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Ion-pair Extraction of Pyrocatechol Violet into Chloroform with Quaternary Ammoniun Salts

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An extraction method was first examined for establishing possible distributions of surface-active dodecyltrimethylammonium chloride (DTMAC) and non-surface active tetrabutylammonium chloride (TBAC) between aqueous and organic phases. Both quaternary ammonium salts seem to be present in the form of a free ion in the aqueous phase and in the forms of an ion pair(monomer) and a dimer in the organic phase. A possible distribution of DTMAC in the organic phase was confirmed spectrometrically by following the formation of a 1 : 1 DTMAC–iodine adduct in chloroform solution. On the basis of the possible distribution of quaternary ammonium salts, an ion pair forming extraction of Pyrocatechol Violet (PV) can be successfully interpreted in terms of the anion-exchange mechanism.

Spectrophotometric determinations of metal ions with various ligands in the presence of some cationic surfactants have provided some interesting advantages, such as improved sensitivity and/or selectivity, and a considerable reduction in analytical operation. Such analytical methods have been much advanced in practical applications but fundamental studies have been rare. We intended first to confirm possible distribution of water-soluble cationic surfactant species in aqueous and nonaqueous solutions for clarifying some questions, such as what the true roles of the surfactant species are in the formation of ternary metal–ligand–surfactant complexes.

A surfactant solution is a complicated system involving different chemical species equilibrated with each other through ion associations and molecular aggregations. To examine such a complex system, an extraction method has often been used under well-defined conditions because of its flexibilities. H. K. Biswas and B. M. Mandal[1)] successfully analyzed their experimental data of extraction of hexadecyltrimethylammonium bromide with a dyestuff, on the condition that the quaternary ammonium salt was present in the form of free ion in an aqueous phase and an ion pair(monomer) in an organic phase at the low concentration (10^{-5} mol dm^{-3}). In the present study, extractions of two different types of quaternary ammonium salts from aqueous chloride solutions into chloroform were studied in order to establish possible distributions of their chemical species in both solutions. Surface-active dodecyltrimethylammonium chloride (DTMAC) was selected to provide a more complicated system than that of H. K. Biswas and B. M. Mandal because of its relatively higher cmc. A part of the extraction results was confirmed by following the reaction of DTMAC with free iodine in chloroform. And finally, the extraction of Pyrocatechol Violet (PV) with both quaternary ammonium salts was studied on the basis of the possible distributions of quaternary ammonium species.

Experimental

Reagent. A DTMAC solution was prepared by dissolving a weighed amount of DTMAC in distilled water or purified chloroform. The solution was diluted precisely to 100 cm^3 and was used without further dilution. A TBAC solution was prepared by dissolving about 7 g of TBAC in 250 cm^3 of distilled water and standardized by Mohr's argentimetric titration before use. Stock solution of PV (2.50×10^{-3} mol dm^{-3}) and Thymol Blue (TB) (5.00×10^{-4} mol dm^{-3}) were prepared with Dotite PV and TB for a pH indicator, respectively. They were dried to a constant weight under vacuum. An iodine solution (1.00 g dm^{-3}) in chloroform was prepared for each experimental run and was used without dilution. Chrlorform, of chemically pure reagent grade, was purified by the ordinary method and kept in an amber glass bottle; 0.5% (v/v) of ethanol was added as a stabilizer. The other chemicals, of guaranteed reagent grade or chemically pure reagent grade, were used without further purification.

Procedure. *Determination of Distribution of DTMAC and TBAC*: Ten cubic centimetres of an aqueous phase, containing a fixed amount of DTMAC or TBAC, sodium chloride and hydrochloric acid, was equilibrated with 10 cm^3 of purified chloroform in a 50 cm^3 glass-stoppered test tube by shaking for about 20 min (the first extraction). The quaternary ammonium salt extracted was spectrophotometrically determined as its 1 : 1 ion pair with TB extracted at pH 6.5 into chloroform. From this determination and the original amount of quaternary ammonium salt, distribution ratios of DTMAC and TBAC in the first extraction were calculated.

Reaction of DTMAC with Iodine in Chloroform: A desired amount of DTMAC solution and iodine solution in chloroform were mixed to be diluted precisely to 10 cm^3 with purified chloroform. Absorbance of the solution was measured in a quartz cell with 1 cm path length at 364 nm.

