

Recovery of Fine Ilmenite Particles from Beach Sand by Liquid-Liquid Extraction

by

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Abstract

In this fundamental study on the recovery of fine mineral particles by liquid-liquid extraction, the concentration of fine ilmenite particles at the iso-octane/water interface has been investigated using surfactants under different pH. Sodium oleate, sodium laurylbenzenesulfonate and stearylammmonium acetate were used as surfactants to control the wettability of ilmenite particles and to stabilize the iso-octane/water emulsion system in the extraction process.

It was found that one hundred percent recovery of the ilmenite was obtained with the optimum pH and surfactant addition regardless of the surfactant used in this study. The distribution of neutral oleate and amine molecules between the aqueous and organic phases was examined by colorimetry. A good correlation was observed between ilmenite recovery and the concentration distribution of surfactant species.

1. Introduction

In the mining of alluvial tin deposits, which are the most important mineral resources in Southeast Asia, accessory heavy minerals found in association with cassiterite were also recovered. These minerals include ilmenite, monazite, xenotime, zircon, struverite and so on. Dressing plants of alluvial tin mines normally produce cassiterite concentrate by gravity separation techniques, and the other minerals recovered as by-products are separately concentrated from tailings of tin concentrate by the combination of magnetic and electrostatic separation techniques. However, it is very difficult to recover fine particles in the beach sand by using the above separation techniques, and it is also well-known that very fine mineral particles are difficult to float in conventional flotation machines. As mineral particles become finer, a fine particle may never make contact with a bubble because of the presence of an energy barrier in the vicinity of the air/water interface¹⁾.

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It was thought that by using an oil phase instead of air, the energy barrier would be decreased so that fine particles could be concentrated at the oil/water interface more readily than at the air/water interface. One such method might be the extraction of fine solid particles from aqueous suspensions into an oil phase, i.e., liquid-liquid extraction.

The basis of all these processes is directly related to the stabilization of emulsions with finely divided solid particles. Extensive studies on the behaviour of fine particles at the oil/water interface have been carried out by a number of research workers²⁾⁻⁷⁾. For example, Shergold and Mellgren carried out the investigation into the interfacial phenomena in the quartz/water/iso-octane system in the presence of dodecylammonium salt⁸⁾⁹⁾, and also the hematite/water/iso-octane system in the presence of sodium dodecylsulphate¹⁰⁾. The liquid-liquid extraction technique has been adopted by Lai and Fuerstenau¹¹⁾ who studied the alumina/dodecylsulfonate system. Zambrana and his collaborators¹²⁾ investigated the application of liquid-liquid extraction to the recovery of fine cassiterite particles of minus 10 microns.

In the present study of liquid-liquid extraction, the recovery of fine particles of hydrophilic ilmenite was determined after separating an iso-octane/water mixture(emulsion) into its two phases. Sodium oleate, alkylbenzenesulfonate and alkylamine salt were used to change the wettability of the ilmenite and to effect emulsification of the oil-water mixture. Furthermore, the effect of the distribution of neutral oleic acid and amine molecules between oil and aqueous phase were investigated by colorimetry.

2. Materials

Selected pieces of a high purity natural ilmenite from Malaysia were used in this study. From the result of the X-ray diffraction measurement of the ilmenite sample, it was confirmed that the ilmenite was pure enough for the purpose of this study. Pure ilmenite was ground in a laboratory vibratory ball mill. The ground sample was sieved and minus 44 micron fraction was prepared. The specific surface area of minus 44 micron sample was 3.22 m²/g, as determined by B.E.T. method. All aqueous solutions were prepared from distilled and extra purified (by ion exchange process) water.

Sodium oleate (NaOl), sodium laurylbenzenesulfonate (SLBS) and stearyl-ammonium acetate (SAA) were used as surfactants. Iso-octane (2, 2, 4-trimethylpentane), of better than 99 % purity, supplied by Nakarai Tesque Inc., was used. The adjustment of pH was made with hydrochloric acid and sodium

hydroxide. All chemicals mentioned above were of reagent grade.

3. Experimental Procedure

The first step in the extraction procedure was to condition 1gm of ilmenite sample with an appropriate volume of aqueous solution for 20 minutes using a shaking apparatus. During the shaking process, the separatory funnel was sealed with a glass sleeve in order to avoid air contamination of the solution. After the aqueous phase conditioning, iso-octane of a given volume was added to make 100 ml of the liquid mixture. This oil-water-solid mixture was then shaken for 20 more minutes. At the end of the shaking period, the mixture was allowed to stand for 5 minutes to separate the water phase from the oil phase. The water phase was drained into a beaker, and the equilibrium pH was measured. Then the residual solids in the water phase were separated in a centrifugal machine, dried in a vacuum dessicator and then weighed. Finally percent of recovery of fine ilmenite particles in the oil phase was determined.

