Diagrams of Existence of Chloramines and Bromamines in Aqueous Solution

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Ultraviolet spectrophotometric analysis of haloamines produced by mixing aqueous halogen and ammonia solutions allowed distribution diagrams for the various species to be established as a function of pH and log R (R = [initial halogen]/[initial ammonia]). These diagrams are interpreted by using a model involving reversible reactions between the different compounds, whilst neglecting their decomposition. The reactions (equilibrium constants in parentheses) controlling concentrations of the species are as shown in equations (1)—(6). These equilibria and

$$X_2 + H_2O \rightleftharpoons HXO + H^+ + X^- \quad (1)$$

$$HXO \rightleftharpoons H^+ + XO^- \quad (2)$$

$$NH_3 + H^+ \rightleftharpoons NH_4^+ \quad (3)$$

$$NH_2X + H_2O \rightleftharpoons NH_4^+ + XO^- \; (K_{hm}) \quad (4)$$

$$2NH_2X + H^+ \rightleftharpoons NHX_2 + NH_4^+ \; (K_{md}) \quad (5)$$

$$3NHX_2 + H^+ \rightleftharpoons 2NX_3 + NH_4^+ \; (K_{dt}) \quad (6)$$

the law of N and X^+ mass conservation led to a non-linear system of eight equations with eight unknowns, solved by iteration. Experimental values of the constants, derived from isocontent curves between two species, are (at 25 °C): $K_{hm}(Cl) = 4 \times 10^{-7}$ mol dm^{-3}, $K_{hm}(Br) = 1 \times 10^{-7}$ mol dm^{-3}, $K_{md}(Cl) = 5.2 \times 10^6$ dm^3 mol^{-1}, $K_{md}(Br) = 8 \times 10^7$ dm^3 mol^{-1}, $K_{dt}(Cl) = 1.7 \times 10^4$ dm^3 mol^{-1}, $K_{dt}(Br) = 1.5 \times 10^5$ dm^3 mol^{-1}. Satisfactory agreement was found between calculated and measured values for the various species.

CHLORINE and bromine are well known oxidizing and germicidal agents used for water disinfection. Monitoring the oxidizing power of the medium is related to the nature and the concentration of the species formed and involves characterization of the various compounds. In addition to X_2, water dissolution of halogen gives rise to the forms X_3^-, HXO, and XO^-, whose respective proportions can be calculated and depend on temperature, pH value, and halide concentration. Relative unstable haloamines are formed in the presence of ammonia, according to the reactions below.

$$HXO + NH_3 \rightleftharpoons NH_2X + H_2O$$

$$HXO + NH_2X \rightleftharpoons NHX_2 + H_2O$$

$$HXO + NHX_2 \rightleftharpoons NX_3 + H_2O$$

Thus, the type of haloamines formed depends on the concentration of halogen in relation with that of ammonia, but these equilibria do not account for the effect of the medium. Now, the nature and the quantity of haloamines formed is affected by the pH.[1-5] Monohaloamine NH_2X is predominant in alkaline solution; mixtures are obtained in neutral medium but with a higher proportion of dihaloamine NHX_2, whereas trihaloamine NX_3 becomes predominant in acidic medium. This can be explained by the reactions shown below.

$$2NH_2X + H^+ \rightleftharpoons NHX_2 + NH_4^+$$

$$3NHX_2 + H^+ \rightleftharpoons 2NX_3 + NH_4^+$$

The set of previous reactions, together with the equilibria relating the various forms of the halogen–water system, constitute a model for the interpretation of experimental results of the halogen–ammonia–water system.

This ideal reversible system does not, however, entirely fit the observed facts. Allowance should be made for rates of formation and interconversion of haloamines on one hand, and reactions of irreversible decomposition on the other. The rates of formation of haloamine are pH-dependent and are generally high,[6-8] while the rates of decomposition of existing haloamines are relatively slow. Besides, a significant decomposition ratio of halogen at the +1 degree of oxidation was found during their formation under certain conditions. The system comprises, therefore, numerous evolving species, which are related to reversible and fast reactions, rather than irreversible or slow ones. So, our study is based on a system in equilibrium, after a given period of contact, the zero being defined at the time when the reagents have been mixed.

This investigation consists chiefly of spectrophotometric measurements of all forms of halogen and haloamines occurring in aqueous solution in well defined conditions of time, temperature, pH, and molar ratio of initial halogen to initial ammonia, $R = [Hal_i]/[Amm_i]$; subsidiary voltammetric and colorimetric[9] measurements have also been made. The titration results make it possible to plot experimental diagrams of existence for the different forms of free and nitrogen combined halogen. It is possible to derive therefrom the constants characterizing the equilibrium state between the various species, to draw their zones of predominance, compare their experimental and theoretical distributions, and finally extrapolate the results to much more dilute solutions, where measurement of the concentrations becomes impossible.

EXPERIMENTAL

Preparation of Halogen and Haloamine Solutions.—Halogen solutions were prepared by dissolving gaseous chlorine (supplied by l'Air Liquide Corporation) or liquid bromine (reagent grade) in distilled water. This halogen stock solution, with a concentration of *ca.* 5 × 10^{-2} mol dm^{-3}, was stored away from light, and titrated by thiosulphate iodometry before use. The solution of initial halogen Br_i, Cl_i was prepared by diluting the former to 5 × 10^{-4} mol dm^{-3}. The haloamines were obtained at fixed temperature in buffered medium, by pouring together solutions of initial halogen and ammonium sulphate with 1 × $10^{-4} \leqslant [NH_4^+] \leqslant$ 5 × 10^{-2} mol dm^{-3}.

Procedure.—After a few minutes of contact between the reagents, part of the solution was placed in a silica cell, to be analysed by means of a double-beam modular spectrophotometric set-up (Mac Kee Pedersen Instruments and Ateliers Centraux des Mines de Potasse d'Alsace). pH Values of the solutions were checked during each analysis (Tacussel electrodes and pH-meter). The identification and titration of haloamines as a function of time, with a view to performing kinetic studies, was achieved by developing an open flow cell, ensuring steadiness of local concentrations, enabling voltammetric and optical absorption measurements to be made.[10]

U.V. Absorption Spectra.—Spectra of halogen–water systems. All forms of halogen, and haloamines with chromophoric groups, can therefore be subjected to spectrophotometric analysis. The identification of haloamines through their absorption spectra requires previous knowledge of the spectra of the chlorine–water and bromine–water systems. The computer programs, as well as Figures of molar absorption coefficients, the predominance domains, and experimental and theoretical distributions are in Supplementary Publication No. SUP 23156 (32 pp.).* All the spectra are confined to 205 nm by the absorption of the halide, of the components of buffer solutions, and also by the range of detection of the photomultipliers. The spectra of the different forms of aqueous bromine are like those of chlorine. They are shifted to higher wavelengths in comparison to chlorine, whereas Br_3^- is more absorbing than Cl_3^-. The absorption maxima observed for the various species and their molar absorption coefficients (Table 1) agree fairly well with reported data.[11-15]

TABLE 1

Absorption maxima of the species

	X = Cl			X = Br		
Species	λ_M/nm	ϵ_M/dm^3 mol^{-1} cm^{-1}	Ref.	λ_M/nm	ϵ_M/dm^3 mol^{-1} cm^{-1}	Ref.
XO^-	292	*ca.* 350	11	333	*ca.* 350	11
	ca. 290	350	12	329	345	*
	292	350	*			
HXO	*ca.* 230	*ca.* 100	11	*ca.* 260	*ca.* 100	11
	ca. 235	100	12			
	233	97	*	260	160	*
X_2	*ca.* 325	75	13	390	141	14
	323	68	*	392	175	*
X_3^-	*ca.* 220	*ca.* 10 000	13	267	25 000	15
	ca. 325	193				
	233	18 500	*	266	35 000	*
	325	85				
NH_2X	245	416	16	278	390	5
	244	445	17			
	245	455	5	278	380	*
	244	457	*			
NHX_2	297	265	16	232	1 900	5
	294	267	17	*ca.* 290		
	206	2 100	5			
	295	300				
	207	1 700	*	232	1 900	*
	294	280				
NX_3	340	255	16	258	4 600	5
	336	272	17			
				323	940	
	220	8 100	5			
	340	260				
	221	6 100	*	258	4 800	
	337	285		323	490	*

* This work.

