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An Application of the Phase-inversion-temperature Method to the Emulsification of Cosmetics. I. Factors Affecting the Phase-inversion Temperature

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Recently, the PIT (phase-inversion-temperature) system was originated and developed by Shinoda and his collaborators as a guide to surfactant selection. In order to apply the PIT system to the cosmetic field, the effects of various factors on the PIT have been reinvestigated using cosmetic materials. POE alkyl ethers, whose distribution of EO chain lengths is broad, are widely used in cosmetics. In such a case, the effect of the distribution of the EO chain lengths is important. When a surfactant with a distribution of EO chain lengths was used, the PIT was lowered by an increase in the concentration of the surfactant, but when a monodisperse surfactant without any distribution was used, the PIT scarcely varied with the concentration of the surfactant. In the case of the surfactant with a distribution of EO chain lengths, however, if the ratio of oil to surfactant was kept constant, the PIT scarcely varied with the ratio of oil phase to water phase. This relationship can be used in estimating the PIT in the case of the practical production of an emulsion.

An emulsion stabilized with a certain non-ionic surfactant changes its type from the oil-in-water type (O/W) to the water-in-oil type (W/O) as the temperature rises. The emulsion tends to form a W/O type because the affinity of the ethylene oxide (EO) chain of the surfactant for water is weakened at higher temperatures.

The phase-inversion temperature (PIT), at which the emulsion inverts its phase, has been adopted by Shinoda[1] as a guide for choosing a suitable type of emulsifier and for estimating the effects of additives because of its precise indication of the characteristics of the emulsion.

The factors which affect the PIT of the emulsion are[1-12]:

1. the nature of the hydrophilic and lipophilic moieties of the surfactant;
2. the mixing of the surfactants;
3. the nature of the oil;
4. the nature of the additives of the oil and water phases;
5. the concentration of the surfactant;
6. the ratio of oil phase to water phase, and
7. the distribution of EO chain lengths in the surfactant.

In the present study the effects of the above-mentioned factors on the PIT were investigated using cosmetic materials in order to establish the application of the PIT system[1] to the emulsification of cosmetics.

Furthermore, as the PIT is greatly affected by the distribution of EO chain lengths in the surfactant when an oil-soluble surfactant on the market is used, a comparison test was carried out with monodisperse surfactants.

Experimental

Samples. Liquid paraffin, whose Saybolt viscosities were 50 sec, 70 sec and 350 sec at 100°F, dodecane (purity: 98.9%), tetradecane (purity: 99.5%), and squalane were used as the oil bases.

POE ($\bar{n}$=3.7, 4.8, 6.2, 6.9, 8.1 mol) oleyl ether, POE ($\bar{n}$=4.8, 5.9, 6.7, 7.5) stearyl ether, POE ($\bar{n}$=4.0, 5.0 mol) lauryl ether (Nihon Emulsion Co.), and POE (n=4.0, 5.0, 6.0, 7.0, 8.0 mol) lauryl ether (Nikko Chemical Co.; purity: 95—98%, a monodisperse surfactant) were used.

Solid paraffin (mp 62.8°C), oleic acid (purity: 88.0%), oleyl alcohol (purity: 79.5%), lauryl alcohol (purity:

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[1] K. Shinoda, *Nippon Kagaku Zasshi*, **39**, 435 (1968); K. Shinoda, B/O, No. 51, 5th International Congress of Surface Active Substances, Barcelona, Spain (1968).

[2] M. Aoki, A. Kamata and T. Matsuzaki, *Yakugaku Zasshi*, **83**, 1132 (1963).

[3] K. Shinoda and H. Arai, *J. Phys. Chem.*, **68**, 3485 (1964).

[4] H. Arai and K. Shinoda, *Nippon Kagaku Zasshi*, **86**, 299 (1965).

[5] M. Aoki and T. Matsuzaki, *Yakugaku Zasshi*, **87**, 761 (1967).

[6] M. Aoki and T. Matsuzaki, *ibid.*, **87**, 765 (1967).

[7] K. Shinoda, *J. Colloid Interfac. Sci.*, **24**, 4 (1967).

[8] H. Arai and K. Shinoda, *ibid.*, **25**, 396 (1967).

[9] K. Shinoda and H. Arai, *ibid.*, **25**, 429 (1967).

[10] K. Shinoda and H. Takeda, *ibid.*, **32**, 642 (1970).

