Review

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Exploration of Universal Index to Characterize Surfactant Potency: Integrated Surfactant Potency as an Alternative Index to Hydrophilic–Lipophilic Balance

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The hydrophilic–lipophilic balance (HLB) of a surfactant, one of the most widely used indices of its potency for a given application, is a measure of surfactant partitioning tendency between oil and water. The HLB number shows a good correlation with the properties of the poly-oxyethylene-type nonionic surfactants and provides significant benefits to the development of advanced emulsification technology, while sometimes causing problems in formulation development and manufacturing processing for other types of surfactants. To avoid such a misfit between HLB number and solution properties, we developed "Integrated Surfactant Potency (ISP)" as an alternative index to HLB based on the chromatography technique by using thin layer chromatography (TLC). An appropriate method to determine ISP was investigated in detail and confirmed that ISP will be able to predict the properties of a surfactant solution such as critical micellar concentration, cloud point, and liquid crystal structures associated with the HLB of the surfactant. Our objective is to establish this TLC method to be utilized in many industrial fields to provide solutions through the proper selection of surfactants.

Key words: hydrophilic–lipophilic balance (HLB), HLB number, required HLB, Integrated Surfactant Potency (ISP), thin layer chromatography (TLC), poly-oxyethylene (POE) surfactant, critical micelle concentration (CMC), poly-glycerin surfactant, cloud point (CP), phase inversion temperature (PIT), emulsification

Note: This review article is intended to deliver our research journey from building up the objectives, tracing our progress to establish ISP (Integrated Surfactant Potency) as an alternative index to HLB, and then finding potential applications. We hope this review will give readers with some hints for their own research in cosmetic science and technology.

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1. Introduction

Surface active agents (surfactants) are the essential fundamental substances in controlling interfacial properties to achieve the desired formulation and are defined in the ***ISO 862 Surface active agents—Vocabulary***[1] as ***a chemical compound possessing surface activity which, dissolved in a liquid in particular in water, lowers the surface tension or interfacial tension, by preferred adsorption at the liquid/vapor surface, or other interfaces.*** *Additionally, the note explains:* ***a chemical compound including in its molecule at least one group with an affinity for markedly polar surfaces, ensuring in most cases its dissolution in water, and a non-polar group which has little affinity for water***. And surface activity is defined as ***the action of a substance that modifies the physical (mechanical, electrical, optical, etc.) properties of a surface or an interface and reduces its surface tension or interfacial tension***. (Bold italic text is copied from the definition listed under ISO 862.[1])

The hydrophilic–lipophilic balance (HLB) of a surfactant, one of the most widely used indices of its potency for a given application, is a measure of a surfactant's partitioning tendency between oil and water. The HLB number shows a good correlation with the properties of poly-oxyethylene (POE)-type nonionic surfactant solutions and has provided significant benefit to the development of advanced emulsification technology. The HLB number scale, introduced by Griffin in 1949,[2,3] was the first successful attempt at quantitative characterization based on extensive experiments using the POE surfactants, although it is often encountered that the classification of surfactants by HLB numbers does not help to make predictions for the optimum emulsification. Although alternative methods to calculate the HLB number, for example, Davies' method[4,5] or organic conceptual diagrams,[6,7] have been proposed, the HLB values obtained by these methods are incompatible with each other. To resolve the misfit between the HLB number and the solution properties, we developed a new method by using chromatography techniques to introduce a novel index, Integrated Surfactant Potency (ISP).

2. Pros and Cons of HLB

In the past few decades, many POE surfactants have been investigated for their fundamental properties, such as melting point and solubility in water or oil, as well as their practical properties, such as cloud point (CP), solubilization, liquid crystal (LC) formation, and emulsification. These are some of the most useful pros of the HLB concept. The HLB concept for the POE surfactants has contributed to the practical use of these POE surfactants in advanced applications across many industrial fields. Table 1 presents applications corresponding to the HLB number range.

The HLB number is an index that indicates the affinity of a surfactant toward a solvent; for example, a higher number means it is more attractive to water (hydrophilic). It is well known as a practical example of the HLB number that the type and suitable amount of the POE surfactant can be estimated to emulsify any kind of oil with water. In addition, the HLB number shows a good correlation with the cloud temperature, or CP, and phase inversion temperature (PIT), providing significant benefit to the development of advanced emulsification technology. The HLB number scale, introduced by Griffin,[2] was the first ever successful attempt to quantitatively characterize POE surfactants.

Griffin established the HLB number by his extensive experiments using the POE surfactants. It is well understood that the POE chain has a unique interaction with water, which decreases with temperature due to conformational changes and dehydration. As the HLB number given by Griffin's definition does not account for these conditional changes, the application of the HLB number to the practical systems faces difficulties relating to the effects of additives, temperature, self-organization, and so on in the HLB number calculated by the provided equation. The HLB number and its calculation are certainly convenient and applicable to many properties but exclusively for the POE surfactants, while they do not always provide suitable HLB value for non-POE surfactants. Therefore, a surfactant with excellent properties but not fitting the HLB system would have difficulty becoming a common surfactant.

To overcome these cons of HLB, we attempted to review the classical HLB number and the substantial issues involving basic properties and applications. By reconsidering the HLB number, we introduced our recent studies on the hydrophilic-lipophilic nature of the surfactants (Fig. 1).

3. Calculations of the HLB Number

A variety of equations have been proposed over the past half-century to calculate the HLB number, of which the first and still commonly used equation was proposed by Griffin.[2] This equation expresses the structural balance between hydrophilic and lipophilic (hydrophobic) groups in a surfactant molecule as a numeric index from 0 to 40 based on multiple experimental emulsifications to find suitable POE surfactants. The equations are useful for POE surfactants,

Table 1 Typical applications corresponding to the HLB number range.

HLB number range	Corresponding application
1.5–3	Anti-foaming agent
1–4	Emulsifier for W/O emulsions
6–8	Wetting agent
10–13	Emulsifier for O/W emulsions
13–15	Detergent
15–18	Solubilizer

HLB, hydrophilic–lipophilic balance; O/W, oil in water; W/O, water in oil

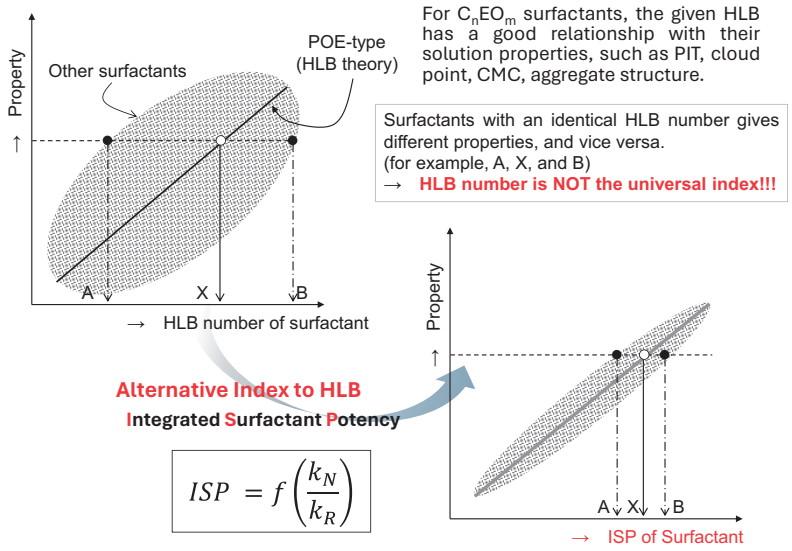


Fig. 1 Controversial point of HLB. HLB is an empirical index developed by Griffin[3] based on the extensive experiments with POE-type nonionic surfactants. The HLB number shows a good correlation with the CP and PIT for POE surfactants, but not for the other types of surfactants. ISP, as an alternative index to HLB, was developed based on thin layer chromatography (TLC).
CMC, critical micellar concentration; HLB, hydrophilic–lipophilic balance; ISP, Integrated Surfactant Potency; PIT, phase inversion temperature; POE, poly-oxyethylene

that is, the HLB numbers of the POE alkyl ethers (C_nEO_m) are given by the following equation, where the HLB number equals the weight fraction of POE moiety in the molecule

$$\mathrm{HLB} = \frac{POE\,(\mathrm{wt.\%})}{5} \tag{1}$$

As described above, these numbers are obtained from the empirical emulsifications, and they are utilized as a convenient tool for industrial applications. On the other hand, Griffin also obtained another equation to calculate the HLB number for fatty acid esters chemically bonded with alcohols as follows[3]:

$$\mathrm{HLB} = 20 \times \left(1 - \frac{S}{A}\right) \tag{2}$$

where S and A are the saponification and acid numbers of the ester, respectively. The HLB number given to polyglycerol fatty acid ester (C_mG_n) as a representative for this equation frequently shows different solution properties even though their HLB numbers appeared to be equivalent. Thus, it is difficult to apply HLB numbers to the mixed surfactant systems, as their assigned values come from different equations.

