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A comprehensive framework for surfactant selection and design for emulsion based chemical product design

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ABSTRACT

The manufacture of emulsified products is of increasing interest in the consumer oriented chemical industry. Several cosmetic, house-hold and pharmaceutical products are in the emulsified form when sold and/or they are expected to form an emulsion when used. Therefore, there is a need for the development of a methodology and relevant tools in order to spare time and resources in the design of emulsion-based chemical products, so that the products can reach the market faster and at a reduced cost. The understanding and modeling of the characteristic behavior of emulsions and their peculiar ingredients is consequently necessary to tackle this problem with computer-aided methods and tools. A comprehensive framework for the selection and design of surfactants, the main responsible for the formation and the stability of emulsions, is presented here together with the modeling of the cloud point, a key-property of nonionic surfactants, with a group-contribution model. The mathematical formulation of a standard product design problem is presented, together with the list of both the pure component properties (related to nonionic surfactants) and the mixture properties (relevant to the overall products as an emulsion) needed for the solution of the design algorithm. These models are then applied together with established predictive models for pure component properties of ionic surfactants and for standard mixture properties such as the density, the viscosity, the surface and the interfacial tension, but also the type of emulsion expected (through the hydrophilic–lipophilic balance), and its stability (through the hydrophilic–lipophilic deviation), forming a robust chemical product design tool. The application of this framework is highlighted for the design of some emulsion based chemical products.

1. Chemical product design

Recently, a substantial shift is observed from materials valued for their purity, to materials sold for their performance behavior [1,2]. To meet these challenges, on a global and local scale, while remaining profitable and maintaining sustainable growth, there has been an increasing interest in the formulation and solution of product design problems [3]. The chemical product tree shown in Fig. 1 gives an idea of the size of this shift: the roots of the tree consist in a limited number of *Raw Materials* which are processed to obtain the commodity products (*Basic Products*). Specialty chemicals (*Intermediate Products*) are then manufactured from the commodities and finally the leaves of the tree represent a large portfolio of higher value products (*Refined Chemicals & Consumer Products*) obtained by processing and/or combining the chemicals of the previous product classes. As one ascends the product tree, the number of products belonging to each category grows exponentially from around 10 for the raw material class, up to almost 30,000 in the last class of higher value added products. This last class is composed of formulations, devices and technology based consumer goods. Formulated products include pharmaceuticals, paints, food, cosmetic, detergents, pesticides, in which 5 to more than 20 ingredients are usually present, representing a wide range of chemical compounds such as polymers, surfactants, solids, solvents, pigments, and aromas [4]. The common practice, in the development of such products, is still the experiment-based and trial-and-error approach. However, a systematic procedure, able to design a higher added value product with enhanced product qualities, represents an efficient alternative, with respect to time and resources, speeding up the product development.

1.1. Formulation design

Many chemical-based personal care products of everyday life such as sun lotions, shower creams, and insect repellents are liquid formulations, while examples of non-personal care products are

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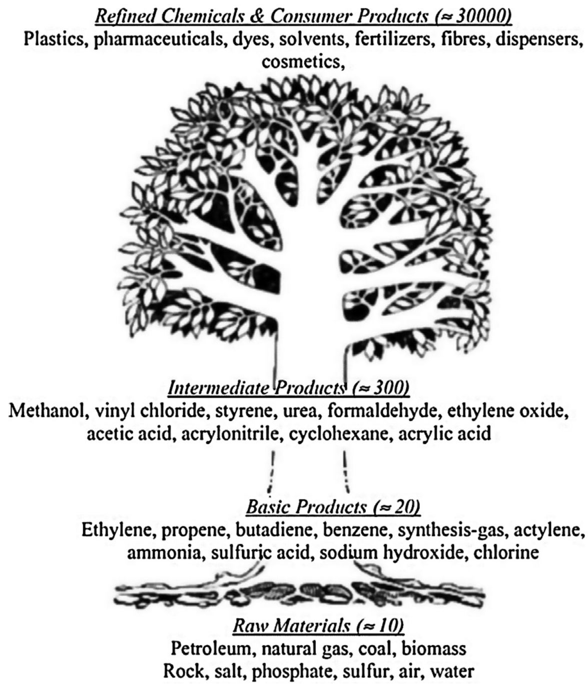

Fig. 1. The chemical product tree: classification of chemical-based products [3].