[11] K. Shinoda and H. Saito, *ibid.*, **26**, 70 (1968).

[12] K. Shinoda edit. Figs. 9 and 11 in Chapter 2 of "Solvent Properites of Surfactant Solutions," Marcel Dekker Inc., New York (1967).

95.0% or over), 2-octyldodecanol (Dehydag Co.), and castor oil (purity: 86.0%) were studied as additives.

Methods. Oil, water, and surfactant were weighed into the same beaker, and then heated with stirring in order to make an emulsion, the total amount being 100 g. The PIT of the emulsion was determined by an electric conductivity device. The reproducibility of the measurements was within ± 1°C.

Results and Discussion

Effect of the HLB Value of the Surfactant and the Nature of Oil on the PIT. Figure 1 shows the effect of the HLB value of the surfactant and the kinds of oils on the PIT. As has already been pointed out by Shinoda and Arai,[3] the PIT's rose almost linearly with the increase in HLB values, and the rising rates were almost identical in all the liquid paraffins used. The PIT's varied with the nature of the oils used, even though surfactants with the same HLB values were used; the greater lipophilic the oil, the higher the PIT. This fact can be explained in terms of the difference in the required HLB values of the oils.

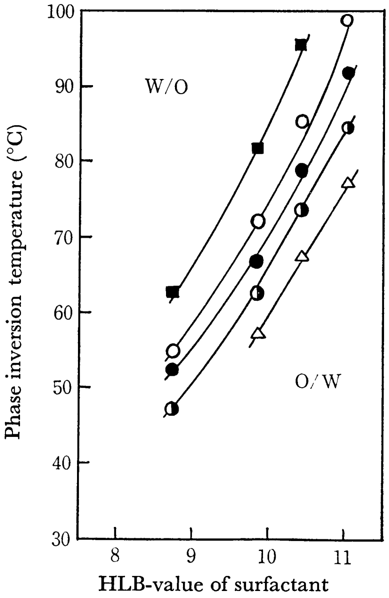

Fig. 1. Effect of different hydrocarbons on PIT *vs.* HLB-value of surfactant.
Surfactant: POE stearyl ether, 5 wt%/system
Phase ratio: 0.5 (wt).
■: squalan, ○, ●, ◑: liquid paraffin (Saybolt vis. 350, 70, 50 at 100°F respectively), △: tetradecane.

Effect of Additives on the PIT. Shinoda *et al.* studied the effect of added salts in water on the PIT,[10] and Aoki *et al.* studied some oil-soluble components.[6] We have studied the effect of additives on the oil phase because cosmetics always contain several additives in the oil phase. Figure 2 shows the effects of some oil-soluble additives on the PIT of a three-component system, consisting of liquid paraffin (70 Saybolt viscosity at 100°F), POE (4.8 mol) oleyl ether, and water. When liquid paraffin was replaced with 20% of solid paraffin, which is a non-polar substance, the PIT rose about 10°C. On the contrary, when it was replaced with only 1% of oleyl alcohol, lauryl alcohol, or oleic acid, which are polar substances, the PIT fell about 20—40°C. When a mixture consisting of solid paraffin and oleyl alcohol (the former raises the PIT, while the latter lowers it) in an appropriate ratio was added to the system, it showed the same PIT as the one to which no additive had been added. Thus, when a small quantity of an additive was added to the oil phase, the PIT rose or fell monotonously according to the quantity added. In the cases of 2-octyldodecanol, castor oil, etc., however, as is shown in Fig. 3, the minimum value of the PIT appeared.

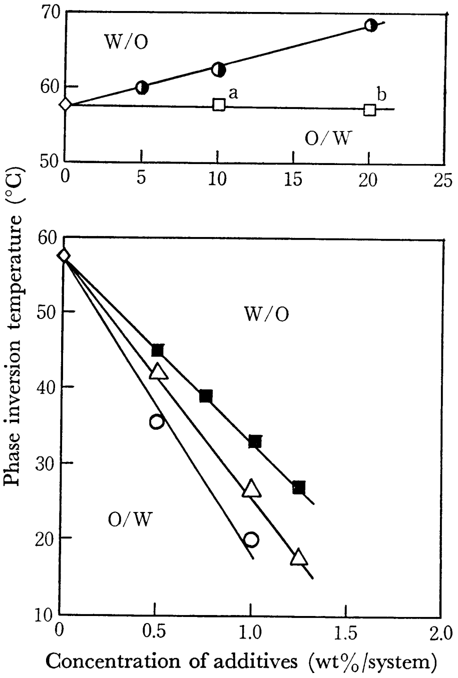

Fig. 2. Effect of different additives on PIT.
Oil: liquid paraffin (Saybolt vis. 70) plus additives.
Surfactant: POE ($\bar{n}$=4.8) oleyl ether, 4 wt%/system.
Phase ratio: 0.5 (wt).
◑: solid paraffin, □: solid paraffin plus oleyl alcohol (a, b: oleyl alcohol 0.23, 0.5 wt%/system respectively), ■: oleyl alcohol, △: lauryl alcohol, ○: oleic acid.

