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Effect of chemical structure on the cloud point of some new non-ionic surfactants based on bisphenol in relation to their surface active properties

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Abstract A series of non-ionic surfactants were prepared from bisphenol derived from acetone (A), acetophenone (AC) and cyclohexanone (CH). The prepared bisphenols were ethoxylated at different degrees of ethylene oxide (27, 35, 43). The ethoxylated bisphenols were non-esterified by fatty acids; decanoic, lauric, myristic, palmitic, stearic, oleic, linoloic and linolinic. Some surface active properties for these surfactants were measured and calculated such as, surface tension [γ], critical micelle concentration [CMC], minimum area per molecule [A_{min}], surface excess [Γ_{max}], free energy of micellization and adsorption [ΔG_{mic}] and [ΔG_{ads}]. At a certain temperature, the cloud point was measured for these surfactants. From the obtained data it was found that; the cloud point is very sensitive to the increase of the alkyl chain length, content of ethylene oxide and degree of unsaturation. The core of bisphenol affected the cloud point sharply and they are ranked regarding bisphenol structure as BA > BCH > BAC. By inspection of the surface active properties of these surfactants, a good relation was obtained with their cloud points. The data were discussed on the light of their chemical structures.

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1. Introduction

Non-ionic surfactants become water soluble by the hydration of ether oxygen of the polyoxyethylene group. The longer chain of ethylene oxides containing ether oxygen is more hydrated and consequently, more solubility. An increase in temperature causes the cleavage of the hydrogen bond between the ether oxygen of the ethylene oxide group and the hydrated hydrogen to the ether oxygen. As a result, the aggregation number of micelles increases and the micelles of polyoxyethylene non-ionic surfactant become larger and larger until they are so large that the solution becomes visibly turbid [1].

The depletion of water from non-ionics decreases their solubility in water [2]. The water depleted non-ionic surfactants solution, therefore, becomes turbid and separates into two immiscible phases a surfactant rich phase and a surfactant lean phase. The phase separation occurs as a result of the density difference between the micelle-rich and micelle poor phases [3]. This sudden onset of turbidity of a non-ionic surfactant solution when the temperature rises is called the ''cloud point''. This turbidity is a reversible process, so that the solution clears again on cooling. In general, non-ionics having a longer polyoxyethylene chain consequently have a higher cloud point, meaning a greater capacity to hydrate. The cloud point of a non-ionic surfactant or glycol solution is the temperature at which the dissolution of solids is no longer complete, and the mixture starts to phase separate and two phases appear, thus becoming cloudy [4]. This behavior is characteristic of non-ionic surfactants containing polyoxyethylene chains, which exhibit reverse solubility versus temperature behavior in water and, therefore, cloud out at some point as the temperature is raised. The cloud point is effected by salinity, being generally lower in more saline fluids [5]. This term is relevant to several applications with different consequences, knowing the cloud point is important for determining storage stability [6]. Storing formulations at temperatures significantly higher than that of the cloud point may result in phase separation and instability [7]. Wetting, cleaning and foaming characteristics can be different above and below the cloud point. Generally, non-ionic surfactants show optimal effectiveness when used near or below their cloud point [8]. Low-foam surfactants should be used at temperatures slightly above their cloud point [9].Cloud point is typically measured using 1% aqueous surfactant solutions. Cloud points range from 0° to 100 °C (32–212 °F), limited by the freezing and boiling points of water. Cloud point is characteristic of non-ionic surfactants. Anionic surfactants are more water-soluble than non-ionic surfactants and will typically have much higher cloud points (above 100 °C). The presence of other components in a formulation can depress or increase the cloud point of a solution. For example, the addition of a coupler or hydrotrope can increase the cloud point of a solution, whereas builders or other salts will depress the cloud point temperature. For standard and low-foam applications [10,11], the cloud point of the product should be just below the used temperature. The cloud point of TRITON CF-32 defoamer is 23 °C (73.4 °F), which should be used around 25–28 °C (77–82 °F) for maximum efficiency. The first object of this work is to prepare some bisphenols such as; bisphenol based on acetone (BA), bisphenol of acetophenone (BAC) and bisphenol of cyclohexanone (BCH). These bisphenols were ethoxylated at different ethylene oxide contents. The ethoxylated products were monoesterified by long chain fatty acids. The second object is to measure surface tension and calculate their surface active properties and then measure their cloud points. The third object of this investigation is to try to find a relation between the surface properties and the cloud point of these surfactants.

2. Experimental

2.1. Preparation of surfactants

Three bisphenols based on acetone (diphenylol propane, bisphenol A), acetophenon and cyclohexanone were prepared and named as; BA, BAC and BCH, respectively. These bisphenols were ethoxylated at different ethylene oxides (27, 35 and 43). The ethoxylated bisphenols were monoesterified by fatty acids, decanoic, lauric, myristic, palmitic, stearic, oleic, linoloic and linolinic. The method of preparation was described clearly in a previous work [12]. Fig. 1 shows the generalized formula and designation of the prepared surfactants.

2.2. Surface tension measurement and calculations of surface active properties

The values of surface tension (γ) were measured at 303 °K for various concentrations of the surfactant. The measured values of (γ) were plotted against the surfactant concentration, ln C. The intercept of the two straight lines designates the critical micelle concentration (CMC), where saturation in the surface adsorbed layer takes place. The main importance of the CMC consists of the fact that, at this concentration, most of the physical and chemical properties of the surfactant solutions present an abrupt variation. The surface active properties of the surfactant, effectiveness (π_{cmc}), maximum surface excess (Γ_{max}) and minimum area per molecule (A_{min}) were calculated using the following equations [13]:

$$\pi_{cmc} = \gamma_o - \gamma_{cmc} \quad (1)$$

$$\Gamma_{max} = -10^{-7}[1/RT][d\gamma/d\ln C]_T \quad (2)$$

$$A_{min} = 10^{16}/[\Gamma_{max} \cdot N_A] \quad (3)$$

$$\Delta G_{mic} = RT \ln CMC \quad (4)$$

$$\Delta G_{ads} = \Delta G_{mic} - [0.6022 \times \pi_{cmc} \times A_{min}] \quad (5)$$

where γ_o is the surface tension measured for pure water at the appropriate temperature and γ_{cmc} is the surface tension at CMC, Γ is the surface excess concentration in mol/dm^2, R is the molar gas constant (R = 8.314 J/(mol K)), T is the

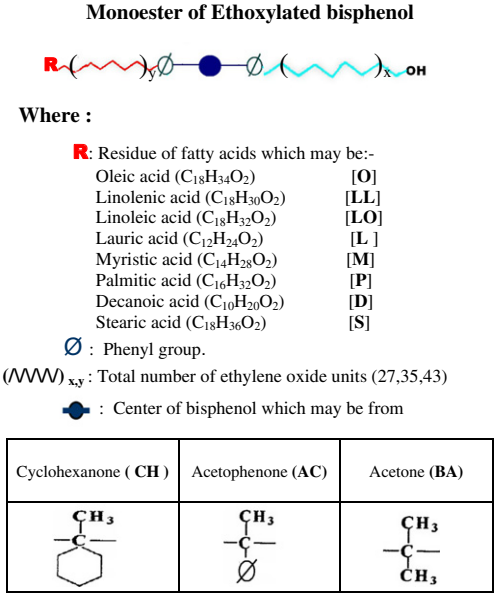

Figure 1 Generalized formula and structure designation.