Phase behavior of TXs/toluene/water microemulsion systems for solubilization absorption of toluene

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Abstract

Triton Xs (TXs) surfactants/cosurfactant/water/oil (toluene) microemulsion systems for enhancing toluene solubilization were proposed and its potential was investigated for toluene removal from gas stream. The results indicated that TX-100 was superior to other TXs surfactants in removing toluene without cosurfactant. The efficiency of cosurfactants for improving toluene solubilization capacity follows the order: amine > alcohol > acid. According to the factor analysis, the linear cosurfactants are better than the branched ones. The effects of hydrophile-lipophile balance (HLB), salt (NaCl) concentration and temperature on the formation of microemulsion system were also discussed. The results suggested that the optimum value of HLB was 15, the effect of NaCl concentration on the system was inconspicuous and the lower temperature enhanced the solubilization capacity. Nonionic surfactant-based microemulsions had a significant absorption enhancement for toluene, indicated by as much as 82.72% of toluene in phase composition diagram, which will have a great prospect in air pollution treatment.

Key words: microemulsion; phase behavior; absorption; toluene

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Introduction

Volatile organic compounds (VOCs) are the source of serious environmental issues and toluene is one of the most representative organic pollutants. VOCs emissions have been subjected to more and more stringent legislation (Hadjoudj et al., 2004). There are many techniques available to control VOCs emission (e.g., thermal or catalytic incineration, adsorption on activated carbon, biological, or membrane processes) with advantages and limitations (Fourmentin et al., 2006). Among them, absorption method is one of the most economical technologies, with a removal efficiency of 95%–98% (Lawson and Adams, 1999). The enhancement of VOCs solubility in water can be achieved in the presence of surfactants. Kim et al. (2001) reported that when the addition of fresh polyoxyethelene sorbitan ester (Tween) 81 solution (0.3%, *W/V*) into a jet loop reactor, over 90% absorbtion of toluene can last for 48 hr with inlet toluene 1000 μL/L or less. The function of surfactant was to enhance the solubility of hydrophobic organic compounds. However, the solubilization capacity of microemulsion far exceeds the capacity of micelle solutions formed with surfactants. The solubilization capacity of the oil-in-water (O/W) surfactants is 5% or 2 oil molecular per surfactant molecular, and the O/W microemulsions is 60% or 10–25 oil molecular per surfactant molecular

(Armand et al., 1990; Placet et al., 2000; Chen and Liu, 2002; Hadjoudj et al., 2004; Ozturk and Yilmaz, 2006). Hence, an absorption reactor filled with the microemulsion may be more efficient than single surfactant solution. The capacity of nonionic surfactant microemulsions in trapping VOCs was studied in present study.

Microemulsion is a system of water, oil and an amphiphile, which is a single optically isotropic and thermodynamically stable liquid solution (Rajib and Paul, 2005). For simple aqueous systems, the formation of microemulsion is dependent on the type and structure of surfactant (Alany et al., 2000; Rudolph et al., 2000; Hsu and Nacu, 2003; Rodriguez et al., 2004; Fanun, 2007; Metha et al., 2007). Microemulsions have attracted considerable attention in many applications, such as cosmetics, foods, pharmaceuticals, pesticides, coating materials in the last decade (Chernik, 2000; Yaghnur et al., 2002). However, there is almost no application in environmental treatment. For this reason, the study focused on the absorption of VOCs based on nonionic surfactant microemulsions. Toluene was taken as oil phase, which simplified the composition of microemulsion, and apt to desorption.

Solubilization and interfacial properties of microemulsions depend upon pressure, temperature and the nature and concentration of the components. The determination of phase stability diagrams (or phase maps), and the location

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of different structures formed within these water (salt)-oil-surfactant-cosurfactant systems in terms of variables are, therefore, very important. In using an adequate mode of representation, it is possible to describe not only the limits of existence of the single and multiphase regions, but also to characterize the equilibrium between phases (tie-lines, tie-triangles, critical points, etc.).

