Hydrophile-Lipophile Balance of Surfactants and Solid Particles

Physicochemical Aspects and Applications

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Preface

The amphiphilicity is a fundamental characteristic of any surfactant, which becomes evident in various surface and bulk properties, for example, adsorption, micelle formation, formation of stable liquid films in foams and emulsions, wetting films, lipid membranes, formation of vesicles (liposomes), in the distribution of matter between heteropolar phases, in the operation of various biologic systems, etc.

To access the quantitative measure of the amphiphilicity, the so-called hydrophile-lipophile balance is widely used, which in a certain way reflects the relative efficiency of the heteropolar parts of the surfactants.

The most commonly used characteristics of the hydrophile-lipophile balance with respect to the application of surfactants are Griffin's HLB numbers and Davies' HLB numbers. These numbers were introduced in response to technological needs, where a quantitative characterisation of a surfactant was required to facilitate the choice and selection of the particular compound in a specific application (the development of a detergent compositions and solubilisers, stabilisation of foams and emulsions, etc.)

The studies dealing with the concept of the hydrophile-lipophile balance were mainly concerned with establishing correlations between Griffin's or Davies' HLB numbers and various properties of surfactants, the substantiation or criticism of the Griffin's HLB system, the refinement of various methodological details of experimental measurements or theoretical calculations of HLB numbers, and with the proper account for various factors (molecular structure, medium, temperature etc.) which have been ignored in the HLB numbers system. It should be noted that the applicability of the system of HLB numbers is often overestimated. Clearly, any complex phenomena, and, in particular, the stabilisation of emulsions or detergency, cannot be characterised by a single parameter of a surfactant irrespective of the temperature and ambient medium.

It should also be noted that, following Davies, many authors considered the calculated Davies' and Griffin's HLB numbers as the same quantities. This point of view cannot, however, cannot be shared. Generally speaking, these two systems of numbers represent different hydrophility scales.

From the viewpoint of the physical chemistry of surfactants, it appears that the problem of the search, establishing and study of the practically important characteristics of the hydrophile-lipophile balance which, as applied to surfactants, possess a simple and unambiguous physical meaning, and are applicable to all types of surfactants (micellar and non-micellar, ionic and non-ionic) is much more important.

It was stressed by P.A. Rebinder that "… the development of a quantitative theory of hydrophile-lipophile balance … should be considered as the most important goal of the physical chemistry of surfactants. The solution of this problem should lead to the scientific foundations for the estimation of the efficiency of the developed application of surfactants". Here two aspects of the problem should be kept in mind: the choice of a general and physically meaningful characteristic which employs both the balance of the heteropolar parts of a surfactant and the amount (force) of the "lever arm" of the balance, and the application of the constituents of this balance and the hydrophile-lipophile balance value to give an explanation for various surface and bulk properties (with respect to micelle formation or adsorption) and more complicated phenomena, for example the formation of vesicles, microemulsions, emulsions, foams etc.

The energetic treatment of the hydrophile-lipophile balance can possibly be the most general and useful concept, because all colloid and surface phenomena are closely related with the energetic characteristics of surfactants. This approach, however not consequently, was adopted already in the concept of Davies' numbers for functional groups of surfactants.

In his studies, Davies introduced the energetic treatment of the hydrophile-lipophile balance when comparing the empirical group numbers corresponding to the functional groups of surfactants, and the activation barrier for the breaking of emulsion films.

In recent years, a quite extensive scope of knowledge was accumulated in the area of the energetic characteristics of surfactant molecules and their particular parts with respect to adsorption, micelle formation, distribution between bulk phases etc. However, the hydrophile-lipophile balance concept based on these characteristics by no means became widespread.

The main idea of the proposed book is the energetic concept of hydrophile-lipophile balance as applied to surfactants and solid particles (acting mainly as stabilisers of emulsions). At the same time, the monograph systematises a number of other branches of studies regarding the hydrophile-lipophile balance.