Spectra of haloamines. The study of the spectra permits the characterization of the different chloramines and bromamines by separate absorption bands, whose maxima were specified by Metcalf [16] and Galal-Gorchev and Morris [5] respectively. Absorption spectra for each chloramine, obtained alone or when not possible, formed in the mixture in large proportion, have been determined (data in the Supplementary Publication). The spectra of bromamines look like those of chloramines, but are shifted to higher wavelengths.†

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

† In order to record these spectra, we used solutions of Br_i with a low bromide concentration (about 1 × 10^{-4} mol dm^{-3} in acidic medium) to minimize Br_3^- formation, as its very high absorption might conceal that of other species, notably NBr_3. As regards chloramines, Cl_3^- does not interfere, its concentration being negligible for $[Cl^-] \leqslant 1 \times 10^{-3}$ mol dm^{-3}.

RESULTS

Domains of Existence of Halogens and Haloamines.—Generalisations. An overview of the results and the means to interpret them can be obtained by constructing a diagram of existence of halogens and haloamines in a three-dimensional frame of reference. The pH values were plotted as abscissa, log R as ordinate, and the halogen X^+ content due to a given species (combined or not to nitrogen) on the third co-ordinate axis. This content is defined as the ratio (%) of halogen X^+ concentration of a given species to that of the halogen concentration initially introduced.

$$\%\ X^+ \text{ in the } NX_3 \text{ form} = 100 \cdot 3[NX_3]/[Hal_i]$$

$$\%\ X^+ \text{ in the } NHX_2 \text{ form} = 100 \cdot 2[NHX_2]/[Hal_i]$$

$$\%\ X^+ \text{ in the } NH_2X \text{ form} = 100 \cdot [NH_2X]/[Hal_i]$$

A partial decomposition of the species yields various products, in particular X^- formed at the expense of X^+. The main reaction of decomposition is that shown below. Given the overall reaction of Hal_i and Amm_i, the percentages of X^+ shown below can be expressed.

$$2NH_3 + 3XO^- \longrightarrow N_2\uparrow + 3X^- + 3H_2O$$

$$\underset{\substack{\text{Initial}\\ \text{halogen}}}{Hal_i} + \underset{\substack{\text{Initial}\\ \text{ammonia}}}{Amm_i} \longrightarrow \underbrace{NX_3 + NHX_2 + NH_2X}_{\substack{\text{Residual combined}\\ \text{halogen}}} + \underbrace{X_2 + X_3^- + HXO + XO^-}_{\substack{\text{Residual free}\\ \text{halogen}}} + \underbrace{X^- + N_2\uparrow + \ldots}_{\text{Decomposition}} + \underbrace{NH_3 + NH_4^+}_{\substack{\text{Residual}\\ \text{ammonia}}}$$

$$\%\ X^+ \text{ in the form of residual free halogen} = 100([X_2] + [X_3^-] + [HXO] + [XO^-])/[Hal_i]$$

$$\%\ X^+ \text{ lost by decomposition} = 100([Hal_i] - 3[NX_3] - 2[NHX_2] - [NH_2X] - [X_2] - [X_3^-] - [HXO] - [XO^-])/[Hal_i]$$

The values plotted on the diagrams result from u.v. absorption measurements carried out at 25 °C, after 5 to 10 min contact time between the reagents, for numerous pH and log R values. In the plane pH–log R, the asterisked curves indicate quasi-equal contents (50%) of two species, when those of others can be neglected (Figures 1 and 2), thus delineating zones of predominance for a given species.

Domain of existence of chlorine and chloramines. The interpretation of spectrophotometric measurements relating to chlorine and chloramines (Figure 1) confirms data reported by Chapin[3] and Metcalf.[16] Thus, for log $R \leqslant 0$, the existing species are those shown below.

$\text{pH} < 3 \longrightarrow$ predominance of NCl_3

$3 < \text{pH} < 4 \longrightarrow NCl_3 + NHCl_2$

$4 < \text{pH} < 5 \longrightarrow$ predominance of $NHCl_2$

$5 < \text{pH} < 8 \longrightarrow NHCl_2 + NH_2Cl$

$\text{pH} > 8 \longrightarrow NH_2Cl$

When log $R > 0$, the domains of the various species shift to higher pH values, in particular NCl_3 still exists for pH $>$ 8. More precisely, the domain of NCl_3 is located on the left and above a curve passing through points A (pH 2.6, log $R = -2$), B (pH 4.1, log $R = 0$), and C (pH 6, log $R = 0.38$). The species NH_2Cl is predominant on the right of a boundary passing near points D (pH 5, log $R = -2$) and E (pH 7.3, log $R = 0$). Between these two limits $NHCl_2$ is preponderant, but the decomposition ratio is important, reaching 54% around the point defined by co-ordinates pH 6.5, log $R = -0.3$.

Absorption measurements achieved on solutions after the reagents had reacted for 1 h showed slightly decreasing contents of all compounds, and minor displacements of the zones of preponderance. By resorting to other methods however, certain predominance boundaries can be modified, *e.g.* by pouring an NH_2Cl solution, prepared before use under optimum conditions (pH 9, $R = 0.1$), into various media buffered to definite pH values. The boundary between the NH_2Cl and $NHCl_2$ zones remains unchanged, whereas that between $NHCl_2$ and NCl_3 is shifted by about 2 pH units to the left, to more acidic media, and that between NH_2Cl and ClO^- is slightly displaced to the right, to more alkaline media, in agreement with data reported by Gray.[17] These differences might be explained by slow kinetics for the conversion of $NHCl_2$ into NCl_3 and the hydrolysis of NH_2Cl into ClO^-.

Domains of existence of bromine and bromamines. The set of contents relating to bromine and bromamines (Figure 2) allows the delimitation of domains for the various species, corresponding fairly well to the ones found by Johnson and Overby.[18] Only NBr_3 forms in low proportion at pH $<$ 2.7, irrespective of R; *i.e.* a zone where Br_2 is predominant.

Above the curve defined by points A (pH 3.4, log $R = -2$), B (pH 5, log $R = 0$), and C (pH 7, log $R = 0.38$), NBr_3 is found in high proportion. Below a line joining points D (pH 6, log $R = -2$) and E (pH 8.2, log $R = 0$), NH_2Br is preponderant. In the intermediate zone $NHBr_2$ is formed preferentially but is very unstable. Indeed, a very high ratio of decomposition, which may exceed 90%, occurs in a zone defined as $6 < \text{pH} < 8.5$ and $-1 < \log R < 0.2$.

By comparing the measurements performed on solutions, at 5 min and 1 h after preparation for both Cl and Br, decomposition as a function of time was found to be more pronounced for bromamines than for chloramines, and no marked shift of predominance boundaries for the bromamines was noticed. In contrast to chloramines, all bromamines were transformed very quickly by pH change. Thus, when modifying the procedure, *e.g.* by introduction of NBr_3 solution into alkaline medium or NH_2Br solution into acidic medium, results similar to those achieved by pouring the reagents together into a medium with the same pH value can be obtained.

