

Separation of PET and PVC by Flotation

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Separation of PET and PVC is a key technology to achieve effective plastics recycling but no efficient and economically feasible method has been developed yet. The application of flotation was investigated by many researchers but the causes of the selectivity were not clarified. This paper described the adsorption mechanism of wetting agents onto plastics, using the agents which have various polarity and hydrocarbon chain length. It was found that (1) hydrophobic interaction played a predominant role for the adsorption, (2) anionic wetting agents could be adsorbed onto negatively charged plastics with the polar radicals oriented outer part of the plastics, then often depressed plastics more effectively than cationic agents, and (3) PET and PVC could be separated with dodecylamine hydrochloride and sodium dodecylsulfonate in the concentration ranges of 1.0×10^{-6} – 5.0×10^{-5} and 2.0×10^{-6} – 1.0×10^{-5} mol/l, respectively.

Keywords: PET, PVC, Flotation, Wetting agent, Adsorption mechanism, Hydrophobic interaction, Electrostatic interaction

Introduction

Waste plastics treatment is one of the most important problems to be solved in resources recycling both for materials recycling and energy recovery. Many processes have been developed for the separation of plastics but most of them are based on the difference in their specific gravity. However, separation of PET and PVC which is a key technology in plastic recycling is remained difficult because of their similar specific gravity and cannot be achieved by any types of gravity separation methods. Electrostatic separation is a choice for their separation but the efficiency is easily influenced by humidity and dust particles in the circumstances and by impurity particles which are adsorbed on waste plastic particles.

The application of flotation to the plastics separation has been investigated from old days but the mechanism, how wetting agents can be adsorbed selectively onto plastic surface, has not been clarified yet. In this study, the effect of hydrophobic and electrostatic interactions between plastic surface and wetting agents on the flotation behavior is discussed. In the experiment, several types of wetting agents with different ionic property and hydrocarbon chain length were used.

Sample materials

PET samples used in flotation test were fresh bottles of 1.5 liter capacity which were manufactured by the Toyo Seikan Kaisha Ltd. The average thickness and specific gravity of the PET samples were measured 0.38 mm and 1.370, respectively. The Hishi-plate (HP-101) of 0.50 mm thickness manufactured by the Mitsubishi Chemical Corp. was used as PVC sample of which the specific gravity was measured 1.467. Both plastic samples were cut one by one manually, by using ceramic knife, into 10.0 mm size of square fractions for the flotation tests.

Experimental

Flotation tests were carried out in the Kyoto University type cell (made of glass) with 1800 ml deionized and distilled water and 50 plastic fractions for one batch of flotation tests. Conditioning with wetting agents was carried out for 10 min in the same flotation cell with the same volume of water and the number of plastic fractions as in the flotation tests. Sodium alkylsulfonates and alkylamine hydrochlorides with different length of hydrocarbon chain were used as wetting agents (see Table 1). After conditioning, MIBC was added into the cell (8.917×10^{-5} mol/l), then flotation was started. Plastic samples floated were recovered by mesh ladle after each 1 min to know the flotation kinetics and flotation was terminated after 10 min from the start. Solution pH was not controlled by any regulators both in conditioning and flotation stages.

Table 1 Wetting agents used in the experiments.

Cationic wetting agents	Mole. weight	CMC* ($\times 10^{-3}$ mol/l)	HLB*
n-Butylamine hydrochloride, (AC4) CH ₃ (CH ₂) ₃ NH ₃ Cl	109.60	-	9.57
n-Hexylamine hydrochloride, (AC6) CH ₃ (CH ₂) ₅ NH ₃ Cl	137.65	-	7.62
2-Octylamine hydrochloride, (AC8) CH ₃ (CH ₂) ₇ NH ₃ Cl	165.71	40.0	6.33
n-Dodecylamine hydrochloride, (AC12) CH ₃ (CH ₂) ₁₁ NH ₃ Cl	221.81	13.0	4.73
Anionic wetting agents	Mole. weight	CMC* ($\times 10^{-3}$ mol/l)	HLB*
1-Sodium butylsulfonate, (SS4) CH ₃ (CH ₂) ₃ SO ₃ Na	160.17	-	12.87
1-Sodium hexylsulfonate, (SS6) CH ₃ (CH ₂) ₅ SO ₃ Na	188.22	-	10.95
1-Sodium octylsulfonate, (SS8) CH ₃ (CH ₂) ₇ SO ₃ Na	216.27	155	9.53
1-Sodium decylsulfonate, (SS10) CH ₃ (CH ₂) ₉ SO ₃ Na	244.33	41.0	8.43
1-Sodium dodecylsulfonate, (SS12) CH ₃ (CH ₂) ₁₁ SO ₃ Na	272.38	10.0	7.56