The distribution of the neutral species between two oil and water phases was measured in the following manner. At first 3 ml of iso-octane was added to 17 ml of surfactant solution at 25 °C, and the oil/water mixture was shaken for 2 hr, after which the concentration of the surfactant species in the water phase was measured by colorimetry, then the concentration of the surfactant in the oil phase was determined. In the colorimetry process, Nile blue¹³⁾⁻¹⁵⁾ for oleate species and picric acid¹⁶⁾ for stearylammonium species were used. Here since SLBS is a strong electrolyte, it was fully ionized through all the range of pH used except at very low pH value¹⁷⁾. Therefore no measurement was made with respect to the distribution of sulfonate species between the two liquid phases.

4. Results and Discussion

4-1. Effect of oil/water ratio and pH without surfactant

First of all, the effect of the oil/water ratio (O/W) on the recovery of ilmenite in the absence of the surfactant was investigated. In this case the pH was the natural pH from 5.9 to 6.4. The result is shown in Fig. 1. As shown in Fig. 1, maximum recoveries are obtained in the O/W range of 15/85 to 20/80, and the addition of iso-octane above 20/80 and below 15/85 results in a decrease in the recovery of ilmenite. Based on the result obtained above, the O/W was fixed at 15/85 for the following experiments.

Fig. 2 presents the recovery of ilmenite in the oil phase as a function of pH in

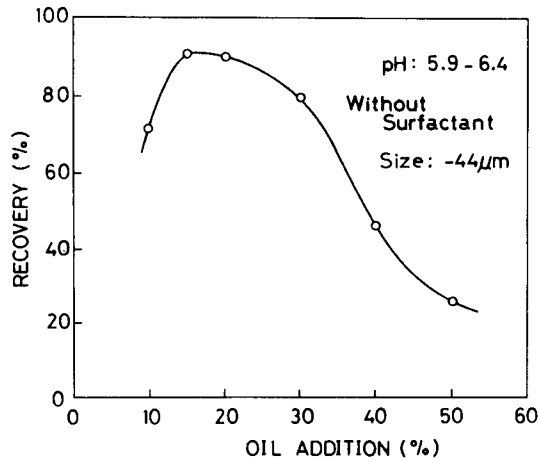


Fig. 1. Effect of oil/water ratio on the recovery of ilmenite without surfactant.

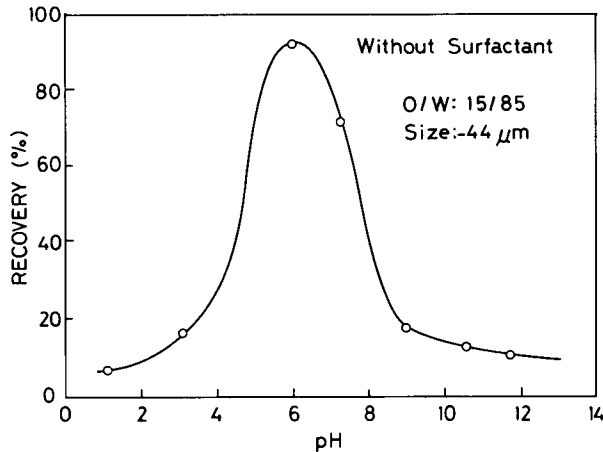


Fig. 2. The recovery of ilmenite in the oil phase as a function of pH without surfactant.

the absence of a surfactant. As shown in Fig. 2, the recovery reaches a maximum around pH 6, rapidly decreases as the pH increases above 6 and decreases below 6.

The zeta potential of ilmenite particles¹⁸⁾ in the absence of a surfactant using the electrokinetic method is presented in Fig. 3 as a function of pH. It can be seen in Fig. 3 that the zero point of charge (zpc) of ilmenite is around pH 6. Consequently in the pH range below and above 6 there is repulsion between the particles so that the concentration of ilmenite particles at the oil/water interface is prevented in the pH range except at the zpc. Thus the recovery decreases.

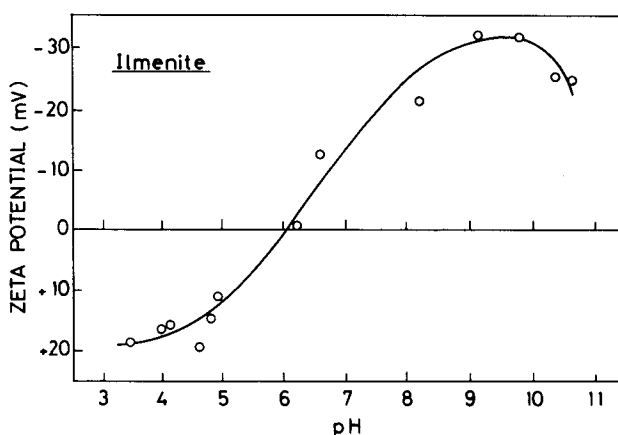


Fig. 3. Zeta potential of ilmenite as a function of pH.

