostatic Surface Potential and Critical Micelle Concentration Relationship for Ionic Micelles

Healy, Drummond, Grieser, Murray, 1990



Fernandez, Fromherz, 1977

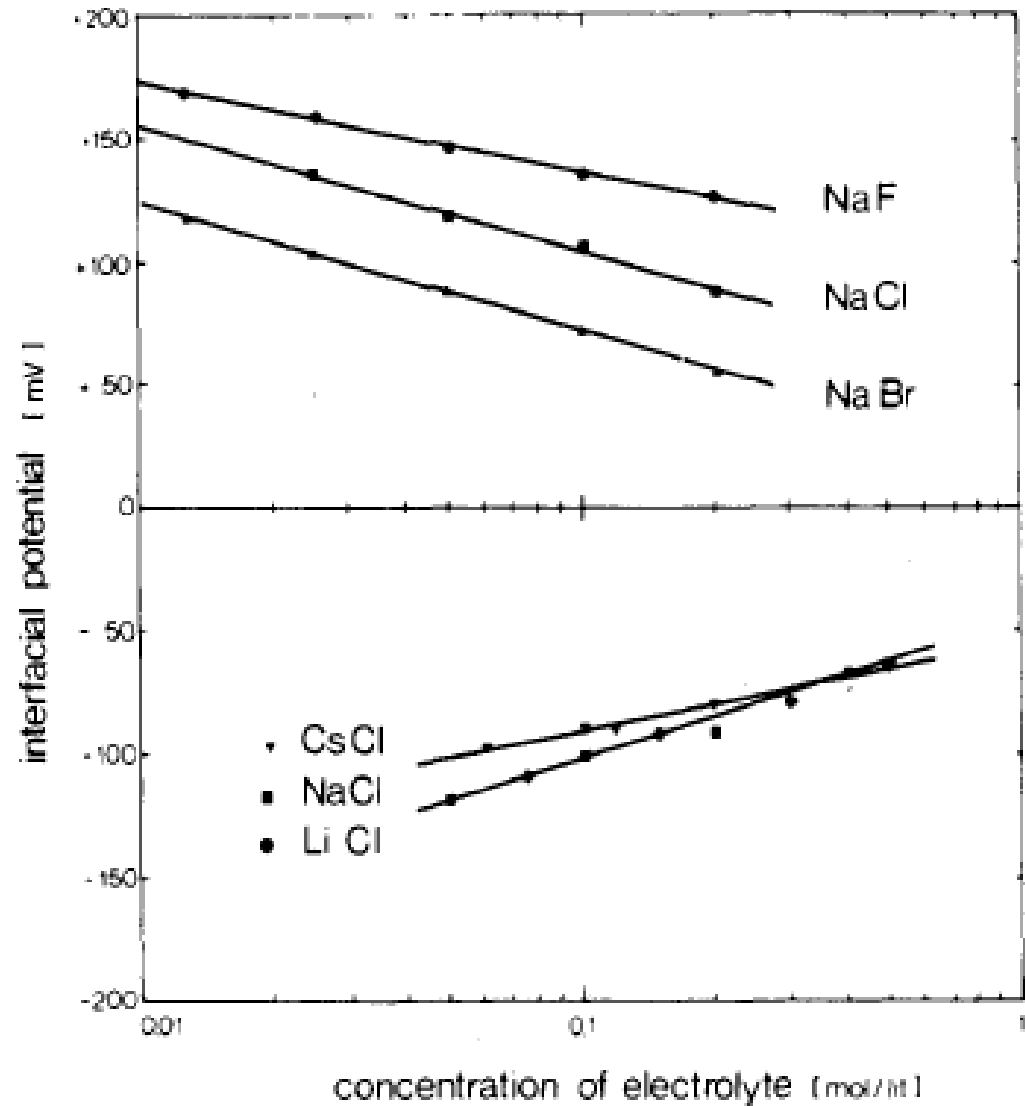
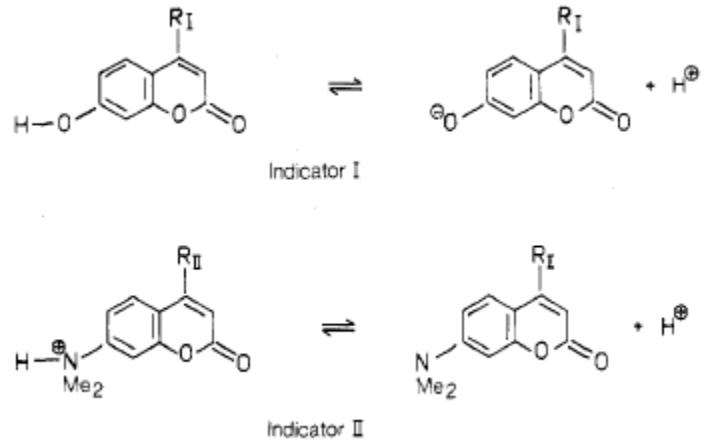
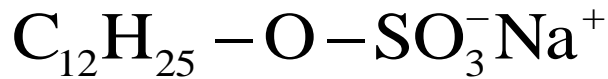


Figure 6. Electrical potential at micelle surface vs. concentration of foreign electrolyte. The upper three curves refer to 2 mM solutions of cetyltrimethylammonium bromide (CTAB), where the potentials are detected by indicator I, using eq 13. The lower three curves refer to 10 mM solutions of sodium dodecyl sulfate (SDS), where the potentials are detected similarly by indicator II.

In an anionic surfactant micelles:



Lukanov, Firoozabadi,
2014

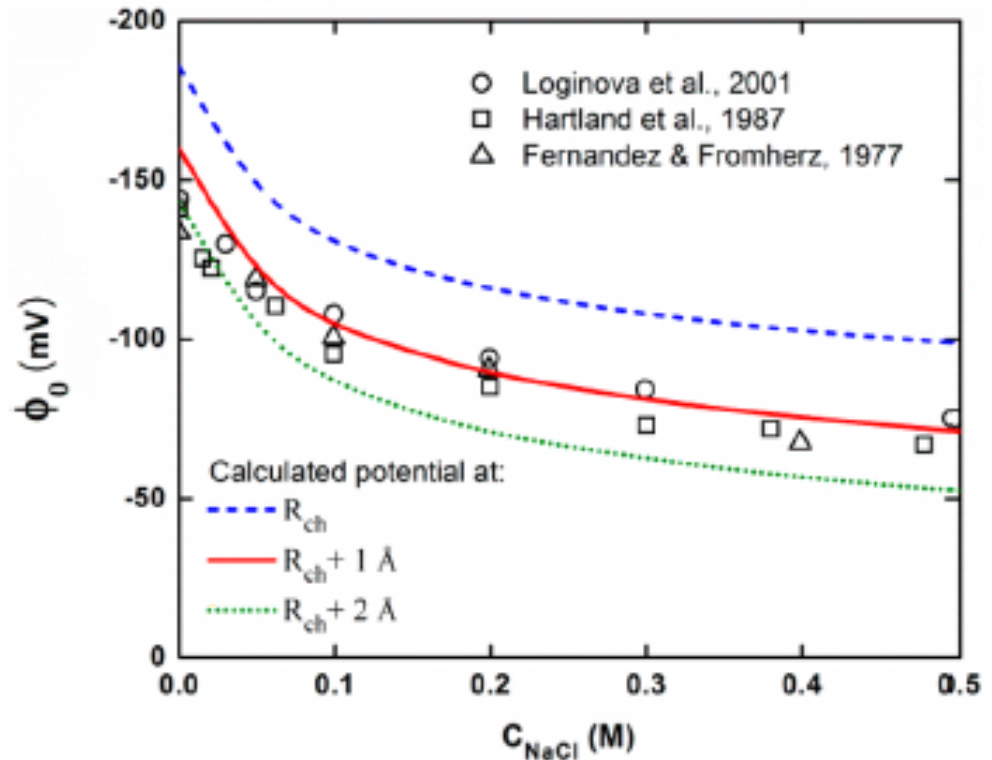
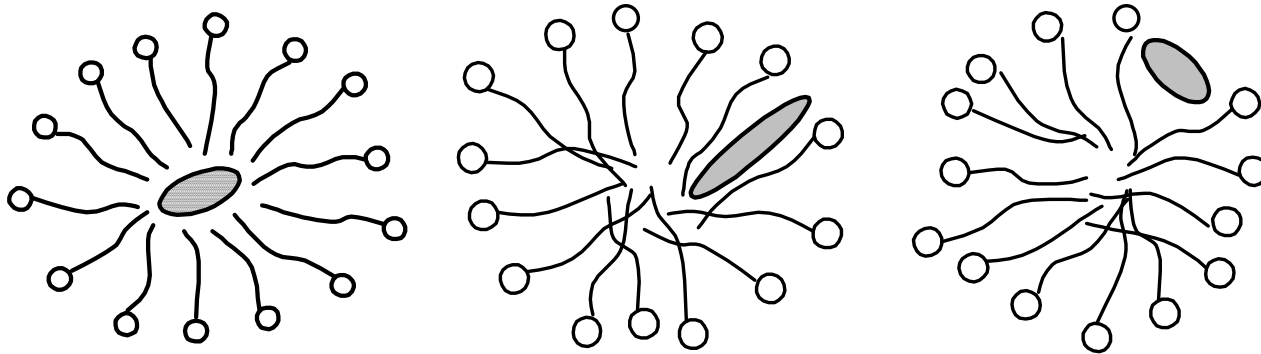
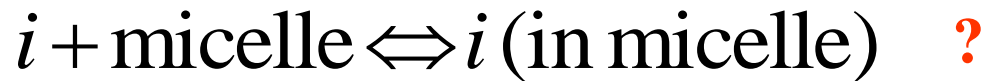


Figure 8. Comparison between the predicted and experimental^{56–58} micelle surface electrostatic potential, ϕ_0 , for SDS micelles at 25 °C and at an SDS concentration of 10 mM as a function of NaCl concentration. The predicted potentials are for the micelle surface of charge at R_{ch} (blue dashed line), 1 Å from it (solid red line) and 2 Å from it (dotted green line).

Incomplete binding of reactants by micelles



Binding constant:

$$K_b = \frac{1}{c_{\text{surf}} - \text{CMC}} \frac{[i_m]_t}{[i_w]_t}$$

}

m – in micelle

w – in water phase

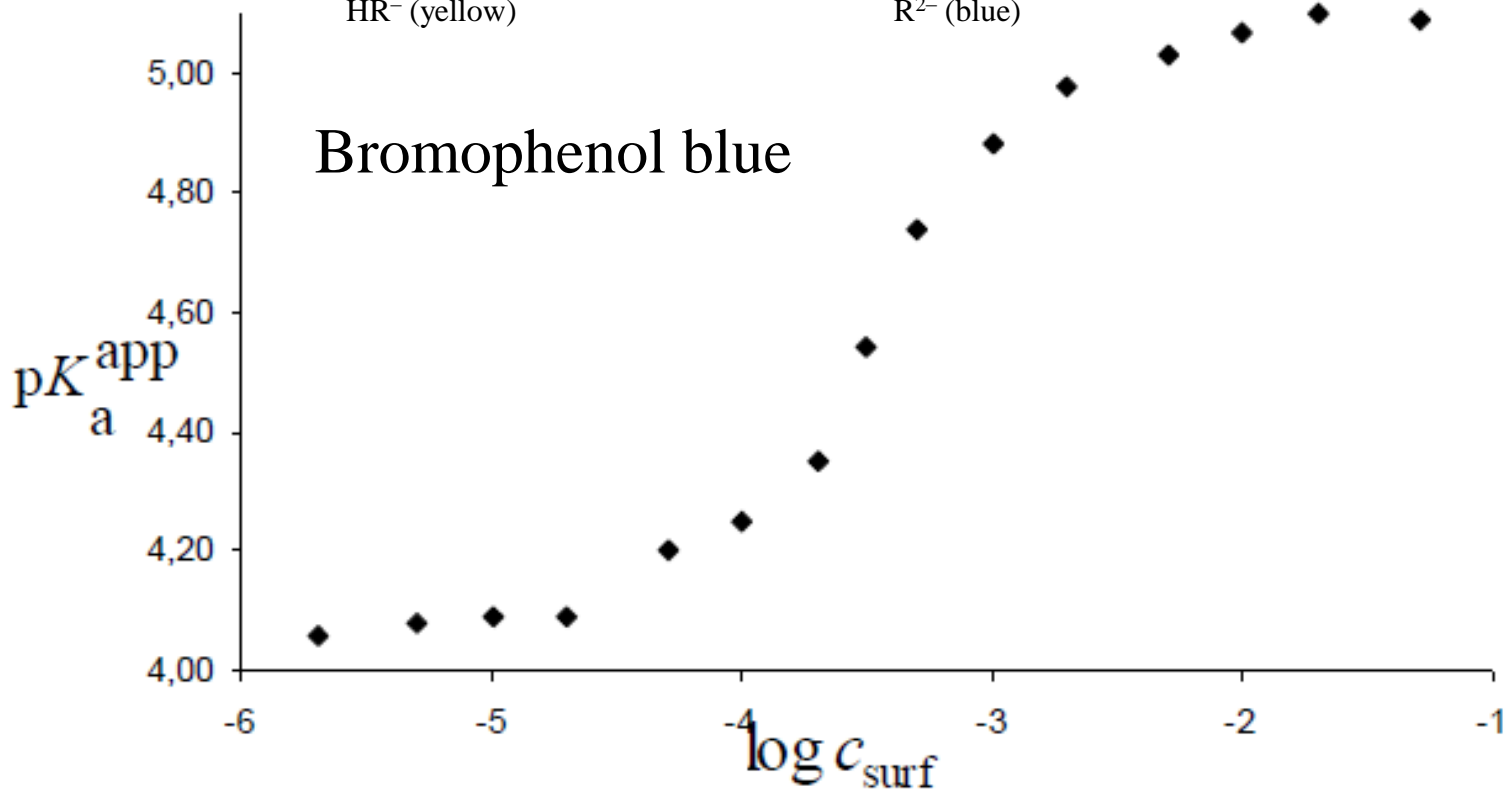
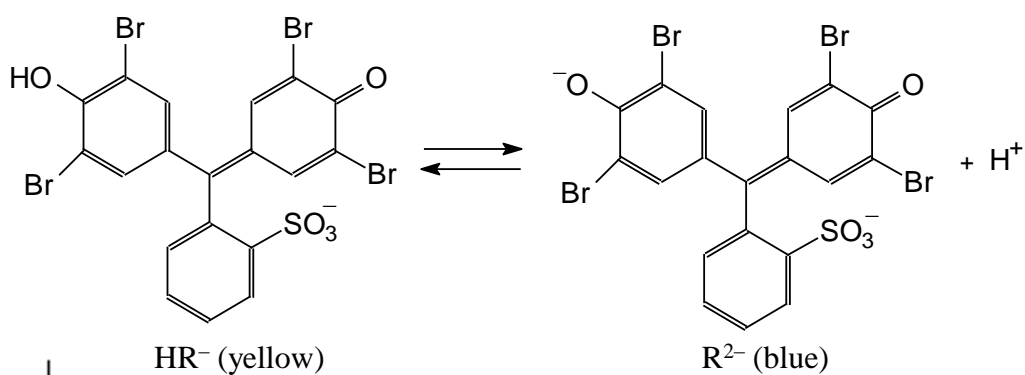
t – per total volume