DISCUSSION

Choice of a Model.—The domains of existence of halogens and haloamines can be accounted for by a model involving the equilibrium reactions between the various species, whilst leaving out their decomposition. The comparison of the experimental and the theoretical contents of the various compounds requires calculation of $[X_2]$, $[HXO]$, $[XO^-]$, $[NH_2X]$, $[NHX_2]$, $[NX_3]$, $[NH_3]$, $[NH_4^+]$ from the following data: concentrations in initial halogen $[Hal_i]$, in initial ammonia $[Amm_i]$, in halide $[X^-]$, the pH value of the solution, and the

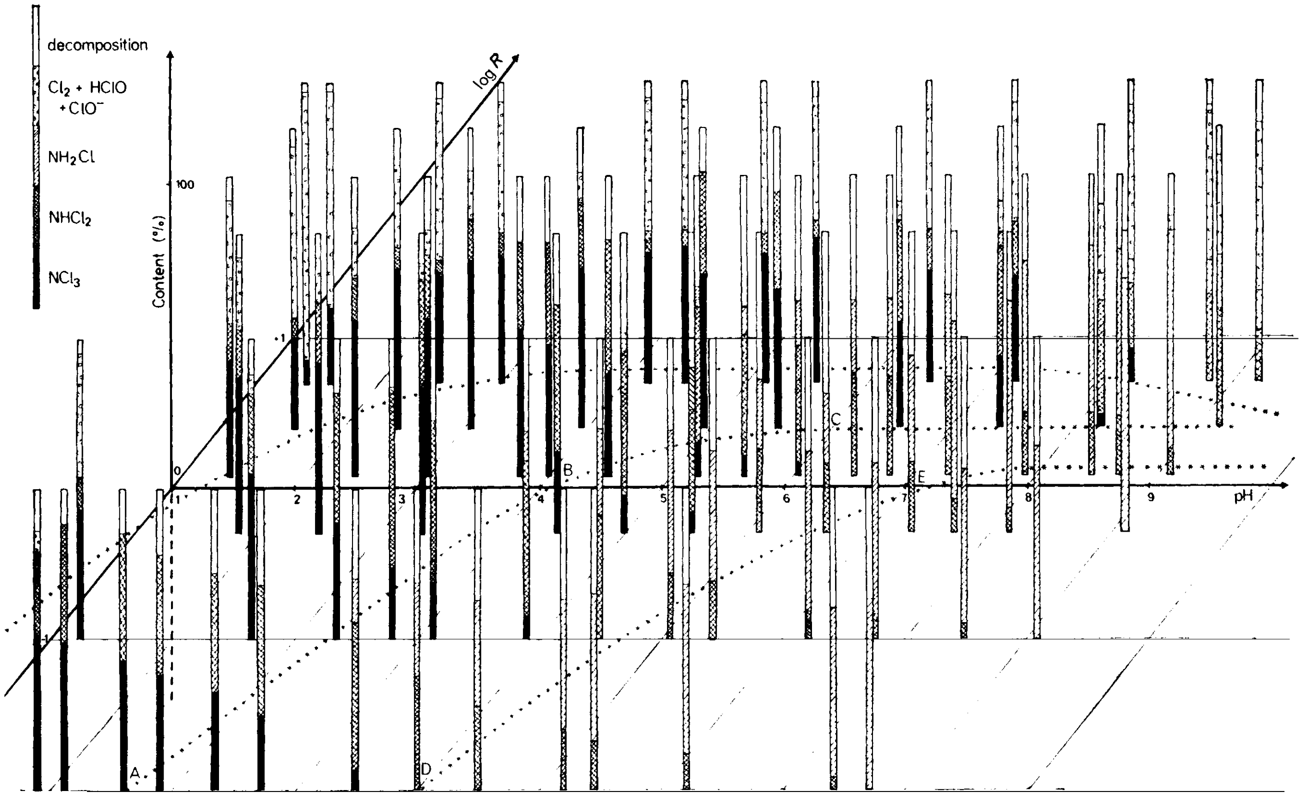

FIGURE 1 Experimental existence diagram of chlorine and chloramines as a function of pH and log R (after 10 min and at 25 °C) $[Cl_i]$ *ca.* 5×10^{-4}, $[Cl_i^-]$ *ca.* 1×10^{-3} mol dm^{-3}; (* * *) preponderance boundaries

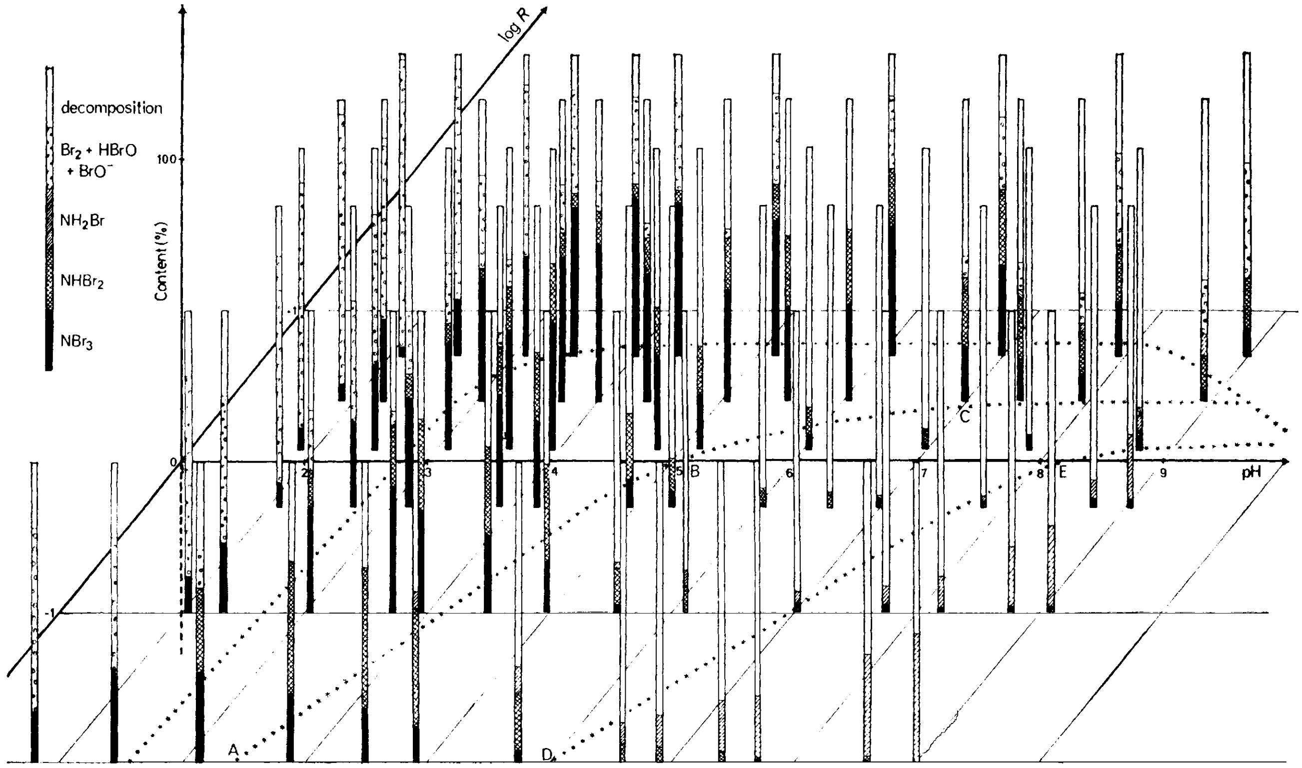

FIGURE 2 Experimental existence diagram of bromine and bromamine as a function of pH and log R (after 10 min and at 25 °C): $[Br_i]$ *ca.* 5×10^{-4}, $[Br_i^-]$ *ca.* 1×10^{-4} mol dm^{-3}; (* * *) preponderance boundaries

equilibrium constants of a minimum number of reactions.* We chose equilibria which allow the different unknowns to be related by the simplest possible equations (1)—(6). Also, the law of mass conservation makes it possible to express the conservation of halogen (X^+) and nitrogen in all their forms [equations (7) and (8)].