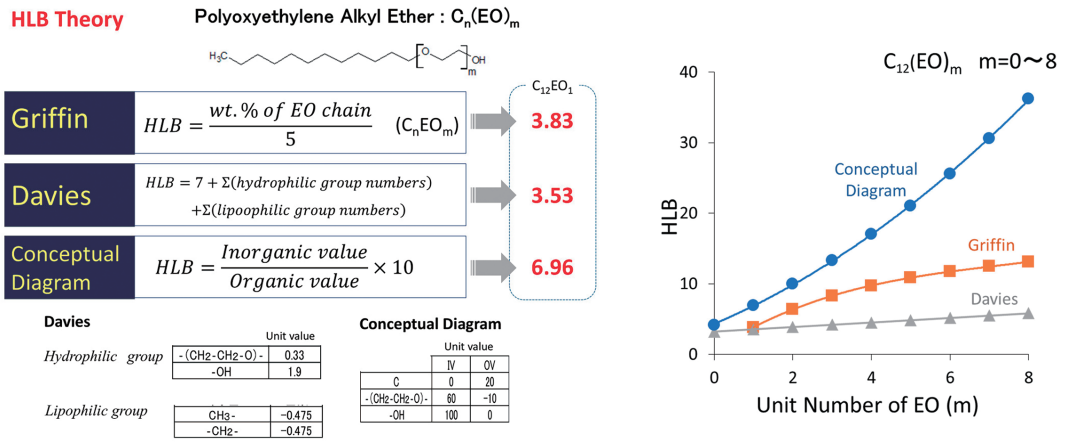


Fig. 2 HLB numbers calculated by different equations for POE surfactants. There is no consistency among HLB numbers estimated from these theories.
HLB, hydrophilic–lipophilic balance; POE, poly-oxyethylene

Davies's method,[4,5] one of the traditional methods to calculate HLB, is based on the unit value given to each functional group as either a hydrophilic or lipophilic element, and the HLB of the molecule can be calculated as the summation of all unit values

$$\mathrm{HLB} = 7 + \sum(\text{Unit value of hydrophilic group}) + \sum(\text{unit value of lipophilic group}) \tag{3}$$

The representative unit values are shown in Fig. 2. This versatile equation can calculate the HLB number even for ionic surfactants, although the resulting HLB value may not predict the properties of the surfactant solution as expected.

Another distinctive equation commonly used for the HLB calculation is based on the "organic conceptual diagram."[6,7] The primary objective of this method was to figure out complex properties of organic compounds via intermolecular interactions. The conceptual diagram consists mainly of "organic value (OV)" and "inorganic value (IV)," which respectively relate to the intermolecular forces generated by van der Waals interaction and electrostatic interaction, and the combination of these 2 values corresponds to the HLB number

$$\mathrm{HLB} = \frac{\sum IV}{\sum OV} \times 10 \tag{4}$$

The representative OV and IV are shown in Fig. 2.

Let us compare the HLB numbers of $C_{12}EO_m$ calculated by Equations (1), (3), and (4). Figure 2 shows the change in the HLB number as a function of the EO chain length (m). As expected, the HLB number monotonically increases with m, suggesting that the hydrophilicity of $C_{12}EO_m$ becomes greater. Even though there are discrepancies in HLB values between the equations, these discrepancies increase further with increasing EO numbers. Namely, for $C_{12}EO_5$, Griffin's HLB value is 10.8, whereas Davies's equation (3) gives 4.9, which underestimates compared to Griffin's equation. On the other hand, the HLB value calculated from the organic conceptual diagram's equation (4) is 21.1, overestimating contrastively. No matter which is the correct HLB value, it is a fact that these different equations result in different answers. This is a crucial problem when industrial applications are exercised because we rely on the HLB number of the surfactant regardless of its origin.

Despite the recent market trend favoring nature-friendly surfactants to replace petroleum-derived materials, POE surfactants still dominate emulsifiers. One reason is that there is no sufficiently accurate general index, like the HLB number for POE, to define the intrinsic properties of prospective surfactants with intended properties. Careful thought and constructive examination are needed to fill this gap. For example, an interesting phenomenon is known where polyglycerol fatty acid esters in diluted solution show a specific CP within a limited range of HLB, which is incompatible with the POE surfactants.[8] Furthermore, Kunieda et al.[9] and Sagitani et al.[10] reported that PIT was found in the polyglycerol-type surfactant/water/oil ternary system, and that the HLB of the polyglycerol surfactant is tunable by

temperature. This implies that polyglycerol surfactants possess similar basic properties such as CP and PIT, but these differ from those of POE surfactants. In summary, the HLB concept was established for the POE surfactants working within the family of POE structures, but there must be a way to interrelate the HLB concept to the surfactants with different chemical species to compare or combine their functions.

Figure 1 shows a conceptual figure representing the above context. The horizontal axis (*X*) is the HLB number of a surfactant, and the vertical axis (*Y*) is a property of the surfactant solution, such as CP, PIT, phase state, and so on. The proportional line in Fig. 1 represents the relationship between *Y* and *X* for POE surfactants. With this, one can predict the properties of the POE surfactant solution if their HLB values are given. On the other hand, for most of the surfactants except the POE type, HLB numbers correspond to specific properties of their solutions that deviate, as shown from *A* to *B* in Fig. 1. Thus, it would be difficult to predict the properties based on the HLB number. In the case of getting the desired property of the surfactant solution, we can choose a specific surfactant within the POE-type surfactants (HLB = *X* in Fig. 1) while being obliged to have several choices among the other surfactants (HLB = *A* or *B* or …). Although conceptually explained here, "HLB dependence" may fail to make a proper assessment to utilize the surfactant in the real formulation development.

4. Our Journey to Explore Quantitative HLB Index

Chromatography has been applied for quantitative analysis of the surfactants by using reversed-phase chromatography.[11] During the development of N-acyl amino acids as sustainable and nature-friendly surfactants in the 1980s to 1990s, we found an interesting correlation between hydrophobicity measured by reversed-phase high-performance liquid chromatography (HPLC) (*T*) and their interfacial activities, such as micelle formation CMC and deformation of biomembranes as hemolysis (concentration to cause 50% hemolysis of human red blood cells), shown in Figs. 3–5.[12] These activities can be expressed by the general equation $\ln(X) = A - B_n$, where *X* represents each activity and *n* is the chain length (-CH_2-) of the surfactant.

Hydrophobicity (*T*) can be calculated from the retention time of each surfactant (t_R) and the mobile solvent (t_0) and correlated to the free energy change of each phenomenon by the equations shown below, where k_R is the capacity constant. Although *T* is empirical data, it can be correlated to the partition constant *K* and the free energy change of the phenomenon. Table 2 shows the effect of hydrophobicity change (*B*) by alkyl chain length for 3 surfactants.

As a result of this hydrophobicity analysis, we confirmed the usefulness of chromatography for the determination of surfactant potency.

