C12 hydroxyester ethoxylates as nonionic surfactants

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Abstract: A series of ethoxylates of 2,2,4-trimethyl-1,3-pentanediol mono-isobutyrate representing a synthetic C12 hydroxyester hydrophobe was obtained. The solubility parameters, surface tension and critical micelle concentrations for model solutions were investigated. The new surfactants were found to produce extremely low foam levels and a non-standard surface interfacial behavior was determined. It was observed that the ethoxylates of the C12 hydroxyester formed an oriented monolayer at the interface regardless of their average polyaddition degree. Such behavior is different from the surface activities of commonly known linear nonionic surfactants and it indicates self-organization of the surfactants at the interface. This feature offers possibility for application of these surfactants in nanotechnology as well as in the conventional cleaning processes.

Keywords: Nonionic surfactants • C12 hydroxyester • Surface tension • Nanotechnology

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1. Introduction

2,2,4-Trimethyl-1,3-pentanediol mono-isobutyrate is a hydrophobic organic solvent used as a coalescent in water-based architectural paint formulations. The content of the coalescent in water-based paints is usually between 1 to 5%. Although precise data is not available in the literature, global production of such paints may be estimated as c.a. 100 kt per year. As a result, the C12 hydrophobe solvent containing one labile hydrogen group is an available bulk production chemical suitable for ethoxylation. The C12 alcohol-ester is obtained in a sequence of chemical reactions. In the first reaction, isobutyraldehyde (isobutanal) is used as the raw material for aldol condensation, with the subsequent Cannizaro and Tisztechenko reaction [1], as shown in Fig. 1. The C12 synthetic alcohol-ester is further subjected to ethoxylation. A general reaction diagram was presented in Fig. 2.

Preliminary studies showed that the ethoxy derivatives of 2,2,4-trimethyl-1,3-pentanediol mono-isobutyrate exhibited some typical properties of nonionic surfactants [2,3]. A basic characteristic of any surfactant is its amphiphilicity, which is described by different concepts. The oldest one is based on the hydrophilic-lipophilic balance (HLB). HLB indicates the relative strength of the hydrophilic and hydrophobic portions of the molecule and characterizes the relative affinity of surfactants for aqueous and organic phases [4]. A high HLB value generally indicates good surfactant solubility in water, while a low HLB value signifies a lower aqueous solubility and higher relative affinity for the organic phase. The most commonly used expressions of the HLB of surfactants are Griffin’s HLB [5] and Davies’s HLB values [6]. Griffin introduced the hydrophilic-lipophilic balance in an empirical and quantitative scale. Griffin’s HLB number was later expanded by Davies, who introduced a scheme to assign HLB group numbers for different chemical groups composing one surfactant molecule. In fact, the
HLB does not take into account several physiochemical parameters [7]. For instance, temperature, electrolyte concentration, oil type, chain length, and co-surfactant concentration can all modify the geometry of the surfactant at an interface. Salager et al. [8] proposed a concept of HLD (hydrophilic-lipophilic deviation), which takes into account all the above effects. HLD is dimensionless numerical expression of the so-called surfactant affinity difference (SAD), i.e., of the free energy change of a surfactant molecule when transferred from oil to water [9,10]. It is linked to the partition coefficient of the surfactant [11] and can be expressed as a linear function of the various formulation variables [12].

The HLD concept has been proven to be successful when applied to the system composed of pure oil phase and certain kinds of surfactants. However, it is still difficult to use it in crude systems because of the complex variety of components. Therefore, the old HLB concept is still used due to its simplicity.

Surfactants reduce the surface tension of water by adsorbing at the liquid-gas interface. They also reduce the interfacial tension between oil and water by adsorbing at the liquid-liquid interface. Many surfactants can also assemble in the bulk solution as aggregates. The concentration at which surfactants begin to form micelles is known as the critical micelle concentration (CMC). Surfactants are also foaming agents, which when present in small amounts, facilitate the formation of foam, or enhance its colloidal stability by inhibiting the coalescence of bubbles [13].

Surfactants with weak main property have area per headgroup size dependent heavily on the surfactant, for example, the bending constant of the film is high. Therefore, special properties of these compounds anti-foam, emulsion with fixed radii, and possibility of formulating microemulsions. This group of properties was noticed first by Rushfort et al. [14]. Additionally, Testard and Zemb [15,16] studied these compounds for dilution properties by using double chain cationic surfactants. A theory has been established more recently by Mortensen, who compared different methylated forms of cholesterol [17].

