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An Equilibrium Study of Reactions Involving a Cationic Surfactant and Various Counterions: Prediction of Ion Selectivity

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Abstract

The thermodynamic equilibrium constants for the reactions between the cationic surfactant, ethylhexadecyldimethylammonium bromide, EHDA–Br, and various anions were determined using spectrophotometric and specific ion electrode measurements. The sequence of stability of $EHDA^+$ in the presence of the anions X^- studied is $Br^- < F^- < H_2PO_4^- < NO_3^- < C_6H_5O^- < I^-$. The sequence of stability of EHDA–X is the reverse of this. The $EHDA^+$ stability sequence is the same as the order of selectivity expected during foam fractionation from published results for Br^-, I^-, NO_3^-, and for $H_2PO_4^-$ and $C_6H_5O^-$, i.e., I^- preferred over NO_3^-, which is preferred over Br^-, etc. The stability and selectivity sequences are interrelated by the steric hindrance of $EHDA^+$ in the presence of the anions X^- at the bubble surface.

INTRODUCTION

Foam fractionation has been widely studied as a technique for removing counterions from aqueous solutions. Of particular interest is the removal of nitrate, iodide, and bromide (*1*) and of phosphate and phenol (*2–5*) by foam fractionation with the quarternary ammonium surfactant, ethylhexadecyldimethylammonium bromide, EHDA–Br. Studies by Grieves (*2*) include the effects on the removal of a particular anion by addition of a

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second anion, usually sulfate or chloride. A competition between the counterions present in solution is established, reducing the removal of the original anion. Grieves has utilized a ratio termed the "relative fractionation" parameter (*2*) which can indicate the relative effectiveness of various anions in removal of $EHDA^+$ from aqueous solution under conditions of competition. Experiments also indicate that removal of counterions from solution is extremely pH-dependent in the case of phenol and orthophosphate (*2–5*). Investigations concerning the selectivity of one anion in preference to another in foam fractionation have been carried out. Shinoda and Fujihira (*6*) studied the relative adsorbability of the ions Cl^-, Br^-, NO_3^-, ClO_3^-, CH_3COO^-, and SO_4^{2-} in the presence of ammonium surfactants. More recently, Grieves (*1*) has determined the selectivity coefficient for NO_3^- vs Br^- and for I^- vs Br^-. The effects of strong inorganic acids and bases on the batch foam fractionation of EHDA–Br have been investigated (*7*) and competition from OH^- is not evident below pH 11.

In their studies of foam fractionation, several workers have made assumptions concerning the equilibrium situation between the surfactant $EHDA^+$ and the counterions. Grieves (*1*) assumed that ion-pair formation occurs between surfactant and counterions present in solution. The surfactant cation–counterion complex then diffuses to the air–solution interface and is there adsorbed. On the other hand, Nguyen and Phillips (*8*) assumed that $EHDA^+$ is adsorbed, and calculated resultant surface potentials.

This study was intended, firstly, to provide additional evidence on the nature of the adsorbed species, and, secondly, to investigate the nature of the equilibria between the cationic surfactant EHDA–Br and the anions F^-, Br^-, I^-, NO_3^-, $H_2PO_4^-$, and $C_6H_5O^-$ and to establish a relationship between the equilibrium constant and the selectivity of a given anion.

EXPERIMENTAL

All solutions were freshly prepared with double distilled water, ethylhexadecyldimethylammonium bromide (EHDA–Br), and the potassium salt of the anion of interest except in the case of the phenolate anion for which C_6H_5OH was used. Concentrations of the salts ranged from 2×10^{-4} to 1×10^{-5} *M* and concentrations of surfactant varied between 1.9×10^{-4} to 1×10^{-5} *M*. The surfactant concentrations were chosen to be below the critical micelle concentration (cmc). The cmc of EHDA–Br in 2.0×10^{-4} *M* NaI was found to be 4.8×10^{-4} *M* at 24°C, and substitution of the salts KBr or KNO_3 would raise this value (*9*). The cmc of EHDA–Br in distilled water was determined as 7.9×10^{-4} *M* at 24°C from surface tension and conductivity data (*10*). Based on a two-phase titration technique using bromophenyl blue as the titrant (*11*), the surfactant was found to be more than 98% active and no further purification was performed. The pH of surfactant–salt mixtures was between 5.7 and 6.1 due to dissolved CO_2. This represents about two orders of magnitude difference between the salt concentrations and the concentration of HCO_3^-; hence no interference from HCO_3^- would be expected. Adjustment of pH to 11.0 in the case of phenolate was accomplished by using minute amounts of KOH.

