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The Stability of O/W Type Emulsions as Functions of Temperature and the HLB of Emulsifiers: The Emulsification by PIT- method

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The properties of emulsions containing 3 wt % of polyoxyethylene nonylphenylether per system were studied as functions of temperature, composition, and the hydrophile-lipophile balance (HLB) of emulsifiers. It has been found that (a) the size of emulsion droplets changes remarkably with temperature and HLB of emulsifiers, (b) the diameter of droplets is very small but less stable towards coalescence close to the phase inversion temperature (PIT), (c) relatively stable O/W type emulsions are obtained when the PITs of respective systems are about 20º - 65ºC higher than the storage temperature, (d) a stable and fine emulsion is obtained by rapid cooling of an emulsion emulsified at the PIT, which process we shall designate **"emulsification by the PIT - method",** and (e) the optimum stability of an emulsion is relatively insensitive the change of the HLB values or PITs of emulsifiers, but the instability of an emulsion is very sensitive to the PIT of the system. It seems difficult to determine the optimum HLB value of an emulsifier accurately from the stability vs HLB value relation. On the other hand, since the change in the stability of an emulsion is sensitive to the temperature near the PIT, the selection of an emulsifier according to the PIT may be more accurate and reliable.

INTRODUCTION

In the preceding paper the phase diagram and the dispersion types of water- cyclohexane systems containing 3 and 7 wt% of polyoxyethylene (9.7) nonylphenylether were studied as a function of temperature.(1)

The present investigation was undertaken (1) to determine the mean droplet diameter and the stability of emulsions as functions of temperature and the hydrophile-lipophile balance (HLB) of the emulsifier, and (2) to determine the correlations among the optimum temperature for stable emulsification, the optimum hydrophilic chain length, and the PIT of emulsifiers. In addition, the "emulsification by the PIT-method," which affords more uniform and stable emulsions, was created.

EXPERIMENTAL

Materials The cyclohexane used was extra pure grade material. Polyoxyethylene nonylphenylethers used were research samples furnished from Kao Soap Co. through the kindness of Dr. H. Arai. These samples were used without purification, so that present results are directly applicable to the practical use of emulsifiers. The comparison between the properties of the purified material and the commercial material will be published elsewhere.

Procedures. About 6 gm of sample composed of oil, water, and noionic surfactant was sealed into an ampoule (inner diameter 16.5 mm) and the ampoule was shaken gently in order to attain approximate dissolution equilibrium at first. After 1 hour the ampoule was shaken 20 times in 5 sec with 15 cm amplitude followed by 5 sec settling, and this process was repeated 6 times in 55 sec. The mean volume diameter was determined by observation through a phase contrast microscope. (The mean volume diameter $D = \sqrt[3]{\sum n_i D_i^3 / \sum n_i}$).

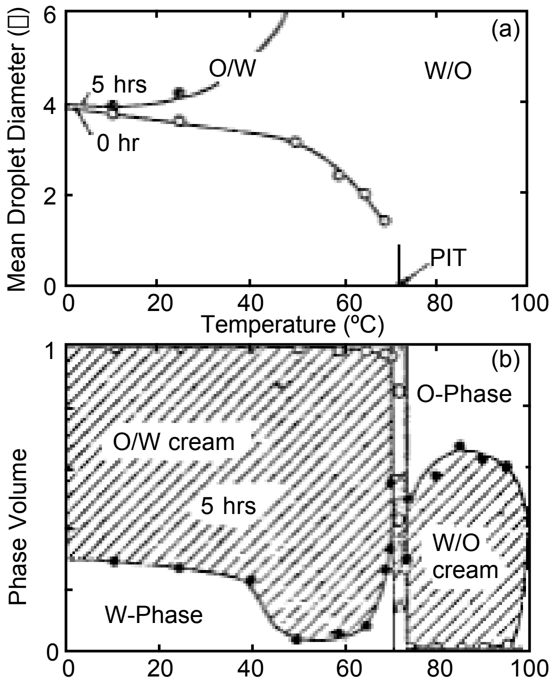

Fig1. (a) (Upper). The effect of temperature on the mean volume diameter of emulsions containing 3 wt% polyoxyethylene (9.7) nonylphenylether, 48.5 wt% cyclohexane and 48.5 wt% water immediately after (0 hour) and 5 hours after emulsification. (b) (Lower). The effect of temperature on the volume fractions of oil, cream, and water phases in the same system. After emulsification with a single emulsifier the system was maintained at the temperature indicated for 5 hours.

