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(54) Title: METHOD FOR SEPARATING EMULSIONS

(57) Abstract: A method for breaking an emulsion of an ionic liquid which is a salt that is in the liquid state at a temperature below 1500C, and an oil, comprising the steps of (a) irradiating the emulsion with microwave radiation; (b) separating the emulsion into an ionic liquid phase and an oil phase; and (c) recovering at least one of the phases.



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METHOD FOR SEPARATING EMULSIONS

The present invention relates to a method for separating emulsions of ionic liquids and oils.

5 Many ionic liquids readily separate from oils to form two phase systems. Such ionic liquids may be used for extracting sulfur containing compounds from gasoline or diesel (desulfurization), extracting olefins from alkanes, and as liquid catalysts for oligomerization and polymerization of olefins. However, in practice, many common ionic liquids form emulsions with oils on mixing, and the demulsification and separation of the ionic liquid and oil phases can be problematic.

The use of microwave radiation to aid demulsification of water-in-oil and oil-in-water emulsions is known. For example, US 4,528,629 describes a method for enhancing the separation of hydrocarbon and water from an emulsion or dispersion thereof comprising the steps of subjecting said emulsion or dispersion to microwave radiation in the range of one millimeter to 30 centimetres and heating the microwave irradiated emulsion or dispersion to a separating temperature using conventional heating means. The method is said to be applicable to both oil external and water external systems i.e. water-in-oil and oil-in-water emulsions respectively. US 6,077,400 relates to a method of breaking an oil-in-water emulsion feedstock into its constituent oil and water phases using radio frequency (RF) microwave energy. However, there are fundamental differences between water (a weakly ionized molecular liquid) and ionic liquids (comprised wholly of dissociated cations and anions). Accordingly, the solvent properties of water do not provide a guide to the solvent properties of ionic liquids or to their behaviour in biphasic systems, particularly with respect to the formation of ionic liquid/oil emulsions. Ionic liquids have been shown to readily absorb microwave radiation through dipole-dipole and ionic conductance mechanisms giving rise to exceptionally efficient heating and rapid local increases in temperature. This characteristic of ionic liquids has been utilized in their applications as solvents for synthesis (see Westman, "Preparation and use of ionic liquids in microwave-assisted chemical transformations", United States Patent 6,596,130 July 22, 2003) and for dissolving cellulose (see "Dissolution of cellulose with ionic liquids", R. P. Swatloski, S. K. Spear, J. D. Holbrey and R. D. Rogers, J. Amer. Chem. Soc., 2002, 124, 4974-4975; US 6,808,557 and US 6,824,599). However, none of these references deal

with the separation of ionic liquid/oil emulsions nor the necessity for increasing or enhancing the rate of separation therefrom.

It has now been found that microwave irradiation of ionic liquid/oil emulsions may be used to effect demulsification and separation of the ionic liquid and oil phases.

5 Accordingly, the present invention relates to a method for breaking an emulsion of an ionic liquid which is a salt that is in the liquid state at a temperature below 150°C, and an oil, comprising the steps of

- (a) irradiating the emulsion with microwave radiation;
- (b) separating the emulsion into an ionic liquid phase and an oil phase; and
- 10 (c) recovering at least one of the phases.

Without wishing to be bound by any theory it is believed that microwave irradiation of the ionic liquid/oil emulsion induces or enhances breaking of the emulsion through preferential heating of the ionic liquid phase resulting in breaking of the interfacial film present in the emulsion and coalescence of the emulsion droplets. Thus,

15 demulsification of ionic liquid/oil emulsions using microwave irradiation substantially improves both the extent of separation of the phases and the rate at which the phases separate.

The emulsion may be an "ionic liquid-in-oil emulsion" comprising droplets of a discontinuous ionic liquid phase dispersed in a continuous oil phase or an "oil-in-ionic liquid emulsion" comprising droplets of oil dispersed in a continuous ionic liquid phase.

20 Suitably, the ionic liquid-in-oil emulsion contains from 1 to about 50% by weight ionic liquid based on the total weight of the emulsion. Suitably the oil-in-ionic liquid emulsion contains greater than 50% by weight ionic liquid. Preferably, the emulsion is an ionic liquid-in-oil emulsion. Suitably both phases resulting from the breaking of the emulsion

25 are recovered.