Concentrations of iodide, bromide, nitrate, and phenolate were determined from absorption measurements obtained on a four-digit display Unicam SP 1700 UV spectrophotometer. Optimum wavelengths for absorption measurements were 230, 198, 210, and 235 nanometers for iodide, bromide, nitrate, and phenolate, respectively. A slit width of 0.30 mm giving a bandwidth of 0.90 nm was considered adequate for the resolution required. Calibration graphs were prepared for each salt and analysis of compounds of known concentrations gave agreement to within 3.5% of the expected concentration. All measurements were recorded at 24°C using 1.000 cm quartz curvettes.

Specific ion electrodes were also used to determine some concentrations. A general halide electrode calibrated for bromide and connected to an Orion specific ion meter model 407 gave potential readings for Br^-; a four-digit readout Orion model 701 was used to determine F^- potentials. Tests indicated that the fluoride electrode was specific for F^- in solutions containing at least a tenfold excess of other halides. To minimize the effect of drift in the 407 model, the average potential measurements of standard solutions obtained before and after a series of mixtures was used for calibration; there was no appreciable drift in the readings obtained on the 701 model. Measurements were recorded at room temperature. Since the degree of protonation of phosphate is pH dependent, a pH of 5.6–5.8 ensured that the only form of phosphate in solution was the monovalent anion $H_2PO_4^-$ (*12*).

Results

Table 1 outlines the results obtained from least squares treatment of the data required for an absorption vs concentration calibration graph for the various anions.

To determine the equilibrium constant for the reaction between surfac-

TABLE 1

Absorption Calibration Data for Various Anions[a]

Anion	ε	A_0	λ (nm)
Nitrate	7713.3 ± 269.2	0.012	210
Iodide	12172.4 ± 170.2	0.004	230
Bromide	10232.8 ± 230.0	0.009	198
Phenolate	9085.0 + 197.7	0.003	235

[a] ε is the slope of the calibration graph (the molar extinction coefficient). The error limits represent the 95% confidence limits in the slope. A_0 is the background absorption. λ is the optimum absorption wavelength.

tant and salt, solutions of EHDA–Br whose concentrations were below the cmc in the salt solution were mixed with the individual salts. The surfactant–salt reaction is

$$\text{EHDA–Br} + \text{KX} \rightleftarrows \text{EHDA–X} + \text{KBr} \tag{1}$$

where X represents an anion listed in Table 1. The concentration of free anion was then determined by application of Beer's law to the absorbance measurements. Knowledge of the original concentrations of salt and surfactant were also required to calculate the equilibrium constant K:

$$K = \frac{[\text{EHDA–X}][\text{KBr}]}{[\text{EHDA–Br}][\text{KX}]} \tag{2}$$

Table 2 presents experimental data obtained from absorption measurements for the reaction of surfactant with salt.

The average values of the equilibrium constants for the reaction between EHDA–Br and the above salts are shown in Table 3. It was not possible to determine the equilibrium constant for the reaction between surfactant and phenol at pH 5.9 since overlap occurred between the calibration band ($\lambda_{\max} = 210$ nm) and the band at $\lambda_{\max} = 200$ nm.

Determination of the dissociation constant of the surfactant EHDA–Br was accomplished by two methods, absorption measurements and measurements of the electrode potential of a halide ion electrode in the presence of bromide. The dissociation reaction and the corresponding dissociation constant are

$$\text{EHDA–Br} \rightleftarrows \text{EHDA}^+ + \text{Br}^- \tag{3}$$

$$K = \frac{[\text{EHDA}^+][\text{Br}^-]}{[\text{EHDA–Br}]} = \frac{[\text{Br}^-]^2}{[\text{EHDA–Br}]} \tag{4}$$

TABLE 2

Data for Reaction between Surfactant and Various Anions[a]

