PALM OIL-BASED MICROEMULSIONS STABILISED BY NON-IONIC SURFACTANTS

ISMAIL AB. RAHAT

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ISMAIL AB. RAMAN

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Dedication to:

My wife, my kids, i.e., Mohd Ikhwan, Mohammed Idzham, Mohammad Izzat, Siti Nur Athirah and Siti Nur Afiqah, and both my parent and parent in law.

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ISMAIL BIN AB. RAMAN

September 2006

Chairperson: **Professor Hamdan b. Suhaimi, Ph.D**

Members : **Associate Professor Ku Halim Ku Bulat, Ph.D**
Professor Anuar b. Kassim, Ph.D

Faculty : **Science and Technology**

There are growing interests in microemulsions system where the hydrocarbon oils (or mineral oils) have been replaced by the oils derived from natural resources, such as fatty acid esters (FAE), medium chain triglycerides (MCT) and long chain triglycerides (LCT) due to their renewable, biodegradable, non-flammable, harmless to the environment and less or non-toxic to end users. However, palm oil and its derivatives have not yet been used for preparing microemulsions for practical applications. Thus, this study aims at delineating the range of conditions under which the palm oil and its derivatives such as palm fatty acid methyl esters or palm oil methyl esters (PFAME or POME), palm kernel-medium chain triglycerides (PK-MCT) and palm olein (P.Olein) form microemulsions with non-ionic surfactants system. The effects of adding co-surfactants on the ternary phase behaviour of palm-based microemulsions have also been investigated, emphasizing the application of non-toxic co-surfactants, such as 1,2 alkanediols [e.g., hexylene glycol (or 1,2 hexanediol), butylene

glycol (or 1,2 butanediol) and ethylene glycol (or 1,2 ethanediol)] and glycerols. Furthermore, the formation of microemulsions was characterised for the O/W, bicontinuous and W/O microemulsions by the conductivity, viscosity and droplets size measurements.

The screening processes (i.e., miscibility tests, binary phase diagrams and formation of microemulsions by addition of 1-pentanol) on selected non-ionic surfactants found that the alkyl (C_{12-14}) alcohol ethoxylates (6.5EO) was suitable for producing larger microemulsions region than the polyoxyethylene (POE) (20) sorbitan monooleate and polyethylene glycol (PEG) 600 monooleate. The C_{12-14} alcohol ethoxylates (7EO) and mixed C_{12-14} alcohol 7EO/2EO were also chosen for the formation of microemulsions with palm oil derivatives for comparison studies

The studies of schematic phase behaviour of palm oil derivatives in C_{12-14} alcohol ethoxylates (6.5EO) determined that the extent of microemulsion formation and destabilisation of liquid crystalline phases decreased in the sequence PFAME (or POME) > PK-MCT and increased with temperature. There was an increase in the temperature for the onset of the W + L_1 region (the partial miscibility or clouding of a very dilute surfactant solution with L_1) by ca. 10°C or more for PFAME and PK-MCT. The temperature for the onset of the W + L_α region (the partial miscibility of a very dilute surfactant solution with L_α phase) was hardly affected. Furthermore, the capacities of solubilisation were

tetradecane ~ PFAME > PK-MCT in C_{12-14} alcohol ethoxylates (6.5EO) solutions. The study of solubilisation was an exploratory work for obtaining the Gibbs phase diagram for the water-oil-surfactant systems.

The ternary phase diagrams of palm oil derivatives formed in C_{12-14} alcohol ethoxylates (6.5EO), and later in C_{12-14} alcohol ethoxylates (7EO) documented various phase regions as functions of composition and temperature for the three-component systems. The capacities of solubilisation were PFAME (or POME) > PK-MCT in C_{12-14} alcohol ethoxylates (6.5EO) and/or C_{12-14} alcohol ethoxylates (7EO) solutions. The degree of mixing (or solubilising) in the various phases decreased with increasing molecular size of oil, but it increased with temperature.

