

An improved method for the determination of HLB properties of nonionic surfactants

Roland Nagy, Réka Kothencz, Rubina Sallai, László Bartha

Abstract—The nonionic surfactants have received an increasing attention in the industrial field. The partial solubility in water of the own-developed and own-synthesized vegetable oil-based nonionic surfactants was examined. The solubility is one of the key properties of the surfactants. The new fiber-optic spectrophotometric analytical method was found appropriate and beneficial to determine the water number and the HLB value of the nonionic surfactants. Two series of nonionic surfactants were studied by different HLB methods (conventional, numerical- and a developed method). A new method was developed inspired by the method of Becher et al. which approximates better the theoretical HLB value.

Index Terms— biopolymer, hydrophilic-lipophilic balance, method development, nonionic surfactant

1 INTRODUCTION

In the past few decades the importance of the researches related to the surfactants increased, mainly because of the development of cosmetic and household industry [1], [2].

However, the surfactants are also used for the preparation of polymer composites. Starch is widely applied in the preparation of biopolymer mixtures because of its low price and suitable degradation characteristics. Currently formaldehyde-based adhesives, phenol-formaldehyde and urea-formaldehyde are used as wood adhesives [3], [4]. The application of nonionic surfactants is also considerable in this area. The requirements regarding the emulsifiers are determined by different characteristics of the given area. Due to their amphipatic character, one of the key properties of the surfactant molecules is the solubility in water or in oil [5]. Thus, it is important to determine these properties to choose the appropriate utilization area [6].

The relation between the emulsifying effect and the dispersed particle size in oil/water emulsions was studied by Yamamoto et al [7]. The capacity of the emulsification and the solubility depend on the HLB value of a given nonionic surfactant which information is necessary for its practical application.

The HLB (hydrophilic-lipophilic balance) concept was introduced by Griffin [8]. The HLB of an emulsifier is a number which expresses the ratio of water-soluble and oil-soluble groups in the molecule. The method of Greenwald et al. was employed to determine the Water Number of each surfactant. In this method the surfactant was dissolved in benzene-dioxane mixture containing 4 v/v% of benzene. Then the stirred solution was titrated with double-distilled water from a microburette until a persistent turbidity was obtained. The amount of water added at this point is known as the 'Water Number' (WN). Greenwald et al. gave a figure with the linear relationships between HLB and WN for 18 surface active compounds in two surfactant families of polyhydric alcohol esters: ethylene oxide adducts and those without ethylene oxide [9].

The aim of our work was to study the characteristics of surfactants by laboratory method, particularly their solubility in water [10]. The purpose of our development was the application of the advanced spectrophotometric method and to find options to replace the benzene in the process of sample preparation. It was an important aspect to find a solvent instead of

carcinogenic benzene which provides also precise results.

2 MATERIALS

For several years researches are being carried in order to develop surfactants for industrial purpose in the Department of MOL Hydrocarbon and Coal Processing of the University of Pannonia. The development of suitable test methods for the qualification of our proprietary surfactants was performed. As a part of this research the need of a reliable measurement of water solubility of surfactants came to the fore. The possibility of using fiber-optic AvaSpec spectrophotometer for the characterization of water solubility of surfactants was investigated. The properties of vegetable oil-based ester type nonionic surfactants used in the measurements are given in Table 1.

TABLE 1
PHYSICAL AND CHEMICAL PROPERTIES OF NONIONIC SURFACTANTS

	T-1	T-2	T-3	T-4	T-5	T-6	T-7
Kinematic viscosity, mm ² /s	8.8	13.3	10.2	4.4	8.8	25.2	35.9
Acid number, mg KOH/g	23.5	4.6	13.6	7.4	1.84	3.0	6.3
Saponification number, mg KOH/g	119.3	177.2	175.6	116.7	171.0	142.1	136.7

The characteristics of surfactants containing mainly fatty acid-alkanolamine-monoderivative, ester or amide are shown in Table 2.

