

**The comparison between the PIT system and the HLB-value system to
emulsifier selection**

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RÉSUMÉ

Un système basé sur la température d'inversion des phases (TIP) pour la sélection des agents émulsionnants a été développé et comparé au système de la valeur HLB. Le rapport hydro-lipophile (HLB) d'un agent de surface non-ionique change avec la température et provoque l'inversion des phases d'une émulsion, quand les deux propriétés sont égales. La TIP varie avec les conditions d'essais et fournit des informations concernant les types d'huiles, le volume des phases, la concentration des agents émulsionnants, l'effet de la température etc. La valeur HLB ne fournit pas d'informations pareilles. La TIP est également en relation étroite avec d'autres propriétés.

ZUSAMMENFASSUNG

Ein Phasen-Inversions-Temperatur (PIT)- System wurde zur Auswahl eines Emulgators entwickelt und verglichen mit dem HLB-Wert System. Das hydro-lipophile Verhältnis (HLB) eines nicht ionischen Tensids verändert sich mit der Temperatur und bewirkt die Phasenumkehr einer Emulsion, wenn beide Eigenschaften gleich sind. Die PIT variiert mit den experimentellen Bedingungen und ermöglicht Informationen über Öltypen, Phasenvolumen, Konzentration der Emulgatoren, Temperatureffekt etc. Der HLB-Wert liefert keine solchen Informationen. Die PIT steht auch in enger Beziehung zu anderen Eigenschaften.

SUMMARY

A phase inversion temperature (PIT) system for selecting an emulsifier has been developed and compared with the HLB-value system. The hydrophile-lipophile balance (HLB) of a nonionic surfactant changes with the temperature and the inversion of an emulsion type occurs at which these two properties just balance. The PIT changes with the experimental conditions and affords information on the types of oils, the phase Volume, the concentration of emulsifiers, the effect of temperature etc., but the HLB-value does not afford such information. PIT is also closely related with the other properties.

Introduction

It is the most important theme in the studies of emulsions to select an emulsifier which will satisfactorily emulsify the chosen ingredients at a given temperature. For this purpose, the hydrophilic-lipophilic balance (HLB) of emulsifier is an useful index. Clayton (¹) has drawn attention to the concept of balanced emulsifying agents as embodied in a series of patents dating back to 1933. However, the concept of HLB in early stages was qualitative.

HLB-value

Schemes designed to put this concept on a qualitative basis have been advanced: there are the HLB-values of Griffin (^{2,3}) and the H/L numbers of Moore and Bell (⁴) etc. In order to indicate the HLB of a surfactant, an HLB-value is assigned to each surfactant based on the analysis of the surfactant. But in practice, HLB means the balance of surfactant at an oil-water interface. Accordingly, the HLB-value should change with the types of oils and with the additives to water or oil phase. The required HLB-value of an oil is determined to adjust the gap between the assigned HLB value and the actual HLB of respective systems. The HLB-value of a surfactant is also a function of temperature, because the interaction between water and hydrophilic group or oil and lipophilic group changes with temperature. However, it is not easy to determine an exact HLB-values of respective surfactants, because the emulsion stability (from which the required HLB-value is derived empirically) does not change sensitively with the change of the HLB-values of surfactants. The situation is explained by Griffin as follows: << In its present form, the HLB (value) system lacks exactness. A suitable simple laboratory method of measuring HLB-values or surfactant accurately is needed ... >> (²). The original method of determining HLB-values involves a long and laborious experimental procedure (²). In order to save time for determining the HLB-values, empirical equations which permit the calculation of the HLB-values for certain types of nonionic agents were developed. Becher et al. devised several rapid methods to determine the HLB-value, i.e., 1) spreading coefficient in a particular oil-water system (⁵), and 2) the ratio of the retention times of ethanol and hexane in gas-liquid chromatograph containing respective surfactants (⁶).

