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The Effect of the Nature of Inorganic Ions on Hydrocarbon Flotation

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Abstract

The liquid hydrocarbons hexadecane and pseudocumene (1,2,4-trimethylbenzene) were removed from their O/W-type emulsions by flotation. The effect of different inorganic salts (NaCl, Na_2SO_4, Na_3PO_4) on the removal efficiency was investigated. It was shown that the inorganic salt effect on flotation efficiency is connected with their influence on the double-layer thickness and on the adsorption of surface-active ions.

INTRODUCTION

The effect of hydrocarbons removal from their emulsions by the flotation method depends on the forces exerted between a hydrocarbon droplet and a bubble. Those forces may be devided into three groups: hydrodynamic forces such as interception, repulsive forces due to electric double layer interactions, and London-van der Waals adhesive forces resulting from intermolecular attraction (*1-5*). Chemical additives to the flotation system did not change the first two forces very much (*1*). However, the double layer repulsion is very strongly dependent on the added chemical species and their concentration. The nature of the added substance plays an important role in the flotation process. It is known that surface-active substances as well as inorganic salts may enhance or depress flotation efficiency (*1-9*).

It has been stated by many authors (*4–6*, *9*, *10*) that the effect of inorganic ions is connected with decreasing of the bubble size and the coalescence of droplets, and it is known that the better the flotation efficiency, the smaller the bubbles and the larger the particles. This is a general observation not only for oil emulsion flotation.

Anfruns (*2*) stated that the collection rate of spherical glass particles was increased about three times when potassium chloride was added to the water in an amount of 1 mg/dm^3. Strickland (*4*) found that an increase of sodium chloride concentration to 3% significantly increases oil recovery. He also found a decrease of bubble diameter from 1 mm in distilled water to about 0.4 mm at 3% sodium chloride concentration. Similar results were presented by Sylwester et al. (*5*) who stated that an increase of NaCl concentration from 1 to 10 wt% decreases the bubble diameter from 0.7 to 0.2 mm.

The addition of inorganic salt also causes drop coalescence, which gives better flotation efficiency. Saito et al. (*6*) found that the flotation of the emulsion containing 1000 ppm of mineral oil gives a raffinate containing less than 10 ppm of oil when 0.5% of NaCl, Na_2SO_4, or $NH_4H_2PO_4$ was added.

The effect of inorganic ions on flotation is connected with their influence on the thickness of the diffuse part of the electric double layer as well as on the electric potential of the particle and the bubble surfaces. The thickness of the double layer limits the possibility of a near approach of an oil droplet and a bubble. The dnesity of the electrostatic charge of both surfaces influences the electrostatic repulsive or attractive forces. Thus the valence of the inorganic ions and their concentration are the most important parameters influencing flotation efficiency. Sato et al. (*1*) found that flotation efficiency may be improved in $CaCl_2$ and $AlCl_3$ solutions by increasing their concentration from 10^{-5} to 10^{-2} mol/dm^3 or slightly decreasing their concentration in NaCl solution. These observations were in agreement with their results: the lower the zeta potential, the better the flotation efficiency.

It has been stated by many authors (*1*, *6*) that the best flotation was achieved when the pH value of the mineral oil emulsions was about 4, which corresponds to about a zero charge on the particle and on the bubble surfaces.

It has been stated repeatedly that oil droplets dispersed in water have a negative charge on their surface (*1*, *11–13*), and that the air bubble surface is negatively charged in water (*1*, *10*). This negative charge is probably due to preferential adsorption of hydroxyl ions or preferential desorption of hydrogen ions from the surface, as suggested by Davis and Rideal (*14*). Strongly adsorbing surface-active ions may increase this negative charge if they are of the anionic type, or depress it if they are cations. Surface-active cations at a proper concentration may "recharge" those surfaces to a positive charge. This was confirmed by Collins (*15*) and Usui (*10*) whose experiments used cetyltrimethylammonium bromide (CTAB).

The purpose of this work was to find the correlation between the valency of inorganic anions and the efficiency of hydrocarbon flotation from aqueous emulsions containing ionic surfactants.

