Adsorptive Equilibrium Relationships of Bubble-Foam Separation

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기포-포말분리에서의 흡착평형관계 연구

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Summary

The adsorption energy and the equilibrium concentration relationship between the surface phase and the bulk phase of sodium lauryl sulphate (SLS) which was an anionic surfactants in the bubble-foam separation was investigated.

Sodium lauryl sulphate solution in this experimental condition behaved like that an ideal solution and equilibrium concentration relationship of the gas and liquid interfacial adsorption could be written as

$$C_S = C_B \cdot e^{\lambda/RT}$$

From the analysis of batch foaming which was considered the rising interstitial bulk liquid carried up, the following equation was derived.

$$\delta (e^{\lambda/RT}-1) = \frac{r}{3G} \left[(C_D V_D)_\theta - \int_0^{V_D} C_B dV_D \right] / \int_0^\theta C_B d\theta$$

The values of adsorption energy which was calculated by the above equation was 4.2kcal/mol.

國文抄錄

본 연구에서는 음이온 계면활성제인 SLS를 사용한 회분식 기포-포말 흡착분리 실험을 통하여 흡착평형관계에 대하여 고찰하였다. SLS용액은 실험농도범위에서 이상용액으로 거동하며, 기-액계면 흡착의 평형농도

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관계는 다음으로 주어졌다.

$$C_S = C_B \cdot e^{\lambda/RT}$$

또한 계면활성물질의 기포-포말흡착분리에서 포말에 동반되는 본체액을 고려한 회분해석으로 부터 계면
활성물질의 기-액계면 흡착열을 보다 정확히 구할 수 있는 다음과 같은 식을 유도하였다.

$$\delta (e^{\lambda/RT}-1) = \frac{r}{3G} [(C_D V_D)_\theta - \int_0^{V_D} C_B dV_D] / \int_0^\theta C_B d\theta$$

이 식으로 부터 구한 SLS의 기-액계면 흡착열은 4.2kcal/mol이었다.

Introduction

One important aspect of chemical engine-
ering consists of understanding and improving
the various techniques of separating materials.
There are a number of common separation
methods such as distillation, extraction,
chemical precipitation and ion exchnage, etc.
These separation methods can not be widely
applied in the very low concentration.
However, the bubble-foam adsorptive separa-
tion method using surfactants is one of the
most effective technigues for the removal of
the dilute contaminants and the recovery of
the dilute useful components from waste water
(David and Kennedy, 1979).

In recent years, many researchers (Harper
and Lemlich, 1965; Pinfold, 1970; Kato and
Kusunoki, 1977) have studied about bubble
foam separation which the theoretical principle
is based on the classical adsorption theorem
of gibbs (Davies and Rideal, 1963; Lemlich,
1972; Smith and Van Ness, 1989) derived from
thermodynamic considerations, because the
process is very simple and effective at the
dilute concentration. A great deal of workers
have been reported on the removal obj-

ectionable surfactants and certain other
impurities from waste water (Huang and
Talbot, 1973; Ferguson and Hinkle, 1974;
Kobayashi, 1975; Suh and Lee, 1984), the
technique for selective separation of certain
complex organic materials such as proteins
(Schnepf and Gaden, 1959; Lemlich, 1972),
and microfloatation of bacteria enzyme (Rubin
et al., 1966; Lemlich, 1972), the climination
of the radioactive contaminants from nuclear
wastes (Schonfeld and Kibbey, 1967; Lemlich,
1972), etc.

However, less attention have been paid to
the equilibrium concentration relationship
(Grieves, 1963; Lemlich, 1972) between sur-
face phase and bulk phase. Considering the
equilibrium concentration relationship between
surface phase and bulk phase, workers have
overlooked the rising interstitial liquid in their
analysis and have treated the upflow as
consisting entirely of surface phase. This can
lead to gross miscalculations since the amount
of the solute carried up by the rising
interstitial liquid can be very important.

From the analysis around the overhead flow
of the batch foam separation under the
assumption of ideal solution and the monol-
ayer adsorption mechanism, two equilibrium
equations based on to be ignored and not to

be ignored the amount of liquid accompanied by the rising bubbles were derived.

In order to investigate the accuracy of the equilibrium concentration relationship between the surface phase and bulk phase, the experimental data was achieved by using tall separation column filled with the aqueous solution of Sodium Lauryl Sulphate (SLS) as surfactants in batchwise operation.