Hydrolysis of halogen

$$X_2 + H_2O \rightleftharpoons HXO + H^+ + X^- \qquad (1)$$
$$K = [HXO][H^+][X^-]/[X_2]$$

Dissociation of hypohalous acid

$$HXO \rightleftharpoons H^+ + XO^- \qquad (2)$$
$$K_a = [H^+][XO^-]/[HXO]$$

Basicity of ammonia

$$NH_3 + H^+ \rightleftharpoons NH_4^+ \qquad (3)$$
$$K_b = [NH_4^+]/[NH_3][H^+]$$

Hydrolysis of monohaloamine

$$NH_2X + H_2O \rightleftharpoons NH_4^+ + XO^- \qquad (4)$$
$$K_{hm} = [NH_4^+][XO^-]/[NH_2X]$$

Conversion of mono- into di-haloamine

$$2NH_2X + H^+ \rightleftharpoons NHX_2 + NH_4^+ \qquad (5)$$
$$K_{md} = [NHX_2][NH_4^+]/[NH_2X]^2[H^+]$$

Conversion of di- into tri-haloamine

$$3NHX_2 + H^+ \rightleftharpoons 2NX_3 + NH_4^+ \qquad (6)$$
$$K_{dt} = [NX_3]^2[NH_4^+]/[NHX_2]^3[H^+]$$

$$[Amm_i] = [NH_3] + [NH_4^+] + [NH_2X] + [NHX_2] + [NX_3] \qquad (7)$$

$$[Hal_i] = [X_2] + [HXO] + [XO^-] + [NH_2X] + 2[NHX_2] + 3[NX_3] \qquad (8)$$

A non-linear system of eight equations with eight unknowns was obtained. We solved this system by an iterative algorithm proposed by Bard and King.[19]

Equations of isocontent curves and calculation of equilibrium constants. The knowledge of the constants K, K_a, K_b, K_{hm}, K_{md}, and K_{dt} is required for solving the system of equations. The values of the first three constants are well known [20-22] and the three other ones can be determined experimentally from the curves of isocontent.

Equations of the isocontent curves of the halogen–water system. All the equations of isocontent curves corresponding to species, taken two by two, allow the delineation of predominance boundaries for each compound. In the absence of ammonia, the species are reduced to X_2, HXO, and XO^-. In acidic medium, this last species can be left out, and equation (8) is simplified.

$$[Hal_i] = [X_2] + [HXO]$$

For equal contents of X_2 and HXO, the equation of the isocontent curve is obtained by substituting the concentrations of both species by their values in equation (1).

$$[X_2] = [HXO] = 0.5[Hal_i] \quad K = [H^+][X^-]$$
$$pH = \log([X^-]/K) \qquad (a)$$

In neutral medium, the existing species being HXO and XO^-, equation (8) becomes $[Hal_i] = [HXO] + [XO^-]$ and for equal contents between both compounds, equation (2) is written with substitution of concentrations by their values.

$$[HXO] = [XO^-] = 0.5[Hal_i] \quad K_a = [H^+]$$
$$pH = \log(1/K_a) = pK_a \qquad (b)$$

Determination of K_{md}. The determination of K_{md} can be carried out from the domain boundary between NH_2X and NHX_2 (curve DE of Figures 1 and 2). As a matter of fact, near the boundary the species are restricted to NH_2X, NHX_2, NH_4^+, and H^+. Equations (7) and (8) are simplified as shown below. For a 50% content of X^+

$$[Amm_i] = [NH_4^+] + [NH_2X] + [NHX_2]$$
$$[Hal_i] = [NH_2X] + 2[NHX_2]$$

in the forms NH_2X and NHX_2, the equations are further simplified and under these conditions the equilibrium constant K_{md} is written as shown. Hence the equation (c)

$$2[NHX_2] = [NH_2X] = 0.5[Hal_i]$$
$$[NH_4^+] = [Amm_i] - 0.75[Hal_i]$$
$$K_{md} = ([Amm_i] - 0.75[Hal_i])/[Hal_i][H^+]$$

the isocontent curve between NH_2X and NHX_2 is obtained. The average experimental value calculated

$$pH = \log(K_{md}R/1 - 0.75R) \qquad (c)$$

from the isocontent curve DE is then (at 25 °C) for chloramines, $K_{md} = (5.2 \pm 0.6) \times 10^6$ dm^3 mol^{-1}; for bromamines, $K_{md} = (8 \pm 2) \times 10^7$ dm^3 mol^{-1}.

Determination of K_{dt}. In proximity of the curve ABC (Figures 1 and 2), the existing species are restricted to NX_3, NHX_2, NH_4^+, and H^+. Equations (7) and (8) can be simplified as before and for a 50% content of X^+ in the

$$[Amm_i] = [NH_4^+] + [NHX_2] + [NX_3]$$
$$[Hal_i] = 2[NHX_2] + 3[NX_3]$$

forms NX_3 and NHX_2, the equations become those shown below. When values are substituted in the expression for the equilibrium constant of equation (6) an expression for K_{dt} is obtained. Hence the isocontent curve between NX_3 and NHX_2 is represented by equation (d).

$$3[NX_3] = 2[NHX_2] = 0.5[Hal_i]$$
$$[NH_4^+] = [Amm_i] - 0.417[Hal_i]$$
$$K_{dt} = 1.78([Amm_i] - 0.417[Hal_i])/[Hal_i][H^+]$$
$$pH = \log(0.56 \cdot K_{dt} R/1 - 0.417R) \qquad (d)$$

The average experimental value obtained from the isocontent curve ABC is for chloramines, $K_{dt} = (1.7 \pm 0.2) \times 10^4$ dm^3 mol^{-1}; for bromamines, $K_{dt} = (1.5 \pm 0.2) \times 10^5$ dm^3 mol^{-1}.

Determination of K_{hm}. The constant K_{hm} can be calculated indirectly from experimental results obtained either in very acidic or very alkaline medium; our calculations are performed in this latter case, connected with formation of monohaloamine, in accordance with

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* The square brackets denote the concentration, considered as equivalent to the activity, the species being very dilute.

reaction (9). If this equilibrium is assumed to result

$$XO^- + NH_3 \rightleftharpoons NH_2X + OH^- \qquad (9)$$
$$K_f = [NH_2X][OH^-]/[XO^-][NH_3]$$

from combination of equilibria (3), (4), and that of water dissociation, characterized by constants K_b, K_{hm}, and K_e respectively, K_f is then expressed as shown. In this very

$$K_f = K_bK_e/K_{hm}$$

alkaline medium, where the system is restricted to XO^-, NH_2X, NH_3, and OH^-, equations (7) and (8) can again be simplified. Supposing the contents of NH_2X and

$$[Amm_i] = [NH_3] + [NH_2X]$$
$$[Hal_i] = [NH_2X] + [XO^-]$$
$$\text{with } K_e = [H^+][OH^-]$$

XO^- to be equal, equations (7) and (8) become those shown below. If $[NH_2X]$, $[XO^-]$, and $[NH_3]$ are replaced by their values in the equation relative to equilibrium (9), K_f is now written as shown and the equation

$$[NH_2X] = [XO^-] = 0.5[Hal_i]$$
$$[NH_3] = [Amm_i] - 0.5[Hal_i]$$
$$K_f = K_e/[H^+]([Amm_i] - 0.5[Hal_i])$$
$$pH = \log \{K_f[Hal_i](1/R - 0.5)/K_e\} \qquad (e)$$

of the isocontent curve between NH_2X and XO^- can be written in the form (e). From a sufficient number of experimental points of this curve, an average value of K_f can be derived for chloramines, $K_f = (44 \pm 8)$; for bromamines, $K_f = (1.8 \pm 0.4) \times 10^2$. This implies for chloramines, $K_{hm} = (4.0 \pm 0.7) \times 10^{-7}$ mol dm^{-3}; for bromamines, $K_{hm} = (1.0 \pm 0.2) \times 10^{-7}$ mol dm^{-3}.

Calculation of other equilibrium constants. Other equilibrium reactions of X^+ halogen transfer between the various compounds, taken by pairs, can be considered. These additional equilibria obtained by a linear combination of the independent equilibria (1)—(6) make it possible to obtain equations of other curves of isocontent, required for delineation of predominance boundaries of each species. These are the equilibria (10)—(17).