EXPERIMENTAL

The influence of chloride, sulfate, and phosphate ions on the removal of hexadecane or pseudocumene (1,2,4-trimethylbenzene) has been investigated. Experiments were carried out with the addition of cethyltrimethylammonium bromide (CTAB, 1.5×10^{-4} mol/dm^3) or sodium dodecylbenzenesulfonate (NaDBS, 1.5×10^{-4} or 5×10^{-4} mol/dm^3). Flotation processes were carried out continuously in a column described earlier (*8*, *9*). The process parameters were as follows: the height of the column was 120 cm, the height of the liquid phase was 95 cm, the feeding solution flow rate was 1.8 dm^3/h, and the gas flow rate was 5 dm^3/h.

The concentrations of hydrocarbons in the emulsion and in the raffinate were determined by the GLC method (*9*) by applying the proper analysis temperature: for hexadecane 458 K and for pseudocumene 333 K.

The efficiency of the flotation process was expressed as a percentage of hexadecane removal from the emulsion. The zeta potential of hydrocarbon droplets in the systems investigated was measured by means of microelectrophoresis. The electrophoretic mobility was measured in an apparatus similar to that described by Stachurski (*13*). The zeta potential was calculated by means of the Smoluchowski equation.

RESULTS AND DISCUSSION

The results presented in Fig. 1 report the pseudocumene flotation runs in which an anionic surfactant, NaDBS, was used. The adsorption of DBS anions on both droplet and bubble surfaces increases the electrostatic repulsion between the bubble and the particle. As a consequence, the worse flotation efficiency is observed for processes using NaDBS and inorganic salts (Curves 1, 2, and 3) compared with processes using only inorganic salts (Curve 4). In Fig. 1 it is also observed that if the hydrocarbon concentration is higher than about 140 mg/dm^3, the best

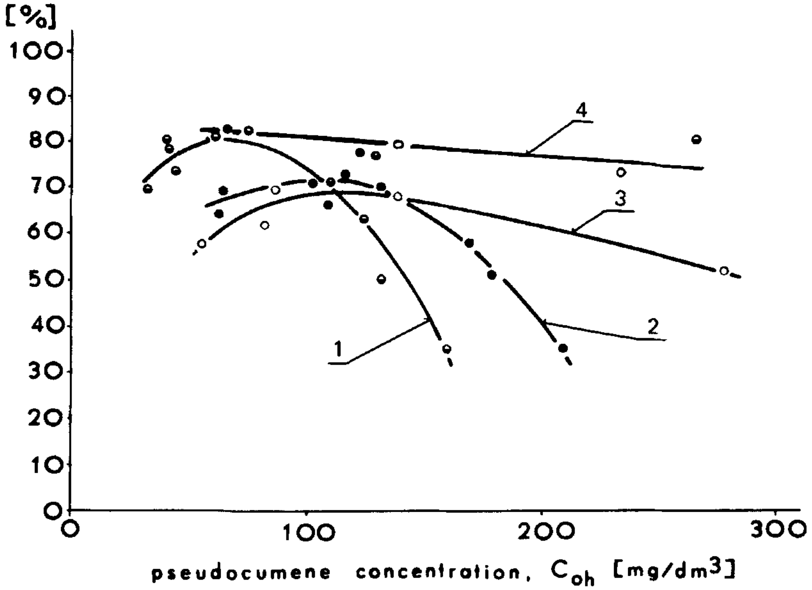

FIG. 1. Removal of pseudocumene during the flotation processes with sodium dodecylbenzenesulfonate; dependence on hydrocarbon concentration in the initial emulsion. NaDBS concentration, 5×10^{-4} mol/dm^3; inorganic salts concentration, 0.01 mol/dm^3. (○) NaCl, (●) Na_2SO_4, (○) Na_3PO_4. (1), (2), (3): with NaDBS; (4): without NaDBS.

removal takes place in the presence of Na_3PO_4 and the worse effect is observed in the presence of NaCl. If the pseudocumene concentration in emulsion is lower than about 140 mg/dm^3, NaCl causes the best effect and Na_3PO_4 the worse effect in flotation efficiency.

The observed dependencies are connected with the mixed mechanism of pseudocumene flotation. Pseudocumene has an aqueous solubility and vapor pressure similar to mesitylene. Thus we may state, similarly to mesitylene (*16*), that two simultaneous processes take place during pseudocumene emulsion flotation: evaporation of the molecules dissolved in water into the bubbles and hydrocarbon droplets capture by rising bubbles due to hydrodynamic forces. We have stated previously (*16*) that the evaporation process predominates in less concentrated emulsions.

