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Physicochemical study of nanoemulsions of aqueous cellulose acetate propionate, cellulose acetate butyrate and tween80 with castor, olive and linseed oils from temperature (293.15 to 313.15) K

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ABSTRACT

Physicochemical properties, such as, density, viscosity, surface tension, friccohesity for oil-in-water nanoemulsions (NEs) formed by castor (CO), olive (OO) and linseed oils (LO), respectively, with cellulose acetate propionate (CAP), cellulose acetate butyrate (CAB) and tween 80 (Tw80) are reported at various temperatures ranging from 293.15 K to 313.15 K. The aqueous solutions of the non-ionic surfactants used are CAP, CAB and Tw80 along with co-surfactants ethyl alcohol, ethyl acetate, ethylene glycol and Tw40. Surface tension, viscosity and friccohesity data were obtained from density, pendant drop number and viscous flow time. The surface tension value is used to calculate surface excess concentration and area per molecule. Particle size and activation energy were calculated from viscosity. The parameters viscosity, surface tension, friccohesity, particle size, surface excess concentration and activation energy were regressed for their limiting values. Overall, this manuscript focuses on the effect of temperature, structure of oil and surfactant on the formulation, properties and stability of NEs.

1. Introduction

Nanoemulsion (NE) is one of the most challenging and fascinating research areas due to their immense application potential [1]. Emulsions are metastable dispersions of surfactant stabilized liquid droplets dispersed in another immiscible liquid termed as dispersion medium [2–4]. In the formation of emulsions, the components are mixed in appropriate proportions. NEs are kinetically stable dispersion containing nano-sized droplet (<100 nm) [5–7] of dispersed phase stabilized by one or two surfactants [8,9]. Due to strong Brownian motion of nanoscale size droplets, the NEs are incredibly resistant to creaming and sedimentation and become kinetically stable by a surfactant that inhibit coalescence [10,11]. Due to their ease of preparation and peculiar properties such as, small droplet size, high surface area and high bioavailability, NEs have attracted huge attention in multi-disciplinary research e.g., drug designing, paint, oil industry and as a potential vehicle for delivery of active pharmaceutical ingredients, cosmetics, personal care products as well as other bioactives [12–14]. The properties of NEs depend not only on thermodynamic conditions such as temperature, pressure and composition, but also on method of preparation i.e. order of addition of various components [13,15]. The most commonly used method for preparation of NEs are low energy emulsification, high pressure homogenization, microfludization, ultra sonication and phase inversion method [16,17].

In this manuscript, we have used non-ionic surfactants CAP, CAB and Tw80, respectively, along with co-surfactants ethyl alcohol, ethyl acetate, Tw40 and ethylene glycol for getting stable emulsions. Since surfactants are responsible for fractionating and then emulsifying the oil in water, we had chosen the surfactants with increasing alkyl chain length, to vary hydrophilic and hydrophobic interactions (HbI) for effective dispersion. In the HbI approach, the hydrophilic part of oil and surfactants have become additive factor and favorable for emulsification of oil by developing additive forces between water and oil that leads to stability of NEs. Ethyl alcohol and ethyl acetate are added to dissolve surfactants, whereas, ethylene glycol and Tw40 are used to enhance the stability of NEs. We have noticed that when surfactant is added to aqueous phase, the surface tension is found to be very low thus clearly indicating that surfactant molecule is going completely to an interface and responsible for utilizing the surface energy. There is an urgent need to study structural interactions of dispersed phase, dispersion medium and surfactants. Their physiochemical parameters, such as, density, viscosity, surface tension and friccohesity should also be studied in details either through. Herein we have studied the effect of temperature, on the formulation, stability and particle size of NEs formed by CO, OO, LO oils and CAP, CAB, Tw80 surfactants in the presence of co-surfactants ethyl alcohol, ethyl acetate, Tw40 and ethylene glycol. Castor oil is a