In present study, the effect of cosurfactant, temperature and salt on water solubilization in a nonionic quaternary model system was discussed. Phase behavior of nonionic microemulsions was also investigated using the pseudoternary phase diagram. Triton Xs (TXs) have more remarkable solubilization, and prone to form microemulsion with cosurfactant free. The formation of microemulsion solution is dependent on the absorption of toluene, and the proportion of surfactant-cosurfactant-water under a certain circumstance. Large microemulsion region area will form with the presence of toluene in solution. The purpose of the current study was to propose a standard of screening microemulsion systems stress the potential of these microemulsions as delivery system, and to describe their phase behavior. This study provides a new technology in air pollution treatment using microemulsion systems.

1 Materials and methods

1.1 Materials

The surfactants TX-100, TX-305, and TX-405, were obtained from American Sigma Aldrich Fluka. Propanol, butanol, pentanol, butyric acid, n-butylamine, ethanolamine, diethanolamine, triethanolamine, n-methyl diethanolamine, NaCl, and toluene were purchased from China National Medicines Corporation. All reagents were analytical grade and used without purification. The physico-chemical parameters for cosurfactants are presented in Table 1. Double distilled water of conductance less than 2 μS/cm was used for the preparation of microemulsion samples.

1.2 Preparation of microemulsion precursors

In the phase diagram, the system includes water (W), oil (O), nonionic surfactant (C), cosurfactant (D), salt (E). The weight fraction of the surfactant and cosurfactant in the mixture of surfactant, cosurfactant and water was nominated as $\alpha = (C + D)/(C + D + W)$, weight fraction of the salt in salt and water was denoted as $\beta = E/(W + E)$, and weight fraction of the surfactant in surfactant and cosurfactant was nominated as $\gamma = C/(C + D)$. Samples were firstly prepared individually by mixing the required weights of surfactant and cosurfactant (according to the Hydrophile-lipophile balance (HLB) value of surfactant and cosurfactant, mixed configured to samples with different γ values). Then surfactant, cosurfactant, and water (α = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9) were shaken vigorously in thermostat oscillator for 2 hr to ensure proper mixing and kept at desired temperature.

1.3 Phase diagrams

The four-component systems were described on a pseudo-ternary phase diagrams. Figure 1 shows the example of these phase diagrams. The four-component system includes water (W), oil (O), nonionic surfactant or surfactant mixed with cosurfactant (S). Four independent variables, and other parameters such as temperature (T), salt (NaCl), and HLB value were involved. The phase diagram constructs three of the four parameters in three dimensions, and the other factors were kept constant. The prepared samples were put into thermostatic bath (± 0.5 K) with constant stirrer to ensure the solution mixed completely. After 5 min, 50 μL of toluene was injected into samples. Toluene was added until the solution has become turbidity, and the samples were checked after complete phase change was detected by direct visual inspection (Rajib and Paul, 2005). Desired amounts of toluene, surfactant, and water were pur into test tubes and sealed immediately. The proportion was drawn in the phase diagram, and the points were connected using a line as the boundary of microemulsion region.

1.4 Solubilization parameters

The most useful parameter to characterize microemulsion is the size of microemulsion region area. The microemulsion region area was used to compare the solubi-

Table 1 Physico-chemical parameters for the cosurfactants

Cosurfactant	Number of carbon atoms	C (%)	HLB value	Boiling point (K)	F_b
Propanol	3	37.1	7.5	370	0
Butanol	4	64.9	7	389	0
Pentanol	5	68.2	6.5	411.1	0
Butyric acid	4	54.5	7.6	438	0
n-Butylamine	4	65.8	14.5	351	0
Ethanolamine	2	39.3	17.3	443	0
Diethanolamine	4	45.7	18.3	318.3	0
Triethanolamine	6	48.3	19.1	321.3	1.33
n-Methyl diethanolamine	4	40.3	17.7	313.3	0.8

C: carbon atom; F_b: branching factor; HLB: hydrophile-lipophile balance.
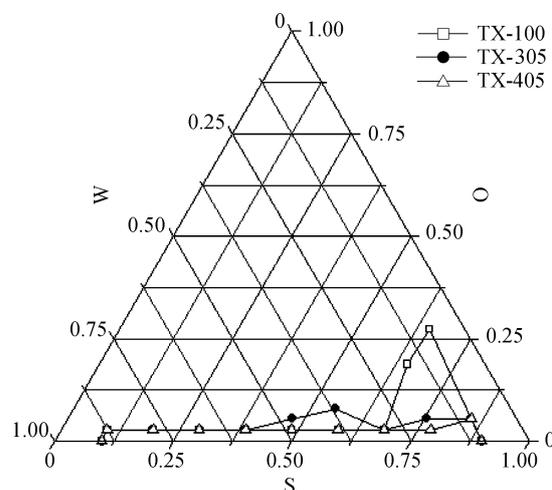

