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SEPARATING CYCLOALKANES USING AQUEOUS SOLUTIONS OF CUCURBITURIL MACROCYCLES

Abstract

Embodiments of the present disclosure include methods for separating cycloalkanes comprising contacting a petroleum solution including one or more cycloalkanes with an aqueous solution including a cucurbituril macrocycle to produce a first aqueous phase and a first organic phase, wherein the cucurbituril macrocycle is selective for extraction of at least one of the one or more cycloalkanes.

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Background/Summary

BACKGROUND

[0001] With the increasing demand for chemicals driven by the rapid development of industries, such as the petrochemical and pharmaceutical industries, innovative materials and technologies are essential to improve the efficiency, quality, and safety of these processes.

[0002] Hydrocarbons such as cycloalkanes are often used as principal raw materials for the production of plastics, fertilizers, pharmaceuticals, and more. Most hydrocarbons used in these industries are derived from crude oil. Through multiple steps of distillation and refining processes, crude oil can be reformed into high value hydrocarbons. However, these processes are energy-intensive and laborious, which not only account for half of the industrial energy use and the third largest source of industrial carbon dioxide emission but also represent up to 40 to 70% of production costs. Additionally, only a few of the crude oil separated fractions, 8-14%, is used for further refining, with less than 20% conversion into the final products. Exploring economic and sustainable strategies to obtain high-value hydrocarbons from crude oil poses an important challenge in industry and academia. Crude oil naturally contains a variety of hydrocarbon compounds. However, due to the complexity of its composition, it is challenging to obtain a high-purity product through distillation and rectification. Recent research has developed techniques for successful separation of light hydrocarbon fractions from crude oil using energy-saving membrane technology. However, these size-exclusion-based membrane separations face challenges in separating moderately sized individual hydrocarbons from crude oil. On the other hand, adsorptive separation using porous adsorbents shows promise in selectively separating highly pure single hydrocarbons from simple mixtures based on differences in size, shape, polarity, and affinity. However, this approach faces challenges when applied to separations of petroleum/crude oil due to its overly complex composition, which hinders achieving both high selectivity and strong affinity simultaneously. Furthermore, the heterogeneous adsorption and desorption processes require high-temperature and low-pressure conditions to enhance mass transfer rates, which implies additional operational costs and energy consumption.

SUMMARY

[0003] According to one aspect of the present invention, a method of separating cycloalkanes comprising contacting a petroleum solution including one or more cycloalkanes with an aqueous solution including a cucurbituril macrocycle to produce a first aqueous phase and a first organic phase, wherein the cucurbituril macrocycle is selective for extraction of at least one of the one or more cycloalkanes.

[0004] According to another aspect of the present invention, a liquid-liquid extraction solvent comprising an aqueous solution of a cucurbituril macrocycle, wherein the cucurbituril macrocycle is selective for the extraction of at least one cycloalkane and wherein the cucurbituril has the following chemical structure:

##STR00001## [0005] wherein a.sup.1 indicates the point of attachment to b.sup.1, a.sup.2 indicates the point of attachment to b.sup.2; n is 1-20, X is O, S, or NH; and R.sup.1 and R.sup.2 are independently selected from the group consisting of hydrogen, H, optionally substituted C.sub.1-C.sub.30 alkyl group; optionally substituted C.sub.2-C.sub.30 alkenyl group; optionally substituted C.sub.2-C.sub.30 alkynyl group; optionally substituted C.sub.2-C.sub.30 carbonylalkyl group; optionally substituted C.sub.1-C.sub.30 thioalkyl group; optionally substituted C.sub.1-C.sub.30 alkylthiol group; optionally substituted C.sub.1-C.sub.30 hydroxyalkyl group; optionally substituted C.sub.1-C.sub.30 alkylsilyl group; optionally substituted C.sub.1-C.sub.30 aminoalkyl

group; optionally substituted C.sub.1-C.sub.30 aminoalkylthioalkyl group; optionally substituted C.sub.5-C.sub.30 cycloalkyl group; optionally substituted C.sub.2-C.sub.30 heterocycloalkyl group; optionally substituted C.sub.6-C.sub.30 aryl group; optionally substituted C.sub.6-C.sub.30 arylalkyl group; optionally substituted C.sub.4-C.sub.30 heteroaryl group; and optionally substituted C.sub.4-C.sub.30 heteroarylalkyl group.

Description

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] FIG. **1**A illustrates a flowchart of a liquid-liquid extraction process for separating cycloalkanes, in accordance with one or more embodiments of the present invention.

[0007] FIG. **1**B illustrates a flowchart of a liquid-liquid extraction process for separating cycloalkanes, in accordance with one or more embodiments of the present invention.

[0008] FIG. **2** illustrates a schematic diagram of a liquid-liquid extraction system for separating cycloalkanes, in accordance with one or more embodiments of the present invention.

[0009] FIG. **3** illustrates a schematic diagram of another liquid-liquid extraction system for separating cycloalkanes, in accordance with one or more embodiments of the present invention.

[0010] FIG. **4** depicts four .sup.1H NMR spectra of a petroleum solution (labelled i), a water phase solution following the first extraction using CB[7] (labelled ii), an organic phase solution from the second extraction using CB[7] (labelled iii), and pure cyclohexane, methylcyclohexane, and methylcyclopentane dissolved in CDCl.sub.3 (labelled iv).

[0011] FIG. **5**A depicts three GC-MS spectra of a petroleum solution, an organic phase solution, and pure cyclohexane, methylcyclohexane, and methylcyclopentane dissolved in CDCl.sub.3 (labelled “Standard samples”).

[0012] FIG. **5**B depicts an expanded view of the three GC-M S spectra of FIG. **5**A.

[0013] FIG. **5**C depicts a GC-MS spectrum of water phase from the second extraction using CB[7] at pH 14.

[0014] FIG. **5**D depicts a GC-MS spectrum of water phase from the second extraction using CB[7] at pH 1.

[0015] FIG. **5**E depicts a GC-MS spectrum of water phase from the second extraction using CB[7] in 1.0 M NaCl solution.

[0016] FIG. **5**F depicts a GC-MS spectrum of water phase from the second extraction using CB[7] in a seawater solution.

[0017] FIG. **5**G depicts a GC-MS spectrum of water phase from the second extraction using CB[5] in 4 M HCl solution.

[0018] FIG. **5**H depicts a GC-MS spectrum of water phase from the second extraction using CB[6] in 4 M HCl solution.

[0019] FIG. **5**I depicts a GC-M S spectrum of and water phase from the second extraction using CB[8] in 4 M HCl solution.

[0020] FIG. **6**A illustrates a computer-generated model of single crystal structures of a guest-host complex between cyclohexane and CB[7] resulting from single crystal X-ray diffraction (SCXRD) analysis.

[0021] FIG. **6**B illustrates a computer-generated model of single crystal structures of a guest-host complex between cyclohexane and CB[7] resulting from SCXRD analysis.

[0022] FIG. **6**C illustrates a computer-generated model of single crystal structures of a guest-host complex between methylcyclohexane and CB[7] resulting from SCXRD analysis.

[0023] FIG. **6**D illustrates a computer-generated model of single crystal structures of a guest-host complex between methylcyclohexane and CB[7] resulting from SCXRD analysis.