By ionic liquid is meant a salt that is in the liquid state at a temperature below 150 °C, preferably, at a temperature below 100°C. The ionic liquid salt is comprised wholly of dissociated ions and is therefore a conductor of electricity. Ionic liquids have substantially no vapour pressure and are consequently odorless. For a more detailed description of ionic

30 liquids see J. L. Anthony, J. F. Brennecke, J. D. Holbrey, E. J. Maginn, R. A. Mantz, R. D. Rogers, P. C. Trulove, A. E. Visser and T. Welton, "Physicochemical Properties of Ionic Liquids" in Ionic Liquids in Synthesis, Wiley-VCH, Eds P. Wasserscheid and T. Welton.

Other publications which give details of ionic liquids which may form emulsions treatable by the process of the present invention, include US 6,596,130, US 6,824,599, WO 02/079212 and WO 2004/016631. The contents of all prior art publications referred to herein are incorporated herein by reference.

5 Any ionic liquid capable of forming an emulsion with an oil may be present in the emulsion processed according to the invention. In general, the ionic liquid will be substantially insoluble in the oil phase and will not have significant surfactant properties. By "insoluble" in the oil phase is meant that the ionic liquid has a solubility in the oil phase of less than 100 ppm, preferably less than 50 ppm, more preferably, less than 25 ppm, for
10 example, less than 10 ppm.

The oil phase of the emulsion may for example be selected from crude oils, crude oil blends, crude oil distillates, vegetable oils, animal oils, synthetic oils, lubricant oils and mixtures thereof.

It is envisaged that the emulsion may comprise minor amounts of water, for
15 example, 0.1 to 5 weight % water. Some or all of the water may be absorbed into the ionic liquid phase of the emulsion.

The method of the present invention is particularly suitable for breaking unwanted emulsions that arise when an ionic liquid is employed as an extract phase or as a liquid catalyst. For example, crude oils or crude oil distillate fractions often contain naturally
20 occurring surfactants. Accordingly, an emulsion may arise spontaneously when a mixture of the crude oil or crude oil distillate and an ionic liquid is subjected to shearing (thereby imparting the energy required to form the ionic liquid/oil emulsion). The ionic liquid phase of such spontaneously formed emulsions may have been contacted with the crude oil or crude oil distillate in order to extract unwanted components of the crude oil or crude oil
25 distillate, for example, organic acids such as naphthenic acids, or sulfur containing compounds. Where the oil is a lubricant, an emulsion may also arise when an ionic liquid is contacted with the lubricant in order to extract contaminants such as metal particles, metal ions or combustion residues, and the resulting mixture is subjected to shearing.

Microwave radiation is defined herein as electromagnetic radiation in the frequency
30 range of 300 MHz to 300 GHz (having wavelengths in the range 1 to 1000 nm). The wavelength of the microwave radiation is preferably chosen so as to optimize the penetration of the microwave radiation into the emulsion. The penetration of the

microwave radiation increases with increasing wavelength (and hence decreasing frequency). However, in practice, the frequency of microwave radiation that is licensed for use in industrial processes is restricted to 2.4 GHz and 0.6-0.7 GHz thereby avoiding the risk of the emitted microwave radiation disrupting communications equipment.

- 5 The emulsion is subjected to microwave irradiation in step (a) for a time sufficient to break the emulsion. It has been found that microwave irradiation of the emulsion significantly reduces the time taken for separation of the ionic liquid and oil phases, for example, from days to minutes.

Suitably, the emulsion may be irradiated with microwave radiation in a tank where
10 the residence time of the emulsion in the tank is 5 to 20 minutes. Alternatively, the emulsion may be irradiated as it flows through a tubular apparatus having a microwave reactor arranged such that microwaves penetrate radially into the flowing emulsion.

Suitably, the emulsion is subjected to microwave irradiation at ambient pressure. Suitably, the microwave radiation preferentially heats the ionic liquid phase of the
15 emulsion to a temperature of at least 50°C, preferably, to a temperature in the range 60 to 100°C.