$$pK_a^{\text{app}} = \text{pH}_w + \log \frac{[\text{HA}_w]_t + [\text{HA}_m]_t}{[\text{A}_w]_t + [\text{A}_m]_t}$$

$$pK_a^{\text{app}} = \text{pH}_w + \log \frac{[\text{HA}_w]_t \{1 + K_{b,\text{HA}} (c_{\text{surf}} - \text{CMC})\}}{[\text{A}_w]_t \{1 + K_{b,\text{A}} (c_{\text{surf}} - \text{CMC})\}}$$

$$pK_a^{\text{app}} = pK_a^{w*} + \log \frac{1 + K_{b,\text{HA}} (c_{\text{surf}} - \text{CMC})}{1 + K_{b,\text{A}} (c_{\text{surf}} - \text{CMC})}$$

$$\frac{1 - 10^{(pK_a^{w*} - pK_a^{\text{app}})}}{c_{\text{surf}} - \text{CMC}} = - \underline{K_{b,\text{A}}} + 10^{(pK_a^{w*} - pK_a^{\text{app}})} \underline{K_{b,\text{HA}}}$$



$$\frac{1 - 10^{(\text{p}K_{\text{a}}^{\text{w}*} - \text{p}K_{\text{a}}^{\text{app}})}}{c_{\text{surf}} - \text{CMC}} = -K_{\text{b,A}} + 10^{(\text{p}K_{\text{a}}^{\text{w}*} - \text{p}K_{\text{a}}^{\text{app}})} K_{\text{b,HA}}$$

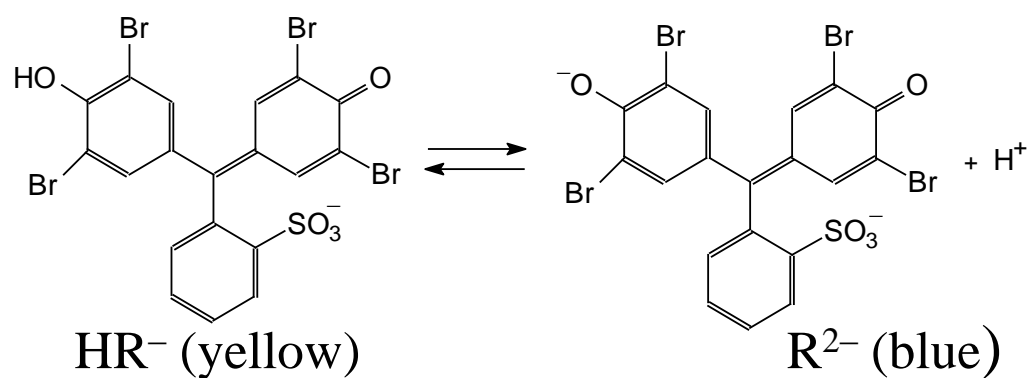


Table 1. The values of binding constants/ M^{-1} of mono- and dianions of bromophenol blue and the calculated $\text{p}K_{\text{a}}^{\text{app,c}}$ values in solutions of non-ionic surfactants [15,97]

Surfactant	$c_{\text{surf}}, \text{M}$	$10^{-3} K_{\text{b,HB}^-}$	$10^{-3} K_{\text{b,B}^{2-}}$	$\text{p}K_{\text{a},2}^{\text{app,c}}$
Brij 35 ^a	$1 \times 10^{-4} - 0.01$	12	1.2	5.10 ± 0.03
Triton X – 100 ^a	$5 \times 10^{-4} - 0.005$	11	1.7	5.00 ± 0.02
Triton X – 305 ^a	$1.3 \times 10^{-3} - 0.005$	2.4	0.13	4.88 ± 0.03
Nonyl phenol 12 ^b	$2 \times 10^{-4} - 0.004$	20	2.7	4.80 ± 0.03
Tween 80 ^b	$1.5 \times 10^{-4} - 0.05$	13	0.90	5.09 ± 0.03

^a Ionic strength $I = 0.01 \text{ M}$; ^b $I = 0.05 \text{ M}$.

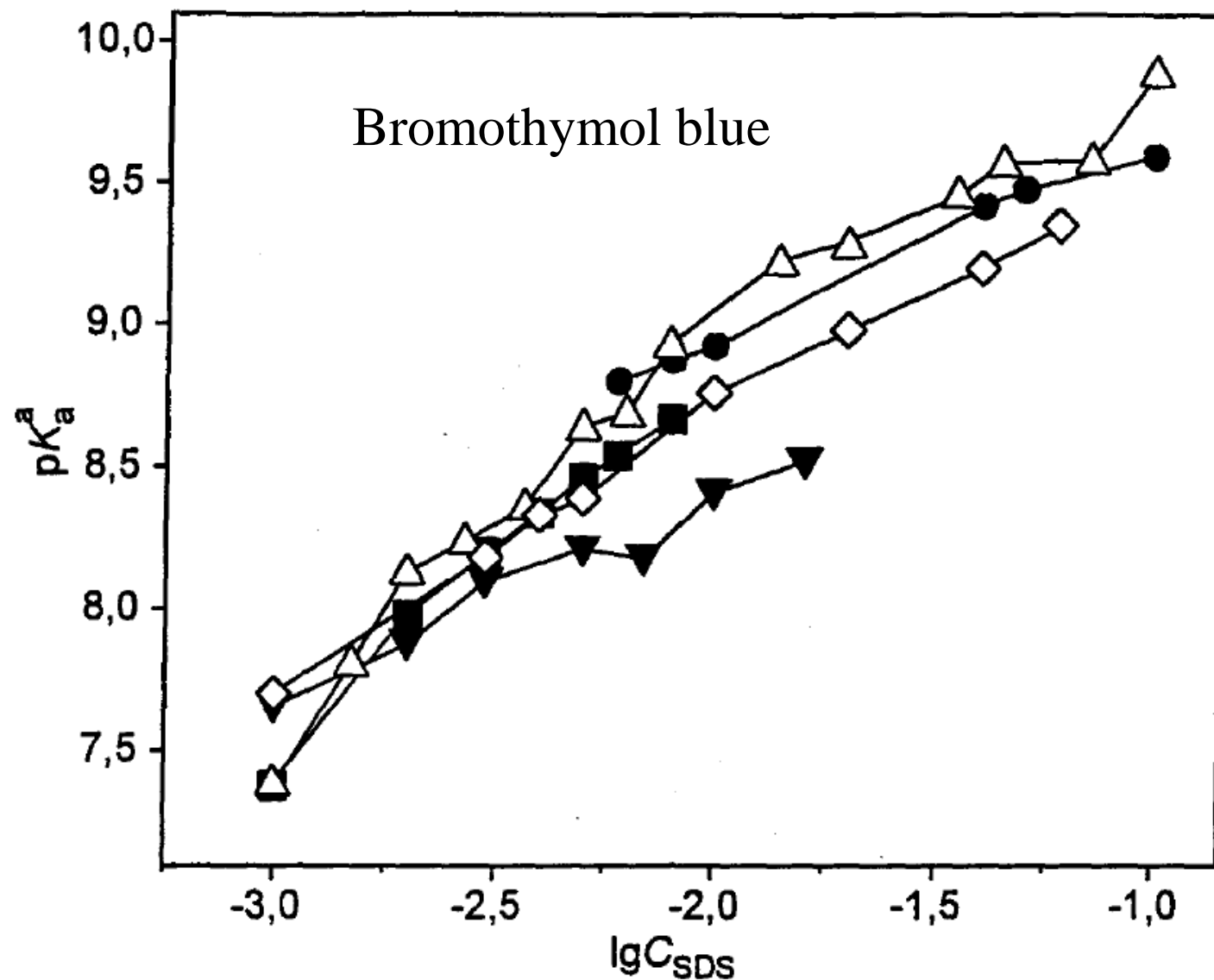


Figure 1. The dependence of pK_a^a of bromothymol blue on $\log C_{\text{SDS}}$ at ionic strength 0.2 mol dm^{-3} : \blacksquare – tris buffers; \bullet – borax buffers; Δ – phosphate buffers; \blacklozenge – phosphate buffers, 0.2 mol dm^{-3} of pentanol; \diamond – borax buffers, 90% SDS + 10% Brij 35.

Relation between $K_{b,i}$ and P_i

$$P_i = \frac{a_i^m}{a_i^w} = \frac{n_i^m V_w}{n_i^w f_i^w V_m}; \quad K_{b,i} = \frac{n_i^m V_t}{n_i^w n_{\text{surf}}^m}; \quad V_t \approx V_w$$

$$P_i = \frac{a_i^m}{a_i^w} = K_{b,i} (c_{\text{surf}} - CMC) \frac{V_w}{V_m f_i^w};$$

$$P_i = K_{b,i} \frac{s}{f_i^w};$$

$$s = \frac{n_{\text{surf}}^m}{V_m}; \quad \leftarrow \text{surfactant concentration in micelles}$$

$$pK_a^{\text{app}} = \text{pH}_w + \log \frac{[\text{HA}_w]_t \left\{ 1 + K_{b,\text{HA}} (c_{\text{surf}} - \text{CMC}) \right\}}{[\text{A}_w]_t \left\{ 1 + K_{b,\text{A}} (c_{\text{surf}} - \text{CMC}) \right\}}$$

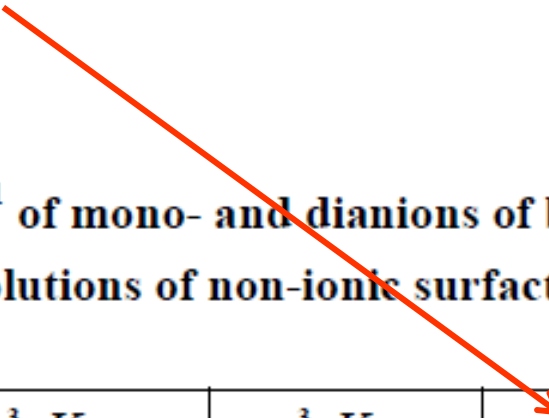
$$pK_a^{\text{app}} = \text{pH}_w + \log \frac{[\text{HA}_m]_t \left\{ 1 + K_{b,\text{HA}}^{-1} (c_{\text{surf}} - \text{CMC})^{-1} \right\}}{[\text{A}_m]_t \left\{ 1 + K_{b,\text{A}}^{-1} (c_{\text{surf}} - \text{CMC})^{-1} \right\}}$$

$$pK_a^{\text{app}} = pK_a^{\text{a,c}} + \log \frac{1 + K_{b,\text{HA}}^{-1} (c_{\text{surf}} - \text{CMC})^{-1}}{1 + K_{b,\text{A}}^{-1} (c_{\text{surf}} - \text{CMC})^{-1}}$$

apparent dissociation constant under conditions of complete binding

Apparent dissociation constant under conditions of complete binding

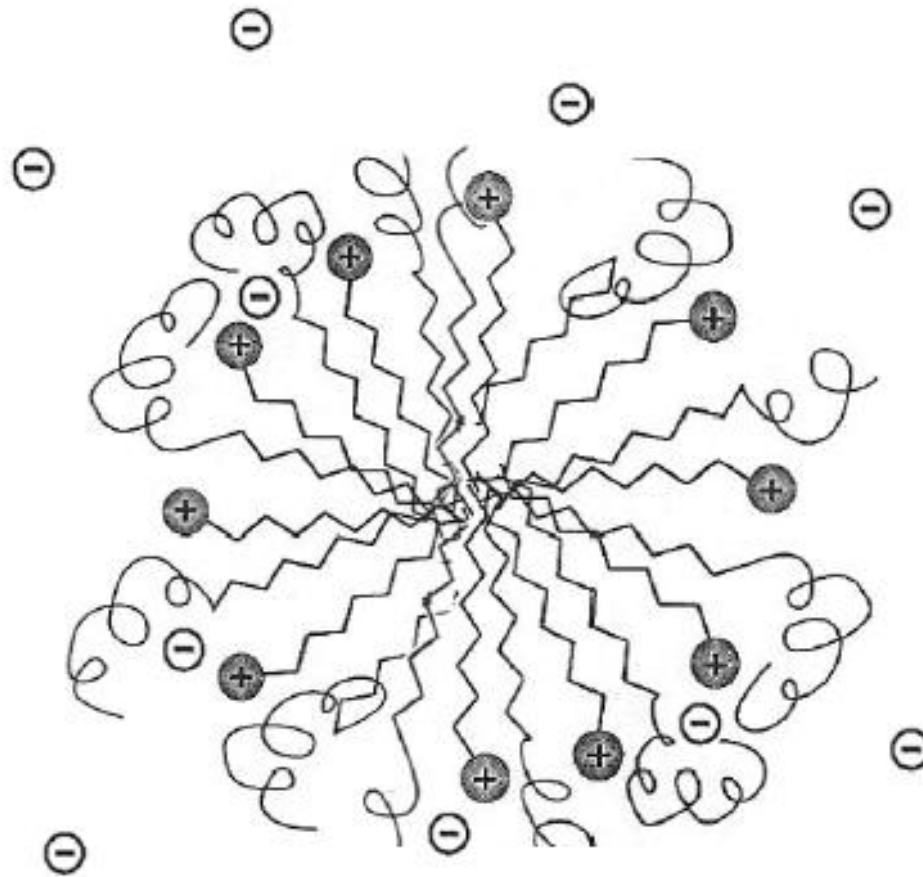
Table 1. The values of binding constants/ M^{-1} of mono- and dianions of bromophenol blue and the calculated $pK_a^{\text{app,c}}$ values in solutions of non-ionic surfactants [15,97]