* CMC: Critical Micelle Concentration

* HLB : Hydrophilic-Lipophilic Balance

Results and discussion

Importance in hydrophobic interaction

Experimental results of flotation tests are shown in Figures 1-4 as relationships between flotation rate and the concentration of wetting agent. Solution pH was measured 6 – 7 under any flotation conditions. It is clear that the depression of plastic particles occurs at concentrations much less than their CMCs for all wetting agents. Since PET and PVC surfaces are reported [4,5] charged negatively in natural pH, it is considered that wetting agents are concentrated near the plastic surfaces which are negatively charged, even (anionic) sodium sulfonates to form probably (reverse) hemi-micelle on the surface. It can be demonstrated that hydrophobic interaction plays much more significant role for the wetting agents to be concentrated near plastic surface than electrostatic interaction.

From the figures, in case using sulfonates, the order of the magnitude of flotation rate is SS12 < SS10 < SS6 < SS8 < SS4 both for PET and PVC and the order in case of

amines is SS12 < SS8 < SS6 < SS4 also for both plastics. It is clear that hydrocarbon chain length of wetting agents is strongly influential to decrease flotation rate, which indicates that the hydrophobic interaction between wetting agent and plastic surface plays a dominant role in the attraction of the two phases in plastics flotation.

Comparing the flotation rates between PET and PVC with the same wetting agent (especially AC8, AC12, SS10 and SS12), PET shows larger values than PVC. The degree of hydrophobicity is considered smaller on PET surface than on PVC surface because solubility parameters can be calculated 22.0 and 19.7 (MJ/m³)^{1/2} for PET and PVC, respectively. It is well recognized that the higher the hydrophobic interaction between plastic surface and wetting agent, the lower the flotation rate is.

Jacobash [4] reported that the amount of cationic surfactants required to reverse the surface potential of plastic surface is larger for the plastics having relatively lower hydrophobicity than for those of higher hydrophobicity. Polarity of plastics, in other words hydrophobicity, is also considered predominant to control the flotation behavior.

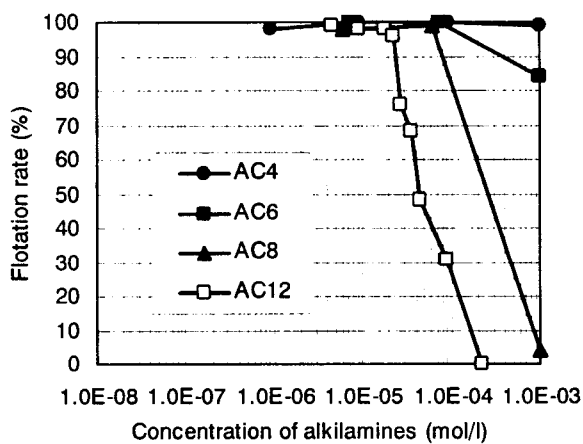


Figure 1 Flotation rate of PET as a function of alkylamine concentration.

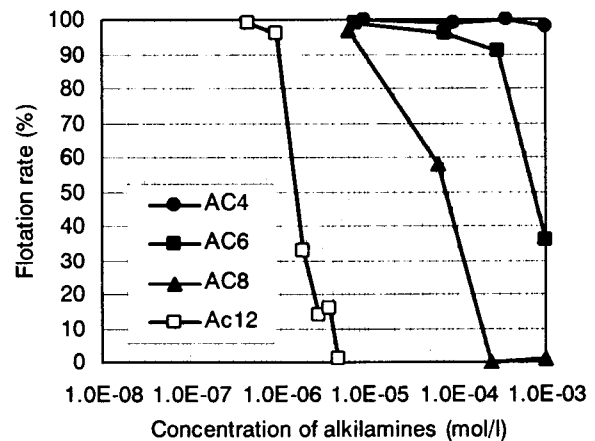


Figure 3 Flotation rate of PVC as a function of alkylamine concentration.

