Study on Formation of Oil-in-Water (O/W) Pickering type Emulsion via Complexation between Diesel and β-Cyclodextrin

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With use of β-cyclodextrin, Pickering type oil-in-water (O/W) emulsions were prepared using diesel sample obtained from an oil refinery plant. With considering the emulsion stability test, the effects of the two influential factors were quantitatively determined using statistical modeling. Inclusion complex (IC) formed between the βCD and diesel was structurally characterized using several instrumental techniques and the results in terms of the emulsifying role of the formed ICs were discussed.

1. Introduction

Several functions are ascribed to use of drilling fluids in rotary drilling operation for oil and gas wells such as removal of cuttings, controlling-balancing formation pressure, suspending solids, etc. (Vega et al. 2012). The complex physicochemical nature of a fluid gives special view on the relationships exist between the fluid characteristics and the successfulness of drilling process execution. Considerable attentions in recent years have directed towards emulsion-based drilling fluids subject and the efforts were directed to find responses to some undesirable properties exhibited by use of water-based drilling fluids (Kumar Jha et al. 2014). Surfactants with reference to their chemical nature and the concentration used, play critical roles in stabilization of emulsions while concerns over the environmental safety of the materials used by industries has intensified search on the use eco-friendly surfactants for petroleum industry (Chike-Onyegbula et al. 2012). Successful preparation of biodegradable drilling fluids with use of starch, gum arabic, guar gum, and polyanionic cellulose have been reported while the performance of hydrocolloids considerably was improved by addition of some chemicals such as bentonite to the mud formulation (Olatunde et al. 2012). Cyclodextrins (CDs) as the starch derivatives produced by certain bacteria through catalytic action of the cycloglucanotransferase enzyme, have unique molecular structure: the cone shaped cyclic structure provides an internal empty space available for being occupied preferably by an organic compound (Hashizaki et al. 2009). The formed complex is an example of supramolecular self-assembly process occurring spontaneously upon molecular associations without involvement of covalent bonds and described in terms of several weak forces (van der Waals, hydrophobic, hydrogen bond, and dipole-dipole) which cooperatively being involved in the complexation process (Gao et al. 2006). This uniqueness molecular structure has given CDs versatile applications and considerable emphasize is to study the mechanism of the action in terms of system's the stabilization in the presence of two immiscible liquids (Noël et al. 2014). The inclusion complex (IC) molecules thus with its hydrophobic-hydrophilic character, behave like nanosized solid particles in an oil-water mixture and express emulsifying activity and in fact the attachment of the fine solid particles to the interface in the Pickering emulsions depends on the degree of the particles' hydrophilicity or hydrophobicity determinable by measuring the relevant contact angle (Fennema 1985). Hydrophobic nanosilica and organically modified nanoclay have been successfully used for preparation of the model invert emulsion drilling fluids (Agarwal et al. 2013). With reference to analyze the preparation of emulsion-based drilling mud using eco-friendly additives, the present work was undertaken to study formation of diesel-in-water emulsion (O/W) using βCD as an emulsifier. In controlling the stability of the emulsions in terms of the influential factors (βCD concentration, diesel to water ratio 'O:W' and time of homogenization) statistical analysis was used and the

complexation between diesel and βCD for the optimized O/W emulsion was characterized using different analytical techniques namely XRD, DSC, FTIR, H NMR, and SEM.

2. Materials and methods

2.1 Materials

The diesel sample used in the present study, was provided from the Tehran Oil Refinery Company (TORC) and some of its specifications are as follows: 826.2 kg/m^3 as the density at 15 ºC; 2.5 cSt as the kinematic viscosity at 37.8 ºC; 0.826 as the specific gravity. All the reagents including βCD (Sigma-Alderich) were of the analytical grade and purchased from the local market.

2.2 Methods

2.2.1 Emulsion preparation

Diesel-in-water emulsions were prepared at room temperature using HO4 Edmund Buhler 7400 Tubingen homogenizer (Germany), where the speed and time of the homogenization were set at 11000 RPM and 2 min, respectively. According to the details given in Table 1a, two ratios of diesel to water and two levels of βCD emulsifier were used (see 2.2.3 section for the details). The βCD was first dissolved in an appropriate volume of the distilled water and within 10 min after the diesel as the oily phase was added at once to the homogenizer vessel (25 ml as the emulsion total volume) and the homogenization was proceeded at 11000 RPM for 2 min. Emulsion stability test was used to characterize the prepared emulsions.