The aim of this work was to investigate the main characteristic of ethoxylation products of 2,2,4-trimethyl-1,3-pentanediol mono-isobutyrate as novel nonionic surfactants.

2. Experimental Procedure

2.1. Materials
The following chemicals were used as raw materials for the syntheses:
- 2,2,4-trimethyl-1,3-pentanediol mono-isobutyrate, purity 99.0% (molecular weight M_w=216), from Opole Technical University according to the method described elsewhere [18]. For simplicity, instead of 2,2,4-trimethyl-1,3-pentanediol mono-isobutyrate, the abbreviation “C12 hydroxyester” or “C12 alcohol-ester” is further used in this work;
- Oxirane (M_w=44), 99.9% pure, manufactured by PKN ORLEN S.A., Plock, Poland;
- Sodium hydroxide, analytical grade, from POCh S.A., Gliwice, Poland;
- Butyldiglycol ether, 99% pure, manufactured by PCC “Rokita” Chemical Works, Brzeg Dolny, Poland.

HLB calibration curve was performed by using the Tween surfactants from Croda International Plc., as listed below:
- TWEEN 81 – PEG 5 sorbitan monooleate,
- TWEEN 80 – PEG 20 sorbitan monooleate,
- TWEEN 20 – PEG 20 sorbitan monolaureate,
- TWEEN 85 – PEG 20 sorbitan trioleate. A series of known and used in commercial practice surfactants were applied as reference materials:

1. Oxyethylated rapeseed methyl ester of average polyaddition degree, \( N_{av} = 10 \) (average molecular weight, \( M_w = 740 \)), trade name FAMEN N10, manufactured at ICSO Chemical Production, Kedzierzyn-Kozle, Poland.

2. Oxyethylated rapeseed methyl ester, \( N_{av} = 6 \) \( (M_w = 564) \), FAMEN N6, manufactured at ICSO Chemical Production, Kedzierzyn-Kozle, Poland.

3. Oxyethylated rapeseed oil, 80% EO \( (M_w = 4425) \), produced by MEXEO Co., Kedzierzyn-Kozle, Poland.

4. Oxyethylated alcohol C11-C15, \( N_{av} = 5 \); ROKANOL DB5 \( (M_w = 425) \), manufactured at PCC Rokita Chemical Works, Brzeg Dolny, Poland.

5. Oxyethylated alcohol C11-C15, \( N_{av} = 7 \); ROKANOL DB7 \( (M_w = 513) \), manufactured at PCC Rokita Chemical Works, Brzeg Dolny, Poland.

6. Oxyethylated alcohol C12-14, \( N_{av} = 10 \); ROKANOL L10 \( (M_w = 664) \), manufactured at PCC Rokita Chemical Works, Brzeg Dolny, Poland.

2.2. Methods

2.2.1. Synthesis

Laboratory-scale ethoxylation was carried out in a 1-liter autoclave equipped with mechanical stirrer, heating mantle and cooling coil. The synthesis was performed using method described elsewhere \[19,20\]. NaOH was used as the catalyst at a concentration of 0.4% as calculated per starter material. Following dehydration by nitrogen purge at 120°C, a desired amount of ethylene oxide was introduced at 120-130°C. Afterwards, the reaction product was kept at the reaction temperature for additional 60 minutes, then cooled down to 60°C and neutralized with acetic acid. The obtained products were used for the planned investigation, and no further treatment or separation took place (100% reaction yield).

2.2.2. Gas chromatography determination

The composition of ethoxylation products was determined by means of gas chromatography, using a Perkin Elmer GC apparatus model 9000 equipped with a flame-ionization detector and column with packing, 1/8 inch in diameter and 1.8 m in length, packed with OV-17 on Chromosorb WHP 100/120 mesh. The following separation conditions were used: column temperature programmed from 70°C and, after 1 min of isotherm, to 300°C, at a rate 8°C min\(^{-1}\), injector temperature 300°C, detector temperature 400°C, and Argon as carrier gas.

2.2.3. Hydrophilic-Lipophilic Balance (HLB)

HLB is an important parameter characterizing a surfactant that can indicate its appropriate applications. Because HLB is difficult to determine experimentally, instead, cloud point and Relativity Solubility Number (RSN) were used to represent the hydrophile-lipophile balance.