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triglyceride of ricinoleic acid, as the main constituent with one double bond (DB) in a chain contains hydroxyl functionality [18]. Olive oil is a triglyceride of mainly oleic acid (one DB in chain), has high nutritive value and contains a variety of compounds having antioxidative activity. As compared to other oils, olive oil has more stability towards oxidation [19]. Linseed oil (flaxseed oil) is a triglyceride of mainly α-linolenic acid (three DB in chain) [20] and is used in some pain relieving ointments. Hence, it is of utmost importance to study the formation and properties of NEs formed by such essential oils having significant pharmaceutical applications. In this manuscript, we have focused on structural impacts of non-*π* conjugated oil, surfactant and influence of varying temperature on formulation and stability of NEs by monitoring various physiochemical properties, such as, viscosity, surface tension, particle size, surface area and friccohesity.

2. Experimental section

2.1. Materials

Chemicals were used as received, without any further purification (Table S_1) (supplementary information) (S·I.). Analytical grade ethyl alcohol and ethylene glycol were used in formulation and the solutions are prepared Milli-Q water of 5×10^{-6} S cm^{-1}. Weight measurements were carried out by using Mettler Toledo New Classic MS electronic balance with ±0.0001 g accuracy.

2.2. Method of preparation of nanoemulsions

NEs were prepared by low energy method by spontaneous mixing of dispersion medium (water) to organic phase with constant stirring with magnetic stirrer (500 rpm) for 60 min at room temperature (25 ± 1 °C) [21]. Concentration of each component used in the preparation of NEs is given in **Table S_2 (S.I.)**.

2.3. Apparatus and procedure

Densities were measured by using Anton Paar 'Density and Sound velocity meter' DSA 5000 M. The temperature inside the densimeter was controlled to $\pm 1 \times 10^{-3}$ K, with a built-in Peltier device. The instrument was calibrated with Mili-Q water and dry air. Before and after each measurement, the tube was washed with acetone and dried uninterruptedly till a persistent oscillation period was obtained, by passing dried air through a tube using air pump. The repeatability in density was found to be 1×10^{-3} kg m^{-3} [21].

Viscous flow time and pendant drop numbers were measured with Borosil Mansingh Survismeter (calibration no. 06070582/1.01/C-0395, NPL, India) for viscosity and surface tension measurements respectively at $T = 293.15$ to 313.15 K. The temperature inside the survismeter was controlled by Lauda Alpha KA 8 thermostat with ±0.05 K. The pendant drop number was counted with an electronic counter while viscous flow time was recorded with an electronic timer of ±0.1 s accuracy. The survismeter was properly washed with Milipore water and acetone and was dried completely before viscosity and surface tension measurements [22–24]. The reported viscosity and surface tension are an average of three repeated measurements with 0.00028 mPa s and 0.03 mN m^{-1} combined uncertainty respectively.

UV spectra of aqueous-CAP, CAB and Tw80 and CO–CAP, OO–CAP, LO–CAP, CO–CAB, OO–CAB, LO–CAB, CO–Tw80, OO–Tw80 and LO–Tw80 were recorded with UV–Visible spectrophotometer (Spectro 2060 plus model) from 200 to 600 nm at room temperature in a cuvette of 1 cm path length. Their absorbance (A) for λ_{max} 200 to 600 nm was measured. The A, η and γ data focus on hydrophobicity and interaction of surfactant with oils.

3. Results and discussion

3.1. Viscosity

Viscosities were calculated with Eq. (1) [25,26]

$$\eta = \left[\left(\frac{t}{t_0}\right)\left(\frac{\rho}{\rho_0}\right)\right]\eta_0 \tag{1}$$

The t and $t_{0,}$ ρ andρ_0, η and $\eta_0$are viscous flow time, density and viscosity of sample and solvent respectively. Viscosity, density and surface tension of pure water are given in **Table S_3 (S.I.)** [27–31]. Viscosities of aqueous co-surfactants, aqueous surfactants without oil and NEs are given in **Tables S_4, S_5A (S.I.) and 1** respectively.