Experimental

The separation column used was constructed from a long vertical glass tube, 4.32cm inside diameter, over its 260cm length, a bubbler which was used to form small and fairly uniform bubbles, and a drain valve. A schematic diagram of the apparatus was shown in Fig.1. The bubbler was an air disperser in a 3.44cm OD with 16 holes with a 0.025cm ID. The separation column was filled to the height of 250cm with a fresh dilute solution of sodium lauryl sulfate in distilled water through the bottom of the column.
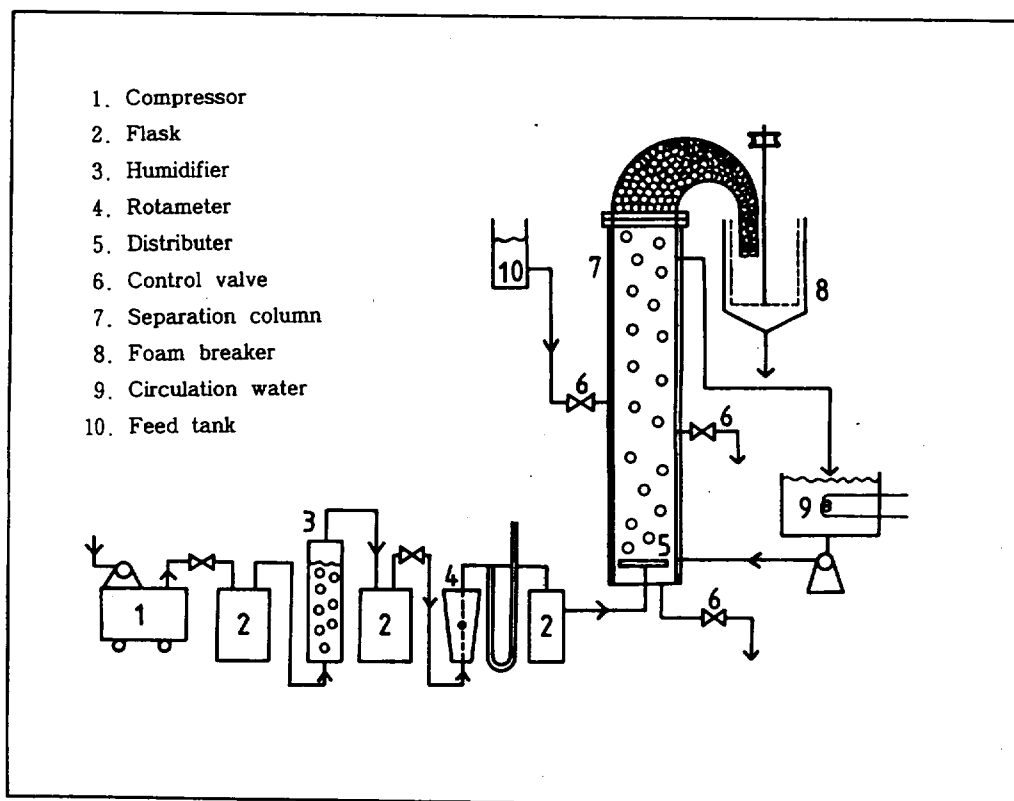
1. Compressor
2. Flask
3. Humidifier
4. Rotameter
5. Distributer
6. Control valve
7. Separation column
8. Foam breaker
9. Circulation water
10. Feed tank

Fig. 1. Schematic diagram of the bubble–foam adsorptive sepatation.

Each initially charged concentrations of solution was 0.5×10^{-3}, 1.0×10^{-3}, 1.5×10^{-3}, and 2.0×10^{-3}mol/l, respectively. The compressed

air from the compressor passed through a needle valve and rotameter for control and measurement of air flow rate. The air flow

rate was 600ml/min (±3% error). The air was introduced to the separation column through the bubbler at the bottom of the column.

The foam generated by rising bubbles moved up and eventually was directed into the foam breaker. The centrifugal foam breaker was housed in 13.5cm outerside diameter by 7 cm high basket, the basket rotated at 1, 200rpm. The collapsed foam liquid(foamate) was thrown against the sides of the bowl and collected in a small graduated cylinder. The volumes and concentrations of the liquid pool and the collapsed foam liquid were measured every 20 minutes.