Acid hydrolysis of monohaloamine into hypohalous acid and ammonium ion

$$NH_2X + H_2O + H^+ \rightleftharpoons HXO + NH_4^+ \qquad (10)$$
$$K_{ma} = [HXO][NH_4^+]/[NH_2X][H^+]$$

Acid hydrolysis of dihaloamine into hypohalous acid and ammonium ion

$$NHX_2 + 2H_2O + H^+ \rightleftharpoons 2HXO + NH_4^+ \qquad (11)$$
$$K_{da} = [HXO]^2[NH_4^+]/[NHX_2][H^+]$$

Alkaline hydrolysis of dihaloamine into hypohalite ion and ammonia

$$NHX_2 + 2OH^- \rightleftharpoons 2XO^- + NH_3 \qquad (12)$$
$$K_{di} = [XO^-]^2[NH_3][H^+]^2/[NHX_2]K_e^2$$

Acid hydrolysis of trihaloamine into hypohalous acid and ammonium ion

$$NX_3 + 3H_2O + H^+ \rightleftharpoons 3HXO + NH_4^+ \qquad (13)$$
$$K_{ta} = [HXO]^3[NH_4^+]/[NX_3][H^+]$$

Alkaline hydrolysis of trihaloamine into hypohalite ion and ammonia

$$NX_3 + 3OH^- \rightleftharpoons 3XO^- + NH_3 \qquad (14)$$
$$K_{ti} = [XO^-]^3[NH_3][H^+]^3/[NX_3]K_e^3$$

Transformation of trihaloamine into halogen and ammonium ion

$$NX_3 + 3X^- + 4H^+ \rightleftharpoons 3X_2 + NH_4^+ \qquad (15)$$
$$K_{th} = [X_2]^3[NH_4^+]/[NX_3][X^-]^3[H^+]^4$$

Transformation of dihaloamine into halogen and ammonium ion

$$NHX_2 + 2X^- + 3H^+ \rightleftharpoons 2X_2 + NH_4^+ \qquad (16)$$
$$K_{dh} = [X_2]^2[NH_4^+]/[NHX_2][X^-]^2[H^+]^3$$

Transformation of monohaloamine into halogen and ammonium ion

$$NH_2X + X^- + 2H^+ \rightleftharpoons X_2 + NH_4^+ \qquad (17)$$
$$K_{mh} = [X_2][NH_4^+]/[NH_2X][X^-][H^+]^2$$

Other conceivable combinations were not retained, as equations of isocontent curves resulting therefrom are pH-independent or involve three X^+ species instead of two. Values of the constants of the various equilibria are summarised in Table 2, where K, K_a, K_b are taken from the literature. As seen already, the values of K_{md}, K_{dt}, K_f were derived from experimental results, while those of the other constants are connected with K, K_a, K_b, K_{md}, K_{dt}, K_f.

TABLE 2

Equilibrium constants of the reactions between the various species

Equilibrium	Constant	Typical values at 25 °C	
		X = Cl	X = Br
(1)	K	4.0×10^{-4} mol^2 dm^{-6}	7.2×10^{-9} mol^2 dm^{-6}
(2)	K_a	4.0×10^{-8} mol dm^{-3}	1.8×10^{-9} mol dm^{-3}
(3)	K_b	1.8×10^9 dm^3 mol^{-1}	
(4)	K_{hm}	4.0×10^{-7} mol dm^{-3}	1×10^{-7} mol dm^{-3}
(5)	K_{md}	5.2×10^6 dm^3 mol^{-1}	8×10^{-7} dm^3 mol^{-1}
(6)	K_{dt}	1.7×10^4 dm^3 mol^{-1}	1.5×10^5 dm^3 mol^{-1}
(9)	K_f	44	1.8×10^2
(10)	K_{ma}	10	55
(11)	K_{da}	1.9×10^{-5} mol dm^{-3}	2.8×10^{-4} mol dm^{-3}
(12)	K_{di}	5.8×10^{28}	1.9×10^{30}
(13)	K_{ta}	6.5×10^{-10} mol^2 dm^{-6}	6.2×10^{-10} mol^2 dm^{-6}
(14)	K_{ti}	4.3×10^{40}	4.9×10^{44}
(15)	K_{th}	10 dm^{12} mol^{-4}	1.7×10^{15} dm^{12} mol^{-4}
(16)	K_{dh}	1.2×10^2 dm^9 mol^{-3}	5.4×10^{12} dm^9 mol^{-3}
(17)	K_{mh}	2.5×10^4 dm^6 mol^{-2}	4.0×10^8 dm^6 mol^{-2}

Equations of other isocontent curves. Adopting the previous method of calculation, which involves neglecting the species not contributing to equilibriums (10)—(17), and in considering equal X^+ contents for the various species taken by pairs, different equations of isocontent curves such as (f)—(m) are obtained.

$$pH = \log \{K_{ma}/[Hal_i](1/R - 0.5)\} \qquad (f)$$

for boundary NH_2X–HXO

$$\mathrm{pH} = \log\{K_{\mathrm{da}}/[\mathrm{Hal_i}]^2(1/R - 0.25)\} \quad \text{(g)}$$
for boundary NHX_2–HXO

$$\mathrm{pH} = 0.5\log\{K_{\mathrm{di}}[\mathrm{Hal_i}]^2(1/R - 0.25)\} \quad \text{(h)}$$
for boundary NHX_2–XO^-

$$\mathrm{pH} = \log\{1.33K_{\mathrm{ta}}/[\mathrm{Hal_i}]^3(1/R - 0.167)\} \quad \text{(i)}$$
for boundary NX_3–HXO

$$\mathrm{pH} = 0.33\log\{1.5K_{\mathrm{ti}}[\mathrm{Hal_i}]^3(1/R - 0.167)\} \quad \text{(j)}$$
for boundary NX_3–XO^-

$$\mathrm{pH} = 0.25\log\{1.33K_{\mathrm{th}}[X^-]^3/[\mathrm{Hal_i}]^3(1/R - 0.167)\} \quad \text{(k)}$$
for boundary NX_3–X_2

$$\mathrm{pH} = 0.33\log\{K_{\mathrm{dh}}[X^-]^2/[\mathrm{Hal_i}]^2(1/R - 0.25)\} \quad \text{(l)}$$
for boundary NHX_2–X_2

$$\mathrm{pH} = 0.5\log\{K_{\mathrm{mh}}[X^-]/[\mathrm{Hal_i}](1/R - 0.5)\} \quad \text{(m)}$$
for boundary NH_2X–X_2

Predominance domains of species. Consideration of the equations of isocontent curves between two species shows that (a) and (b) are pH-dependent; (c) and (d) are dependent on pH and R. The curves (e)—(j) also depend upon the concentration of initial halogen, whereas (k)—(m) are at the same time dependent on pH R, $[\mathrm{Hal_i}]$, and $[X^-]$. By fixing $[\mathrm{Hal_i}]$ and $[X^-]$, all these curves can be plotted in two-dimensional space (pH, log R) (Figures 3 and 4). The relative positions of the curves show whether two particular species are actually predominant in a domain of given pH and log R. They also show if a theoretical isocontent curve merges with the predominance boundary relating to the two species considered or if, on the contrary, those two species foreseen by the isocontent curve cannot exist, given the predominance of other species. Thus, in Figures 3 and 4, all the theoretical isocontent curves are represented by thin lines and theoretical predominance by thick continuous ones. These lines are broken in the zone where occurrence of other species cannot be disregarded. The curves (***) constitute the experimental boundaries of the zones of predominance, taken from the diagrams of existence of halogens and haloamines. Satisfactory agreement was found between experimental and theoretical values of these boundaries, and likewise with the experimental values reported by Johnson and Overby for bromamines and represented by dotted lines in Figure 4.

The calculation of the isocontent curves for concentrations of initial halogen of 1×10^{-4}, 1×10^{-5}, 1×10^{-7} mol dm^{-3} respectively shows that the domains of tri-, then di-, and finally mono-haloamine were found to narrow down successively with dilution in $[\mathrm{Hal_i}]$ (see SUP 23156).

Distribution of halogen (X^+) *between the various species.* After the study of the diagrams of existence of halogens and haloamines in two-dimensional space (pH, log R), where the determination of predominance boundaries allows a qualitative interpretation of the results, we investigated in the vertical planes, the contents of the various species as a function of the pH and R values.

Computation of the contents of the various species inside these domains requires resolution of the system of equations with eight unknowns. An iterative calculation was performed (see SUP 23156) by taking the values given to the constants K, K_a, K_b, K_{hm}, K_{md}, K_{dt} in Table 2, for pH 0—14, and for six fixed molar ratios: R = 5, 2.5, 1.2, 0.5, 0.1, and 0.01. Experimental and theoretical distributions of free chlorine and chloramines as a function of pH for one value of R are shown in Figure 5 and they were plotted against log R for one fixed pH value in Figure 6 (see SUP 23156). In order to allow comparison with the calculated contents, the experimental contents favoured on these Figures refer to the residual halogen, while in the diagrams of existence of species the contents were referred to the initial halogen.