Surfactant	c_{surf}, M	$10^{-3} K_{b,HB^-}$	$10^{-3} K_{b,B^{2-}}$	$pK_{a,2}^{\text{app,c}}$
Brij 35 ^a	$1 \times 10^{-4} - 0.01$	12	1.2	5.10 ± 0.03
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Nonyl phenol 12 ^b	$2 \times 10^{-4} - 0.004$	20	2.7	4.80 ± 0.03
Tween 80 ^b	$1.5 \times 10^{-4} - 0.05$	13	0.90	5.09 ± 0.03

^a Ionic strength $I = 0.01 M$; ^b $I = 0.05 M$.

Mixed surfactant micelles



A schematic sketch of the section of a spherical (cationic + nonionic) mixed surfactant micelle

Rubin (basing on the theory of regular solutions):

$$y^2 \ln(\text{cmc}^* x / \text{cmc}_{\text{ionic}} y) = (1 - y)^2 \ln[\text{cmc}^* (1 - x) / \text{cmc}_{\text{nonionic}} (1 - y)]$$

y - molar fraction of the ionic surfactant in micelles, x – molar fraction in the system

The pK_a values of indicators in mixed micelles

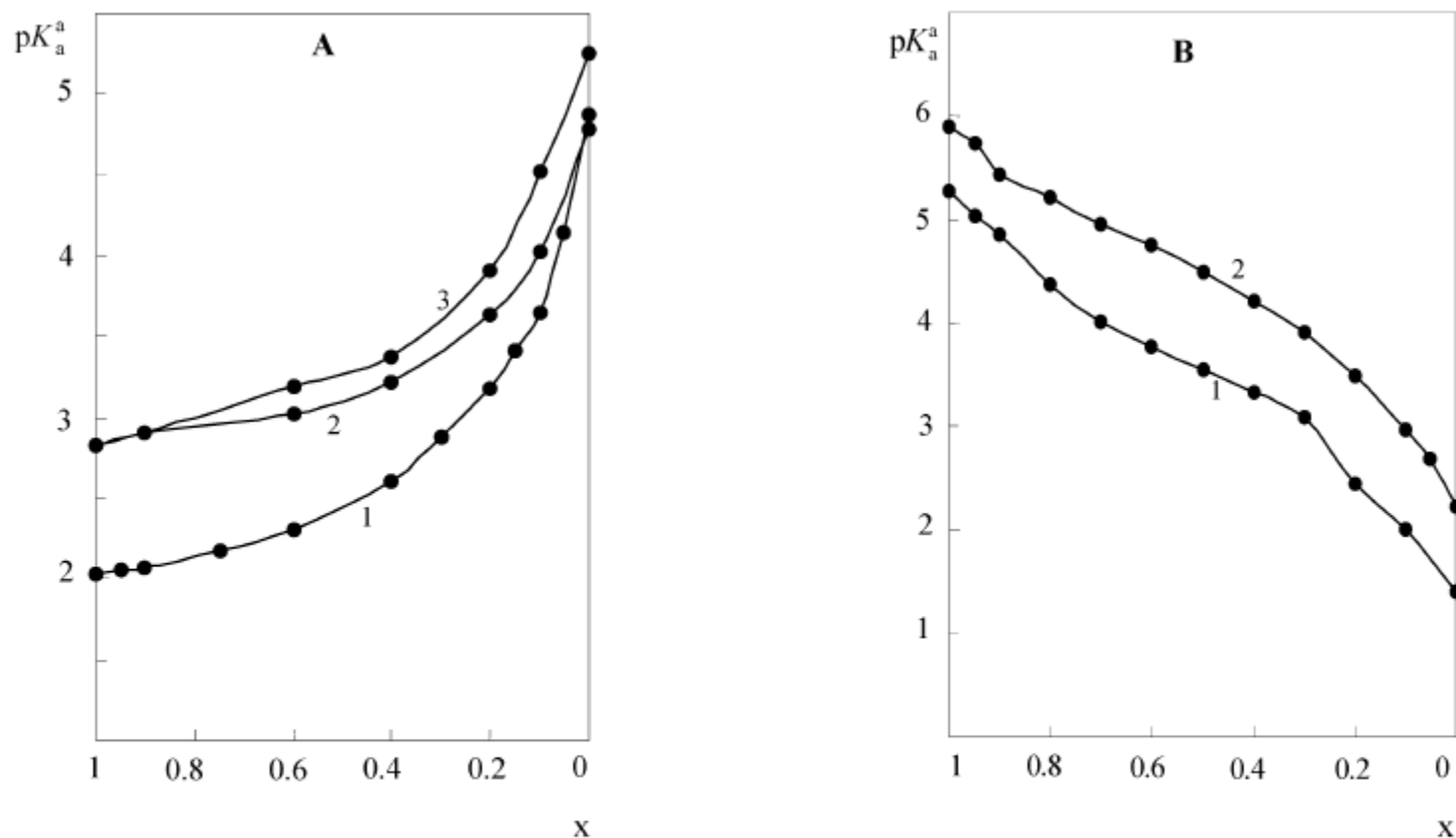
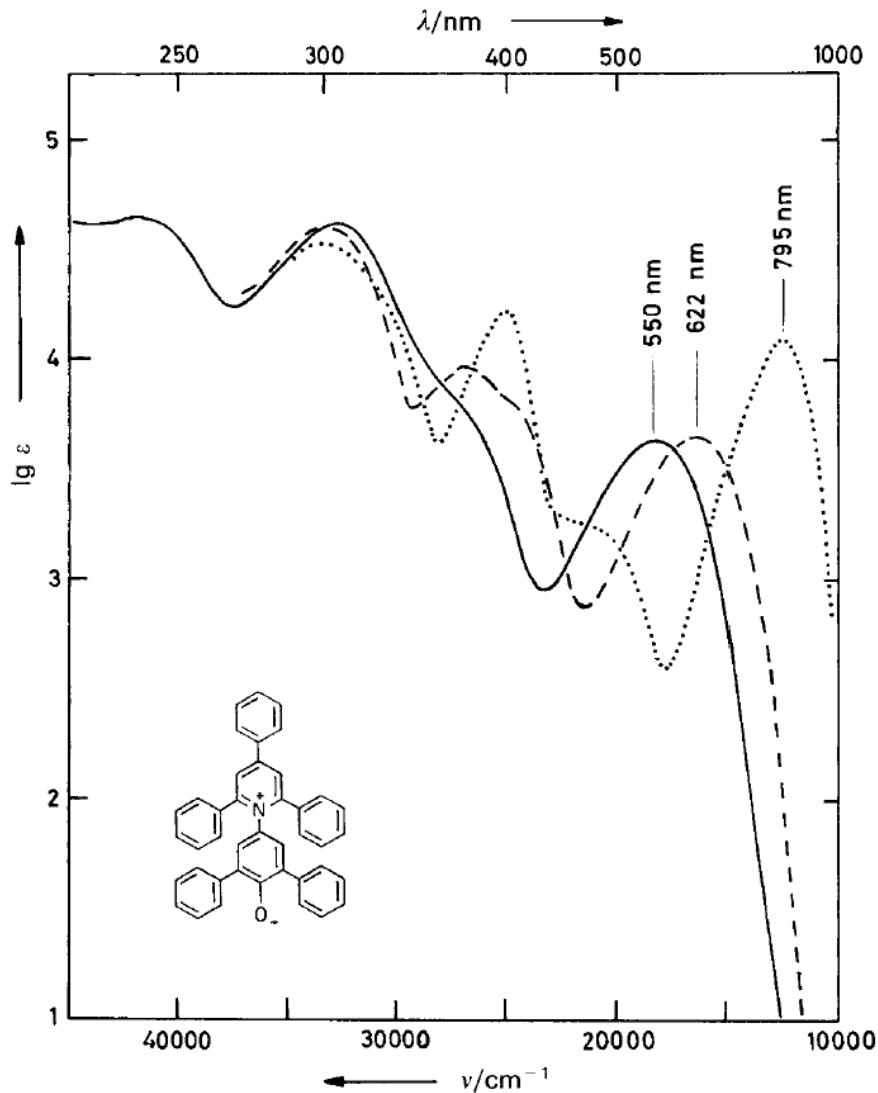


Fig. 4 (A) pK_{a2}^{ac} of bromophenol blue as a function of the molar fraction of CTAB in its mixtures with Nonylphenol-12 (1, 2) and Tween-60 (3) at total concentration of surfactants of 0.003 M and $I = 0.01$ M (NaCl + buffer) (1) and 0.05 M (NaBr + buffer) (2,3). (B) pK_{a0}^{ac} of methyl yellow (1) and hexamethoxy red (2) as a function of the molar fraction of SDS in its mixtures with Nonylphenol-12 at total concentration of surfactants of 0.02 M and $I = 0.01$ M (NaCl + buffer); 25 °C (Data from ref. [281]).

Solvent Polarity. **Solvatochromism**



The position of the absorption band maxima of electronic spectra depends on the solvent nature

Fig. 6-2. UV/Vis absorption spectrum of 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate in ethanol (—), acetonitrile (---), and 1,4-dioxane (·····) at 25 °C [10, 29].

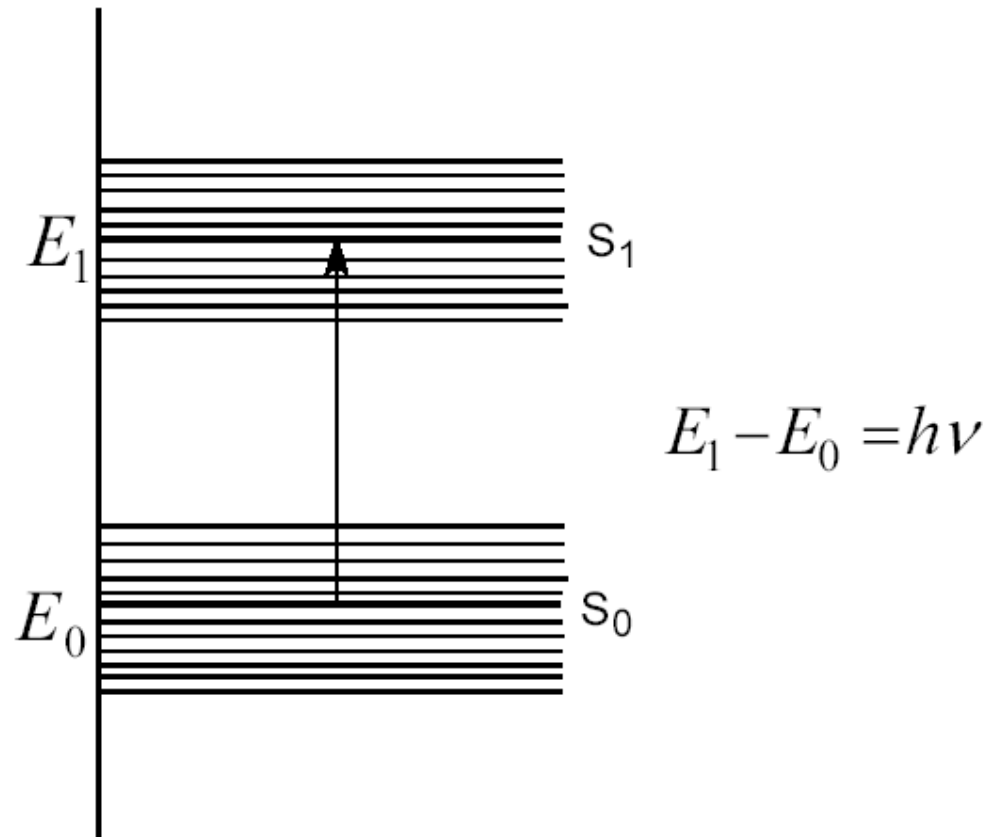
Light absorption is an intramolecular process

