

On the Stability of Microfoams

YONG-LI YAN*[†], JIE-RONG CHEN and YONG-WEI WANG[‡]

*School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an 710049, P.R. China
E-mail: yylhill@163.com*

Microfoams are finding increasing applications in separation processes. The stability of microfoams is a key parameter in these processes. The aim of this work is to derive the drainage mechanisms of microfoams by measuring drainage rates of the dispersions. Results show that the drainage of liquid from microfoams is divided into two stages of independent mechanisms. The primary drainage follows zero-order chemical reaction kinetics, while the second stage involving the films rupture and the bubbles coalesce is comparatively much slower. The effects of surfactant concentration used to produce microfoams in the presence of the electrolyte, such as sodium chloride, on the stability of the suspensions were also studied. The ordered molecular microstructures emerge when the concentrations of surfactant are above the value of the critical micellar concentration in the system, which plays an important role in stabilizing foam lamellae. The effect of the addition of sodium chloride on the stability of microfoams varies with the concentration of salt added in the continuous phase.

Key Words: Microfoams, Stability, Drainage, Zero-order chemical reaction kinetics, Sodium chloride.

INTRODUCTION

Microfoams can be described as spherical, micron-sized gas bubbles dispersed in an aqueous surfactant solution. The volumetric gas content is not more than 74 % and the size of the bubbles are less than 100 μm . Microfoams are recognized as Kugelschaum foams (wet foams). As such they were first called as microfoams¹, but latter renamed as colloidal gas aphrons².

Sebba³ postulated that these microbubbles are different from conventional foams. He proposed that microfoams consist of a gaseous inner core surrounded by a thin aqueous surfactant film or shell composed of two surfactant layers and in addition, a third surfactant layer that stabilizes this structure. He also claimed that the higher stability of microfoam dispersions compared with conventional foams could be explained by this proposed structure³. However, as yet, there have been no studies that have provided conclusive evidence of this or indeed any other structure.

[†]College of Chemistry and Chemical Engineering, Xi'an Shiyu University, Xi'an 710065, P.R. China.

[‡]Shaanxi Yanchang Petroleum Co. Ltd., Xi'an, 710069, P.R. China.

Despite the lack of understanding of the structure and stabilizing mechanisms of microfoam dispersions, it has been reported that these dispersions: (1) possess a large interfacial area; (2) exhibit relatively high stability; (3) separate easily from the bulk liquid phase; and (4) have similar flow properties to those of water³.

Based on these properties, researchers have considered various applications for microfoams, with a particular focus on separation processes. There have been a number of reported applications for microfoams including: intensification of mass transfer in aqueous two-phase systems for enzyme extraction⁴, protein recovery⁵⁻⁷, flotation of yeast cells⁸⁻¹⁰, soil flushing¹¹⁻¹³, clarification of suspensions¹⁴, predispersed solvent extraction of dilute products¹⁵⁻¹⁸, removal of sulphur crystals¹⁹, removal of metals from aqueous solutions²⁰⁻²³, coflotation and solvent sublimation processes²⁴ and separation of organic dyes from waste water²⁵⁻³⁰.

These applications for which microfoams have been employed by various investigators demand generalized characterization of microfoams with respect to its lifetime (stability) and effect of other variables. The life span of microfoams needed depends upon its applications. The stability of microfoams is affected by various operating parameters such as pH, presence of electrolyte and stabilizers, *etc.*

Stability is an important characteristic of microfoams, which will be influenced by their structure. Sebba³ stressed that due to his proposed structure the coalescence of microfoams is delayed and hence these dispersions exhibit higher stability as compared to conventional foams. There are limited theoretical and experimental investigations dedicated to the stability of microfoams. In the completed work stability measurements for microfoams were presented in terms of liquid drainage rates. A model was developed for the prediction of liquid drainage rates of foams is applied for the prediction of liquid drainage rates of microfoam dispersions^{31,32}. Also a modification to this model, proposed by Save and Pangarkar, that accounts for possible structural differences of microfoams is applied³³. Amiri and Woodburn made a systematic attempt to characterize microfoams¹⁹. Roy *et al.*²⁶ and Chaphalkar *et al.*³⁴ have reported some data on stability and bubble size distribution of microfoams but no relationship is proposed.

In previous reports (mentioned above), the focus has been made mainly on the measurements of microfoams stability and discussion on the influence of a number of process parameters on stability. Unfortunately, the drainage mechanism of microfoams has not been addressed in the literature up to now. The objective of this work was to explore the stability behaviours by measuring drainage rates of microfoams.