The first chapter summarises the known surface and bulk properties of surfactants which are directly related to the hydrophile-lipophile balance concept and are used either to determine the HLB numbers or to provide an independent measure of the hydrophile-lipophile balance. Along with the systematic exposition of known properties of surfactants, this chapter contains new theoretic data concerning the calculation of interfacial tension, determination of the adsorption of surface-active electrolytes, estimation of the energy of adsorption, and also summarises the studies performed by the author in relation with the Antonov's rule, Traube's rule and the comparison of the contribution to Gibbs' energy for various structural groups of surfactant molecules as applied to their transfer from bulk phases through the dividing surface to micelles and other bulk phases.

The second chapter systematises the most important properties of emulsions (properties of films, phase inversion, and the kinetics of flocculation and coalescence) which are directly related to the stability of emulsions, to the formulation of HLB numbers by Davies, and to the concept of the HLB temperature (phase inversion temperature, PIT) introduced by Shinoda.

The third chapter presents a comprehensive analysis of the systems of Griffin's and Davies' HLB numbers (experimental evaluation and calculation of HLB numbers and a comparative analysis of the original systems and modifications proposed by various authors), the determination of the characteristics of the hydrophile-lipophile balance based on the energetic properties of surfactants (distribution coefficients, work of adsorption and energy of micelle formation).

In the fourth chapter, the methods are described which are used to express hydrophile-lipophile balance for solid particles of various nature and dispersity (macroscopic, gel-like or colloid-disperse) employed as emulsifying agents or foam stabilisers, and the properties of emulsions stabilised by solid particles.

The fifth chapter briefly summarises some practical applications of the concept of the hydrophile-lipophile balance in various branches of science and technology.

The author acknowledges the contributions made by his co-workers, namely T.V. Mikina A.I. Bulavchenko, L.L. Kuznetsova, S.M. Selitskaya, V.D. Mal'kov and T.N. Khaskova, to the studies related to the hydrophile-lipophile balance concept, summarised in this book.

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Penza, May 2000 Pyotr M. Kruglyakov

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Introduction

The concepts of lyophilicity and lyophobicity (or, as applied to aqueous media, hydrophilicity and hydrophobicity) are commonly used in colloid chemistry.

At the early stages of the studies of disperse systems, the terms 'lyophilicity' and 'lyophobicity' were used to discriminate between systems which possess weak affinity of the disperse phase to the medium (suspensoids) and those displaying a pronounced interaction between the particles and the medium (emulsoids). From the modern point of view, lyophobic colloidal solutions and other dispersions are thermodynamically non-equilibrium systems, while lyophilic colloids are equilibrium systems.

Another meaning is ascribed to the terms 'lyophilicity' and 'lyophobicity' with respect to the phenomena of wetting and stabilisation of emulsions by solid particles. In this case the hydrophility (or hydrophobicity) of the particle is characterised by the contact angle θ for the selective wetting, that is, for the contact of the solid surface with a pair of immiscible heteropolar liquids (e.g., water/oil), or by other parameters, for example the work of wetting, quantitatively related to the wetting angle. The surface is called hydrophobic (oleophilic) if it is better wetted by non-polar liquids, $\theta > 90°$. Alternatively, if it is better wetted by water, $\theta < 90°$, the surface is called hydrophilic (oleophobic). Hereinafter the wetting angle is counted through the polar liquid.

According to these two concepts of lyophilicity, the behaviour of quartz, for example, corresponds to hydrophilic (oleophobic) particles with respect to wetting by water; at the same time the sol of SiO_2 (or SiO_2 suspensions) in water demonstrates the properties of a hydrophobic colloidal system.

The concept of hydrophile-lipophile balance as the quantitative measure of the amphiphilicity of surfactants (primarily emulsifying agents) arose much later (in the late 40s and early 50s), especially in connection to the synthesis and application of non-ionic surfactants, for example, oxyethylated derivatives of alcohols, acids and alkyl phenols.

In particular, W. Clayton in his well-known monograph *The Theory of Emulsions and their Technical Treatment* ([1] p. 243) refers to patents in which substances are proposed that prevent splashing of liquid margarine, and emulsifying agents with balanced contents of hydrophilic and hydrophobic groups.

In these years, in the studies of non-ionic surfactants [2-5] it was shown that the existence of a definite hydrophile-hydrophobe balance (the ratio of the mean number of moles of ethylene oxide to the number of hydrophobic fragments, e.g. methylene groups) is required to achieve the optimum condition of wetting, detergency, emulsifying and de-emulsifying action, solubilisation, foam formation etc. This concept was subsequently extended over other classes of surfactants; at the same time, the quantitative measure of the hydrophile-lipophile balance for these substances is still controversial.