The magnitude of the interfacial surface not covered by surfactant molecules is a very important parameter for evaporation efficiency. Consider the pseudocumene emulsion at concentrations below 140 mg/dm^3. If the molar concentrations of salts are the same, the NaDBS adsorption is lower in NaCl solutions, and thus the uncovered surface of the bubble is larger and the removal efficiency is higher than in Na_2SO_4 and Na_3PO_4 solutions.

If the pseudocumene concentration is above 140 mg/dm^3, the process of droplet capture by a bubble predominates. Its efficiency depends on the possibility of the near approach of a droplet to a bubble, which depends on the thickness of the diffuse part of the electric double layer. The higher the counterions concentration, the thinner the diffused layer and the better the flotation effect. In the case of NaDBS, the Na^+ ions are counterions, and in 0.01 M Na_3PO_4 solutions their concentration is 3 times higher than in 0.01 M NaCl solution. This explains why the best flotation efficiency with Na_3PO_4 is over the range of pseudocumene concentrations above 140 mg/dm^3.

Some experiments were performed on pseudocumene emulsion flotation with CTAB (Table 1). As expected, this cationic surfactant permits better removal than does NaDBS at the same concentration.

By analyzing the results presented in Table 1, we note that the flotation efficiency is worse in the presence of NaCl and surfactants than when only NaCl is present. The opposite case is observed when sodium phosphate is added. The removal effect was better when surfactants were used than when they were absent. No substantial differences for the processes with and without surfactants were observed in the presence of sodium sulfate.

An explanation of the observed relations may be made on the basis of zeta potential measurements (Table 2).

TABLE 1
Flotation Efficiency of Pseudocumene from Its Emulsions Containing Surfactants and Inorganic Salts

Inorganic salt (0.1 mol/dm^3)	Surfactant (1.5×10^{-4} mol/dm^3)	Flotation efficiency (%)
NaCl	—	78-87
	CTAB	68-73
	NaDBS	68-78
Na_2SO_4	—	74-86
	CTAB	81-89
	NaDBS	74-88
Na_3PO_4	—	72-87
	CTAB	92-94
	NaDBS	76-85

TABLE 2
Zeta Potential of Hydrocarbon Droplet

Inorganic salt (0.01 mol/dm^3)	Pseudocumene ζ (mV)	Pseudocumene $\Delta\zeta^b$ (mV)	Hexadecane ζ (mV)	Hexadecane $\Delta\zeta^b$ (mV)
	In Water			
—	−48.2	0	−52.2	0
NaCl	−35.5	+12.7	−47.7	+5.4
Na_2SO_4	−29.0	+19.2	−48.5	+4.6
Na_3PO_4	−79.4	−31.9	−101.5	−48.4
NaOH^a	—	—	−109.9	−57.7
	In NaDBS Solution of 2 × 10^{-5} mol/dm^3			
—	−56.2	0	−62.3	0
NaCl	−105.0	−48.8	−103.5	−41.2
Na_2SO_4	−100.2	−44.0	−101.9	−39.6
Na_3PO_4	−115.0	−58.8	−107.1	−44.8
NaOH^a	—	—	−117.1	−54.8
	In CTAB Solution of 1 × 10^{-5} mol/dm^3			
—	+51.7	0	+43.7	0
NaCl	+111.0	+59.3	+98.1	+54.4
Na_2SO_4	+49.3	−2.4	+36.6	−7.1
Na_3PO_4	+18.6	−33.1	−3.3	−47.0

[a] NaOH concentration equals 0.0075 mol/dm^3.
[b] $\Delta\zeta = \zeta$ with salt − ζ without salt.

The zeta potential values presented are related to 0.01 *M* salts solutions. It was not possible to determine the zeta potential in more concentrated solutions; however, on the basis of the values in 0.01 *M* solutions, we can predict its change when the salts concentration is increased.

The zeta potential of hydrocarbon droplets in salts solutions without surfactants will have similar values for 0.1 and 0.01 salts concentrations. In the case of CTAB, the zeta potential may become more "positive" in 0.1 *M* than in 0.01 *M* NaCl solution because of the greater adsorption of the surface-active cation. In CTAB solutions containing Na_3PO_4 the zeta potential will change to more "negative" values when the salt concentration is increased from 0.01 to 0.1 *M* because of a greater hydroxyl ions content.

When the salt concentration is increased in Na_2SO_4 + CTAB solutions, the positive potential will be reduced because the counterions adsorption increase in the double layer will be greater than the increase of adsorption of the surface-active ions.