Table 1: The two independent variables and their selected levels (coded and actual values) used in the present study (a). Arrangement of the 2^2 replicated factorial design with the additional repeated center point is also shown (b). The actual and predicted values of the emulsion stability index in percentage (ESI%) are given (b).

(a)

Independent variables	Coded levels and their actual amount	
	-1	+1
x_1: O/W ratio (v:v%)	40/60	50/50
x_2: β-CD concentration (w/v%)	0.75	1.25

(b)

Exp. No.	Coded levels		ESI%	
	x_1	x_2	Actual	Predicted
1	-1.0	-1.0	75	75
2	-1.0	-1.0	75	75
3	1.0	-1.0	89	87.5
4	1.0	-1.0	86	87.5
5	-1.0	1.0	76	76.7
6	-1.0	1.0	77.5	76.7
7	1.0	1.0	91	91
8	1.0	1.0	91	91
9	0	0	84	82.6
10	0	0	84	82.6

2.2.2 Emulsion stability

Test for ESI determination was as follows (Mirhosseini et al. 2008): ESI%= (HE-(HS+HC))/HE×100
where HE is the initial emulsion height, HC and HS are indicative of creaming and sedimentation as two forms of the gravitational separation in emulsions. Thus HC is the height of creaming layer and HS is the height of sedimentation phase.

2.2.3 DOE and data analysis

Test for ESI determination At first the screening experiments were performed using one-factor-at-a-time procedure to consider the four influential factors on the O/W emulsions in terms of ESI%: time and speed of homogenization, oil:water ratio, and the amount of βCD. The effects of time and speed of homogenization were studied separately by setting time at 1 min while amount of βCD and the O:W ratio were at 1 w/v% and at 30/70 v/v%, respectively. By obtaining the optimum level of homogenization speed at 11000 RPM, the time of homogenization was considered next at the five different levels and the optimum time of homogenization was determined as 2 min.The minimum and maximum levels of O:W ratio (x_1) and βCD content (x_2) were determined based on the results of the preliminary study (Table 1a). Ten experiments were performed (2^2 replicated factorial design with the additional repeated center points) (Table 1b).

2.2.4 Instrumental analyses

The inclusion complex formed between βCD and diesel molecules was characterized using several instrumental techniques: DSC analysis with use of Mettler-Toledo DSC 823e (STARe SW version 9.10 software, Switzerland) under nitrogen atmosphere (N_2 flow: 80 ml/min). The DSC instrument was calibrated using aluminium crucibles and the indium sample was accurately weighed and placed in the 40 μl crucible. Two different heating rates were used in the DSC analysis: 10 °C/min was from 30 °C to 300 °C for βCD monomer and the formed IC and 2 °C/min was from 30 °C to 50 °C for the diesel sample. The FTIR spectra were obtained using KBr pellets and Nicolet iS10 FTIR spectrometer in the spectral region of 4000-400 cm^{-1} (32 scans with the resolution 4 cm^{-1}). The crystalline phase of the each test system (βCD, diesel, and IC) in terms of X-ray diffraction pattern (XRD) was determined using Equinox 3000 (Inel, France) with a Cu-Kα (1.5418 Å) as the source of X-ray radiation operating at a voltage of 40 kV and a current of 40 mA. H NMR spectra of the test samples were recorded on a Bruker spectrometer operating at 500 MHz radiation frequency with D_2O solvent. The formed precipitate separated by the centrifugation of the emulsion (optimum O/W emulsion- see 2.2.3 section) was shaped into a pellet-like configuration and the pellet was immersed in the diesel oil and by placing 4 μl of dis.H_2O onto the shaped pellet, the formed contact angle from the precipitate with the diesel-water interface thereafter, was measured at the room temperature using a contact angle measuring system (OCA 15 plus with the SCA20 software, Dataphysics Instruments, GmbH, Filderstadt, Germany).