EXPERIMENTAL

For the typical microfoam dispersion formulation, the anionic surfactants were sodium dodecylbenzene sulfonate (SDBS, AR grade) with a CMC value of 1.5 mM purchased from Xi'an Chemical Reagent Factory. Sodium chloride (NaCl, AR grade) was supplied by Shanghai Chemical Co. All aqueous phases were prepared from

freshly deionized water (School of Medicine, Xi'an Jiaotong University, China) with a conductivity of < 0.5 mS/cm that has been filtered through a 0.2 mm filter.

Preparation: Microfoam suspensions were generated using a high-speed stirrer. The surfactant solution was stirred at high speed (8000 rpm), starting with 100 mL of surfactant solution, until a constant volume of white creamy microfoams was prepared. These microfoams can be kept dispersed under low stirring conditions (around 1000 rpm). In this study, we chose sodium dodecylbenzene sulfonate (SDBS) as the surfactant and deionized water with and without an electrolyte (sodium chloride, NaCl) as the continuous phase for microfoam suspension.

Stability measurement: The liquid drainage rates were measured by reading the volume of the liquid drained as a function of time. This was measured by transferring microfoam suspension into a 500 mL graduated cylinder. When all the microfoams had burst and drained, the final height was measured. This corresponded to the original water volume in the microfoam dispersions. The water content of the microfoam dispersions at intermediate times was calculated as the difference between this volume and the volume corresponding to the clear liquid interface at that time. The stability was measured in terms of half-life, the time required for half of the liquid content to drain. Various surfactant concentrations were used ranging from 0.15 mM to 35 mM. The effect of electrolyte concentration was also considered.

RESULTS AND DISCUSSION

The results of drained liquid from microfoams as a function of time with NaCl and without NaCl were presented in Figs. 1-3, respectively. In these figures, the curve is divided into two segments of drainage at a certain point. The primary drainage is rapid and almost linear with time. It is followed by a secondary drainage involving the thinning of films. The second stage is deviated from the straight line, which is comparatively much slower as seen from Figs. 1-3. It can therefore be concluded that, for these microfoams, the drainage of liquid does not control microfoam decay. The liquid films rapidly drain down to a small thickness, beyond which drainage appears to be extremely slow or completely arrested. At the conclusion of the rapid draining period, the entire microfoam volume appears to contain liquid lamellae of more or less uniform film thickness. This makes film rupture equally at all places in the systems.

Two mechanisms are responsible for fluid flow in microfoam systems. Flow in the films is driven by the capillary pressure, while the flow in the plateau border channels occurs due to gravity. In conventional foam, as liquid starts draining at the top, the major driving force is capillary pressure rather than gravitational force. Hence liquid starts travelling in radial direction under capillary pressure instead of channeling in the downward direction. By this action, net downward movement of liquid starts at constant rate in all the capillaries and results in complete drainage. In the case of microfoams, bulk liquid drains rapidly under gravity till the formation

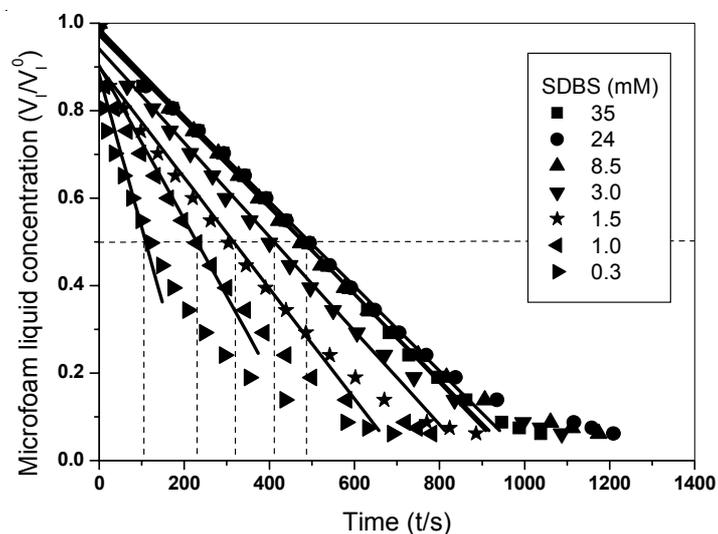


Fig. 1. Liquid drainage of microfoams with time in deionized water at various surfactant concentrations (note: solid lines fitted by linear regression)