4-2. Effect of sodium oleate

4-2-1. The effect of pH and oleate concentration on the recovery of ilmenite — Fig. 4 shows the effect of pH on the recovery of ilmenite in the presence of various concentrations of NaOl. When NaOl is used as a surfactant, a maximum recovery can be obtained around pH 6 similar to that in the absence of NaOl. However, as the addition of NaOl gives a perfect recovery at a concentration of only 5 mg/l, the effect of NaOl is recognized to be marked. Though the recovery tends to increase with an increasing concentration of NaOl in the acidic solution below pH 6, it is

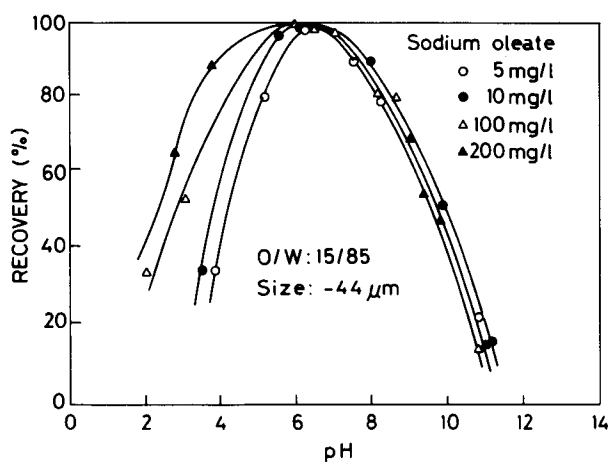


Fig. 4. Effect of concentration sodium oleate in the water phase on the recovery of ilmenite as a function of pH.

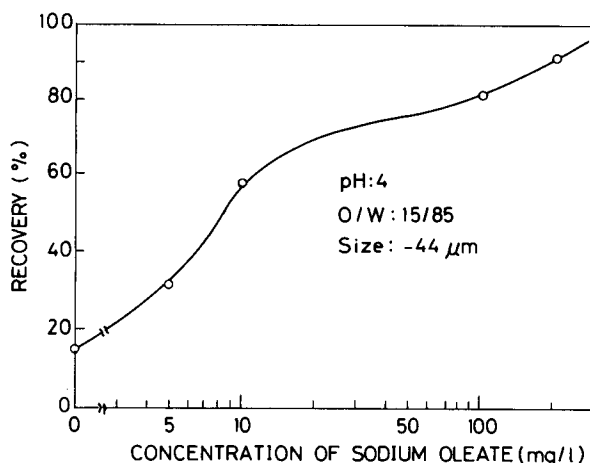


Fig. 5. Effect of concentration of sodium oleate in the aqueous phase on the recovery of ilmenite at a given pH of 4.

found that the recovery is independent of NaOl concentration in alkaline solution above pH 6.

Fig. 5 shows the effect of NaOl concentration on the recovery of ilmenite at a constant pH of 4. It is recognized that the recovery tends to increase with an increasing of the NaOl concentration, comparable with the recovery of only 15% in the absence of NaOl at pH 4.

4-2-2. The distribution of NaOl for an iso-octane/water system — The distribution of neutral oleic acid molecules is observed when NaOl is used as a surfactant for the iso-octane/water system. It is known that the carboxylic ions are prone to hydrolysis, and consequently oleate ions (Ol^-) keep their equilibrium with oleic acid (HOl) as



The K_a value ¹⁹⁾ of the oleic acid (K_{HOl}) is given as

$$K_{HOl} = \frac{[H^+][Ol^-]}{[HOl]_w} = 10^{-5.5} \quad (2)$$

where $[HOl]_w$ denotes the concentration of the neutral oleic acid in the water phase.

The distribution of neutral oleic acids between the water phase and the oil phase can be expressed as

$$[HOl]_w = D \cdot [HOl]_o \quad (3)$$

where $[HOl]_o$ is the concentration of oleic acid in the oil phase and D indicates a

partition coefficient.