Salt	Absorption	$[\text{EHDA-Br}]_0$	$[X^-]_0$	$[X^-]$	K
KNO_3	0.150	4.153×10^{-6}	1.836×10^{-5}	1.789×10^{-5}	3.33×10^{-3}
	1.389	1.252×10^{-4}	1.878×10^{-4}	1.785×10^{-4}	4.16×10^{-3}
	1.415	6.261×10^{-5}	1.878×10^{-4}	1.819×10^{-4}	3.38×10^{-3}
	1.563	6.290×10^{-5}	2.066×10^{-4}	2.011×10^{-4}	2.64×10^{-3}
KI	0.271	9.024×10^{-5}	2.280×10^{-5}	2.193×10^{-5}	3.82×10^{-4}
	0.301	7.826×10^{-5}	2.537×10^{-5}	2.440×10^{-5}	4.99×10^{-4}
	1.216	7.826×10^{-5}	1.015×10^{-4}	9.957×10^{-5}	4.90×10^{-4}
	1.352	3.990×10^{-5}	1.121×10^{-4}	1.107×10^{-4}	4.32×10^{-4}
$C_6H_5O^-$ (pH = 11.0)	0.800	5.336×10^{-5}	8.958×10^{-5}	8.773×10^{-5}	7.60×10^{-4}
	0.795	6.670×10^{-5}	8.958×10^{-5}	8.718×10^{-5}	1.03×10^{-3}
	1.586	1.334×10^{-4}	1.792×10^{-4}	1.742×10^{-4}	1.10×10^{-3}

[a] The subscript 0 indicates initial concentrations, and $[X^-]$ is the molar concentration of the anion X^- after reaction with surfactant.

TABLE 3

Equilibrium Constants for the Reaction between EHDA-Br and Nitrate, Iodide, and Phenolate.

Anion	K
NO_3^-	$3.38 \pm 0.50 \times 10^{-3}$
I^-	$4.51 \pm 0.63 \times 10^{-4}$
$C_6H_5O^-$	$9.60 \pm 1.92 \times 10^{-4}$

TABLE 4

Data for the Dissociation of EHDA-Br[a]

Absorption	$[\text{EHDA-Br}]_0$	$[Br^-]$	K ($\times 10^3$)
1.034	1.064×10^{-4}	1.002×10^{-4}	1.62
1.236	1.334×10^{-4}	1.199×10^{-4}	1.06
1.264	1.330×10^{-4}	1.226×10^{-4}	1.45

[a] $[\text{EHDA-Br}]_0$ is the original molar concentration of surfactant, $[Br^-]$ is the concentration of bromide in solution after dissociation.

Data from the spectroscopic determination of bromide concentrations are shown in Table 4. The average value of the dissociation constant of EHDA-Br obtained from absorption data is $1.37 \pm 0.20 \times 10^{-3}$.

In the second series of experiments, specific ion electrodes were used to determine the dissociation constant of EHDA-Br and the equilibrium constant for the reaction between surfactant and the anions F^- and $H_2PO_4^-$. Calibration graphs of the log of the molar concentration of fluoride or bromide vs electrode potential were prepared and least squares data obtained (see Table 5).

TABLE 5

Electrode Calibration Data for Various Anions[a]

X^-	Electrode used	ε	C_0
Br^-	Halide	$-1.734 \pm 0.044 \times 10^{-2}$	-3.116
$H_2PO_4^-$	Halide	$-1.782 \pm 0.065 \times 10^{-2}$	-3.207
F^-	Fluoride	$-1.856 \pm 0.047 \times 10^{-2}$	-3.687

[a] ε is the slope of the calibration graph. The error limits represent the 95% confidence limits in the slope. C_0 is the log of the concentration of F^- or Br^- which gives an electrode potential of 0 mV.

TABLE 6

Experimental Values and Results of Calculations for Specific Ion Electrode Measurements[a]

Anion (X^-)	$[\text{EHDA-Br}]_0$	$[X^-]_0$	Potential (mV)	[Halide]	K
Br^-	1.056×10^{-4}	—	58.7	7.347×10^{-5}	1.68×10^{-4}
	2.113×10^{-4}	—	42.2	1.420×10^{-4}	2.91×10^{-4}
$H_2PO_4^-$	4.240×10^{-5}	1.054×10^{-3}	77.0	2.635×10^{-5}	4.21×10^{-2}
	5.300×10^{-5}	1.054×10^{-3}	73.0	3.105×10^{-5}	4.30×10^{-2}
F^-	4.242×10^{-5}	1.381×10^{-4}	13.8	1.140×10^{-4}	2.78×10^{-1}
	4.242×10^{-5}	6.905×10^{-5}	31.7	5.304×10^{-5}	1.83×10^{-1}

[a] K for the anion Br^- is found from Eq. (4). K for the anions $H_2PO_4^-$ and F^- is found from Eq. (2). The subscripts 0 indicate initial concentrations. [Halide] is the halide concentration (Br^- for EHDA–Br dissociation and $X^- = H_2PO_4^-$; F^- for $X^- = F^-$) after reaction with surfactant.

