

Recovery of Fine Monazite Particles by Liquid-Liquid Extraction

by

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Abstract

As a fundamental study with regards to the recovery of fine mineral particles by liquid-liquid extraction, the effect of sodium dodecylbenzenesulfonate (SDBS) as a surfactant has been investigated in terms of pH, SDBS concentration, zeta potential, contact angles, interfacial tensions and work of adhesion.

Maximum recoveries were obtained at pH around 7 and SDBS concentration of $1 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$. In alkaline solutions, the recovery of monazite decreased regardless of the SDBS concentration as the pH was increased above 7. An increase in the SDBS concentration up to $1 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ resulted in an increase in the recovery. It was considered that in the pH range below 7, an increase in the SDBS concentration brought about a higher coulombic adsorption density of the surfactant ions on the monazite particles which were charged positively, and resulted in higher recoveries.

So as to examine a relationship between the oil-wettability and the recovery, contact angles and interfacial tensions were also measured in terms of pH and SDBS concentration. Based on the results obtained above, the work of adhesion was calculated. It was found that the work of adhesion was considerably related to the monazite recovery of the liquid-liquid extraction.

1. Introduction

Monazite, which includes light rare earth elements such as cerium, lanthanum and neodymium etc., is a mineral of the rare earth phosphate and is one of the most important rare earth minerals in the industrial field. Monazite is widely distributed in the world, especially in the beach sands around Southeast Asia. It is produced together with xenotime, zircon, cassiterite, ilmenite and so on. These minerals are recovered by means of a combination of magnetic, electrostatic and gravity separations. However, the finer these minerals are, the more difficult is the separation between them by the above methods.

As a method of recovering fine particles, the flotation process is usually applied, but it becomes more difficult to recover fine particles less than several microns¹⁾.

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Consequently, a liquid-liquid extraction in which fine solid particles suspended in water concentrate at the oil/water interface has been applied, based on the stability of emulsion of finely divided solids.

Extensive studies of the liquid-liquid extraction for the recovery of fine mineral particles were made by Lai and Fuerstenau²⁾ (for alumina/alkyl-sulfonate system) and Shergold and Mellgren (for quartz/dodecylamine^{3,4)} and hematite/dodecylsulfate⁵⁾ systems). Zambrana et al.⁶⁾ applied a liquid-liquid extraction for the recovery of minus ten micron cassiterite. Marnakis et al.⁷⁾ made the study of activation and/or depression of lattice cations and some anions for tungsten minerals.

In this study, the application of liquid-liquid extraction to fine monazite, which is one of the beach sand minerals, is discussed in terms of the interfacial tensions, the contact angles, the work of adhesion of oil onto solid surface and the adsorption of surfactant ions at the oil/water interface.

2. Materials

Monazite from Indonesia was used in this experiment. The result of the measurement of X-ray diffraction indicated that no impurity was included in the monazite sample. The monazite sample ground by a vibratory ball mill was sieved and a minus 44 micron fraction was prepared. The mean particle diameter of the sample, as examined by the Andreasen pipet, was 13.4 micron and its specific surface area was 3.81 m²/g by the B.E.T. method.

Throughout this experiment extra pure grade of sodium dodecylbenzenesulfonate (SDBS) as a surfactant, and guarantee grade of hydrochloric acid, sodium hydroxide and sodium chloride were used.

3. Experimental Procedure

3.1 Measurement of monazite recovery

At first 1 g of minus 44 micron monazite was conditioned for 20 min in 85 ml of distilled and ion-exchanged water which include a pH modifier, SDBS and NaCl all together placed in a separate funnel and mounted on a shaking apparatus. After conditioning, 15 ml of iso-octane was added to make 100 ml of the liquid mixture, which was then shaken out for 20 min in order to make an oil-in-water emulsion. Then the mixture was allowed to stand for 5 min in order to separate the oil phase from the water phase, in which residual particles were centrifuged,

dried in a vacuum drier and weighed. Thus, the recovery of fine monazite particles in the oil phase was determined.