PIT (HLB-temperature)

If we adopt a characteristic property of emulsions, such as phase inversion temperature, as a measure of HLB, it naturally reflects the effects of the sizes and types of hydrophilic groups and lipophilic groups of the surfactant, and affords informations on the effect of the concentration of emulsifier, the phase volume, the additives in both water and oil phases, the temperature etc. I believe we should adopt the PIT as the most suitable property of a measure of the HLB of nonionic surfactant (^{7,8}). Emulsions stabilized with nonionic agents are W/O types at high temperatures but change to an O/W type at low temperatures. This phenomenon is evidence that the hydrophilic-lipophilic balance of nonionic surfactant changes appreciably with temperature.

The hydration forces between the hydrophilic moiety of surfactant and water are stronger at the lower temperature so that the surfactant is more hydrophilic, and the adsorbed monolayer at an oil-water interface may have convex curvature towards water. When the hydration between the hydrophilic moiety of surfactant and water diminishes, the surfactant is more lipophilic at the higher temperature and the adsorbed monolayer at an oil-water interface may have concave curvature towards water (⁷).

Hence, the PIT is considered to be the temperature at which the hydrophilic-lipophilic property of a surfactant just balances. PIT may be designated as << HLB temperature >>. The selection of a suitable emulsifier by the PIT system is similar to the HLB-value system in regard to the selection on the basis of hydrophile-lipophile balance.

The comparison between the PITs and HLB-values

The phase inversion temperature of an emulsion is the temperature at which the hydrophilic and lipophilic property of the nonionic surfactant balances, and the HLB of the surfactant changes with temperature. Hence, a correlation between the PIT (HLB-temperature) and the HLB value is expected. The relation is shown in Fig. 1.

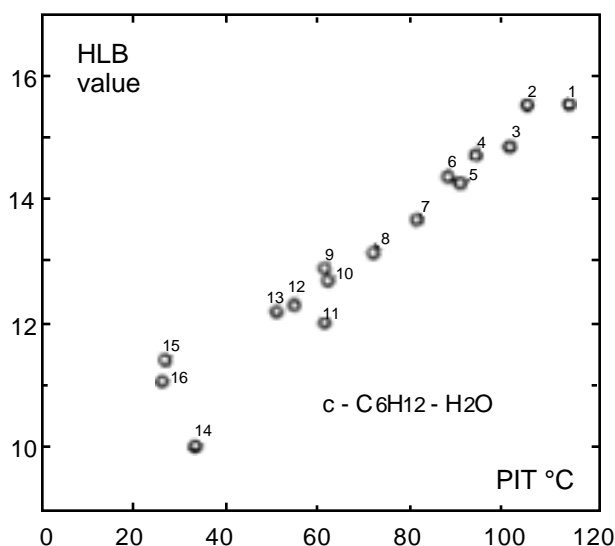


Fig. 1. The correlation between the HLB values of nonionic surfactants and the phase inversion temperatures in c-C₆H₁₂-H₂O emulsions stabilized with the surfactants. (3wt %/system).

- | | |
|---|--|
| 1, Tween 40; | 9, i-R ₈ C ₆ H ₄ O(CH ₂ CH ₂ O) _{8,5} H; |
| 2, i-R ₉ C ₆ H ₄ O(CH ₂ CH ₂ O) _{17,7} H; | 10, i-R ₁₂ C ₆ H ₄ O(CH ₂ CH ₂ O) _{9,7} H; |
| 3, Tween 60, | 11, R ₁₂ O(CH ₂ CH ₂ O) _{6,3} H; |
| 4, i-R ₉ C ₆ H ₄ O(CH ₂ CH ₂ O) _{14,0} H; | 12, i-R ₁₂ C ₆ H ₄ O(CH ₂ CH ₂ O) _{9,4} H; |
| 5, i-R ₁₂ C ₆ H ₄ O(CH ₂ CH ₂ O) ₁₅ H; | 13, i-R ₉ C ₆ H ₄ O(CH ₂ CH ₂ O) _{7,4} H; |
| 6, R ₁₂ O(CH ₂ CH ₂ O) _{10,8} H; | 14, i-R ₁₂ O(CH ₂ CH ₂ O) _{4,2} H; |
| 7, i-R ₈ C ₆ H ₄ O(CH ₂ CH ₂ O) ₁₀ H; | 15, i-R ₈ C ₆ H ₄ O(CH ₂ CH ₂ O) ₆ H; |
| 8, i-R ₉ C ₆ H ₄ O(CH ₂ CH ₂ O) _{9,7} H; | 16, i-R ₉ C ₆ H ₄ O(CH ₂ CH ₂ O) _{6,2} H; |

As the PIT changes markedly with the types of oils, the correlation between the HLB values and the PITs in different oil-water emulsions differs each other as shown in Figure 2.