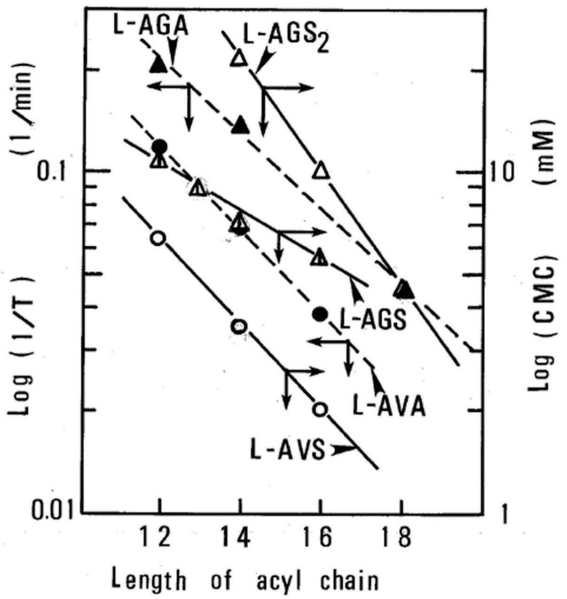
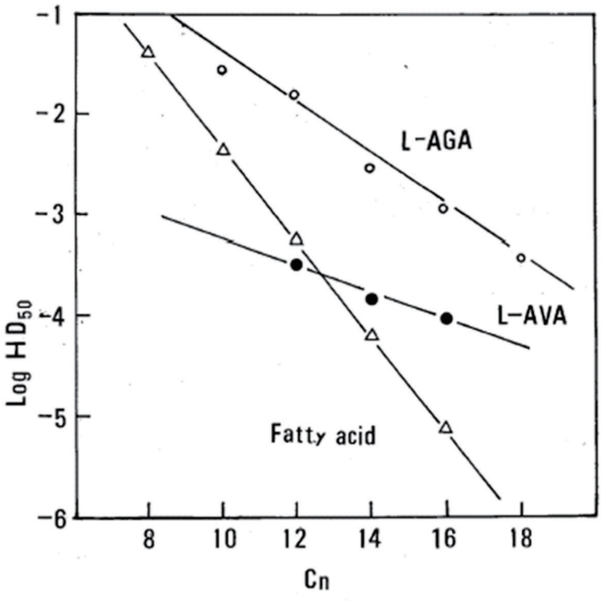


Fig. 3 Relation between log (1/*T*) or log (CMC) and chain length for N-acylamino acids. L-AGA (▲), L-AGS (△), L-AGS2 (△), L-AVA (●), L-AVS (○).

CMC, critical micellar concentration; L-AGA, N-acyl-L-glutamic acid; L-AGS, mono sodium N-acyl-L-glutamate; L-AGS2, disodium N-acyl-L-glutamate; L-AVA, N-acyl-L-valine; L-AVS, sodium N-acyl-L-valinate



Relation between HD_{50}(M) and carbon number in acyl group

○: L-AGA (N-Acyl-L-glutamic acid)
●: L-AVA (N-Acyl-L-valine)
△: Fatty acid

Fig. 4 Relation between HD_{50} (M) and carbon number in the acyl group.
HD_{50}, concentration to cause 50% hemolysis of human red blood cells

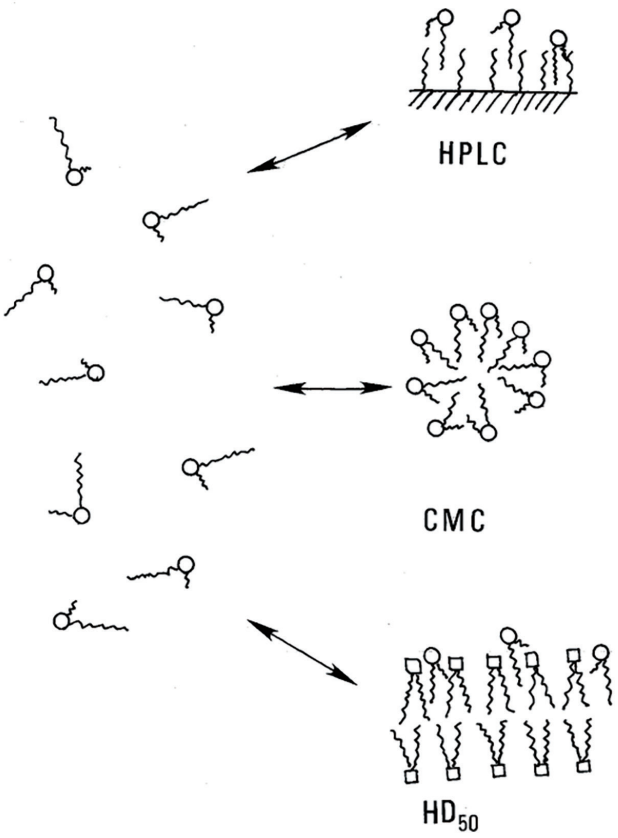


Fig. 5 Schematic illustration of hydrophobic interactions.
CMC, critical micellar concentration; HD_{50}, concentration to cause 50% hemolysis of human red blood cells; HPLC, high-performance liquid chromatography

Table 2 Relation between cmc, HD_{50}, or $1/k'$ and carbon number of N-acylamino acid.

Sample	cmc (M)[1)]		HD_{50} (M)[2)]		$1/k'$[3)]	
	A	*B*	*A*	*B*	*A*	*B*
N-acyl-L-valine	−0.69	0.13	−1.81	0.14	−1.28	0.15
N-acyl-L-glutamic acid	0.67	0.17	1.04	0.24	−1.6	0.14
Fatty acid	1.74	0.29	2.30	0.46	—	—

[1)]cmc, critical micelle concentration; HD_{50}, concentration to cause 50% hemolysis of human red blood cells; HPLC, high-performance liquid chromatography.

[2)]Capacity constant by HPLC.

[3)]Concentration at 50% hemolysis.

$$T = t_R - t_0$$
$$K' = T/t_0 = (t_R - t_0)/t_0$$
$$K' = Cs/Cm \times Vs/Vm$$
$$\ln k' = \ln Cs/Cm + \ln Vs/Vm$$
$$\Delta G^{o}_{x} = -RT\ln k$$
$$= -RT\ln Cs/Cm$$

$\log X = A - B_n$, where n represents the number of carbon atoms and X represents cmc, HD_{50}, or $1/k'$.

5. Advanced Empirical HLB Determination by ISP

Surfactants consist of hydrophilic and lipophilic groups that are covalently bonded. Therefore, it is conceivable that a single method would be difficult to accurately characterize the nature of every functional group. There are many reports concerning the polarity and hydrophilicity–lipophilicity of surfactants by using reversed-phase chromatography.[11)] However, the method never managed to establish a practical index because of the limited number of surfactants applied and the laborious and time-consuming nature of the task. On the other hand, we have proposed a novel method using TLC and systematically evaluated ionic and nonionic surfactants.[12,13)] In addition, it was ensured that this TLC method had good consistency with the HPLC method.[14)] Esquena and Solans examined our TLC method for the POE alkyl ethers and confirmed it is compatible with the calculated HLB numbers of these surfactants.[15)]

Based on these studies, we have attempted the theoretical evolution of this TLC method. The originality and ingenuity in our study lie in using 2 TLC plates with different polarities, normal and reverse phases, that provide individual R_f values as shown in Figs. 6 and 7.

The intrinsic capacity constant (k) of a surfactant is calculated by Equation (5)

$$k = \frac{1}{R_f} - 1 \tag{5}$$

Thus, each k value is obtained for the normal and reverse phases, and their ratio (k_N/k_R: k_N for normal phase and k_R for reverse phase) represents the "correlation index of hydrophilicity–lipophilicity." The selection and combinatorial approach of the TLC plate (stationary phase) and the mobile phase led to a comprehensive index that includes contributions of every functional group of the surfactant molecule partitioning in the mobile phase and interacting with the stationary phase. In addition, by using a given eluent as the mobile phase, the effect of solvation of the object substance can be estimated. Eventually, we developed a new index, "ISP", representing surfactant properties as functions of k_N and k_R

$$ISP = f\left(\frac{k_N}{k_R}\right) \tag{6}$$

This relational expression seems like the HLB calculation using the organic conceptual diagram,[6,7)] whereas our proposed method enables the empirical analysis of the substance itself.