RESULTS AND DISCUSSION

The effect of emulsification temperature oil on the mean volume diameter of O/W type emulsions of the ternary system composed of 3 wt% of polyoxyethylene (9.7) nonylphenyl-ether, 48.5 wt% of water, and 48.5 wt% of cyclohexane has been studied and shown in Fig. la (upper figure). The volume fractions of oil cream and water phases of the same system 5 hr after agitation are shown in Fig. 1b (lower figure). Cream phase means an O/W type below the PIT and a W/O type above the PIT. (The PIT of this system was 72ºC).

As can be seen in Fig. 1a, the mean volume diameter was smallest close to the PIT and monotonically increased with the temperature decrease. In course of time, the droplet diameter increases rapidly close to the PIT, because the coalescence proceeds very rapidly near the PIT, but it increases much more slowly at lower temperature, because the coalescence rate is slow and the viscosity of the medium is larger. It is evident from Fig. 1b that the mean volume diameter, coalescence rate, etc., of an emulsion stabilized with a definite nonionic emulsifier vary remarkably with temperature. As for the O/W type emulsion, the drainage rate was slow at about 20ºC below the PIT, but for the W/O type emulsion it was slow at about 10º-20ºC above the PIT. As the PIT varies with the types of oils and the hydrophilic chain lengths of nonionic emulsifiers, it is readily understood that the optimum PIT, i.e., the optimum hydrophilic chain length of emulsifier, is required to get a better emulsion for respective oils and temperature.

The interaction between the hydrophilic moiety and water increase with the temperature decrease, so that the increase of hydrophilic chain length of the emulsifier may have an effect similar to the temperature decrease of the system. In order to confirm this view, the effect of the hydrophilic chain length (the PITs) of a series of noionic agents on the mean volume diameter and the stability of emulsions of an O/W type has been studied and plotted in Fig. 2a and 2b.

The higher the PIT of the emulsifier above the experimental temperature, the larger the emulsion droplets. This finding is consistent with the results obtained in Fig. 1, i,e., the lower the emulsification temperature, the larger the droplet diameter of a system stabilized with a definite emulsifier. It is concluded from Fig. 2 that emulsifiers the PITs of which are about 25º - 70ºC higher than storage temperature yield the most satble emulsions. Thus, it is possible to screen a suitable emulsifier for given ingredients at a given temperature by the use of the PIT data.

Emulsification by PIT Method. It is readily anticipated from the experiments shown in figs. 1 and 2 that a better emulsion can be obtained if a sistem is shaken at first close to the PIT (about 2º - 4ºC below the PIT is the best) to fine dispersion and then rapidly cooled down

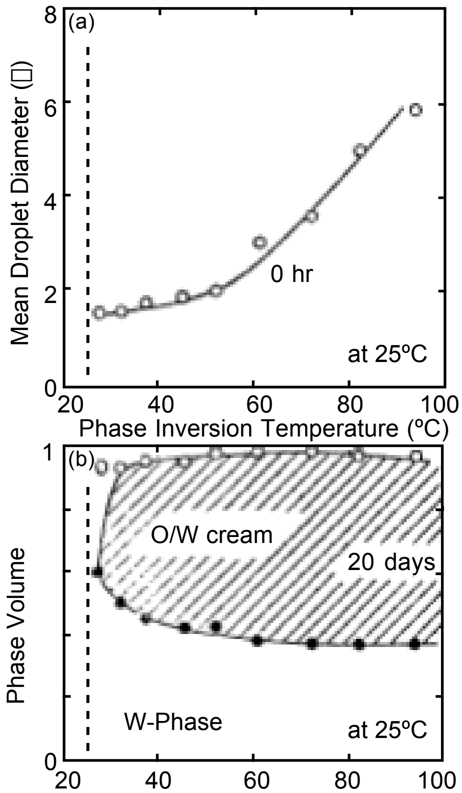

Fig. 2. (a) The effect of PIT (hydrophilic chain length) of emulsifier on the mean volume diameter of emulsions containing 3 wt% polyoxyethylene (6.3 - 14.6) nonylphenylethers, 48.5 wt% cyclohexane and 48.5 wt% water. (b) The effect of PIT of emulsifier on the volume fraction of oil, cream, and water phases 20 days after emulsification. (Emulsified and stored at 25º using a series of polyoxyethylene nonylphenylethers the PITs of which vary from 27º to 94ºC).

to storage temperature, at which the coalescence rate is slow. We designate this process as "emulsification by the PIT-method". In order to test this method, the effect of emulsification temperature on the mean volume diameter was studied in three systems in which the volume ratios of oil vs water were 1, 1/4, an 1/9 respectively. The results are plotted in Fig. 3. It is clear that emulsification at the PIT (slightly below) always affords smaller droplets of O/W type. On the contrary, emulsification at a temperature higher than the PIT means emulsification to a W/O type at first and then inversion to an O/W type by cooling. Present results tell us that "emulsification by the inversion method" is not as good as "emulsification by the PIT-method".