Theoretically, it is known that the minimum oil volume (as determined by a closely-packed water-in-oil emulsion of uniform spherical droplets) is around 26 %⁸⁾ of the total volume. Consequently, in order to make an oil-in-water emulsion in the liquid-liquid extraction process, it is necessary to choose the oil volume such that it is less than 26% of the total volume. Throughout this experiment the oil volume was kept at 15% of the total.

3.2 Contact angles

To evaluate the wettability of the monazite surface, contact angles were measured by means of the tilting plate method. In this case, monazite was crystal polished with diamond paste and was inserted in the cell at the interface between the iso-octane and pH-modified SDBS solution. The contact angles measured were across the aqueous phase and refer to the advancing contact angles.

3.3 Interfacial tensions

The interfacial tensions of the interface between the iso-octane and SDBS solution were determined by the drop weight method. The correction factors for this method have been given by Harkins and Brown⁹⁾.

4. Results

4.1 Effect of concentration of SDBS on monazite recovery

Fig. 1 shows the effect of pH in the presence of various SDBS concentrations on the recovery of monazite. In the case where SDBS was used as a surfactant, as shown in Fig. 1, the recovery was maximum in the pH range from 6 to 7. The recovery, as the pH was increased above 7, rapidly decreased. In the acidic region of pH below 7, an increase in the SDBS concentration resulted in an increase in the monazite recovery.

In Fig. 2, the monazite recovery by the extraction into the oil phase from the solution at a given pH of 5 is presented as a function of the SDBS concentration. It is recognized that at pH 5 the recovery tends to increase as the SDBS concentration increases up to $1 \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$. It is a maximum of 95% in the range of the SDBS concentration from 4×10^{-5} to $2 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$. However, the addition of SDBS above $2 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ causes a decrease in the recovery.

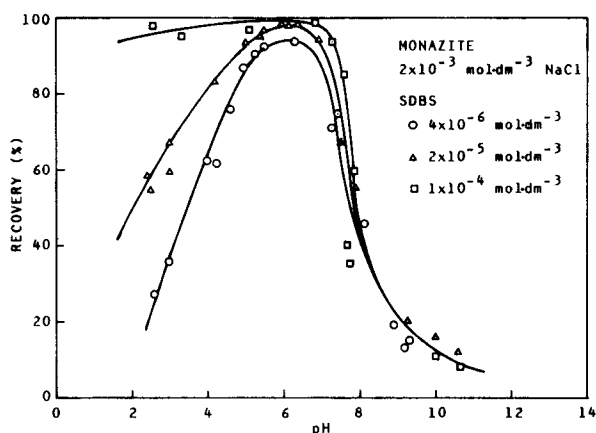


Fig. 1. The recovery of monazite in the oil phase as a function of pH at various SDBS concentrations and 15 volume percent iso-octane (ionic strength 2×10^{-3}).

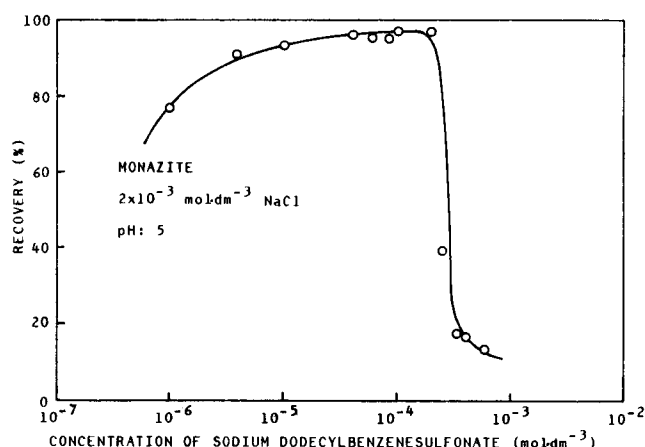


Fig. 2. The recovery of monazite in the oil phase as a function of the SDBS concentration at pH 5 and 15 volume percent iso-octane (ionic strength 2×10^{-3}).