Now involving both neutral and ionic species in two phases, a distribution coefficient (K_d) can be defined as

$$K_d = \frac{\text{Total oleate in the water phase}}{\text{Total oleate in the oil phase}} = \frac{[\text{HOI}]_w + [\text{OI}^-]}{[\text{HOI}]_o} \quad (4)$$

By substitutions from Equations (2) and (3), Equation (4) is rewritten as

$$K_d = \frac{K_{\text{HOI}}}{D[\text{H}^+]} + \frac{1}{D} \quad (5)$$

If $[\text{H}^+] \ll K_{\text{HOI}}$, that is, $\text{pH} \gg 5.5$, Equation (5) can be approximately simplified as

$$\log K_d = \text{pH} + (\log K_{\text{HOI}} - \log D) \quad (6)$$

Therefore if the logarithm of K_d is plotted as a function of pH after the concentration of oleate species in water and/or oil phases is determined, a straight line should be obtained with a unit slope and an intercept of $(\log K_{\text{HOI}} - \log D)$.

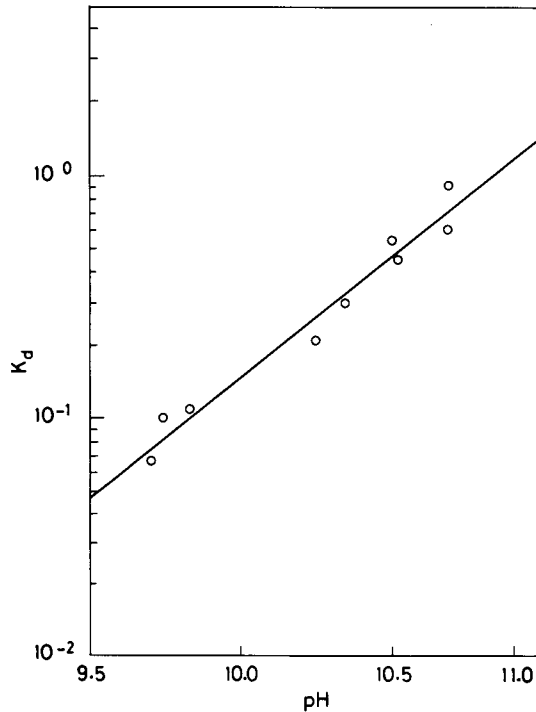


Fig. 6. Relationship between distribution coefficient and pH at a total oleate concentration of 1×10^{-3} mol/l.

Fig. 6 shows the experimental plot of $\log K_d$ against pH for values of the iso-octane and the water volumes of 3 ml and 17 ml respectively. The slope obtained from the line in the alkaline solution above pH 9.5 was + 0.997 and the value of D calculated from the intercept was 1.98×10^5 . Using this value of D, calculations were carried out to determine concentrations of $[\text{HOI}]_w$, $[\text{OI}^-]$ and $[\text{HOI}]_o$ for a total NaOI concentration of 1×10^{-3} mol/l, which refers to the concentration added initially in the water phase. The result of these calculations is presented in Fig. 7. As shown in Fig. 7, in the pH range above 10.7 the anionic oleate ion predominates over any oleate species, whereas the neutral oleic acid in the oil phase is predominant at pH values below 10.7. The concentration of the neutral oleic acid in the water phase is much lower than that of any other species above pH 5.5 and is higher than that of the oleate ion. If Fig. 4 is compared with Fig. 7, it is obvious that though $[\text{HOI}]_o$ is predominant in the acidic solution below pH 5.5, the electrostatic adsorption of the oleate ion below pH 6 gives hydrophobic surfaces to the limenite particles which are positively charged, and the penetration of the hydrocarbon chain of the surfactant into the oil drop easily takes place, so that the recovery can be increased as the NaOI concentration is increased. On the other

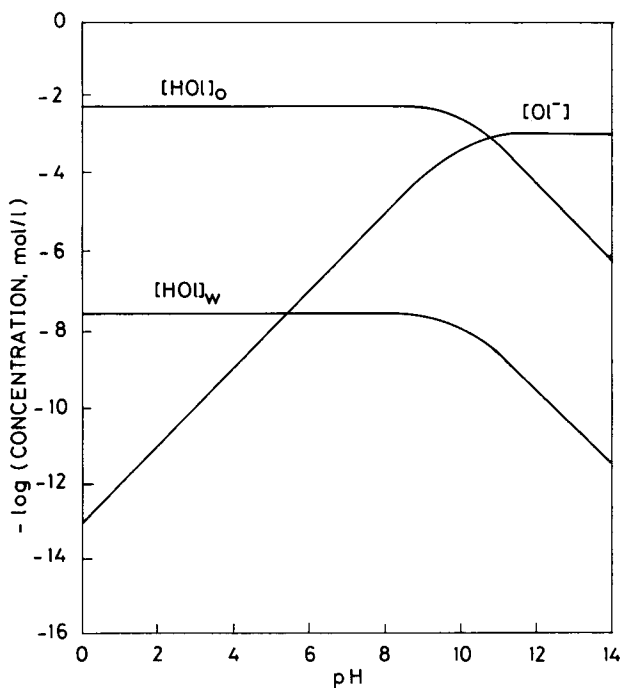


Fig. 7. Concentration of oleate species as a function of pH at a total oleate concentration of 1.0×10^{-3} mol/l.

hand, since in the alkaline solution the oleate species exist in the form of ions, they are prevented from adsorbing on the negatively charged ilmenite particles, so that the recovery of ilmenite becomes independent of the NaOl concentration.