Similarly, experimental and theoretical distributions of free bromine and bromamines as a function of pH for R fixed are specified in Figure 7, whereas they are represented as a function of log R for one pH value in Figure 8. In all Figures the measured and calculated curves of distribution are in satisfactory agreement, particularly the position of predominance boundaries is thus confirmed.

The total content of residual halogen and haloamines, shown by these curves (***) in Figures 5—8, allows us to substantiate correlations between decomposition ratio, pH value, log R, and distribution of X^+ among the species. Taken as a whole, the results reveal a much higher decomposition for bromamines than chloramines; it increases with NHX_2 content and reaches a maximum for pH *ca.* 7.5 and $R \leqslant 1$.

The partition of X^+ among the various species in a very dilute medium, impossible to analyse, was calculated for chlorine under the conditions determined in Figure 9. Bromine showed a similar behaviour (see SUP 23156). The curves of distribution confirm and specify the qualitative results of the predominance zones found for these media.

Thermodynamic Properties.—The values of K_{hm}, K_{md}, K_{dt} allow the Gibb's free-energy calculations for the formation of NH_2X, NHX_2, and NX_3 in very dilute aqueous solution (with the activity coefficients of all species close to unity). The calculated values (kJ mol^{-1})

Chloramines

$$\Delta G_f^\ominus\,(NH_2Cl) = +84.0 \pm 0.4$$
$$\Delta G_f^\ominus\,(NHCl_2) = +209.2 \pm 1.2$$
$$\Delta G_f^\ominus\,(NCl_3) = +341.4 \pm 1.8$$

Bromamines

$$\Delta G_f^\ominus\,(NH_2Br) = +84.3 \pm 0.5$$
$$\Delta G_f^\ominus\,(NHBr_2) = +203.0 \pm 1.5$$
$$\Delta G_f^\ominus\,(NBr_3) = +329.6 \pm 2.5$$

at 25 °C are listed above. From these data, standard redox potentials can be obtained for the electrochemical equilibria (18)—(20).

$$NH_2X + 2H^+ + 2e^- \rightleftharpoons X^- + NH_4^+ \quad (18)$$
$$NHX_2 + 3H^+ + 4e^- \rightleftharpoons 2X^- + NH_4^+ \quad (19)$$
$$NX_3 + 4H^+ + 6e^- \rightleftharpoons 3X^- + NH_4^+ \quad (20)$$

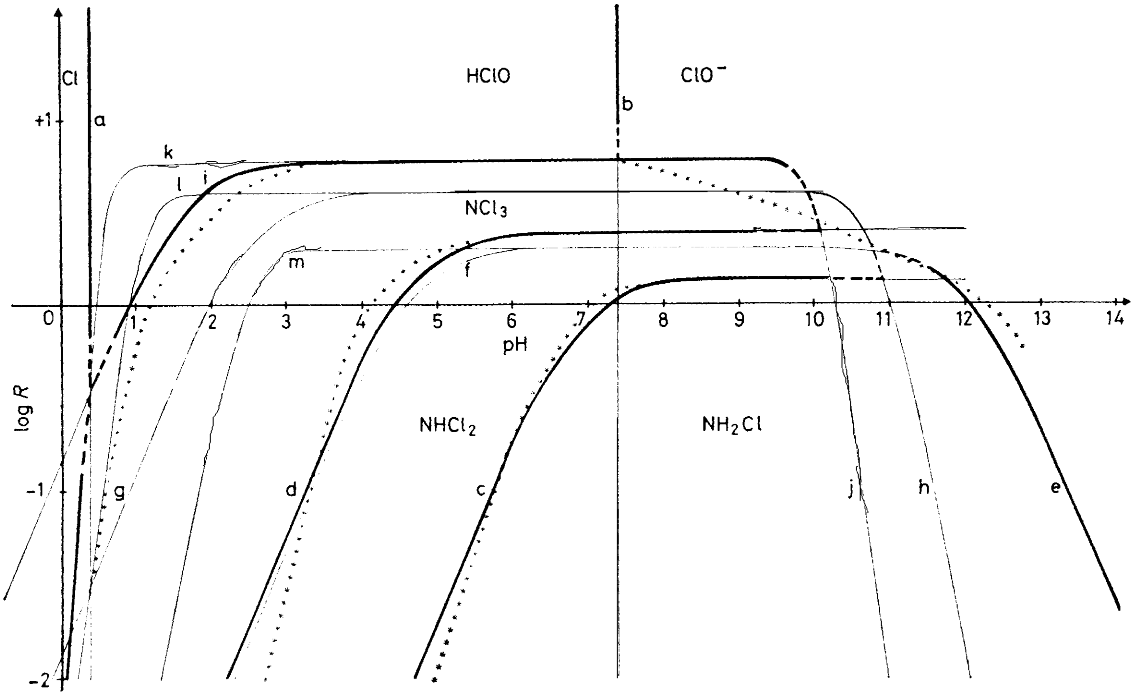

FIGURE 3 Experimental and theoretical predominance domains of chlorine and chloramines as a function of pH and log R: $[\mathrm{Cl_I}]$ *ca.* 5×10^{-4}, $[\mathrm{Cl_I^-}]$ *ca.* 1×10^{-3} mol dm^{-3}; (———) theoretical isocontent curves, (▬▬▬) theoretical preponderance boundaries, (* * *) experimental preponderance boundaries

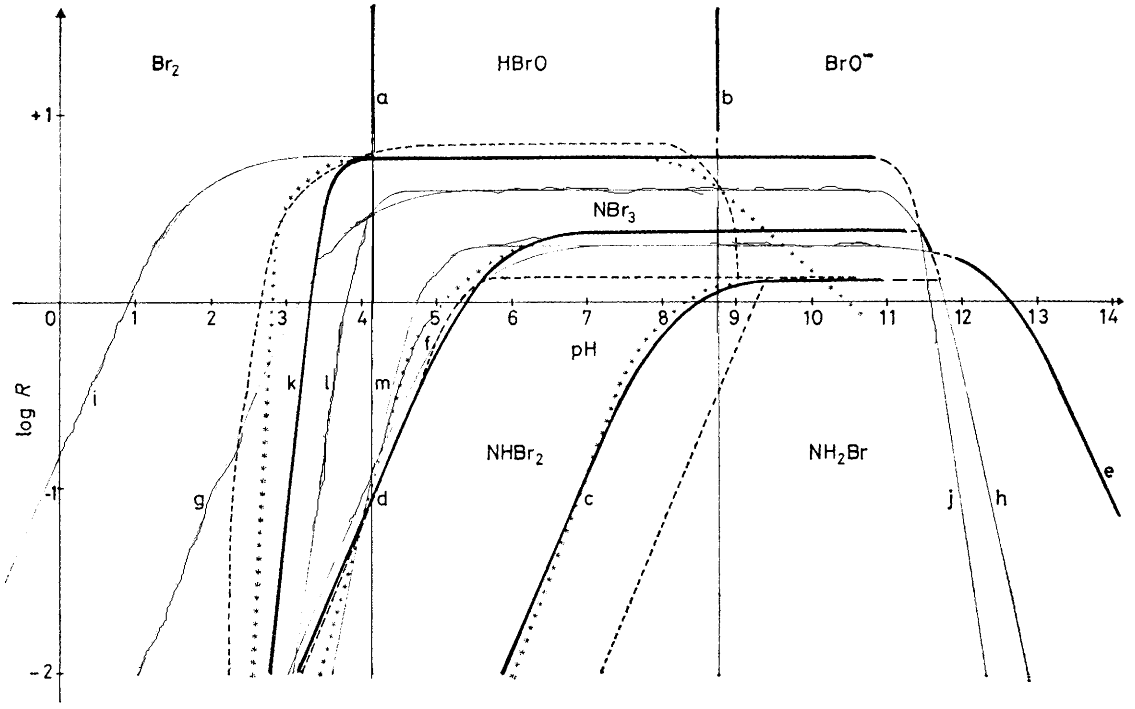

FIGURE 4 Experimental and theoretical predominance domains of bromine and bromamines as a function of pH and log R: $[\mathrm{Br_I}]$ *ca.* 5×10^{-4}, $[\mathrm{Br_I^-}]$ *ca.* 1×10^{-4} mol dm^{-3}; (———) theoretical isocontent curves, (▬▬▬) theoretical preponderance boundaries, (* * *) experimental preponderance boundaries, (— — —) preponderance boundaries after Johnson and Overby [18]