After sampling liquid pool the same volume was fed again. The concentrations of liquid pool and collapsed foam liquid were measured with a Beckman Conductivity Bridge(cell constant 0.2). The calibration curve of concentration versus conductivity was plotted in Fig.2.
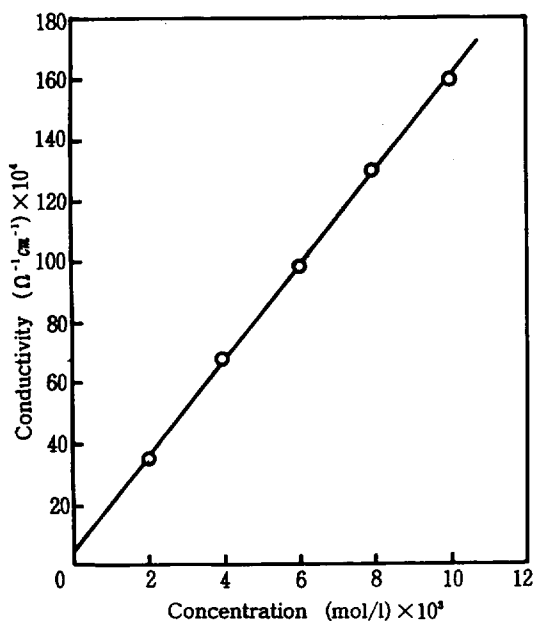

Fig. 2. Concentration versus conductivity at 25℃.

Bubble diameters were measured by means of millimeter scale mounted on the column wall. The arithmetic mean diameter of 100 bubbles was 0.25cm. The results obtained were remarkably reproducible.

Results and Discussion

By passage of bubbles through the liquid pool it is possible to present a new gas surface to the solution continuously. It results from the ability of surfactants to lower the surface tension of water, the adsorption of rising bubbles at the liquid-air interface, and the production of the stable foam.

As a consequence of positive surface tension exisisting at a liquid-air interface, air bubbles dispersed in a liquid pool will spontaneously tend to adopt a spherical shape independently of the particular method used for obtaining the dispersion.

We can neglect any other changes which may occur simultaneously, in particular, bubble coalescence, in batch operation at very low gas rates. Provided the foaming is carried out sufficiently slowly in a long column of liquid pool, the time of air bubble ascension is quite sufficient for establishing equilibrium in foaming between bulk phase and surface phase.

1) Analysis of batch foaming

It can be assumed that the concentration of solution is so dilute that the solution is an ideal fluid and the saturation of the surface phase adsorbed with a monolayer. So the equilibrium relationship between surface phase and bulk phase(Lemlich, 1972) is determined by thermodynamic consideration like that;

The chemical potential of solute in the bulk

phase is

$$\mu_B = \mu_B^{\cdot} + RT \ln C_B \qquad (1)$$

and in the surface phase

$$\mu_B = \mu_S^{\cdot} + RT \ln C_S \qquad (2)$$

At equilibrium, the chemical potential associated with the great concentration of solution at the interface equals the chemical potential of bulk solution, so that equating Eq. (1) and Eq. (2)

$$\mu_B^{\cdot} - \mu_S^{\cdot} = -RT \ln(C_B/C_S) = \lambda \qquad (3)$$

Thus, the maximum concentration of the surface active component is determined by the chemical potential difference, the heat of desorption and the concentraion in the bulk phase. Eq. (3) may be written as

$$C_S = C_B \cdot e^{\lambda/RT} \qquad (4)$$

Lemlich (1972) offered a mathematical analysis of batch foaming. The analysis is basically a material balance on the batch foam adsorptive separation system. Let V be the volume of bulk phase. If differential volume dV_B is foamed from the bulk phase, then, by material balance,

$$(V_A - dV_B)(C_B - dC_B) + dV_S(C_S + dC_s) = C_B V_B \qquad (5)$$

Simplifying and dropping second-order differentials, this becomes

$$\frac{dV_B}{V_B} = \frac{dC_B}{(C_S - C_B)} \qquad (6)$$

The composition of the bulk and surface or

foam phase is given by the equilibrium relationship of Eq. (4), i.e., $C_S = C_B \cdot e^{\lambda/RT}$.

Substituting in Eq. (4) into Eq. (6) for C_S and integrating

$$\ln\left(\frac{V_{Bo}}{V_B}\right) = \frac{1}{e^{\lambda/RT} - 1} \ln\left(\frac{C_{Bo}}{C_B}\right) \qquad (7)$$

Eq. (7) is the relationship between the volume and composition over the bulk phase assuming that equilibrium is achieved in foaming between the bulk and surface phases. This also provides a method for experimentally determining λ, the heat of desorption, provided the foaming is carried out sufficiently slowly to achieve equilibrium.