Clearly, the relative efficiency of the polar and apolar parts of surfactant molecule can be expressed via the particular properties of these parts (or the substance as a whole); it should be also kept in mind that different ways of the estimation of hydrophile-lipophile balance can turn to be practically convenient for different processes in which the surfactants play an important role.

Among the parameters which can be employed to estimate the hydrophile-lipophile balance are the structural characteristics (the volume and configuration of the parts of a surfactant), mass-dependent (various functions of mass of hydrophilic or hydrophobic parts) or energy-dependent characteristics (the work of transfer from one phase to another, the work of adsorption from various phases, including those determined in chromatographic processes, the heat of dissolution, the work of micelle formation), and other complex characteristics (the stability and the type of emulsions formed, phase inversion temperature, detergency, solubilisation, etc.)

In turn, the energetic characteristics can be subdivided into direct (primary) and indirect (secondary) parameters. The primary characteristics are related to the surfactant itself (or to its specific parts). These characteristics, however, depend also on the type of the phases, between which the surfactant is distributed and with which it interacts. Among these characteristics are the energy of the transfer of surfactant from one phase to another, the work of surfactant adsorption, the heat of dissolution and the heat of adsorption, the work of micelle formation.

The indirect characteristics refer to the system as a whole, for example, to the water/oil system in the presence of a surfactant, or to different parts of the system. This group includes interfacial tension, spreading coefficient, activity coefficients for water and oil in the presence of the surfactant and some other parameters.

Possibly the most general characteristic of the hydrophile-lipophile balance should be expressible through some fundamental properties, which are immanent to any surfactant, reflects the influence of both parts of the surfactant molecule, and possesses a clear physical meaning. For example, the characteristics related to the micelle formation do not satisfy these requirements, because micelle formation is not immanent to all kinds of surfactants. On the other hand, the stabilising ability (in foams, emulsions, suspensions) or detergency of surfactants, while belonging to the important properties of these substances, also cannot satisfy these requirements because these properties follow from the complex action of several simple properties, evident in complex kinetic processes and equilibrium states.

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Chapter 1

Physicochemical properties of surfactants used in the definition of hydrophile-lipophile balance

1.1. Classification of surfactants with respect to structure and chemical nature

Surfactants are substances which decrease the surface (interfacial) tension. It should be noted, of surfactants with respect to the structure and chemical nature however, that the interface can be chosen in such a way that any particular substance, being in a liquid or vapour phase, or a solution component, can act to decrease the surface or interfacial tension. In a more specific sense, the term "surfactant" denotes amphiphilic organic substances of an asymmetric molecular structure.

Typically, surfactant molecule consists of two parts, which possess properties that are opposite to each other by their nature. One part of the molecule (or ion) is the hydrophilic polar group, for example, $-NH_2$, $-OH$, $-COOH$, $-SO_3H$, $-OSO_3H$, $-COOMe$, $-OSO_3Me$, $-N(CH_3)_3Cl$, $-CH_2CH_2O$.

Another part is formed by a rather long hydrocarbon or hydrofluorine hydrophobic (oleophilic) chain. High molecular-weight surfactants (proteins, polyvinyl alcohols, polyacryl amide etc.) contain alternating hydrophilic and hydrophobic molecular groups distributed along the whole molecule.

These typical surfactants demonstrate always some surface activity at the water/gas and water/oil interface, and are often surface active at the interface between a solution and some solid phases.

With respect to their structure and chemical nature, surfactants can be divided into two major groups - non-ionic surfactants and surface-active electrolytes (colloidal electrolytes) which consist of a long-chain ion (surface active ion) and an ordinary inorganic ion (counterion).

The molecules of non-ionic surfactants contain polar groups unable to dissociate and possessing a significant affinity to water and other polar substances. Usually these groups incorporate atoms of oxygen, nitrogen, phosphorus or sulphur (alcohols, amines, ethers etc.).