The effects of adding 1-pentanol and non-toxic co-surfactants, such as 1,2 hexanediol, 1,2 butanediol, 1,2 ethanediol and glycerol on the ternary phase behaviour of palm-based microemulsions were also investigated. 1,2 hexanediol has shown better synergy effect as non-toxic co-surfactant than 1-pentanol, 1,2 butanediol, 1,2 ethanediol and glycerol for lowering the curvature and/or interfacial tension of the oil-aqueous phases to form palm-based microemulsions with non-ionic surfactants system, thus, form the largest microemulsion region. Therefore, the 1,2 alkanediols (i.e., 1,2 hexanediol, 1,2 butanediol and 1,2 ethanediol) and glycerol have potential to be applied as the alternative co-surfactants to replace the medium chain aliphatic alcohols (e.g., 1-pentanol) in palm-based microemulsions for applied formulations.

Finally, we also determined the physical characterisations of palm-based microemulsions formed with C_{12-14} alcohol ethoxylates (7EO), mixed C_{12-14} alcohol ethoxylates (7EO/2EO) and 1,2 hexanediol. We conclude that the amounts of water in the systems had directly or obviously affected the values of the conductivity, viscosity and droplets size of the microemulsion solutions formed in both methods for PFAME/C_{12-14} alcohol ethoxylates (7EO)/1,2 hexanediol/water and PFAME/mixed C_{12-14} alcohol ethoxylates (7EO/2EO)/1,2 hexanediol/water systems. The co-surfactant had only affected the values of conductivity, viscosity and droplets size of the microemulsion solutions at very high concentrations. Furthermore, these physical characterisations indicate types of microemulsions formed, i.e., O/W, bicontinuous and/or W/O microemulsions.

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PEMBENTUKAN MIKROEMULSI DARI BAHAN TERBITAN MINYAK SAWIT DENGAN MENGGUNA SURFAKTAN BUKAN-IONIK SEBAGAI BAHAN PENSTABIL

ISMAIL AB. RAMAN

September 2006

Pengerusi : **Profesor Hamdan Suhaimi, Ph.D**

Ahli : **Profesor Madya Ku Halim Ku Bulat, Ph.D**
Profesor Anuar Kassim, Ph.D

Fakulti : **Sains dan Teknologi**

Terdapat minat yang tinggi oleh penyelidik dan industri bagi menggantikan minyak/pelarut dari terbitan bahan petroleum di dalam sistem mikroemulsi dengan minyak/pelarut dari terbitan bahan semulajadi, seperti ester asid lemak (fatty acid esters, FAE), triglisida rantai sederhana (medium chain triglycerides, MCT), dan triglisida rantai panjang (long chain triglycerides, LCT) kerana bahan-bahan tersebut bersifat semulajadi, tidak mudah terbakar, kurang merosakkan sekitaran dan tidak toksik kepada pengguna/pekerja. Walaubagaimanapun, terbitan minyak sawit belum ada digunakan bagi pembentukan larutan mikroemulsi bagi penggunaan secara praktikal/komersial. Dengan ini, kajian telah memfokuskan kepada penghasilan larutan mikroemulsi dari bahan-bahan ester metil asid lemak sawit (palm fatty acid methyl esters, PFAME) atau ester metil minyak sawit (palm oil methyl esters, POME), triglisida rantai sederhana isirong sawit (palm kernel-medium chain triglycerides, PK-MCT) dan minyak oljen sawit (palm olein, PO) dengan surfaktan jenis bukan-ionik sebagai bahan

penstabil. Kesan penambahan bahan ko-surfaktan keatas perubahan kepada fasa segitiga mikroemulsi adalah juga dikaji, dengan memfokuskan kepada penggunaan ko-surfaktan tidak toksik seperti 1,2 heksandiol (atau heksilin glikol), 1,2 butandiol (atau butilin glikol), 1,2 etandiol (atau etilin glikol) dan gliserol. Seterusnya, pembentukan mikroemulsi juga telah ditentukan sebagai mikroemulsi jenis O/W, atau W/O dengan teknik konduktiviti, kelikatan dan saiz partikel.