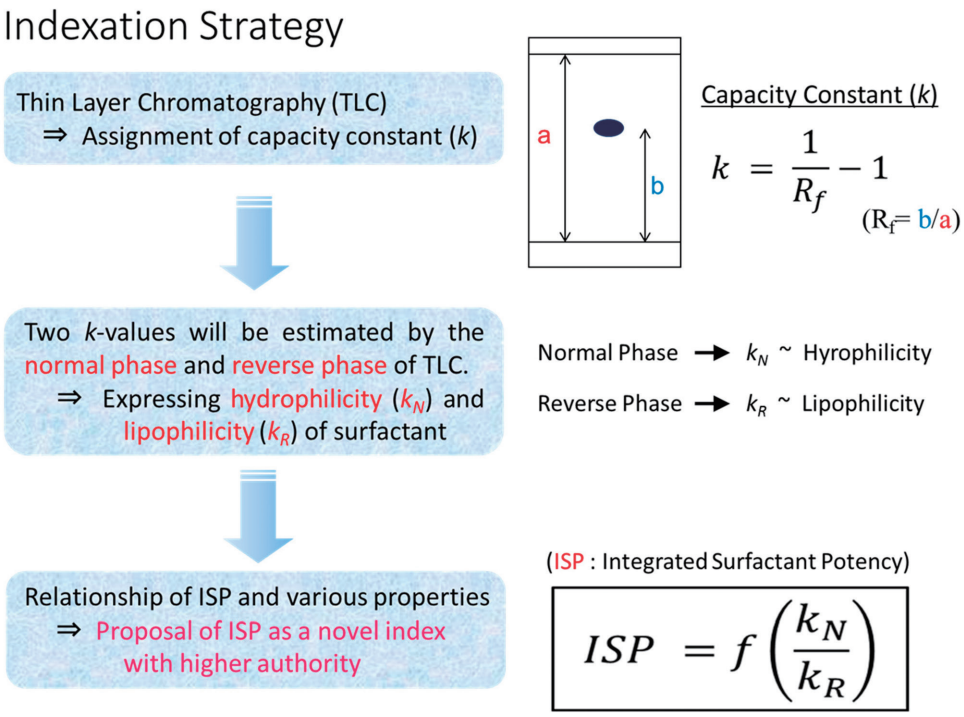


Fig. 6 Exploration of alternative parameter for HLB.
HLB, hydrophilic–lipophilic balance

6. Determination of ISP by the TLC Method[16,17]

To confirm the validity of this TLC method, the new index, k_N/k_R, was examined for POE lauryl ether ($C_{12}(EO)_m$, m = 0, 2, 3, 4, 5, 6, 7, 8, provided by Nikko Chemicals, Japan), and polyglycerin lauric acid ester ($C_{12}G_m$, m = 1, 2, 3 provided by Taiyo Kagaku, Japan) under the conditions shown in Figs. 7–9.

Figures 8 and 9 show TLC chromatograms of $C_{12}(EO)_m$ and $C_{12}G_m$ at room temperature (~25°C), and the capacity constants (k_N and k_R) of each surfactant are plotted in Figs. 10A and 10B. Since the migration distance of the surfactant (spot position) on the TLC plate depends on ambient conditions such as temperature and humidity (data not shown), the k values are always calibrated by the standard material, $C_{12}(EO)_4$. All TLC measurements were carried out at room temperature (~25°C). The normal phase k_N as an indicator of hydrophilicity showed a proportional increase with EO or G numbers as expected, following the equation $\ln(k_N) = A \times m - B$, where A reflects the hydrophilicity of the unit. As the value of A is 0.33 for $C_{12}(EO)_m$ and 1.20 for $C_{12}G_m$, glycerin (G) is a stronger hydrophilic group than oxyethylene (EO).

Reversed-phase k_R as an indicator of lipophilicity also showed a proportional increase with EO or G number (m) fitting the equation $\ln(k_R) = A' \times m - B'$, where A' reflects the lipophilicity of each hydrophilic group, that is, EO or G, and A' is larger for G at 0.43 than for EO at 0.095. This lipophilicity in the hydrophilic group is never accounted for in the regular HLB estimation, and this is the key point of the advanced feature of ISP as a quantitative and general (universal) index of surfactant potency.

ISP as a novel empirical index can be calculated by Equation (6) as

$$ISP = f\left(\frac{k_N}{k_R}\right). \quad (6)$$

There is a linear relationship between $\ln(k_N/k_R)$ and the number of hydrophilic groups in the surfactant molecule, as shown in Fig. 11, suggesting that the contribution per glycerin unit in $C_{12}G_m$ for ISP as a surfactant potency is approximately 2.8 times larger than the EO unit in $C_{12}(EO)_m$. This result is in close concordance with the work reported by Sagitani on the characterization of polyglycerol dodecyl ether. He reported that single glycerol units are approximately equivalent to the 3 oxyethylene units for HLB.[10]

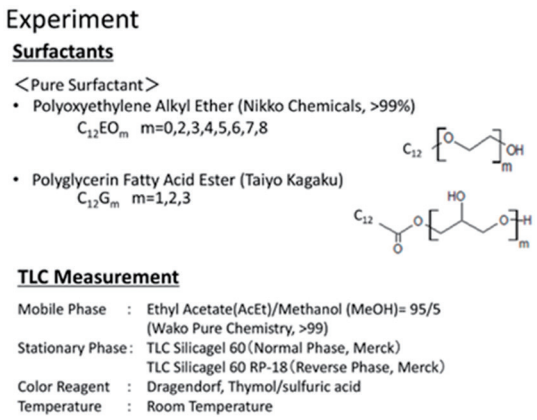


Fig. 7 Experimental condition for TLC chromatogram.
TLC, thin layer chromatography

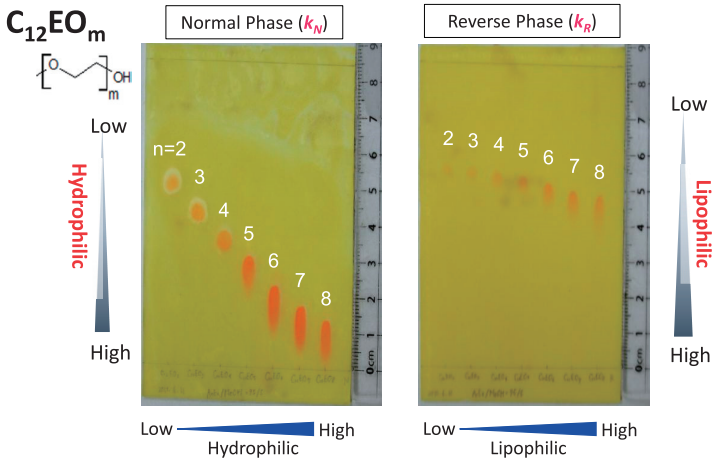


Fig. 8 TLC chromatogram for $C_{12}EO_m$ and the changes in k_N and k_R with EO chain length. The spot position monotonically decreases with increasing EO chain length for both normal and reverse TLC plates. The results suggest that POE groups have a lipophilic nature.
EO, oxyethylene; TLC, thin layer chromatography

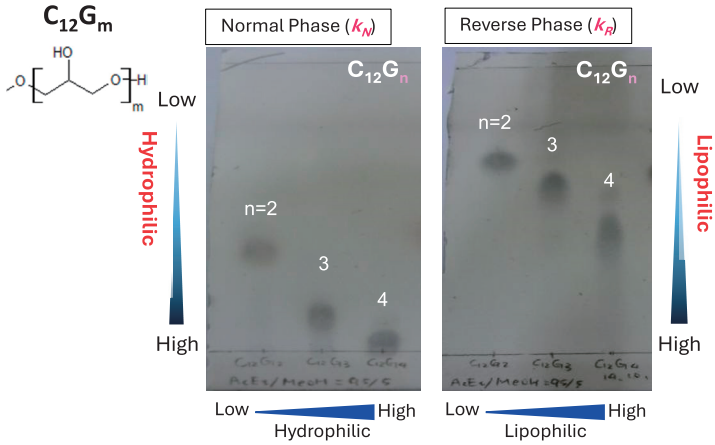


Fig. 9 TLC chromatogram for $C_{12}G_m$ and the changes in k_N and k_R with G chain length. The spot position monotonically decreases with increasing G chain length for both normal and reverse TLC plates. The results suggest that the G group has a lipophilic nature.
G, glycerin; TLC, thin layer chromatography