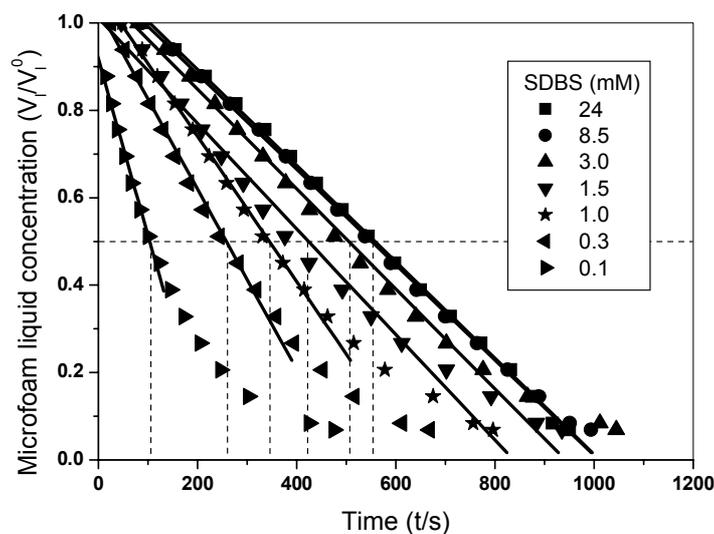


Fig. 2. Liquid drainage of microfoams with time in 2.0 mM NaCl aqueous solution at various surfactant concentrations (note: solid lines fitted by linear regression)

of conventional foam beyond which drainage rate decreases. Further drainage of the liquid in the lamellae and plateau borders continues under the influence of capillary pressure and plateau border suction. When the liquid film becomes sufficiently thin (less than $0.1 \mu\text{m}$) the effects of the London-van der Waals forces and the repulsive force of any electrostatic double layer also become important. Eventually, the films rupture and the bubbles coalesce.

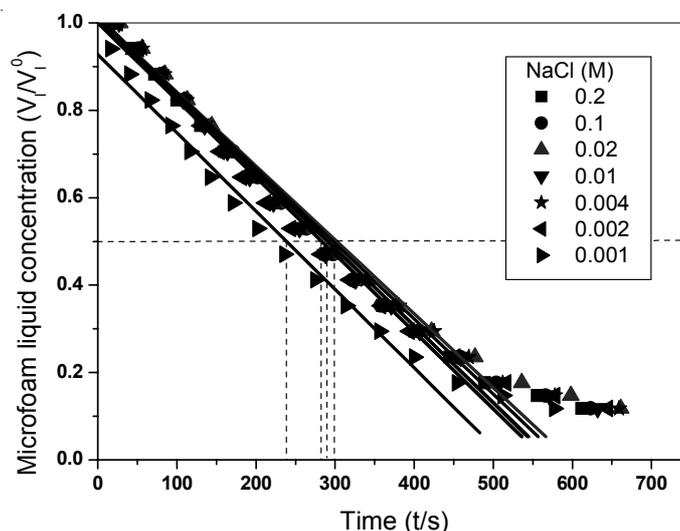


Fig. 3. Liquid drainage of microfoams with time in 0.3 mM SDBS aqueous solution at various NaCl concentrations (note: solid lines fitted by linear regression)

The drainage of liquid takes place through the gravity present between the bubbles, through which bulk liquid flows. This is followed by the secondary drainage in which thinning of microfoams films takes place. The present model was developed to explain the primary drainage.

The kinetics of this proposed drainage process, as indicated in Figs. 1-3 by the liquid volume concentration of microfoams, V_1 , with time, t , have been found to follow pseudo-zero-order reaction kinetics.

$$-\frac{dV_1}{dt} = k \quad (1)$$

where V_1 and V_1^0 are the liquid volume remaining in the microfoams at time t and $t = 0$, respectively. t is the time elapsed since the microfoam phase was initially dispersed and k is the rate constant. Equation 1 can be integrated to obtain:

$$V_1 = V_1^0 - kt \quad (2)$$

Thus the rate constant k can be obtained from a plot of V_1 vs. t . The half-life of the microfoams can be calculated from the rate constant using:

$$t_{1/2} = \frac{V_1^0}{2k} \quad (3)$$

where $t_{1/2}$ is the mean half-life of microfoams.

The V_1 vs. t curves do represent a zero-order process. As shown in Figs. 1-3, a plot of liquid volume concentration remaining in the microfoams against time yields a straight line. Therefore, the calculated values of half-life ($t_{1/2}$) were found to be dependent of the initial volume of liquid remaining in the microfoams.