Effect of the Concentration of the Surfactant and the Ratio of Oil Phase to the Water Phase on the PIT. The relationship between the concentration of the surfactant and the PIT was in-

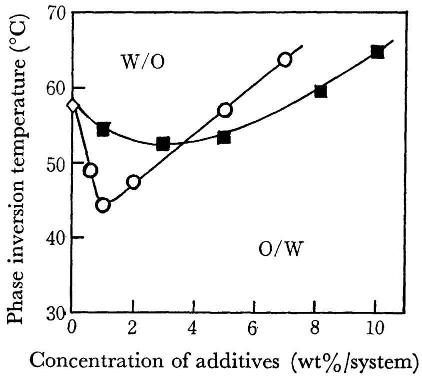

Fig. 3. Effect of castor oil and 2-octyldodecanol on PIT.
Oil: liquid paraffin (Saybolt vis. 70) plus additives.
Surfactant: POE ($\bar{n}$=4.8) oleyl ether, 4 wt%/system.
Phase ratio: 0.5 (wt).
○: castor oil, ■: 2-octyldodecanol.

vestigated by Shinoda *et al.*[3,9,10] using POE alkyl phenyl ether. In the present study, this relationship was reinvestigated using POE alkyl ether, whose distribution of EO chain lengths is broad. The results are shown in Fig. 4. As the concentration of the surfactant increased, the PIT was lowered very steeply compared with the case[3] of POE alkyl phenyl ether. Especially in the case of a surfactant with a shorter EO chain, the falling rate of the PIT was remarkable. It was found that the effect of the distribution of EO chain lengths on the PIT is greater when the average EO chain length is shorter.

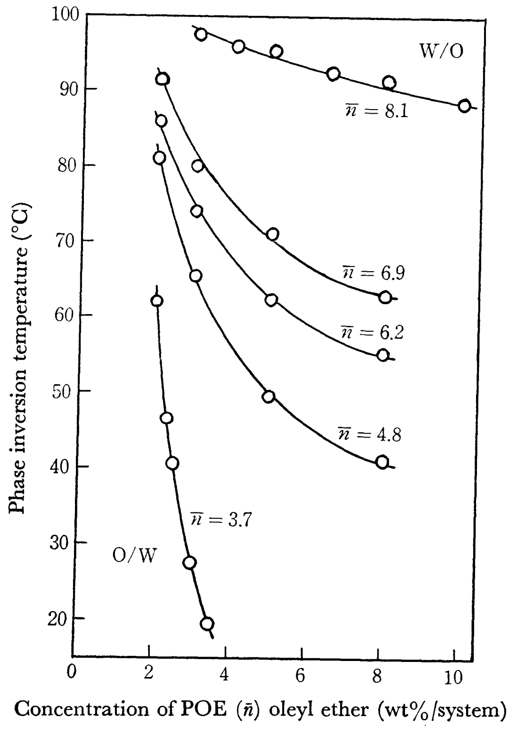

Fig. 4. Effect of ethylene oxide chain length on PIT *vs.* concentration of POE oleyl ether.
Oil: liquid paraffin (Saybolt vis. 70).
Phase ratio: 0.5 (wt).