Further measurement was on the surface morphological structure of βCD and the formed IC both which were characterized by scanning electron microscope (SEM) using AIS-2100 (Seron Technology, Korea) analyzer. Emulsion particle size (expressed as the diameter) was also measured using a laser light scattering instrument (Mastersizer 2000, Malvern Instruments, UK). Mean diameter in terms of volume weighted mean ($d_{43}=\frac{\sum n_i d_i^4}{\sum n_i d_i^3}$) and surface weighted mean ($d_{32}=\frac{\sum n_i d_i^3}{\sum n_i d_i^2}$) were reported, where n_i is the number of particles having diameter of d_i

3. Results and discussion

3.1 Statistical model

With reference to the findings shown in Table 1 the analysis of variance (ANOVA) and the least squares techniques were used to treat the experimental data. The adequacy of the data fitting and the model prediction were then determined and the two factor interaction model (2FI), shown below was found to be adequate (Design Expert software version 7):

$$y_i = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum \sum_{i<j} \beta_{ij} x_i x_j + \varepsilon \qquad (1)$$

where y_i is the predicted response, x is the predictor, βs are the regression model coefficients, and ε represents the error term (Vining 1998). The results of the suggested model is presented in Figure 1.
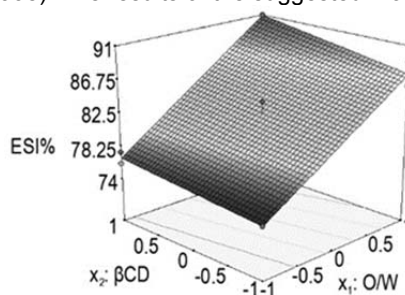

Figure 1: The three dimensional plot of the emulsion stability index as a function of O/W ratio and the amount of βCD (see the section materials and methods for the emulsion preparation details). Modeling was with use of Eq(1): ESI% =82.56+6.69x_1+1.31x_2+0.44x_1x_2.

3.2 Structural characterization

Differential scanning calorimetry (DSC) as one of the thermo-analytical techniques uses a controlled temperature program through which the sample exposes to the heat flow thus it is possible to determine the flow of the involved heat into (endothermicity of the process) or out of the sample (exothermicity). Figure 2a presents DSC curves and the endothermic peak at 92 °C seen for βCD, is indicative of the dehydration process. Removal of water from the βCD cavity and its association with surrounding water molecules are

steps in the complexation and likliness of the hydrophobic interactions occurrence as a result, would be considerable while hydrogen bonding, Van der Waals forces are also involved in the IC formation (Saenger 1980). Shifting of a peak with or without broadening, appearance or disappearance of certain peak(s), all are expected structural behavior which may occur upon receiving the programmed heat by the substance through DSC technique. These thermogram observations with reference to macrocycle structure of CDs indicate that physical properties of the entrapped molecules within the βCD cavity have changed (i.e., confirmation of the IC formation). The peak at 92 °C shifted to the lower temperatures and showed broadening appearance, as it is seen in the diesel-βCD thermogram (Figure 2b). A small endothermic peak at 220 °C observed for βCD (before degradation of cyclic structure of βCD at 300 °C) shifted to the higher temperature (227 °C) for the diesel- βCD complexation and its broadening appearance is clearly observable in Figure 2b. The DSC plot for the diesel sample shows no peak in the range of the test temperatures (Figure 2c).

Results of monitoring FTIR pattern for the free form of βCD, diesel sample and the formed IC are presented in Figure 3. Distinct peaks for the βCD seen at 3384 and 2926 cm^{-1} are corresponded to alcoholic -OH and aliphatic C-H bands, respectively. The relative intensity of the transmittance band at 1652 cm^{-1} is corresponded to H-O-H bending vibrations of the associated water molecules (Geetha et al. 2009). Bands at 1157 and 1080 cm^{-1} are assigned to the motions of C-O, C-O-C of glucose units of βCD upon the energy absorption (Pavia et al. 1976; Geetha et al. 2009). Changes of cyclodextrin bands of the IR spectra are slight upon complex formed between CD and the organic compound and the assigned bands to the entrapped part of the guest molecules within the CD's inside are usually masked by the bands of CD spectra (Davarpanah and Vahabzadeh, 2012).
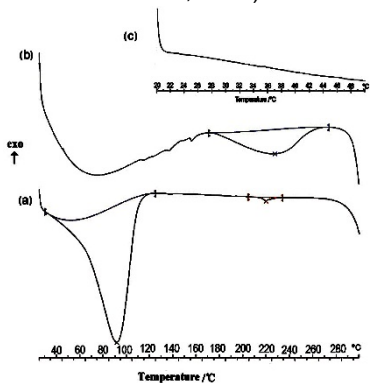