Extraction of PV with DTMAC and with TBAC: Fifteen cubic centimetres of an aqueous phase, containing PV (5.00×10^{-4} mol dm^{-3} except for the varying concentration), DTMAC or TBAC, sodium chloride and hydrochloric acid, was equilibrated with 15 cm^3 of purified chloroform in a 50 cm^3 glass-stoppered test tube by shaking for 10 min. Absorbances of the aqueous and chloroform layers were measured at 445 and 440 nm, respectively, after separating the clear liquid phases.

Results and Discussion

Partition of DTMAC and TBAC between Aqueous and Chloroform Phases. We first examined an extraction of surface-active DTMAC from an aqueous chloride solution into chloroform at a constant pH and at a fixed total concentration of chloride ion, but at various total concentrations of DTMAC. Figure 1 shows that

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TABLE 1. INTERCEPT AND SLOPE OF LINEAR D *vs.* C_w GRAPHS

DTMAC			TBAC		
C°_{Cl} / mol dm^{-3}	Intercept	Slope / dm^3 mol^{-1}	C°_{Cl} / mol dm^{-3}	Intercept	Slope / dm^3 mol^{-1}
0.05	0.209	205	0.75	0.215	16.6
0.10	0.440	422	1.0	0.381	26.0
0.15	0.669	712	1.3	0.432	56.0
0.20	0.897	1070	1.5	0.554	86.7
0.30	1.353	1980	1.6	0.579	107
0.40	1.800	3180			
0.50	2.260	4660			

pH 1.5 (DTMAC), pH 1.0 (TBAC).

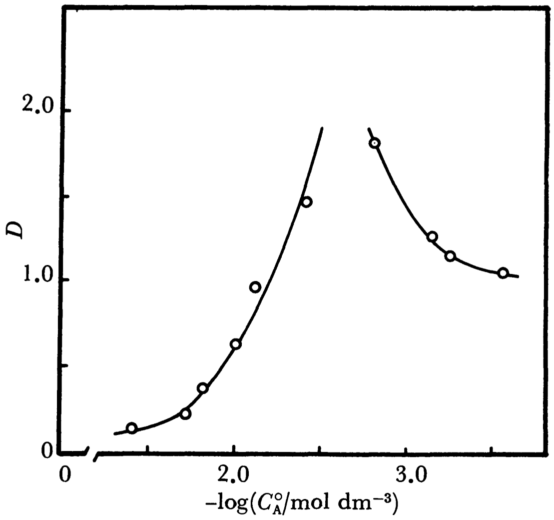

Fig. 1. Distribution ratio of DTMAC between aqueous and chloroform phases.
pH 1.8 and $C^\circ_{Cl}=0.20$ mol dm^{-3}.

the distribution ratio of DTMAC is influenced through the formation of higher aggregates in the organic phase than in the aqueous phase at a concentration lower than 2.5×10^{-3} mol dm^{-3}. These dependences reverse at higher concentrations. Because of a violent emulsification which occurred at concentrations above 2.5×10^{-3} mol dm^{-3}, our extraction method was exclusively applied to examinations at a lower concentration than this one.

The distribution ratios of DTMAC and TBAC were determined as a function of the total concentration of quaternary ammonium salt and chloride ion at a constant pH of an aqueous phase. The distribution ratio of both quaternary ammonium salts was increased with an increase of the total concentration of them and of chloride ions. This concentration dependence suggests that the extraction was enhanced with quaternary ammonium salt itself and with chloride ion. A higher aggregate of quaternary ammonium salt may be formed in a chloroform layer than in an aqueous phase. The present extraction system can be thus interpreted in terms of the following equilibria: formation of an ion pair of quaternary ammonium salt in the aqueous phase, partition of it into the chloroform layer, and formations of its aggregates such as a dimer and a trimer in chloroform. The distribution ratio of quaternary ammonium salt, D, can be written as,

$$D=\frac{[\mathrm{ACl}]_o+2[(\mathrm{ACl})_2]_o+3[(\mathrm{ACl})_3]_o+\cdots}{[\mathrm{A}^+]_w+[\mathrm{ACl}]_w}, \tag{1}$$