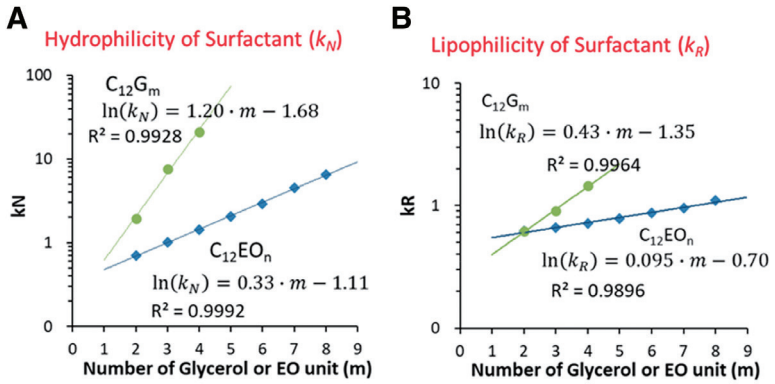


Fig. 10 Relation of capacity constants (k_N and k_R) of each surfactant for $C_{12}(EO)_m$ or $C_{12}G_m$. Normal phase k_N as an indicator of hydrophilicity showed a proportional increase with EO or G numbers as expected, following the equation $\ln(k_N) = A \times m - B$, where A reflects the hydrophilicity of the unit. As the value of A is 0.33 for $C_{12}(EO)_m$ and 1.20 for $C_{12}G_m$, G is a stronger hydrophilic group than EO. Reversed-phase k_R as an indicator of lipophilicity also showed a proportional increase with EO or G number (m) fitting the equation $\ln(k_R) = A' \times m - B'$, where A' reflects the lipophilicity of each hydrophilic group, that is, EO or G. A' is larger in G at 0.43 than EO at 0.095. This lipophilicity in the hydrophilic group is not accounted for in regular HLB estimation, and this is the key point of the advanced feature of ISP as a quantitative and general (universal) index of surfactant potency.
EO, oxyethylene; G, glycerin

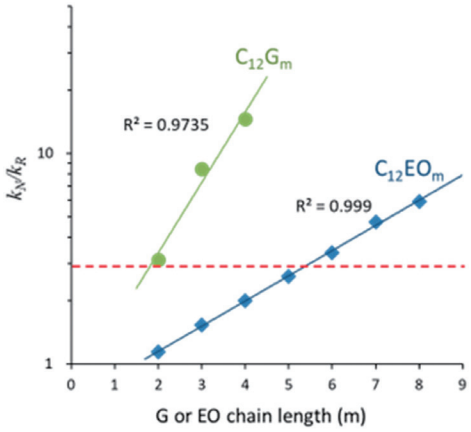


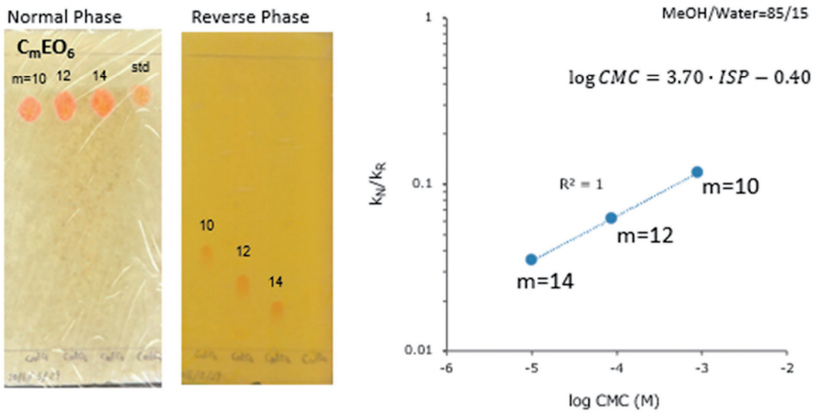
Fig. 11 Relationship between ISP = $\ln(k_N/k_R)$ and the number of hydrophilic groups in the surfactant molecule. There is a linear relationship between $\ln(k_N/k_R)$ and the number of hydrophilic groups in the surfactant molecule, suggesting that the contribution per glycerin unit in $C_{12}G_m$ for ISP as a surfactant potency is approximately 2.8 times larger than the EO unit in $C_{12}(EO)_m$.
IEO, oxyethylene; G, glycerin; ISP, Integrated Surfactant Potency

7. Influence of Lipophilic Chain Length on the ISP[17)]

As explained before, many primary surfactant properties, such as micelle formation (CMC), capacity constant (k) in chromatography, hemolysis, denaturation of proteins, and so on, are mainly caused by hydrophobic interactions with other hydrophobic substances, and are expressed by the general equation with hydrophobic chain length as $\ln(X) = A - B_n$, where X is a parameter for each property and n is the number of -CH_2- in the hydrophobic group.

As shown by the TLC chromatogram in Fig. 12, a significant effect of n was observed in reversed-phase TLC for $C_n(EO)_6$ with n = 10, 12, and 14. On the other hand, by normal phase TLC, the effect of n was negligible. Then, ISP = $\ln(k_N/k_R)$ showed the expected type of $\ln(X) = A - B_n$ relationship, as ISP = $0.384 - 0.132 \times n$. Also, a linear relationship between ISP as $\ln(k_N/k_R)$ and log(cmc) was found.

Such fundamental amphiphilic nature expressed by ISP was observed for alkyl sulfonate, which is an anionic surfactant, as shown in Figs. 13 and 14. Considering these results for ISP as $\ln(k_N/k_R)$ and log(cmc), we can expect the utilization of ISP as a universal index to characterize surfactant potency.



$$ISP = \ln(k_N/k_R) = 0.384 - 0.132\ n$$

Fig. 12 Influence of lipophilic chain length on ISP and CMC.
CMC, critical micellar concentration; ISP, Integrated Surfactant Potency

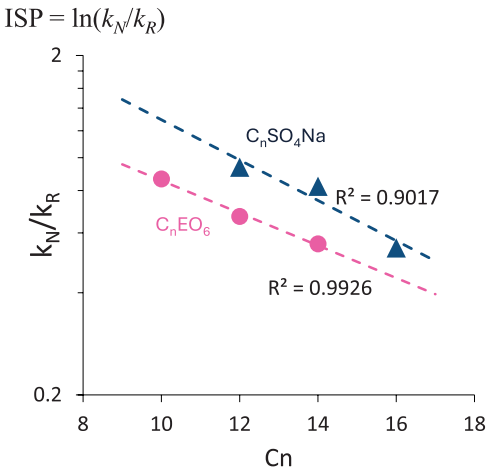


Fig. 13 Effect of lipophilic chain length on the ISP. ISP decreased linearly with chain length both for POE surfactant (C_nEO_6) and alkyl sodium sulfate (C_nSO_4Na).
ISP, Integrated Surfactant Potency; POE, poly-oxyethylene

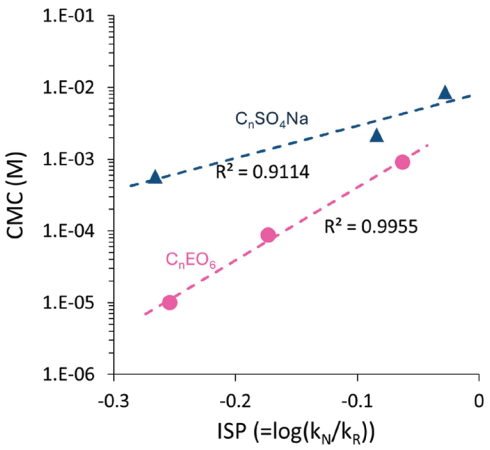


Fig. 14 Relationship between log (CMC) and ISP for POE surfactant (C_nEO_6) and alkyl sodium sulfate (C_nSO_4Na).
CMC, critical micellar concentration; ISP, Integrated Surfactant Potency; POE, poly-oxyethylene