4-3. Effect of sodium laurylbenzenesulfonate

Fig. 8 shows the effect of SLBS, used as a surfactant, on the recovery of ilmenite as a function of pH. In the case of SLBS it is recognized that the recovery rapidly

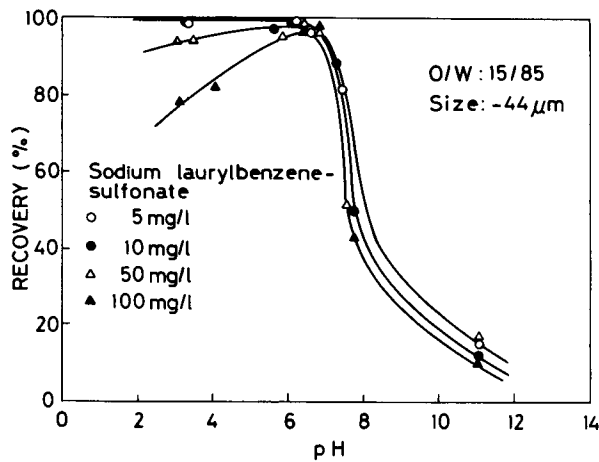


Fig. 8. Effect of concentration of sodium laurylbenzenesulfonate in the water phase on the recovery of ilmenite as a function of pH.

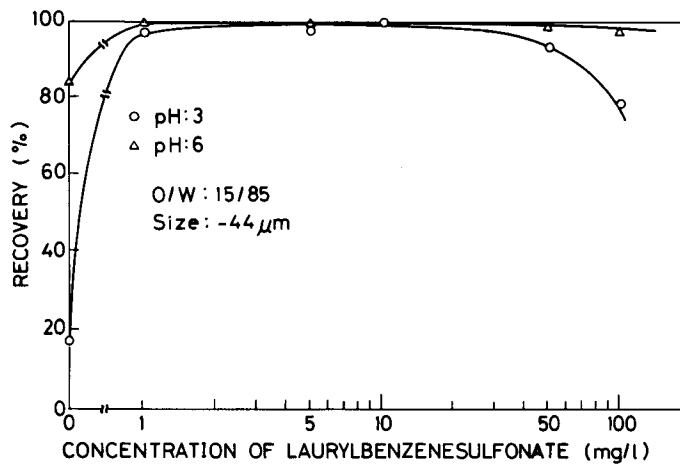


Fig. 9. Effect of concentration of sodium laurylbenzenesulfonate in the water phase on the recovery of ilmenite at given pH's of 3 and 6.

decreases when the pH increases above 6. In the acidic solution at pH below 6, the addition of only 10 mg/l SLBS leads to the recovery of approximately 100 %, but the addition of SLBS above 10 mg/l is apt to decrease the recovery. This tendency is presented in Fig. 9. Fig. 9 shows the influence of the SLBS concentration on ilmenite recovery at two different pH's, 3 and 6. As shown in Fig. 9, it can be seen that ilmenite recoveries are decreased with the increase of SLBS concentration over 50 mg/l though perfect recoveries are able to achieve at pH 3 within the range of the SLBS concentration from 1 to 10 mg/l. From those results it is found that there is an optimum range of SLBS concentration in order to obtain high recoveries of ilmenite.

As to decreases in recoveries at high concentrations of the surfactant, as explained by Mackenzie²⁰, it can be considered that since the adsorption density at both oil/water and water/solid interfaces increases, no sweep of the surfactant at the oil/water interface takes place, therefore the lipophilic group of the surfactant ion adsorbed on the particle is prevented from penetrating into the oil drop.