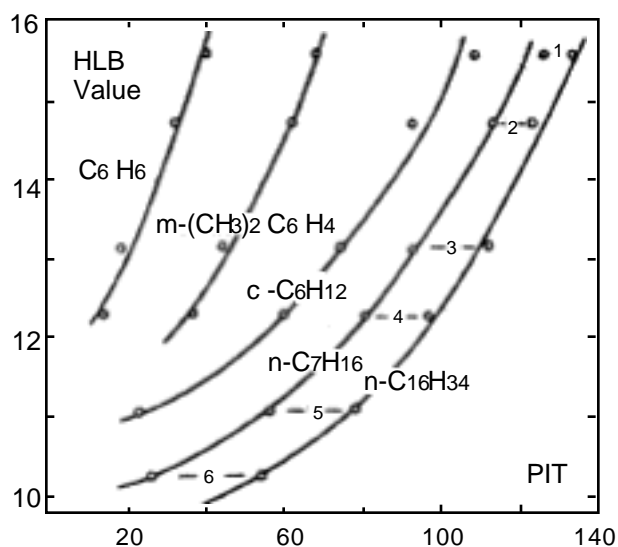


Fig. 2. The correlation between the HLB values and the PITs in various oil-water (1 : 1 emulsions stabilized with nonionic surfactants. (1.5 % per system).

- | | |
|--|---|
| 1, $i\text{-R}_9\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_{17.7}\text{H}$; | 4, $i\text{-R}_9\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_{7.4}\text{H}$; |
| 2, $i\text{-R}_9\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_{14.0}\text{H}$; | 5, $i\text{-R}_9\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_{6.2}\text{H}$; |
| 3, $i\text{-R}_9\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_{9.6}\text{H}$; | 6, $i\text{-R}_9\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_{5.3}\text{H}$; |

As the HLB of a surfactant at different oil-water interfaces differs, a correction for types of oil is necessary in HLB-value system which is known as << Required HLB values of oils >>. The PIT, on the other hand, reflects the types of oils, and no correction is needed. Figure 2 is useful for finding the << Required HLB-value of oils >>, because the HLB-value of surfactants whose PITs are 20-60°C higher than storing temperatures are the << Required HLB-value >> (⁹). The required HLB-values estimated from PIT system and those recommended by Atlas (¹⁰) are compared in Table 1.

PIT reflects also the differences of the types of hydrophilic and/or lipophilic groups. The comparison between the PIT system and the HLB-value system in regard to the informations on various factors are summarized in Table 2.

As the PIT is an experimental quantity, it affords all the information about experimental condition. It is difficult, however, to know the effect of temperature on the types of emulsion stabilized with ionic surfactant.

Phase volume, the kinds of gegenions etc., have more pronounced effect. We should assign a high PIT to an ionic surfactant which gives O/W type emulsions in order to express a high HLB-value of the surfactant and vice versa. HLB-value of-surfactant, in principle, can not afford any information of any variable, but empirical correction such as the <<required HLB value of oils>>, <<required HLB-value of water containing salts>>, etc. is possible particularly by the aid of the PIT data. Both systems are thus compatible.