4.2 Effect of pH and SDBS concentration on contact angles

To evaluate the wettability of the monazite surface, contact angles were determined by the tilting plate method. In Fig. 3, the contact angle between the oil/water and water/solid interfaces across the water phase is presented as a function of pH in the presence of two different SDBS concentrations. As can be seen in Fig. 3, the contact angle is maximum around pH 7 and decreases above 7 at both concentrations, which indicates that the hydrophobicity of the solid is reduced.

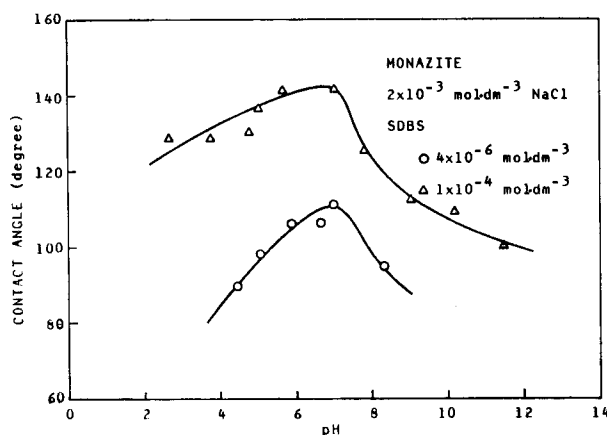


Fig. 3. The contact angle of iso-octane/water/monazite system as a function of pH at two different SDBS concentrations.

At low concentration of SDBS, the contact angles decrease when the pH decreases below 7. Large contact angles, however, are kept at a high SDBS concentration, resulting in a high hydrophobicity at the surface.

Fig. 4 shows the effect of the SDBS concentration on the contact angle between the oil/water interface and the monazite surface across the aqueous phase at a given pH of 5 in the presence of $2 \times 10^{-3} \text{ mol·dm}^{-3}$ NaCl. As shown in Fig. 4, contact angles were kept constant up to an SDBS concentration of $2 \times 10^{-5} \text{ mol·dm}^{-3}$. With SDBS concentrations ranging from 2×10^{-5} to $1 \times 10^{-4} \text{ mol·dm}^{-3}$, the contact angle increases with an increasing SDBS concentration. As the SDBS concentration was

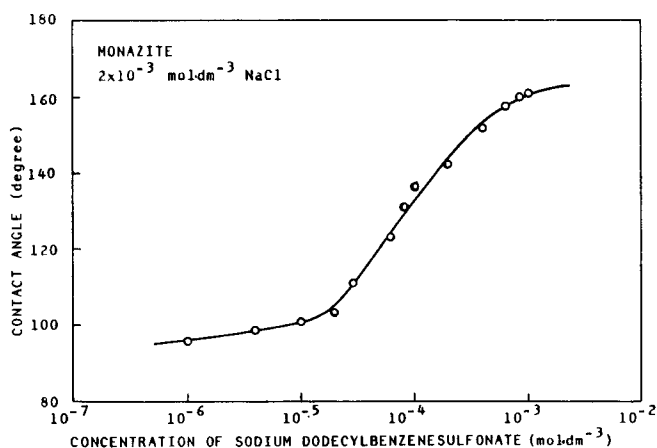


Fig. 4. The contact angle of iso-octane/water/monazite system as a function of the SDBS concentration at pH 5 (ionic strength 2×10^{-3}).

increased above $1 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$, the contact angles also slowly increased.

4.3 Effect of SDBS concentration on oil/water interfacial tension

The interfacial tension was determined by the drop weight method. Because SDBS is a strong electrolyte, it is fully ionized in an aqueous solution. Under the experimental conditions used, no sulfonate was extracted into the iso-octane phase and the interfacial tension remained approximately constant at the pH values used. Consequently, all the experiments were carried out at natural pH from 5.5 to 5.8 without any adjustments.

Fig. 5 shows the effect of the SDBS concentration on the iso-octane/water interfacial tension. It can be seen that there is a linear relationship between the interfacial tension and the logarithm of the SDBS concentration above $2 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$.

