ADSORPTIVE STUDIES OF AQUEOUS ZINC IONS BY FOAM FRACTIONATION IN SIMPLE MODE

R. KONDURU

CANMET, EMR, P.O. Bag: 1280, Devon, Alberta, Canada, T0C 1E0

This paper discusses the application of a foam fractionating column operating strictly in simple mode. The system chosen was zinc and sodium lauryl sulphate. Using the correct way of operating a foam fractionating column in simple mode, as was discussed in a separate paper by the same author, the combined influence of collector and metal ion concentrations on zinc surface excess was studied. Even a small amount of collector was found to be sufficient to saturate the bubble surface. However, for higher bulk zinc concentrations a higher collector concentration was required to maximize the zinc surface excess. The bulk zinc concentration and solution pH mutually affected the zinc surface excess. While a bulk zinc concentration of $0.15 \, \text{mol/m}^3$ was found to be optimum to maximize the zinc surface excess, a pH of 4.0 provided optimum surface excess for any bulk zinc concentration.

Introduction

Adsorptive bubble separation techniques—the generic name of which was first proposed by Lemlich in 1966[6]—are practiced as bubble and foam separation methods. Foam separation, while being a less familiar purification/separation method, occupied an important role in wastewater treatment, more specifically for the removal of trace metals such as cadmium, chromium, copper, iron, lead, manganese, mercury, nickel and zinc, with the aid of surfactants.[13] There are two important types of foam separation: (a) foam fractionation for removing soluble matter, and (b) froth flotation for removing insoluble matter.[7]

Walling *et al.*[22] first published a study of the separation of calcium and sodium ions in a vertical foaming column. Sebba[18] introduced a low-gas flow rate or gentle bubbling foam separation technique known as ion-flotation. He mentioned that the surfactant should be added in stoichiometric amounts to exist as simple ions. Wace and Banfield[21] studied the foam separation of radioactive metals with surface excess as an important parameter. Rubin and Gaden[16] presented various systems, including 18 metals that could be separated by foam fractionation. Grieves *et al.*[4] employed foam fractionation in the treatment of radioactive wastes. Rubin[15] published on the removal of trace metals (iron, copper and lead) by foam separation using NaLS as surfactant. Rubin and Lapp[17] investigated the foam separation of lead with NaLS. Kubota *et al.*[9] studied extensively the foam fractionation of cadmium. Carlson and Moussavi[2] published on the chelation and foam separation of metal ions such as cadmium, zinc and lead from waste solutions. Porta *et al.*[12] studied the separation of copper ion species in aquatic systems by foaming.

Most of the aforementioned papers discussed much about the adsorption of aqueous metal ions employing continuous-type foam fractionation in higher mode—thus lacking information on simple-mode foam fractionation.

The only publications available in the literature related to tapered column simple-mode apparatus are: Dick and Talbot,[3] St. Eloi,[20] Huang and Talbot[5] and Siy and Talbot.[19] Dick and Talbot[3] published on the fractionation of copper by using a surfactant as well as an auxiliary ligand. Huang and Talbot[5] reported results on the removal of copper, cadmium and lead ions from dilute aqueous solutions by foam fractionation. St. Eloi[20] reported on the foam fractionation of zinc with NaDBS as a collector along with excess sodium chloride. He reported that zinc concentration increased with lower surfactant concentration. Siy and Talbot[19] published on the foam fractionation of zinc with NaDBS, reporting that the order of increasing effectiveness in the removal of zinc ions by various forms of DBS^- is $KDBS < NaDBS < LiDBS < HDBS$. While these papers discussed the adsorption of metal ions in simple mode foam fractionation, there was no evidence that data were collected strictly under simple mode operation.

Experiments in the present work were therefore conducted to study the adsorption of metal ions, using the correct way of operating a foam fractionating column strictly in simple mode[8], with the aid of a collector.

1. Theory and Discussion

1.1 Principle of foam fractionation

Foam fractionation is based on the principle that the surface-active material is carried up by bubbles introduced into the liquid pool as illustrated step-by-step[7] in Fig. 1. **Figure 1(a)** shows a typical liquid pool that contains a surface-active substance which often is called the collector. Gas with an appropriate flowrate is introduced into the system through a bubbler which generates bubbles. A single bubble introduced into the system can be imagined as shown in **Fig. 1(b)**. Each gas bubble submerged in liquid is surrounded by collector ions. Surface-active solutes, having great affinity by nature to travel to the surface, move to the bubble surface and orient with their hydrophobic (non-polar) end towards the gas phase, and with their hydrophilic (polar) end towards the liquid phase as shown in **Fig. 1(c)**. The bubble is not stationary in the liquid pool but travels to the liquid surface, carrying up some solute particles with it as shown in **Fig. 1(d)**. The principle holds good for all bubbles and so they combine together to form the foam which is collapsed from the foam-liquid interface as shown in general in Fig. 1(a).