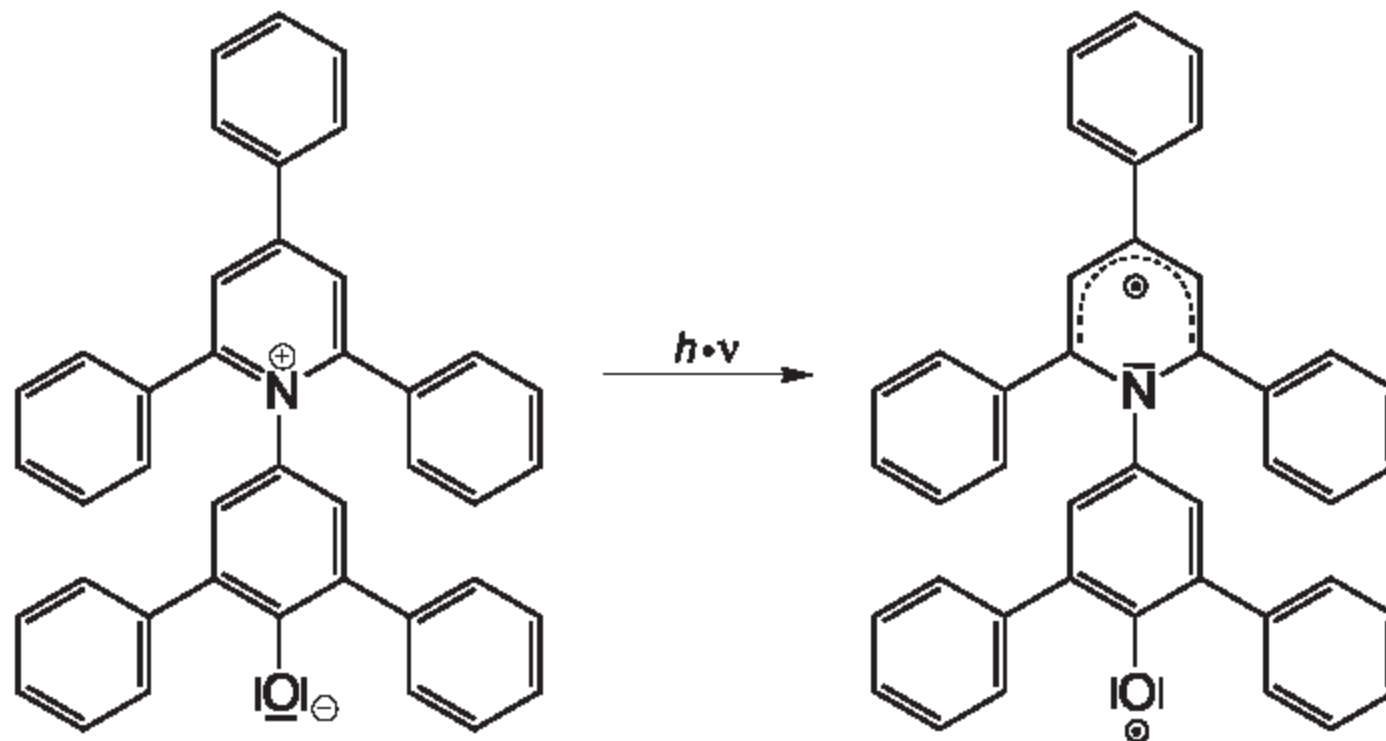
The Franck – Condon principle: time of molecular vibrations is about 10^{-12} s, whereas the time of electron transition is about 10^{-15} s.

Energy of a quant:

$$E = h\nu, \quad h = 6.6256 \times 10^{-34} \text{ J s}$$

$$\nu = \frac{c}{\lambda}; \quad c = 2.997925 \times 10^8 \text{ m s}^{-1}$$

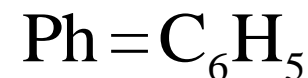
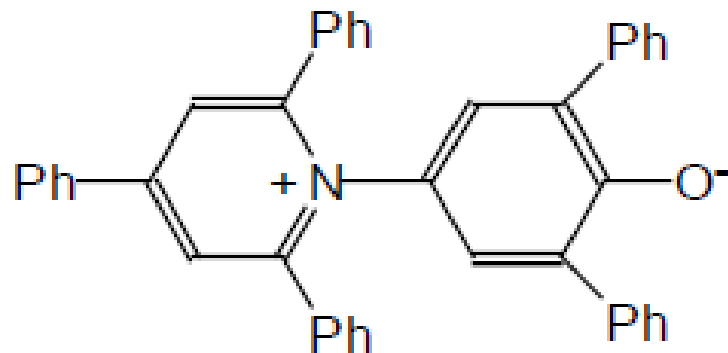




Solvent	$(\text{C}_6\text{H}_5)_2\text{O}^{\text{a)}$	$\text{C}_6\text{H}_5\text{OCH}_3$	CH_3COCH_3	$i\text{-C}_5\text{H}_{11}\text{OH}$	$\text{C}_2\text{H}_5\text{OH}$	CH_3OH	$\text{H}_2\text{O}^{\text{a)}$
$\lambda_{\text{max}}/\text{nm}$	810	771	677	583	550	516	453
Solution colour	–	yellow	green	blue	violet	red	–
Solvent polarity	—————→						

^{a)} Solubility very low.

Pyridinium N-phenolate (Reichardt's dye)



$$E_{\text{T}} = hc\tilde{\nu}N_{\text{A}} = \frac{28591}{\lambda} (\text{kcal mole}^{-1})$$

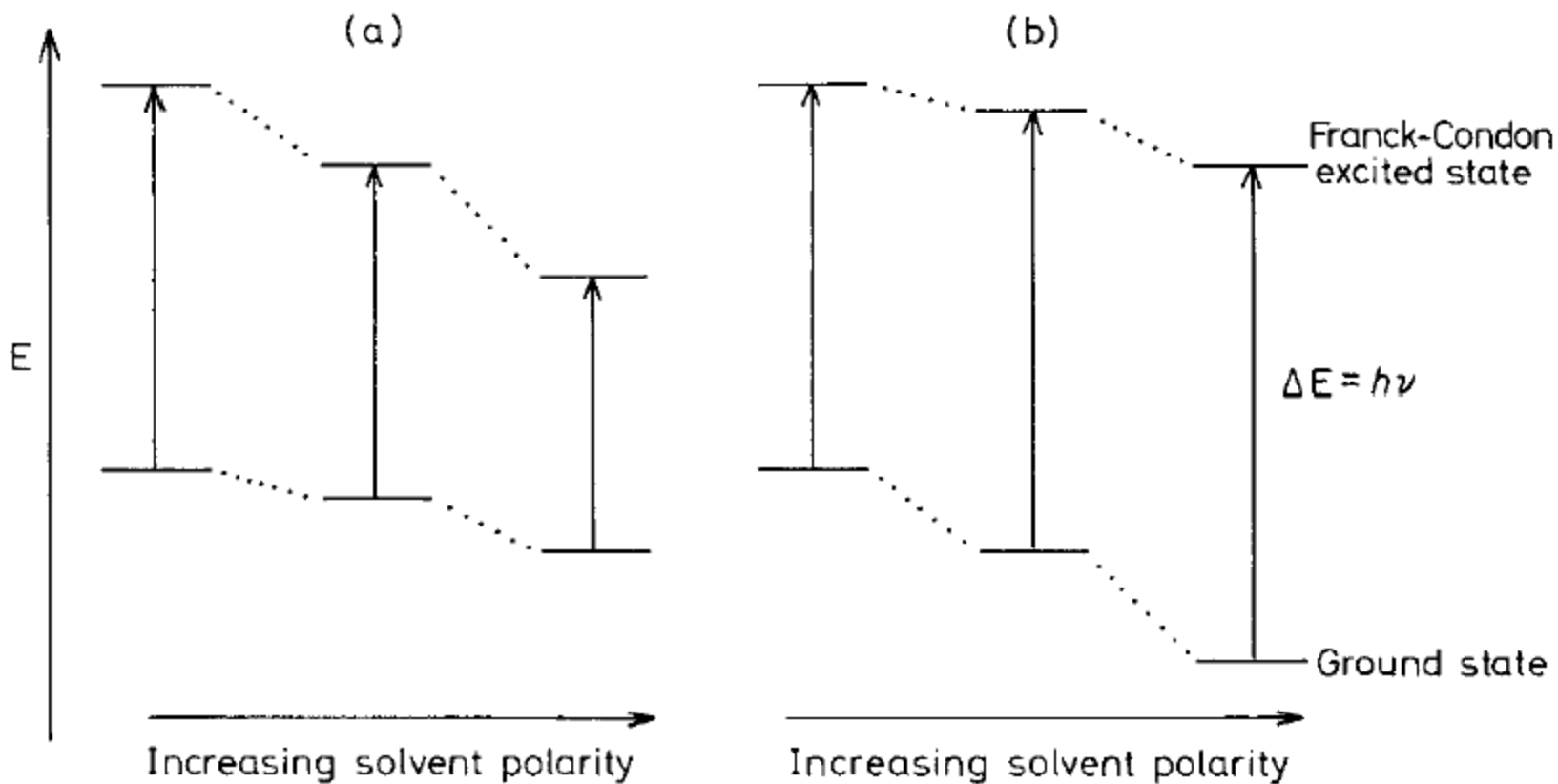
$\tilde{\nu}$ – wavenumber in cm^{-1} ; λ – wavelength in nm

$$E_{\text{T}}^{\text{N}} = \frac{E_{\text{T}} - 30.7}{32.4}$$

Solvent influence on absorption spectra :
positive (a) and negative (b) solvatochromism

$$\mu_g < \mu_e$$

$$\mu_g > \mu_e$$



Solvatochromic polarity scale of solvents (several examples)

Solvent	E_T^N
Water	1.000
Methanol	0.762
Ethanol	0.654
Acetonitrile	0.460
Dimethyl sulfoxide	0.444
Acetone	0.355
1,4-Dioxane	0.164
n-Hexane	0.009
Tetramethylsilane	0.000

Main idea of solvatochromic dyes application to surfactant micelles consists in comparison with organic solvent

Micellar system ^a	λ_{\max}/nm (E_T^N)
None (water)	453 (1.000)
SDS ^d	497 (0.828)
SDS, 0.40 NaCl	497 (0.828)
SDS, 0.003 M $n\text{-C}_{10}\text{H}_{21}\text{N}(\text{C}_2\text{H}_5)_3^+\text{HSO}_3^-$	503 (0.807)
SDS, 0.01 M $\text{N}(n\text{-C}_4\text{H}_9)_4\text{I}^e$	505 (0.800)
SDS – 1-pentanol – benzene (ME) ^f	502 (0.810)
SDS, 50 °C	502 (0.810)
$n\text{-C}_{13}\text{H}_{27}\text{OSO}_3\text{Na}$, 50 °C	511 (0.779)
$n\text{-C}_{14}\text{H}_{29}\text{OSO}_3\text{Na}$, 50 °C	502 (0.810)
$n\text{-C}_{16}\text{H}_{33}\text{OSO}_3\text{Na}$, 50 °C	510 (0.783)
$n\text{-C}_{10}\text{H}_{21}\text{SO}_3\text{Na}$, 0.40 NaCl	501 (0.814)
$n\text{-C}_{10}\text{H}_{21}\text{SO}_3\text{Na}$ (0.02 M)	496 (0.832)
$n\text{-C}_{10}\text{H}_{21}\text{SO}_3\text{Na}$ (0.03 M)	507 (0.793)
$n\text{-C}_{16}\text{H}_{33}\text{SO}_3\text{Na}$, 50 °C	505 (0.800)
$n\text{-C}_{12}\text{H}_{25}\text{C}_6\text{H}_4\text{SO}_3\text{Na}$	495 (0.835)
$n\text{-C}_{12}\text{H}_{25}\text{C}_6\text{H}_4\text{SO}_3\text{Na}$, 50 °C	495 (0.835)
$n\text{-C}_{12}\text{H}_{25}(\text{OC}_2\text{H}_4)_3\text{OSO}_3\text{Na}$	495 (0.835)

Nonyl phenol 12 (nonionic surf.)	538 (0.693)
Tween 80 – 1-pentanol – <i>n</i> -hexane (ME) ⁱ	545 (0.672)
Tween 80 – 1-butanol – <i>n</i> -hexane (ME) ⁱ	535 (0.702)
Triton X 100 – 1-butanol – <i>n</i> -hexane (ME) ⁱ	543 (0.678)
Brij 35 – 1-butanol – <i>n</i> -hexane (ME) ⁱ	554 (0.645)
Tween 80 – cyclohexanol – <i>n</i> -hexane (ME) ⁱ	544 (0.674)
Tween 80 – 1-butanol – cyclohexane (ME) ⁱ	545 (0.672)
<i>n</i> -C ₁₆ H ₃₃ N ⁺ (CH ₃) ₂ (CH ₂) ₃ SO ₃ ⁻ (0.001 M)	550 (0.657)
CTAB ^h	540 (0.687)
CTAB, 0.40 NaCl	543 (0.678)
CTAB, 0.01 M C ₇ H ₇ SO ₃ Na ^e	540 (0.687)
CTAB, 50 °C	542 (0.681)
CTAB (0.003 M), 4.00 KCl	562 (0.623)
<i>n</i> -C ₁₆ H ₃₃ NC ₅ H ₅ Br	535 (0.702)
CPC ^j	538 (0.693)
<i>n</i> -C ₁₈ H ₃₇ N(CH ₃) ₃ Cl, 30 °C	543 (0.678)

