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MANUFACTURING OF PARAFFIN EMULSIONS BY PHASE INVERSION STABILIZED WITH MIXED EMULSIFIERS

KATONA Jaroslav, DOKIĆ Petar, DOKIĆ Ljubica

UNIVERSITY OF NOVI SAD
FACULTY OF TECHNOLOGY
COLLOID CHEMISTRY
SERBIA & MONTENEGRO

SUMMARY:

A systematic investigation of the procedure and conditions for paraffin emulsification in water by phase inversion method was undertaken in order to obtain stable technical emulsions and to find out what emulsifier properties, i.e. final emulsion characteristics and phase inversion are independent.

The emulsions were stabilized by an emulsifier mixture composed of polyglicol ethers with different paraffin chain length, nonylphenil polyglicol ethers of different polyoxyethylene chain length, oleic acid and triethanolamine.

Varying the composition and mutual ratio of the emulsifier mixture, its concentration and phase inversion temperature, a number of emulsions which were different in stability, rheological and dispersion characteristics were prepared. On the basis of viscosity, particle size distribution and stability measurements, the composition of the emulsifier mixture, most suitable procedure and phase inversion temperature for manufacturing of stable paraffin emulsions have been determined. These examinations also indicated complexity of phase inversion and specific role of individual components of the emulsifier mixture.

KEYWORDS:
emulsion, phase inversion, PIT

1. INTRODUCTION

Emulsions are at least two-phase liquid-liquid systems, where one liquid (disperse phase) is dispersed in another (continual phase) in the form of minute droplets. Since the emulsification of two immixable liquids involves a tremendous rise in the surface energy, such emulsions are unstable and third component is needed to stabilize the system. This is usually an emulsifier-small, amphiphilic molecule with tendency to accumulate on the two liquid's interface. Choice of the emulsifier and its concentration determine final emulsion properties (i.e. particle size distribution, rheological properties etc.) to a great extent.

Although emulsification process can be done in a number of ways, this usually engages utilization of mechanical energy (stirrer, colloid mil, homogenizer etc.). However, more often than not, this requires a great amount of energy input, especially at industrial scale, which is obviously a considerable disadvantage when looking from commercial point of view. Emulsion formation by means of phase inversion method might give solution to that problem.

Phase inversion refers to phenomenon that an oil-in-water emulsion (O/W) is transferred into a water-in-oil (W/O) emulsion, or vice versa [1]. It can be one of two types: Transitional inversion induced by changing factors which affect affinity of the emulsifier towards the two phases of the system, e.g. temperature and/or electrolyte concentration [2, 3]. Catastrophic inversion which is induced by increasing the volume fraction of the disperse phase [4]. Transitional inversion can also be induced by changing the HLB number of the surfactant at constant temperature using surfactant mixtures [5]. Both mechanisms are closely related to the formation of double emulsions [6,7].

Even though emulsion formation by phase inversion method is said to be no more mysterious and uncontrollable process [8], it still remains a rather complex phenomenon dependent on a numerous parameters.

In this paper, precise phase inversion method for the emulsification of paraffin in water has been presented. Influence of emulsifier mixture's content and concentration on rheological properties as well as particle size distribution have been discussed.

2. MATERIALS AND METHODS

Paraffin in water emulsions were prepared by means of phase inversion method. The emulsions consisted of paraffin (melting point 52-54°C), bidistilled water, oleic acid (OA), triethanolamine (TEA) and one, or the mixture of two, of the nonionic emulsifiers given in Table 1. Values of hydrophile-lipophile balance numbers (HLB) of the emulsifiers as well as phase inversion temperatures (PIT) of emulsion of paraffin oil having 1% of the emulsifier are also given:

TABLE 1. NONIONIC EMULSIFIERS USED IN THE EMULSION PREPARATION

NONIONIC EMULSIFIERS	HLB	PIT [°C]
Polyoxyethylenealkylethers		
Polyoxyethylene(4.2)laurylether (POE-LE)	10	50
Polyoxyethylene(8)(C_{10}/C_{16}/C_{20})ether (POE-AE8)	3.4	
Polyoxyethylene(11)(C16/C20)ether (POE-AE11)	4.0	
Nonylphenylpolyoxyethylenes (NPPE)		
NPPE-3	7.5	
NPPE-6	10.9	75
NPPE-8	12.3	95
NPPE-9	13.3	100
NPPE-12	14	115

