Phase behaviour and physicochemical study of Karanj oil-ethanol microemulsion as alternative renewable biofuel

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Vegetable oil reverse micelle microemulsions as an alternative method for biodiesel production has been studied to eliminate transesterification reaction and avoid unpurified glycerol formation. The sorbitane oleate ester surfactants due to high solubilization capacity in oils have formed reverse micelle microemulsions with karanj oil and ethanol. The phase behaviour of span 80 and 85 based Karanj oil-ethanol microemulsion have been studied with their physicochemical parameters i.e. density and viscosity for formulating optimized systems as biofuel. The kinematic viscosity being an important physicochemical parameter elucidate karanj oil-ethanol microemulsion a better biofuel with span 80 than with span 85 as their resultant viscosities were in close agreement with ASTM biodiesel standards. It has been found that the microemulsiﬁcation is a sustainable method for producing biofuels without chemical reactions as green fuel.

Keywords: Microemulsion, Phase behaviour, Biofuels, Kinematic viscosity

Introduction

The rapid depletion of petroleum reserves and their inherent environmental pollution issues have led to development of alternative energy resources, such as biofuel a greener and environment friendly fuel. The vegetable oils have emerged as an alternative source of green fuels globally due to several advantages such as renewable and non-toxic nature1-3. The soybean, peanut, sunflower, rape, coconut, karanj, neem, cotton, mustard, jatropha, linseed and caster oils have shown a performance quite comparable with diesel fuels4-7. Triglycerides are primary component of vegetable oils responsible for high viscosity due to which long term use of neat vegetable oils affects the engine durability resulting in injector coking and ring sticking8,9. In addition, vegetable oils also have higher cloud and pour points that cause problems in cold weather conditions10. Several methodologies have been applied to overcome these difficulties for preparing biodiesel such as dilution, microemulsion (ME), pyrolysis and transesterification11-14. The biodiesel obtained through these methods are biodegradable and environmentally friendly with disadvantages like high cost, poor cold flow properties and increasing nitrogen oxides (NOx) in exhaust emissions15,17. Transesterification is widely applied for biodiesel production in which triglycerides react with alcohols with catalysts producing glycerol as a byproduct. Purification or conversion of glycerol into a value added product is an expensive process and its disposal causes environmental pollution18,19. Therefore, microemulsiﬁcation of oils could be applied to prevent formation of glycerol and biofuels obtained are transparent and thermodynamically stable. Considering above mentioned criticalities, the densities and viscosities of spans based KO-ethanol microemulsions (MEs) with phase behaviour at $T = (298.15, 303.15, 308.15$ and $313.15)$ K and ambient pressure to bring them to a usable form have been made.

Experimental Section

Materials and Methods

Non-edible grade KO was acquired from Agarwal oils (Udaipur, Rajasthan, India) and its chemical composition was analyzed by gas chromatography (GC) with flame ionization detector (FID), given in Table 1. KO has shown 84.7 g/100 g and 4.88 mg KOH/g, iodine and acid values respectively. Ethanol ($\geq 99.8\%$), span 80 (HLB number 4.3) and span 85 (HLB number 1.8) (Sigma–Aldrich) were used as received.

Microemulsion preparation

Binary mixtures of ethanol in KO from 0 - 100 % (w/w) were prepared with an accuracy of ± 0.0001 g
using Mettler Toledo New Classic MS with continuous stirring at 500 RPM. Solutions up to 15 % were transparent and thermodynamically stable and above which were cloudy. Above 15 % ethanol, variable amounts of the span were added to formulate transparent and thermodynamically stable MEs. The KO-ethanol-span mixtures were continuously stirred at 500 RPM and placed into a water bath to check MEs stability from 298.15 to 313.15 K.

**Ternary phase diagram**

For study of phase behaviour and stability of MEs, ternary phase diagram was used where three vertices of the equilateral triangle represent the three components of ME. The two vertices at the bottom depict weight percent of KO at left side and of ethanol at right, while the upper vertex represents span. The composition at each point in diagram depicts % weight of three components A, B, C as under:

\[x\% A + y\% B + z\% C = 100\%\]

Miscibility curve is plotted between the liquid phases of the MEs. The region above the curve is a single phase transparent and thermodynamically stable ME system with minimum surfactant.

**Density and viscosity measurements**

Density (\(\rho\)) of pure components and mixtures were measured using Anton Paar DSA 5000M densimeter whose temperature was controlled to ± 0.001 K built-in Peltier device. Sensitivity of instrument corresponds to ± 5·10^-3 kg·m^-3 precision in density. Densimeter was calibrated with Millipore water and densities are an average of three consecutive measurements reproducible to ± 6·10^-3 kg·m^-3 uncertainties.

Viscosity measurements were done with Borosil Mansingh Survivimeter^21^25 (Cal.no. 06070582/1.01/ C-0395, NPL, India) by flow time method having Lauda Alpha KA 8 thermostat with ± 0.05 K control. The survismeter was calibrated using reported viscosity for ethanol and water. After attainment of thermal equilibrium, the viscous flow times were recorded with ± 0.1s uncertainty. Viscosity is an average of three consecutive measurements with ± 0.0001 mm²·s⁻¹ uncertainties.