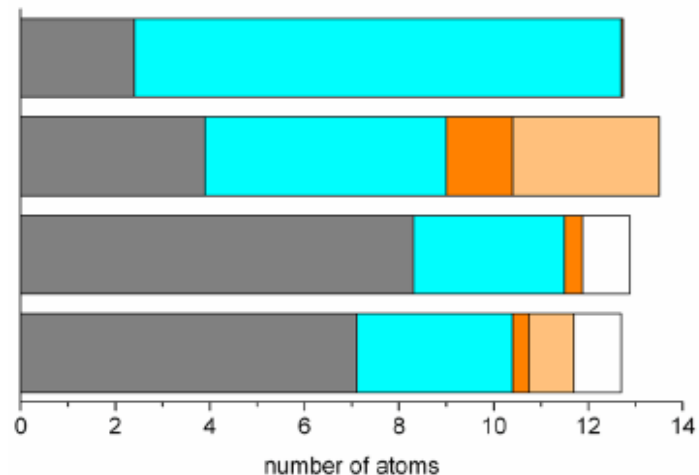
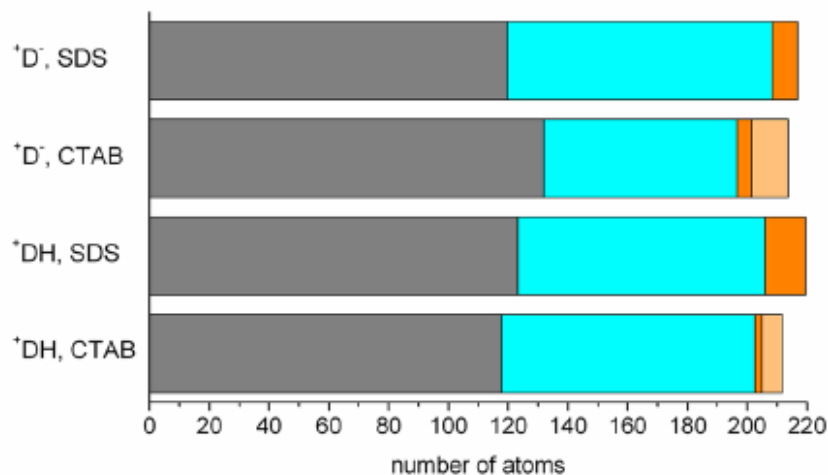
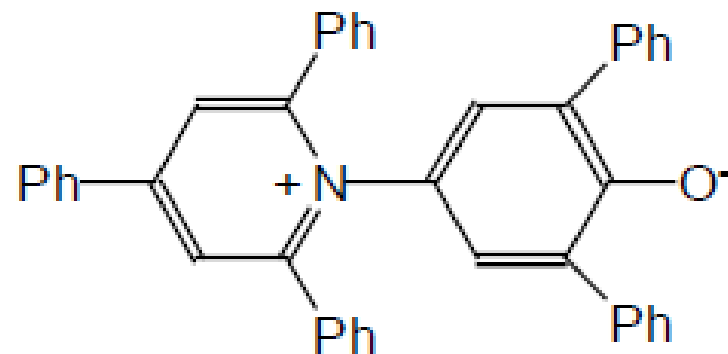
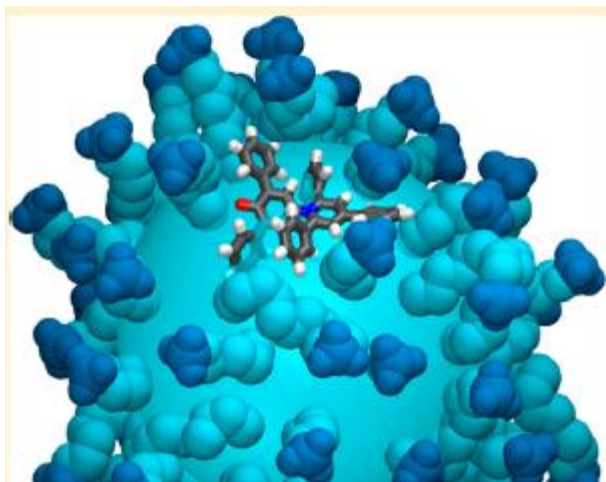
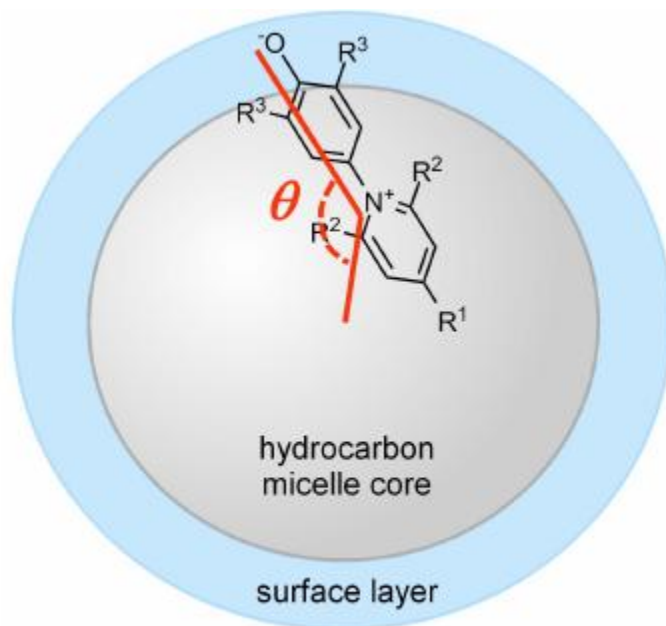


Figure 5. Average numbers of various atoms in microenvironments of the whole dye molecule (left) and the O atom (right). The sections of bars correspond to (left to right) the micelle core atoms (gray), the water atoms (cyan), the headgroup weight atoms (orange), the headgroup H atoms (light orange), and the bonded H atom (white).

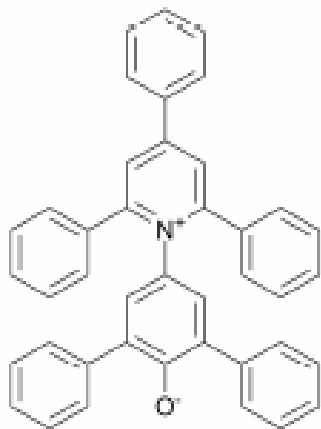
Molecular dynamics simulations allow revealing (predicting) the locus of the solvatochromic indicators within the micellar phase



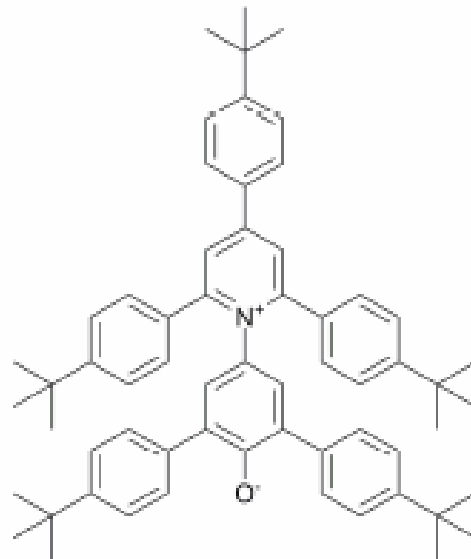
Definition of the angle θ that characterizes the inclination of the dye molecules.

Different solvatochromic betaine dyes

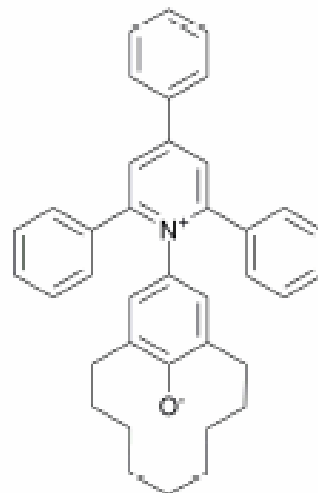
A:



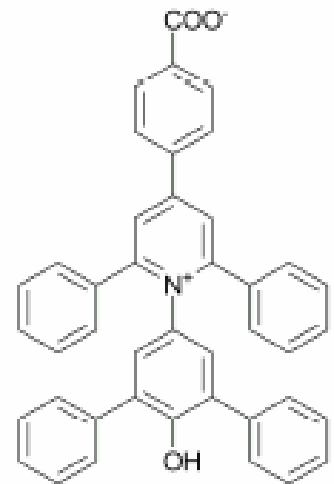
RD-Ph (I)



RD-PhtBu (V)

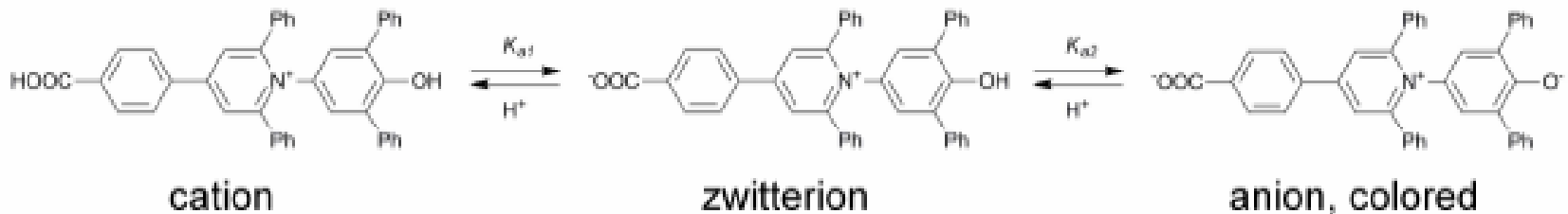


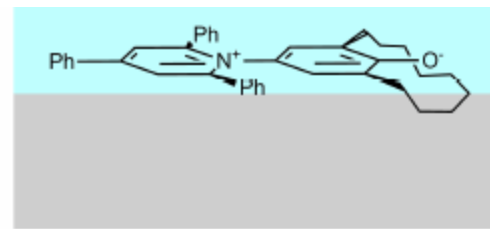
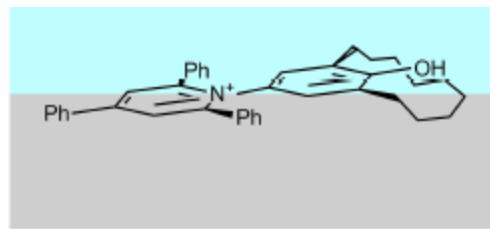
RD-cyclo9 (VI)



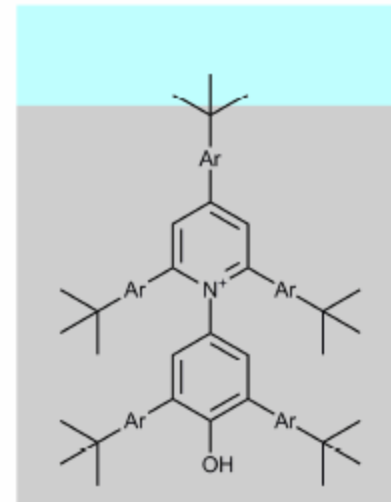
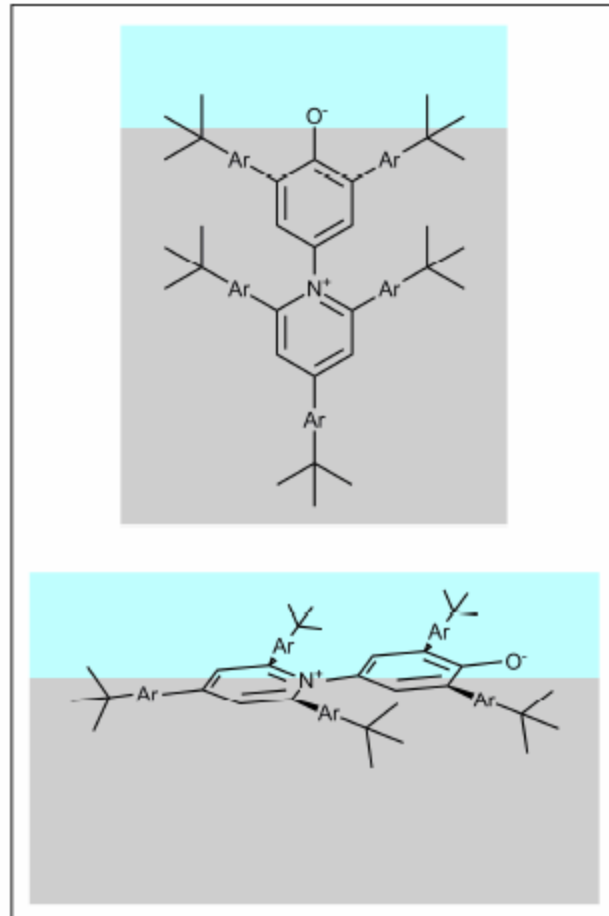
RD-COOH (VII)

B:

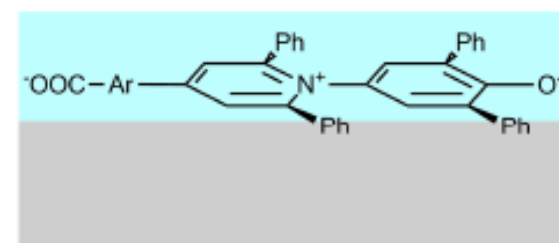
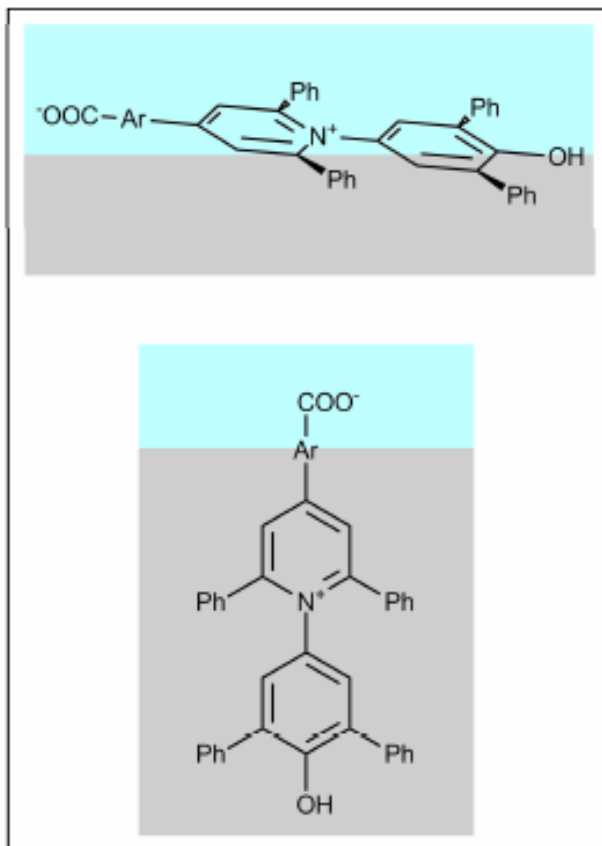
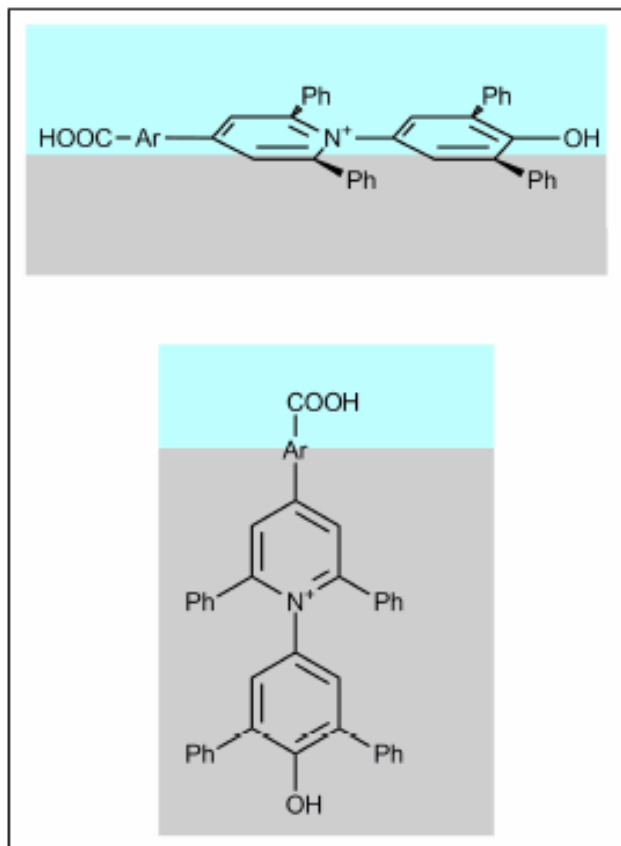




A



B



C

SURFACE ACIDITY OF WATER

Several years ago, this problem was on the boil because some theoretical papers predicted the acidic character of the water/air interface, whereas the experimental measurements of the zeta-potential of air (or argon) bubbles indicated a substantial negative charge. The last is probably caused by HO⁻ ions.

PNAS USA 2007

Water surface is acidic

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Biochemistry, Academy of Sciences of the Czech Republic and Center for Bic
Czech Republic; and †Department of Chemistry, Oklahoma State University, Stillwater

Edited by Mark A. Ratner, Northwestern University, Evanston, IL, and approved Mark

Water autolization reaction $2\text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}^-$ is a textbook process of basic importance, resulting in $\text{pH} = 7$ for pure water. However, pH of pure water surface is shown to be significantly lower, the reduction being caused by proton stabilization at the surface. The evidence presented here includes *ab initio* and classical molecular dynamics simulations of water slabs with solvated H_3O^+ and OH^- ions, density functional studies of $(\text{H}_2\text{O})_{48}\text{H}^+$ clusters, and spectroscopic isotopic-exchange data for D_2O substitutional impurities at the surface and in the interior of ice nanocrystals. Because H_3O^+ does, but OH^- does not, display preference for surface sites, the H_2O surface is predicted to be acidic with $\text{pH} < 4.8$. For similar reasons, the strength of some weak acids, such as carbonic acid, is expected to increase at the surface. Enhanced surface acidity can have a significant impact on aqueous surface chemistry, e.g., in the atmosphere.

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The surface of neat water is basic

James K. Beattie,* Alex M. Djerdjev and Gregory G. Warr

Received 28th March 2008, Accepted 28th May 2008

First published as an Advance Article on the web 18th September 2008

DOI: 10.1039/b805266b

Theoretical studies which conclude that the surface of neat water is acidic (with a $\text{pH} \leq 4.8$), due to the preferential adsorption of hydronium ions, are contrary to the available experimental evidence. Air bubbles in water have a negative charge, as do hydrophobic oil drops in water, and streaming potential measurements on inert surfaces such as Teflon in water show a similar negative surface charge. In each case the pH dependence of the zeta potential has an isoelectric point between $\text{pH} 2-4$. An isoelectric point of $\text{pH} 4$ implies

Direct simulation o
because of the activati
study of bulk autoioni

On the interfacial and dynamical properties of the hydroxide ion

The natures of the aqueous hydroxide and hydronium ions are clearly of special interest to broad areas of science. Recent theoretical and experimental advances have permitted these species to be examined at a greatly enhanced level of detail in both aqueous solutions and in size-selected clusters. While there is fairly general agreement regarding the behavior of hydronium, recent papers on hydroxide have generated considerable controversy. Several FRONTIERS articles have addressed molecular-level details regarding the interfacial propensity, transport properties, and reorientation dynamics of hydroxide, revealing the crucial role of hydrogen bond rearrangements in the first and second solvation shells. In this issue, two new FRONTIERS articles address these same subjects from new perspectives, and two Comments from prominent figures in

that exist between members of that community and chemical physicists regarding the interfacial properties of hydroxide. Such welcome dialogue illustrates the deceptively complex nature of this fundamental anion.

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Chemical Physics Letters 458 (2008) 255–261



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Frontiers article

Is the liquid water surface basic or acidic? Macroscopic vs. molecular-scale investigations

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Department of Chemistry, University of California, Berkeley, CA 94720-1460, United States

This paper is published as part of Faraday Discussions

volume 141:

Water – From Interface
Bulk

DISCUSSIONS

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General discussion

Introductory Lecture

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Pavel Jungwirth, *Faraday Discuss.*, 200

DOI: [10.1039/b816684f](https://doi.org/10.1039/b816684f)

Papers

[The surface of neat water is basic](#)

James K. Beattie, Alex M. Djerdjev and

Warr, *Faraday Discuss.*, 2009

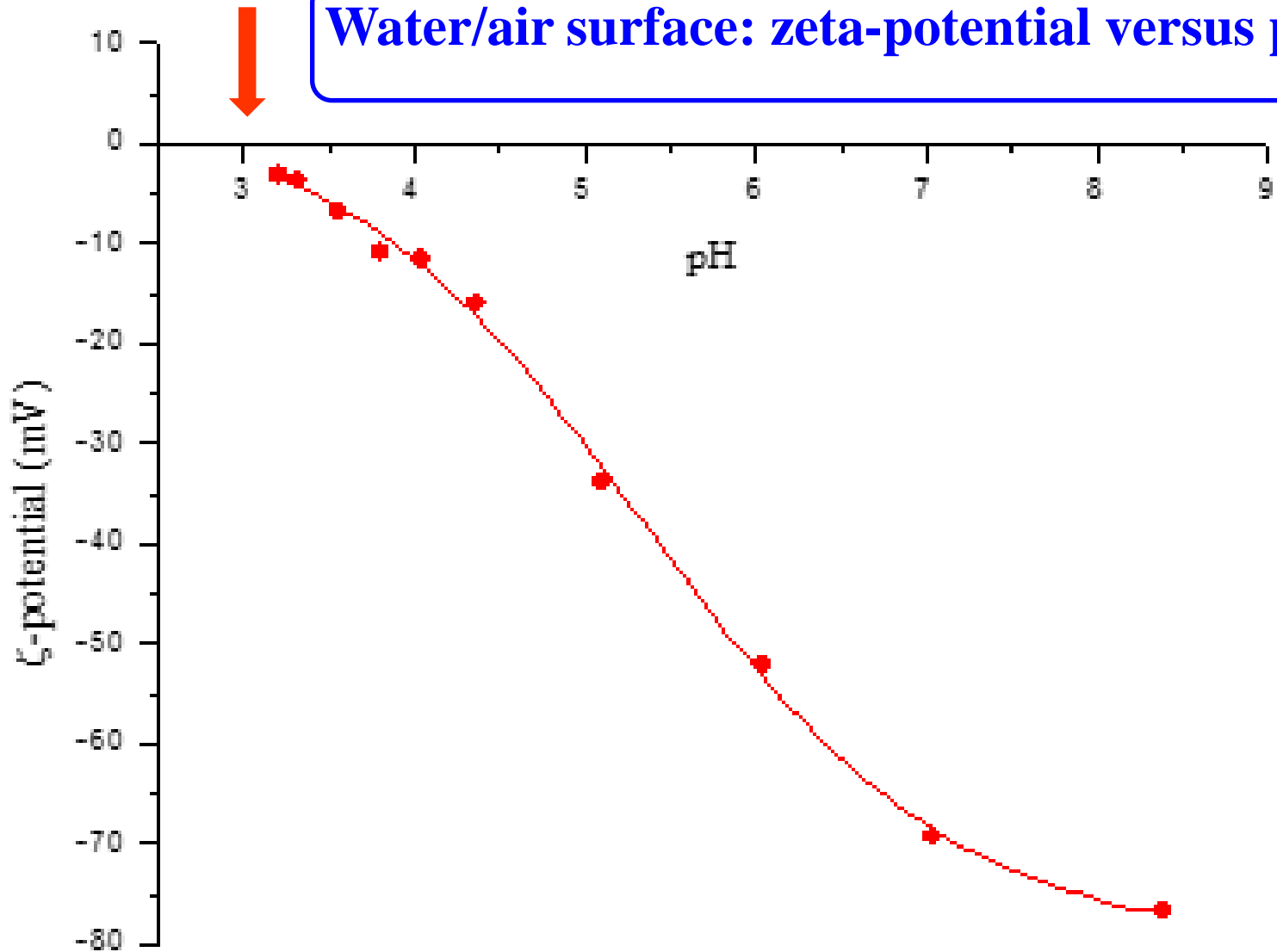
DOI: [10.1039/b805266b](https://doi.org/10.1039/b805266b)

Professor Finney opened the discussion of the introductory lecture by Professor Jungwirth: The ΔG values given for both H_3O^+ (-3 kcal mol^{-1} and OH^- ($+1 \text{ kcal mol}^{-1}$) each came with an “error” of $\pm 1 \text{ kcal mol}^{-1}$. Assuming this “error bar” is a standard error, this means that the 95% probability ranges of both these values overlap. Bearing in mind also the fact that these ΔG values are of the order of a few kT , this implies that the physical implications of the outcome of the simulations will be very sensitive to the simulations themselves (force fields, long range corrections, sample size *etc.*). I worry that too strong conclusions might be being drawn from the simulations.

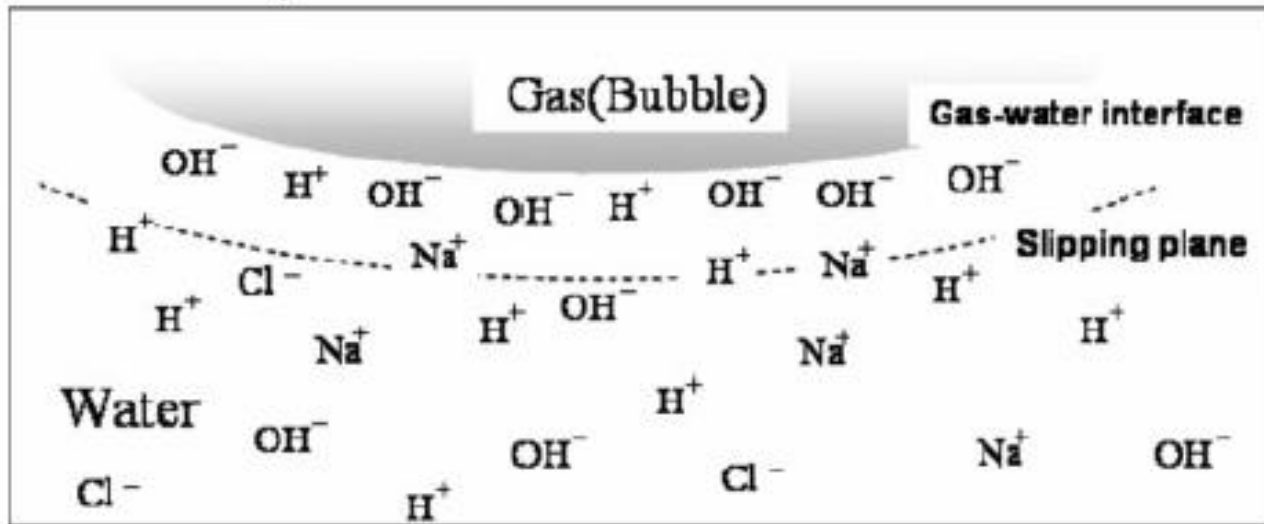
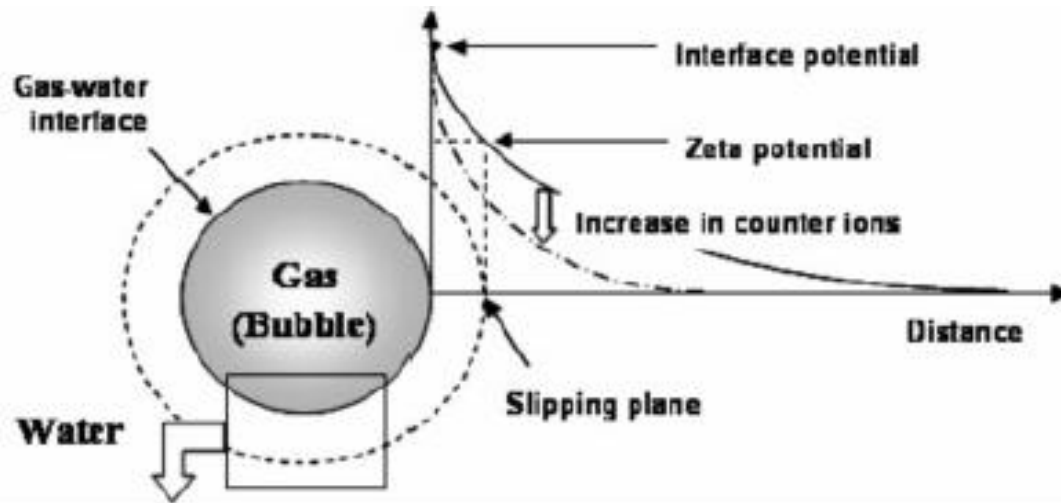
Also, calculations were reported for (a) the singly hydrated proton H_3O^+ and (b) the unhydrated OH^- group. Are these necessarily the entities that should be considered? Have calculations been done for *e.g.* H_5O_2^+ , H_7O_3^+ , H_3O_2^- *etc.*? If so, what were the results?