Following procedure for the emulsion preparation was employed: All of the emulsions were prepared in the amount of 200g. Each emulsion contained 50g of paraffin, while the amount of oleic acid, TEA and the non-ionic emulsifiers were varied. The mixture of paraffin, oleic acid and the non-ionic emulsifier was put in a jacketed vessel thermostated at 90°C. After the mixture had melted and reached temperature of 80°C, an impeller stirrer was immersed in. The stirrer speed was approximately 1300rpm. Subsequently, the melted mixture was gradually being added particular amounts of boiling water. A W/O emulsion was formed in the first place. However, after sufficient amount of water had been added, phase inversion took place and O/W emulsion was produced. Following the addition of entire amount of water, temperature of the thermostating water was lowered to 15°C. When the emulsion temperature reached 60°C, pH value was checked and adjusted to 7.5 by addition of TEA. Cooling and steering of the emulsion was stopped when the emulsion temperature dropped to 30°C.

Rheological measurements were carried out on rotational viscositymeter "Haake RV 3" (Germany).

Initial and long-term stability was determined visually i.e. observing whether there was phase separation or not.

Particle size distribution of the emulsions was determined by means of microphotography.

3. RESULTS AND DISCUSSION

With the aim of developing an exact procedure for making stable 25% (wt/wt) paraffin in water emulsions by phase inversion method a large number of emulsions of different composition were prepared.

During the emulsification some of the parameters were held constant (way and rate of mixing, way and sequence of components addition) while the others were varied (emulsification temperature, rate of addition of water phase, cooling of inverted emulsions and composition of the emulsifiers' mixtures). Overall concentration of the emulsifiers' mixtures was between 5-8% (wt/wt). Concentration of the emulsifiers used was varied in the following intervals (%, wt/wt): 0.25-4, 3, 1-4, 1—3, 2-4, 0.5-4, 1-1.5, 1-1.5, 0.5-4, 1.5-4.5 for POE—LE, POE-AE8, POE-AE11, NPPE-3, NPPE-6, NPPE-8, NPPE-9, NPPE-12, OA, and TEA respectively. Water concentration was ranged between 67 and 70% (wt/wt).

Certain number of the emulsions proved to be unstable since phase separation occurred either during emulsification procedure or immediately after an emulsion had been prepared. In the like manner, some emulsions phase separated after a few hours, days or weeks. Nevertheless, by the systematic change of the emulsifying parameters, precise method for the preparation of stable paraffin in water emulsions has been defined. In addition to the detailed description of the method in experimental part of this work, for the sake of convenience it is also presented in Fig. 1.