where A^+, ACl, $(ACl)_2$, and $(ACl)_3$ are a free quaternary ammonium ion, an ion pair of it with chloride ion (monomer) and its molecular aggregates, a dimer and trimer, respectively. Two subscripts, w and o, denote the aqueous phase and the organic layer. From the material balance of quaternary ammonium salt and the experimental conditions, Eq. 1 can be rewritten

$$D=\left(\frac{KPC^\circ_{Cl}}{1+KC^\circ_{Cl}}\right)+2K_2\left(\frac{KPC^\circ_{Cl}}{1+KC^\circ_{Cl}}\right)^2C_w + 3K_3\left(\frac{KPC^\circ_{Cl}}{1+KC^\circ_{Cl}}\right)^3C_w^2+\cdots, \tag{2}$$

where K, P, K_2, and K_3 are the formation constant of the ion pair in the aqueous phase, its partition coefficient, and the formation constants of the dimer and the trimer in the chloroform layer, respectively. C°_{Cl} represents the total concentration of chloride ion in the extraction system and C_w that of quaternary ammonium salt in the aqueous phase. This equation predicts a linear or a curved graph on D *vs.* C_w diagram at every constant C°_{Cl} value.

A practical plotting of D against C_w gave a series of straight lines with varying slopes and intercepts as a function of C°_{Cl} for both quaternary ammonium salts. Their results suggests that quaternary ammonium salt can be present in the monomeric and dimeric forms in chloroform under the conditions studied. K. Inoue *et al.*[2] and K. Inoue and Y. Baba[3] have reported a similar result in their paper of extraction equilibria of hydrochloric and acetic acids with a long-chain alkylamine. From Table 1, intercepts of these lines were directly proportional to C°_{Cl}, so that the first term of Eq. 2 can be regarded as KPC°_{Cl}, that is, $KC^\circ_{Cl}\ll1$. This is supported by the fact that a linear graph with a small intercept is obtained by plotting slopes of the serial straight lines against $C^{\circ 2}_{Cl}$. These suggest that a free quaternary ammonium ion is a predominant species in the aqueous phase. Under these conditions, the distribution ratio of quaternary ammonium salt can be expressed by

$$D=KPC^\circ_{Cl}+2K_2(KPC^\circ_{Cl})^2C_w. \tag{3}$$

From these linear relations, the extraction constant of the ion pair of quaternary ammonium salt, *KP*, and its dimerization constant, K_2, can be estimated as 4.45 and 440 $dm^3\ mol^{-1}$ for DTMAC and as 0.35 and 140 $dm^3\ mol^{-1}$ for TBAC, respectively.

Table 2. Intercept and slope of linear plots of $C^\circ_A/(A_s-\varepsilon_{I_2}\cdot C^\circ_{I_2})$ against $(A_s-\varepsilon_{I_2}\cdot C^\circ_{I_2})$

$C^\circ_{I_2}$ / $mol\ dm^{-3}$	Intercept / $mol\ dm^{-3}$	Slope / $mol\ dm^{-3}$
3.28×10^{-4}	6.98×10^{-4}	1.16×10^{-3}
7.91×10^{-4}	3.42×10^{-4}	1.02×10^{-4}
1.16×10^{-3}	3.10×10^{-4}	3.50×10^{-5}
2.32×10^{-3}	2.52×10^{-4}	1.17×10^{-5}
8.58×10^{-3}	1.51×10^{-4}	8.28×10^{-6}

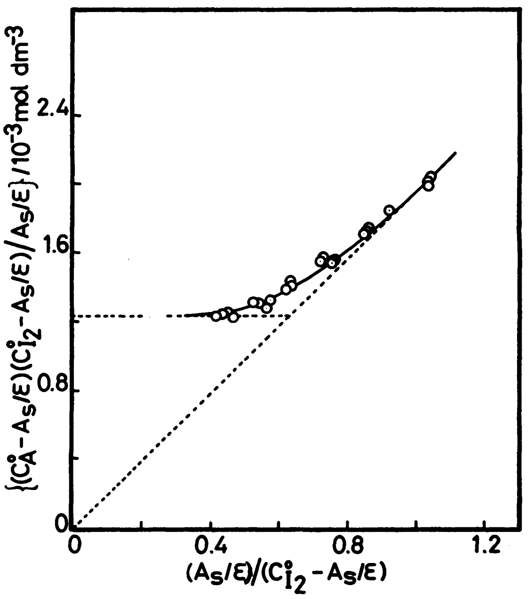

Fig. 2. $(C^\circ_A-A_s/\varepsilon)\cdot(C^\circ_{I_2}-A_s/\varepsilon)/(A_s/\varepsilon)$ *vs.* $(A_s/\varepsilon)/(C^\circ_{I_2}-A_s/\varepsilon)$ plot.