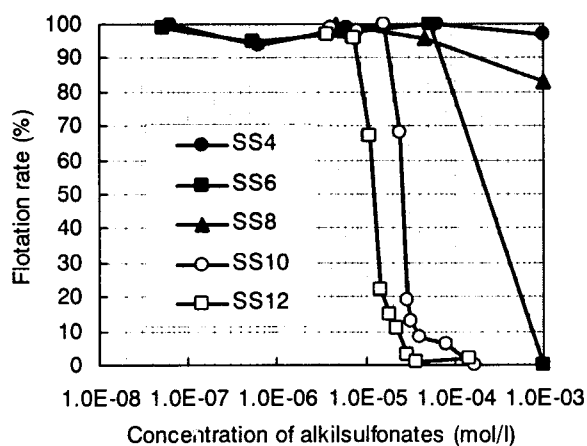


Figure 2 Flotation rate of PET as a function of alkylsulfonate concentration.

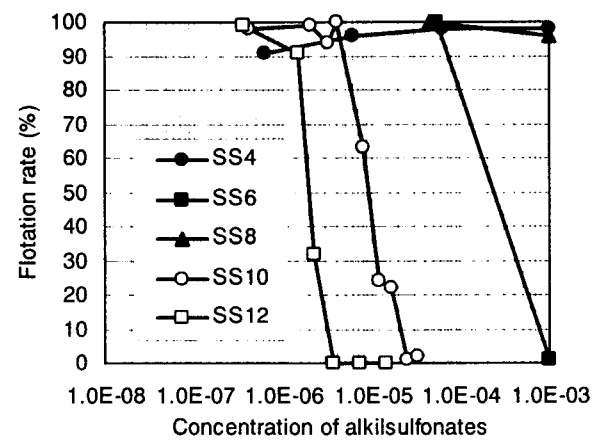


Figure 4 Flotation rate of PVC as a function of alkylsulfonate concentration.

Effect of electrostatic interaction

Considering electrostatic interaction between plastic surface and wetting agent, one can easily imagine that cationic wetting agents are more easily adsorbed onto the plastic surface which is negatively charged. However, flotation rates with anionic sulfonate ions often show higher values than those with cationic amines. For example, in case of PET, the effectiveness of depression is $SS6 > AC6$, $SS8 = AC8$, and $SS12 > AC12$, and in case of PVC, $SS6 > AC6$, $SS8 < AC8$, and $SS12 = AC12$. Generally speaking, sulfonates are more effective than amines in the range of short hydrocarbon chain length (C6) and once become less effective or equal than/to amines in the range of middle length of hydrocarbon chain (C8–10), then sulfonates are again back to be more effective or equal than/to amines in the range of long hydrocarbon chain (C12). These phenomena are considered to be able to be explained by the following adsorption mechanism.

Cationic amine ions can be adsorbed onto plastic surface both by hydrophobic and electrostatic interactions, thus some of them may also be adsorbed onto plastics in the form, laying on the plastic surface and/or keeping hydrocarbon chain oriented outer part of the plastic surface.

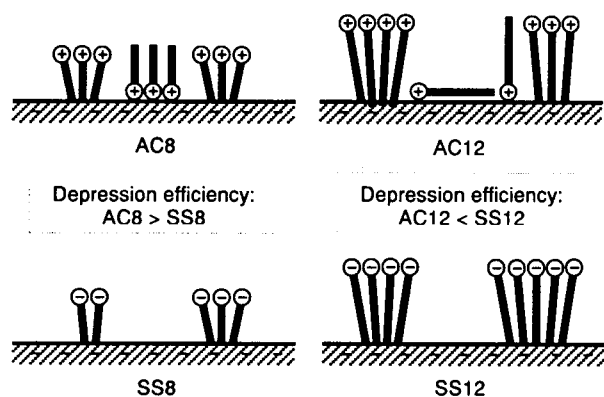


Figure 5 Adsorption model onto PET for wetting agents of various polarity and hydrocarbon chain length.