As can be seen from Table 2, the zeta potential of pseudocumene droplets in "NaCl + CTAB" solutions is much higher (+101 mV) than that of pseudocumene droplets in NaCl solutions (−35.5 mV). We did not measure the zeta potential of a bubble surface in the above-mentioned solutions; however, on the basis of some references (*1*, *10*, *12*, *17*), it is expected that the sign and values of zeta potentials of the bubbles in both solutions will be similar to those of hydrocarbon droplets in those solutions.

Thus, in solutions containing only NaCl, the electrostatic repulsive forces between the droplet and the bubble are lower than similar forces in solutions containing NaCl and CTAB. This is the reason why CTAB worsens flotation efficiency in sodium chloride solutions. An analogous situation is observed in the case of NaDBS.

In the case of Na_3PO_4 there is the opposite situation. A large amount of hydroxyl ions exist in Na_3PO_4 solution [for example, in 0.01 *M* Na_3PO_4 solution the OH^- ions concentration equals 0.0075 mol/dm^3 (*18*)], which makes the particle charge more negative than in water.

Table 2 also presents the zeta potential values of hexadecane droplets in NaOH solution of such a concentration that the OH^- ions content is the same as it is in 0.01 *M* Na_3PO_4 solution. Note that the zeta potential is similar in both cases (for example: −101.5 and −109.9 mV). This allow us to state that OH^- ions are responsible for the particle potential in Na_3PO_4 solutions.

The zeta potential of pseudocumene droplets in Na_3PO_4 solution has a much greater value (−79.4 mV) than in "Na_3PO_4 + CTAB" solution (+18.6 mV). Thus the electrostatic repulsive forces between a droplet and a bubble should be lower in "Na_3PO_4 + CTAB" solution than in a solution containing only Na_3PO_4. The better flotation efficiency observed in cases where CTAB is added to the sodium phosphate solution is the result of a large reduction in the repulsive interaction of the electric double layers.

As shown in our earlier investigations (*9*), hexadecane flotation is much worse than the flotation of aromatic hydrocarbons (*8*). To improve hexadecane removal, a higher inorganic salts concentration than in pseudocumene flotation and a cationic surfactant (CTAB) were used. An inorganic salts concentation of about 0.1 mol/dm^3 causes such a large double layer compression that the hydrodynamic particle capture by a bubble increases significantly.

It may be seen in Fig. 2 that the flotation of hexadecane droplets gives about 50% removal from pure water and about 40 to 90% from solutions containing CTAB and inorganic salts. The flotation efficiency also depends on the kind of inorganic ions present in the system. The addition of NaCl causes the worse effect (40–65%), while Na_3PO_4 and Na_2SO_4 allow satisfactory removal of hexadecane (70–92%). The results of flotation efficiency agree with zeta potential measurements (Table 2), because the repulsion between bubbles and hexadecane droplets is higher in solutions of CTAB containing NaCl than in solutions containing Na_2SO_4 or Na_3PO_4.

CONCLUSIONS

It was shown that inorganic salts affect flotation efficiency very strongly. This effect is connected with their influence on the electric double layers of the bubbles and droplets. The coalescence of droplets is a visible result of that influence. It is seen in Fig. 3 that the NaCl used in the flotation process increases the content of hexadecane droplets bigger than 5 μm in diameter in the raffinate from 16 to 26 wt%. In the case of Na_2SO_4, about 84 wt% of the big droplets in the raffinate are obtained; in the case of Na_3PO_4, about 91 wt%.

The zeta potential measurements are also very important for interpretation of the flotation results obtained, as well, i.e., the modification of