The effect of surfactant concentration on the stability of microfoams was shown in Figs. 1, 2 and 4, respectively. The Fig. 2 also shows the effect of adding 2.0 mM NaCl. Whether the salt is added or not, both plots in the Figs. 1 and 2 indicate a similar tendency to the stability of these dispersions. When the concentration of surfactant is below 8.5 mM, the microfoams stability increases sharply as shown in Fig. 4. At the concentration of surfactant beyond this value, the curve becomes more flat, which means that the concentration of surfactant has a little effect on the stability of microfoams when the concentration of surfactant is much greater than the value of CMC (CMC: the concentration above which micelle formation becomes appreciable) of the surfactant.

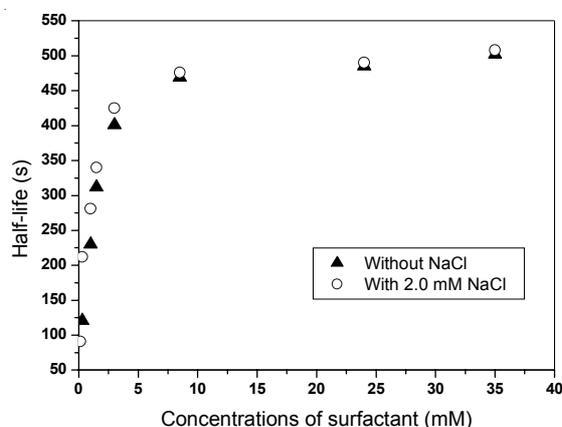


Fig. 4. Effect of SDBS concentration on stability of microfoams

The change in the stability of microfoams is most significant at low concentration. At very low concentrations, below 1.0 mM, microfoams, if formed, is highly unstable. The bubbles separate and coalesce almost as readily as they are formed. As mentioned earlier, SDBS has a CMC of 1.5 mM in distilled and deionized water³⁵. Thus as surfactant concentration drops below this value, there would be insufficient surfactant molecules at the bubbles interface to lower the Gibbs-Maragoni elasticity that would otherwise have stabilized the film.

At higher concentration of surfactant, there is a sharp increase on the stability of microfoams comparatively to that of lower concentration of surfactant. This may be attributed to the occurrence of organized molecular structures within the thin film when the concentrations of surfactant are above the value of CMC in the system. The organized molecular structures comprise of micelles, bilayers and even liquid crystals, which cause thinning of the film to occur, through a stepwise drainage mechanism known as stratification. These give an entirely different drainage pattern compared to films containing low levels of surfactants³⁶.

The organized molecular structures, produced from micelles of ionic or non-ionic surfactants in aqueous solution, provide an additional contribution to the disjoining

pressure. These micelle layers flow out of the film surface into the Plateau borders causing step-wise thinning, with each step corresponding to specific concentration. It is concluded that the ordered molecular microstructure played an important role in stabilizing microfoam lamellae.

When microfoams are generated using ionic surfactants, the salt concentration (ionic strength) has an important effect on drainage rates of microfoam dispersions. Fig. 2 shows the effect of adding 2.0 mM NaCl in the system on drainage rates of microfoam dispersions. Similarly, the plot as shown in Fig. 2 was found to be accorded with the zero-order chemical reaction kinetics in that there is almost a linear dependence between the liquid volume concentration, V_1 and the film life span (t). It is apparent from Fig. 4 that there is an increase of half-life comparatively in the process of microfoam drainage after adding 2.0 mM NaCl in the system. The most significant increase was observed at low surfactant concentrations.