[0024] FIG. **6**E illustrates a computer-generated model of single crystal structures of a guest-host

complex between methylcyclopentane and CB[7] resulting from SCXRD analysis.
[0025] FIG. **6**F illustrates a computer-generated model of single crystal structures of a guest-host complex between methylcyclopentane and CB[7] resulting from SCXRD analysis.
[0026] FIG. **7** illustrates a graph showing the results of fluorescence titration while adding CB[7] to the mixture of CH and BC.
[0027] FIG. **8** illustrates a chart showing results of other fluorescence titration using C5-C8 hydrocarbons with CB[7], wherein binding constants are expressed as Log(K.sub.a) and hydrocarbons are graphically depicted and arranged by molecular weight.
[0028] FIG. **9**A illustrates a 3-dimensional chart showing binding constants of CB[7] with different hydrocarbons multiplied by water solubility against number of carbon molecules contained therein, wherein a-h differentiate hydrocarbons with shared number of carbon molecules.
[0029] FIG. **9**B illustrates a 3-dimensional chart showing binding constants of CB[7] with different hydrocarbons multiplied by water solubility and hydrocarbon content in petroleum solutions/crude oil against number of carbon molecules contained therein, wherein a-h differentiate hydrocarbons with shared number of carbon molecules.

DETAILED DESCRIPTION

Definitions

[0030] The terms recited below have been defined as described below. All other terms and phrases in this disclosure shall be construed according to their ordinary meaning as understood by one of skill in the art.
[0031] As used herein, the terms “petroleum solution” and “crude oil” refer to a liquid solution containing petroleum, petrochemicals, or a multiplicity of hydrocarbons.
[0032] As used herein, the term “cycloalkanes” refers to monocyclic aliphatic hydrocarbons. Examples of cycloalkanes include cyclic hydrocarbons having molecular formula C.sub.nH.sub.2n, wherein n is an integer. Specific examples of cycloalkanes include cyclopropane, cyclobutene, cyclopentane, cyclohexane, cycloheptane, cyclooctane, cyclononane, and cyclodecane. Further examples of cycloalkanes include cyclic hydrocarbons with one or more functional groups. Specific examples of these include methylcyclopropane, methylcyclobutene, methylcyclopentane, methylcyclohexane, methylcycloheptane, methylcyclooctane, methylcyclononane, and methylcyclodecane, These shall not be construed as limiting the scope of the term “cycloalkane” as used herein.
[0033] As used herein, the term “cucurbituril” and/or “cucurbituril macrocycle” generally refers to a macrocyclic molecule having a central cavity and comprising glycoluril monomer units linked by methylene (—CH.sub.2—) bridges. In some embodiments, the central cavity of cucurbituril is symmetric or substantially symmetric and/or hydrophobic. Unless provided otherwise, the term includes hydrates, salts, derivatives, and analogues of cucurbituril. For example, the term includes cucurbituril macrocycles having the chemical structure of formula (2):
##STR00002## [0034] or hydrates, salts, and/or analogues thereof, wherein: [0035] a.sup.1 indicates the point of attachment to b.sup.1; [0036] a.sup.2 indicates the point of attachment to b.sup.2; [0037] n is from 1 to 20; [0038] X is O, S, or NH; and [0039] R.sup.1 and R.sup.2 are independently selected from the group consisting of hydrogen, optionally substituted C.sub.1-C.sub.30 alkyl group; optionally substituted C.sub.2-C.sub.30 alkenyl group; optionally substituted C.sub.2-C.sub.30 alkynyl group; optionally substituted C.sub.2-C.sub.30 carbonylalkyl group; optionally substituted C.sub.1-C.sub.30 thioalkyl group; optionally substituted C.sub.1-C.sub.30 alkylthiol group; optionally substituted C.sub.1-C.sub.30 hydroxyalkyl group; optionally substituted C.sub.1-C.sub.30 alkylsilyl group; optionally substituted C.sub.1-C.sub.30 aminoalkyl group; optionally substituted C.sub.1-C.sub.30 aminoalkylthioalkyl group; optionally substituted C.sub.5-C.sub.30 cycloalkyl group; optionally substituted C.sub.2-C.sub.30 heterocycloalkyl group; optionally substituted C.sub.6-C.sub.30 aryl group; optionally substituted C.sub.6-C.sub.30 arylalkyl group; optionally substituted C.sub.4-C.sub.30 heteroaryl group; and optionally

substituted C.sub.4-C.sub.30 heteroarylalkyl group.
[0040] An unsubstituted cucurbituril refers to a cucurbituril in which R.sup.1 and R.sup.2 are both hydrogen in all the glycoluril units of formula (2). A substituted cucurbituril refers to a cucurbituril in which at least one of R.sup.1 and R.sup.2 is other than a hydrogen for at least one glycoluril unit of formula (2). A cucurbituril, whether substituted or unsubstituted, can be referred to herein as a "cucurbit[n]uril" or "CB[n]," where n represents the number of glycoluril monomer units present in the macrocycle. Examples of suitable cucurbiturils include, without limitation, the following: cucurbit[2]uril, cucurbit[3]uril, cucurbit[4]uril, cucurbit[5]uril, cucurbit[6]uril, cucurbit[7]uril, cucurbit[8]uril, cucurbit[8]uril, cucurbit[9]uril, cucurbit[10]uril, cucurbit[11]uril, cucurbit[12]uril, cucurbit[13]uril, cucurbit[14]uril, cucurbit[15]uril, cucurbit[16]uril, cucurbit[17]uril, cucurbit[18]uril, cucurbit[19]uril, cucurbit[20]uril, analogues thereof, and combinations thereof.
[0041] A cucurbituril can include substituted and unsubstituted glycoluril monomer units. Such cucurbiturils refer to a cucurbituril in which R.sup.1 and R.sup.2 are both hydrogen in at least one glycoluril unit of formula (2) and in which R.sup.1 and R.sup.2 is other than a hydrogen for at least one glycoluril unit of formula (2). Such cucurbiturils can be referred to herein as a "cucurbit[s,u]uril," where s represents the number of substituted glycoluril monomer units and u represents the number of unsubstituted glycoluril monomer units.
[0042] As used herein, the term "host-guest complex" generally refers to a supramolecular assembly containing a macrocyclic host species and a guest species bound together via non-covalent interactions. Examples of non-covalent interactions include, without limitation, hydrophobic forces, electrostatic forces, van der Waals forces, hydrogen bonding, and the like. The macrocyclic host species is usually characterized by a cavity within which at least a portion of the guest species resides.
[0043] As used herein, the term "alkyl" refers to a straight- or branched-chain or cyclic hydrocarbon radical or moiety comprising only carbon and hydrogen atoms, containing no unsaturation, and having 30 or fewer carbon atoms. The term "cycloalkyl" refers to aliphatic cyclic alkyls having 3 to 10 carbon atoms in single or multiple cyclic rings, preferably 5 to 6 carbon atoms in a single cyclic ring. Non-limiting examples of suitable alkyl groups include methyl group, ethyl group, propyl group, isopropyl group, cyclopropyl group, butyl group, isobutyl group, sec-butyl group, tert-butyl group, cyclobutyl group, pentyl group, neo-pentyl group, cyclopentyl group, hexyl group, cyclohexyl group, 2-ethylhexyl, cyclohexylmethyl group, heptyl group, octyl group, nonyl group, decyl group, dodecyl group, tridecyl group, tetradcyl group, pentadecyl group, hexadecyl group, heptadecyl group, octadecyl group, nonadecyl group, cyclopentyl group, cyclohexyl group, and the like. Additional examples of cycloalkyl groups include cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclopentenyl, cyclohexenyl, cyclohexadienyl, cycloheptatrienyl, norbornyl, norpinyl, norcaryl, adamantyl, and spiro[4.5]decanyl groups, as well as their homologs, isomers, and the like. Alkyls can be substituted or unsubstituted. When the term is used with the "substituted" modifier, one or more hydrogen atoms has been independently replaced by any of the substituents disclosed herein.
[0044] As used herein, the term "heteroalkyl" refers to an alkyl as defined above having at least one carbon atom replaced by a heteroatom. Examples of cycloheteroalkyl groups include, among others, morpholinyl, thiomorpholinyl, pyranyl, imidazolidinyl, imidazolinyl, oxazolidinyl, pyrazolidinyl, pyrazolinyl, pyrrolidinyl, pyrrolinyl, tetrahydrofuranyl, tetrahydrothiophenyl, piperidinyl, piperazinyl, and the like. Heteroalkyls can be substituted or unsubstituted. When the term is used with the "substituted" modifier, one or more hydrogen atoms has been independently replaced by any of the substituents disclosed herein, or a substituent is bonded to a heteroatom, or both.
[0045] As used herein, the term "alkenyl" refers to a straight-or branched-chain hydrocarbon radical or moiety comprising only carbon and hydrogen atoms and having at least one carbon-carbon double bond, which can be internal or terminal. Non-limiting examples of alkenyl groups