Reaction of DTMAC with Free Iodine in Chloroform. To confirm the above conclusion, the reaction of DTMAC with isolated iodine was followed spectrophotometrically in a chloroform solution. An iodine solution in chloroform showed an absorption maximum near 514 nm and one near 364 nm on the absorption spectra in the absence and presence of DTMAC, respectively. Since only one isosbestic point is found on the spectra, only one DTMAC–iodine adduct may be formed on adding DTMAC into an iodine solution. This adduct composition was found to be the 1 : 1 molar ratio by the continuous variation method.

In the presence of an excess of free iodine, absorbance of the solution at 364 nm increased linearly with the total concentration of DTMAC, C°_A. A slope of this linear graph increased with an increase of the total concentration of free iodine, $C^\circ_{I_2}$. In the presence of an excess of DTMAC, a similar linear graph was obtained on an absorbance-$C^\circ_{I_2}$ diagram. We considered for simplicity that quaternary ammonium salt was present in three different forms: a monomer, a dimer and a 1 : 1 adduct of monomeric DTMAC with free iodine, and that iodine was present as two species: free iodine and the 1 : 1 DTMAC–iodine adduct in the chloroform solution. Since $C^\circ_{I_2}=[I_2]_o$ in the presence of an excess of free iodine, the absorbance of the solution can be approximated as

$$A_s = \varepsilon_{I_2}\cdot C^\circ_{I_2} + \varepsilon\cdot[ACl\cdot I_2]_o, \tag{4}$$

where $[I_2]_o$ is the actual concentration of free iodine in the solution and ε_{I_2} and ε are molar absorptivities of free iodine and the 1 : 1 DTMAC–iodine adduct at 364 nm, respectively. On the other hand, in the presence of an excess of DTMAC, the absorbance of free iodine, $\varepsilon_{I_2}\cdot[I_2]_o$, was negligible as compared with that of the adduct because of small values of ε_{I_2} and $[I_2]_o$. Thus, absorbance of the solution can be approximated as $A_s=\varepsilon\cdot[ACl\cdot I_2]_o$. Taking account of the dimerization of DTMAC and the formation of the 1 : 1 DTMAC–iodine adduct, the following equations can be derived in the presence of an excess of free iodine and of DTMAC, respectively:

$$\frac{C^\circ_A}{A_s-\varepsilon_{I_2}\cdot C^\circ_{I_2}} = \frac{1+K_f\cdot C^\circ_{I_2}}{\varepsilon\cdot K_f\cdot C^\circ_{I_2}} + \frac{2K_2}{\varepsilon^2\cdot K_f^2\cdot C^{\circ 2}_{I_2}}(A_s-\varepsilon_{I_2}\cdot C^\circ_{I_2}) \tag{5}$$

and

$$\frac{(C^\circ_A-A_s/\varepsilon)\cdot(C^\circ_{I_2}-A_s/\varepsilon)}{A_s/\varepsilon} = \frac{1}{K_f} + \frac{2K_2}{\varepsilon^2\cdot K_f^2\cdot C^{\circ 2}_{I_2}}\cdot\frac{A_s/\varepsilon}{C^\circ_{I_2}-A_s/\varepsilon}, \tag{6}$$