4-4. Effect of stearylammonium acetate

4-4-1. Influence of pH and SAA concentrations — The effect of pH in the presence of various concentrations of SAA is illustrated in Fig. 10. The recovery curve in the case of SAA has a tendency opposite to that of SLBS in Fig. 8, i.e., it is recognized that a perfect recovery is obtained at an optimum SAA concentration of 50 mg/l in the alkaline range above pH 6, whereas the recovery decreases when the pH decreases below 6. This tendency is made obvious by the following

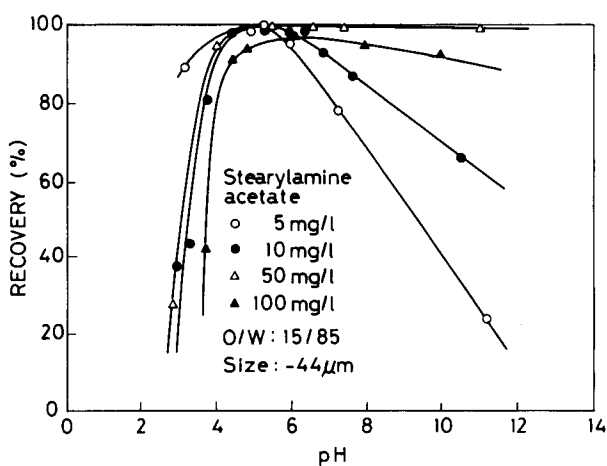


Fig. 10. Effect of concentration of stearylamine acetate in the water phase on the recovery of ilmenite as a function of pH.

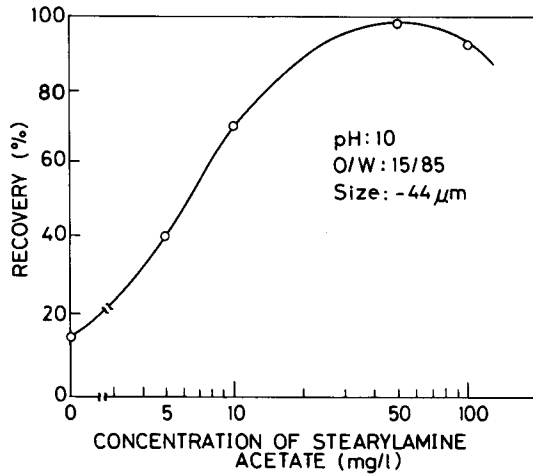


Fig. 11. Effect of concentration of stearylamine acetate in the water phase on the recovery of ilmenite at a given pH of 10.

figure. Fig. 11 shows the effect of the SAA concentration on the recovery at a given pH of 10. As shown in Fig. 11, the ilmenite recovery increases when the SAA concentration increases and reaches a maximum of approximately 100 % at 50 mg/l of SAA. However, the recovery conversely decreases as the SAA addition is increased above 50 mg/l. From the result obtained above, it is found that in the alkaline solution above the optimum pH of 6 there is an optimum range of the SAA concentration similar to the case of SLBS.

4-4-2. Distribution of SAA for an iso-octane/water system — It is known that neutral stearylamine molecules (RNH_2) are soluble in neutral oil such as iso-octane but insoluble in water²¹. If the amine is added in the iso-octane/water system, the distribution of neutral amines takes place between two liquid phases²².

The acidic dissociation of the stearyl ammonium ion (RNH_3^+) can be presented as



The dissociation constant (K_{SAA}) is given as

$$K_{\text{SAA}} = \frac{[\text{RNH}_2]_{\text{w}}[\text{H}^+]}{[\text{RNH}_3^+]} \quad (8)$$

where $[\text{RNH}_2]_{\text{w}}$ is the concentration of the neutral amine in the water phase. The distribution between the two liquid phases is defined as

$$[\text{RNH}_2]_{\text{o}} = D \cdot [\text{RNH}_2]_{\text{w}} \quad (9)$$

where D is a partition coefficient and $[\text{RNH}_2]_o$ is the concentration of the neutral amine in the oil phase.

Involving both neutral and ionic species in two liquid phases, a distribution coefficient (K_d) can be defined as

$$K_d = \frac{\text{Total amine concentration in water}}{\text{Total amine concentration in oil}} \\ = \frac{[\text{RNH}_2]_w + [\text{RNH}_3^+]}{[\text{RNH}_2]_o} \quad (10)$$

Substituting Equations (8) and (9), Equation (10) is rewritten

$$K_d = \frac{[\text{H}^+]}{D K_{\text{SAA}}} + \frac{1}{D} \quad (11)$$

If $[\text{H}^+] \gg K_{\text{SAA}}$, i.e., $\text{pH} \ll 10.6$, Equation (11) can be simplified as