include: —CH═CH.sub.2 (vinyl), —CH═CHCH.sub.3, —CH═CHCH.sub.2CH.sub.3, —CH.sub.2CH═CH.sub.2 (allyl), —CH.sub.2CH═CHCH.sub.3, —CH═CH—C.sub.6H.sub.5, —CH═CH—, —CH═C(CH.sub.3)CH.sub.2—, and —CH═CHCH.sub.2—. The groups, —CH═CHF, —CH═CHCl, —CH═CHBr, and the like. Examples of alkenyl groups include ethenyl, propenyl, butenyl, pentenyl, hexenyl, butadienyl, pentadienyl, hexadienyl groups, and the like. Alkenyls can be substituted or unsubstituted. When the term is used with the "substituted" modifier, one or more hydrogen atoms has been independently replaced by any of the substituents disclosed herein.

[0046] As used herein, the term "alkynyl" refers to a straight- or branched-chain hydrocarbon radical or moiety comprising only carbon and hydrogen atoms and having at least one carbon-carbon triple bond, which can be internal or terminal. The groups —C≡CH, —C≡CCH.sub.3, and —CH.sub.2C≡CCH.sub.3, are non-limiting examples of alkynyl groups. Examples of alkynyl groups include ethynyl, propynyl, butynyl, pentynyl, hexynyl, and the like. Alkynes can be substituted or unsubstituted. When the term is used with the "substituted" modifier, one or more hydrogen atoms has been independently replaced by any of the substituents disclosed herein.

[0047] As used herein, the term "carbonylalkyl" refers to a carbonyl group bonded, as a substituent, to an alkyl.

[0048] As used herein, the term "thioalkyl" and "alkylthio" refers to the group —S-alkyl.

[0049] As used herein, the term "hydoxyalkyl" refers to a hydroxyl group bonded, as a substituent, to an alkyl group.

[0050] As used herein, the term "alkylsilyl" refers to an alkyl group bonded, as a substituent, to a silyl group.

[0051] As used herein, the term "aminoalkyl" refers to an amino group bonded, as a substituent, to an alkyl.

[0052] As used herein, the term "aminoalkylthioalkyl" refers to an amino group bonded, as a substituent, to an alkyl group that is bonded, as a substituent, to a thioalkyl group.

[0053] As used herein, the term "aryl" refers to a monocyclic or polycyclic aromatic hydrocarbon radical or moiety comprising only carbon and hydrogen atom, wherein the carbon atoms form an aromatic ring structure. If more than one ring is present, the rings may be fused, not fused, or bridged. The term does not preclude the presence of one or more alkyl groups attached to the first aromatic ring or any additional aromatic ring present. The point of attachment can be through an aromatic carbon atom in the ring structure or a carbon atom of an alkyl group attached to the ring structure. Non-limiting examples of aryl groups include phenyl (Ph), toyl, xylyl, methylphenyl, (dimethyl)phenyl, —C6H4-CH2CH3 (ethylphenyl), naphthyl, and the monovalent group derived from biphenyl. Further examples of aryl groups having only aromatic carbocyclic ring(s) include phenyl, 1-naphthyl (bicyclic), 2-naphthyl (bicyclic), anthracenyl (tricyclic), phenanthrenyl (tricyclic), pentacenyl (pentacyclic), and like groups. Examples of polycyclic ring systems in which at least one aromatic carbocyclic ring is fused to one or more cycloalkyl and/or cycloheteroalkyl rings include, among others, benzo derivatives of cyclopentane (i.e., an indanyl group, which is a 5,6-bicyclic cycloalkyl/aromatic ring system), cyclohexane (i.e., a tetrahydronaphthyl group, which is a 6,6-bicyclic cycloalkyl/aromatic ring system), imidazoline (i.e., a benzimidazolinyl group, which is a 5,6-bicyclic cycloheteroalkyl/aromatic ring system), and pyran (i.e., a chromenyl group, which is a 6,6-bicyclic cycloheteroalkyl/aromatic ring system). When the term is used with the "substituted" modifier, one or more hydrogen atoms has been independently replaced by any of the substituents disclosed herein.

[0054] Asused herein, the term "heteroaryl" refers to an aryl having at least one aromatic carbon atom in the ring structure replaced by a heteroatom. The term does not preclude the presence of one or more alkyl groups attached to the first aromatic ring or any additional aromatic ring present. The point of attachment can be through an aromatic carbon atom or aromatic heteroatom in the aromatic ring structure or a carbon atom of an alkyl group attached to the aromatic ring structure.

Non-limiting examples of heteroaryl groups include furanyl, benzofuranyl, isobenzylfuranyl, imidazolyl, indolyl, isoindolyl, indazolyl, methylpyridyl, oxazolyl, pyridyl, pyrrolyl, pyrimidyl, pyrazinyl, quinolyl, quinazolyl, quinoxalinyl, thienyl, and triazinyl. Additional examples of heteroaryl groups include, for example, the 5- or 6-membered monocyclic and 5-6 bicyclic ring systems such as pyrrolyl, furyl, thienyl, pyridyl, pyrimidyl, pyridazinyl, pyrazinyl, triazolyl, tetrazolyl, pyrazolyl, imidazolyl, isothiazolyl, thiazolyl, thiadiazolyl, isoxazolyl, oxazolyl, oxadiazolyl, indolyl, isoindolyl, benzofuryl, benzothienyl, quinolyl, 2-methylquinolyl, isoquinolyl, quinoxalyl, quinazolyl, benzotriazolyl, benzimidazolyl, benzothiazolyl, benzisothiazolyl, benzisoxazolyl, benzoxadiazolyl, benzoxazolyl, cinnolinyl, IH-indazolyl, 2H-indazolyl, indolizinyl, isobenzofuyl, naphthyridinyl, phthalazinyl, pteridinyl, purinyl, oxazolopyridinyl, thiazolopyridinyl, imidazopyridinyl, furopyridinyl, thienopyridinyl, pyridopyrimidinyl, pyridopyrazinyl, pyridopyridazinyl, thienothiazolyl, thienoxazolyl, thienoimidazolyl groups, and the like. Further examples of heteroaryl groups include 4,5,6,7-tetrahydroindolyl, tetrahydroquinolinyl, benzothienopyridinyl, benzofuropyridinyl groups, and the like. Heteroaryls can be substituted or unsubstituted. When the term is used with the “substituted” modifier, one or more hydrogen atoms has been independently replaced by any of the substituents disclosed herein, or a substituent is bonded to a heteroatom, or both.