where K_f and K_2 are formation constants of the adduct and the dimeric DTMAC, respectively. A series of straight lines on the $C^\circ_A/(A_s-\varepsilon_{I_2}\cdot C^\circ_{I_2})$ *vs.* $(A_s-\varepsilon_{I_2}\cdot C^\circ_{I_2})$ diagram indicate the validity of Eq. 5. Table 2 summarizes the intercept and slope of these straight lines determined by the least-square regression method. A linear graph was then drawn by plotting the intercept against $1/C^\circ_{I_2}$. From the intercept and the slope of this graph, the molar absorptivity and the formation constant of the 1 : 1 DTMAC–iodine adduct were estimated as $\varepsilon=7622\ dm^3\ mol^{-1}\ cm^{-1}$ and $K_f=711\ dm^3\ mol^{-1}$, respectively. Logarithmic plot of the slope *vs.* $C^\circ_{I_2}$ also gave a straight line with a slope of -1.97. From the intercept of this graph, the formation constant of the dimeric DTMAC was found as $K_2=683\ dm^3\ mol^{-1}$, closed fairly to that of $K_2=440\ dm^3\ mol^{-1}$ estimated through the extraction experiment. On the other hand, a reversed L-shaped curve appeared on the $(C^\circ_A-A_s/\varepsilon)\cdot(C^\circ_{I_2}-A_s/\varepsilon)/(A_s/\varepsilon)$ *vs.* $(A_s/\varepsilon)/(C^\circ_{I_2}-A_s/\varepsilon)$ diagram (Fig. 2). This suggests that a monomeric DTMAC is the dominant species at DTMAC concentrations below about $9.0\times10^{-4}\ mol\ dm^{-3}$ and the dimeric one is dominant above this concentration. From the constant value of the graph, the formation constant of the adduct was also estimated as $K_f=797\ dm^3\ mol^{-1}$, closed to that of $K_f=711\ dm^3\ mol^{-1}$. And from the slope of the linearly increasing part of the curve, the formation constant of the dimeric DTMAC was found to be $K_2=626\ dm^3\ mol^{-1}$, comparable to that of $K_2=638\ dm^3\ mol^{-1}$. These results lead to the same conclusion as that of the extraction experiment of DTMAC.

Extraction of PV with DTMAC and with TBAC from Aqueous Phase into Chloroform. PV was extracted into chloroform with DTMAC or with TBAC but only with difficulty without such quaternary ammonium salts. Depending upon the pH value of the aqueous phase, two different PV species could be extracted into chloroform. They were extractable at a pH lower than 6 and between pH 7 and 11, and showed absorption bands near 450 and 610 nm on the spectra. For the PV species extracted at a pH above 7, time-dependent absorptions spectra were observed, so that the extraction of PV with DTMAC and TBAC was examined more in detail at a low pH. The literature[4–6] reports a stable PV species in the low pH range to be a protonated form with three dissociative hydroxyl groups (H_3L^-). In the range lower than pH 2, another PV species with an absorption band near 560 nm newly appeared in the aqueous phase. This was regarded as a more protonated form of the H_3L^- species, such as H_4L or H_5L^+. Comparing the absorption spectra of chloroform and aqueous solutions containing PV, we considered that the H_3L^- species was the extractable species of PV with quaternary ammonium salt in this pH range. Since very similar absorption spectra were observed in the absence and presence of the quaternary ammonium salt, we conclude that no PV species interacting with it was present in the aqueous phase equilibrated once with chloroform. No aggregated form of the PV species may be present in either phase because the ratio of absorbances of the two related phases stayed constant at any concentration of PV(C°_L). Even in the presence of a large excess of quaternary ammonium salt, quantitative extraction of PV could occur only with difficulty in the present study. Thus, an absorbance ratio of both phases, $Y = A_{So}/A_{Sw}$, was used for analyzing experimental data, instead of a distribution ratio. Figure 3 shows a parabolic curve on the Y vs. C°_A diagram for the DTMAC–PV system. This suggests the formation of an aggregated DTMAC species involving only one PV molecule in a chloroform layer. A similar curve was observed for the TBAC–PV system. We considered that PV species were present in the form of H_3L^-, H_4L, and H_5L^+ in the aqueous phase and H_3LA and $H_3LA \cdot ACl$, regarded as anion-exchanged forms of ACl and $(ACl)_2$, in the chloroform layer. According to Beer's law and linear additivity of absorbances, the absorbance ratio, Y, can be expressed as

$$Y = \frac{\varepsilon_o \cdot [H_3LA]_o + \varepsilon_o' \cdot [H_3LA \cdot ACl]_o}{\varepsilon_{w(3)} \cdot [H_3L^-]_w + \varepsilon_{w(4)} \cdot [H_4L]_w + \varepsilon_{w(5)} \cdot [H_5L^+]_w}, \tag{7}$$