paints, pesticides and drugs. These can be classified as "consumer-oriented products" since their needs, on the basis of which they are designed, are defined by the consumers. Therefore these products need to satisfy multiple needs of the consumers [5]. A sunscreen lotion, for example, must provide protection against sunburns and skin cancer, but must also prevent skin aging, and be, for example, long lasting, safe, easily applicable, with good sensorial properties (color and odor) [6]. Because a single chemical is unlikely to satisfy these multiple needs, a blend of several chemicals is usually sought. A formulation may then contain materials from different classes of chemicals, such as polymers, surfactants, solvents, pigments and aromas. These classes of chemicals are usually classified as follows [5]:

- *Active ingredients*: these chemicals are the most important ones in the formulation, because they satisfy the main needs of the product, thus defining the function of the product itself. For example, the function of a sunscreen lotion is to protect the skin against the UV radiation.
- *Solvent mixture*: it is usually present in high concentration in the formulation and has the function of dissolving the active ingredients and other chemicals in the formulation, ensuring the product to be a single liquid phase and to be properly delivered. The solvent mixture must evaporate after application.
- *Additives*: these chemicals are usually present in low concentration and they satisfy the secondary needs of the product, enhancing the end-use product properties. Examples are pigments and aromas, to enhance the sensorial properties of the formulation.

The presence of several classes of chemicals to be included in the formulation design leads to the necessity of a step-by-step hierarchical design methodology, in order to avoid any combinatorial explosion due to the high number of possible candidate formulations to be generated and screened, systematically and efficiently, while at the same time excluding "blind" trial-and-error solutions. Several methodologies and frameworks have been developed, in order to address the need for the solution of a formulation design problem, with the aid of adequate property models and computer-aided tools. Raman and Maranas [7] addressed the problem incorporating topological indices for correlating the necessary physico-chemical properties, while Chemmangattuvalappil et al. [8] applied combined property clustering and group-contribution techniques. Teixeira et al. [9] directed their attention toward structured products (more specifically microencapsulate perfumes for textile application), while Charpentier [10] focused on the multi-scale problem generated by the introduction in the methodology of economic, social and environmental constraints. Fig. 2 shows the work-flow diagram of the computer-aided design/verification stage, based on "define target – match target" paradigm as presented by Conte et al. [5], highlighting input, output and tools used for each step. The methodology employs the "reverse design" technique. The defined target properties of the product are then the known variables and input for the property models. Appropriate property models are needed to estimate the target properties of the candidates so that they are evaluated and then accepted or rejected. At the same time the mixture compositions that satisfy the product constraints are determined, using suitable mixture property models as well as phase stability algorithms. As shown in Fig. 2, if in any task a solution is not found, it is possible to return to a previous task to refine the problem definition.

1.2. Emulsion design

Formulations can also have other physical forms [11]: suspensions containing insoluble chemicals dispersed in the liquid with the help of a dispersant; emulsions where solid constituents have been emulsified through selected emulsifiers together with solvents and additives; solid products such as pharmaceutical tablets or soap bars. In chemical product design, Cussler and Moggridge [2] distinguish between commodities, chemical devices, molecular products and microstructured products, where the term "microstructure" refers to a chemical organization on the scale of micrometers, belonging to the colloidal domain and incorporating polymer solutions, foams, gels and emulsions. The performances of such products are related not only to the presence of active ingredients and additives in the formulation, but also to the product's structural and material properties [12]. Among the microstructured products, emulsified products are the most relevant, particularly in the food and cosmetic industries. Emulsions are defined as mixtures of two normally immiscible liquids, kinetically stabilized by emulsifiers (most often surface active agents, better known as surfactants) that lie on the interface between the two phases. Active ingredients and additives are usually dissolved in the continuous and/or dispersed phases, according to the needs of the products. Bernardo and Saraiva [13] proposed a simultaneous approach to address product and process design, with special attention to cosmetic emulsions, while Bagajewicz et al. [14] extended a generic approach [15] to consider price-competitive markets. Recently, a systematic procedure, which is applicable to the design of emulsified formulated products, has been proposed by Mattei et al. [16] and it is further extended in this work (see Fig. 2).

For emulsion-based chemical product design, the solvent(s) design task (Task 3a) provides as output two non-miscible liquid phases and an additional task (Task 3b: Surfactant(s) design) is needed. Necessarily, some of the models applied for the definition of the target properties might differ when considering an emulsified product, rather than a homogeneous formulation. In particular, surfactants are key chemicals in most emulsified formulations and a wide range of peculiar properties need to be considered when designing or selecting chemicals such as surfactants [17].