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ORIGINAL CONTRIBUTION

Constant vapor pressure evaporation from emulsions

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Abstract The evaporation from three phases in equilibrium in a three-component emulsion was investigated. The calculations considered the fact that the composition of three phases and that of the vapor is determined by the system per se, leaving only the gross composition of the emulsion to be varied. The total composition was established for one scenario, the evaporation taking place with no change in the composition of the emulsion. The relative amounts of the three phases to satisfy this condition were calculated using two methods, and the complexity of the methods was compared.

Keywords Emulsions · Evaporation · Vapor pressure · Phase diagrams · Detergents

Introduction

It is a true privilege to contribute this article to the issue honoring Professor Janos Fendler. Janos, "the renaissance man" has not only made pioneering and lasting contributions to colloid science, but for me personally, the brilliance and vivacity of the Fendler couple brightened the long and cold winters in the hostile environment up North.

As for the theme of the present contribution, the evaporation of emulsions is important within a wide field of applications [1–4] This significance is strongly felt in the area of general cosmetics [5, 6] and, naturally, even more so for fragrance emulsions [7]. Of the other applications worthy of notice, the use of emulsions as vehicles to prepare solid particles [8–10], an approach that resulted in a rich literature on the preparation of nano-particles, may be mentioned.

Evaporation from emulsions is, hence, an industrially essential process and has consequently given rise to extensive fundamental research on the process as such, especially in two-phase emulsions. Over the past decade, the chemistry faculty at the University of Hull, as a leading group, has investigated basic aspects of evaporation from a variety of emulsions [11–14] and microemulsions [15]. One key insight obtained into emulsion evaporation is that oil evaporation from oil drops in an oil-in-water emulsion proceeds by dissolution of the oil into the thin water film present at the emulsion surface, followed by diffusion and release into the vapor. The oil drops do not break through into the emulsion surface before evaporation [11, 12].

In parallel with these efforts and as a consequence of the Scandinavian research into amphiphilic phase diagrams came the early realization that a large number of emulsions actually contain additional phases [16], followed by a most significant increase in the research on the phase diagrams of amphiphile systems [17–23]. As one of the results of this research, the recent report demonstrating even simple emulsions to go through drastic phase changes during evaporation [24] should be mentioned. This result led to research into the involvement of colloidal structures with long range order in the evaporation process [7].

Recently, the research on the evaporation of emulsions was expanded to include an algebraic system to extract information from phase diagrams [25]. The initial approach [26] took advantage of the fact that one compound, the surfactant, does not evaporate to a significant extent. One of the conclusions in the cited contribution [26] drew attention to the fact that evaporation from several phases in

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equilibrium enabled the formulation of emulsions evaporating with constant vapor pressure during extended times.

As this condition is of pre-eminent interest in the area of fragrance formulations, it was considered justified with an extension of the research into the fundamentals of evaporation from emulsions under constant vapor pressure, and a preliminary investigation into a simplified system was recently published [20]. The present contribution analyzes the basic factors during evaporation from three-phase emulsions under the condition that the exhaustion of the three phases is simultaneous.

The system

The system is illustrated in Fig. 1. It consists of three compounds A, B, and C, and inside the system, the three phases 1, 2, and 3 exist in equilibrium. The composition of the phases is expressed as (A_ν, B_ν, C_ν), in which ν=1–3.

The emulsion composition is (A_E, B_E, C_E) and that of the vapor composition at equilibrium is (A_V, B_V, C_V).

Some general conditions

The entire treatment of this problem rests on two basic conditions. The composition of the vapor and the composition of the three phases are decided by the compounds per se and cannot be changed unless new compounds replace the ones used. This leaves the total composition of the emulsion as the only variable.

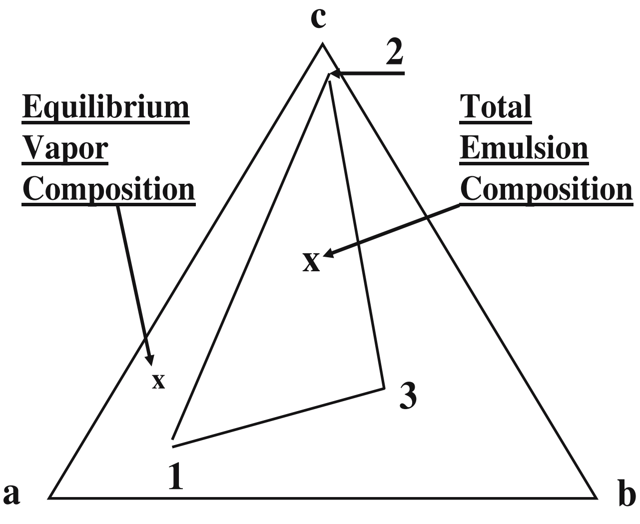

Fig. 1 The emulsion system of the compounds *A*, *B*, and *C* with a three-phase region of phases 1 to 3. The total emulsion composition is marked with a capital *X* and the composition of the vapor with lower case *x*