[0055] As used herein, the term “aralkyl” refers to an alkyl having at least one hydrogen atom replaced by an aryl or heteroaryl group. Non-limiting examples of aralkyls are: phenylmethyl (benzyl, Bn) and 2-phenyl-ethyl. The point of attachment can be through a carbon atom of the alkyl group or through an aromatic carbon atom or aromatic heteroatom in the aromatic ring structure of the aryl or heteroaryl group attached to the alkyl group. Aralkyls can be substituted or unsubstituted. When the term is used with the “substituted” modifier, one or more hydrogen atoms has been independently replaced by any of the substituents disclosed herein, or a substituent is bonded to a heteroatom, or both.

[0056] As used herein, the term “alkaryl” refers to an aryl or heteroaryl having at least one hydrogen atom replaced by an alkyl or heteroalkyl group. The point of attachment can be an aromatic carbon atom or aromatic heteroatom in the aromatic ring structure or a carbon atom of an alkyl group attached to the ring structure. Alkaryls can be substituted or unsubstituted. When the term is used with the “substituted” modifier, one or more hydrogen atoms has been independently replaced by any of the substituents disclosed herein, or a substituent is bonded to a heteroatom, or both.

[0057] As used herein, the term “heteroaralkyl” refers to a heteroaryl bonded, as a substituent, to an alkyl group.

[0058] As used herein, the term “heteroalkaryl” refers to a heteroalkyl bonded, as a substituent, to an aryl group.

[0059] As used herein, the terms “halide,” “halo,” and “halogen” refer to —F, —Cl, —Br, or —I.

[0060] As used herein, the term “substituent” and “substituted” refers to all permissible substituents of the compounds described herein. In the broadest sense, the permissible substituents include acyclic and cyclic, branched and unbranched, carbocyclic and heterocyclic, aromatic and nonaromatic substituents of organic compounds. Examples of substituents include, without limitation, nothing, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, alkenyl, substituted alkenyl, alkynyl, substituted alkynyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, aralkyl, substituted aralkyl, alkaryl, substituted alkaryl, haloaryl, substituted haloaryl, alkoxy, substituted alkoxy, alkenyloxy, substituted alkenyloxy, alkynyloxy, substituted alkynyloxy, aryloxy, substituted aryloxy, aralkoxy, substituted aralkoxy, heteroaryloxy, substituted heteroaryloxy, acyloxy, substituted acyloxy, acyl, substituted acyl, halo (—F, —Cl, —Br, —I, etc.), hydrogen (—H), carboxyl (—COOH), hydroxy (—OH), oxo (═O), hydroxyamino (—NHOH), nitro (—NO.sub.2), cyano (—CN), isocyanate (—N═C═O), azido (—N.sub.3), phosphate (e.g., —OP(O)(OH).sub.2, —OP(O)(OH)O—, deprotonated forms thereof,

etc.), mercapto (—SH), thio (═S), thioether (═S—), sulfonamido (—NHS(O).sub.2—), sulfonyl (—S(O).sub.2—), sulfinyl (—S(O).sub.2—), amino, alkylamino, vinyl, allyl, any combinations thereof, and the like.

[0061] Additional examples of substituents include, but are not limited to, —NC, —S(R.sup.0).sub.2.sup.+, —N(R.sup.0).sub.3.sup.+, —SO.sub.3H, —SO.sub.2R.sup.0, —SO.sub.3R.sup.0, —SO.sub.2NHR.sup.0, —SO.sub.2N(R.sup.0).sub.2, —COR.sup.0, —COOR.sup.0, —CONHR.sup.0, CON(R.sup.0).sub.2, C.sub.1-40 haloalkyl groups, C.sub.6-14 aryl groups, and 5-14 membered electron-poor heteroaryl groups; where R.sup.0 is a C.sub.1-20 alkyl group, a C.sub.2-20 alkenyl group, a C.sub.2-20 alkynyl group, a C.sub.1-20 haloalkyl group, a C.sub.1-20 alkoxy group, a C.sub.6-14 aryl group, a C.sub.3-14 cycloalkyl group, a 3-14 membered cycloheteroalkyl group, and a 5-14 membered heteroaryl group, each of which can be optionally substituted as described herein. Additional examples of substituents include, but are not limited to, —OR.sup.0, —NH.sub.2, —NHR.sup.0, —N(R.sup.0).sub.2, and 5-14 membered electron-rich heteroaryl groups, where R.sup.0 is a C.sub.1-20 alkyl group, a C.sub.2-20 alkenyl group, a C.sub.2-20 alkynyl group, a C.sub.6-14 aryl group, or a C.sub.3-14 cycloalkyl group.

[0062] As used herein, the term “percent transferred” refers to the % by mass of a species A transferred from a solution B to a solution C based on the total weight of species A in solution B prior to the transfer.

[0063] As used herein, “CB[7]” refers to cucurbit[**7**]uril; “OX” refers to ortho-xylene; “MX” refers to meta-xylene; “PX” refers to para-xylene; “OX@CB[7]” refers to a complex including ortho-xylene and cucurbit[7]uril; “MX@CB[7]” refers to a complex including meta-xylene and cucurbit[7]uril; and “PX-@CB[7]” refers to a complex including para-xylene and cucurbit[7]uril.

[0064] As used herein, “substantially free of” means having less than, approximately, or between any two of 0%, 0.5%, 1%, 2%, 3%, 4%, 5%, 6%, 7%, 8%, 9%, or 10%.

DISCUSSION

[0065] The present invention relates to the selective separation of one or more cycloalkanes from one or more petroleum solutions and, in particular, to the use of cucurbituril macrocycles, which are selective for one or more cycloalkanes, in liquid-liquid extraction systems and processes. As described herein, cucurbituril macrocycles may be included in aqueous solutions and used as liquid-liquid extraction solvents to separate some of the most challenging cycloalkane mixtures in industry, including petroleum solutions which include a large variety of hydrocarbons and inorganic impurities. The liquid-liquid extraction systems and processes disclosed herein can be performed under ambient temperature and ambient pressure, with substantially lower energy requirements than conventional separation processes. Furthermore, unlike conventional cycloalkanes separation processes, the liquid-liquid extraction systems and processes disclosed herein can separate cycloalkane mixtures with high selectivity and/or high specificity, without the use of highly toxic and corrosive solvents.

[0066] While not wishing to be bound to a theory, it is believed that the separation of cycloalkanes from petroleum solutions can involve the formation of a host-guest complex in which the cucurbituril macrocycle is the host and the cycloalkane to be extracted is the guest. For example, in some embodiments, the liquid-liquid extraction process can include a step in which a petroleum solution is contacted with an aqueous cucurbituril solution. Being selective for the extraction of at least one cycloalkane, the cucurbituril macrocycle can be used to effectuate the transfer and/or extraction of the at least one cycloalkane from the petroleum solution to the aqueous solution through the formation of the host-guest complex. It is believed that, upon contacting the petroleum solutions with the aqueous cucurbituril solution, the cycloalkane to be extracted is taken up into and bound within the cavity of the cucurbituril macrocycle where it resides and is stabilized by various non-covalent interactions. As described below, the cycloalkane can be released from the cavity of the cucurbituril macrocycle using an organic solvent.