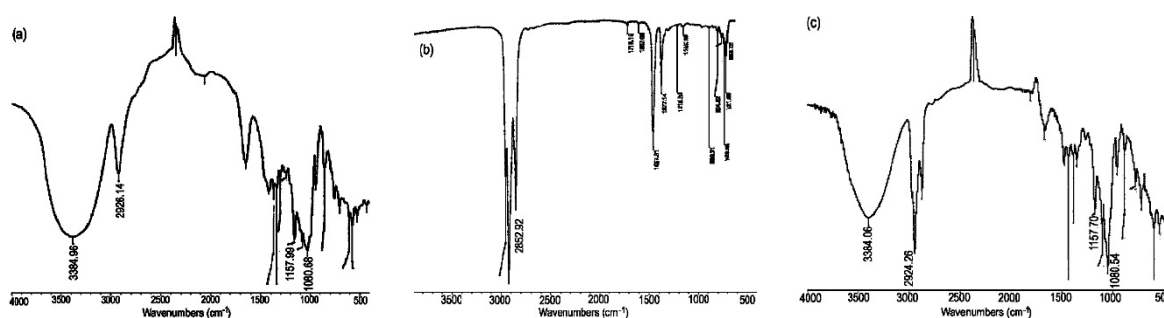Figure 2: DSC thermogram of βCD (a), and the formed IC (b), diesel (c).

Figure 3: FTIR spectra of free form of βCD (a), diesel (b), and the formed IC (c).

Figure 4 shows the H NMR spectra obtained for the three compounds analyzed in the present study. Petroleum diesel is complex mixture of hydrocarbons with aliphatics as the main fraction, protons of CH_3 group terminating the aliphatic chains give the signals between 0.5-1 ppm while the resonance of protons of the methylene group express signals at 1-3 ppm (Zhu et al. 2015). The findings shown in Figure 4 are in favor of purity of the diesel sample used in the present work. Marked decrease in H NMR signals of aliphatic methyl and methylene groups of diesel fuel sample is observable upon complexation of diesel with the βCD. The inclusion complexation affected the aliphatic nature of the diesel, where marked decrease in the peak intensity of hydrogen signals of the methyl and methylene groups were observed (Figure 4). While the H NMR signals of βCD in the formed IC were remained almost unchanged. Further note is on the Table 2 showing hydrogen

signals in the form of chemical shifts associated with the free form of βCD, diesel sample, and the formed IC (βCD-diesel) with reference to the IC's signals.

Table 2: H NMR chemical shifts of the protons associated with different carbon atoms of free form of the βCD and of the formed IC (βCD-diesel) sample.

	H1	H2	H3	H4	H5	H6
βCD	4.9884	3.5048	3.7193	3.4990	3.5724	3.7966
Formed IC	4.9596	3.4768	3.8495	3.4768	3.5415	3.7638
Δδ	0.0288	0.0280	-0.1302	0.0222	0.0309	0.0328

Variation shifts seen in the Δδ values are indicative of complexity of the test molecular systems involving cyclodextrin as being able to entrap the guest substance which part of it can undergo an oscillatory motion inside the cavity while part of it is free to vibrate, thus changes of intermolecular distances are likely event (Fronza et al. 1996). The Δδ for protons of C3 located inside the hydrophobic cavity of βCD was lowest. Also resonance of protons of C5 clearly gives signal in the IC spectrum.
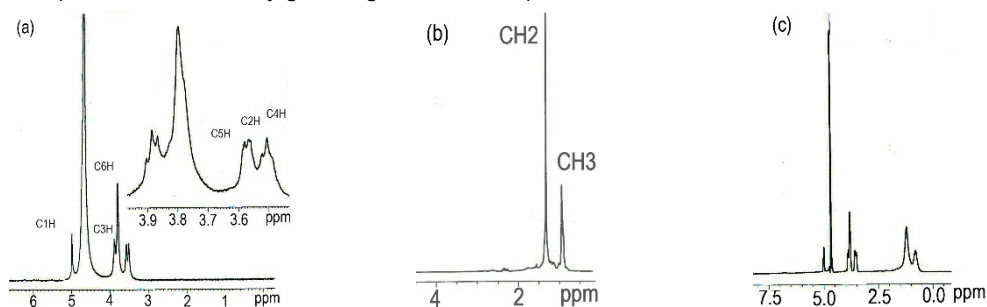

Figure 4: H NMR spectra of free form βCD (a), diesel (b), and the formed IC (c).