8. Application of ISP as an Alternative Index to HLB Number[16,17)]

To expand the utilization of ISP beyond micelle formation, factors affecting emulsification are examined in relation to ISP as an alternative index to the HLB number. It is well known that the CP for C_nEO_m increases with increasing EO units (m) but nonlinearly, then saturates to an upper limit temperature for long alkyl tails. This is one of the cons, or demerits, of the HLB number in designing a desired emulsion formulation. As shown in Fig. 15[16)], ISP and CP of 1 wt.% $C_{12}EO_m$ aqueous solution show a linear relationship, which indicates ISP's quantitative nature in representing intrinsic surfactant potency. PIT is a more specific empirical index for POE surfactants, and PIT in C12G2/water/dodecane system is shown in Fig. 16.[16)]

Sagitani[10)] reported similar PIT for diglyceryl dodecyl ether (C_{12}-O-G_m) in the same water/dodecane system and explained that a single glycerol unit is approximately equivalent to the 3 oxyethylene units for HLB.[10)] As such, ISP could be a reliable index to represent surfactant potency based on the empirical hydrophilic and hydrophobic balance and correlates well with the physicochemical property (X), which follows the general equation of $\ln(X) = A - B_n$. Furthermore, ISP can be converted to the known HLB number of C_nEO_m surfactant if its property follows $\ln(X) = A - B_n$. In the next section, we will show the practical application of ISP for emulsification.

Furthermore, PIT of 3 wt.% $C_{12}G_2$ (C_{12} di-glycerin ester) in the water/$C_{12}G_2$/dodecane system was approximately 45°C, as shown in Fig. 18, and lies on the line of C_nEO_m close to C_nEO_5, as shown by the red triangle in Fig. 15. This is in quite good concordance with the result shown in Fig. 11, suggesting that the contribution per glycerin unit in **C12Gm** is approximately 2.8 times larger for ISP (surfactant potency) than the EO unit in $C_{12}(EO)_m$.

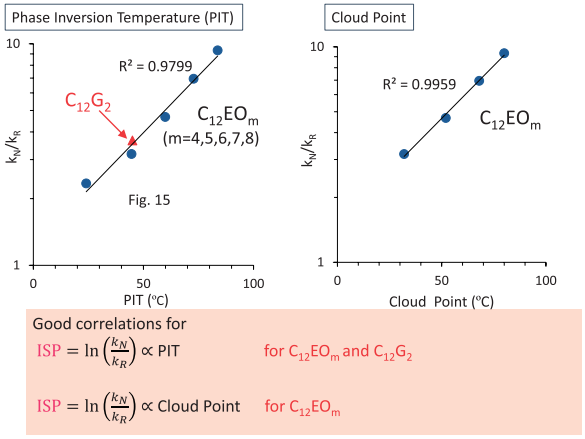


Fig. 15 Relationship between ISP and the cloud point of 1 wt.% $C_{12}EO_m$ and $C_{12}G_2$.
ISP, Integrated Surfactant Potency; PIT, phase inversion temperature

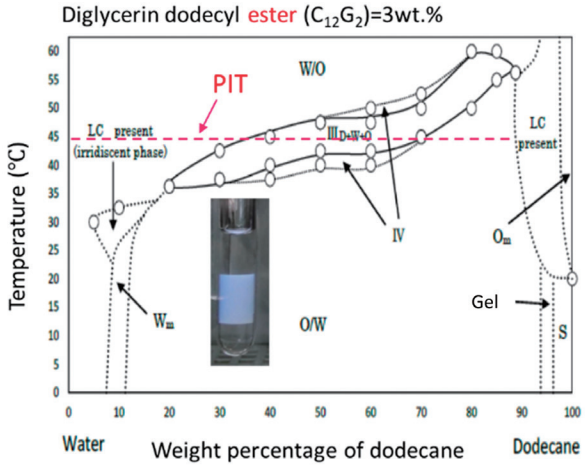


Fig. 16 PIT in the $C_{12}G_2$/water/dodecane system.
O/W, oil and water; PIT, phase inversion temperature; W/O, water and oil

9. Emulsification Test[16,17]

It is well known that a stable and finely dispersed emulsion can be prepared by knowing the required HLB of the oil and adjusting the HLB of surfactant mixtures to the oil's requirement. Based on this concept, an emulsification test was carried out for the model formulations A and B with a surfactant/water/liquid paraffin = 4/56/40 wt.% system as shown in Fig. 17. Formulation A was prepared by using the estimated HLB number 11 for $C_{12}G_2$, derived from its ISP value (3.7) converted to the HLB of $C_{12}EO_m$, as shown in Fig. 17. This was then combined with Span (HLB 4.7) to adjust the HLB to 10, which corresponds to the required HLB of the oil. Formulation B was prepared by using an HLB of 8.5 for $C_{12}G_2$, which is provided by the Griffin's method, and adjusted with Tween (HLB 14.9). Formulation A gave a finely dispersed stable emulsion, while Formulation B, as a common method, did not provide a desirable emulsion, as shown in Fig. 17. Thus, ISP is a promising alternative index to the HLB number.

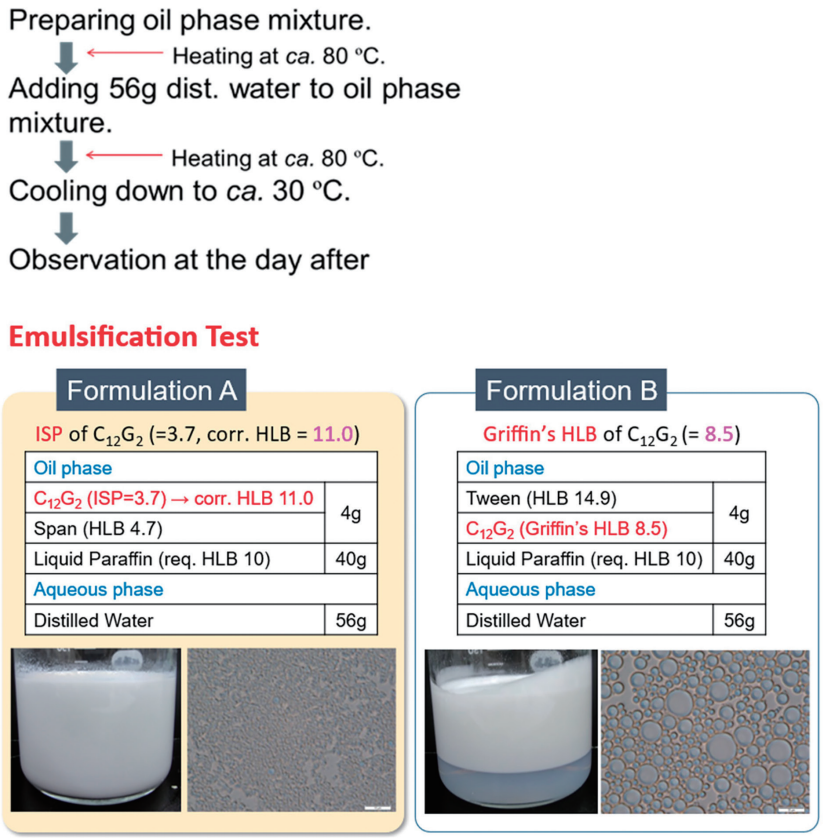


Fig. 17 Emulsification for test formula with required (4.7) of liquid paraffin for adjusted surfactant combination. General emulsification tests using Tween (HLB 14.9) and Span (4.7) are carried out to evaluate $C_{12}G_2$ with unknown HLB. ISP of $C_{12}G_2$, which is taken as a hydrophilic surfactant, gives a more stable emulsion than the Griffin's HLB, which corresponds to a lipophilic surfactant.
HLB, hydrophilic–lipophilic balance; ISP, Integrated Surfactant Potency; hydrophilic–lipophilic balancehydrophilic–lipophilic balancehydrophilic–lipophilic balance

10. Extension of ISP to the Mixed Surfactants and Commercial Surfactants[17]

As explained above, the basic potency of ISP as a novel index to characterize surfactant potency and its prospective application to the commercial surfactants is discussed in this section. As commercial surfactants are mixtures of many components, we have tried to apply the ISP concept to the mixtures of POE surfactants with the assumption that ISP_{mix} can be calculated by $ISP_{mix} = ISPmix = \Sigma\left(\frac{k_N}{k_R} \times A_i \times I_i\right)$, where A_i is the fraction of area and I_i is the intensity factor obtained from the TLC chromatogram. The experimental design is shown in Fig. 18. This experiment was designed to confirm

the assumption by using a mixture of pure $C_{12}EO_m$ to prepare a known composition and to compare the experimental results with the theoretical calculations. As shown in Figs. 19 and 20, the experimental ISP_{mix} showed good concordance with the calculated values.

