

ORGANIC SYNTHESIS
AND INDUSTRIAL ORGANIC CHEMISTRY

The Effect of NaCl Concentration on the Phase Inversion Temperature and Droplet Sizes of Liquid Paraffin Nanoemulsions

Ali Mohammad Astaraki^{a,*} and Farideh Shirvani^b

^a Department of Chemistry, Islamic Azad University, Doroud, 68816-99999 Iran

^b Department of Chemistry, Payame Noor University, Delijan Center, Delijan, 19395-3697 Iran

*e-mail: am.astaraki@yahoo.com

Received August 14, 2019; revised April 14, 2020; accepted May 18, 2020

Abstract—In this study, nano-emulsions were prepared by phase inversion temperature within the system liquid paraffin /Span80-Tween80/–water and also the effect of NaCl concentrations on phase inversion temperature (PIT) system and droplet sizes of liquid paraffin were studied. The changes in electrical conductivity with temperature for emulsions with 10 wt % liquid paraffin, 12 wt % surfactant mixture of Span80 and Tween80 and 0.01 to 0.5 M NaCl aqueous solution were measured by conductivity meter, and middle temperature within the range of extra reduction in conductivity as PIT in each case was considered. The results show that, with increasing concentration of NaCl from 0.01 to 0.5 M, PIT decreased logarithmically from 62 to 53°C, and also the mean droplet size of paraffin increased from 21.1 to 30.3 nm respectively. Nano-emulsions also are transparent.

Keywords: nano-emulsion, phase inversion temperature, emulsification, surfactant

DOI: 10.1134/S1070427220060191

INTRODUCTION

Nano-emulsions are transparent or semi-transparent systems which, approximately, cover droplet size of 50 to 200 nm [1, 2]. They also mentioned as mini-emulsion nano-emulsion [3, 4]. Nano-emulsions are kinetically stable. Despite of this fact, long-term physical stability of nano-emulsions (without aggregation or coagulation) has made them unique and sometimes as near to thermodynamic stability, may be attributed to them. Three methods is also wont to produce nano-emulsions, employing a high-pressure homogenizer (with appropriate selection of surfactants and co-surfactants), using low-energy emulsification at a constant temperature or the applying of the principle of phase inversion temperature (PIT)[5, 6].

The phase inversion temperature method (PIT) is particularly interesting because it's a low energy method and without organic solvent. The last two experimental

conditions essentially for application within the field of nanomedicine, cosmetics and pharmaceutical sciences, drug encapsulation to prevent damage during the process are appropriate. As an example, because the process is comparatively simple and low energy consumption may be easily performed on an industrial scale. The PIT method is provided by Shinoda and Saito. Using the special ability of surfactants, usually nonionic (NS) like polyethoxylated surfactants, by modifying the tendency for water and oil as a function of temperature, they undergo phase inversion. Furthermore, it is called transitive emulsion phase inversion that it happens within the fixed combination when the surfactant relative tendency changes for the varied phases due to temperature gradual modification. As an example, when the temperature rises, oil in water emulsion (O/W) are going to be exposed to the phase inversion during which water-in-oil (W/O) emulsion are going to be produced. Within the transition zone between macro-emulsions, namely for

temperatures that non-ionic surfactants show an identical tendency for two mixture phase, the ternary system represented a really low surface tension and curvature; for example, micro-emulsions produce bicontinuous and nano-scale systems [7]. Thus, the PIT method involves the sudden separation of microemulsion bicontinuous within the PIT by cooling rapidly [8–10] or by sudden diluting in water or oil [11–14] that the nano-emulsions are immediately produced [15]. The nano-emulsion is attracted for applying in various industrial fields, for instance, for polymerization reaction medium, personal health and cosmetics, health, and agricultural chemicals, as a result of following reasons: firstly, a really small droplet sizes cause much lower weight and influence of Brownian forces may prevent any coagulation or sedimentation of the droplets. Secondly, dimensions tiny droplets and high kinetic stability make nano-emulsion suitable for effective delivery of the active agents (due to high surface area) and penetrating the skin uneven tissue [16]. In contrast with the micro-emulsions which for their production need the high surfactant concentration (usually within the range of 10–30 wt %), nano-emulsions may be made at the typical surfactant concentration (in weight range of 4–8%) [8].

MATERIALS AND METHODS

Material. Span 80 and Tween 80 surfactants, liquid paraffin (extra pure), NaCl (purity 99.999%) were obtained from the German Merck company. Double distilled water was used for the preparation of NaCl aqueous solutions.