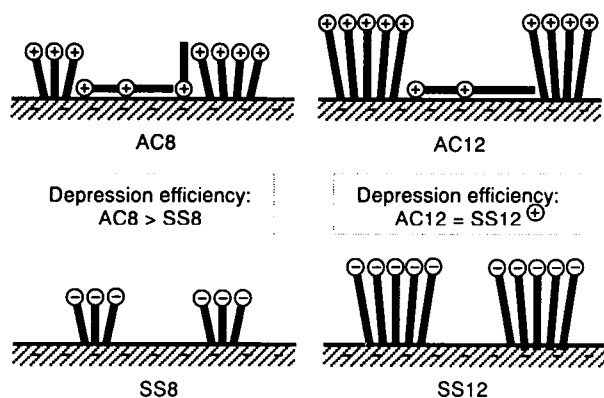


Figure 6 Adsorption model onto PVC for wetting agents of various polarity and hydrocarbon chain length.

On the other hand, since anionic sulfonate ions are adsorbed only by hydrophobic interaction, most of them must be adsorbed in the form keeping polar (hydrophilic) radical oriented outerpart of the plastic surface. Accordingly, sulfonates often have higher ability to depress plastics than amines, even if the number of adsorbed ions is less than amines. As mentioned above, PVC have more hydrophobic surface than PET, in other words, the hydrophobic interaction with wetting agents is higher for PVC than for PET when the same wetting agent is used. These considerations are schematically described in Figure 5 and 6.

Although we have obtained no distinct evidence for this adsorption model yet, such as the amount of wetting agent adsorbed, orientation of wetting agent on plastic surface, this mechanism is considered to be reasonable from the conventional theories of interfacial chemistry.

Flotation kinetics

In general, flotation rate is considered to follow first order kinetics [6] in ore flotation. However, in plastics flotation, there are several factors which are different from the case of ore flotation, such as surface hydrophobicity of particles, particle size and shape, adsorption mechanism of surfactants, and so on. Examples of the relation between flotation rate and time are shown in Figure 7 and 8.

In the cases of amines, flotation rate is almost saturated at a certain value of flotation time, and the rate curves (to flotation time) show almost concave in the cases of sulfonates. In plastic flotation, a lot of air bubbles must be attached onto relatively large plastic surface (size of plastic particles is much larger than that of air bubbles in this study) for the plastic particles to be floated. From the results of various kinetic data, it can be said that the flotation rate at a certain time is determined by the detachment rate of air bubbles from plastic surface, especially in sulfonate flotation. Hydrodynamic effect of water flow in the flotation cell would also influential to the flotation rate, but no obvious evidence could be obtained from this viewpoint.

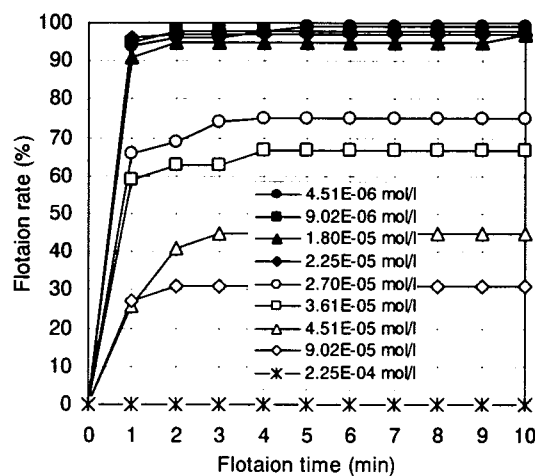


Figure 7 Flotation rate as a function of flotation time using AC12 for PET.

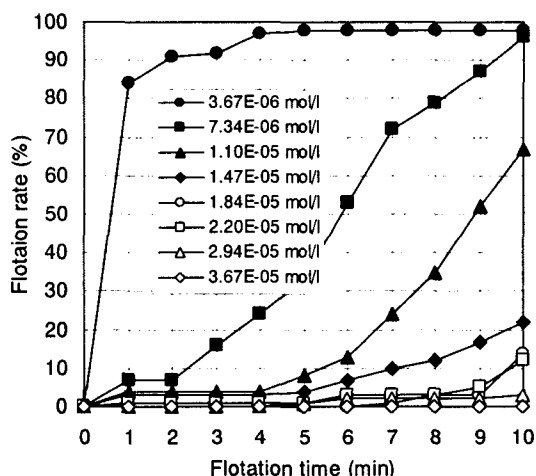


Figure 8 Flotaion rate as a function of flotation time using SS12 for PVC.