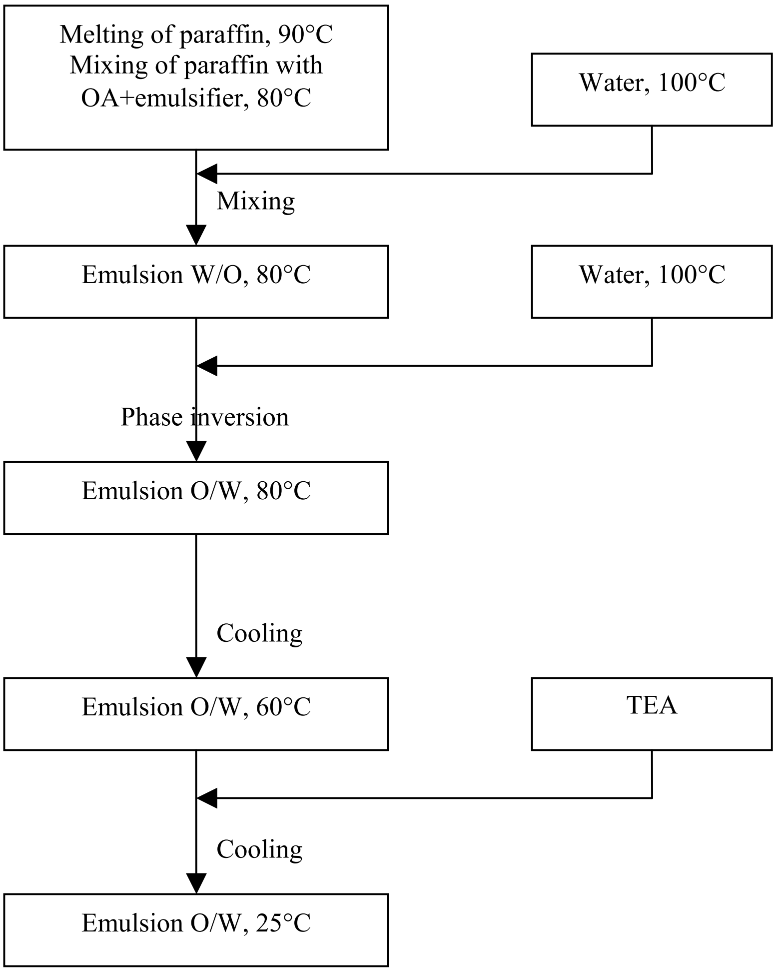

Fig. 1. The scheme for paraffin emulsion preparation by phase inversion method

Among all the emulsions tested only those containing emulsifiers' mixtures were stable. Demanding long-term stability had the emulsions stabilized by POE-LE and NPPE with polyoxyethylene chain of medium length (NPPE-8 and NPPE-9). This is understandable when bearing in mind Bancroft's rule on one side, [3] and that solubility of polyoxyethylen based emulsifiers strongly depend on both hydrophilic chain length and temperature [4] on the other. Namely, since the NPPE-3 and NPPE-6 solubility in water was insufficient, especially at high temperatures, phase separation occurred following the phase inversion of a W/O emulsion. On the other hand, NPPE-12, as well as POE-AE8 and POE-AE11 solubility in oil phase was not good enough, and consequently W/O emulsion, which is prerequisite for the O/W emulsion manufacturing, could not be formed.

Compositions of the emulsifiers' mixtures which gave stable emulsions, calculated HLB values and phase inversion temperatures (PIT) are given in Table 2.

Table 2. Composition of the emulsifier mixtures (in % wt/wt) in some stable paraffin emulsions

Emulsifier	Emulsion				
	1	2	3	4	5
PO-LE	1	0.5	0.5	0.5	-
NPPE-8	2	1.5	1	-	-
NPPE-9	-	-	-	1	-
POE-AE11	-	-	-	-	1.5
Oleic acid	1.5	2	2	2	2
TEA	2.5	3.5	2.5	1.5	1.5
HLB	9.7	9.3	8.5	7.9	5.5
PIT (°C)	80	84	80	83	-

The HLB values of emulsifier mixtures (HLB_{mix}) so as the corresponding PIT values (PIT_{mix}) were calculated using equitation 1 and 2, respectively.

$$HLB_{mix} = \sum \frac{g_i}{\sum g_i} HLB_i \quad [1]$$

$$PIT_{mix} = \sum \frac{g_i}{\sum g_i} PIT_i \quad [2]$$

Where g_i is mass fraction of the emulsifier used; HLB_i is HLB values of the emulsifier as found in literature or calculated from the group numbers [2].

One can notice, Table 2., that calculated PIT values of the emulsions was around 80°C, which was at the same time temperature of emulsification. This implies that, though phase inversion was of the catastrophic type (i.e. due to excess of water volume), it happened in the vicinity of transitional locus. It has been reported that at the PIT interfacial tension reaches minimum so as the droplet size of the just inverted emulsion. However, the small droplets are unstable and they coalesce very rapidly. By rapid cooling of the emulsion that is prepared at the temperature near the PIT, very stable and small emulsion droplets could be produced [8,9].

Namely, phase inversion is closely related to multiple emulsion formation. As the phase inversion process proceeds, the greater amount of continuous phase is being dispersed as an internal phase in the disperse phase. In one moment, effective volume of the disperse phase reaches maximum value and coalescence happens so that the disperse phase becomes continuous, while the internal phase becomes disperse phase of the newly formed phase inverted emulsion. When catastrophic phase inversion that happens fairly away from the transitional locus is encountered, submicron droplets of the newly dispersed phase are given rise to rapid coalescence and the emulsion of rather large droplets is formed. Yet, when transitional or catastrophic phase inversion in the vicinity of the transitional locus takes place, emulsion of submicron droplets can be formed [1, 4, and 10].

This could be also the explanation for the rather small droplets diameters obtained by the developed method nevertheless low mechanical energy input.

Corresponding particle size distribution parameters of stable paraffin in water emulsions are given in Table 3. Probability density curves are given in Fig. 2.

Table 3. Particle size distribution parameters of some stable paraffin emulsions

Parameters	Emulsion				
	1	2	3	4	5
Mean diameter (□m)	0.76	1.50	1.53	1.94	2.12
Variance (□m)	0.06	0.26	0.36	0.67	0.41
Specific surface (m^2/g)	6.31	3.14	2.74	2.24	2.25
Most frequent diameter (□m)	0.68	1.44	1.29	1.59	1.81
Asymmetry	0.44	0.40	0.63	0.73	0.40