When the system contains non-surface active solutes such as metal ions, they can be electrostatically attracted to the bubble surface by a negatively charged surface-active agent—specifically, an anionic surfactant. As explained above, the surface-active solutes go to the surface of the bubble and orient with their negative charge as shown in **Fig. 1(e)**. To neutralize the charge on the bubble surface, metal ions move to the surface and orient with their positive charge as shown in **Fig. 1(f)**. Thus an electrical double layer is formed around the surface of each bubble introduced into the liquid pool. Positive ions will be attracted towards the surface and negative ions will be repelled from the surface as shown in **Fig. 1(g)**. Thus each bubble introduced into the liquid pool brings some metal ions from the bulk to the surface as shown in **Fig. 1(b)**.

1.2 Equilibrium concept

The equilibrium of concern in foam fractionation is that of solutes between the bubble surface and the bulk liquid. There must be sufficient residence time of bubbles to establish such surface equilibrium. If a surfactant is to be sufficiently concentrated under equilibrium conditions, the adsorbed surface molecules must generally occupy an area of about $50 \times 10^{-10} \, m^2/mol$, which corresponds to a surface excess of $3.0 \times 10^{-6} \, mol/m^2$. For an anionic surfactant such as NaLS, Rubin and Jorne[14] reported that the surface excess is $2.7 \times 10^{-6} \, mol/m^2$.

Whenever the foam is generated in a liquid pool under controlled conditions, the collapsed foam,
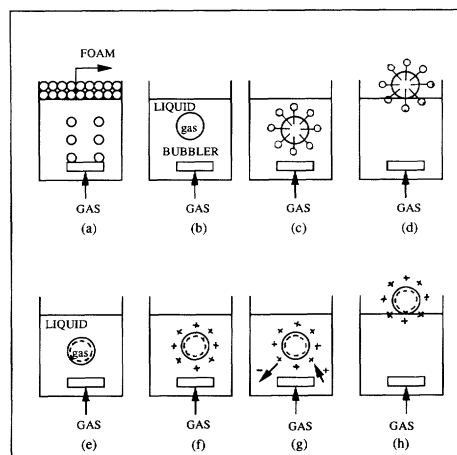

Fig. 1. Principle of foam fractionation

which is made of surface region and bulk region, is richer in surfactant and metal ions than the parent bulk liquid. The volume of the surface region is very small when compared to that of the bulk region. The equilibrium is established between the surface region and the region of the interstitial liquid among bubbles, which is assumed to have the same composition as the pool liquid. It is also known that the equilibrium between the surfactant and the counter ions at the interface governs the necessary fractionation[1,21]. The number of theoretical stages in the foam fractionation is considered to be an important and complex aspect, and there are limited theoretical expressions and graphical procedures available in the literature to determine it.[10] The liquid pool is generally considered to be one theoretical stage (it resembles the reboiler in a distillation column). In the current research topic, the column is treated as "a single equilibrium stage" with the assumption that there are no stages to measure in the foam column. That means the foam is not enriched due to the bubble coalescence or drainage. In other words, the column is operated strictly in simple mode.

1.3 Mass balance

Simple-mode foam fractionation can be carried out either in batchwise or in continuous flow operation. In some practical cases recycling of the foam would become unfavorable because the collector micelles would not be dissociated when returned to the pool liquid—suggesting that a batch operation is advantageous. The surface phenomena for a batch column are studied through performing the following mass balance on the collapsed foam[7]:

$$V_f C_f = S\Gamma + V_f C_b \qquad (1)$$

For a properly designed bubbler of n capillaries which is capable of generating N bubbles per minute per capillary, the surface generation rate (S) is given by:

$$S = nN(\pi d^2) \qquad (2)$$

where d is the bubble diameter. Eq. (2) was written under the assumption that the bubble surface in the pool liquid is always spherical (small gas bubbles introduced into a liquid pool will spontaneously tend to adopt a spherical shape[16]). The gas flowrate (Q) is given by:

$$Q = (nN)(1/6)\pi d^3 \qquad (3)$$

The bubble diameter (d) can be calculated from Eq. (3) and thereafter S can be determined from Eq. (2). Hence Eq. (1) becomes:

$$\Gamma = (V_f/S)(C_f - C_b) \qquad (4)$$

Eq. (4) is applicable to both metal ions and surfactant ions since the mass balance is valid for all components of the system. It is also based on the assumption that there was sufficient contact time for each bubble to become saturated. Eq. (4) is purposefully written with the term "(V_f/S)" because the maintainance of an optimal (V_f/S) ratio would reliably keep the operation in simple mode.[8]