Fig. 3 illustrated the effect of NaCl concentration on the behaviour of microfoam drainage. The kinetics of this drainage process, as shown in Fig. 3 by the decrease in the liquid volume concentration of microfoams, V_1 , with time, t , have also been found to follow pseudo-zero-order reaction kinetics. The effect of NaCl concentration in the continuous phase on the half-life of dispersed microfoams was shown in Fig. 5. It can be seen that values of $t_{1/2}$ increase with increasing ionic strength till the concentration of NaCl up to 0.1 M. The electrolyte increases the effective concentration of the surfactant and lowers the CMC of ionic surfactants. The result is the formation of smaller bubbles and increases in surfactant concentration density at the bubble interfaces, factors that improve the stability of microfoams. At concentrations of NaCl beyond 0.1 M, there is a decline with an increase in the concentration of NaCl. This is because addition of an electrolyte to the surfactant solution causes compression of the electrical double layers associated with the surface films, such addition decreases their mutual repulsion. This is believed to account for the decreased thickness of the liquid films with increase in electrolyte concentration and hence for the decreased stability of the microfoams. According to Sebba's proposed structure³ for microfoams, the outer interface of the 'soapy-shell' is stabilized by a bilayer of ionic surfactant molecules. These create an electrical double-layer, due to the charges on the surfactant head groups, which together with the Gibbs elasticity of this thin liquid film is responsible for the greater stability of dispersed microfoams compared to normal foam droplets. The electrostatic repulsion of the highly charged droplets and the mechanical stability of the liquid film prevent microfoam coalescence. Upon the addition of salt to the dispersion these electrical double-layers are compressed, hence the microfoams formed are initially smaller than those dispersed in deionized water. However, with increasing salt concentration the electrical double-layer is increasingly destabilized and it is suggested that this causes the 'soapy-shell' around the gas core to be stripped off the microfoams. This would therefore reduce the energy barrier to droplet coalescence, allowing the gas cores of the microfoams to fuse upon collision and thus leading to the type of process indicated

by the data in Fig. 5. For 'soapy-shells' stabilized by anionic or cationic surfactants, this mechanism would be expected to show a strong dependence on continuous phase ionic strength³⁷.

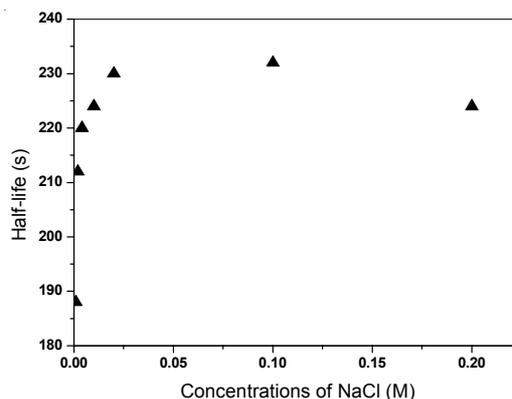


Fig. 5. Effect of NaCl concentration on stability of microfoams

Conclusion

(i) Two distinct stages of microfoams liquid drainage by independent mechanisms were identified from analysis of the relationship between the microfoam liquid drainage and time. The primary drainage was found to be well described by an equation developed from zero-order chemical reaction kinetics for the first time. The pseudo-zero-order kinetics model can be applied not only to the continuous phase of deionized water, but also to the presence of salt in the continuous phase. The second stage involving the thinning of films is comparatively much slower.

(ii) Microfoams exhibit relatively high stability as the concentrations of surfactant go beyond the value of CMC in the aqueous solution. This is because the ordered molecular microstructures within soap film were produced from micelles of ionic or nonionic surfactants in a system. These supramolecular structures provide an additional contribution to the stabilizing microfoam lamellae, which give an entirely different drainage mechanism known as stratification.

(iii) The salt concentration (ionic strength) has a significant effect on stability of microfoams as microfoams are prepared using ionic surfactant. There are different effects of salt added on stability of microfoams with different ranges of concentrations of the electrolyte. At low salt concentrations, microfoams stability can be enhanced by the addition of NaCl. The electrolyte increases the effective concentration of the surfactant and lowers the CMC of ionic surfactants. The result is the formation of smaller bubbles and increase in surfactant concentration density at the bubble interfaces, factors that improve the stability of microfoams. Conversely, microfoams stability can be deteriorated by the presence of NaCl at higher salt concentrations. Since addition of the electrolyte to the surfactant solution causes compression of the electrical double layers associated with the interface films, such addition decreases their mutual repulsion.

ACKNOWLEDGEMENTS

This project has been financially supported by China Postdoctoral Science Foundation Funded Project (NO.20060400299) and Shaanxi Province Science & Technology Research Program (NO.07JK367).