Professor Jungwirth replied: The confidence level of our $\pm 1 \text{ kcal mol}^{-1}$ statistical error in the free energy calculation is better than 85% (see also analogous calculations by Kubar *et al.*¹ or Yang *et al.*²). Therefore, our free energy values for hydronium and hydroxide with their statistical uncertainties do not overlap with each other, not even in the 95% probability range mentioned by Professor Finney. Concerning the hydrated proton, we performed classical MD calculations for both limiting cases, *i.e.* H_3O^+ (Eigen) and H_5O_2^+ (Zundel). The surface free energy minima for the two species are within 1 kcal mol^{-1} from each other. We did not simulate the delocalized form of hydroxide, H_3O_2^- . It would be worthwhile doing so, particularly in the light of *ab initio* DFT-based MD simulations which suggest an abundance of a rather delocalized form of hydroxide at the interface.

Water/air surface: zeta-potential versus pH

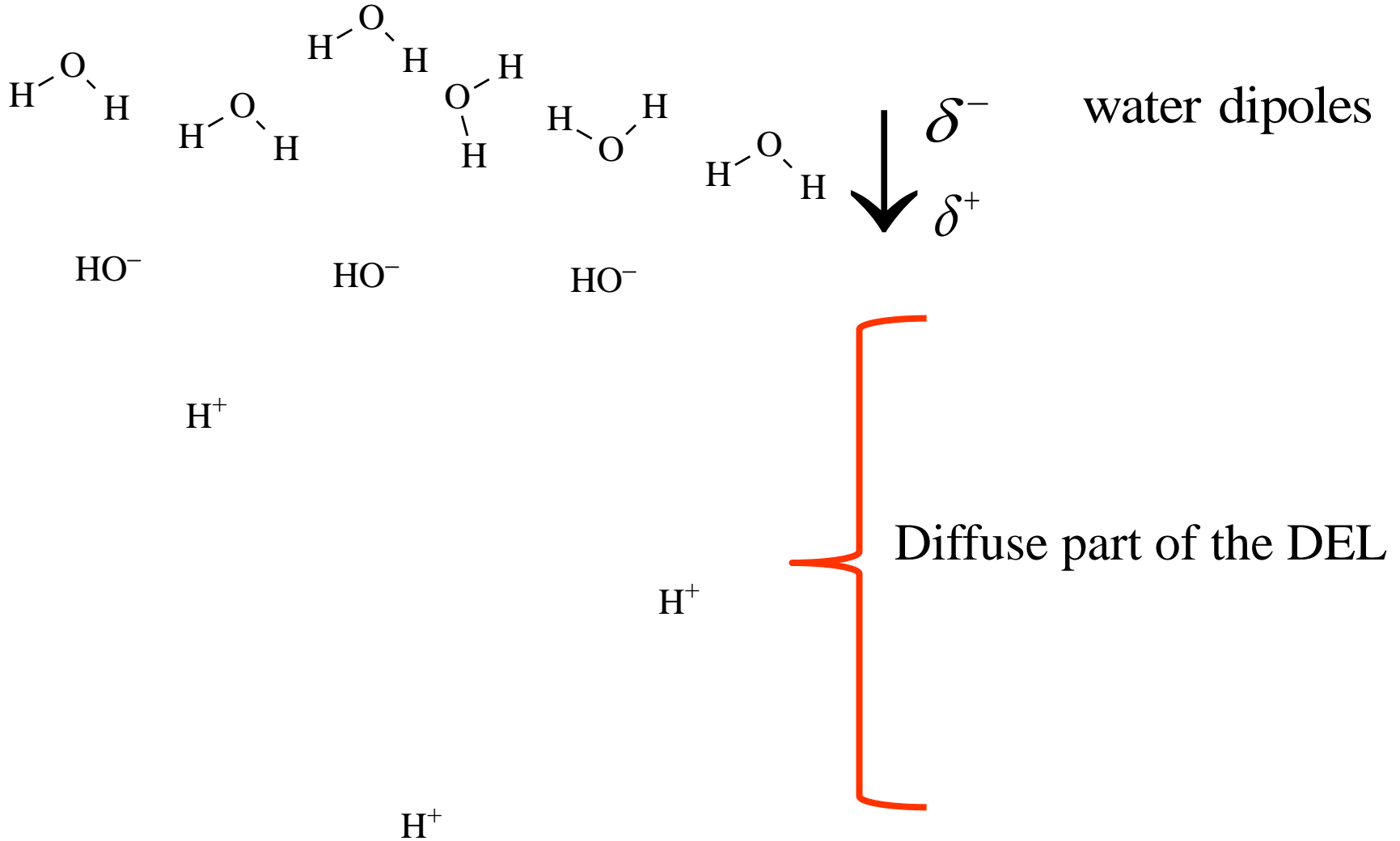


(Prof. James Beattie; Sydney, Australia)



Takahashi, 2005

The structure of water surface



$$\text{pH}_s = \text{pH}_b - \log P_{\text{H}^+}^0 + \frac{\Psi F}{2.303RT}$$

$$\log P_{\text{H}^+}^0 = -\log \gamma_{\text{H}^+}$$

Unfortunately, some authors write:

$$\text{pH}_s = \text{pH}_b + \frac{\Psi F}{2.303RT} \quad ?$$

$$P_{\text{H}^+} = \frac{[\text{H}_s^+]}{[\text{H}_b^+]} = P_{\text{H}^+}^0 \exp\left(-\frac{\Psi F}{RT}\right) \quad P_{\text{HO}^-} = \frac{[\text{HO}_s^-]}{[\text{HO}_b^-]} = P_{\text{HO}^-}^0 \exp\left(\frac{\Psi F}{RT}\right)$$

$$\frac{[\text{HO}_s^-]}{[\text{H}_s^+]} = \frac{P_{\text{HO}^-}^0 [\text{HO}_b^-]}{P_{\text{H}^+}^0 [\text{H}_b^+]} \exp\left(\frac{2\Psi F}{RT}\right)$$

Takahashi,
2005

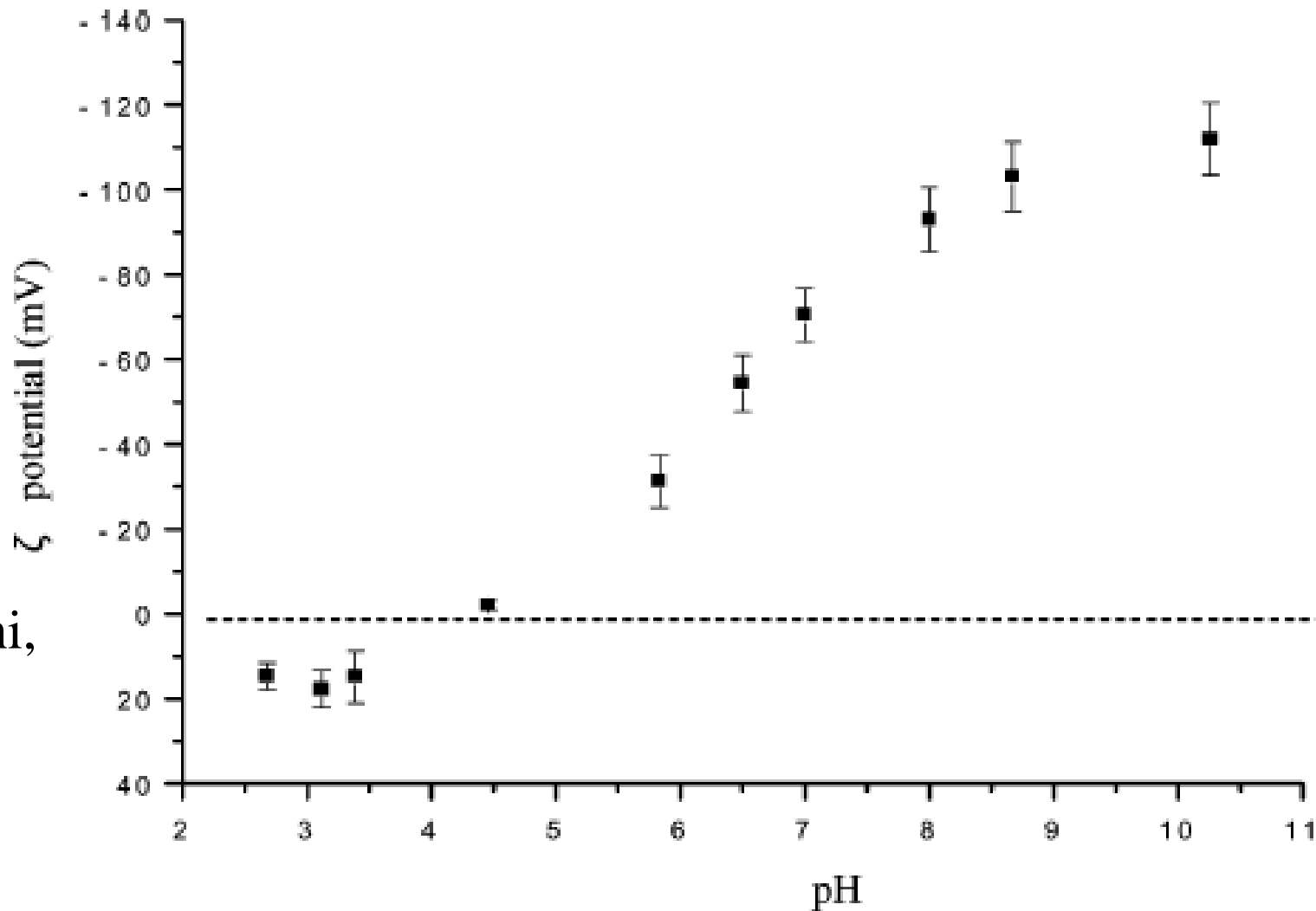


Figure 11. Relationship between the ζ potential of the microbubbles and the pH of the water, determined by HCl and NaOH. The surface charge of the gas–water interface was strongly affected by the pH of the water. The result indicated the important role of H^+ and OH^- in the surface charge.

The pH of the isoelectric state (so-called isoelectric point) is about 3 or 4, as reported by different authors

$$\frac{[\text{HO}_s^-]}{[\text{H}_s^+]} = \frac{P_{\text{HO}^-}^0 [\text{HO}_b^-]}{P_{\text{H}^+}^0 [\text{H}_b^+]} \exp\left(\frac{2\Psi F}{RT}\right)$$

b means “bulk”, or water phase

Therefore, at this pH: $[\text{HO}_s^-] = [\text{H}_s^+]$; $\Psi = 0$; $\exp\left(\frac{2\Psi F}{RT}\right) = 1$;

$$[\text{H}_b^+] \approx (10^{-3} - 10^{-4}) \text{M}$$

$$\frac{P_{\text{HO}^-}^0}{P_{\text{H}^+}^0} \approx \frac{10^{-3}}{10^{-11}} = 10^8 \quad \text{or} \quad \approx \frac{10^{-4}}{10^{-10}} = 10^6$$

Table 4
The $[\text{HO}_3^-]/[\text{H}_3^+]$ ratio calculated using Takahashi's data [8]^a.

pH_b	ζ, mV^b	$[\text{HO}_3^-]/[\text{H}_3^+]$
3.39	+14.1	0.029
4.46	-2.5	1.09
6.52	-54.9	202
6.98	-71.6	546
8.01	-93.8	1.2×10^4
10.26	-112.3	8.4×10^7

^a Calculated for the isoelectric point $\text{pH}_b = 4.40$; $P_{\text{HO}_3^-}^0/P_{\text{H}_3^+}^0 = 1.58 \times 10^5$.

^b The ζ values were used in calculations via Eq. (12) instead of Ψ .

In addition to the numerous discussions, an attempt was made by Tahara's group to apply an acid-base indicator .