TABLE 1
The comparison between the Atlas-required HLB-values and the HLB-values estimated from PIT

Types of Oils	HLB - Values (Atlas)	HLB - Values (PIT)
Mineral Oil (Paraffinic)	10	10
Propene Tetramer	14	12
Kerosene	14	12
Trichlorotrifluorethane	14	12.5
Cyclohexane	15	13
Carbontetrachloride	16	13
Xylene	14	14.5
Toluene	15	15.5
Benzene	15	16.5

The informations of various factors reflected on the PIT

The effect of the concentration of surfactant and the types of oils on the PIT in emulsions stabilized with nonionic surfactant are shown in Fig. 3 (⁸). The effect of the hydrophilic

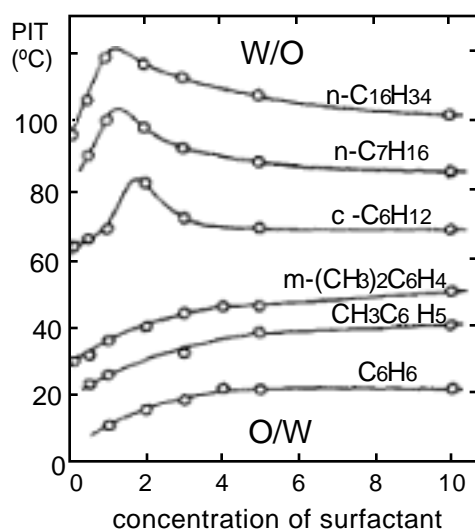


Fig. 3. The effect of the types of oils on the PIT of emulsions (1:1) vs. the concentration of $i - R_9C_6H_4O(CH_2CH_2O)_{9,6} H$; (wt % in water).

TABLE 2
The comparison between the PIT system and the HLB value
system in regard to the information on various factors

PIT	Factors	HLB Value
o	Hydrophilic - lipophilic balance	●
o	Types of hydrophilic moiety	*
o	Types of lipophilic moiety	*

o	Types of oils	●
o	Additives in water and/or oil phase	*
o	Concentration of emulsifier	*
o	Phase volume	*
o	Temperature	*
o	Emulsion types	●

o	Correlation with the other properties	▲

▲	In the case of ionic surfactants	▲

o	Information is available accurately	
●	Information is available less accurately	
▲	Crude information is available	
*	Almost no information is available	

chain length of nonionic surfactant and the effect of phase volume on the PIT are shown in Fig. 4⁽¹¹⁾.

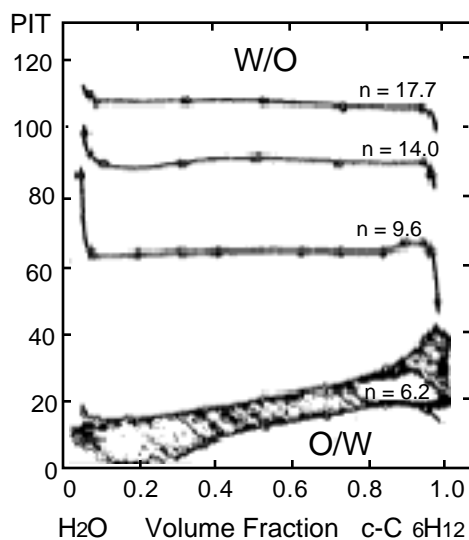


Fig. 4. The effects of the hydrophilic chain length of nonionics $i\text{-R}_9\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$; and phase volume on the PIT of cyclohexane vs. water emulsions.

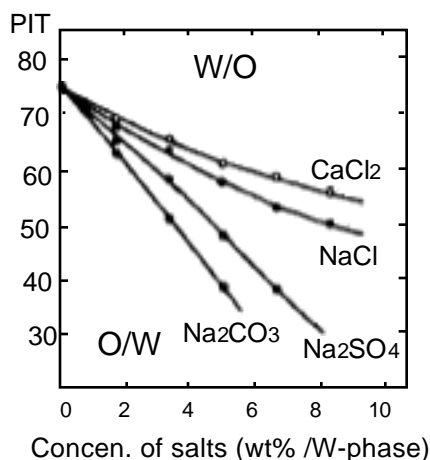


Fig. 5. The effects of added salts on the PIT of $c\text{-C}_6\text{H}_{12}\text{-H}_2\text{O}$ emulsions (1:1 volume) stabilized with $i\text{-R}_9\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_{9.6}\text{H}$; (3wt % in water).