As to the first condition, the fraction of compound A within the vapor is equal to

$$A_V = P_A M_A / (P_A M_A + P_B M_B + P_C M_C) \quad (1)$$

with the inherent assumption that the evaporated vapor is in equilibrium with the three phases and that the atmosphere into which the evaporation takes place does not contain one of the compounds A to C in a permanent manner.

Secondly, the emulsion formulation must, with necessity, be located within the three-phase region. It is germane to allude to the fact that the locale of the vapor composition is not restricted in this manner but may reside anywhere in the diagram. However, in the present treatment, the vapor composition is located within the three-phase region because of the special restriction.

The line for evaporation originates at the total composition of the emulsion, (A_E, B_E, C_E), and its direction is an extension of a line from the vapor composition, (A_V, B_V, C_V). Its equation is

$$A = A_V + (A_E - A_V)(B - B_V)/(B_E - B_V) \quad (2)$$

Equation 2 does not define the direction of the change in composition; it does not distinguish a move from (A_E, B_E, C_E) towards (A_V, B_V, C_V), the opposite direction from the evaporation path. Limiting the equation to describe evaporation requires only one complementary condition

$$|A - A_V| > |A_E - A_V| \quad (3)$$

or identical conditions for components B and C.

Evaporation pattern

Several evaporation scenarios are tractable by this approach, but the following analysis is restricted to the case for which the evaporation does not change the emulsion composition.

Equation 2 offers an immediate solution to the condition for an emulsion, which evaporates with no change in the total composition of the emulsion, as long as there is material left in all three phases. The condition for this state is immediately evident if Eq. 2 is written

$$A = A_V + B(A_E - A_V)/(B_E - B_V) - B_V(A_E - A_V)/(B_E - B_V) \quad (4)$$

As $(A_E-A_V)/(B_E-B_V) \neq 0$, the obvious solution is $A=A_V$ combined with $B=B_V$, which, hence, is the condition for evaporation at constant composition of the emulsion. It should be noticed that the relation $(A_E-A_V)/(B_E-B_V) \neq 0$ holds also as the emulsion coordinates approach the one for the vapor composition, when both expressions within the parenthesis approach zero. The ratio between them remains constant for infinitely small values of the denominator and the numerator because the variation of the two factors is linear. In this evaporation case, the vapor composition is located within the three-phase region.

As pointed out, the composition of the vapor and of the three phases are dependent on the emulsion components, and the aim of the exercise to achieve the simultaneous evaporation of the phases is accomplished by using a formulation equal to the vapor composition. Hence, the only matter of interest remaining is the amount of the three phases (m_1, m_2, m_3) in equilibrium resulting in the total emulsion composition as required. This can be obtained by solving the equation system in which the amounts of the emulsion components is given by adding the amount of the component in each phase according to Laughlin [27] or by using the recently introduced algebraic approach [25]. Although the latter system is to its most advantage when the coordinates vary, it was considered of interest to compare the complexity of expressions for a static problem like the one in question.

In the following equations, the entire terms are used. The author is well aware that the equation system is more directly solved by using matrix algebra, but the present discussion is concerned with a direct comparison of the final expressions, and the resulting equations are presented in toto.

The equation system

$$\begin{aligned} A_V &= m_1A_1 + m_2A_2 + m_3A_3 \\ B_V &= m_1B_1 + m_2B_2 + m_3B_3 \\ C_V &= m_1C_1 + m_2C_2 + m_3C_3 \end{aligned} \tag{5}$$

the solution is

$$m_1 = [(A_VB_2 - A_2B_V)(A_3C_2 - A_2C_3) - (A_VC_2 - A_2C_V)(A_3B_2 - A_2B_3)]/ \\ [(A_1B_2 - A_2B_1)(A_3C_2 - A_2C_3) - (A_1C_2 - A_2C_1)(A_3B_2 - A_2B_3)] \tag{6}$$