2) Analysis of batch foaming considered the interstitial liquid carried up.

The surface concentration of bubbles which ascends through the liquid pool may be greater than that of the bulk liquid. The foam generated by rising bubbles directed into the foam breaker and collapsing there. Then the collapsed foam (foamate) contains not only surface phase but also the interestitial bulk liquid carried up.

In the case of bubbles of approximately uniform spherical shape, denoting the volume of the liquid pool V_B, its concentration C_B, the volume of surface phase V_S, its concentration C_S, the volume of interstitial bulk liquid in the bubble walls V_A, the volume of foamte V_D, and its concentration C_D; then V_D is equal to $V_S + V_A$.

If differential volume dV_B is foamed from the bulk phase over a short period of time $d\theta$, then, by material balance the following equation is obtained.

$$(V_A - dV_B)(C_B - dC_B) + dV_S(C_S + dC_S)$$
$$+ dV_A(C_A + dC_A) = C_B V_B \qquad (8)$$

It it is assumed that the thickness of surface phase (δ) does not vary, the differential volume of surface phase, dV_S may be written as

$$dV_S = \frac{3\delta G}{r} \, d\theta \qquad (9)$$

After substituting of Eq. (4) and Eq. (9) into Eq. (8), simplifying and dropping second order differentials, this becomes

$$d(C_D V_D) = C_B \frac{3\delta G}{r}(e^{\lambda/RT} - 1) \, d\theta + C_B dV_D \qquad (10)$$

Intergrating Eq. (10) under the assumption of constant thickness (δ) and rearranging, this becomes

$$\delta(e^{\lambda/RT} - 1) = \frac{r}{3G} \left[(C_D V_D)_\theta - \int_0^{V_D} C_B dV_D \right] / \int_0^\theta C_B d\theta \qquad (11)$$

On the condition that the foaming was carried out sufficiently slowly to achieve equilibrium, the experimental data was achieved by using tall separation column filled with liquid pool of sodium lauryl sulphate.

The experimental results were plotted in Fig.3 through Fig.8. Using the experimental data within the concentration range which the foams could be produced continuously, the change of the bulk liquid concentration and the foamate concentration with time were plotted in Fig.3 and Fig.4, respectively. As shown in Fig.3 and Fig.4, the values decreased drastically with the increase of time in this experimental range. The change of the

foamate volume with time was plotted in Fig.5 and the change of the concentration of bulk liquid with overflow volume was plotted in Fig.6.

Fig.7 was plotted according to Eq. (7). As shown in Fig.7, all the points in this graph was scattered quitely. This plot was not satisfied with a linear relations sufficiently, because the collapsed foam (foamate) contains not only suface phase but alos the interestitial bulk liquid carried up. However, if it was plotted according to Eq. (11) which was derived from the aanlysis of batch foaming which was considered the rising interstitial bulk liquid liquid carried up, all the values fell at about the same points nearly, as shown in Fig.8, and the graph was satisfied with a linear relations sufficiently. As the result, the value of the adsorption energy calculated by the Eq. (11) would be constant within the
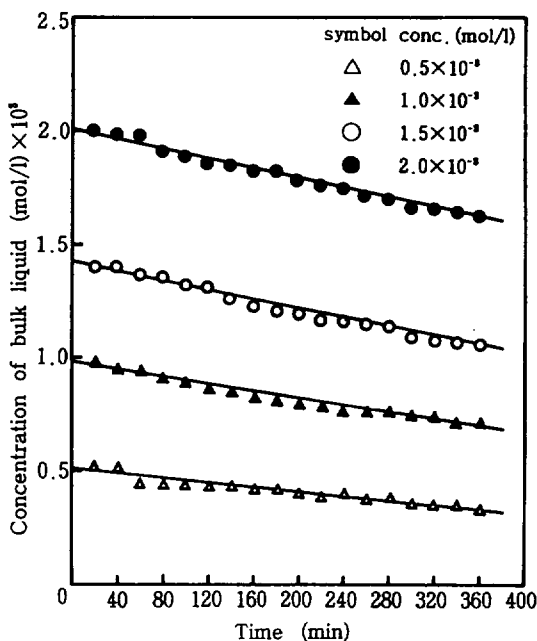