REFERENCES

1. F. Sebba, *J. Colloid Interface Sci.*, **35**, 643 (1971).
2. F. Sebba and S.M. Barnett, Proceedings of the Second World Congress of Chemical Engineering, Montreal, Vol. 4, p. 27 (1981).
3. F. Sebba, Foams and Biliquid Foams-Aphrons, John Wiley & Sons, New York, p. 63 (1987).
4. S.V. Save, V.G. Pangarkar and S.V. Kumar, *Biotechnol. Bioeng.*, **41**, 72 (1993).
5. P. Jauregi, S. Gilmour and J. Varley, *Chem. Eng. J.*, **65**, 1 (1997).
6. P. Jauregi and J. Varley, *Biotechnol. Bioeng.*, **59**, 471 (1998).
7. M. Noble, A. Brown, P. Jauregi, A. Kaul and J. Varley, *J. Chromatogr. B*, **711**, 31 (1998).
8. M.A. Hashim, B. Sengupta and M.B. Subramaniam, *Bioseparation*, **5**, 167 (1995).
9. M.A. Hashim, B.S. Gupta, S.V. Kumar, R. Lim, S.E. Lim and C.C. Tan, *J. Chem. Technol. Biotechnol.*, **71**, 335 (1998).
10. M. Noble and J. Varley, *J. Chem. Technol. Biotechnol.*, **74**, 231 (1999).
11. D. Roy, S. Kongara and K.T. Valsaraj, *J. Hazard. Mater.*, **42**, 247 (1995).
12. D. Roy, R.R. Kommalapati, K.T. Valsaraj and W.D. Constant, *Wat. Res.*, **29**, 589 (1995).
13. R.R. Kommalapati, K.T. Valsaraj, W.D. Constant and D. Roy, *J. Hazard. Mater.*, **60**, 73 (1998).
14. M.B. Subramaniam, N. Blakebrough and M.A. Hashim, *J. Chem. Technol. Biotechnol.*, **48**, 41 (1990).
15. F. Sebba, *Sep. Sci. Technol.*, **20**, 331 (1985).
16. F. Sebba, *Chem. Engineer*, **March**, 12 (1986).
17. Y.D. Wang, M. Chen, L.L. Xu and Y. Dai, *Chin. J. Chem. Eng.*, **8**, 103 (2000).
18. W. Hu, Y. Sun, R.Q. Ye, S.S. Wu and H.L. Liu, *Chin. J. Chem. Eng.*, **11**, 367 (2003).
19. M.C. Amiri and E.T. Woodburn, *Trans. Ins. Chem. Eng.*, **68A**, 154 (1990).
20. S. Ciriello, S.M. Varnett and F.J. Deluise, *Sep. Sci. Technol.*, **17**, 521 (1982).
21. L.M. Cabezon, M. Cabellero and J.A. Perez-Bustamante, *Sep. Sci. Technol.*, **29**, 1491 (1994).
22. J.J. Cilliers and D.J. Bradshaw, *Miner. Eng.*, **9**, 235 (1996).
23. Y.D. Wang, H.Z. Wen, Y.Y. Huang and Y.Y. Dai, *J. Chem. Eng. (Japan)*, **34**, 1127 (2001).
24. M. Caballero, R. Cela and J.A. Perez-bustamante, *Sep. Sci. Technol.*, **24**, 629 (1989).
25. D.L. Michelsen, K.W. Ruettimann, K.R. Hunter and F. Sebba, *Chem. Eng. Commun.*, **48**, 155 (1986).
26. D. Roy, K.T. Valsaraj and S.A. Kottai, *Sep. Sci. Technol.*, **27**, 573 (1992).
27. C. Zhang, K.T. Valsaraj, W.D. Constant and D. Roy, *Sep. Sci. Technol.*, **31**, 1463 (1996).
28. M.A. Hashim and B.S. Gupta, *Bioresour. Technol.*, **64**, 199 (1998).
29. D.W. Lee, H.H. Won and Y.H. Kyung, *Sep. Sci. Technol.*, **35**, 1951 (2000).
30. S. Basu and P.R. Malpant, *Sep. Sci. Technol.*, **36**, 2997 (2001).
31. P.A. Haas and H.F. Johnson, *Ind. Eng. Chem. Fundam.*, **6**, 225 (1967).
32. P. Jauregi, G.R. Mitchell and J. Varley, *AIChE J.*, **46**, 24 (2000).
33. S.V. Save and V. G. Pangarkar, *Chem. Eng. Commun.*, **127**, 35 (1994).
34. P.G. Chaphalkar, K.T. Valsaraj and D. Roy, *Sep. Sci. Technol.*, **28**, 1287 (1993).
35. C. Zhang, K.T. Valsaraj, W.D. Constant and D. Roy, *Sep. Sci. Technol.*, **31**, 1059 (1996).
36. V. Bergeron, *J. Phys.: Condens. Matter*, **11**, R215 (1999).
37. G.J. Lye and D.C. Stuckey, *Colloids Surfaces A*, **131**, 119 (1998).