[0067] The use of aqueous cucurbituril solutions as liquid-liquid extraction solvents offers

numerous advantages over conventional liquid-liquid extraction solvents. For example, porous cucurbituril macrocycles, such as cucurbit[7]uril (CB[7]), may be used. In addition, most conventional porous adsorbents-based adsorption separation techniques face challenges separating different but similarly-sized hydrocarbons due to having fixed pore sizes. These challenges are exacerbated when faced with the complexity of petroleum's typical composition which hinders both high selectivity and strong affinity simultaneously. However, the aqueous cucurbituril solutions disclosed herein, with their tunable properties and structures, can be used to separate a variety of cycloalkane mixtures and thus exhibit broader utility and range than conventional porous materials. For example, aqueous solutions of cucurbit[7]uril can be used to separate one or more of cyclohexane, methylcyclohexane, and methylcyclopentane, achieving more than 99% specificity after a single extraction cycle for certain separations. An additional advantage is that cucurbituril macrocycle exhibits higher chemical, moisture, and thermal stability than conventional porous materials, such as zeolites, metal-organic frameworks, porous coordination polymers, covalent organic frameworks, porous organic cages, and the like. The cucurbituril macrocycle can also be recovered and reused/recycled in one or more extraction cycles without any loss in performance.

[0068] An example of a cucurbituril macrocycle that can be used for the selective extraction of at least one cycloalkane from at least one petroleum solution includes macrocycles with the following structural formula:

##STR00003## [0069] wherein: [0070] a.sup.1 indicates the point of attachment to b.sup.1; [0071] a.sup.2 indicates the point of attachment to b.sup.2; [0072] n is 1-20; [0073] X is O, S, or NH; and [0074] R.sup.1 and R.sup.2 are independently selected from the group consisting of hydrogen, H, optionally substituted C.sub.1-C.sub.30 alkyl group; optionally substituted C.sub.2-C.sub.30 alkenyl group; optionally substituted C.sub.2-C.sub.30 alkynyl group; optionally substituted C.sub.2-C.sub.30 carbonylalkyl group; optionally substituted C.sub.1-C.sub.30 thioalkyl group; optionally substituted C.sub.1-C.sub.30 alkylthiol group; optionally substituted C.sub.1-C.sub.30 hydroxyalkyl group; optionally substituted C.sub.1-C.sub.30 alkylsilyl group; optionally substituted C.sub.1-C.sub.30 aminoalkyl group; optionally substituted C.sub.1-C.sub.30 aminoalkylthioalkyl group; optionally substituted C.sub.5-C.sub.30 cycloalkyl group; optionally substituted C.sub.2-C.sub.30 heterocycloalkyl group; optionally substituted C.sub.6-C.sub.30 aryl group; optionally substituted C.sub.6-C.sub.30 arylalkyl group; optionally substituted C.sub.4-C.sub.30 heteroaryl group; and optionally substituted C.sub.4-C.sub.30 heteroarylalkyl group.

[0075] FIG. **1**A is a flowchart of a liquid-liquid extraction process **100**A for separating cycloalkanes, in accordance with one or more embodiments of the invention. The liquid-liquid extraction process of the present invention can utilize the cucurbituril macrocycle presented above. As shown in FIG. **1**A, in some embodiments, the liquid-liquid extraction process **100**A can comprise contacting **101** a petroleum solution **103** including one or more cycloalkanes, with an aqueous solution **105** including a cucurbituril macrocycle, wherein the cucurbituril macrocycle is selective for the extraction of at least one of said cycloalkanes. Contacting **101** may be performed to obtain a solution **107** including at least one cycloalkane from the petroleum solution **103**. In some embodiments, contacting **101** the petroleum solution with the aqueous solution produces a first aqueous phase and a first organic phase, wherein the first aqueous phase includes the cucurbituril macrocycle and at least a portion of the cycloalkane extracted from the petroleum solution. In some embodiments, to recover the cycloalkane from the first aqueous phase, the first aqueous phase is contacted with an organic solution to produce a second aqueous phase and a second organic phase, wherein the second organic phase includes at least a portion of the cycloalkane from the first aqueous phase (and/or from the original petroleum solution). In some embodiments, the second organic phase can be referred to as a raffinate. In some embodiments, the second aqueous phase includes the cucurbituril macrocycle and is recycled and/or reused for use in one or more separation cycles (e.g., of a liquid-liquid extraction process).

[0076] Referring now to FIG. **1**B, a flowchart of a liquid-liquid extraction process **100** for

separating cycloalkanes is presented, in accordance with one or more embodiments of the present invention. As shown in FIG. **1**B, the liquid-liquid extraction process **100** can comprise one or more of the following steps: providing **102** an petroleum solution including at least one cycloalkane and further providing an aqueous solution including a cucurbituril macrocycle; extracting **104** at least a portion of the cycloalkanes from the petroleum solution, using the aqueous solution, to produce a first aqueous phase and a first organic phase, wherein the first aqueous phase includes at least a portion of the cucurbituril macrocycle from the aqueous solution and the portion of the cycloalkanes extracted from the petroleum solution; recovering **106** at least a portion of the cycloalkanes from the first aqueous phase, using an organic solution, to produce a second aqueous phase and a second organic phase, wherein the second aqueous phase includes at least a portion of the cucurbituril macrocycle from the first aqueous phase and wherein the second organic phase includes the portion of the cycloalkanes recovered from the first aqueous phase; and recycling and/or reusing **108** the second aqueous phase for one or more extraction cycles.

[0077] Providing **102** includes providing a petroleum solution including at least one cycloalkane and further providing an aqueous solution including a cucurbituril macrocycle.

[0078] The petroleum solution can include one or more cycloalkanes, including at least one of the cycloalkanes to be extracted. In some embodiments, the one or more cycloalkanes to be extracted may include cycloalkanes with one or more functional groups attached to ring carbon atoms. In some embodiments, the one or more cycloalkanes to be extracted may include one or more of cyclohexane, methylcyclohexane, and methylcyclopentane. In some embodiments, the petroleum solution may also contain one or more of linear hydrocarbons, acyclic hydrocarbons, cyclic hydrocarbons, branched hydrocarbons, unbranched hydrocarbons, carbocyclic hydrocarbons, heterocyclic hydrocarbons, aromatic hydrocarbons, and aliphatic hydrocarbons. In some embodiments, the petroleum solution may contain one or more of the following hydrocarbons: n-pentane; cyclopentane; 2,2-dimethylbutane; 2,3-dimethylbutane; 2-methylpentane; 3-methylpentane; n-hexane; methylcyclopentane; benzene; cyclohexane; n-heptane; cycloheptane; methylcyclohexane; toluene; p-xylene; m-xylene; o-xylene; cyclooctane; 1,2,3-trimethylbenzene; and 1,2,4-trimethylbenzene.