$$\log K_d = -\text{pH} - (\log K_{\text{SAA}} + \log D) \quad (12)$$

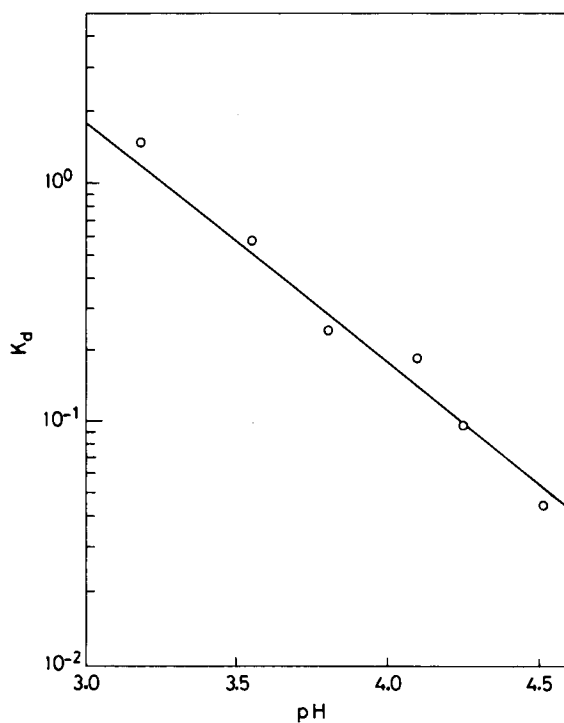


Fig. 12. Relationship between distribution coefficient and pH at a total amine concentration of 1.0×10^{-4} mol/l.

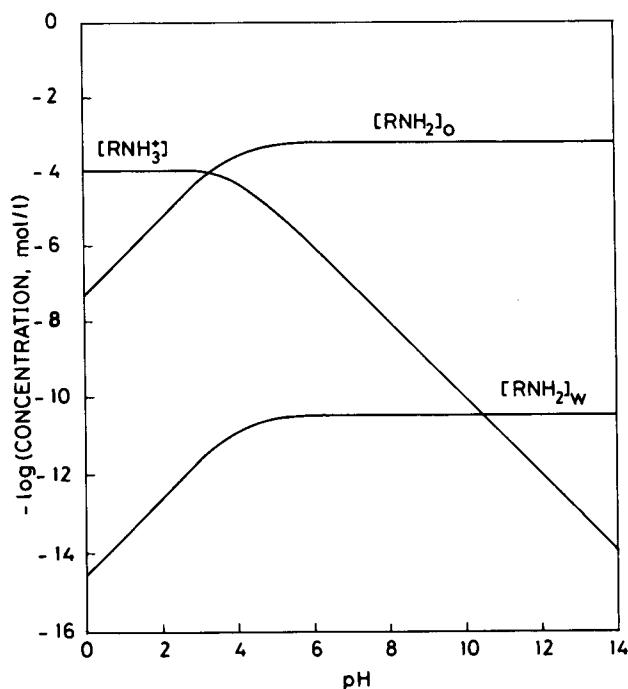


Fig. 13. Concentration of amine species as a function of pH at a total amine concentration of 1.0×10^{-4} mol/l.

When the logarithm of K_d is plotted against pH, a straight line with a slope of -1 and an intercept of $-(\log K_{SAA} + \log D)$ can be obtained.

Fig. 12 shows the experimental plot of the logarithm of K_d as a function of pH for values of the oil and the water phase volumes of 3 and 17 ml respectively. The slope obtained from the line was -1.01 and the value of D calculated from the intercept was 2.03×10^7 . Using this value of D , calculations were made to determine $[RNH_2]_w$, $[RNH_3^+]$ and $[RNH_2]_o$ for a total SAA concentration of 1×10^{-4} mol/l. This result is presented in Fig. 13. As shown in Fig. 13, stearylammionium ion is predominant in the acidic range below pH 3.5, whereas the neutral amine predominates over any other species in the system above pH 3.5. The concentration of neutral amine in water is much lower than any other species in the pH range below 10.6 and is higher than that of stearylammionium ion above pH 10.6.

When Fig. 10 is compared with Fig. 13, though the concentration of stearylamine in the oil phase is predominant above pH 3.5, the cationic amine adsorbs on the ilmenite particles charged negatively in alkaline solution at pH above

6 and the hydrophobic hydrocarbon chain of the ion can easily penetrate into the oil drop, so that the ilmenite recovery increases as the SAA concentration added in water is increased. On the other hand, with respect to the decrease in the recovery at high SAA concentrations, similar to the case of SLBS, it can be thought that as the adsorption densities at both oil/water and water/solid interfaces increase, the hydrocarbon chain of the ion adsorbed on the solid is prohibited from penetrating the oil droplet.