Table 6 presents the results of measurements obtained from the fluoride and halide electrodes.

The pH of the surfactant–orthophosphate mixture was 5.1 to 5.6, in which interval more than 99% of the orthophosphate exists as the monovalent anion $H_2PO_4^-$ (*12*). The average values of K for the reaction between EHDA–Br and the anions $H_2PO_4^-$ and F^- are $4.25 \pm 0.85 \times 10^{-2}$ and $2.30 \pm 0.35 \times 10^{-1}$, respectively. The average value for the dissociation constant of EHDA–Br obtained from electrode measurements is $2.30 \pm 0.34 \times 10^{-4}$. Combining this value with that obtained from absorption data, an average of $8.00 \pm 1.20 \times 10^{-4}$ is obtained for the dissociation constant of EHDA–Br. Additional evidence which indicates that this surfactant is not completely dissociated in aqueous solution is obtained by plotting the equivalent conductivity of EHDA–Br vs the square root of the equivalent concentration. The graph (Fig. 1) shows a sharp increase in the equivalent conductivity as the concentration decreases. This behavior is typical of a moderate to weak electrolyte (*13*). The data used to plot this graph were calculated from specific conductivity data (*10*).

DISCUSSION

The thermodynamic equilibrium constants or formation constants (K_1) for the reaction between the surfactant EHDA–Br and various anions have

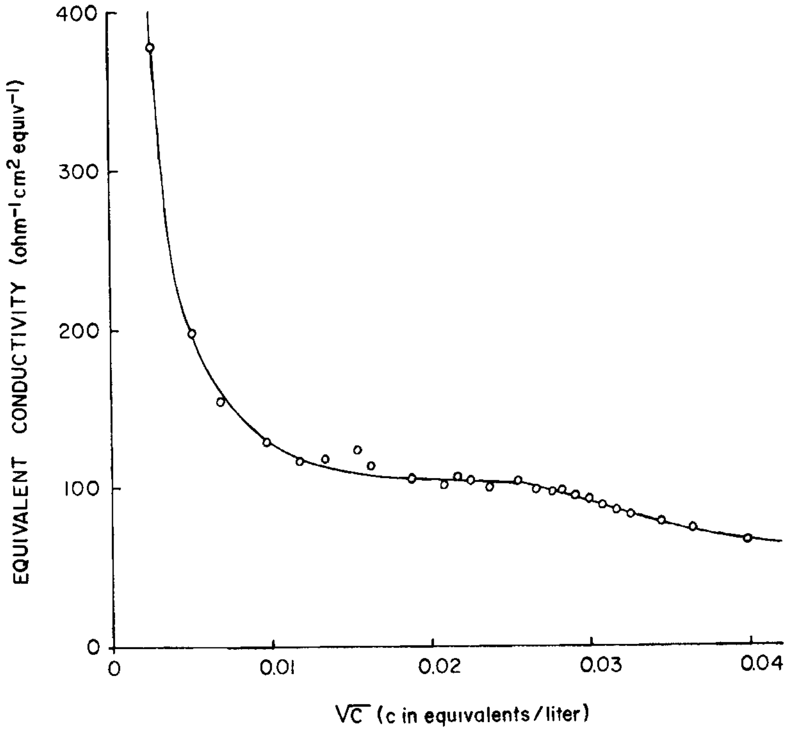

FIG. 1. Equivalent conductivity plot for EHDA–Br.

been determined. The general reaction is

$$\text{EHDA–Br} + \text{X}^- \rightleftarrows \text{EHDA–X} + \text{Br}^- ; \qquad K_1 = \frac{[\text{EHDA–X}][\text{Br}^-]}{[\text{EHDA–Br}][\text{X}^-]}$$

The dissociation constant (K_2) of EHDA–Br was also determined.

$$\text{EHDA–Br} \rightleftarrows \text{EHDA}^+ + \text{Br}^- ; \qquad K_2 = \frac{[\text{EHDA}^+][\text{Br}^-]}{[\text{EHDA–Br}]}$$

From the values of K_1 and K_2, the dissociation constants (K_3) for the compounds EHDA–X may be calculated and used as a basis for comparison of their relative stabilities. The general dissociation reaction is

$$\text{EHDA–X} \rightleftarrows \text{EHDA}^+ + \text{X}^- ; \qquad K_3 = \frac{[\text{EHDA}^+][\text{X}^-]}{[\text{EHDA–X}]}$$

The general dissociation constant is obtained by taking the ratio K_2/K_1.