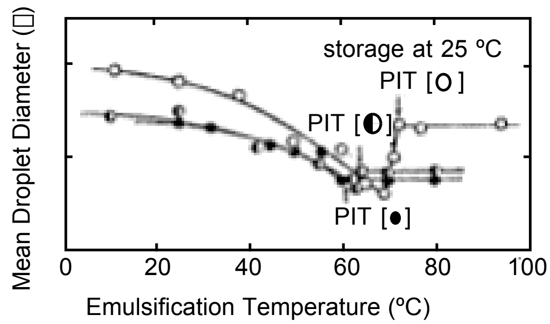

Fig. 3. The effect of phase volume ratio on the mean volume diameter of emulsions containing 3 wt% per system of polyoxyethylene (9.7) nonylphenylether emulsified at temperature indicated and cooled down to 25ºC for observation. The weight ratios of water to cyclohexane were 1/1, O; 4/1, ◐; and 9/1, ●.

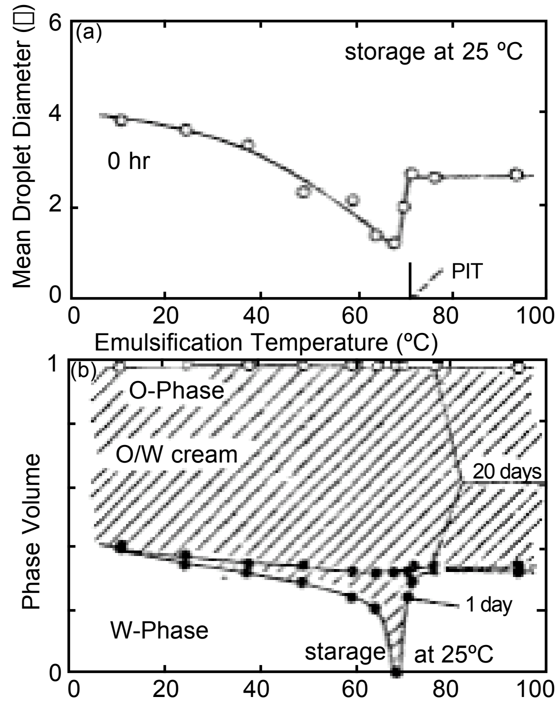

Fig. 4. (a) The effect of the emulsification temperature on the mean volume diameter of emulsions containing 3 wt% polyoxyethylene (9.7) nonylphenylether, 48.5 wt% cyclohexane, and 48.5 wt% water. (b) The effect of the emulsification temperature on the volume fractions of oil, cream, and water phases of the same emulsion 20 days after agitation. After emulsification with a single emulsifier the system was stored at 25ºC.

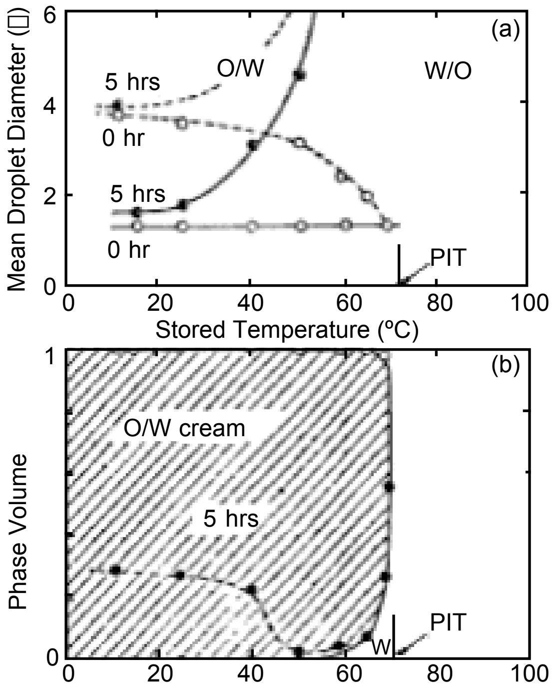

Fig. 5. (a) The mean volume diameter of O/W type emulsions (3 wt% polyoxyethylene (9.7) nonylphenylether, 48.5 wt% cyclohexane, and 48.5 wt% water) emulsified at the PIT and then cooled to and held at the temperature indicated. Holding times were 0 hour and 5. Dotted curve illustrates the mean droplet diameter of the same system emulsified and stored at one temperature. (b) The effect of storage temperature on the volume fractions of the oil, cream, and water phases of the system prepared as in 5(a) and stored 5 hours.