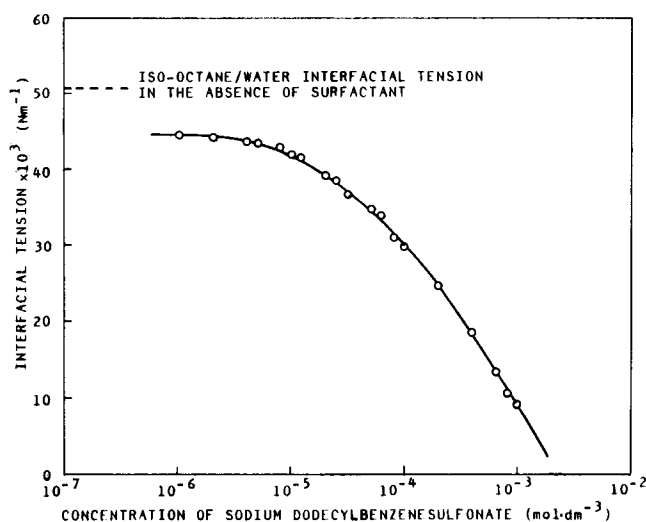


Fig. 5. The iso-octane/water interfacial tension as a function of the aqueous concentration of SDBS (ionic strength 2×10^{-3}).

5. Discussions

5.1 Effect of pH

The contact angle is considered to be one of the important factors that governs the recovery of solids in the liquid-liquid extraction process¹⁰⁾. When Fig. 1 is compared with Fig. 3, it can be seen that a maximum recovery of monazite is obtained around pH 7, where the contact angle is also maximum. When the pH

increases above 7, both the recovery of monazite and the contact angle rapidly decrease. In the case of high SDBS concentration, high recoveries and large contact angles are maintained in the acidic range below pH 7. A little addition of the SDBS causes decreases both in the recoveries and in the contact angles when the pH is decreased below 7.

Fig. 6 shows the zeta potential of monazite particles as a function of pH without any surfactants. It is found that the zero point of charge (zpc) of monazite used is around 7. Based on the result above, within the pH range below 7, the electrostatic adsorption of dodecylbenzenesulfonate ions (DBS^-) results in an increase in the contact angle, that is, in the hydrophobicity of the particles. Conversely, in the pH range above 7 where the monazite particles are charged negatively, DBS^- is prevented from adsorbing electrostatically on the particles, which leads to a decrease in the contact angles i.e. a decrease in the hydrophobicity at the surface and results in low recoveries.

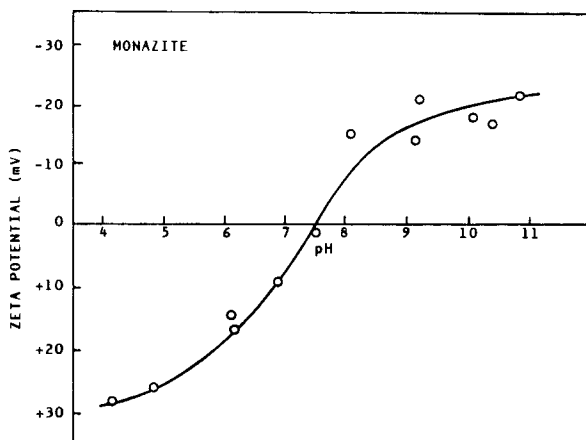


Fig. 6. Zeta potential of monazite as a function of pH.

However, it is necessary to evaluate the work of adhesion of oil onto the mineral surface which is derived from the interfacial tension and the contact angle when the wettability of the solid surface is taken into account³⁾. The work of adhesion gives the work necessary to separate a unit area of oil/solid interface into two oil/water and water/solid interfaces, briefly indicating an affinity between the oil and the solid in the aqueous solution. Consequently, an increase in the work of adhesion gives an increase in the lipophilicity of the solid in the aqueous solution. The work of adhesion for oil onto the solid is related by Dupre's equation¹¹⁾ and is presented as

$$W_A = \gamma_{ow} + \gamma_{sw} - \gamma_{so} \quad (1)$$

where W_A is the work of adhesion, γ_{ow} is the interfacial tension of the oil/water interface, γ_{sw} is the interfacial tension of the solid/water interface and γ_{so} is the interfacial tension of the solid/oil interface. If the ϑ_{ow} is the contact angle of oil/water interface across the aqueous phase, the three interfacial tensions at equilibrium are related to Young's equation¹¹⁾ as follows.