Good information about the size distribution and arrangements of atoms/molecules are obtainable from the diffractogram and in the present study the microscopic structure of the test compounds was analyzed using XRD. The XRD diagram in Figure 5 shows the relevant spectrum for each of the test compounds. The precipitated fraction obtained in the O/W emulsions due to the βCD-diesel complexation, composed of the nano-sized materials which performed as solid-like particles and able to stabilize the emulsions against coalescence. X-ray diffractogram of βCD, as a highly crystalline material, in Figure 5 shows main diffractions at a <10º, 12º-14º, 18º, and >20º (2θ). The peaks indexes would be useful in monitoring their presence/absence along with their intensity. Considerable increase of the intensity at about 18º (2θ) with marked decrease of the intensity at
10º-14º (2θ) and at <10º (2θ) seen in the X-ray diffractogram of the formed IC (Figure 5) are indicative of newly formed crystalline substance as the result of the βCD interactions with the diesel in the O/W emulsions. These peak indexes have been reported in the literature (Davarpanah and Vahabzadeh, 2012). The SEM analysis is well suited for visualization of the surface morphology and Figure 6 shows the SEM photomigrographs of the
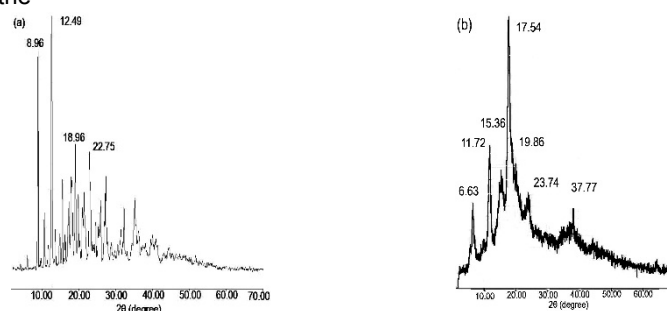

Figure 5: Powder XRD patterns of free from βCD (a), and the formed IC (b).

βCD in the free form and as the formed IC. βCD particles shown in Figure 6a, as the pieces with no definite shape dispersed irregularly within a matrix while βCD lost its surface integrity upon complexation with diesel molecules (Figure 6b).
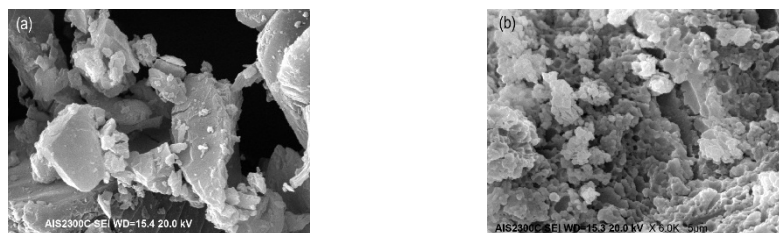
Figure 6: SEM images of free form βCD (a) and the formed IC (b).

4. Conclusions

As has mentioned in the present study the IC which formed with βCD-diesel and being separated as the precipitate by centrifugation, actually acted as the fine solid particles where the distribution of these types of particles is under influence of systems' interfacial tension. Measuring the contact angle (θ) in these situations is indicative of wetting characteristic of the particles and the findings in the present study in terms of the measuring this emulsion property, confirmed the O/W emulsion formation (θ~30º) and this was in agreement with the relevant results reported in the literature (Hashizaki et al. 2009). The emulsion stability data in this study were analyzed statistically and the influential factors were described in terms of first degree polynomial prediction equation. The IC of the optimized O/W emulsion was structurally characterized. Further note on the statistical modeling and use of the suggested model was to examine the size distribution of the emulsion particles where, 73 % of the particles at the diameter in the range of 10-100 μm with 19.74 μm as the d_{43} (d_{32}=5.83 μm).

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