The η values of aqueous surfactant solutions of CAP, CAB and Tw80 are almost 2 times, 1.5 and 1.5 times higher than water **(Table S_5) (S.I.)** at their respective temperature. Higher η value infers that along with CAP, CAB and Tw80, ethyl alcohol, ethyl acetate, ethylene glycol and Tw40 promote HbHbI as well as hydrophilic interaction (HI). Thus, their mixtures could be termed as pre-cursor for emulsification. In general, from 293.15 to 298.15, 298.15 to 303.15, 303.15 to 308.15 and 308.15 to 313.15 K the η values of aqueous surfactants decreased by 16.62, 14.26, 16.19 and 12.53% respectively for CAP, 14.06, 12.73, 12.23 and 13.05% respectively for CAB and 14.45, 12.66, 13.83 and 12.23% respectively for Tw80 **(Table S_6 A) (S.I.)**. The η of aqueous surfactants as CAP > Tw80 > CAB from 293.15 to 303.15 and 313.15 K and CAP > CAB > Tw80 at 308.15 K, **(Fig. S_1 A) (S.I.)** depicts that binding activities of CAP, CAB and Tw80 from 293.15 to 303.15 and at 313.15 K remain the same. CAP with higher η values (by 22 and 23% compared to Tw80 and CAB respectively) **(Table S_7 A) (S.I.)** proves that it develops stronger HI with stronger binding with water, ethyl alcohol, ethyl acetate, ethylene glycol and Tw40 due to shorter alkyl chain. Therefore, a structure develops in the mixture whose flow through a rigid and uniform capillary takes longer time with stronger frictional forces on an adjacent layer or laminar flow. The η value of Tw80 infers that 3-OH in its hydrophilic head **(Fig. S_2 B) (S.I.)** strengthens the HI than CAB at 293.15 to 303.15 and 313.15 K but at 308.15 K, it seems that longer alkyl chain of Tw80 developed a tendency to move to interface by weakening HI and resulting lower η **(Table S_5 A) (S.I.)**. Fig. 1A–C illustrates that η of NEs continuously decreases with increase in temperature with almost the same $\Delta\eta/\Delta T$. In general, from 293.15 to 298.15, 298.15 to 303.15, 303.15 to 308.15 and 308.15 to 313.15 K the η values decreased by 16.38, 13.90, 15.92 and 13.94% respectively for NEs of CAP, 14.49, 13.03, 12.86 and 12.01% respectively for NEs of CAB and 14.86, 13.18, 13.59 and 12.24% respectively for NEs of Tw80 **(Table S_8 A) (S.I.)** which infers that whatever structural development takes place in NEs at optimum temperature, almost the same structural arrangement exists with weaker inter-molecular forces.

The temperature dependence η is not a straight or linear but it is polynomial which shows that the emulsion droplets probably reorient smoothly. With CAP and CAB, the η values of oil as LO > CO > OO (Fig. 1A–B) are the same from 293.15 to 313.15 K and with Tw80 the sequence of η is as LO > OO > CO (Fig. 1C) infers that with increase in DB of oils the value of η increases (Table 1). In general, η of oils (OO–LO and CO–LO), increased by 1.33 and 0.49% respectively with CAP, 2.08 and 0.97% respectively with CAB, 4.59 and 5.68% respectively with Tw80 **(Table S_9 A) (S.I.)**. The data reveal that π bond helps in developing HI with formation of hydrogen bonds between oil and water molecules resulting increase in the frictional force with increased η. The CO with one DB and –OH develops HI but strength remains lower than HI of LO having three DB. The lower η value of OO than CO with CAP and CAB by 1.62 to 1.11% respectively elucidates the effect of –OH in strengthening HI with hydrogen bond formation between water molecules and –OH of CO and lower η value of CO than OO with Tw80 by 1.15% infers that –OH impact is diminished with stronger HbTw80. The η of surfactants with oils as CAP > CAB > Tw80 (Fig. 1A–C) is attributed to stronger

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