2. Experimental

2.1 Experimental apparatus

The apparatus of a tapered foam fractionating column was described in detail with an appropriate schematic diagram elsewhere[8]. In summary, an air inlet system with measuring device was connected to a properly designed bubbler which generated uniform spherical bubbles in the liquid pool of a tapered column.

2.2 Experimental procedure

For any required concentrations of surfactant (NaLS) and metal ion (zinc), the dilute feed solution was prepared with deionized distilled water. The pH of the feed solution was adjusted to the desired value by using HNO_3, NaOH or both. The optimal operating conditions[8] of the simple-mode apparatus, as given in **Table 1**, were maintained to generate bubbles in the liquid pool. The column was charged with feed solution and, after reaching steady form-liquid interface, the foam was collapsed into the receiver, which was later analysed for the concentration of zinc with an atomic absorption spectrophotometer.

Table 2 shows the range of several parameters encountered during experimentation.

2.3 Foam breakage

Approximately one week was needed for the foam to break naturally. In the present experimentation the foam was broken rapidly by freezing it for a period of about 1000 s followed by thawing for another 1000 s to obtain a clear solution.[7] This procedure saved considerable time in the experimentation. After the breakage of the foam, the solution was ready to be analysed.

Table 1. Optical operating conditions—simple mode

Air flowrate [m^3/s]	$= 1.5 \times 10^{-6}$
Height of foam-liquid interface [m]	$= 0.32$
Foam generation rate [m^3/s]	$= 3.3 \times 10^4$
Surface generation rate [m^2s]	$= 3.5 \times 10^{-3}$
(V_f/S) ratio [m]	$= 9.4 \times 10^{-6}$
Bubble diameter [m]	$= 2.56 \times 10^{-3}$
Number of capillaries [—]	$= 5$
Diameter of capillary [m]	$= 1.78 \times 10^{-4}$
Length of capillary [m]	$= 6.00 \times 10^{-3}$

Table 2. Range of parameters

S No.	Parameter	Units	Range
1	C_b	[mol/m^3]	0.01 to 1.73
2	C_c	[mol/m^3]	0.17 to 1.73
3	C_f	[mol/m^3]	0.05 to 1.77
4	C_f/C_b	[—]	1.0 to 4.4
5	pH	[—]	1.8 to 7.6
7	$\Gamma \times 10^6$	[mol/m^2]	0.04 to 1.46

2.4 Precautions

(a) The major caution was taken in keeping the (V_f/S) ratio deliberately constant at its optimal value. This was accomplished by simply maintaining the operating conditions given in Table 1. The (V_f/S) ratio is the amount of foam collected per unit interfacial area. For a given apparatus, the amount of foam could vary according to the entrainment of bubbles or due to the geometry of bubbles. However this discrepancy was overcome with the aid of the (V_f/S) ratio. The apparatus otherwise would produce inconsistent data.

(b) The foam-liquid interface was held constant with extra caution by adjusting the leveling bulb thoughout the operation.

(c) Proper care was taken to pass air through the bubbler prior to operation so that the capillaries of the bubbler were not blocked or wetted by pool liquid.

3. Experimental Results and Discussion

3.1 Collector and metal ion concentrations

The combined influence of collector and metal ion concentrations on zinc surface excess is depicted in **Fig. 2**. Each experiment was conducted with one collector concentration and one bulk zinc concentration exactly as explained in the experimental procedure. The surface excess was computed from Eq. (4).

In foam fractionation, the adsorption of collector-ions causes co-adsorption of equivalent counter-ions so that both collector and counter ions would be extracted from the bulk to the surface.