Then, an experiment for the commercial POE lauryl ether (BL-4.2:C_{12}POE, Nikko Chemicals) was investigated. The most important and difficult part was the complete separation of components by TLC chromatogram. After some trials for the selection of the mobile phase, we succeeded in quantitatively separating and qualifying each component in BL-4.2 using AcOEt/acetone/H_2O = 55/35/10, and then converting it to the k_N of AcOEt/MeOH = 95/5, as shown in Fig. 21. With this composition, we could calculate k_R as plotted in Fig. 22. The experimental ISP of major components in BL-4.2, EO_m with m = 1, 2, 3, 4, showed good concordance with the calculated values as shown in Fig. 22.

As a summary of Fig. 22, the following points are confirmed, which indicate the usefulness of the practical application of ISP:

1. A linear relationship between ISP and CP for a single surfactant is observed.
2. ISP (Obs = Calc) for mixed surfactants lies on this line.
3. ISP (Obs) for commercial surfactants, with conversion of k_N and composition analysis with Mobile Phase 2, showed good agreement with the linear relationship between ISP and CP.

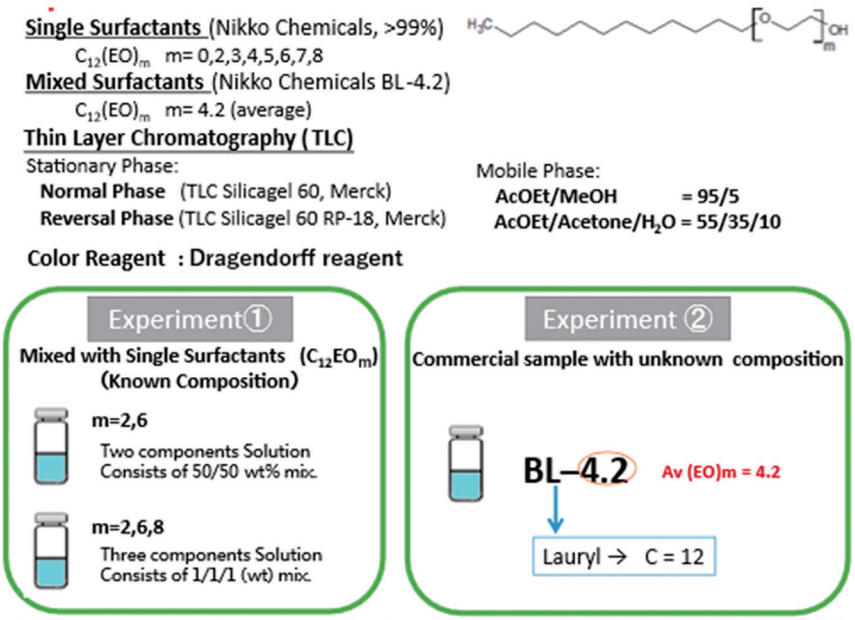


Fig. 18 Extension of ISP to the mixed surfactants and commercial surfactants. Experiment 1 is designed to confirm the assumption by using a mixture of pure $C_{12}EO_m$ to compose a known composition.
ISP, Integrated Surfactant Potency

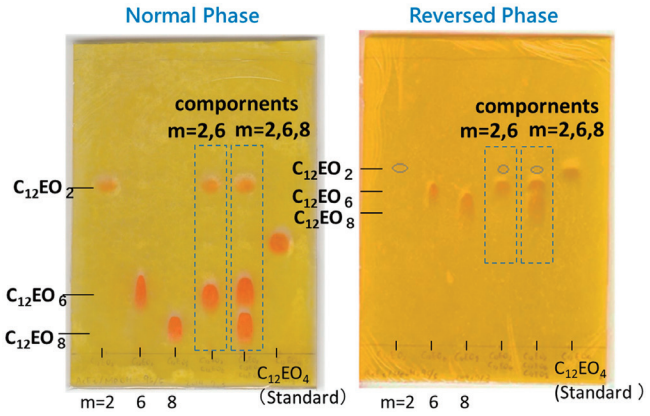
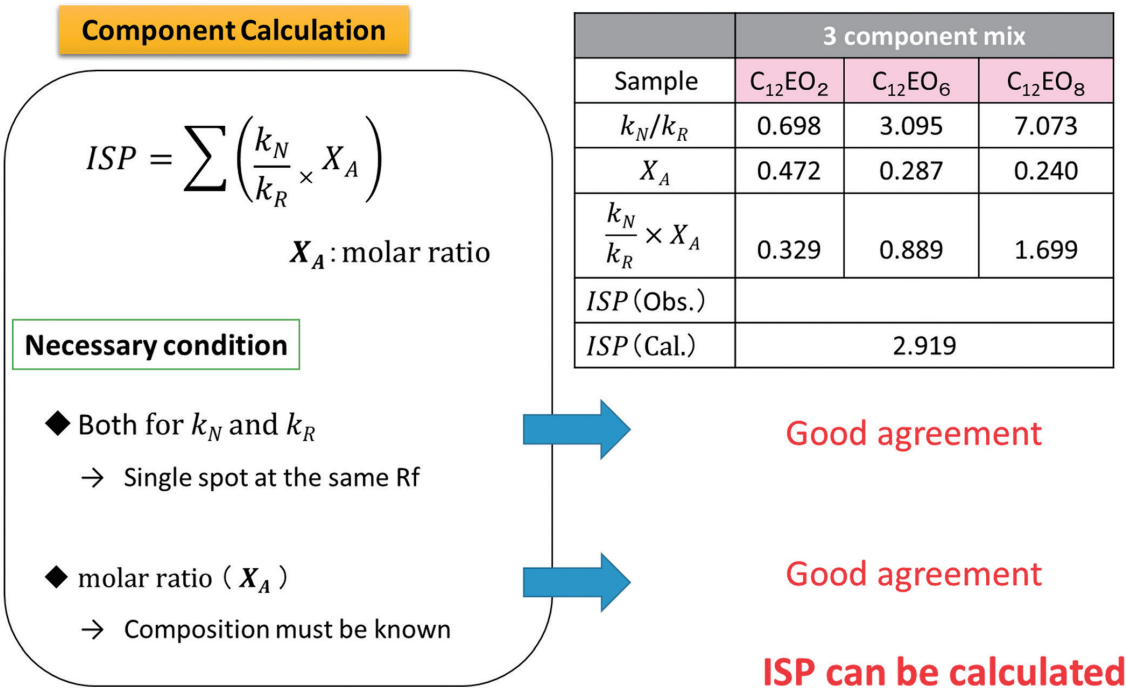


Fig. 19 TLC chromatogram of Experiment 1 for mixed single surfactants ($C_{12}EO_n$).
TLC, thin layer chromatography



	3 component mix		
Sample	$C_{12}EO_2$	$C_{12}EO_6$	$C_{12}EO_8$
k_N/k_R	0.698	3.095	7.073
X_A	0.472	0.287	0.240
$\frac{k_N}{k_R} \times X_A$	0.329	0.889	1.699
ISP (Obs.)			
ISP (Cal.)	2.919		

Fig. 20 Result of Experiment 1 for mixed single surfactants ($C_{12}EO$). For both k_N and k_R, spots are found at the same R_f for each single component, and an equal molar ratio is confirmed for the mixture so that ISP can be calculated for the mixture.
ISP, Integrated Surfactant Potency