The cloud point is the temperature below which a single phase of molecular or micellar solution exists. Above the cloud point, a surfactant loses sufficient water solubility resulting in a cloudy dispersion \[21\]. Cloud temperature was found by heating the prepared solution till clouded, followed by reading the temperature at which the test solution was cleared upon cooling, where: cloud temperature (BDG) denotes the cloud temperature of a 5 g sample in 45 g of a 25% solution of butyldiglycol, and cloud temperature (H\(_2\)O) denotes the cloud temperature of a 1% solution of a surfactant sample in demineralized water.

Relativity Solubility Number (RSN) was determined experimentally by the Greenwald method \[22\]. Until then, the hydrophile-lipophile character of the surfactant was determined by water titration of the surfactant solution using a specific system of organic solvents.

1.00 g of the test ethoxylate was dissolved in 30 mL of a 4% benzene solution in dioxane. The solution was then titrated by means of a digital burette with distilled water until the point where the first permanent clouding of the system took place. The volume of added water is referred to as „water number” \( (w_n) \). The measurement was carried out at room temperature.

A similar method was used to determine the water numbers for the Tween 85, 81, 80, 20 series of surfactants (esters of fatty acids and ethoxylated derivatives of sorbitol), based on which the standard curve was found. The resulting conversion data is shown in Table 1. The resulting standard curve is shown in Fig. 3.

2.2.4. Foaming properties

Foaming properties were evaluated by the Sun method \[23,24\] in which pumping the air through the surfactant solution was maintained at a constant volume rate. 500 mL of each solution was transferred to the cylinder immediately after air was admitted into the system. The rate of aeration, adjusted to within seconds, was kept constant. The foam height was adjusted to a constant level within 4 minutes. The stability of the foam was determined by stopping the air to the column and recording the time taken for the foam to disappear.
### 3. Results and Discussion

A product series of the ethoxylated C12 hydroxyester was synthesized by introducing various amounts of oxirane per mole of the starter material. Sodium hydroxide was applied as the catalyst. The syntheses were performed with a 15-minute induction period and the obtained ethoxylates represented typical polydispersed mixtures of homologues, as exemplified by a lower molecular weight product sample of average polyaddition degree equal to 3 (N<sub>ew</sub> = 3) (Fig. 4). The characteristic solubility parameters of the obtained ethoxylation products are shown in Table 2.

A surfactant’s hydrophilicity is mostly defined by the hydrophilic-lipophilic balance (HLB) values. According to Griffin [6], HLB of typical alcohol ethoxylate is calculated theoretically as a percentage of the poly-ethoxylate chain in the surfactant molecule (HLB=EO%/5). To compare surface activities of surfactants of different hydrophobic structure to that of conventional alcohol ethoxylates, experimental measurement of what is referred to as an “effective HLB” should be examined.

In the case of linear fatty alcohol oxyethylates, the theoretical HLB values overlap with the results of experimental measurements determined as the Relative Solubility Number (RSN). This is also well correlated with other nonionic surfactants such as Tweens (Table 1). It is shown in Fig. 5 that the examined oxyethylates of the C12 hydroxyester exhibit remarkably lower RSN number, as compared to the responding theoretical HLB values. This means, for instance, that adequately higher amounts of ethylene oxide must be added to the C12 hydroxyester in order to achieve an equivalent effective HLB relative to the conventional nonionic surfactants.

Table 3 presents parameters of surface activity of the tested series of a prior-art group of surfactants (a), compared with oxyethylates of the C12 hydroxyester (b) in aqueous solution. Representative plots of surface tension as a function of log C (C – concentration of surfactant, mol L<sup>-1</sup>) are shown in Fig. 6. The surface tension isotherms fit well by the Szyszkowski equation: \( \gamma = \gamma_0 + B_{sz} \ln \left( \frac{C}{C + 1} \right) \), where: \( \gamma_0 \) is the surface tension of solvent (water), \( B_{sz} \) and \( A_{sz} \) are the adsorption coefficients (\( B_{sz} \) is the constant characteristic for a series of homologues, and \( A_{sz} \) is the constant characteristic for a compound). Surface excess concentrations at the saturated interface \( \Gamma_{max} \) were calculated from the equation: \( \Gamma_{max} = \frac{\gamma_0 B_{sz}}{RT} \), where: \( R \) is gas constant and \( T \) the absolute temperature. The minimum surface occupied by a molecule at the interface \( A_{min} \) were calculated from equation: \( A_{min} = \frac{1}{\Gamma_{max} N_A} \), where: \( N_A \) is the Avogadro number.