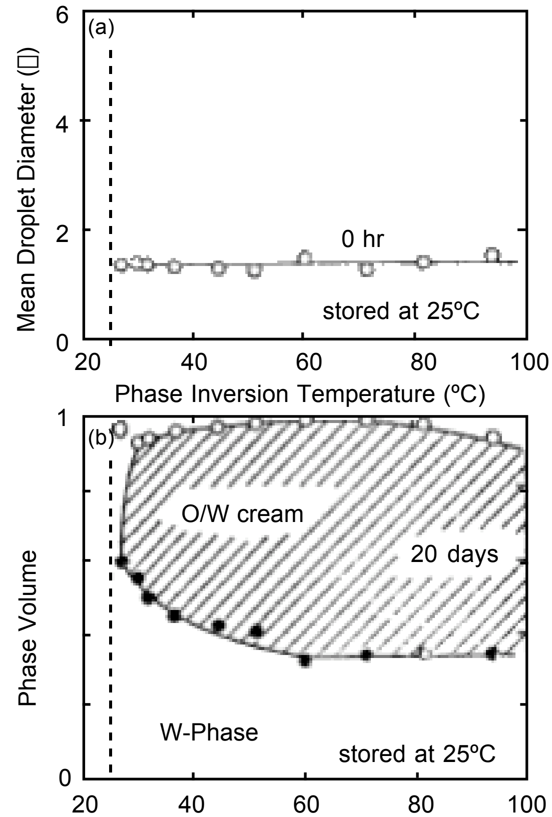

Fig. 6. (a) The effect of the PIT, i.e., the hydrophilic chain length, of the emulsifier on the mean volume diameter of emulsions containing 3 wt% of polyoxyethylene nonylphenylethers, 48.5 wt% cyclohexane, and 48.5 wt% water. (b) The volume fractions of the oil, cream, and water phases of the above systems 20 days after agitation (emulsified at the PIT and stored at 25ºC).

In the usual "emulsification by the inversion method" an emulsifier is dissolved in the oil phase. The emulsion may then be formed by adding water directly to the mixture. In this case, a W/O emulsion is formed at first and then inverted to an O/W type by the addition of further water. On the other hand in "emulsification by PIT-method", emulsifier, oil and water are mixed at the same time at slightly below the PIT. An O/W type emulsion may be formed at this temperature, and then the emulsion is cooled down to the storage temperature. In this respect also, the PIT is an important characteristic property of emulsion.

As the effect of phase volume is not significant, the stability of an emulsion as a function of emulsification temperature has been observed for a system which contains equal amounts of oil and water and is plotted in Fig. 4. Although the effect of emulsification temperature on the stability of the emulsion judged from the phase volumes of oil, cream, an water phases is not very distinct, emulsification at a higher temperature (especially near the PIT) and cooling to storage temperature are effective in obtaining fine and uniform dispersions.