where ε_o, ε_o', $\varepsilon_{w(3)}$, $\varepsilon_{w(4)}$, and $\varepsilon_{w(5)}$ are molar absorptivities of the species, H_3LA, $H_3LA \cdot ACl$, H_3L^-, H_4L, and H_5L^+, respectively. Using equilibrium constants of extraction reaction and dimerization of ACl, extraction reactions of PV with ACl and with $(ACl)_2$ by anion exchange, and protonation of the H_3L^- species in an aqueous phase, the following equation was derived:

$$Y = \frac{\varepsilon_o K_{ex(1)} KP[A^+]_w + \varepsilon_o' K_2 K_{ex(2)} K^2 P^2 C^\circ_{Cl} [A^+]^2_w}{\varepsilon_{w(3)} + \varepsilon_{w(4)} K_{H(4)} [H^+]_w + \varepsilon_{w(5)} K_{H(4)} K_{H(5)} [H^+]^2_w}, \tag{8}$$

where $K_{ex(2)}$ and $K_{ex(2)}$ are extraction constants of PV with ACl and with $(ACl)_2$, and $K_{H(4)}$, and $K_{H(5)}$ are successive protonation constants of the H_3L^- species. Under the experimental conditions, $C^\circ_A \gg C^\circ_L$, so that the following relation is approximately valid:

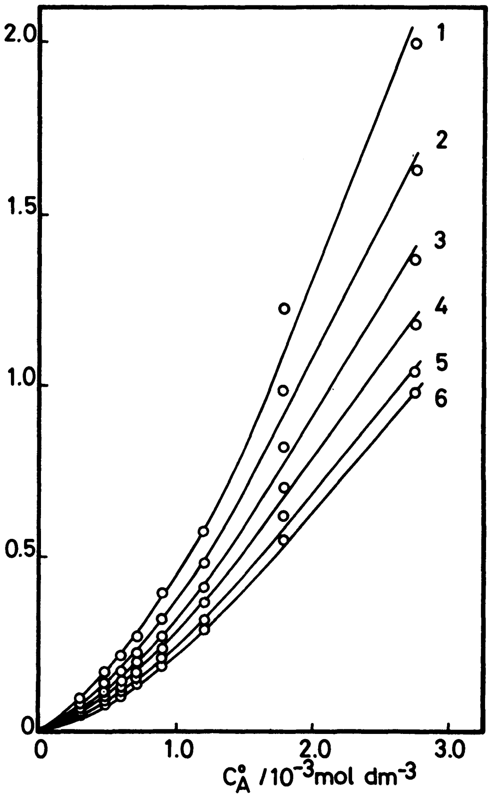

Fig. 3. Y vs. C°_A plot for DTMAC.
pH 2.3, $C^\circ_L = 4.03 \times 10^{-5}$ mol dm^{-3} and C°_{Cl}: 1; 0.10, 2; 0.20, 3; 0.30, 4; 0.40, 5; 0.50, 6; 0.60 mol dm^{-3}.

$$C^\circ_A = [A^+]_w + [ACl]_o + 2[(ACl)_2]_o,$$

that is,

$$C^\circ_A = (1 + KPC^\circ_{Cl})[A^+]_w + 2K_2(KPC^\circ_{Cl})^2[A^+]^2_w. \tag{9}$$

Since KP and K_2 are known, $[A^+]_w$ could be calculated at any C°_{Cl} from this equation. Equation 8 predicts that a series of straight lines with the same intercept but with the C°_{Cl}-dependent slopes may be obtained by plotting $Y/[A^+]_w$ vs. $[A^+]_w$ at a constant pH of the aqueous phase. This prediction was experimentally confirmed for the DTMAC–PV system. The intercept and slope of the regression line are listed in Table 3. The values of $(\varepsilon_o/\varepsilon_w)K_{ex(1)}$ and $(\varepsilon_o'/\varepsilon_w)K_{ex(2)}$ were estimated as 46 and 855 from these values. However, extraction constants, $K_{ex(1)}$ and $K_{ex(2)}$, were difficult to be determined because of our failure to find the molar absorptivities. For the TBAC–PV system, a