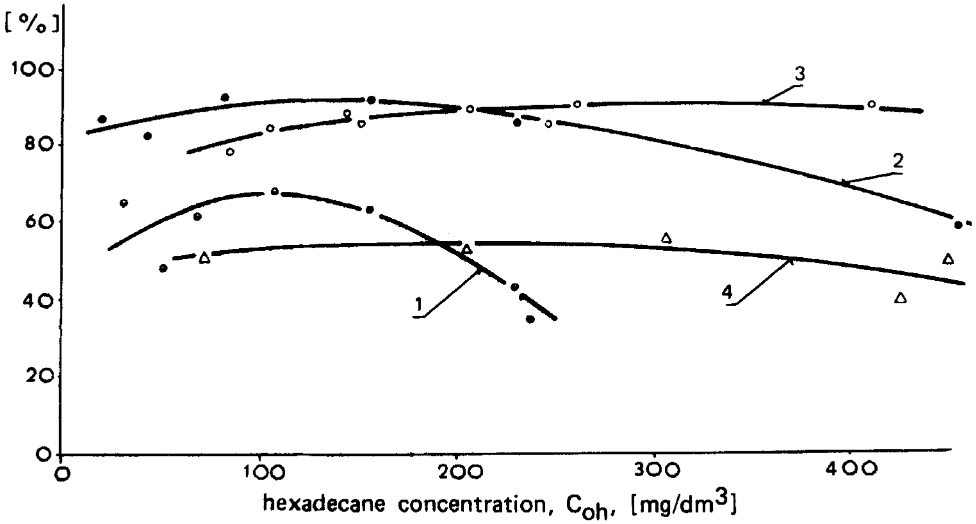

FIG. 2. Removal of hexadecane during the flotation processes with cetyltrimethylammonium bromide; dependence on hydrocarbon concentration in the initial emulsion. CTAB concentration, 1.5×10^{-4} mol/dm^3; inorganic salts concentration, 0.1 mol/dm^3. (1) NaCl, (2) Na_2SO_4, (3) Na_3PO_4, (4) without salt and without CTAB.

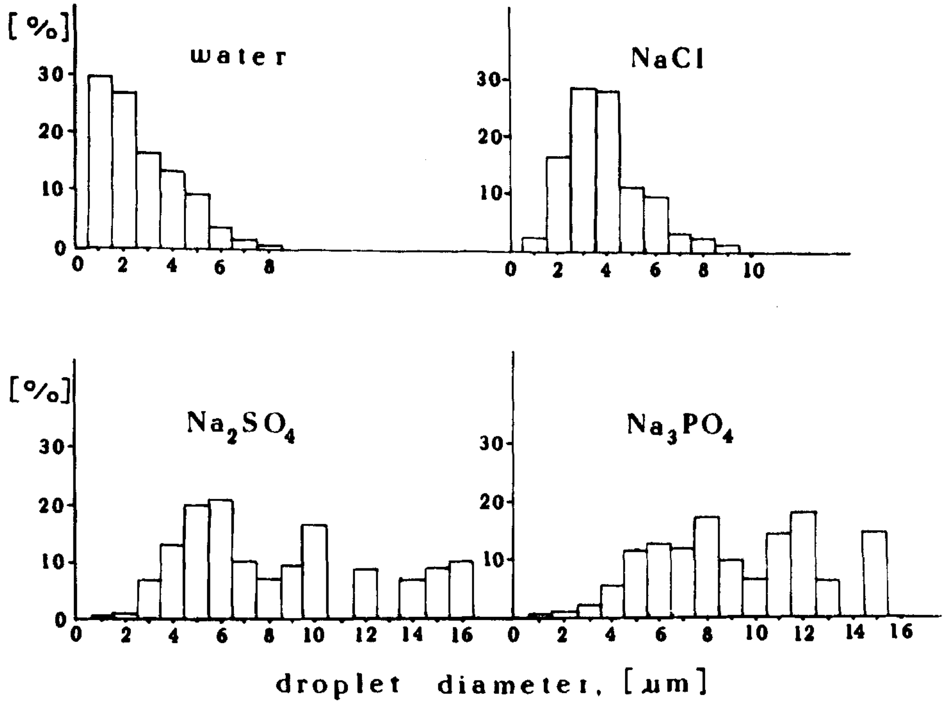

FIG. 3. Drop size distribution of hexadecane in raffinates from flotation processes with the use of cetyltrimethylammonium bromide and different inorganic salts. CTAB concentration, 1.5×10^{-4} mol/dm^3. Salts concentration, 0.1 mol/dm^3.

the flotation parameters by chemical additives. Figure 4 shows that the zeta potential of hexadecane droplets in CTAB solutions depends on the surfactant concentration, and reaches close to a zero value at CTAB concentrations of about 1.3×10^{-7} mol/dm^3. The flotation experiments at that CTAB concentration gives the raffinate with such a low hexadecane concentration that it could not be determined by the analytical method used (below 0.8 ppm). This means that the removal efficiency exceed 99%.

Inorganic salts also influence low volatile hydrocarbon flotation because of their effect on surfactant adsorption processes at the interfaces. The better adsorption is improved by salt addition, the worse is the removal of hydrocarbons because of the evaporation process. This is especially noticeable for low concentration emulsions.