5. Conclusions

In this study on the recovery of fine ilmenite particles by liquid-liquid extractin, the concentration of minus 44 micron ilmenite particles has been investigated in order to obtain the fundamental conditions with surfactants such as oleate, alkylbenzenesulfonate, and alkylammonium salts. The results obtained can be summarized as follows:

- (1) The effect of the oil/water ratio on the recovery of ilmenite has been investigated. The maximum recovery can be obtained in the range of an oil/water ratio of 15/85 to 20/80. In addition, it has been confirmed that the optimum pH for the extraction, in the absence of a surfactant, is at the zpc of ilmenite, and the recovery decreases rapidly at pH above and below 6. Regarding the reason for the above, it can be considered that ilmenite particles are prohibited from concentrating at the iso-octane/water interface due to the repulsion between particles charged positively or negatively except at the zpc of ilmenite.
- (2) The recovery is maximum at pH 6 with NaOl used as a surfactant. In this case NaOl is so effective that the recovery may reach approximately 100 % at the concentration of only 5 mg/l. Further, a distribution of oleate species for the iso-octane/water system has been investigated. A partition coefficient of neutral oleic acid obtained is 1.98×10^5 . Using this value, concentrations of oleate species both in water and in iso-octane have been determined.
- (3) When SLBS is used as a surfactant, the ilmenite recoveries markedly decrease at any SLBS concentrations as the pH increases above 6. Although perfect recoveries can be obtained at SLBS concentrations below 10 mg/l in the pH ranges below 6, the recovery decreases with the increase of SLBS concentration over 10 mg/l. A decrease in the recovery at high SLBS concentrations can be interpreted by the use of a "sweeping-penetration" model.
- (4) Using SAA as a surfactant, the recovery of ilmenite is reduced below pH 6, but the ilmenite can be recovered perfectly in the oil phase at an optimum concentration of 50 mg/l above pH 6. However, an addition of SAA above 50 mg/l in alkaline

solution results in a decrease in the recovery. This can be explained similarly to the case of SLBS by using the sweeping-penetration model. Further, a distribution of SAA for the iso-octane/water system has been investigated. The value of the partition coefficient of strarylamine obtained is 2.03×10^7 , which is used to determine concentrations of amine species distributed between the oil and water phases.

References

- 1) B. V. Derjaguin and S. S. Dukkin; *Trans. Inst. Min. Met.*, **7**, 221 (1961)
- 2) S. U. Pickering; *J. Chem. Soc.*, **91**, 2001 (1907)
- 3) T. R. Briggs; *Ind. Eng. Chem.*, **13**, 1008 (1921)
- 4) F. E. Weston; *Chem. Age.*, **4**, 604 (1921)
- 5) D. F. Cheesman and A. King; *Trans. Faraday Soc.*, **34**, 594 (1938)
- 6) J. H. Schulman and J. Leja; *Trans. Faraday Soc.*, **50**, 598 (1954)
- 7) J. H. Hildebrand; *J. Phys. Chem.*, **45**, 1303 (1941)
- 8) O. Mellgren and H. L. Shergold; *Trans. Inst. Min. Met.*, **75**, C267 (1966)
- 9) H. L. Shergold and O. Mellgren; *Trans. Soc. Min. Eng. AIME*, **247**, 149 (1970)
- 10) H. L. Shergold and O. Mellgren; *Trans. Inst. Min. Met.*, **78**, C121 (1969)
- 11) R. W. M. Lai and D. W. Fuerstenau; *Trans. Soc. Min. Eng. AIME*, **241**, 549 (1968)
- 12) G. Z. Zambrana, R. T. Medina, G. B. Gutierrez and R. R. Vergas; *Inter. J. Miner. Process.*, **1**, 335 (1974)
- 13) S. D. Dixit and A. K. Biswas; *Trans. Soc. Min. Eng. AIME*, **244**, 173 (1969)
- 14) R. Goiffon and M. Couchoud; *Ann. Biol. Clin.*, **11**, 327 (1953); *Chem. Abst.*, **47**, 12129h (1953)
- 15) T. Mizuniwa, K. Iwao, I. Matsuoka and Y. Hotta; *Nippon Kogyo Kaishi*, **93** [1072], 435 (1977)
- 16) A. S. Pearce and E. I. Streatfield; *Analy. Abst.*, **247**, 149 (1970)
- 17) F. F. Aplan and D. W. Fuerstenau; "Froth Flotation," 50th Anniversary Volume, AIME, New York (1962), 170
- 18) Y. Nakahiro, Y. Noguchi and T. Wakamatsu; *Fusen*, **34** [1], 3 (1987)
- 19) K. L. Sutherland and I. M. Wark; "Principles of Flotation," AIME, New York (1955), 174
- 20) J. M. W. Mackenzie; *Trans. Soc. Min. Eng. AIME*, **247**, 202 (1970)
- 21) P. L. de Bruyn; *Trans. Soc. Min. Eng. AIME*, **202**, 291 (1955)
- 22) H. L. Shergold and O. Mellgren; See Ref. 9.