TABLE 3. INTERCEPT AND SLOPE OF LINEAR GRAPH OF $Y/[A^+]_w$ AGAINST $[A^+]_w$ FOR DTMAC

C°_{Cl} mol dm^{-3}	Intercept dm^3 mol^{-1}	Slope dm^6 mol^{-2}
0.1	209	0.724 × 10^6
0.2	218	1.38 × 10^6
0.3	193	2.13 × 10^6
0.4	199	2.95 × 10^6
0.5	208	3.66 × 10^6
0.6	191	4.76 × 10^6

$C^\circ_L = 4.03 \times 10^{-5}$ mol dm^{-3} and pH 2.3.

series of linear graphs was drawn at a fixed C°_{Cl} on the $Y/[\mathrm{A}^+]_\mathrm{w}$ *vs.* $[\mathrm{A}^+]_\mathrm{w}$ diagram. Their different intercepts and slopes, calculated by the least-square regression method, are shown in Table 4. The reciprocals of the intercept and the slope was well correlated linearly to the square of hydrogen ion concentration. This suggests a simultaneous protonation of the $\mathrm{H_3L^-}$ species with two hydrogen ions. I. S. Mustafin *et al.*[6] have reported the simultaneous uptake of two hydrogen ions due to a quinone and a sulfonate groups of the PV molecule. From the intercept and the slope of the linear reciprocal plots, $(\varepsilon_\mathrm{o}/\varepsilon_{\mathrm{w}(3)})K_{\mathrm{ex}(1)}$, $(\varepsilon'_\mathrm{o}/\varepsilon_{\mathrm{w}(3)})K_{\mathrm{ex}(2)}$, $(\varepsilon_\mathrm{o}/\varepsilon_{\mathrm{w}(5)})K_{\mathrm{ex}(1)}/K_{\mathrm{H}(4)}K_{\mathrm{H}(5)}$, and $(\varepsilon'_\mathrm{o}/\varepsilon_{\mathrm{w}(5)})K_{\mathrm{ex}(2)}/K_{\mathrm{H}(4)}K_{\mathrm{H}(5)}$ were determined to be 69, 550, 20 dm³ mol⁻¹ and 127 dm³ mol⁻¹, respectively, for the TBAC–PV system. In this case, the absorbance ratio can be written simply

$$Y=\frac{\varepsilon_\mathrm{o}K_{\mathrm{ex}(1)}KP[\mathrm{A}^+]_\mathrm{w}+\varepsilon_\mathrm{o}'K_2K_{\mathrm{ex}(2)}K^2P^2C^{\circ}_{\mathrm{Cl}}[\mathrm{A}^+]^2_\mathrm{w}}{\varepsilon_{\mathrm{w}(3)}+\varepsilon_{\mathrm{w}(5)}K_{\mathrm{H}(4)}K_{\mathrm{H}(5)}[\mathrm{H}^+]^2_\mathrm{w}}. \tag{10}$$

From these results and discussion, we concluded that both surface-active DTMAC and non-surface active TBAC were present in the form of free ions in an aqueous phase and in the monomeric and dimeric forms in a chloroform layer. The extraction of PV with quaternary ammonium salt could be successfully interpreted by an anion-exchange mechanism on the basis of the distributions of quaternary ammonium salt established. It should be noted that the same distributions could be established for quaternary ammonium salts with and without surface activity. We continue our interest in studying possible distributions of chemical species in the surfactant solution.

TABLE 4. INTERCEPT AND SLOPE OF LINEAR GRAPH OF $Y/[\mathrm{A}^+]_\mathrm{w}$ AGAINST $[\mathrm{A}^+]_\mathrm{w}$ FOR TBAC

$[\mathrm{H}^+]_\mathrm{w}$ mol dm⁻³	Intercept dm³ mol⁻¹	Slope dm⁶ mol⁻²
0.04	19.1	1.15×10^4
0.05	23.2	1.08×10^4
0.10	23.1	9.74×10^3
0.15	20.3	8.92×10^3
0.20	20.1	7.96×10^3
0.25	19.7	7.16×10^3
0.30	14.7	6.84×10^3
0.40	15.7	5.40×10^3
0.50	13.5	4.37×10^3
0.60	10.7	3.84×10^3
0.80	10.2	2.49×10^3
0.98	7.93	1.82×10^3

$C^{\circ}_{\mathrm{L}} = 5.00 \times 10^{-5}$ mol dm⁻³ and $C^{\circ}_{\mathrm{Cl}} = 1.0$ mol dm⁻³.

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