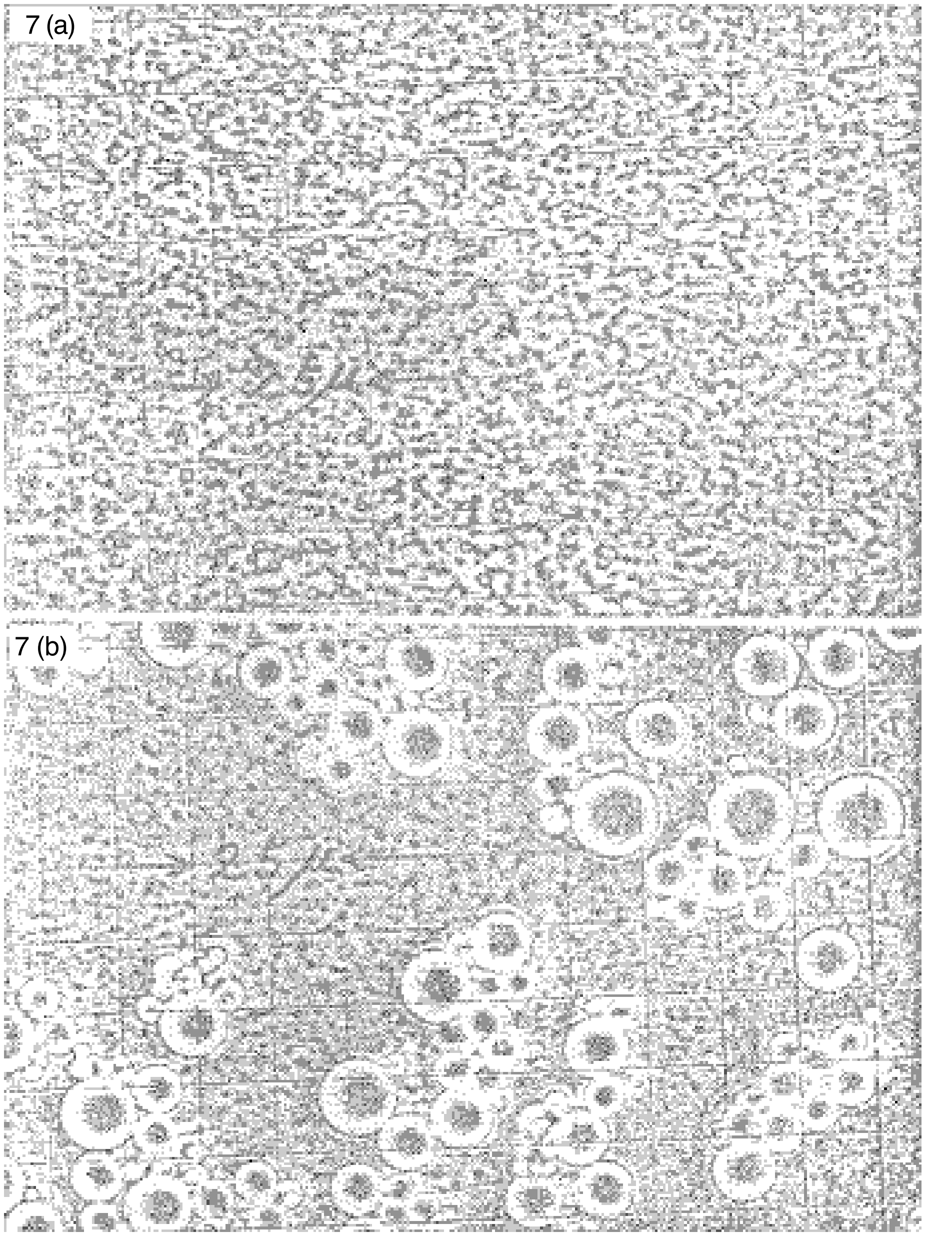

Fig. 7. (a) Emulsion prepared by the PIT-Method, emulsified at 49ºC and cooled down to 25ºC. The PIT of this system was 52ºC. (b) Emulsion prepared by simple shaking at 25ºC.

Comparison of Emulsions Prepared by Simple Shaking and Those by the PIT-Method. The mean volume diameters of emulsions emulsified at the PIT and cooled down to various storage temperature, as well as the phase volumes of oil, cream, and water phases of the same system, are shown in Fig. 5. The mean volume diameter of emulsions made at several temperatures without cooling is also shown for comparison by the dotted line. It is evident from Fig. 5 that (1) the smaller droplets are obtained by emulsification at the PIT regardless of the storage temperature and thus (2), emulsions stored at lower temperatures, at which the coalescence rate is slow, are more stable.

Using a series of polyoxyethylene nonylphenylethers the PITs of which change over a wide temperature range, we applied the emulsification by the PIT-method for the cyclohexane - water system. The mean volume diameter and phase volumes of the respective phases as a function of the PITs of emulsifiers are plotted in Fig. 6. The initial droplet was equally small regardless of the PITs, whereas the emulsions shaken and stored at 25ºC show gradual increase of droplet size with the PIT rise, as shown in Fig. 2. It is concluded from Fig. 6 that emulsifiers the PITs of which are about 20º - 65ºC higher than the storage temperature afford more stable emulsions.

The PIT change from 27º - 94ºC in this experiment corresponds to the change of HLB - value from 11.1 to 14.7. It is clear from Fig. 6 that the optimum HLB value or PIT can not be accurately determined from the stability vs HLB value relation, because the maximum stability is insensitive to the change in HLB value change. On the other hand, the instability of the emulsion is very sensitive to the PIT, so that the selection of a suitable emulsifier by the PIT data is much more accurate and reliable, provided the temperature difference between the storage temperature and the optimum PIT is known. The comparison between the hase-contrast microscopic photographs of emulsions prepared by the PIT-method and by a simple shaking is shown in Fig. 7. The system contains 3 wt% polyoxyethylene (8.6) nonylphenylether, 77.6 wt%water, and 19.4 wt% cyclohexane.

REFERENCES

[1] SHINODA, K., AND SAITO, H., J. Colloid and Interface Sci. 26, 70 (1968).