The Gibbs free energy of adsorption layer was estimated from equation: \( \Delta G_{ads}^0 = -RT \ln A_{sz} \).

A significant feature that has possibilities for practical applications is the ability of surfactants to generate foam in water solutions. Comparative tests were performed to evaluate the foamability of the tested oxyethylates of the C12 hydroxyester and the selected nonionic surfactants, known from state-of-the-art technologies. Dynamic gas flow conditions, using the Sun method, were used for determination of the foaming properties, and the findings are shown in Fig. 7.

It was found that the tested surfactants showed certain properties which allowed their classification as typical nonionic surfactants. However, this type of ethoxylates, in many aspects, appeared to be different from prior-art non-ionic surfactants having a typical linear alkyl chain, as in the case of ethoxylates of aliphatic alcohols, or ethoxylated methyl esters of carboxylic acids. The example was an exceptionally low foamability of the C12 hydroxyster ethoxylates compared with the commonly known surfactants. Their foaming properties were five to ten times less compared to the oxyethylates of aliphatic alcohols. It is a very attractive property in many practical applications. As expected, the foam height decreased proportionally with increasing concentration of less hydrophilic homologues.
In the polyaddition degree range from 11 to 30, the synthesized ethoxylates of C12 hydroxyester, provided HLB between 14 to 17, and RSN between 11 to 14, which is typical of o/w emulsifiers. The length of the linear chain of the hydrophobic portion was only 7 carbon atoms, which suggests a fragment with a relatively low hydrophoby, a property confirmed by high cmc values. However, surface tension was characterized by an extremely low gradient of decrease in the values relative to the increase in the concentrations of the tested surfactants, which resulted in the tension range of 40-45 mN m⁻¹. The branched structure of the hydrophobe containing an internal (polar) ester group is not typical of non-ionic surfactants. As a result, the difference in the efficiency of tension lowering in the range of 40 mN m⁻¹, compared to ethoxylenated aliphatic alcohols, is in the order of one magnitude. In addition to that, the compounds were characterized by the area per molecule of around 10×10⁻¹⁹ m² and their variable number of ethoxylene groups in the range from 11 to 30 modified to a small extent the density of surface packing at the water/air interface.

The values of the constant Bsz obtained from the Szyszkowski isotherms, were comparable to all of

![Figure 3. Standard curve of HLB vs. RSN for model systems of Tween 80, 20, 85, 81 surfactants.](image)
the tested ethoxylates of the C12 hydroxyester in the medium range of polyaddition degrees from 11 to 30. Therefore, no significant changes were observed in the structure of the surface layer, which depended on the length of hydrophilic ethoxylene chains. The constant values of parameter $B_{sz}$ could also be ascribed to the polydispersity of the synthesized surfactants (as shown in Fig. 4), which lead to a preferential adsorption of the molecules with shorter chains.

The dominant role of the hydrophobic portion in the occupied area at the water/air interface eliminated surface adsorption of meandric oligoethoxylene structures, typically formed along the increase in polyaddition degrees by typical ethoxylation products. The discussed phenomenon may be the evidence of an oriented self-organization at the interface of branched polyfunctional molecules of ethoxylates of the C12 hydroxyester. As a consequence of the specific interactions between polar oligoether groups and free hydroxy groups with flatly distributed fragments of branched hydrophobic structures, the formation of a rigid, strongly hydrated monolayer structure in a broad range of concentrations of the discussed surfactants could be expected. Such behavior may lead to major changes in the surface...
properties at the interface, caused by the monolayers of the adsorbed surfactants. This indicates a number of prospective applications in nanotechnology as well as in the common cleaning processes.

4. Conclusions

Physical properties, such as hydrophilic-lipophilic balance, foamability and surface tension, of the nonionic surfactants ethoxy derivatives of 2,2,4-trimethyl-1,3-pentanediol mono-isobutyrate representing a synthetic C12 hydroxyester hydrophobe were studied. Properties of these novel nonionic surfactants were compared with those of some already well known surfactants (TWEEN 20, 80, 81 and 85; oxyethylated rapeseed methyl esters with degrees of polyaddition of 10 and 6; oxyethylated fatty alcohols with degrees of polyaddition of 5, 7 and 10).