TABLE 2
PHYSICAL AND CHEMICAL PROPERTIES OF THE FATTY ACID-
ALKANOLAMINE REACTION PRODUCT TYPE SURFACTANTS

	T-8	T-9	T-10	T-11	T-12	T-13	T-14
Type of surfactant	Alkanolamine reaction products						
Kinematic viscosity, mm ² /s	19.2	18.2	18.6	20.6	19.3	20.9	20.7
Acid number, mg KOH/g	5.4	4.6	4.6	4.2	1.7	2.7	2.3
Saponification number, mg KOH/g	116.8	138.1	139.2	134.2	141.4	134.2	138.7

3 METHOD OF THE DEVELOPMENT

An AvaSpec 2048 standard fiber-optic spectrophotometer with Avalight-DHc compact halogen light source was used for the measurement (Fig1).

Spectrophotometer features:

1. Optical level: Symmetrical Czerny-Turner, 75 mm focal length
2. Wavelength range: 200-1100 nm
3. Resolution: 0,04-20 nm
4. Detector: CCD linear, 2048 pixels

Light source features:

1. Wavelength range: 200-2500 nm
2. Stability: <1 mAU
3. Optical performance (in the fiber): 7μW
4. Temperature range: 5-35°C

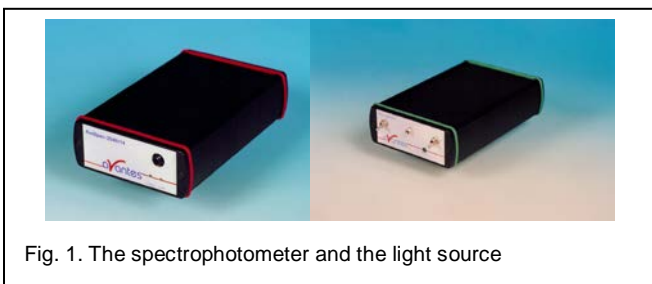


Fig. 1. The spectrophotometer and the light source

Our goal was to provide a new method for the measurement of Water Number by the development of the methods described in the literature, which avoids the use of highly toxic benzene. In addition, the Water Number obtained by the measurements and described in the literature hadn't correlated with the data obtained by calculation based on theoretical chemical structure of the surfactants. It was required to develop a new solvent mixture and a new, more accurate method for detecting the end of titration process.

The Water Number was determined by the method of Becher et al [9]. The conventional analytical method was modified in order to determine the value of HLB.

In the first step of the development of the conventional method cyclohexane was used instead of benzene and the visual

end point detection had been replaced by photometric detection. In our new process of sample preparation the test materials were dissolved in the mixture of cyclohexane-dioxane (with 4% cyclohexane content). Then the sample of the surfactant test material was titrated with distilled water and the transmittance was measured by fiber-optic spectrophotometer. The distilled water was added to the solution of surfactant until it had become permanently cloudy and the further addition of water hadn't decreased the transmittance radically.

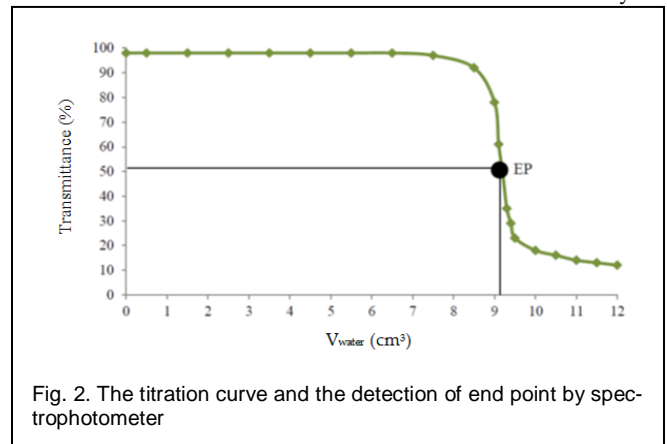


Fig. 2. The titration curve and the detection of end point by spectrophotometer

The current transmittance values were represented as the function of distilled water volumes (cm³) for the evaluation (Fig2). The equivalence point of the obtained curve is the volume which corresponds to the Relative Solubility value (the Water Number) of the surfactant.

4 RESULTS AND DISCUSSION

Two series of nonionic surfactants were prepared which cover a wide range of HLB values:

1. nonionic surfactants which were produced by the reaction of fatty acids with several polyalkylene-glycol type reagents;
2. nonionic surfactants which were fatty acid-alkanolamine reaction products.

The test results obtained by the calculation of HLB values based on different methods are given in Table 3, Table 4 and Fig3. It was determined that the presented method has been used successfully both to test of fatty acid-alkanolamine reaction products and the fatty acid based polyethylene-glycol ester type surfactants.