$$\gamma_{so} = \gamma_{sw} + \gamma_{ow} \cos \vartheta_{ow} \quad (2)$$

Combining Equation 1 with Equation 2, W_A is given as

$$W_A = \gamma_{ow} (1 - \cos \vartheta_{ow}). \quad (3)$$

Equation 3 shows that by measuring the interfacial tension of the oil/water interface and the contact angle of the oil/water interface across the aqueous phase, the work of adhesion can be obtained.

Fig. 7 shows the work of adhesion for iso-octane on monazite as a function of pH calculated from the contact angles (in Fig. 4) and the measurement of the interfacial tension by the use of Equation 3. Comparing Fig. 7 with Fig. 2, in the case where SDBS is used as a surfactant it is recognized that the work of adhesion is well related to the recovery of monazite. Within the range of pH below 7, an increase in the SDBS concentration gives an increase in the work of adhesion and leads to an increase in the recovery of monazite. Conversely, both the work of adhesion and the recovery of monazite decrease at pH above 7. Based on the above result, it can be deduced that the electrostatic adsorption of DBS^- on the monazite particle charged positively in the acidic range below pH 7 contributes to a high hydrophobicity of the particle and hence a good contact between monazite

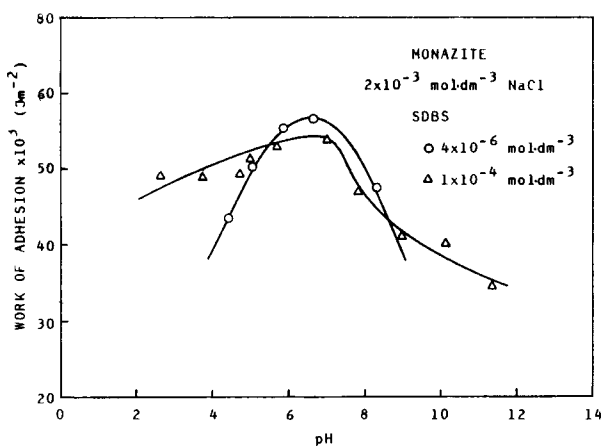


Fig. 7. The work of adhesion for iso-octane on monazite as a function of pH at two different SDBS concentrations (ionic strength 2×10^{-3}).

and iso-octane.

5.2 Effect of SDBS concentration on monazite recovery at pH 5

The contact angle curve shown in Fig. 4 can be divided into three regions, as suggested by Fuerstenau¹³ according to the adsorption isotherm of the surfactant ions for the solid. In the region of a low concentration of SDBS up to $2 \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$, the slope of the contact angle-concentration curve is low, where DBS⁻ ions adsorb individually on the monazite surface which is charged positively. The increase in the contact angle in the region of the SDBS concentration from 2×10^{-5} to $1 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ is due to the formation of hemi-micelles where the surfactant ions adsorbed at the solid/water interface associate with each other. At high concentrations of SDBS above $1 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ the contribution due to the electrostatic attraction disappears because of the reversal of the zeta potential. Hence, the electrostatic repulsion reduces the attraction between the hydrocarbon chains of the surfactant ions, and consequently, less adsorption would take place. Thus, in this region the slope of the contact angle curve decreases. As the hydrophobicity of the solid is directly correlated to the contact angle, it can be considered that the recovery of monazite is increased with an increasing SDBS concentration in solution. Comparing Fig. 2 with Fig. 4, however, the addition of SDBS in solution above $2 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ tends to reduce the recovery of monazite though large contact angles are maintained. For an explanation of this result, it can be considered that less wetting between monazite and iso-octane takes place.