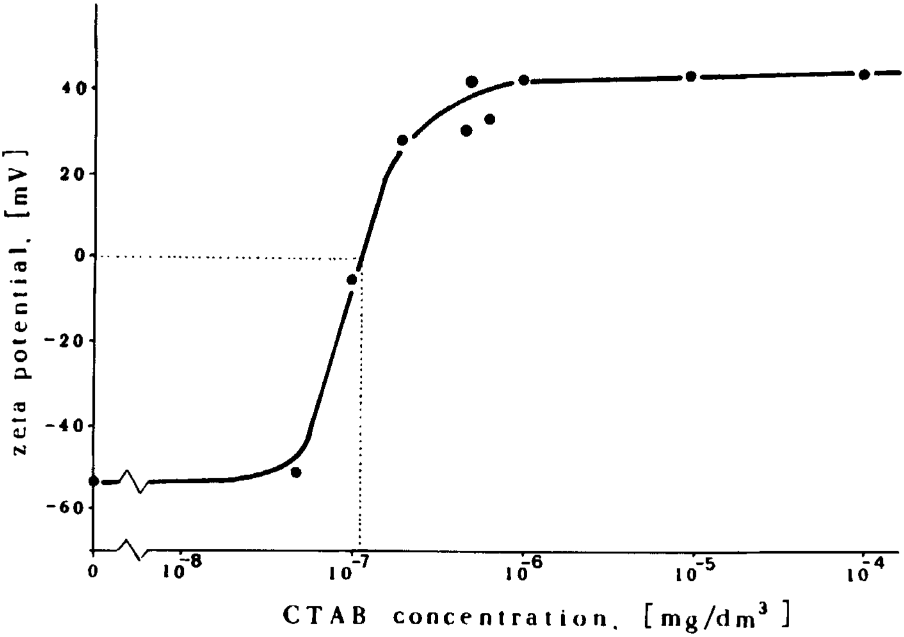

FIG. 4. Zeta potential of hexadecane droplets in water; dependence on the cetyltrimethylammonium bromide concentration.

REFERENCES

1. Y. Sato, Y. Murakami, T. Hirose, H. Yamamoto, and Y. Uryu, *J. Chem. Eng. Jpn.*, *12*(6), 454 (1979).
2. J. F. Anfruns and J. A. Kitchener, *Trans. Inst. Min. Metall.*, *56*, 9 (March 1977).
3. C. Angelidou, E. Keshavarz, M. J. Richardson, and G. J. Jameson, *Ind. Eng. Chem., Process Des. Dev.*, *16*(4), 436 (1977).
4. W. T. Strickland, *Soc. Pet. Eng. J.*, p. 175 (June 1980).
5. N. D. Sylwester and J. J. Byesda, *Ibid.*, p. 579 (December 1980).
6. T. Saito, K. Hagiwara, Y. Ozasa, and Y. Murakami, *Mizushori Gijutsu*, *14*, 823 (1973).
7. L. D. Skrylev, A. G. Niewinskij and A. N. Puritch, *Zh. Prikl. Chim.*, *58*, 2574 (1985).
8. K. B. Medrzycka and W. Zwierzykowski, *Sep. Sci. Technol.*, *19*, 545 (1984).
9. K. B. Medrzycka and W. Zwierzykowski, *Ibid.*, *22*, 1637 (1987).
10. S. Usui and H. Sasaki, *J. Colloid Interface Sci.*, *65*(1), 36 (June 1, 1978).
11. D. K. Chattoraj and A. B. Bull, *J. Phys. Chem.*, *63*, 1809 (1959).
12. M. P. Aronson, M. F. Petko, and H. M. Princen, *J. Colloid Interface Sci.*, *65*(2), 296 (June 15, 1978).
13. J. Stachurski and M. Michalek, *Colloid Surf.*, *15*, 255 (1985).
14. J. T. Davis and E. K. Rideal, *Interfacial Phenomena*, Academic, New York, 1961.
15. G. L. Collins and G. J. Jameson, *Chem. Eng. Sci.*, *31*, 985 (1976).

16. K. B. Medrzycka, *Sep. Sci. Technol., 23,* 565 (1988).
17. R. H. Yoon and J. L. Jordan, *J. Colloid Interface Sci., 113*(2), 430 (October 1986).
18. K. B. Medrzycka, E. Ledóchowska, and W. Zwierzykowski, *Proceedings of the 3rd Discussion Meeting on Physical Chemistry of Finely Dispersed Systems,* Cracow-Mogilany, Poland, October 1984, p. 40.

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