Fig. 1 Pseudoternary phase diagrams for the TXs. S: surfactant or surfactant+cosurfactant mix; O: oil (toluene); W: water.

lization capacity of different microemulsion systems. This diagram can be depicted as an equilateral triangle having the following vertices: 100% water, 100% toluene, and 100% of a binary mixture of surfactant and cosurfactant at a fixed weight ratio (Ezrahi et al., 2005).

The samples were extracted in 50 mL sealed conical flask. The gas phase above the solution was in the range of 20–40 mL. After microemulsion saturated, only a few of toluene was evaporated as indicated in preliminary studies. The maximum relative deviation was 0.19%, the average relative deviation was 0.02%, and error analysis consistent with the previous report (Liu, 2007). Therefore, the experimental error caused by the evaporation of toluene does not affect the experimental conclusions.

2 Results and discussion

2.1 Optimum surfactant

In order to obtain the most appropriate TXs surfactant for the solubilizing toluene, the phase behavior of TXs/butanol/toluene/water system was studied at 303 K. The result is depicted in Fig. 1. The lower part of the phase boundary represents a single-phase part region (microemulsion region area), whereas the upper part is a two-phase region. Usually, surfactant should be saturated with low solubility in oil and water so as to take much effect in oil and water interface. But in the recent study, surfactant was utilized to dissolve oil into water. As shown in Fig. 1, TXs based microemulsions can form without the addition of cosurfactants, and the size of microemulsions region area is in a sequence: TX-100 > TX-305 > TX-405. The reason is that the HLB value of TX-100 and TX-305 are close to the value of toluene. Another reason is the ethoxy (EO) weight fraction. The structure of TXs is shown in Fig. 2, in which R is octyl (C$_8$). The values

of x were 9.5, 30, and 40 for TX-100, TX-305, and TX-405, respectively. The more EO, the better the hydrophilic of surfactant is; in other words, the absorption capacity of toluene is poor. Thus TXs surfactant can be used as absorbent and applied in air pollution treatment, but the absorption capacity was limited.

2.2 Screening of cosurfactants

Cosurfactants can change the surface activity and HLB of surfactants, participate in a micelle and adjusting the polarity of water and oil, and thus affect the system of phase behavior and nature of the microemulsion components. The presence of solubilized hydrocarbon in the surfactant micelles generally increases the solubility of polar compounds in these micelles. The solubilized hydrocarbon causes the micelle to swell, and this may make it possible for the micelle to incorporate more polar material in the palisade layer. On the other hand, the solubilization of such polar material as alcohols, amines, and acids into the micelles of a surfactant appears to increase the solubilization of hydrocarbons.