Fig. 8 shows the influence of SDBS on the work of adhesion for iso-octane on monazite evaluated from the contact angle curve (in Fig. 4) and the measurement of the interfacial tension by the use of Equation 3. As shown in Fig. 8, the work of adhesion is increased as the SDBS concentration is increased up to $1 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$. The further addition of SDBS in the solution above results in a rapid decrease in the work of adhesion i.e. the wettability of monazite by iso-octane is reduced. Comparing Fig. 2 with Fig. 8, within the range of the SDBS concentration where the work of adhesion is markedly reduced in Fig. 8, the recovery of monazite in Fig. 2 is also reduced. Therefore it can be considered that the decrease in the oil/water interfacial tension results in less adhesion for iso-octane on monazite at higher concentrations of SDBS.

Mackenzie¹²⁾ has interpreted a decrease in the recovery at higher concentrations of a surfactant in the extraction process. He used a physical model of a "sweeping-penetration" model for the adhesion between an oil drop and a solid surface, which is derived from steric interactions of ions adsorbed and a free energy of the

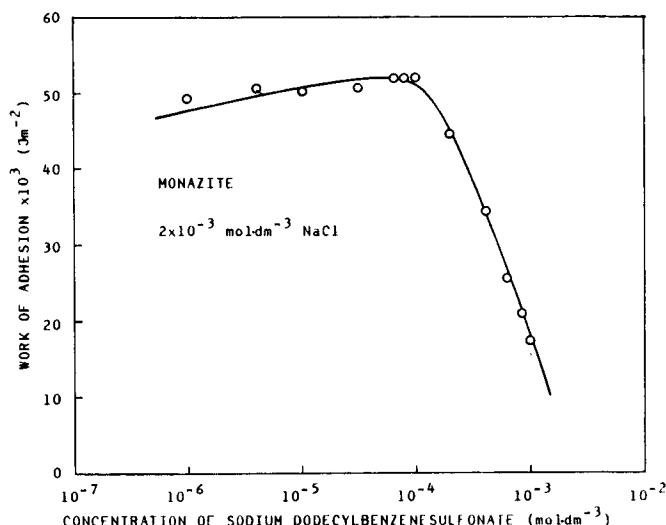


Fig. 8. The work of adhesion for iso-octane on monazite as a function of the aqueous concentration of SDBS at a given pH of 5.

adhesion model. Based on this report, at low concentrations of the surfactant, the adsorption densities at two oil/water and solid/water interfaces are not so great. Hence, the lipophilic group of the surfactant adsorbed at the solid/water interface is easy to penetrate into the oil phase (droplet). At high concentrations, however, dense adsorptions of the ions at two oil/water and solid/water interfaces prevent surfactant ions from sweeping at these interfaces. They also disturb the penetration of the hydrocarbon chains into the oil phase. Under this condition no adhesion between the oil drop and the mineral surface would occur.

The adsorption density at the oil/water interface is related with Gibb's equation¹³⁾ as

$$\Gamma = \frac{1}{RT} \left(\frac{d\gamma}{d \ln C} \right)_T \quad (4)$$

Where Γ is the interfacial excess, R is the gas constant, T is the absolute temperature and C is the concentration of the surfactant. It follows that the adsorption density at the oil/water interface at a given concentration can be obtained by calculating a tangent of the γ -log C curve at the concentration.

Fig. 9 shows the relationship between Γ and the logarithm concentration of SDBS obtained by combining the interfacial tension with Equation 4. It is recognized that the adsorption density reaches a maximum in the range of SDBS concentration from 1×10^{-4} to $2 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$. Thus, the penetration of the lipophilic group of DBS^- adsorbed at the oil/water interface is prevented, and no adhesion between