Determination of phase inversion temperature. Phase inversion temperature was determined through the electrical conductivity method [6, 9, 17, 18] by the conductivity meter Elementor-CP501 model. The emulsion contains 10 wt % paraffin, 12 wt % surfactant mixture of Span80 (0.44) and Tween80 (0.56) [19], and aqueous solutions of 0.01–0.5 M NaCl were prepared at the laboratory temperature. Emulsions were heated gradually and so the conduction was measured as a function of temperature. The center temperature within the range of sharp reduction in conductivity was designated as a phase inversion temperature of O/W to W/O emulsion.

Emulsification by phase inversion temperature method. Oil-in-water nano-emulsions were produced within the way that the oil phase including Span80

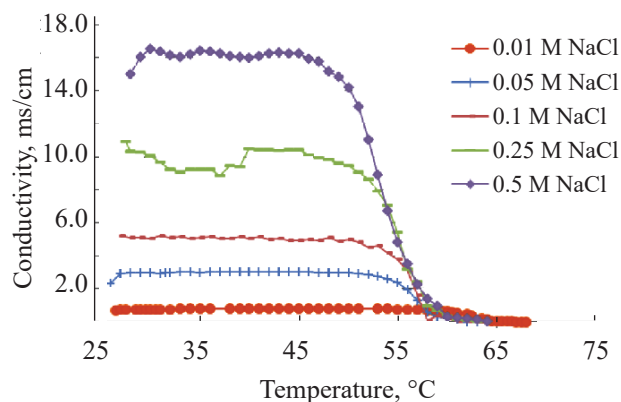


Fig. 1. (Color online) Conductivity as a function of temperature in the nano-emulsions with different concentrations of NaCl solution within the aqueous phase.

and Tween80 surfactants mixture, liquid paraffin, and solution of 0.01–0.5 M NaCl were heated separately to 15°C above PIT; then, at the mentioned temperature, the aqueous phase was poured into the oil phase and also the mixture was taken out of the heating source and was cooled to the equivalent PIT temperature within the environmental conditions by a manual mixer [6, 17, 18, 20]. Consequently, the sample was cooled through the ice bath with a manual mixer. Eventually, the transparent nano-emulsions were obtained.

Determination of droplets size and distribution index of the nanoemulsions particle. Brookhaven instrument Co. (win32) was applied to measure droplets size and polydispersity index (PDI) of the nano-emulsions. This instrument works based on dynamic light scattering (DLS). Input laser light with a wavelength of 657 nm and at an angle of 90° is employed. The tests were administered at 25°C and also the samples were diluted 20 folded by deionized water.

RESULTS AND DISCUSSION

Effect of NaCl concentration on the phase inversion temperature of nanoemulsions. The phase inversion temperature within the emulsions, including 10 wt % paraffin, 12 wt % surfactants mixture Span80 and Tween80, and the solutions of 0.01 to 0.5 M NaCl was measured employing a conductivity meter. The graph of conduction vs. temperature is shown in Fig. 1. According to graphs, the mean temperature within the range of conduction sharp reducing has been considered as PIT of that emulsion (Table 1). It's observed that by a rise in NaCl concentration within the aqueous

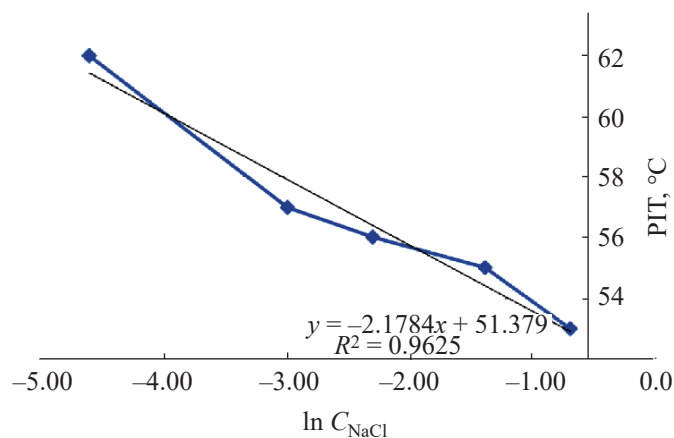


Fig. 2. PIT nano-emulsions as a function of the logarithm of NaCl concentration within the aqueous phase.

phase from 0.01 to 0.5 molar, nano-emulsion PIT reduces from 62 to 53°C.

The PIT nano-emulsions as a function of the logarithm of concentration NaCl within the aqueous phase are plotted in Fig. 2.