[0079] The cucurbituril macrocycle can be dissolved or solubilized in water to obtain an aqueous cucurbituril solution. Examples of water that can be used to form the aqueous cucurbituril solution include, without limitation, tap water, distilled water, reverse osmosis water, and the like. The cucurbituril macrocycle included in the aqueous solution can be selective for the extraction of one or more cycloalkanes from the petroleum solution. In some embodiments, the cucurbituril macrocycle is selective for the extraction of specific cycloalkanes. In some embodiments, cucurbituril macrocycle is more selective for the extraction of specific cycloalkanes than the extraction of other hydrocarbons. In some embodiments, the cucurbituril macrocycle is more selective for the extraction of specific cycloalkanes than the extraction of other aliphatic hydrocarbons. In some embodiments, the other hydrocarbons can include aromatic hydrocarbons.

[0080] In some embodiments, the cucurbituril macrocycle is selective for the extraction of cycloalkanes. In some embodiments, the cucurbituril macrocycle is selective for the extraction of hydrocarbons in addition to cycloalkanes but to a lesser degree than for the extraction of cycloalkanes. In some embodiments, the cucurbituril macrocycle is more selective for the extraction of cycloalkanes than other hydrocarbons in petroleum solutions such as linear hydrocarbons, branched hydrocarbons, and aromatic hydrocarbons.

[0081] In some embodiments, the cucurbituril macrocycle is selective for the extraction of cyclohexane, methylcyclohexane, and methylcyclopentane. In some embodiments, the cucurbituril macrocycle is selective for the extraction of hydrocarbons in addition to cyclohexane, methylcyclohexane, and methylcyclopentane but to a lesser degree than for the extraction of cyclohexane, methylcyclohexane, and methylcyclopentane. In some embodiments, the cucurbituril macrocycle is more selective for the extraction of cyclohexane, methylcyclohexane, and

methylcyclopentane than other hydrocarbons in petroleum solutions such as linear hydrocarbons, branched hydrocarbons, and aromatic hydrocarbons. In some embodiments, cucurbituril macrocycle is more selection for the extraction of cyclohexane, methylcyclohexane, and methylcyclopentane than n-pentane; cyclopentane; 2,2-dimethylbutane; 2,3-dimethylbutane; 2-methylpentane; 3-methylpentane; n-hexane; benzene; n-heptane; cycloheptane; toluene; p-xylene; m-xylene; o-xylene; cyclooctane; 1,2,3-trimethylbenzene; and 1,2,4-trimethylbenzene.

[0082] The aqueous solution may include any of the cucurbituril macrocycles disclosed herein, including those having the structural formula presented above. In some embodiments, the aqueous solution includes cucurbit[7]uril. In some embodiments, the cucurbit[7]uril included in the aqueous solution has the chemical structure of formula (2):

##STR00004## [0083] or hydrates, salts, and/or analogues thereof, wherein: [0084] a.sup.1 indicates the point of attachment to b.sup.1; [0085] a.sup.2 indicates the point of attachment to b.sup.2; [0086] n is 7; [0087] X is O, S, or NH; and [0088] R.sup.1 and R.sup.2 are independently selected from the group consisting of hydrogen, optionally substituted C.sub.1-C.sub.30 alkyl group; optionally substituted C.sub.2-C.sub.30 alkenyl group; optionally substituted C.sub.2-C.sub.30 alkynyl group; optionally substituted C.sub.2-C.sub.30 carbonylalkyl group; optionally substituted C.sub.1-C.sub.30 thioalkyl group; optionally substituted C.sub.1-C.sub.30 alkylthiol group; optionally substituted C.sub.1-C.sub.30 hydroxyalkyl group; optionally substituted C.sub.1-C.sub.30 alkylsilyl group; optionally substituted C.sub.1-C.sub.30 aminoalkyl group; optionally substituted C.sub.1-C.sub.30 aminoalkylthioalkyl group; optionally substituted C.sub.5-C.sub.30 cycloalkyl group; optionally substituted C.sub.2-C.sub.30 heterocycloalkyl group; optionally substituted C.sub.6-C.sub.30 aryl group; optionally substituted C.sub.6-C.sub.30 arylalkyl group; optionally substituted C.sub.4-C.sub.30 heteroaryl group; and optionally substituted C.sub.4-C.sub.30 heteroarylalkyl group.

[0089] In some embodiments, X is O. In some embodiments, X is S. In some embodiments, X is NH. IN some embodiments, R.sup.1 and R.sup.2 are H.

[0090] In some embodiments, the aqueous solution includes cucurbit[s,u]uril, wherein s+u=7. For example, in some embodiments, the aqueous solution includes cucurbit[1,6]uril. In some embodiments, the aqueous solution includes cucurbit[2,5]uril. In some embodiments, the aqueous solution includes cucurbit[3,4]uril. In some embodiments, the aqueous solution includes cucurbit[4,3]uril. In some embodiments, the aqueous solution includes cucurbit[5,2]uril. In some embodiments, the aqueous solution includes cucurbit[6,1]uril.

[0091] In some embodiments, the aqueous solution includes a cucurbituril macrocycle other than cucurbit[n]uril, wherein n is an integer selected from 1 to 6 and 8 to 20. For example, in some embodiments, the aqueous solution includes a cucurbituril macrocycle other than cucurbit[n]uril, where n is from 1 to 4. In some embodiments, the aqueous solution includes a cucurbituril macrocycle other than cucurbit[5]uril. In some embodiments, the aqueous solution includes a cucurbituril macrocycle other than cucurbit[6]uril. In some embodiments, the aqueous solution includes a cucurbituril macrocycle other than cucurbit[8]uril. In some embodiments, the aqueous solution includes a cucurbituril macrocycle other than cucurbit[n]uril, where n is from 9 to 12. In some embodiments, the aqueous solution includes a cucurbituril macrocycle other than cucurbit[n]uril, where n is from 13 to 15. In some embodiments, the aqueous solution includes a cucurbituril macrocycle other than cucurbit[n]uril, where n is from 16 to 18. In some embodiments, the aqueous solution includes a cucurbituril macrocycle other than cucurbit[n]uril, where n is from 19 to 20.

[0092] In some embodiments, the aqueous solution includes cucurbit[6]uril. In some embodiments, cucurbit[6]uril has high selectivity for small hydrocarbons between 3 and 6 carbons long, or C3-C6. In particular, cucurbit[6]uril has high selectivity for n-butane (76.9%). In these embodiments, the method of separating cycloalkanes disclosed herein may be modified to comprise a method for separating small hydrocarbons comprising contacting a petroleum solution including one or more

small hydrocarbons having lengths from C3-C6 from a petroleum solution comprising an aqueous solution including a cucurbit[6]uril to produce a first aqueous phase and a first organic phase, wherein the cucurbit[6]uril is selective for extraction of at least one of the one or more small hydrocarbons.

[0093] In some embodiments, the aqueous solution includes cucurbit[8]uril. In some embodiments, cucurbit[8]uril has high selectivity for long hydrocarbons between 8 and 14 carbons long, or C8-C14. In these embodiments, the method of separating cycloalkanes disclosed herein may be modified to comprise a method for separating small hydrocarbons comprising contacting a petroleum solution including one or more small hydrocarbons having lengths from C8-C14 from a petroleum solution comprising an aqueous solution including cucurbit[8]uril to produce a first aqueous phase and a first organic phase, wherein the cucurbit[8]uril is selective for extraction of at least one of the one or more small hydrocarbons.