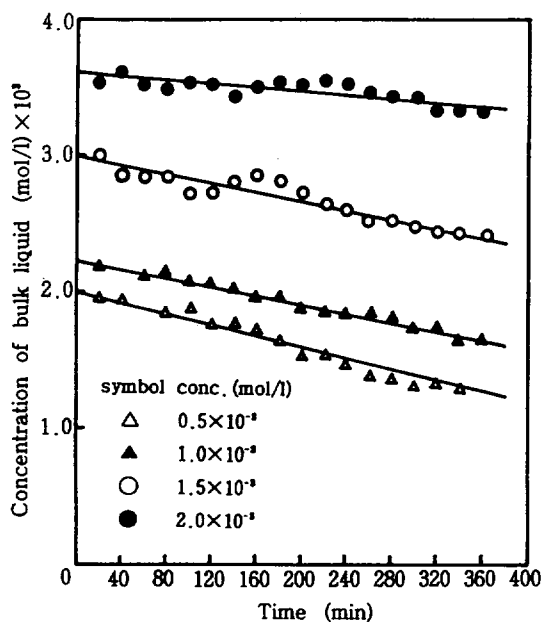
Fig. 3. Bulk liquid concentration change with time.

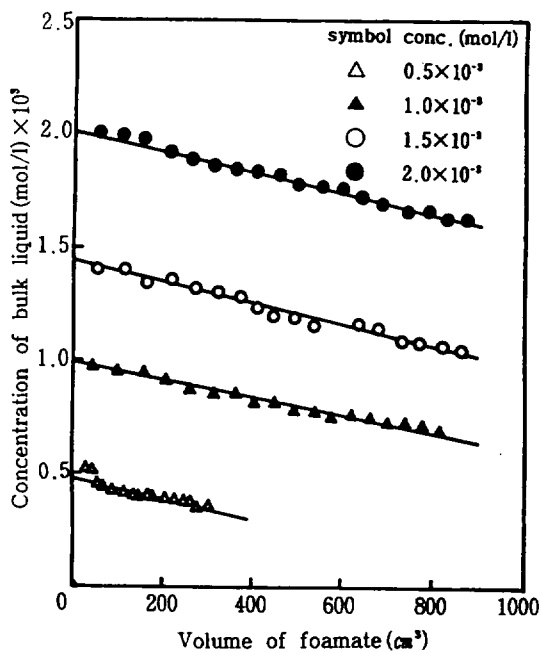Fig. 4. Foamate concentration change with time.

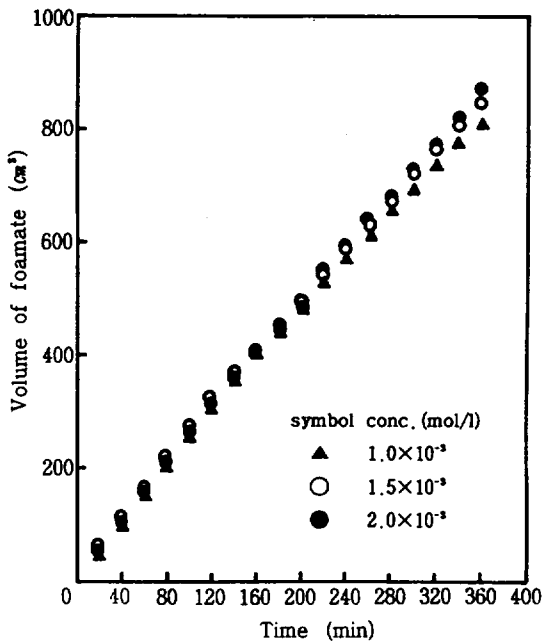Fig. 6. Foamte volume change with bulk liquid concentration.
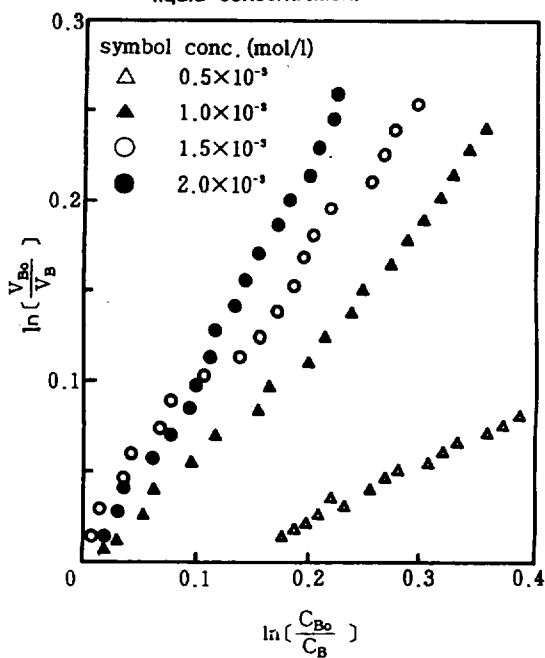

Fig. 5. Foamate volume change with time.