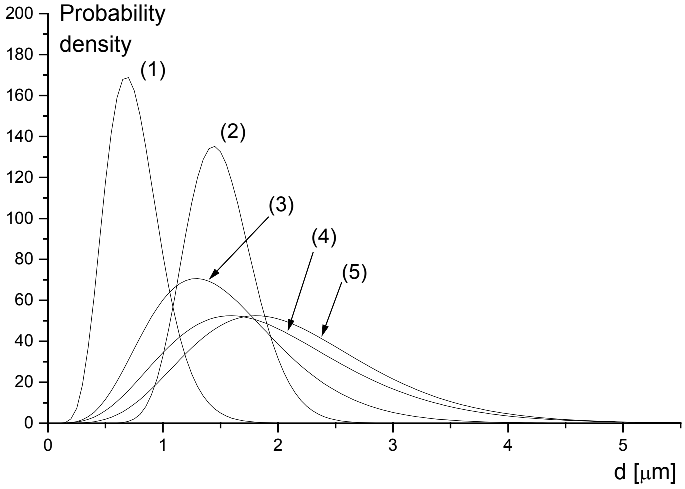

Fig. 2. Curves o particle size distribution (probability density) of the paraffin emulsions stabilized with emulsifiers mixtures of different composition

The higher the overall emulsifier concentration the lower the mean diameter, which is in agreement with [3]. On the other hand, emulsifier concentration affected droplet distribution, as well: droplet distribution was wider when the emulsifier concentration was lower.

As for rheological properties investigations, all of the emulsion showed pseudoplastic (shear thinning) behaviour. In order to determine degree of pseudoplasticity together with high and low shear viscosity (viscosity when shear rate D□∞ and D=0, respectively), experimental date were fitted to the following equitations:

$$\tau = \tau_0 (D+1)^M \qquad [3]$$

$$\eta = (\eta_0 - \eta_N) e^{-KD} + \eta_N \qquad [4]$$

Where □ is shear stress; □0-shear stress when □=0; D-shear rate; M-degree of pseudoplasticity; □-apparent viscosity; □0 and □N low and high shear viscosity, respectively; K-constant. Fitting parameters are given in Table 3.

Table 4. Fitting parameters from the shear stress [3] and viscosity equations [4]

Emulsion	1	2	3	4	5
$\square_0$	0.0480	0.0739	0.8180	0.1052	0.0262
M	0.7808	0.7213	0.4120	0.6356	0.8212
$\square_0$	31.6	32.8	402.3	65.1	17.5
$\square_N$	11.3	10.9	10.6	10.5	7.4
K	$9.1\cdot10^{-3}$	$6.6\cdot10^{-3}$	$4.9\cdot10^{-2}$	$2.8\cdot10^{-2}$	$8.5\cdot10^{-3}$

As it can be seen from Tables 2. and 4, shear thinning of the emulsions depends on the overall emulsifiers' concentration so as on the emulsifiers' mixture used.

Droplet size analysis together with rheological investigations suggests that, although non-ionic emulsifiers used are of crucial importance for the emulsion formation, emulsifying properties of oleic acid and TEA are also contributing to final emulsions properties and could not be neglected.

On the basis of the results outlined, following mechanism of phase inversion may be supposed. Being well soluble in the oil phase, oleic acid enables formation of high concentration W/O emulsion which is stable even if near the catastrophic phase inversion region. POE-LE and NPPE with polyoxyethylene chain of medium length (NPPE-8 and NPPE-9) dissolved in water phase when heated to the 80°C (PIT temperature/ emulsification temperature) becomes soluble in both oil and water phase. This is due to less affinity of water molecules toward polyoxyethylene chains when heated to higher temperatures. This surfactant mobility, through the attached oil phase on the hydrophobic parts of the emulsifiers (nonylphenil/alkyl parts), allows solubilization of a quite amount of oil in the water droplets giving rise to the formation of double emulsions. When certain amount of oil is dispersed in water droplets, their effective volume reaches maximum value and coalescence takes place. Since this catastrophic phase inversion happens in the vicinity of transitional locus, by means of cooling, stable, phase inverted emulsion having small droplets diameters is formed. Besides adjusting the pH value, the addition of TEA close to the end of the emulsification process probably enhances stability of the emulsions via bond formation with oleic acid.

4. CONCLUSION

Precise procedure for emulsion formation by means of phase inversion has been developed. Demanding long term stability had the emulsions stabilized with POE-LE and NPPE with polyoxyethylene chain of medium length (NPPE-8 and NPPE-9). The emulsions obtained had desirable droplet size distribution and rheological properties. The higher the overall emulsifier concentration the lower the mean diameter and the narrower particle size distribution. It was shown that phase inversion method of emulsification enables formation of small droplets of the dispersed phase albeit low mechanical energy input.

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