[0094] A solubilizing agent can optionally be added or included in the aqueous solution of cucurbituril. The solubilizing agent can be used to increase the solubility of the cucurbituril macrocycle in the aqueous solution. In some embodiments, the solubilizing agent includes a metal salt, such as NaCl or CsCl; an ammonium salt, such as NH.sub.4Cl; an acid, such as a mineral or an organic acid (e.g., formic acid, citric acid, or trifluoroacetic acid (TFA)), and/or a polyhydroxylated organic compound, such as sugars (e.g., glucose, sucrose, or cyclodextrins), starch, or glycerol. Other suitable solubilizing agents for increasing the solubility of the cucurbituril macrocycle in aqueous solutions include, for example, coordination complexes, such as hexaamminecobalt (III) chloride.

[0095] In some embodiments, the cucurbituril macrocycle and the one or more cycloalkanes to be extracted (e.g., cyclohexane, methylcyclohexane, and methylcyclopentane) are provided in stoichiometric amounts. In some embodiments, the cucurbituril macrocycle is provided in stoichiometric excess of the one or more cycloalkanes to be extracted (e.g., cyclohexane, methylcyclohexane, and methylcyclopentane). In some embodiments, the one or more cycloalkanes to be extracted (e.g., cyclohexane, methylcyclohexane, and methylcyclopentane) are provided in stoichiometric excess of the cucurbituril macrocycle.

[0096] Extracting **104** includes extracting at least a portion of the one or more cycloalkanes from the petroleum solution, using the aqueous solution of cucurbituril, to produce a first aqueous phase and a first organic phase. In this step, at least a portion of the one or more cycloalkanes is transferred from the petroleum solution to the aqueous solution using a cucurbituril macrocycle, as the cucurbituril macrocycle is selective for the extraction of the said one or more cycloalkanes. In some embodiments, the first aqueous phase includes at least a portion of the cucurbituril macrocycle from the aqueous solution and the portion of the one or more cycloalkanes extracted from the petroleum solution.

[0097] While not wishing to be bound to a theory, it is believed that the mechanism by which at least a portion of the one or more cycloalkanes is transferred from the to be petroleum solution to the aqueous solution of cucurbituril can involve the formation of a host-guest complex, where the host includes the cucurbituril macrocycle and the guest includes the cycloalkane. In some embodiments, the host-guest complex includes a cucurbituril macrocycle having a cavity and the cycloalkane, wherein the extracted cycloalkane at least partially resides in the cavity of the cucurbituril. In some embodiments, the extracted cycloalkane is bound within the cavity of the cucurbituril macrocycle. In some embodiments, the host-guest complex is stabilized by non-covalent interactions. In some embodiments, the cucurbituril macrocycle is selective for the extraction of the one or more cycloalkanes to the extent that no host-guest complexes are formed (at least to any appreciable degree) in which the guest species is a hydrocarbon other than the cycloalkane.

[0098] The first aqueous phase generally includes the aqueous solution of cucurbituril, as well as the portion of the one or more cycloalkanes transferred from the petroleum solution thereto. In

some embodiments, the first aqueous phase includes a host-guest complex in which the cucurbituril macrocycle is the host species and the one or more cycloalkanes to be extracted are the guest species. In some embodiments, the first aqueous phase is substantially free of host-guest complexes in which the cucurbituril macrocycle is the host species and hydrocarbons other than the one or more cycloalkanes are the guest species. In some embodiments, the first aqueous phase is substantially free of hydrocarbons other than the one or more cycloalkanes. For example, in some embodiments, the first aqueous phase is substantially free of hydrocarbons other than cyclohexane, methylcyclohexane, and methylcyclopentane.

[0099] The first organic phase generally includes the petroleum solution less the portion of the one or more cycloalkanes (e.g., cyclohexane, methylcyclohexane, and methylcyclopentane) transferred to the aqueous solution of cucurbituril and/or first aqueous phase. The first organic phase can include other hydrocarbons not transferred from the petroleum solution to the aqueous solution of cucurbituril via extracting **104**. The first organic phase can also include selected-for cycloalkanes (e.g., cyclohexane, methylcyclohexane, and methylcyclopentane) not transferred from the petroleum solution to the aqueous solution of cucurbituril via extracting **104** due to stoichiometrically insufficient cucurbituril macrocycle being used. For example, in some embodiments, the first organic phase includes at least one of the following: cyclohexane, methylcyclohexane, methylcyclopentane, and other hydrocarbons. In some embodiments, the first organic phase includes the portion of cyclohexane, methylcyclohexane, and methylcyclopentane not transferred to the aqueous solution of cucurbituril (if any). In some embodiments, the first organic phase is substantially free of cyclohexane, methylcyclohexane, and methylcyclopentane.

[0100] Extracting **104** can be performed by contacting the petroleum solution and aqueous solution. The contacting can proceed simultaneously or substantially simultaneously, or the contacting can proceed sequentially in any order. In some embodiments, extracting **104** can include admixing the petroleum solution and aqueous solution. In some embodiments, extracting **104** can include agitating the petroleum solution and aqueous solution. In some embodiments, extracting **104** can include mechanically mixing the petroleum solution and aqueous solution. In some embodiments, extracting **104** can include combining the petroleum solution and aqueous solution in a first extraction unit. In some embodiments, extracting **104** can include feeding the petroleum solution and aqueous solution to a first extraction unit. In some embodiments, extracting **104** can include adding the petroleum solution and aqueous solution to the first extraction unit.

[0101] The conditions and duration of extracting **104** should be sufficient to transfer at least a portion of the one or more cycloalkanes to be extracted (e.g., cyclohexane, methylcyclohexane, and methylcyclopentane) from the petroleum solution to the aqueous solution of cucurbituril. In some embodiments, extracting **104** proceeds under ambient conditions (e.g., ambient temperatures and pressures) to reduce or minimize the energy requirements of, and the energy consumed by, the liquid-liquid extraction process. For example, in some embodiments, the petroleum solution and aqueous extractant are contacted at ambient temperatures. In some embodiments, ambient temperatures include temperatures of about 25° C.±5° C. In some embodiments, the petroleum solution and aqueous extractant are contacted at ambient pressures. In some embodiments, ambient pressures include atmospheric pressures. In some embodiments, the contacting duration can range from a few seconds to weeks. In some embodiments, the duration of the contacting is at least, about, or between any two of 5, 10, 15, or 20 minutes. In some embodiments, the contacting of the petroleum solution and aqueous extractant includes or is followed by a settling period of any duration.