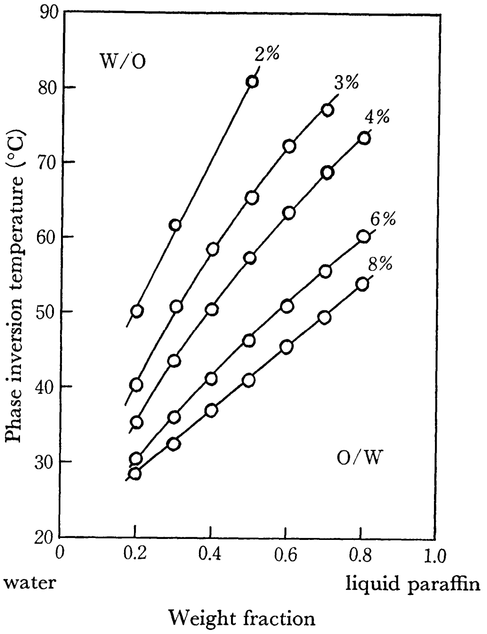

Fig. 5. Effect of concentration of POE ($\bar{n}$=4.8) oleyl ether on PIT *vs.* phase ratio.
Oil: liquid paraffin (Saybolt vis. 70).

The effect of the phase ratio on the PIT was studied using various concentrations of POE oleyl ether, the average EO chain length of which was 4.8 mol. The results are shown in Fig. 5. As the oil-phase ratio became higher, the PIT rose more steeply compared with the case[3] of POE alkyl phenyl ether in a non-polar oil. Furthermore, the lower the concentration of surfactant, the higher the rate of the rise of PIT. However, it can be found from Fig. 5 that when the ratio of the oil to the surfactant is constant, almost the same PIT can be obtained in the same manner as with POE alkyl phenyl ether.[12] For example, the PIT of 50°C is obtained when the oil-phase ratio: concentration of surfactant is 0.2 : 2%, 0.3 : 3%, or 0.4 : 4%.

Therefore, while keeping the ratio of oil to the surfactant fixed, the PIT's were measured at various oil-phase ratios. As is shown in Fig. 6, even though the ratio of oil phase to water phase varied in the range of 0.2—0.8, the PIT was almost constant if the ratio of the oil to the surfactant was fixed. Furthermore, the higher the ratio of the surfactant in the oil phase, the lower the PIT.

In the case of the practical production of emulsion, it would be very convenient if the PIT could be calculated. Therefore, utilizing the above-men-

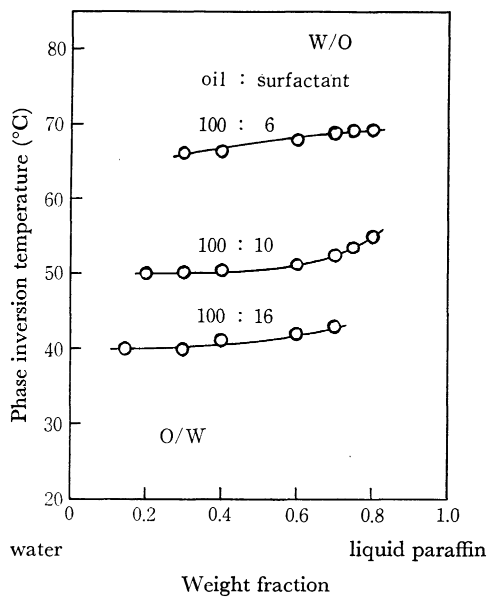

Fig. 6. Effect of phase ratio on PIT in various ratios of surfactant to oil.
Oil: liquid paraffin (Saybolt vis. 70).
Surfactant: POE ($\bar{n}$=4.8) oleyl ether.

tioned relationship, the PIT's were plotted *vs.* the ratio of the oil to the surfactant as well as the ratio of water to the surfactant, as is shown in Fig. 7. It can be found from Fig. 7 that the PIT rises almost linearly with the increase in the ratio of the oil to the surfactant. If such a straight line has been obtained by measuring two PIT's at two different ratios of oil to surfactant, the PIT of a given system can be estimated from its components, *i.e.*, the concentration of the surfactant and the ratio of oil phase to water phase. For example, in the case of a 3% concentration of the surfactant and an oil-phase ratio of 0.3, it can be estimated from Fig. 7 that the PIT is about 50°C.

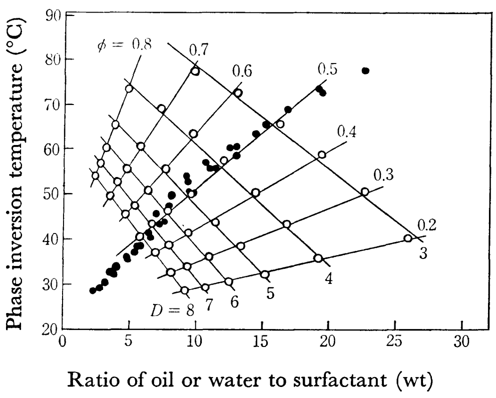

Fig. 7. Correlation between PIT and ratio of oil or water to surfactant.
ϕ: ratio of oil to water (wt).
D: concentration of surfactant (wt%/system).
Oil: liquid paraffin (Saybolt vis. 70).
Surfactant: POE ($\bar{n}$=4.8) oleyl ether.
●: oil/surfactant, ○: water/surfactant.