It was noticed from Fig. 2 that when the collector concentration was very small (say 0.17 mol/m^3), the zinc surface excess gradually increased for a certain range, reached a maximum and then slowly decreased

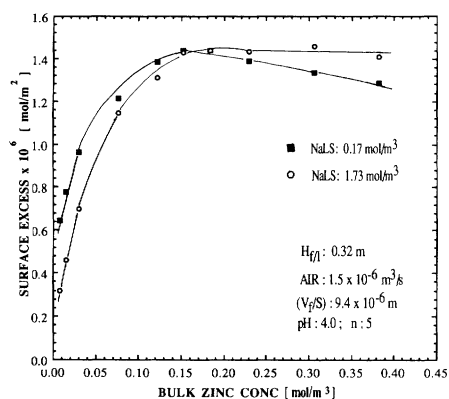Fig. 2. Effect of collector and metal ion concentrations on zinc surface excess
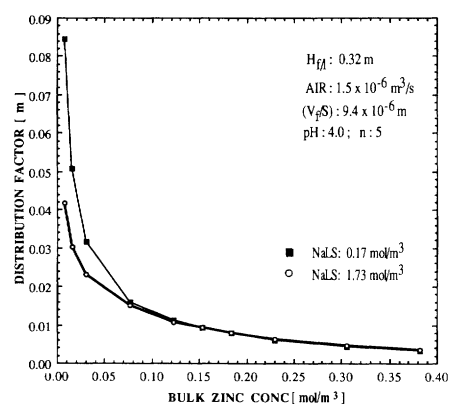

Fig. 3. Effect of collector and metal ion concentrations on distribution factor

Fig. 4. Effect of bulk zinc concentration and pH on zinc surface excess

as the bulk zinc concentration was increased. In the other case, when the collector concentration was very high (say $1.73 \, mol/m^3$), the surface excess gradually increased, reached the same miximum and then remained almost unchanged. It was interpreted, based on the fact that the surface excess reached a maximum possible value, that even a small amount of collector was sufficient to saturate the bubble surface. As the bubble surface was saturated, a further increase in bulk zinc concentration did not further increase the surface excess.

Figure 2 also indicated that the lower collector concentration accomplished higher zinc surface excess up to a bulk zinc concentration of about $0.15 \, mol/m^3$, whereas for higher bulk zinc concentrations a higher collector concentration was required to reach the same maximum. These results seemed reasonable after comparing them with those of Siy and Talbot[19] for the system of zinc and NaDBS.

It was worthwhile to conduct the following test. As the surface excess for lower collector concentration decreased beyond a certain value of bulk zinc concentration, one might expect this tendency even for higher collector concentration when the bulk zinc concentration was increased to an extremely high value. This fact was experimentally checked by working at a stoichiometric bulk zinc concentration of $1.73 \, mol/m^3$. The surface excess dropped to a very low value $(0.039 \times 10^{-6} \, mol/m^2)$ because a very large quantity of sodium hydroxide was consumed for the pH adjustment and thus a large amount of sodium ions competed with the zinc ions in the process of adsorption.

3.2 Distribution factor

The same experimental data in Fig. 2 were further analysed through computating the distribution factor, defined as Γ/C_b, as shown in **Fig. 3**. As the rate of increase of bulk zinc concentration (denominator) was much faster than the rate of increase of surface excess (numerator), the distribution factor continued to fall.

The distribution factor (Γ/C_b), which is also called the degree of separation, dropped because the degree of adsorption (Γ) of zinc diminished with a continuous increase of bulk zinc concentration. Figure 3 also revealed the fact that the lower collector concentration was more effective up to a bulk zinc concentration of about $0.15 \, mol/m^3$, whereas for higher bulk zinc concentrations the collector concentration made no significant difference in terms of the degree of separation.

3.3 Bulk zinc concentration and pH

The mutual influence of bulk zinc concentration and pH, at a fixed collector concentration, on zinc surface excess was studied in a wide range and is depicted in **Fig. 4**. Each experiment was conducted, with one bulk zinc concentration adjusting to a particular pH, strictly under simple-mode operation.

Figure 4 indicated that at any particular pH the surface excess reached maximum for a bulk zinc concentration of $0.15 \, mol/m^3$. When the bulk zinc concentration was very high (say $1.73 \, mol/m^3$) the surface excess dropped to an extremely low value, implying the most difficult chances for zinc while taking part in the adsorption process. As stated previously, for this particular very high bulk zinc

concentration a very large quantity of NaOH was consumed for the pH adjustment and so unusually large amounts of sodium ions competed with zinc ions in the adsorption process. For very low bulk zinc concentrations, say $0.015\,mol/m^3$ and $0.03\,mol/m^3$, there was no significant effect on zinc surface excess up to a pH of 7. But the surface excess started dropping beyond a pH of 7. In the case of $0.38\,mol/m^3$, as the bubble surface was not fully saturated the surface excess curve appeared close to the maximum. However, the bulk zinc concentrations between 0.15 and $0.38\,mol/m^3$ represented an optimum range.