TABLE 7

Formation Constants (K_1) and Dissociation Constants (K_3) for the Compounds EHDA-X

X^-	Br^-	F^-	$H_2PO_4^-$	NO_3^-	$C_6H_5O^-$	I^-
K_1	—	0.23	4.25×10^{-2}	3.38×10^{-3}	9.60×10^{-4}	4.51×10^{-4}
K_3	8.00×10^{-4}	3.48×10^{-3}	1.88×10^{-2}	2.37×10^{-1}	8.33×10^{-1}	1.77

Table 7 gives the values of K_1 and K_3. K_3 for bromide was taken as the average value of the dissociation constants obtained from the two methods mentioned earlier.

Based on the thermodynamic equilibrium constants, the order of stability of the surfactant EHDA$^+$ in aqueous solution in the presence of the anions X^- is $Br^- < F^- < H_2PO_4^- < NO_3^- < C_6H_5O^- < I^-$, and the sequence of stability of the compounds EHDA–X is the reverse of this. Based on the order of this series, it appears that solvated ion size and ion stability are two important, interacting factors which determine the stability of the surfactant EHDA$^+$ in solution. The fluoride ion has the highest hydration energy of the halides and has the highest hydration number. The free energies of hydration of the halides in kcal/mole are F^-, -103.5; Cl^-, -74.8; Br^-, -67.9; and I^-, -59.0 (*14*). The last three halides are relatively close to each other in energy and have much lower free energies of hydration than fluoride. This larger hydration energy is a stabilizing factor for fluoride and in addition to this energy term, additional stability of F^- in solution arises from the greater number of hydrogen bonding interactions which would have to be overcome when the fluoride anion associates with EHDA$^+$. These factors would predominate over anion size to make F^- more stable in solution than Br^-, or alternatively, EHDA$^+$ more stable in the presence of F^- than Br^-. That is, EHDA–F dissociates to a greater extent than EHDA–Br. The hydration numbers for the halides are F^-, 7; Cl^-, 5; Br^-, 5 (*15*); and, for I^- in this series, the expected hydration number is not greater than 5. For similar anions with the same hydration numbers, ion size is important in that the smaller ion can approach the nitronium ion more closely to form a more stable bond. Thus EHDA$^+$ would be most stable in the presence of I^- in aqueous solution.

Ion stability is also an important factor when oxygen-containing anions are considered. In these compounds, an increase in stability of the free anion results from delocalization of electronic charge from one atom onto the whole anion. The valence bond (v.b.) resonance hybrids indicate the delocalization of electrons from atomic orbitals into molecular

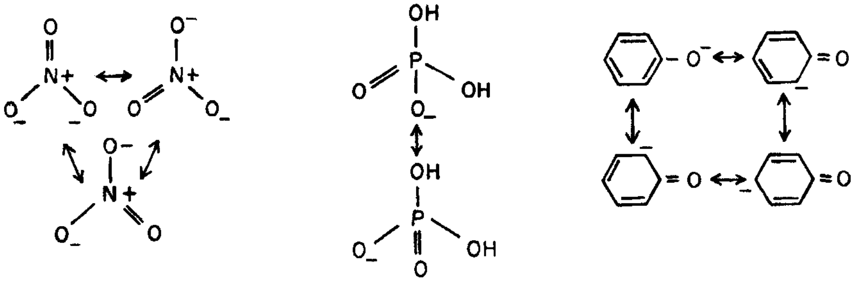

FIG. 2. Resonance structures for the oxo-anions nitrate, phosphate, and phenolate.

orbitals, and the greater the number of v.b. structures that can be drawn for an ion, the greater its stability. (See Fig. 2.) From the above discussion it is clear that the expected order of stability of these oxo-anions in solution is $C_6H_5O^- > NO_3^- > H_2PO_4^-$, hence the order of stability of $EHDA^+$ in the presence of these ions is $C_6H_5O^- > NO_3^- > H_2PO_4^-$. The experimental values for the dissociation constants confirm this sequence. There is no clearly defined rule which specifies when one factor will predominate over another in determining the stability of $EHDA^+$ in the presence of the anions X^-.