**Results and discussion**

**Phase behaviour**

Phase diagram of KO-Ethanol MEs with sorbitane monooleate (span 80, linear) and sorbitane trioleate (span 85, branched) are plotted in Figs. 1 (a) and (b) which show their comparision at 298.15 K. The results have distinguished the surfactants to identify the one with maximum solubilization of ethanol in the oil phase. The results show that branching and the number of OH groups affects the hydrophobicity and hydrophilicity because branching of surfactant increases the oil solubility and OH groups increase the solubility of ethanol. Span 80 contains three OH groups with a straight oleate chain while span 85 contains one OH group with branched trioleate chain. Thus, the oils containing triglycerides are highly hydrophobic with longer and bulkier alkyl chains of triglycerides. Therefore amongst spans, span 80 was identified as a preferred and potential surfactant to achieve a single phase ME as it is required in least amount.

**Physicochemical study**

The effect of increasing ethanol concentration on density of MEs from \(T = (298.15 \text{ to } 313.15)\) K, has been studied. Density decreases with increase in ethanol concentration up to 15 % at a rate of 0.16 %. After 15 % onwards, the rate of decrease in density with span 80 and 85 is 0.13% and 0.04% respectively. It seems that on addition of ethanol up to 15%, the strongest hydrophobic-hydrophobic interactions (\(H_bH_b\)) between oil is weakened due to the development of hydrophilic-hydrophilic interactions (\(HHI\)) between oil and ethanol with decreased density. The higher rate of decrease in density with

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**Table 1—Fatty acid profile of Karanj oil**

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>Chemical name</th>
<th>Molecular weight(g/mol)</th>
<th>% Compositiona</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palmitic (C16:0)</td>
<td>Hexadecanoic</td>
<td>256.42</td>
<td>4.21</td>
</tr>
<tr>
<td>Stearic (C18:0)</td>
<td>Octadecanoic</td>
<td>284.48</td>
<td>3.54</td>
</tr>
<tr>
<td>Oleic (C18:1)</td>
<td>cis-9-Octadecenoic</td>
<td>282.46</td>
<td>62.13</td>
</tr>
<tr>
<td>Linoleic (C18:2)</td>
<td>cis-9,cis-12-Octadecadienoic</td>
<td>280.45</td>
<td>11.78</td>
</tr>
<tr>
<td>Arachidic (C20:0)</td>
<td>Eicosanoic</td>
<td>312.53</td>
<td>3.12</td>
</tr>
<tr>
<td>Eicosenoic (C 20:1)</td>
<td>Gadoleic</td>
<td>310.51</td>
<td>10.56</td>
</tr>
<tr>
<td>Behenic (C22:0)</td>
<td>Docosanoic</td>
<td>340.58</td>
<td>4.45</td>
</tr>
</tbody>
</table>

a analyzed by gas chromatography (GC) with flame ionization detector (FID)
span 80 might be due to a dominance of weaker HHI between ethanol-span over stronger H_bH_b between oil-oil and weaker H_bH_b between span-oil. These interactions develop due to one oleate chain in span 80 and 3:1 ratio of OH in span 80 and ethanol respectively. With span 85, a lower rate of decrease in density could be attributed to an increased H_bH_b with increased hydrophobicity induced by trioleate chain of span and reduced HHI because of 1:1 ratio of OH in span 85 and ethanol respectively.

Kinematic viscosities have decreased with increase in ethanol concentration. In general, initially up to 15 % ethanol addition, the kinematic viscosity decreased sharply within 5 - 15 mm².s⁻¹ and 15 % onwards with span 80 and 85, decreased steadily within 0.9-3.1 and 0.4-1.5 mm².s⁻¹ respectively at 313.15 K. Initially at zero ethanol concentration, only strong H_bH_b prevailed within the oil system. When the concentration of ethanol was increased, the stronger H_bH_b were weakened due to weaker interaction between a larger hydrophobic group of oil and ethyl chain of ethanol. Above 15 % ethanol, a dominance of HHI between ethanol-ethanol increased resulting in phase separation of oil and ethanol. Span was added to mutually solubilize the two phases and a stable ME was obtained where the impact of ethanol concentration on kinematic viscosity is very less due to the counter balancing effect of span which maintains a balance between H_bH_b and HHI. When span 85 was added, the counter balancing effect between the H_bH_b and HHI was less than with span 80 due to the trioleate chain that increased the H_bH_b with higher kinematic viscosities. The kinematic viscosity of MEs with span 80 at 313.15 K with ethanol-oil ratios 65:35, 70:30, 75:25, 80:20, 85:15, 90:10 and 95:5 are in agreement with the standard viscosity of ASTMD6751-02, biodiesel, B100 (1.9-6 mm².s⁻¹). Thus both density and kinematic viscosity behaviour could be supported by two interacting models termed as mutual solubilisation model of KO-ethanol with spans 80 and 85 depicted in Figs. 2 (a) and (b).

**Conclusion**

The physicochemical characterization of spans based Karanj oil-ethanol MEs have depicted them as
potential biofuel. Unlike sulfate-based extended surfactants, ME fuel of spans are an environmentally desirable fuel; since there is no sulfur content in span preventing sulfur oxide (SO$_x$) emissions. Also the MEs were stable without any phase separation up to 313.15 K. The phase behaviour, density and viscosity studies have found that the span 80 based KO-ethanol MEs as the optimum system are stable in range of 298.15-313.15 K. The ethanol:oil ratios of 65:35, 70:30, 75:25, 80:20, 85:15, 90:10 and 95:5 with span 80 have kinematic viscosity meeting the ASTM standard of B100 biodiesel (1.9-6 mm$^2$/s) at 313.15 K. These newly developed KO-ethanol-span 80 MEs could be used as renewable and eco-friendly fuels with high calorific values with suitable surfactant.

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References