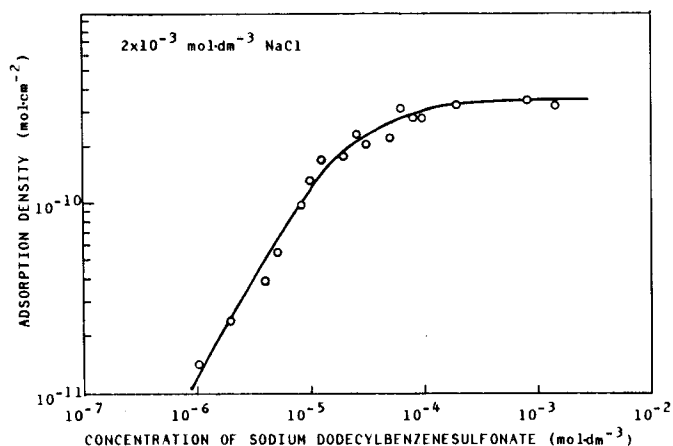


Fig. 9. Adsorption isotherm of SDBS on iso-octane/water interface at natural pH.

oil and monazite takes place. In this case, both the work of adhesion and the recovery of monazite are low.

5.3 Effect of work of adhesion on monazite recovery

Since it is recognized that the wettability of monazite for iso-octane is considerably related with the recovery of monazite, the effect of the work of adhesion on the recovery was examined. The result is presented in Fig. 10. As shown in Fig. 10, an increase in the work of adhesion results in an increase in the recovery. The value of the work of adhesion of $50 \times 10^{-3} \text{ J} \cdot \text{m}^{-2}$ gives a recovery of more

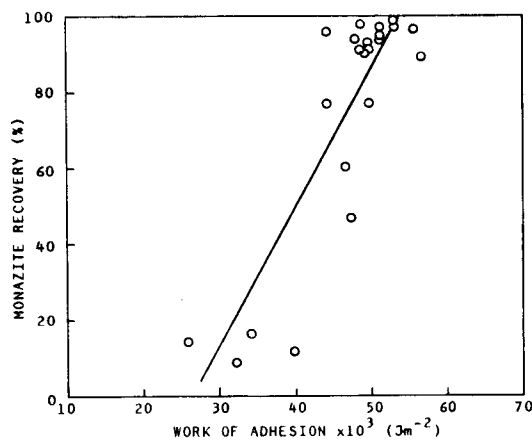


Fig. 10. The effect of the work of adhesion on monazite recovery.

than 90%, and the value of $30 \times 10^{-3} \text{ J} \cdot \text{m}^{-2}$ a recovery of around 10%.

6. Conclusion

As part of the studies regarding the recovery of fine mineral particles, the concentration of minus 44 micron monazite particles with a surfactant of sodium dodecylbenzenesulfonate has been investigated in terms of interfacial tensions, contact angles, the work of adhesion and the adsorption density of the surfactant ions at the oil/water interface. The summaries and conclusions obtained are as follows:

- (1) The pH-contact angle curve and SDBS concentration-contact angle curve have been determined with regards to the contact angles between the oil/water interface and the monazite surface across the aqueous phase.
- (2) Combining the measurement of the interfacial tension of the oil/water interface with Gibb's equation, the adsorption density of dodecylbenzenesulfonate ions at the oil/water interface has been determined.
- (3) In the liquid-liquid extraction of monazite, it is recognized that a good agreement can be obtained among the contact angles, the work of adhesion and the recoveries when the concentration of SDBS is fixed. A maximum contact angle around pH 7 corresponds to the maximum work of adhesion and recovery. In addition the contact angles, the work of adhesion and the monazite recoveries decrease with an increase in the pH above 7. In the acidic solution at pH below 7, the contact angles, the work of adhesion and the recoveries are increased as the SDBS concentration is increased. From the result obtained above, it can be deduced that the hydrophobicity of the solid increases when the electrostatic adsorption of the surfactant ions on the solid increases. Also, it promotes the wetting of monazite by iso-octane, which causes high recoveries with an increase in the concentration of the surfactant.
- (4) It has been pointed out that at a high concentration of SDBS the recovery of monazite is independent of the contact angle. For this reason, it can be considered that the dense adsorption of the surfactant ions at the oil/water interface prevents the hydrocarbon chains of the ions adsorbed on the monazite particle from penetrating into the oil droplet. For that reason, the work of adhesion for iso-octane on the monazite surface, that is, the wettability of monazite for oil is reduced, thus decreasing the monazite recoveries.

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