The above equilibrium constants were obtained in the absence of foam fractionation and they do not represent selectivity coefficients. Experiments to investigate the relative adsorbability of counterions at the bubble surface during foam fractionation have been carried out. Grieves (*1*) has found that the sequence of selectivity coefficients during foam fractionation of the anions studied was $I^- > NO_3^- > Br^-$ using EHDA–Br. Other workers (*6*) have found that the relative adsorbability sequence of various anions was $NO_3^- > Br^- > Cl^-$ during foam fractionation involving two cationic surfactants. Experimental evidence is available which indicates that phenolate is removed in preference to $H_2PO_4^-$ during foam fractionation. Grieves' results (*2*) show that at a pH of 5.9, the removal ratio of phosphate is about 0.42 (42% of phosphate removed) while at a pH of 11.0 the removal ratio of phenolate is about 0.75. At a pH of 5.9, phosphate exists as $H_2PO_4^-$, and at a pH of 11.0, phenol has been converted to phenolate. Addition of sulfate or chloride both provided much less competition with phenolate than with orthophosphate, indicating a higher selectivity for phenolate in the foam fractionation process. Extending the sequence to include the anions studied here, the order of removal of X^- in foam fractionation with EHDA–Br is $I^- > C_6H_5O^- >$

$NO_3^- > H_2PO_4^- > F^- > Br^-$. Comparison of this sequence with that of the stability of the cation $EHDA^+$ in the presence of the anions X^- shows that the two sequences are the same. Thus there is a consistent relationship between the stability of $EHDA^+$ in the presence of an anion and the removal of that anion from solution. For example, $EHDA^+$ is more stable in the presence of $C_6H_5O^-$ than NO_3^-, and $C_6H_5O^-$ is removed in preference to NO_3^-, etc. This relationship indicates that there is a reversal in the stability sequence of $EHDA^+$ in the presence of X^- when the cation is free in solution compared to when the cation is adsorbed at the bubble surface. For example, $EHDA^+$ is stable in the presence of I^- when both are in solution, but when $EHDA^+$ is adsorbed at the solution–air interface, $EHDA^+$ is not stable, resulting in formation of EHDA–I and subsequent removal of I^- from solution. This reversal of $EHDA^+$ stability arises from steric interactions. As a free ion in solution, $EHDA^+$ can undergo a certain amount of distortion from its tetrahedral structure when approached by a counterion. Thus for a series of similar ions, the ion with the smaller radius, in general, can approach closer and form a stronger bond. Ionic size thus plays a more important role than polarizability in this situation. In foam fractionation, an optimum surface excess of $EHDA^+$ is adsorbed on the bubble surface and the degree of distortion now permitted when a counterion approaches is severely restricted sterically. Under these conditions, polarizability would be a main factor in determining selectivity of counterions. Another main factor would be a statistical effect in the case of oxo-anions. The number of resonance structures of an oxo-anion is also the number of ways of forming a bond with a cation since a negative charge is represented at a different atom in each resonance structure. In foam fractionation this statistical or valence effect is more important in selectivity than the stability of the oxo-anion in solution. This effect is comparable to the selectivity of an anion exchange resin for the counterion with the higher valence. Thus selectivity of ions is controlled by a number of factors, and it is difficult to predict which factor will predominate.

The sequence of removal of the anions X^- by $EHDA^+$ during foam fractionation is in general the same as the selectivity sequence of general purpose anion-exchange resins (*16*), indicating that $EHDA^+$ adsorbed on the bubble surface acts as a soluble ion exchanger.

CONCLUSIONS

(1) The species adsorbed at the bubble surface during foam fractionation with EHDA–Br is $EHDA^+$.

(2) Steric hindrance of $EHDA^+$ at the bubble surface compared to hindrance of $EHDA^+$ in solution gives rise to reversal—from surface to solution—in the stability sequence of $EHDA^+$ in the presence of the anions X^-.

(3) In foam fractionation, preference of the cationic surfactant EHDA–Br is for the counterion with the higher polarizability and with the higher valence (statistical effect).

(4) A cationic surfactant behaves as a soluble ion exchanger during the process of foam fractionation.

Acknowledgments

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