N-Butylamine, butanol, butyric acid were used as typical cosurfactant in this study. The experimental temperature was controlled at 303 K, and HLB was 15. These cosurfactants contain straight chains, and the number of carbon is 4. As shown in Fig. 3, the largest microemulsion region area of TX-305 and TX-405 were surfactant mixed with n-butylamine, indicating the microemulsions achieve maximum solubilization capacity for toluene with n-butylamine as cosurfactant. Therefore, the optimum cosurfactant is n-butylamine, and the next is butanol. One explanation is that the lower polarity result in a lower degree of order in the micelle, with a consequent increase in solubilizing power for hydrocarbons; another is that the additives with lesser hydrogen bonding power are solubilized more deeply in the interior of the micelle, and hence expand this region, producing the same effect as a lengthening of the hydrocarbon chain of the micelle-producing molecule.
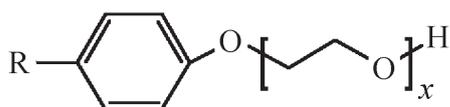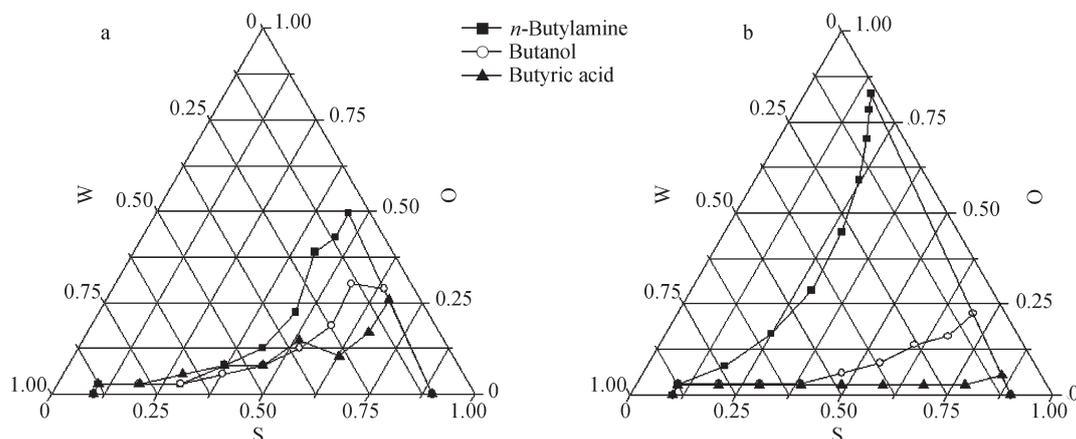
Fig. 2   Structure of TXs.

Fig. 3   Pseudoternary phase diagrams for TX-305/toluene/water system (a) and TX-405/toluene/water system (b) with various cosurfactants.

2.3 Effect of the structure of cosurfactant

The structure of cosurfactant also has remarkable influence on the phase behavior of microemulsion. Thus, eight alcohols were investigated, and branched surfactants may employ the classification of branching suggested by Wormuth and Zushma (1991): (1) Methyl branching – the amphiphile (surfactant or alcohol), has a single hydrophobic chain with one or more methyl or ethyl groups distributed along the main chain. (2) Double-tail branching – the amphiphile, has a main hydrophobic chain attached to the headgroup. A pendant chain with at least three carbon atoms is attached at α and β carbon to the headgroup. We can further extend the classification by distinguishing between equal and unequal "tails" of the amphiphile. (3) Multiple branching – highly branched amphiphiles, is based on some combination of the two former types of branching.

Eight examples of branched amphiphiles are shown in Fig. 4. The experimental temperature was 303 K, and HLB value was 15.

The branching factor (F_b) may be calculated using the suggested equation (Ezrahi et al., 2005):

$$F_b = \frac{1}{d} \sum_i l_i t_i \tag{1}$$

where, d is the length (i.e., the number of carbon atoms) of the amphiphile main chain to which the side groups (or chains) are attached; l_i is the length of the main chain section measured from the free and (i.e., not attached to the headgroup) to the point where it joins the side chain (obviously, $d \geqslant l_i$); and t_i is the length of the i branch (i.e., the side chain). F_b is calculated as follows: one of the chains (in the case of unequal tails, the longer one) is considered as the main chain, whereas the other one is taken as the branched. For the evaluation of secondary branching, i.e., the attaching of side groups to a side chain, the primary branch (the side chain) itself plus the carbon atom of the junction point is considered as an apparent main chain to the secondary branch.
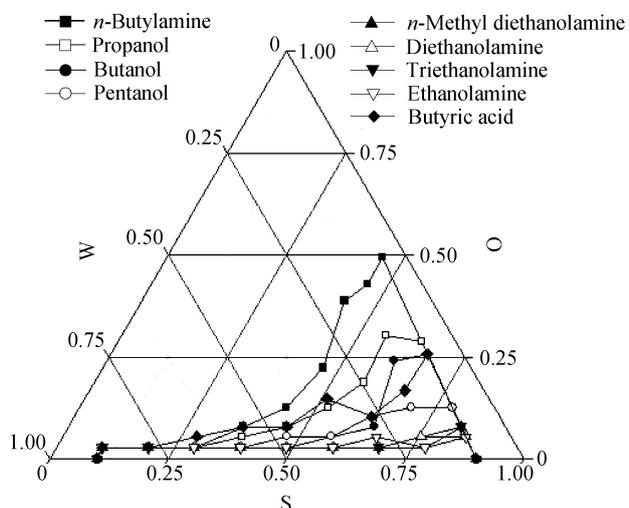
It should be noted that the value of F_b was 0, 1.33, and 0.8 for linear cosurfactants, triethanolamine, and n-methyl diethanolamine, respectively (Table 1). In Fig. 4, triethanolamine and diethanolamine mixed with TX-305 can form microemulsion, and the two microemulsion region areas are the smallest. The linear cosurfactants are superior to the branched for solubilization absorption of toluene. On the other hand, it was easily found that the microemulsion region area is larger with one functional group than two functional groups. A likely explanation is that the structure of TXs system is complex, the main chain is long and they have many branched chain and multi-functional groups. If the cosurfactant is sufficient complicated, it even can not form into microemulsion. Therefore, a simple structure of cosurfactant is favorable.