TABLE 3
SOLUBILITY PROPERTIES OF THE NONIONIC SURFACTANTS

	T-1	T-2	T-3	T-4	T-5	T-6	T-7	Regression coefficient
Solubility in water (%)	55	16	10	82	42	69	74	
HLB ¹	15.3	5.6	4.6	13.5	9	12.4	12.6	0.8906
HLB (C/D) ²	14	6.5	7.0	14.5	10.3	13.1	14.5	0.9385
HLB value ³	13.8	6.5	7.0	15.7	10.2	13.4	13.8	
Δ HLB ⁴	0.2	0.0	0.0	1.2	0.1	0.3	0.7	

Transmittance of distilled water containing 1% surfactant (Reference: 100% distilled water, 0% no light transmission) [11]

¹Datas measured by the conventional method of water number

²Method using C/D=Cyclohexane/Dioxane mixture

³Calculated HLB value based on the estimated molecular structure [8]

⁴ Δ HLB = HLB_{conventional} - HLB_{new}

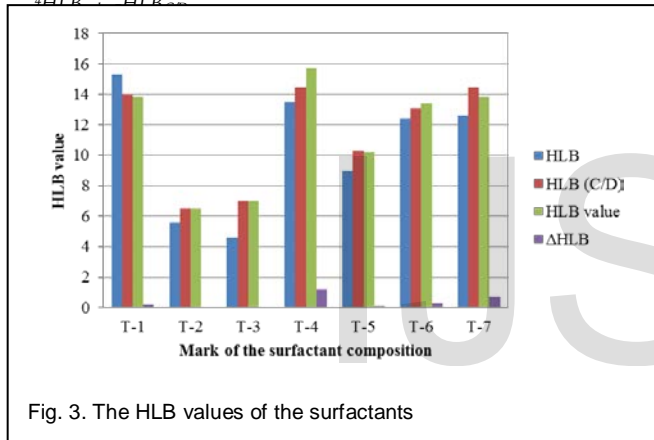


Fig. 3. The HLB values of the surfactants

TABLE 4
SOLUBILITY PROPERTIES OF THE FATTY ACID-ALKANOL-AMINE REACTION PRODUCTS

	T-8	T-9	T-10	T-11	T-12	T-13	T-14	Regression coefficient
Solubility in water (%)	62	58	44	58	42	57	51	
HLB ¹	29.4	14.8	17.3	18	16	18.3	18.7	0.2377
HLB (C/D) ²	10.4	8.9	9.8	10.2	8.3	8.7	8.2	0.0686
HLB value ³	10.3	9.7	8.4	9.6	8.3	9.6	9.0	
Δ HLB ⁴	0.1	0.8	0.6	0.6	0.03	0.9	0.8	

Transmittance of distilled water containing 1% surfactant (Reference: 100% distilled water, 0% no light transmission) [11]

¹Datas measured by the conventional method of water number

²Method using C/D=Cyclohexane/Dioxane mixture

³Calculated HLB value based on the estimated molecular structure [8]

⁴ Δ HLB = HLB_{conventional} - HLB_{new}

The experimental results indicated that there are different levels of correlation (in the interval of 0.8906-0.9385) between the HLB values determined by the different methods.

The best correlation was obtained by the developed method which data approximates the theoretical HLB values (Fig.3, 4) of both type of the nonionic surfactants.

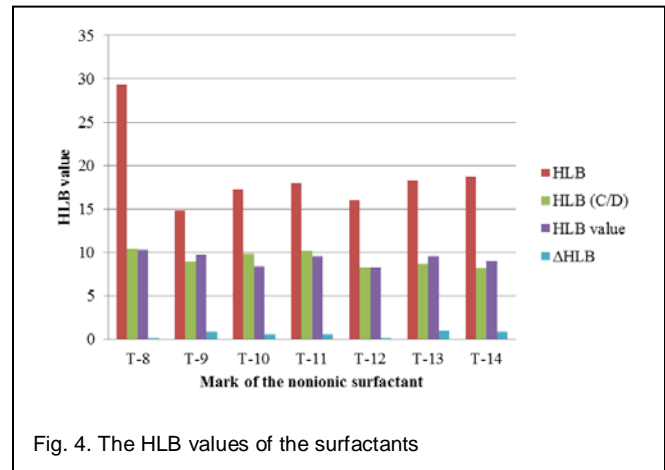


Fig. 4. The HLB values of the surfactants

Based on Fig4 it was observed that the HLB values of the fatty acid-alkanolamine reaction product type surfactants is unusually high. The reason is that the chemical structure and the solubility in water of these surfactants are significantly different from the surfactants having the fatty acid-polyethylene-glycol-ester structure.