$$m_2 = [(A_VB_1 - A_1B_V)(A_3C_1 - A_1C_3) - (A_VC_1 - A_1C_V)(A_3B_1 - A_1B_3)]/ \\ [(A_2B_1 - A_1B_2)(A_3C_1 - A_1C_3) - (A_2C_1 - A_1C_2)(A_3B_1 - A_1B_3)] \tag{7}$$

$$m_3 = [(A_VB_1 - A_1B_V)(A_2C_1 - A_1C_2) - (A_VC_1 - A_1C_V)(A_2B_1 - A_1B_2)]/ \\ [(A_3B_1 - A_1B_3)(A_2C_1 - A_1C_2) - (A_3C_1 - A_1C_3)(A_2C_1 - A_1B_2)] \tag{8}$$

The algebraic approach is based on the information in Fig. 2. The total amount of the emulsion is equal to unity, and the amount in phase 1 is equal to the distance 1V/23-V divided by the distance 1V/23-1 [26]. The primary object is to relate the coordinates for point 1V/23 to the coordinates for phase 1 and the vapor, V. This point is obtained by combining the equation for the line from phase 1 through the vapor composition

$$A = A_V + (A_1 - A_V)(B - B_V)/(B_1 - B_V) \tag{9}$$

with the one between phases 2 and 3

$$A = A_2 + (A_3 - A_2)(B - B_2)/(B_3 - B_2) \tag{10}$$

giving

$$B_{1V/23} = [A_V - A_2 + B_2(A_3 - A_2)/(B_3 - B_2) - B_V(A_1 - A_V)/(B_1 - B_V)]/ \\ [(A_3 - A_2)/(B_3 - B_2) - (A_1 - A_V)/(B_1 - B_V)] \tag{11}$$

The amount of phase 1 becomes

$$m_1 = (B_{1V/23} - B_V)/(B_{1V/23} - B_1) \tag{12}$$

$$m_1 = [A_V - A_2 + (B_3 - B_V)(A_3 - A_2)/(B_3 - B_2)]/ \\ [A_V - A_2 + (B_2 - B_1)(A_3 - A_2)/(B_3 - B_2) + (B_1 - B_V)(A_1 - A_V)/(B_1 - B_V)]. \tag{13}$$

The amounts in phases 2 and 3 are obtained analogously

$$m_2 = [A_V - A_1 + (B_1 - B_V)(A_3 - A_1)/(B_3 - B_1)]/ \\ [A_V - A_1 + (B_1 - B_2)(A_3 - A_1) + (B_2 - B_V)(A_2 - A_V)/(B_2 - BV)] \tag{14}$$

$$m_3 = [A_V - A_1 + (B_2 - B_V)(A_2 - A_1)/(B_2 - B_1)]/ \\ [A_V - A_1 + (B_2 - B_3)(A_2 - A_1)/(B_2 - B_1) + (B_3 - B_V)(A_3 - A_V)/(B_3 - B_V)] \tag{15}$$

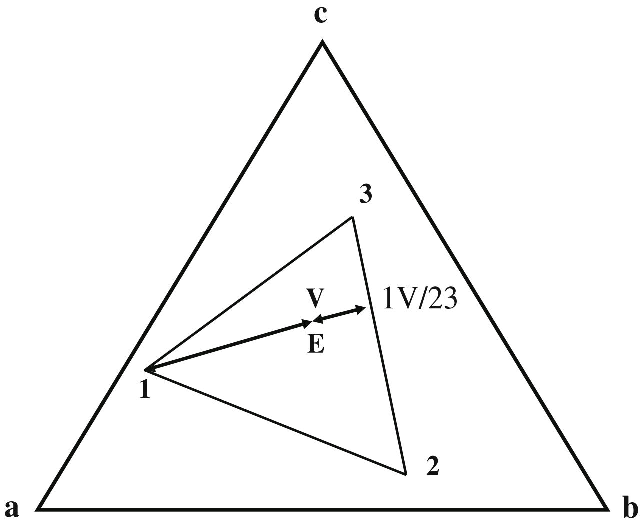

Fig. 2 The weight fraction of phase 1 is obtained as the ratio between the distances 1V/23-V (*E*) and 1V/23-1

Comparing the complete expressions, there is no significant difference in the complexity of them, but for the calculations of single points, the solution of the equation system is to be preferred because the availability of matrix programs facilitates the calculations. For problems involving evaporation or dilution the algebraic system offers distinct advantages because it provides first order expressions of the involved variables with no need for computer programming.

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