3.4 Surface excess versus pH

Refer to Fig. 4, where the mechanism for the effect of pH on surface excess can be explained as follows: at lower pH the concentration of the hydronium ions (H_3O^+) is higher, and the hydronium ions preferentially move to the double layer to neutralize the charge of the collector ions, thereby reducing the zinc surface excess. As the pH was increased, hydronium ion concentration decreased and the zinc surface excess increased. At a pH of 4.0 there was only a little competition from the hydronium ions and hence the zinc surface excess reached a maximum in all cases. The maximum on each curve could also be explained as the optimum pH region for the formation of a co-ordination compound consisting of zinc ions and free lauryl sulphate ions. This fact was originally postulated by Sebba.[18] When pH increased further, sodium ions which were introduced into the system by the addition of NaOH for pH adjustiment competed with zinc ions in the double layer region—thereby reducing the zinc surface excess.

Alternatively, the reason for the reduction of the surface excess in the alkaline region is that a part of the zinc must have been precipitated by combining with OH^- ions of NaOH to form $Zn(OH)_2$. It was experimentally noticed that at higher pH, $Zn(OH)_2$ precipitate was found in the foamate as an insoluble scum. This precipitate was not collected by the foam fractionation technique but by precipitate flotation.

The solubility product/precipitation value is defined as the product of the concentrations of the ions of a substance in a saturated solution:

$$K_{sp} = (Zn^{++})(OH^-)^2 \qquad (5)$$

where K_{sp} = Solubility product
Zn^{++} = conc of zinc in solution
OH^- = conc of hydroxyl in solution
The value of K_{sp} for $Zn(OH)_2$ is available in the literature[11] as 1.8×10^{-14}. From Eq. (5), for a given bulk zinc concentration the concentration of hydroxyl ion (OH^-) was calculated and thereafter the pH of the solution for complete precipitation was determined as shown in Table 3. It was experimentally noticed that the zinc did precipitate at the computed values

Table 3. pH from solubility product

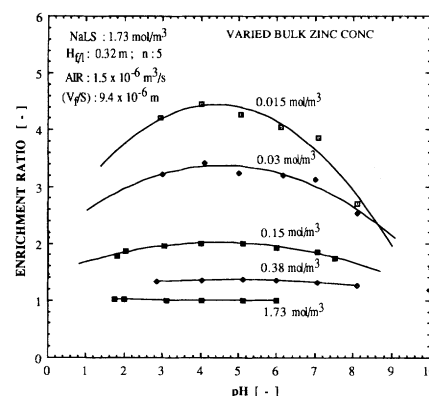| Conc. of Zinc [mol/m³]	pOH [—]	pH [—]
0.015	4.46	9.54
0.03	4.61	9.39
0.15	4.96	9.04
0.38	5.16	8.84
1.73	5.49	8.51

Fig. 5. Effect of bulk zinc concentration and pH on enrichment ratio

of pH.

3.5 Enrichment ratio

The enrichment ratio is the ratio between the concentration of metal in foamate and that in the bulk liquid. Its physical meaning is adsorption efficiency. **Figure 5** was made, from the same data as in Fig. 4, to illustrate the enrichment ratio. From Eq. (4) it is clear that when the data are collected by maintaining a constant (V_f/S) ratio, the enrichment ratio (C_f/C_b) should increase with a decrease in the bulk zinc concentration and vice versa—which was verified from the plot. Siy and Talbot[19] reported that, for the zinc and NaDBS system, the enrichment ratio increased with any decrease in bulk zinc concentration. Rubin[15] also reported in ion flotation studies that, for the copper and NaLS system, the removal should increase by decreasing the metal ion concentration. The tendency of enrichment ratio curves, as anticipated from Eq. (4), coincided with that of surface excess curves.

Conclusion

Non-surface active aqueous zinc ions were made surface-active, strictly under simple mode operation, with the aid of the well-known collector sodium lauryl sulphate.

The combined influence of the collector and zinc ion concentrations on zinc surface excess was studied. Even a small amount of collector was found to be sufficient to saturate the bubble surface. Up to a bulk

zinc concentration of $0.15 \, \text{mol/m}^3$, an extremely low collector concentration ($0.17 \, \text{mol/m}^3$) was proved to be more effective. But for higher bulk zinc concentrations, a higher collector concentration was demanded.