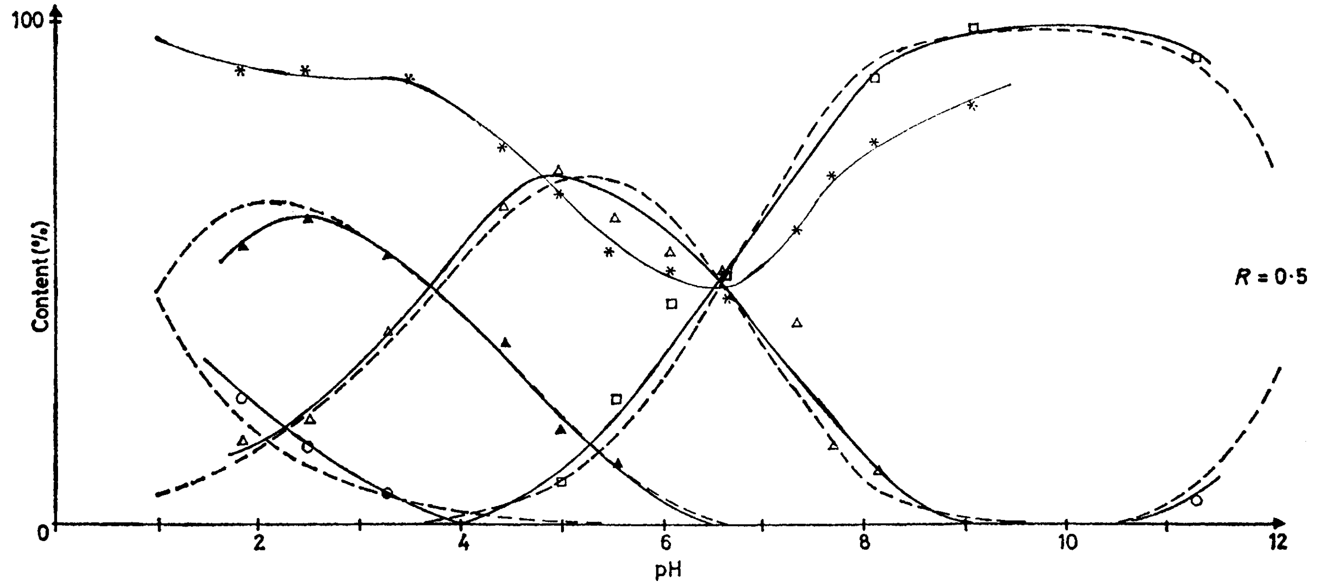

Figure 5 Experimental and theoretical distributions of chlorine and chloramines as a function of pH with R fixed: $[\mathrm{Cl_i}] = 5 \times 10^{-4}$, $[\mathrm{Cl_i^-}] = 1 \times 10^{-3}$ mol dm^{-3}; (— — —) theoretical curves, (———) experimental curves, (— * —) residual content of chlorine and chloramines; experimental points, (▲) NCl_3, (△) $NHCl_2$, (□) NH_2Cl, (○) free chlorine

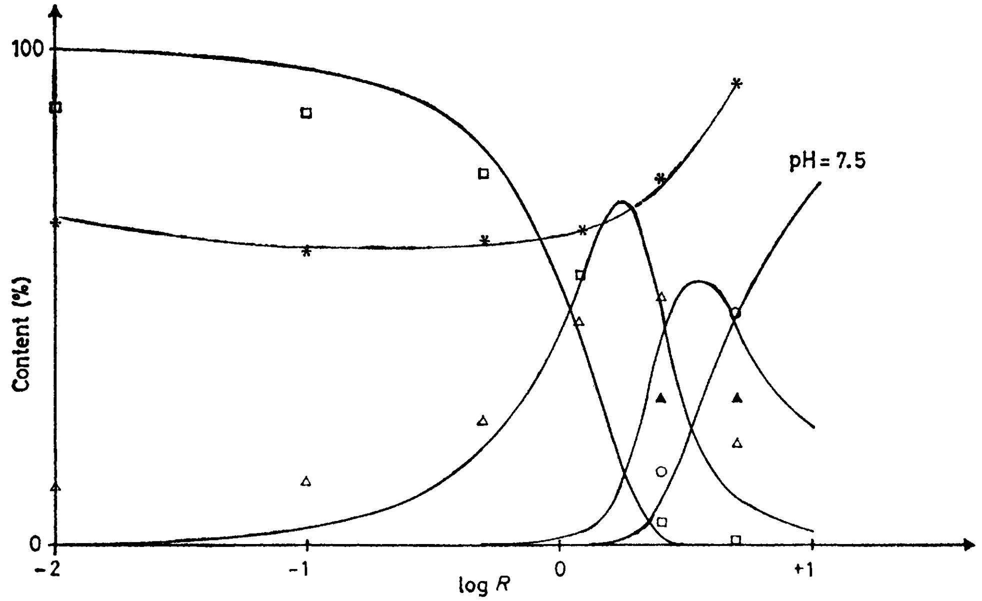

Figure 6 Experimental and theoretical distributions of chlorine and chloramines as a function of log R with pH fixed: $[\mathrm{Cl_i}] = 5 \times 10^{-4}$, $[\mathrm{Cl_i^-}] = 1 \times 10^{-3}$ mol dm^{-3}; (———) theoretical curves, (— * —) residual content of chlorine and chloramines; experimental points, (▲) NCl_3, (△) $NHCl_2$, (□) NH_2Cl, (○) free chlorine

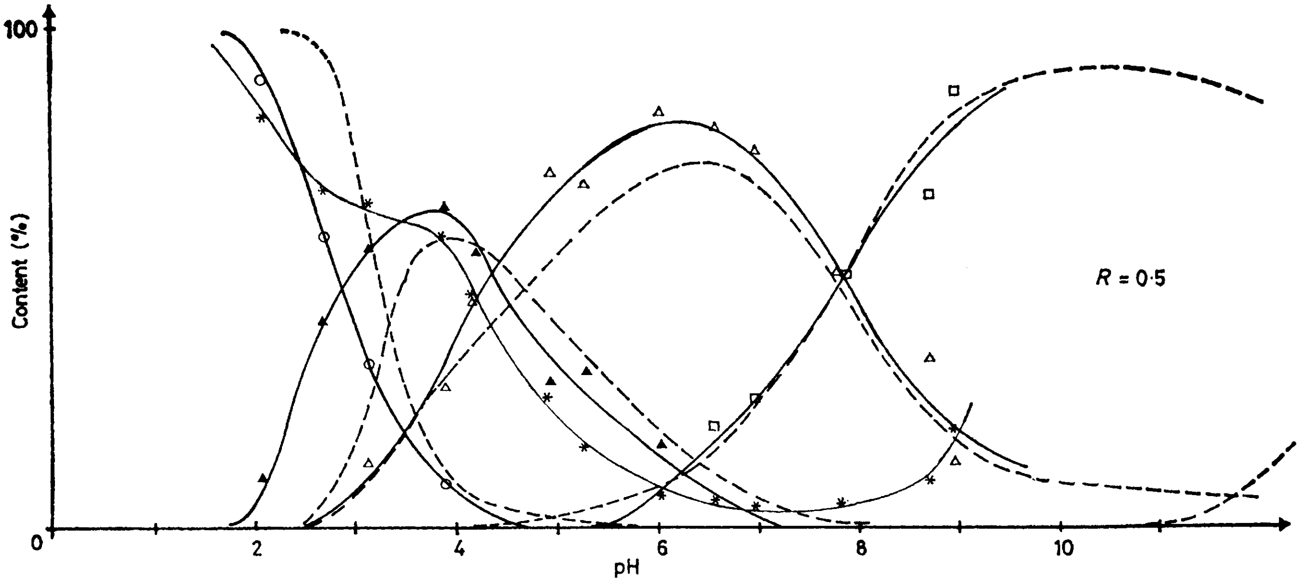

FIGURE 7 Experimental and theoretical distributions of bromine and bromamines as a function of pH with R fixed: $[\mathrm{Br}_i] = 5 \times 10^{-4}$, $[\mathrm{Br}_i^-] = 1 \times 10^{-4}$ mol dm^{-3} (— — —) theoretical curves, (———) experimental curves, (— * —) residual content of bromine and bromamines; experimental points, (▲) NBr_3, (△) $NHBr_2$, (□) NH_2Br, (○) free bromine