2.4 Optimum HLB value

HLB is considered to be the concept relating molecular structure to interfacial packing and film curvature. It is generally expressed as an empirical equation based on the relative proportions of hydrophobic and hydrophilic groups within the molecule and gave quantitative description (Lu et al., 1992).

The phase diagrams of TX-305/butanol/toluene/water system with HLB 13, 14, 15, 16, and 17 (the HLB of surfactant TX-305 is 17, and cosurfactant butanol is 7) are shown in Fig. 6. It is seen that the microemulsion region area have the following order: HLB 15 > HLB 14 > HLB 16 > HLB 13 > HLB 17. Many previous studies indicated that when HLB value of surfactant solution was equal to the HLB value of oil, the solubilization capacity will reach maximum. In this study, the oil was toluene, and the HLB value was 15. Thus, this theory in the TX-305/butanol/toluene/water system is applicable. The whole series of TXs have been studied and the results are similar to TX-305 (Fig. 5).

2.5 Effect of temperature

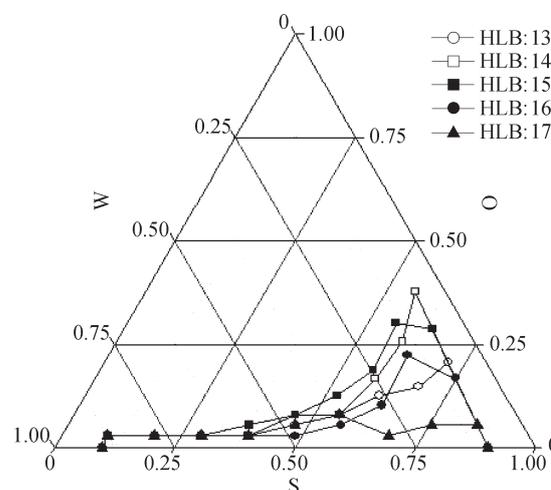The temperature is essential to the stability of microemulsion system, the increase of temperature is known

Fig. 4 Pseudoternary phase diagrams for the TX-305/toluene/water system with various structures of cosurfactants.

Fig. 5 Pseudoternary phase diagrams for the TX-305/butanol/toluene/water system with various HLB values.
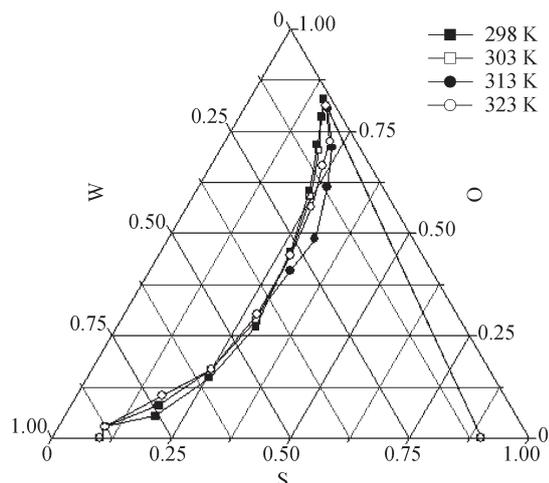
Fig. 6 Pseudoternary phase diagrams for the TX-405/*n*-butylamine/ toluene/water system with various temperatures.
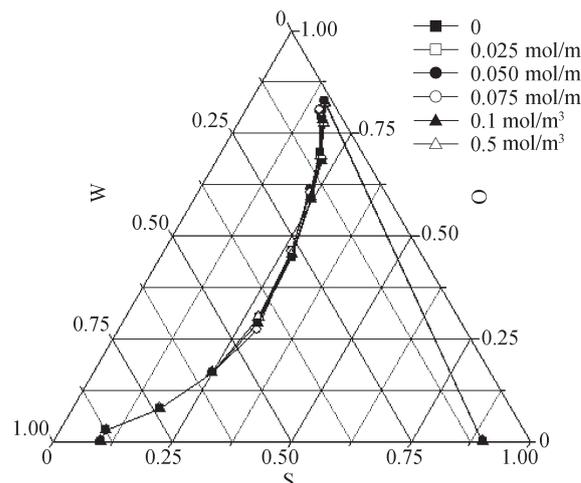