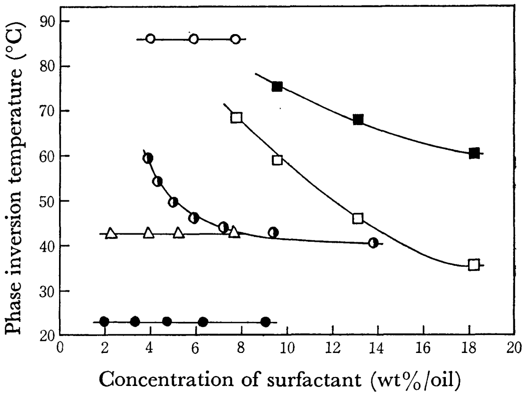

Fig. 8. Effect of distribution of ethylene oxide chain lengths on PIT *vs.* concentration of surfactant.
Oil: dodecane.
Phase ratio: 0.5 (wt.).
Surfactant: POE laurylether.
Monodisperse surfactants: ○: n=8, △: n=5, ●: n=4, ◑: n=8 plus n=4 (1 : 3.4).
Polydisperse surfactants: ■: $\bar{n}$=5, □: $\bar{n}$=4.

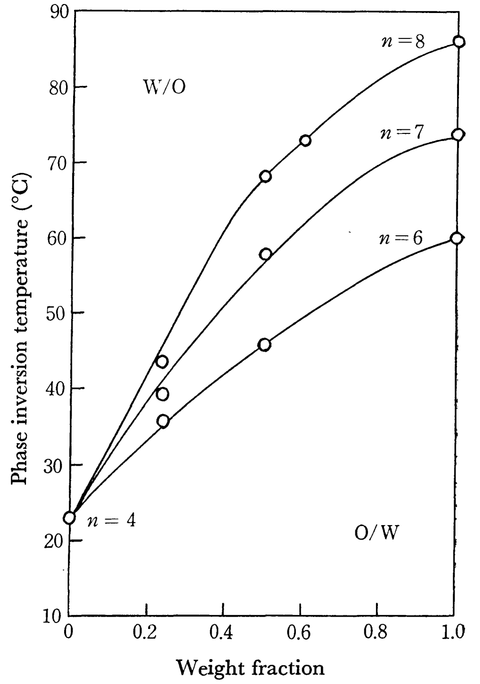

Fig. 9. Effect of mixing of surfactant on PIT.
Oil: dodecane.
Phase ratio: 0.5 (wt).
Surfactant: POE (n) lauryl ether (monodisperse), 4 (wt%/system).

Effect of the Distribution of the EO Chain Lengths in the Surfactant on the PIT. When the concentration of the surfactant was increased, the PIT was lowered, as is shown in Fig. 4. In the case of a surfactant whose average EO chain length is short, the falling rate of the PIT was very high.

Dodecane was used as the oil phase; it was emulsified with POE lauryl ethers with and without the distribution of EO chain lengths. The relationship between the PIT and the concentration of the surfactant is shown in Fig. 8. When a surfactant with a distribution of EO chain lengths was used, the PIT varied greatly with the concentration of the surfactant. However, when a monodisperse surfactant was used, the PIT scarcely varied, though the concentration of surfactant did vary. When a mixed surfactant of POE (n=8 mol) lauryl ether and POE (n=4 mol) lauryl ether, which are both monodisperse surfactants, was used, the PIT rose upon a decrease in the concentration of the mixed surfactant, as in the case of using a surfactant with a distribution of EO chain lengths. It can be assumed that the ratio of a surfactant with a shorter EO chain to one with a longer EO chain decreased at the interface upon a decrease in the concentration of the mixed surfactant, because the CMC of a nonionic surfactant in oil is far higher that the CMC in water; the average EO chain length of a surfactant affecting phase inversion increased, and the PIT rose.

From the same point of view, the relationship between the PIT and the mixing ratio of the surfactants was investigated using monodisperse surfactants. The results are shown in Fig. 9. The curves are convex, and when the surfactants are mixed the PIT moves to a higher position.