Their first work was devoted to the CTAB mono layers on the water surface, and the results were reasonable.

But their results for "bare" water surface were certainly wrong.

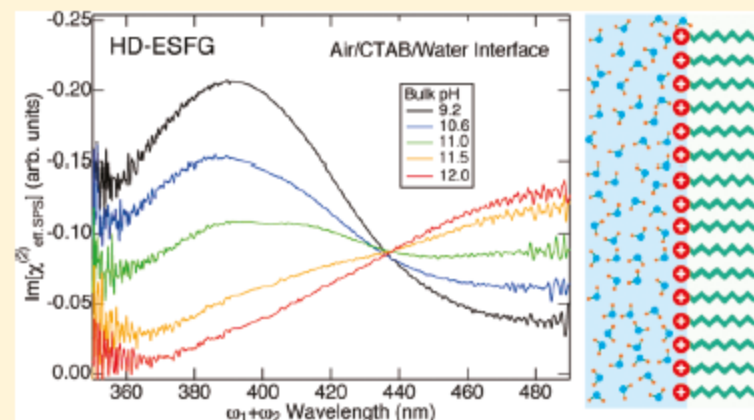
Acid–Base Equilibrium at an Aqueous Interface: pH Spectrometry by Heterodyne-Detected Electronic Sum Frequency Generation

Shoichi Yamaguchi,[†] Kankan Bhattacharyya,[‡] and Tahei Tahara^{*,†}

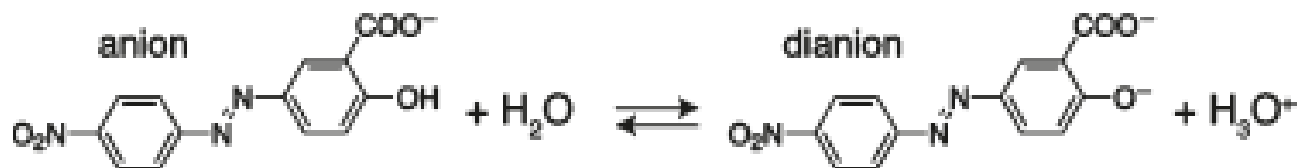
[†]Molecular Spectroscopy Laboratory, Advanced Science Institute (ASI), RIKEN, 2-1 Hirosawa, Wako 351-0198, Japan

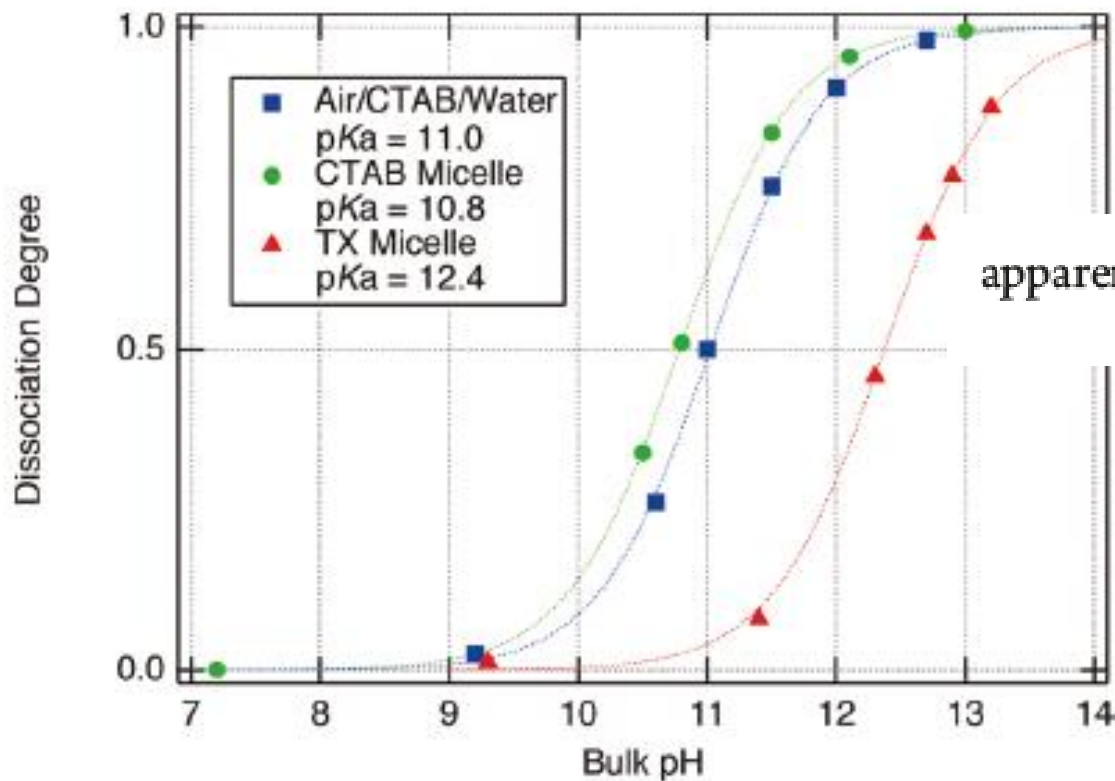
[‡]Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India

ABSTRACT: We applied interface-selective heterodyne-detected electronic sum frequency generation (HD-ESFG) to the pH spectrometry of an air/cationic surfactant/water interface in order to obtain insight into an acid–base equilibrium at the interface. We used an indicator molecule adsorbed at the interface to probe local pH and local effective polarity. We obtained unprecedentedly high quality spectral data of the interfacial pH spectrometry, which clearly indicates that this interface has higher pH than the bulk owing to the positive charge of the head group of the surfactant. In addition, we found that the air/surfactant/water interface and the micelle interface of the same surfactant are essentially equivalent in local pH and local effective polarity.

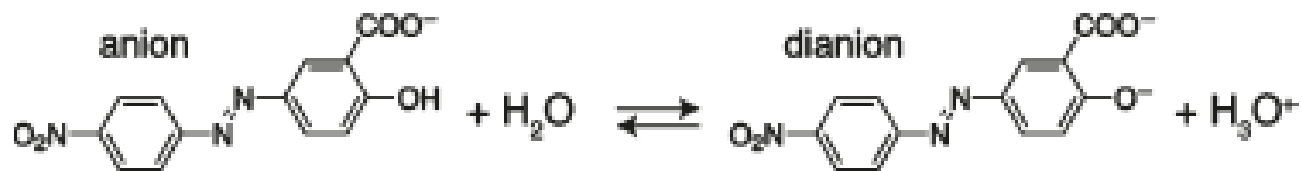


[dx.doi.org/10.1021/jp1113174](https://doi.org/10.1021/jp1113174) | *J. Phys. Chem. C* 2011, 115, 4168–4173





$$\text{apparent } pK_a = \text{bulk pH} - \log_{10} \frac{[A^-]_{\text{int}}}{[HA]_{\text{int}}}$$



The CTAB monolayer displays ca. the same influence as the CTAB micelles in water

An attempt to use the same approach to the

THE JOURNAL OF CHEMICAL PHYSICS 137, 151101 (2012)

Communication: Quantitative estimate of the water surface pH using heterodyne-detected electronic sum frequency generation

Shoichi Yamaguchi,¹ Achintya Kundu,¹ Pratik Sen,² and Tahei Tahara¹

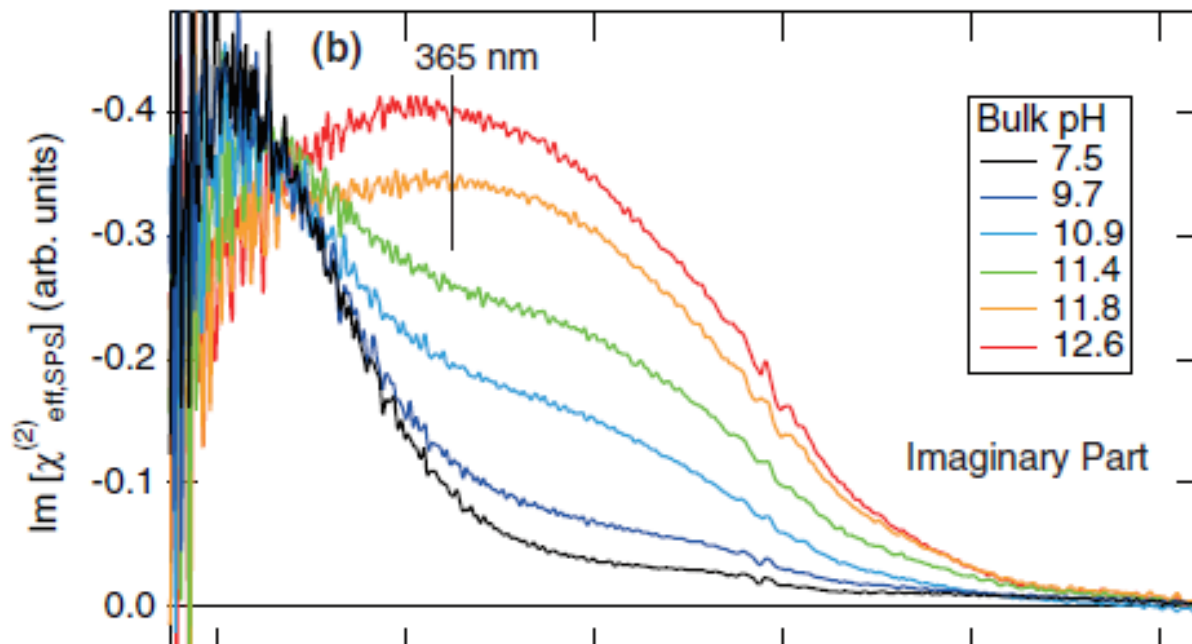
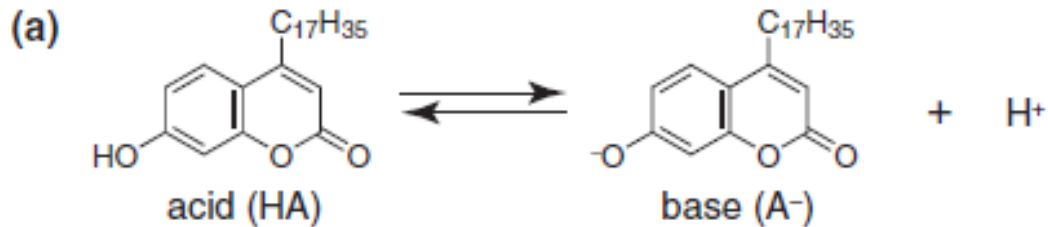
¹*Molecular Spectroscopy Laboratory, RIKEN, Wako 351-0198, Japan*

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Most chemical reactions in water are very sensitive to pH. Many environmentally important chemical reactions are known to take place at the water surface (i.e., air/water interface). However, the pH of the water surface is still controversial. Spectroscopic experiments and theoretical calculations indicate that the water surface is more acidic than the bulk, whereas electrophoretic experiments provide a contrary view. Here, we report that a novel nonlinear optical experiment with a surface-active pH indicator can quantitatively evaluate the pH of the water surface. The result clearly shows that the pH of the water surface is lower than that of the bulk by 1.7. This is the first study to apply a principle of bulk pH measurements to the water surface, and therefore provides a reliable experimental estimate for the pH difference between the water surface and bulk. It is considered that the higher acidity of the water surface plays a key role in marine and atmospheric chemical reactions.

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$$\text{pH}_m - \text{pH}_w = \text{p}K_a^w + \log \frac{P_{\text{HA}}^0}{P_{\text{A}^-}^0} - \log P_{\text{H}^+}^0 - \text{p}K_a^{\text{app}}$$

Processing the data as for surfactant monolayers, Yamaguchi et al. estimated: $\text{pH}_m - \text{pH}_w = -1.7$ and concluded that the surface is acidic.

$$P_i = \frac{a_i^m}{a_i^w} = \exp\left(-\frac{\Phi_i + z_i \Psi F}{RT}\right) = P_i^0 \exp\left(-\frac{z_i \Psi F}{RT}\right)$$

Φ_i is the Stern adsorption potential;

$$pK_a^{\text{app}} = pK_a^w + \log \frac{P_{\text{HA}}^0}{P_{\text{A}^-}^0} - \frac{\Psi F}{2.303RT}; \quad \log \frac{P_{\text{HA}}^0}{P_{\text{A}^-}^0} = \log \frac{\gamma_{\text{A}^-}}{\gamma_{\text{HA}}}$$

$$pH_m - pH_w = \left(pK_a^w + \log \frac{P_{\text{HA}}^0}{P_{\text{A}^-}^0} - \log P_{\text{H}^+}^0 \right) - pK_a^{\text{app}}$$




$$pK_a^m$$

Processing the data as for surfactant monolayers, Yamaguchi et al.

estimated: $pH_m - pH_w = -1.7$

There is a fundamental difference between the acid-base state of the water/air interface and the surface of an ionic surfactant micelle in water or in the water/air interface completely bound by adlayers of ionic surfactants. Indeed, in the last two cases, if $\Psi < 0$, which takes place in anionic surfactant micelles, the concentration of H^+ ions, i.e., hydrated protons, is increasing around the micellar surface: $[H_m^+] > [H_w^+]$. Contrary to it, in micelles of a cationic surfactant, where $\Psi > 0$, the hydroxyl ions are concentrated: $[HO_m^-] > [HO_w^-]$. These relations should be refined by taking into account the P_H^0 values, Eq. (7).

$$pH_s - pH_b = -\log P_{H^+}^0 + \frac{\Psi F}{2.303RT}$$


On “bare” (entire) water surface, this value is extremely low (see above), and therefore $pH_s > pH_b$