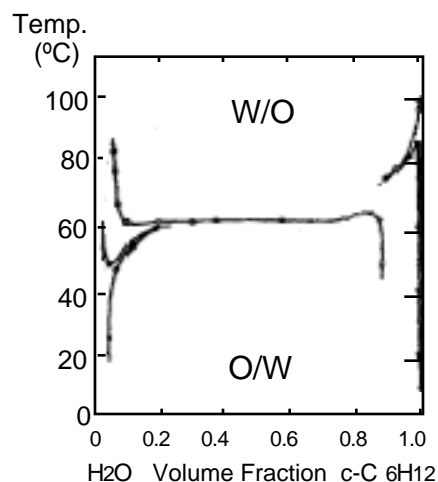


Fig. 6. The Relation between the PIT in emulsion and the optimum temperature for solubilization.

The effect of the concentration and the types of oils on the PIT in emulsions stabilized with nonionic surfactants are shown in Fig. 3⁽⁸⁾. The effect of the hydrophilic chain length of nonionic surfactant and the effect of phase volume on the PIT are shown in Fig. 4 and 6. The effects of added salts on the PIT of emulsions are shown in Fig. 5. The change in PIT by added salts in the water means a change of the HLB, i.e., the change of the required HLB-value for the aqueous solution.

PIT is closely related with the other properties⁽¹²⁾ such as the optimum temperature for the solubilization of oils (or water) in aqueous (or nonaqueous) surfactant solutions^(13,14). Fig. 6 illustrates the relation between the PIT curve and the solubilized regions in aqueous and in oil phases. Optimum solubilization temperatures are close to the PIT.

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DISCUSSION

Question by R. RUYSEN:

Is the P. I. T. system also applicable to the case of sodium palmitate and calcium palmitate?

Answer:

Systems which contain 0-40 % ionic surfactant of bi-valent metal ions, for example calcium dodecylbenzene sulfonate (100-66 % nonionics), was treated similarly, probably because the salt dissolved mostly in oil phase. Small amount of ionic surfactant, such as sodium dodecyl sulfate added to nonionic surfactant enhances the PIT sensitively as you might expect. Systems composed of ionic surfactant alone do not exhibit the clear phase inversion with temperature change, so that the PIT system is not applicable. But, we can assign high PIT value for ionic surfactant which yields an O/W type emulsion and low PIT value which yields a W/O type emulsion just as HLB-value. Phase inversion volume might be a good property to deal with ionic emulsifiers.

Question by E. GRAF:

By what method did you determine the exact phase inversion temperature?

Answer:

Sorry, the time allotted was too short to explain the experimental procedures in my talk. We, at first, prepared a scaled test tube which contained water, oil and emulsifier. Shaked the ampule well at respective temperature to attain the equilibrium distribution of respective components. After coalescence (to promote the coalescence of the droplets, about 2-4°C temperature raise and depression was effective close to the PIT) shaked the system again and determined the emulsion type by visual observation, mostly. Repeated weak shaking and successive observation of the change of volumes of oil and water phases was also helpful. Because the phase volume of continuous phase increases and finally becomes 100 %. Please consult with my paper also. (*K. Shinoda and H. Arai, J. Phys. Chem.*, 68: 3486, 1964).

Question by P. REHBINDER:

Est-ce-que vous avez quelques données nouvelles sur la théorie de la balance lipophile-hydrophile et sur les possibilités du calcul des valeurs de cette balance?

Answer:

No, I did not. Because, the intermolecular forces between complicated molecules may not be expressed properly by the theory. It seems more realistic to me to use experimental figures directly to the emulsifier selection. However, it is not difficult to assign respective values to respective groups and oils in order to obtain empirical equation to estimate the PIT (HLB-temperature) or HLB-value. Thank you very much for your important question.

Question by R. DEFAY:

Is there a theoretical formula which gives the variation of the HLB-value with temperature?

Answer:

No. HLB-value is a value given by Griffin to emulsifier at 25°C (although not clearly stated by him). But, the HLB-value surely decreases with the temperature rise and increases with the temperature depression in nonionic surfactants.

Emulsifiers may have the same HLB-Value at the respective PIT for a given oil. So that it is possible to obtain the relations between the HLB-values at PIT and the HLBvalues at 25°C from Figure 2 (for respective oil-water systems). Thanks for your important question.