As it can be seen, the changes are linear, the equation and the square correlation coefficient will be as follows:

$$\text{PIT} = 2.1784 \ln C_{\text{NaCl}} + 51.379, R^2 = 0.9625.$$

Measurements of droplet sizes of nano-emulsions with different concentrations of NaCl within the aqueous phase. The droplet size and PDI of nano-

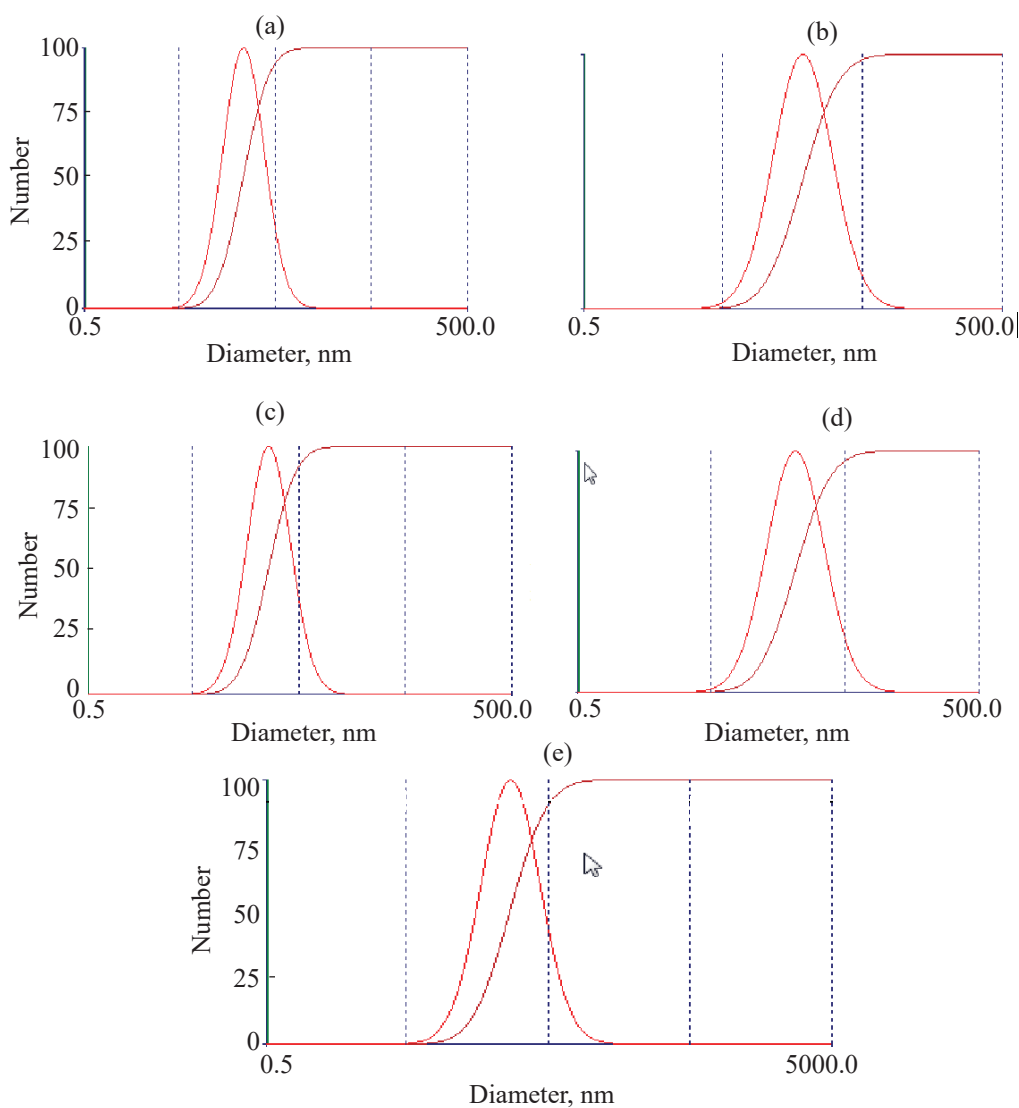


Fig. 3. Mean droplet size distribution vs. number of nano-emulsion for emulsions with different concentrations of NaCl solution within the aqueous phase, M: (a) 0.01, (b) 0.05, (c) 0.1, (d) 0.25 M, and (e) 0.5.

Table 1. The PIT nano-emulsions with different concentrations of NaCl within the aqueous phase

Concentrations of NaCl, M	$\ln C_{\text{NaCl}}$	PIT, °C
0.01	-4.61	62
0.05	-3.00	57
0.10	-2.30	56
0.25	-1.39	55
0.50	-0.69	53

Table 2. The droplet size of nano-emulsions with different concentrations of NaCl solution within the aqueous phase

NaCl concentration, M	Mean droplet sizes, nm	PDI
0.01	21.1	0.282
0.05	26.4	0.298
0.1	24.2	0.293
0.25	29.0	0.270
0.5	30.3	0.277

emulsions containing 10 wt % paraffin, 12 wt % surfactants mixture Span80 and Tween80, and the 0.01 to 0.5 M NaCl solutions were measured by Brookhaven instrument Co. (win32) at 25°C. The results are given in Table 2 and Fig. 3.