Suitably, the emulsion may be subjected to microwave irradiation in the presence of an additional heating source, an electrostatic field, an acoustic field, or combinations thereof in order to further enhance breaking of the emulsion.

- 20 Separation step (b) may be achieved by any means known to the person skilled in the art, for example, by centrifugation, gravity separation, hydrocyclone separation, electrostatic separation or combinations thereof. It is also envisaged that irradiation step (a) and separation step (b) may be carried out together. For example, the ionic liquid/oil emulsion may be subjected to microwave irradiation in a settling tank or in a centrifuge.
25 Generally, the ionic liquid phase will be denser than the oil phase such that the emulsion separates into an upper oil layer and a lower ionic liquid layer.

Optionally, a demulsifier may be added to the emulsion prior to or during the irradiation step (a) to enhance the rate of demulsification. The demulsifier may be selected from any known demulsifier that is not degraded by microwave irradiation. Typically, the
30 demulsifiers utilized during microwave irradiation step (a) will have a molecular weight in the range 500 to 5000, preferably 500 to 2000. In the case of an ionic liquid-in-oil emulsion, the demulsifier suitably has a hydrophilic-lipophilic balance value of above 9,

preferably in the range 9 to 30, for example, 9 to 15. Demulsifiers which will not degrade when exposed to microwave irradiation include those which contain functional groups such as ethers, amines, ethoxylated alcohols, sulfonates and mixtures thereof. A particularly preferred demulsifier is a phenolformaldehyde ethoxylated propoxylated resin.

- 5 In the case of an oil-in-ionic liquid emulsion, the demulsifier suitably has a hydrophilic-lipophilic balance value of less than 8, preferably 3 to 6.

The amount of demulsifier added during microwave irradiation step (a) is preferably in the range of 5 to 100 ppm, preferably, 10 to 25 ppm. Additionally, a delivery solvent may be employed. Where the emulsion is an ionic liquid-in-oil emulsion, the
10 delivery solvent is suitably miscible with the oil phase. Where the oil phase is a crude oil, the delivery solvent may for example be a crude oil distillate boiling in the range of about 70 to 450°C. Where the oil phase is a crude oil distillate fraction, the delivery solvent may for example be the crude oil distillate fraction or a component thereof. It is also envisaged that the delivery solvent may be a conventional solvent that is miscible with the oil, for
15 example an alcohol, ether, or mixture thereof. The delivery solvent may be present in an amount of from 30 to 75% weight in the demulsifier. Where the emulsion is an oil-in-ionic liquid emulsion, the delivery solvent is suitably miscible with the ionic liquid phase.

The present invention will now be illustrated by reference to the following Examples.

20 Example 1

1,3-dimethylimidazolium methyl sulfate was prepared as described in "Efficient, halide free synthesis of new, low cost ionic liquids: Alkylimidazolium salts containing methyl- and ethyl-sulfate anions", J. D. Holbrey, W. M. Reichert, R. P Swatloski, G. A. Broker, W. R. Pitner, K. R. Seddon and R. D. Rogers, Green Chem., 2002, 4, 407-413.

- 25 An emulsified mixture of 1,3-dimethylimidazolium methyl sulfate (2mL) and crude oil from the Harding Field in the North Sea (2mL) was irradiated with microwave radiation using a CEM Explorer (Trade Mark) laboratory microwave reactor resulting in separation of the emulsion into a pale straw colored lower ionic liquid layer and dark upper oil layer. The ionic liquid in oil emulsion had arisen spontaneously upon mixing the ionic liquid with
30 the oil owing to the presence of naturally occurring surfactants in the Harding crude oil.

Example 2

30 mL of Harding crude oil and 30 mL of 1-ethyl-3-methylimidazolium ethylsulfate were blended at 60 °C, stirring with an overhead stirrer at 2000 rpm to form an emulsion.

- 5 2 × 2 mL samples were pipetted into microwave sample tubes. One tube was heated for 1 min in the microwave oven; and the control was heated in a water bath at 50 °C. The sample heated in the microwave showed separation into two phases after one minute of heating. Over the same time period, the sample heated in a water bath showed only initial signs of ionic liquid and oil droplet formation, and required approximately 10
10 min. to achieve comparable separation.