Among the substances of this group of surfactants, the most significant are oxyethylated alkyl phenols, fatty alcohols, fatty acids, amines and block-copolymer surfactants (oxyethylene non-ionic surfactants), in which the polar part of the molecule consists of repeated oxyethylene group $-CH_2-O-CH_2-$ and closing $-OH$, $-COOH$ or $-NH_2$ group.

The most common oil-soluble surfactants which belong to this group are ethers of fatty acids and polyatomic alcohols - pentaerythritol, triethanol amine, unhydro sorbite and unhydro xylite (like Span, Tween etc.)

The ionic surfactants, in turn, can be subdivided into two groups: anionic (anion-active) substances, for which the hydrophobic long-chain part responsible for the surface activity is incorporated into the anion, and cationic (cation-active) surfactants, where the cations are incorporated into the hydrocarbon or other hydrophobic radical which is responsible for the surface activity. Among the anionic surfactants, the most significant are the soaps of carbon acids (RCOOMe), alkyl sulphates (sulphoether salts) $ROSO_3Me$, alkane sulphonates RSO_3Me, alkyl aryl sulphonates $RC_6H_5SO_3Me$, alkyl phosphates $ROPO(OMe)_2$, salts of sulphosuccinic acids. The typical surfactants which belong to this class are sodium dodecyl sulphate, sodium oleate and sodium dodecyl benzene sulphonate.

Among the cationic surfactants, the most common are the salts of (primary, secondary and tertiary) amines, and quaternary salts of ammonium, for example, cetyl ammonium bromide and octadecyl pyridinium chloride.

The ampholytic surfactants, which demonstrate either anionic or cationic properties depending on the properties of the medium (pH), can be regarded to as a particular class. These substances usually comprise some polar groups, for example, dodecyl-β-alanine $C_{12}H_{25}NHC_2H_4COOH$ contains both carboxy group and amino group. Depending on the ambient conditions (primarily on the pH value in aqueous media), in the solution these surfactants can form either surface-active anions or surface-active cations.

Finally, zwitter-ionic surfactants can be regarded as an intermediate between non-ionic and ampholytic surfactants. The polar parts of these molecules, while neutral as the whole, contain opposite charges, separated from each other by another structural elements: here the betaine can be referred to as an example: $RN^+(CH_2C_6H_5)(CH_3)CH_2COO^-$, where R is the hydrocarbon radical possessing 8 to 12 carbon atoms.

As the hydrophobic chain of a surfactant comprises a number of identical elements (CH_2, CF_2, etc.), many of the properties of a surfactant depend additively on the number of such elements, such as vapour pressure, solubility, distribution coefficient, surface activity, adsorption, micelle formation and many others. This additivity is also evident with respect to the variation in the number of oxyethylene groups (EO) in non-ionic oxyethylated surfactants. The additivity usually holds well for straight chains and small variations in the number of structural elements, $\Delta_{nCH_2} = 4 - 5$, sometimes to $\Delta_{nCH_2} = 10$; for higher values of this number, deviations from additivity become evident. The additivity with respect to some properties is violated also when the position of a polar group in the hydrocarbon chain is changed, or when any isomerism is introduced into this chain.

To be efficient, surfactants should not only be amphiphilic, but, in addition, should possess 'strong' and well-balanced hydrophobic and hydrophilic parts, which enable them to remain at the interface, to form micelles, and to participate in other processes. Depending on the strength of both polar and non-polar parts, and on the value of the hydrophile-lipophile balance, the surfactants can be classified with respect to their technological applications (foaming agents, emulsifiers, wetting agents, solubilisers, detergents etc.)

The synthesis, structure and various properties of surfactants are considered in detail in a number of monographs and handbooks [1-8]; the reader can also turn to volumes of the Surfactant Science Series [9-14]. The most recent publication to refer to in respect to a systematisation of surfactants, their synthesis, chemical and physico-chemical characterisation, and practical applications in many technological field is the monograph to be published in this Series [15]. This volume entitled "Surfactants – Chemistry, Interfacial Properties, Applications" will appear in the beginning of 2001 with Elsevier Science B.V., co-authored by B.E. Chistyakov, V.B. Fainerman, D.O. Grigoriev, M.Yu. Pletnev, A.V. Makievski, R. Miller and B.A. Noskov.