As can be seen according to the results, with increasing concentration of the NaCl solution from 0.01 to 0.5 M, the mean droplet sizes increase from 21.1 to 30.3 nm. Moreover, a rise in NaCl concentration within the aqueous phase doesn't have a significant effect on the PDI of nano-emulsions samples.

CONCLUSIONS

According to the results obtained for emulsions with 10 wt % liquid paraffin, 12 wt % surfactant mixture of Span80 and Tween80, and the NaCl solution of different concentrations within the aqueous phase, with increasing concentration of NaCl from 0.01 to 0.5 M, the phase inversion temperature nano-emulsions decreased from 62 to 53°C logarithmically, and therefore the mean droplet size increased from 21.1 to 30.3 nm respectively, which suggests negative effects of increasing NaCl concentrations on the mean droplet size. Also, a rise in NaCl concentration did not significantly effect on the PDI of nano-emulsions.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

REFERENCES

1. Nakajima, H., Tomomossa, S., and Okabe, M., *First Emulsion Conference*, Paris, 1993.
2. Nakajima, H., Solans, C., and Kunieda, H., *Industrial Applications of Microemulsions*, New York: Marcel Dekker, 1997.
3. Ugelstadt, J., El-Aassar, M.S., and Vanderhoff, J.W., *J. Polym. Sci.*, 1973, vol. 11, pp. 503–511.
4. El-Aasser, M. and Asua, J.M., *Polymeric Dispersions*, Netherlands: Kluwer Academic Publications, 1997.
5. Tadros, Th., Izquierdo, P., Esquena, J., and Solans, C., *Adv. Colloid Interface Sci.*, 2004, vols. 108–109, pp. 303–318.
6. Astaraki, A.M., *Russ. J. Appl. Chem.*, 2016, vol. 89, no. 1, pp. 84–89.
<https://doi.org/10.1134/S10704272160010134>
7. Shinoda, K. and Saito, H., *J. Colloid Interface Sci.*, 1968, vol. 26, pp. 70–74.
8. Izquierdo, P., Esquena, J., Tadros, Th.F., Dederen, C., Garcia, M. J., Azemar, N., and Solans, C., *Langmuir*, 2002, vol. 18, pp. 26–30.
9. Izquierdo, P., Esquena, J., Tadros, Th.F., Dederen, J.C., Feng, J., Garcia, M.J., Azemar, N., and Solans, C., *Langmuir*, 2004, vol. 20, pp. 6594–6598.
10. Solans, C., Izquierdo, P., Nolla, J., Azemar, N., and Garcia-Celma, M.J., *Curr. Opin. Colloid Interface Sci.*, 2005, vol. 10, pp. 102–110.
11. Forster, T., Rybinski von, W., and Wadle, A., *Adv. Colloid Interface Sci.*, 1995, vol. 58, pp. 119–149.
12. Pons, R., Carrera, I., Caelles, J., Rouch, J., and Panizza, P., *Adv. Colloid Interface Sci.*, 2003, vol. 106, pp. 129–146.
13. Anton, N., Gayet, P., Benoit, J.P., and Saulnier, P., *Int. J. Pharm.*, 2007, vol. 344, nos. 1–2, pp. 44–52.
14. Anton, N., Benoit, J.P., and Saulnier, P., *J. Drug Del. Sci. Tech.*, 2008, vol. 18, no. 2, pp. 95–99.
15. Anton, N., Benoit, J.P., and Saulnier, P., *J. Controlled Release*, 2008, vol.128, pp. 185–199.
16. Amselem, S., Friedman, D., and Benita, S., *Submicron Emulsions in Drug Targeting and Delivery*, New York: Harwood Academic Publishers, 1998.
17. Astaraki, A.M., Mehrdad Sharif, A.A., Abroomand Azar, P., Abedini Khorrami, S., and Moradi, Sh., *Int. J. Acad. Res.*, 2010, vol. 2, no. 6, pp. 114–119.
18. Mehrdad Sharif, A.A., Astaraki, A. M., Aberoomand Azar, P., Abedini Khorrami, S., and Moradi, Sh., *Arabian J. Chem.*, 2012, vol. 5, pp. 41–44.
19. Liu, W., Sun, D., Li, C., Liu, Q., and Xu, J., *J. Colloid Interface Sci.*, 2006, vol. 303, no. 2, pp. 557–563.
20. Lin, Ee Sh., Duan, X., Liew, J., and Dzuy Nguyen, Q., *Chem. Eng. J.*, 2008, vol. 140, pp. 626–631.