It was found that the difference between the solubility in water of surfactants with different chemical structure measured by the conventional method increased unrealistically because of the benzene content of the solvent mixture.

Therefore, the further development of the method was necessary. Thus, the Water Number defined by the new, experimental method was significantly less. It was shown that the replacement of benzene to cyclohexane decreased this difference to a realistic HLB value.

It was supposed that the cyclohexane influenced favourably the solubility properties by the change of the interaction with the surfactant having a strong polar character.

The difference between the numerical and experimental HLB value reduced notably. The experimental values of HLB obtained by the new method approximates better the theoretical HLB value than that of measured in benzene-dioxane mixture and approaches more the literary values.

5 CONCLUSIONS

Due to the new measurement method the HLB values approximates more the calculated theoretical values. Thus, solubility of surfactants can be defined more specifically by the new method developed in this work. The HLB values of two different chemical types of non-ionic surfactant can be determined more accurately by the described method.

The replacement options of the benzene with cyclohexane was studied which is also significant in terms of safety. An important aspect was to find a new solvent combination which is not carcinogenic but provides accurate results.

The developed titration method is a convenient and easy tech-

nique. The application field of emulsifiers can be quickly estimated. In the further projects there is a chance to extend the use of the new method for other types of nonionic surfactants.

ACKNOWLEDGMENTS

We acknowledge the financial support of the Hungarian State and the European Union under the:

TAMOP-4.2.2.A-11/1/ KONV-2012-0071

REFERENCES

- [1] J Laurier L. Schramm, *Surfactants: Fundamentals and applications in the petroleum industry*, Cambridge University Press, pp. 1-91, 2000.
- [2] D. J. Shaw, *Introduction to Colloid and Surface Chemistry*, Butterworth-Heinemann, pp. 64-78, 1992.
- [3] Jeffrey A. Byars, George F. Fanta, James A. Kenar, "Effect of amylopectin on the rheological properties of aqueous dispersions of starch-sodium palmitate complexes", *Carbohydrate Polymers*, vol. 95, pp. 171-176, 2013.
- [4] Zhaofeng Li, Jian Wang, Li Cheng, Zhengbiao Gu, Yan Hong, Agnieszka Kowalczyk, "Improving the performance of starch-based wood adhesive by using sodium dodecyl sulfate", *Carbohydrate Polymers*, vol. 99, pp. 579-583, 2014.
- [5] Yiangying Wu, Yuming Xu, Tadeusz Dabros, Hassan Hamza, "Development of a method for measurement of relative solubility of nonionic surfactants", *Colloids and Surfaces A: Physicochem. Eng. Aspects*, vol. 232, pp. 229-237, 2004.
- [6] K.S.Birdi, *Surface and colloid chemistry*, Principles and applications, CRC Press Taylor and Francis Group, pp. 5-9, 2010.
- [7] Tatsumi Yamamoto, Hiroyuki Kawasaki, Hidehiro Kumazawa, "Relationship between the dispersed droplet diameter and the mean power input for emulsification in several types of motionless mixers", *Environment Protection Engineering*, vol. 36, pp. 5-21, 2010.
- [8] ICI Americas Inc.: *The HLB SYSTEM, a time-saving guide to emulsifier selection*, ICI, pp. 2-7, 1994.
- [9] Paul Becher, *Emulsions: Theory and Practice*, Oxford University Press, pp. 137-138, 1967.
- [10] Benyamin Yadali Jamaloei, "Insight into the Chemistry of Surfactant-Based Enhanced Oil Recovery Processes", *Recent Patents on Chemical Engineering*, no. 2, pp. 1-10, 2009.
- [11] R. Nagy, R. Sallai, L. Bartha, A. Vago: "Study on solubility of surfactants in water by fiber optic spectrophotometer", *Chemistry & Chemical Technology*, vol. 9, no. 2, 2015.