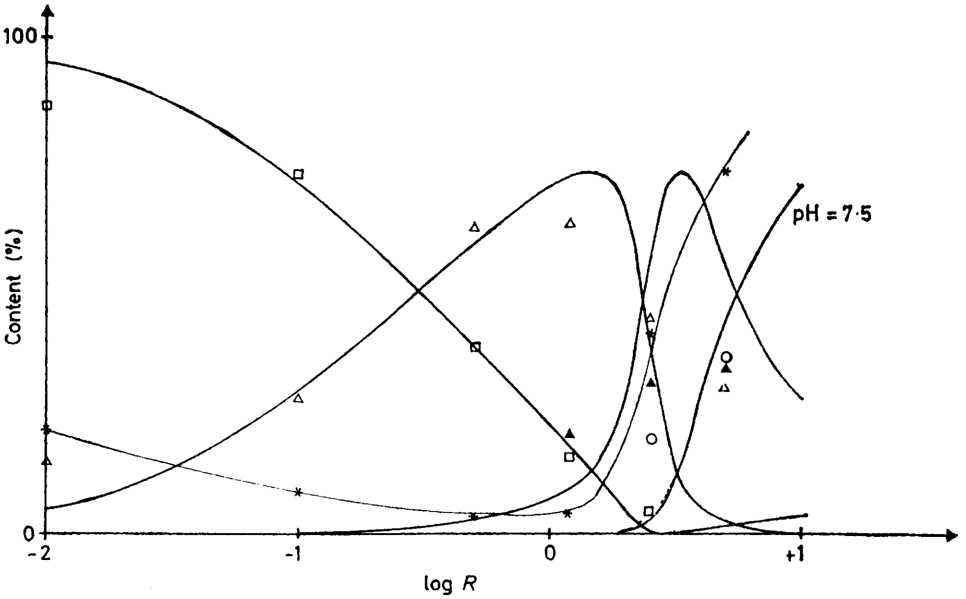

FIGURE 8 Experimental and theoretical distributions of bromine and bromamines as a function of log R with pH fixed: $[\mathrm{Br}_i] = 5 \times 10^{-4}$, $[\mathrm{Br}_i] = 1 \times 10^{-4}$ mol dm^{-3}; (———) theoretical curves, (— * —) residual content of bromine and bromamines; experimental points, (▲) NBr_3, (△) $NHBr_2$, (□) NH_2Br, (○) free bromine

Chloramines

$$E^\ominus\ (18) = 1.527 \pm 0.007\ \text{V}$$
$$E^\ominus\ (19) = 1.428 \pm 0.008\ \text{V}$$
$$E^\ominus\ (20) = 1.407 \pm 0.008\ \text{V}$$

Bromamines

$$E^\ominus\ (18) = 1.382 \pm 0.008\ \text{V}$$
$$E^\ominus\ (19) = 1.265 \pm 0.009\ \text{V}$$
$$E^\ominus\ (20) = 1.239 \pm 0.010\ \text{V}$$

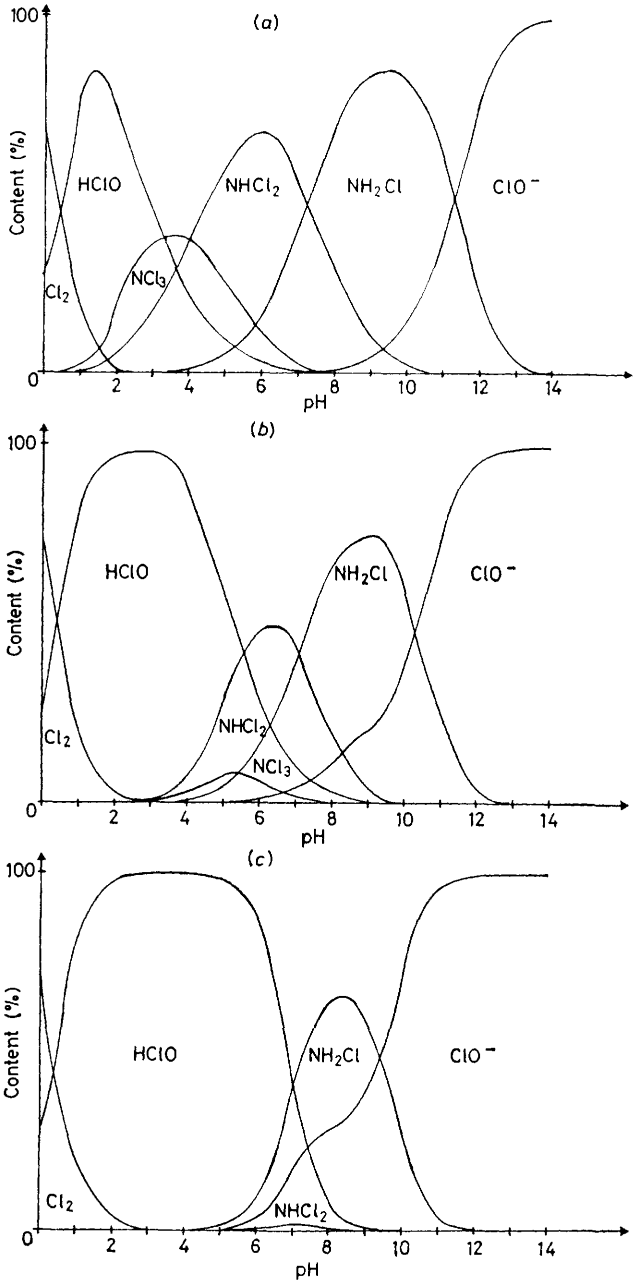

FIGURE 9 Theoretical distributions of chlorine and chloramines for various concentrations in initial chlorine, as a function of pH, with R fixed and $[\text{Cl}^-] = 1 \times 10^{-3}$ mol dm^{-3}: (*a*) $[\text{Cl}_i] = 1 \times 10^{-4}$, $R = 1$; (*b*) $[\text{Cl}_i] = 1 \times 10^{-5}$, $R = 1$; (*c*) $\text{Cl}_i] = 1 \times 10^{-7}$ mol dm^{-3}, $R = 0.1$

CONCLUSION

In spite of difficulties chiefly due to multiple absorption, u.v. spectrophotometry allowed selective and quantitative analysis of all kinds of halogen and haloamines at the +1 degree of oxidation (X_3^-, X_2, HXO, XO^-, NH_2X, NHX_2, NX_3). The experimental values can be correctly interpreted by using a model of reversible reactions, which permits various calculations of theoretical and practical interest. In particular, by controlling a certain number of parameters, such as pH, R, $[\text{Hal}_i]$, $[X^-]$, as well as temperature and time, there is a means both for calculating the contents of all existing species and estimating their decomposition ratio by comparison with experimental diagrams.

Predictions apply to water treatment, notably as regards choice of disinfectant (chlorine or bromine). Better knowledge of halogen–ammonia–water systems should make it possible to avoid the predominance of obtrusive compounds, *e.g.* NCl_3. Selection of initial parameters could also enhance the formation of desirable highly germicidal species, such as HXO, or highly unstable ones, such as $NHBr_2$, resulting in an ammonia elimination.

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