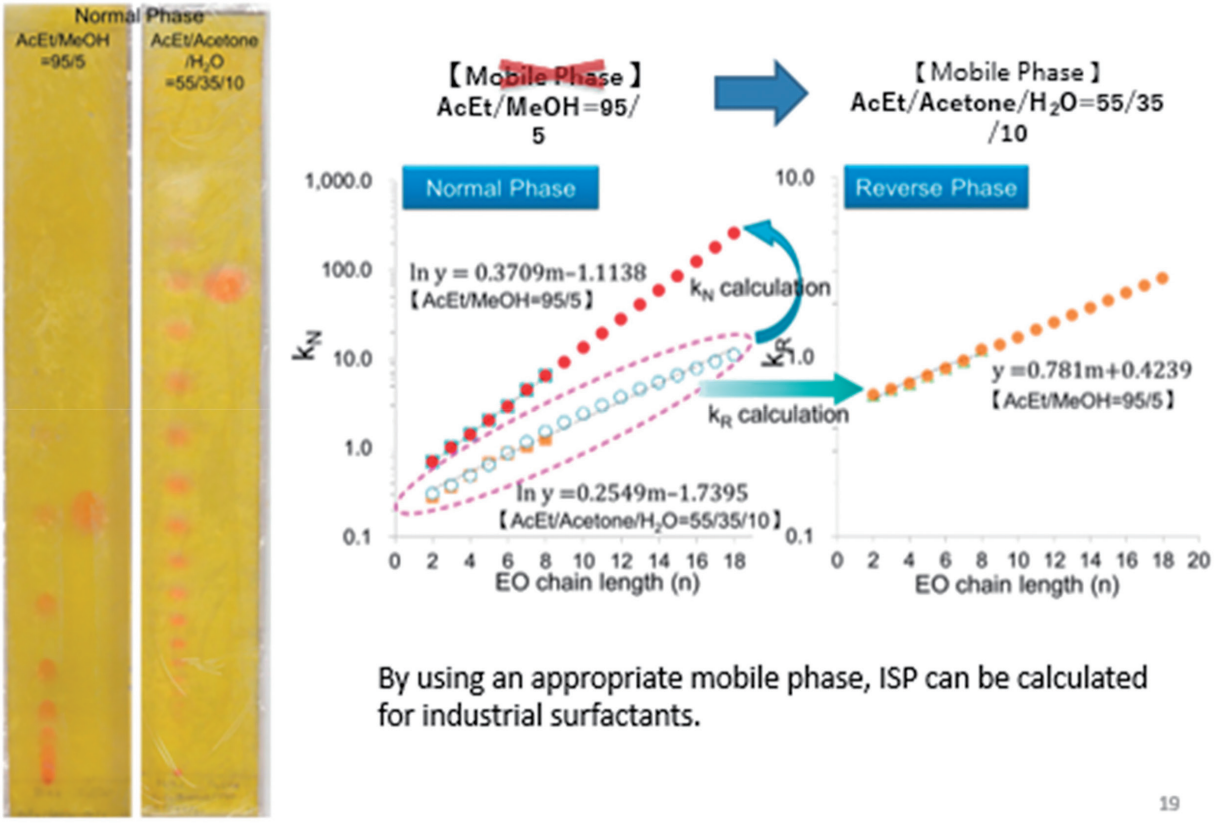


Fig. 21 Application of ISP for commercial surfactants. By using an appropriate mobile phase, ISP can be calculated for industrial surfactants.
EO, oxyethylene; ISP, Integrated Surfactant Potency

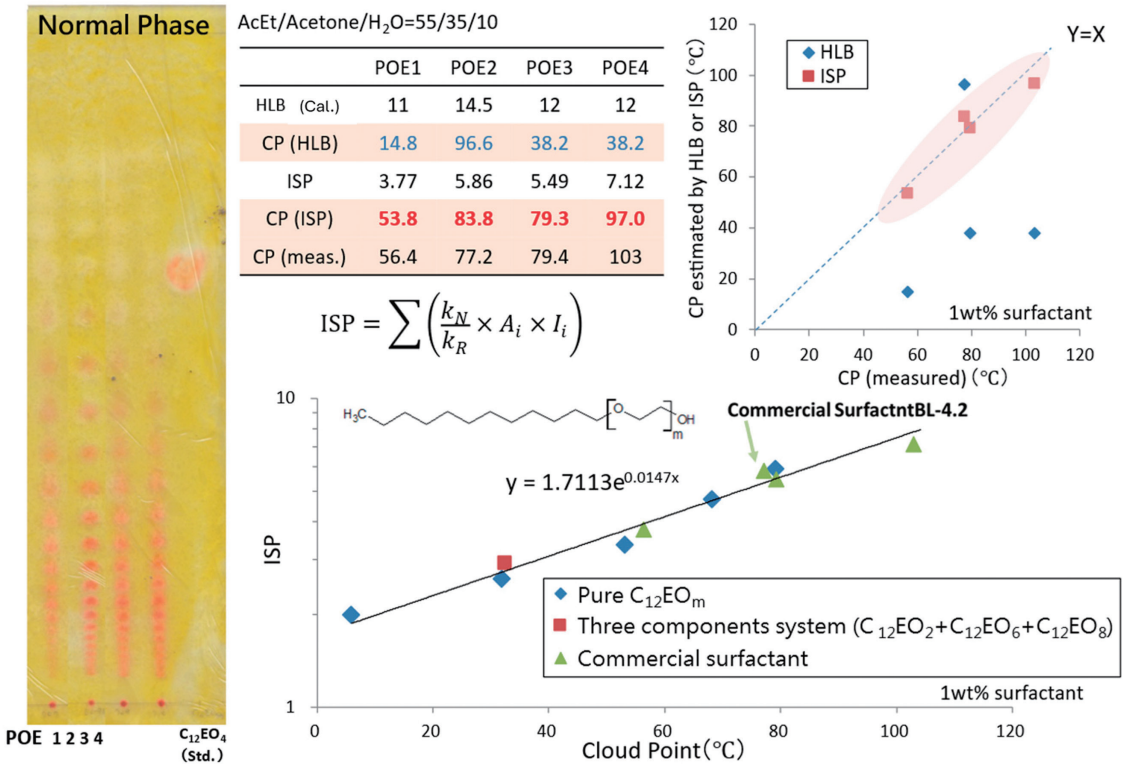


Fig. 22 Application of ISPfor industrial surfactants (POE type). ISP (Obs.) for commercial surfactants with conversion of k_N and composition analysis using Mobile Phase 2 showed good agreement with the linear relationship between ISP and CP.

Cal., calculated; CP, cloud point; HLB, hydrophilic–lipophilic balance; ISP, Integrated Surfactant Potency; meas., measured; Obs., observed; POE, poly-oxyethylene; std., standard

11. Conclusions

We reviewed the classical HLB number and its calculation methods and pointed out the problems that can possibly be encountered during real manufacturing processes. Especially, different equations lead to different HLB numbers, which can put the desired properties of the formulation at risk. To resolve such unnoticed or overlooked misfits between the HLB number and the solution properties and applications such as emulsification, a new method has been proposed by using chromatography techniques. Instead of the HLB number, we proposed an original and useful index, "ISP". The appropriate formula for ISP is being investigated in detail and will be acceptable for all surfactants by modifying the eluent and the stationary phase. In addition, ISP will be able to predict the properties of the surfactant solution such as CMC, CP, and LC structures associated with the HLB of the surfactant. Our objective is to establish this TLC method to be utilized in many industrial fields to provide solutions through the proper selection of surfactants.

Abbreviations: AcOEt, ethyl acetate; CMC, critical micelle concentration; C_mEO_n, polyoxyethylene alkyl ether; C_mG_n, polyglycerin fatty acid ester; C_nSO_4Na, sodium alkyl sulfate; CP, cloud point; HLB, hydrophilic–lipophilic balance; ISP, Integrated Surfactant Potency; LC, liquid crystal; PIT, phase inversion temperature; POE, poly-oxyethylene; TLC, thin layer chromatography

Conflict of Interest: The authors declare there is no conflict of interest to declare.

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