Separation of PET and PVC

As mentioned above, PVC is more easily adsorbed by any wetting agents than PET, thus the separation must be achieved between the two plastic species. Separation efficiency, for PET to be separately floated from PVC, is shown in Figure 9 and 10 as a function of the concentration of wetting agents in both cases of amine and

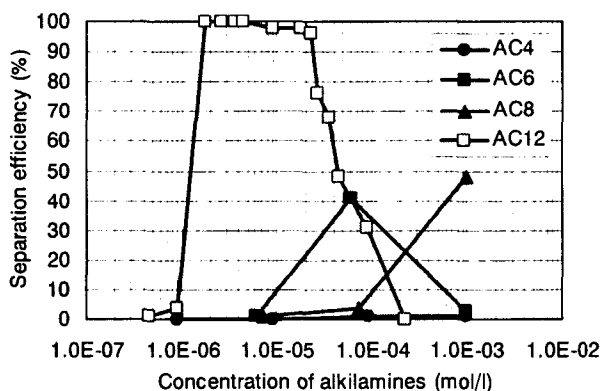


Figure 9 Relation between separation efficiency and alkilamine concentration.

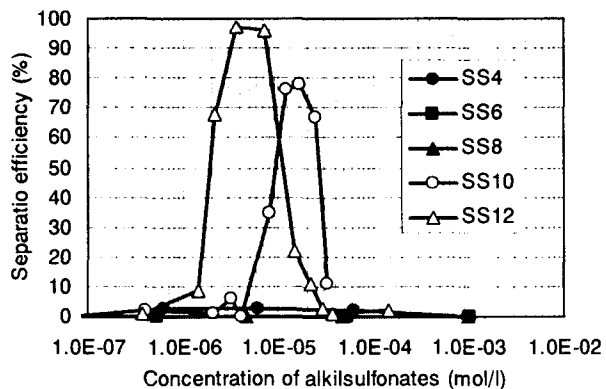


Figure 10 Relation between separation efficiency and alkilsulfonate concentration.

sulfonate flotation. The values were calculated from the data of each single flotation tests. In mixture flotation, which we did not carry out, influence of the interaction between the two plastic species could be estimated negligible, considering the plastic particle size in this study. From the figures, it is recognized that the wetting agents with relatively longer hydrocarbon chains are useful for the separation in both amine and sulfonate flotation. The range of separable concentration of wetting agents is wider in amine flotation than in sulfonate one. The optimum concentration range can be determined approximately 1.0×10^{-6} – 5.0×10^{-5} mol/l for dodecylamine hydrochloride and 2.0×10^{-6} – 1.0×10^{-5} mol/l for sodium dodecylsulfonate.

Conclusion

Plastics flotation was carried out for PET and PVC using simple cationic and anionic wetting agents with different hydrocarbon chain length. The main results obtained are summarized in the following.

- (1) Hydrophobic interaction between plastics and wetting agents plays a predominant role to control flotation behavior under any conditions.
- (2) Anionic sulfonates often showed higher depressing ability than cationic amines, when the hydrocarbon chain is the same length, both for PET and PVC flotation. Hydrophilic (polar) radicals of sulfonate ions can be oriented outer part of the plastic surface and the arrangement is more stable for anionic sulfonates than cationic amines, because the plastic surface is usually charged negatively.
- (3) Flotation kinetics did not follow the first order reaction, different from that of ore flotation. Flotation rate at a certain time would be determined by the detachment rate of air bubbles from plastic surface, especially in sulfonate flotation.
- (4) PET and PVC are considered selectively separated with dodecylamine hydrochloride and sodium dodecylsulfonate in the concentration ranges of 1.0×10^{-6} – 5.0×10^{-5} and 2.0×10^{-6} – 1.0×10^{-5} mol/l, respectively. Selectivity of the two plastics is higher in amine flotation than in sulfonate one.

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