Fig. 7 Pseudoternary phase diagrams for the TX-405/*n*-butylamine/ toluene/water system with various NaCl concentrations.

to induce the hydration level decrease of polyoxyethylene chains, and change the phase behavior of surfactant (Warisnoicharoen et al., 2000). For nonionic surfactant systems, the temperature should be lower than the cloud point of corresponding surfactant, as well as the impact of phase inversion temperature (PIT), which is form of water-oil microemulsions with high temperature sensitivity. In particular, there is a specific PIT and the film curvature changes from positive to negative. PIT can be evaluated using the suggested equation (Eq. (2)) (Kunieda et al., 1985):

$$PIT = K_0(HLB - N_0) + 273 \qquad (2)$$

where, $K_0 \approx 17$ HLB; the value of N_0 based on the type of oil. In this research, oil is toluene, $N_0 = 10.0$, and PIT is 341 K in this section.

The phase diagram of TX-405/*n*-butylamine/toluene/ water system at 298, 303, 313 and 323 K with HLB 15 were prepared and represented in Fig. 6. It shows that the microemulsion region areas decrease with increasing temperature. It has been reported previously the nonionic surfactants become lipophilic at higher temperatures due to the dehydration of the oxyethylene group (Karlstrom, 1985). But in this study surfactant solution does not absorb more toluene at higher temperature. This is most likely ascribed to that the formation of microemulsion solution based on the absorption of toluene. Temperature and pressure are important factors on the absorption capacity or ability; therefore, reducing temperature or enhancing pressure can improve the solubilization capacity. In addition, with temperature increased further, the amount of material solubilized decreased and thus caused an increase in dehydration and a tighter coiling of POE chains, decreasing the space available in the palisade layer and solubilization amount .

2.6 Effect of salt

The phase behavior of TX-405/*n*-butylamine/toluene/ water system has been studied at 303 K with HLB value 15 as a function of different NaCl concentrations ($\beta = 0$,

0.025, 0.05, 0.075, 0.1, 0.5 mol/m^3). Six representative phase diagrams are shown in Fig. 7. It has been found that three-phase body appears in all these systems, and the differences are inconspicuous. For nonionic surfactant without electric charge, the salt does not influence these systems markedly; and the further addition of salt will reduce the solubility and PIT. Therefore, microemulsion region area is smaller with the addition of salt.

On the basis of the results, it can be concluded that nonionic surfactant microemulsions are easy to prepare with the addition of various kinds of cosurfactant, and they can form different microemulsions with various solubilization capacities without the significant solubilization role of toluene. In TX-405/*n*-butylamine/toluene/water system, the proportion of toluene in solution can achieve 82.72%, in other words, 478.7 g of toluene can be absorbed in every 100 g of nonionic microemulsion, but toluene almost insoluble in water. This study reveals that VOCs (especially toluene) absorbed by microemulsions have a great prospect for the development of air pollution treatment.

3 Conclusions

The results of the present study indicate that it is possible to formulate microemulsions as suitable absorbent to remove toluene from gas stream by using TXs surfactants. The findings proved that TX-100 > TX-305 > TX-405, which surfactant with cosurfactant free and based on the solubilization capacity of toluene. The optimum cosurfactant was amine followed by alcohol. Surfactants with linear chain were better than branched ones in forming the microemulsions. Various environmental conditions could control the formation of microemulsions. As an experimental result, the optimum HLB value is 15, the effect of salt solution is inconspicuous, and low temperature can enhance the solubilization capacity.

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