The mutual influence of the bulk zinc concentration and pH on the zinc surface excess was studied. The optimum surface excess was accomplished for a bulk zinc concentration of $0.15 \, \text{mol/m}^3$ over a wide range of pH. At the same time a pH of 4.0 was found to be the optimum for all bulk zinc concentrations studied.

Experimental evidence suggested that the addition of sodium hydroxide in adjusting the pH of feed solution might release sodium ions which would play a competitive role in the process of zinc adsorption.

Nomenclature

C_b	= conc of metal in bulk liquid	$[\text{mol/m}^3]$
C_c	= conc of collector in bulk liquid	$[\text{mol/m}^3]$
C_f	= conc of metal in foamate	$[\text{mol/m}^3]$
d	= bubbler diameter	$[\text{m}]$
$H_{f/l}$	= height of foam-liquid interface	$[\text{m}]$
N	= number of bubbles per sec per capillary	$[\text{s}^{-1}]$
n	= number of capillaries	$[-]$
pH	= negative log of hydrogen ion conc	$[-]$
Q	= air flowrate	$[\text{m}^3/\text{s}]$
S	= surface generation rate	$[\text{m}^2/\text{s}]$
t	= time	$[\text{s}]$
V_f	= foam generation rate	$[\text{m}^3/\text{s}]$
Γ	= zinc surface excess	$[\text{mol/m}^2]$
NaDBS	= sodium dodecyl benzene sulfonate	
NaLS	= sodium lauryl sulphate	

Literature Cited

1) Banfield, D. L., Newson, I. H. and Alder, P. H.: *AIChE Symposium Series*, No. 1, 1.3 (1965).
2) Carleson, T. E. and Moussavi, M.: *Separ. Sci. and Tec*, **23** (**10 & 11**), 1093–1104 (1988).
3) Dick, W. L. and Talbot, F. D.: *Ind & Eng. Chem. Fundamentals*, **10**, 309 (1971).
4) Grieves, R. B., Kelman, S., Oberman, W. R. and Wood, R. K.: *Can. J. of Chem. Eng.*, **40–41**, 252 (1963).
5) Huang, R. C. H. and Talbot, F. D.: *Can. J. of Chem. Eng.*, **51**, 709 (1973).
6) Karger, B. L., Grieves, R. B., Lemlich, R., Rubin, A. J. and Sebba, F.: *Separ. Sci.* **2**, 401 (1967).
7) Konduru, M. R.: M. A. Sc Thesis, University of Ottawa, (1978).
8) Konduru, R.: "Operating a Foam Fractionating Column in Simple Mode," Submitted to *J. Chem. Eng. Japan*, (1992).
9) Kubota, K., Hayashi, S. and Takubo, Y.: *Can J. of Chem. Eng.*, **57**, 591 (1979).
10) Lemlich, R.: "Adsorptive Bubble Separation Techniques," Academic Press, New York, 1, 36, 38 (1972).
11) Lide, D. R.: "Handbook of Chemistry and Physics," 71st edition, CRC Press, 8–39 (1990–91).
12) Porta, A. and Catoggino, J. A.: *Afinidad*, **48(434)**, 247–251 (1991).
13) Rousseau, R. W.: "Handbook of Separation Process Technology," Chapter 17, John Wiley & Sons, 806 (1987).
14) Rubin, E. and Jorne, J.: *Ind. & Eng. Chem. Fundamentals*, **8**, 474 (1969).
15) Rubin, A. J.: *J. Amr. Water Works Ass.*, **60**, 832 (1968).
16) Rubin, E. and Gaden, E. L. Jr.: "Foam Separation," Chapter 5, New Chem. Eng., Separation Techniques, Schoen, H. M. Ed: Interscience, New York, 364 (1962).
17) Rubin, A. J. and Lapp, W. L.: *Analytical Chemistry*, **41**, 1133 (1969).
18) Sebba, F.: *Nature*, **184**, 1062 (1959).
19) Siy, R. D. and Talbot, F. D.: *Can. J. of Chem. Eng.*, **55**, 67 (1977).
20) St. Eloi, R. J.: M.A.Sc Thesis, University of Ottawa, (1972).
21) Wace, P. F. and Banfield, D. L.: *Chem & Proc. Eng.*, **48**, 70 (1966).
22) Walling, C. W., Ruff, E. E. and Thronton, J. L.: *J. Phys. Chem.*, **56**, 989 (1952).