Theoretically obtained value of the hydrophilic-lipophilic balance (HLB) was compared to the Relative Solubility Number (RSN) determined experimentally by the Greenwald method. It is found that the HLB depends linearly on RSN and for TWEEN molecules both values are approximately the same. For the ethoxylated series of C12 hydroxyester, a similar linear dependence is found but with the exception that different values for HLB and RSN are obtained.

These new surfactants produced extremely low foam levels - five to ten times less as compared with the oxyethylated rapeseed oil, rapeseed methyl ester and lauryl alcohol. Graduation in the foam height is properly explained by proportional concentration increase of more hydrophilic homologues with increasing foam height. For the studied ethoxylates of the C12 hydroxyester, a non-standard surface interfacial behavior was also determined. They formed an oriented monolayer at
the interface regardless of their average polyaddition degree. Such behavior is different from the surface activities of commonly known linear nonionic surfactants. This behavior indicates a self organization of the studied surfactants at the interface. This feature offers possibility of applications that these surfactants may have in nanotechnology as well as in the conventional cleaning processes.

References

[1] T.E. Parson, In Kirk-Othmer Encyclopedia of Chemical Technology (Wiley Interscience, New York, 1994)
[2] W. Hreczuch, K. Pyżalski, K. Rolnik, W.J. Tic, Chemik 5, 117 (1999) (In Polish)
[3] W. Hreczuch, W.J. Tic, A. Sokolowski, A. Podolska, Przem. Chem. 8, 934 (2009) (In Polish)
[4] W.C. Griffin, J. Soc. Cosmet. Chem. 1, 311 (1949)
[5] W.C. Griffin, J. Soc. Cosmet. Chem. 5, 259 (1954)
[6] J.T. Davies, E.K. Rideal, Interfacial Phenomena (Academic Press, New York, 1963)
[7] B.P. Binks, In: Modern Aspects of Emulsion Science (The Royal Society of Chemistry, Cambridge, 1998)
[8] J.L. Salager, N. Marquez, A. Graciaa, J. Lachaise, Langmuir 16, 5534 (2000)
[9] J.L. Salager, In: G. Broze (Ed.), Handbook of Detergents - Part A: Properties (Dekker, New York, 1999)
[10] J.L. Salager, R.E. Antón, In: P. Kumar, K. Mittal (Eds.), Handbook of Microemulsions Science and Technology (Dekker, New York, 1999)
[11] N. Márquez, A. Graciaa, J. Lachaise, J.L. Salager, Langmuir 18, 602 (2002)
[12] J.L. Salager, N. Marquez, A. Graciaa, J. Lachaise, Langmuir 16, 5534 (2000)
[13] M.J. Rosen, Surfactants and interfacial phenomena (John Wiley & Sons, Inc, New York, 2004)
[14] D.S. Rushford et al., J. Phys. Chem. 90, 6668 (1986)
[15] F. Testard, Th. Zemb, Langmuir 14, 3175 (1998)
[16] F. Testard, Th. Zemb, J. Colloid Interface Sci. 219, 11(1999)
[17] J. Lemmich, K. Mortensen, J.H. Ipsen, T. Honger, R. Bauer, O.G. Mouritsen, Eur. Biophys. J. 25, 293 (1997)
[18] W.J. Tic, Z. Hehn, Przem. Chem. 12, 580 (2001)
[19] M.J. Schick, Nonionic Surfactants, Surfactant Science Series (Marcel Dekker, Inc. New York, 1967) 11-41
[20] W. Hreczuch, J. Szymanowski, J. Am. Oil Chem. Soc. 73, 73 (1996)
[21] M.J. Schick, Nonionic Surfactants Physical Chemistry (Marcel Dekker, New York, 1987)
[22] H.L. Greenwald, G.L. Brown, M.N. Fineman, Analytical Chemistry 28, 1693 (1956)
[23] M. Bukala, B. Burczyk, J. Chlebicki, Rudy i Metale Niezelazne 12, 615 (1967) (In Polish)
[24] A.A. Yousef, T.R. Boulos, Tenside 6, 322 (1969)
[25] J. Benjamins, A. Cagna, E.H. Lucassen-Reynders, Colloid Surface A 114, 245 (1996)

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