Proses saringan ke atas surfaktan-surfaktan bukan-ionik terpilih mendapati alkil (C_{12-14}) alkohol etoksilat (6.5EO) adalah paling sesuai bagi menghasilkan banyak larutan mikroemulsi, dan diikuti oleh polioksietilin (POE) (20) sorbitan monooleat dan polietilin glikol (PEG) monooleat. Seterusnya, C_{12-14} alkohol etoksilat (7EO) dan campuran C_{12-14} 7EO/2EO juga telah dipilih bagi pembentukan mikroemulsi dengan terbitan minyak sawit.

Kajian secara skematik ciri-ciri fasa yang terbentuk dari campuran terbitan minyak sawit di dalam C_{12-14} alkohol etoksilat (6.5EO) mendapati bahawa proses pembentukan mikroemulsi dan ketidakstabilan fasa kristal cairan meningkat mengikut urutan PFAME (atau POME) > PK-MCT dan juga meningkat berbanding suhu. Suhu bagi permulaan pembentukan kawasan W + L_1 (takat separa larut atau keruh larutan cair surfaktan, L_1) meningkat ~10^0C atau lebih bagi PFAME dan PK-MCT. Suhu bagi permulaan pembentukan kawasan W + L_α (takat separa larut atau keruh larutan cair surfaktan, L_α) terlalu sedikit/tidak

berubah. Seterusnya, kapasiti penglarutan minyak/pelarut di dalam larutan C_{12-14} alkohol etoksilat (6.5EO) adalah tetradekan ~ PFAME > PK-MCT. Kajian penglarutan ini telah diperkembangkan bagi membentuk gambarajah fasa segitiga sistem air-minyak-surfaktan.

Gambarajah fasa segitiga terbitan minyak sawit terbentuk didalam larutan C_{12-14} alkohol etoksilat (6.5EO), dan kemudian didalam larutan C_{12-14} alkohol etoksilat (7EO) memberi gambaran beberapa jenis fasa berbanding fungsi komposisi dan suhu bagi sistem tiga-komponen. Kapasiti penglarutan minyak/pelarut di dalam larutan C_{12-14} alkohol etoksilat (6.5EO dan 7EO) adalah PFAME (atau POME) > PK-MCT. Tahap penglarutan didalam fasa-fasa tersebut berkurangan dengan peningkatan saiz molekul minyak, tetapi meningkat berbanding dengan kenaikan suhu.

Kesan penambahan 1-pentanol dan beberapa jenis ko-surfaktan tidak toksik (1,2 heksandiol, 1,2 butandiol, 1,2 etandiol dan gliserol) ke atas ciri fasa segitiga mikroemulsi berasaskan bahan sawit telah di kaji. 1,2 heksandiol telah menunjukkan kesan sinergi lebih baik sebagai ko-surfaktan tidak toksik berbanding 1-pentanol, 1,2 butandiol, 1,2 etandiol dan gliserol bagi merendahkan ketegangan antara permukaan bagi fasa minyak-air untuk menghasilkan kawasan mikroemulsi yang besar dengan sistem surfaktan bukan-ionik. Jadi, 1,2 alkandiol (1,2 heksandiol, 1,2 butandiol dan 1,2 etandiol) dan gliserol berpotensi untuk digunakan sebagai ko-surfaktan alternatif kepada

alkohol liner (e.g., 1-pentanol) di dalam mikroemulsi berasaskan terbitan sawit untuk penggunaan secara praktikal/komersial.

Akhir sekali, ciri-ciri fisikal mikroemulsi dari terbitan bahan sawit terhasil dengan C_{12-14} alkohol etoksilat (7EO dan campuran 7EO/2EO) dan 1,2 heksandiol juga telah ditentukan. Kesimpulannya, kandungan air di dalam sistem mikroemulsi tersebut telah mempengaruhi dengan jelas nilai konduktiviti, kelikatan dan saiz partikel larutan mikroemulsi yang terhasil dari kedua-dua teknik penyediaan. 1,2 heksandiol memberi kesan yang signifikan kepada nilai konduktiviti, kelikatan dan saiz partikel larutan mikroemulsi hanya pada kepekatan yang tinggi. Seterusnya, pencirian secara fisikal (i.e., konduktiviti, kelikatan dan saiz partikel) telah menentukan jenis mikroemulsi yang terbentuk, iaitu, O/W dan W/O mikroemulsi.