Fig. 7. $\ln \left[\frac{V_{Bo}}{V_B}\right]$ versus $\ln \left[\frac{C_{Bo}}{C_B}\right]$ in Eq. (7).
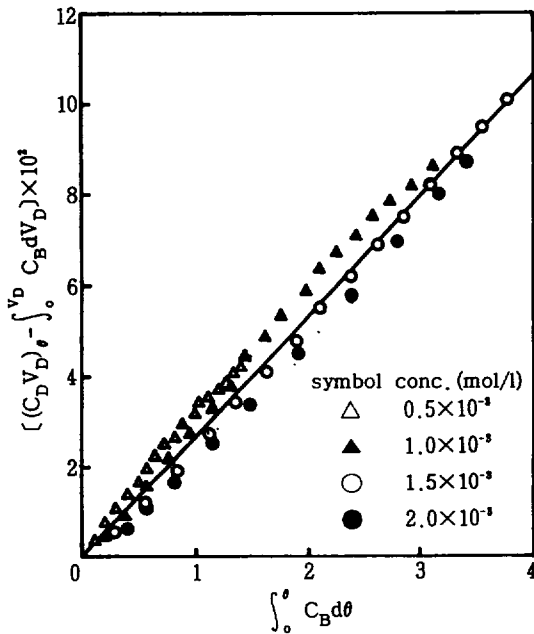
Fig. 8. $[(C_D V_D)_\theta - \int_0^{V_D} C_B dV_D]$ versus $\int_0^\theta C_B d\theta$.

range of the experimental concentration. Based on the present exprimental results, it is shown that Eq. (11) which was derived under the consideration of the bulk liquid accompanied by the bubbles in the batch operation represented more favourable than Eq. (7) to calculate the heat of adsorption in gas-liquid inteface, and it has been confirmed that the two assumptions in the derivation of Eq. (11), ie. ideal solution and monolayer adsorption mechanism are right.

In order to calculate the heat of adsorption in this bubble-foam separation operation using surfactants SLS, we must know the monolayer thickness of surface phase (δ). Monolayer adsorption thickness of LSL was obtained from literature (Davies and Rideal, 1963), the value was $1.8 \times 10^{-7} cm$. The slope in Fig.8 was $0.0267 cm^3/sec$, the flow rate of air (G) was 10 cm^3/sec, and the bubble radius (r) was $0.19 cm$. Then we could the heat of adsorption of SLS

by substitution of these values into Eq. (11). The values of adsoption energy which was calculated by Eq. (11) was 4.2kcal/mol.

Conclusions

By using the experimental data obtained by the batch operation below the concentration of $2 \times 10^{-3} mol/l$ of SLS, the results were obtained as following;

1. Sodium lauryl sulphate solution in this experimental condition behaved like theat an ideal solution and equilibrium concentration relationship of the gas and liquid inteffacial adsorption could be written as

$$C_S = C_B \cdot e^{\lambda/RT}$$

2. From the analysis of atch foaming which was considered the rising interstitial bulk liquid carried up, the following equation was derived.

$$\delta (e^{\lambda/RT} - 1) = \frac{r}{3G} [(C_D V_D)_\theta - \int_0^{V_D} C_B dV_D] / \int_0^\theta C_B d\theta$$

The values of adsorption energy which was calculated by the above equation was 4.2kcal/mol.

Nomenclature

C_B : concentration of bulk liquid (mol/cm^3)
C_D : concentration of foamate (mol/cm^3)
C_S : concentration of surface phase (mon/cm^3)
G : air flow rate (cm^3/sec)
R : gas conatant (cal/mol · K)
r : radius of bubble (cm)

T : absolute temperature (K)

V_A : volume of bulk-phase in foamate (cm^3)

V_B : volume of liquidin bubble column (cm^3)

V_D : volume of foamate (cm^3)

V_S : volume of surface phase (cm^3)

Greek Letters

δ : thickness of surface phase (cm)

θ : time (sec)

λ : difference between chemical potential of solute in bulk phase and chemical potential of solute in surface phase under standard condition (cal/mol)

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