Example 3

- 7 emulsions containing a 1:2 mass ratio of crude oil from the Harding Field and an ionic liquid, were prepared and irradiated with microwave radiation using a CEM Explorer (Trade Mark) laboratory microwave reactor under the following conditions: power: 100
15 watts; ramp time: 60 seconds; hold time: 60 seconds; temperature: 80°C. The ionic liquids in the seven emulsions were prepared by methods similar to those described in "Ionic liquids in synthesis", Peter Wasserscheid, Tom Welton, First Edition, November 2002, ISBN: 3-527-30515-7 - Wiley-VCH, and were: 1-ethyl-3-methylimidazolium methyl sulfate; 1-ethyl-3-methylimidazolium *bis*-trifluoromethanesulfonylimide; 1-octyl-3-
20 methylimidazolium tetrafluoroborate; cholinium *bis*-trifluoromethanesulfonylimide; 1-hexyl-3-methylimidazolium hexafluorophosphate; 1,1-butylmethylpyrrolidinium *bis*-trifluoromethanesulfonylimide; and 1-H-3-methylimidazolium methanoate. In all cases, following irradiation, the emulsion separated into a lower ionic liquid layer and an upper, darker, oil layer.

Claims

1. A method for breaking an emulsion of an ionic liquid which is a salt that is in the liquid state at a temperature below 150°C, and an oil, comprising the steps of
 - 5 (a) irradiating the emulsion with microwave radiation;
 - (b) separating the emulsion into an ionic liquid phase and an oil phase; and
 - (c) recovering at least one of the phases.
2. A method as claimed in claim 1, in which the emulsion is an ionic liquid-in-oil emulsion containing from 1 to 50% by weight ionic liquid based on the total weight of the
10 emulsion, or an oil-in-ionic liquid emulsion containing from 50 to 99% by weight ionic liquid based on the total weight of the emulsion.
3. A method as claimed in either claim 1 or claim 2, in which the ionic liquid is a salt which is in the liquid state at a temperature below 100°C.
4. A method as claimed in any one of the preceding claims, in which the oil phase of
15 the emulsion is selected from crude oils, crude oil blends, crude oil distillates, vegetable oils, animal oils, synthetic oils, lubricant oils and mixtures thereof.
5. A method as claimed in any one of the preceding claims, in which the emulsion is one which has arisen following the use of the ionic liquid as an extract phase or as a catalyst.
- 20 6. A method as claimed in any one of the preceding claims, in which in step (a) the irradiation with microwaves heats the ionic liquid phase of the emulsion to a temperature of at least 50°C.
7. A method as claimed in claim 6, in which in step (a) the irradiation with microwaves heats the ionic liquid phase of the emulsion to a temperature in the range 60 to
25 100°C.
8. A method as claimed in any one of the preceding claims, in which in step (a) the emulsion is subjected to microwave irradiation in the presence of an additional heating source, an electrostatic field, an acoustic field, or a combination thereof.
9. A method as claimed in any one of the preceding claims, in which irradiation step
30 (a) and separation step (b) are carried out together.
10. A method as claimed in any one of the preceding claims, in which a demulsifier is added to the emulsion prior to or during the irradiation step (a).

11. A method as claimed in any one of the preceding claims, in which in step (c) both phases are recovered.

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2006/001998

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D17/04 B01J19/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01D B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6 077 400 A (IMPERIAL PETROLEUM RECOVERY CORP.) 20 June 2000 (2000-06-20) cited in the application the whole document	1-11
A	US 4 582 629 A (CONOCO INC.) 15 April 1986 (1986-04-15) cited in the application the whole document	1-11
A	US 2003/157351 A1 (R.P. SWATLOSKI ET AL.) 21 August 2003 (2003-08-21) paragraphs [0035], [0037], [0050], [0061]	1-11

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 6077400	A	20-06-2000	NONE	
US 4582629	A	15-04-1986	NONE	
US 2003157351	A1	21-08-2003	US 2004038031 A1	26-02-2004