[0102] In some embodiments, the percent transferred of the one or more cycloalkanes to be extracted (e.g., cyclohexane, methylcyclohexane, and methylcyclopentane) from the petroleum solution to the aqueous solution at least, about, or between any two of 90%, 90.5%, 91%, 91.5%, 92%, 92.5%, 93%, 93.5%, 94%, 94.5%, 95%, 95.5%, 96%, 96.5%, 97%, 97.5%, 98%, 98.5%, 99%, 99.5%, or 100%. In some embodiments, the percent transferred is any incremental value or

subrange between 0% and 99%.
[0103] In some embodiments, the percentage transferred of the cucurbituril macrocycle from the aqueous solution to the petroleum solution is less than, about, or between any two of 0.5%, 1%, 2%, 3%, 4%, or 5%. In some embodiments, the percent transferred of the cucurbituril macrocycle from the aqueous solution to the petroleum solution is less than 20%, or any incremental value or subrange between 0% and 20%.
[0104] Optional recovering **106** includes recovering at least a portion of the one or more extracted cycloalkanes (e.g., cyclohexane, methylcyclohexane, and methylcyclopentane) from the first aqueous phase using an organic solution to produce a second aqueous phase and a second organic phase. In this step, at least a portion of the one or more extracted cycloalkanes are transferred from the first aqueous phase to the organic solution using an organic solvent which is selective for the extraction of the one or more extracted cycloalkanes (e.g., cyclohexane, methylcyclohexane, and methylcyclopentane) thereby producing an organic solution (e.g., as the second organic phase) in which the one or more extracted cycloalkanes (e.g., cyclohexane, methylcyclohexane, and methylcyclopentane) are the majority component and the aqueous cucurbituril (e.g., as the second aqueous phase) is regenerated and can be recycled and reused in an additional one or more extraction/separation cycles.
[0105] The organic solution can be selected to break or at least weaken the non-covalent interactions stabilizing or binding the one or more extracted cycloalkanes (e.g., cyclohexane, methylcyclohexane, and methylcyclopentane) within the cavity of the cucurbituril macrocycle (e.g., so as to release said cycloalkane from the cavity of the cucurbituril macrocycle). The organic solution can include a single organic solvent or the organic solution can include a mixture of organic solvents. In some embodiments, the organic solution can include one or more of DCM, p-xylene, o-xylene, cyclooctane, bromocyclohexane, or a mixture thereof.
[0106] The second organic phase can include the organic solution and the portion of the one or more extracted cycloalkanes (e.g., cyclohexane, methylcyclohexane, and methylcyclopentane) transferred from the first aqueous phase.
[0107] Gas chromatograph measurements, among other measurements, can be carried out to determine the relative amount of the one or more cycloalkanes in the second organic phase. For example, in some embodiments, the one or more cycloalkanes include at least, about, or between any two of 90%, 91%, 92%, 93%, 94%, 95%, 96%, 97%, 98%, 99%, or 100% cyclohexane, methylcyclohexane, methylcyclopentane, or some combination of the three.
[0108] The second aqueous phase can include the aqueous solution of cucurbituril less the portion of the one or more cycloalkanes transferred to the organic solution and/or second organic phase. In some embodiments, the second aqueous phase is substantially free of the one or more extracted cycloalkanes, thus regenerating the aqueous solution of cucurbituril which can be recycled and/or reused in additional extraction cycles. In some embodiments, the second aqueous phase is substantially free of at least one of the following cycloalkanes: cyclohexane, methylcyclohexane, and methylcyclopentane. In other embodiments, the second aqueous phase can include trace amounts or less than 5% by weight or volume of cycloalkanes not transferred to the organic solution and/or second organic phase.
[0109] Recovering **106** can be performed by extracting the extracted cycloalkane into the organic solution from the first aqueous phase. For example, in some embodiments, recovering **106** can be performed by contacting the first aqueous phase and the organic solution. The contacting can proceed simultaneously (e.g., substantially simultaneously) or sequentially in any order. In some embodiments, recovering **106** can include admixing the first aqueous phase and the organic solution. In some embodiments, recovering **106** can include agitating the first aqueous phase and the organic solution. In some embodiments, recovering **106** can include mechanically mixing the first aqueous phase and the organic solution. In some embodiments, recovering **106** can include combining the first aqueous phase and the organic solution in a second extraction unit. In some

embodiments, recovering **106** can include feeding the first aqueous phase and the organic solution to a second extraction unit. In some embodiments, recovering **106** can include adding the first aqueous phase and the organic solution to the second extraction unit. In some embodiments, prior to performing recovering **106**, the first aqueous phase and the first organic phase can be separated by centrifugation, filtration, or other similar processes.

[0110] Recycling **108** includes recycling the second aqueous phase produced in recovering **106** and extracting **104**. The aqueous solution of cucurbituril can be regenerated in during recovering **106** through decomplexation of the cucurbituril macrocycle and the one or more cycloalkanes and transfer of the one or more cycloalkanes from the first aqueous phase to the organic solution and/or second organic phase. The second aqueous phase can include the regenerated aqueous solution of cucurbituril which can be recycled **108** for reuse in extracting **104**, during one or more extraction cycles. In some embodiments, prior to performing recycling **108**, the second aqueous phase and the second organic phase can be separated by centrifugation, filtration, or other similar processes.

[0111] In some embodiments, the liquid-liquid extraction process for separating cycloalkanes can include a single step in which the aqueous solution of cucurbituril is contacted with a cycloalkane, wherein the cucurbituril macrocycle and the cycloalkane form a host-guest complex in which the cycloalkane at least partially resides in the cavity of the cucurbituril macrocycle.

[0112] While cycloalkanes are described herein as forming host-guest complexes with the cucurbituril macrocycle, the cucurbituril macrocycle can be selective for hydrocarbons other than cycloalkanes. For example, in some embodiments, the cucurbituril macrocycle is selective for aromatic hydrocarbons. Notably, however, the cucurbituril macrocycle is more selective for cycloalkanes than other hydrocarbons typically found in petroleum solutions, including aromatic hydrocarbons among many others. The selectivity of the cucurbituril macrocycle can be dependent on a variety of different factors, such as thermodynamics, complexation kinetics, dimensional aspects, and so on. For example, factors such as complexation binding constants (K.sub.a), decomplexation rate constants (K.sub.l), aspect ratios based on dimensions (a/b), and the like can be modified and/or adjusted to modulate the selectivity of the cucurbituril macrocycle for hydrocarbons other than cycloalkanes.

[0113] The liquid-liquid extraction process is general and thus the implementation of the liquid-liquid extraction process is not particularly limited. The liquid-liquid extraction process can be implemented using various extraction systems. For example, the liquid-liquid extraction processes can be implemented using extraction towers, mixer-settlers, single-stage unit operations, and/or multi-stage unit operations, such as countercurrent multi-stage cascades. The manner in which the liquid-liquid extraction process is carried out is also not particularly limited. For example, in some embodiments, the liquid-liquid extraction process is implemented in a system operating as a continuous process. In some embodiments, the liquid-liquid extraction process is implemented in a system operating as a batch process. In some embodiments, the liquid-liquid extraction process is implemented in a system operating as a semi-continuous and/or semi-batch process in which at least one unit operation of said system is operated as a continuous process and/or at least one unit operation of said system is operated as a batch process.

[0114] One example of an implementation of the liquid-liquid extraction process is shown in FIG. **2**, which is a schematic diagram of a liquid-liquid extraction system **200** for separating cycloalkanes from petroleum solutions, in accordance with one or more embodiments of the present invention. As shown in FIG. **2**, the liquid-liquid extraction system can comprise a first extraction tower **202** and a second extraction tower **204**. In the illustrated embodiment, the second extraction tower **204** is provided downstream of the first extraction tower **202**. Although not shown, the liquid-liquid extraction system **200** can optionally further comprise other auxiliary components (not shown) including, for example and without limitation, conduits, pipes, diverters, pumps, control systems, sensors, valves, and the like.

[0115] The first extraction tower **202** can be in fluid communication with inlet **210**, inlet **215**, outlet

220, and outlet **225**. In some embodiments, the petroleum solution can enter the first extraction tower **202** through inlet **210**. In some embodiments, the aqueous solution of cucurbituril (and/or second aqueous phase from the first extraction tower **204**) can enter the first extraction tower **202** through inlet **215**. In some embodiments, the first organic phase can exit the first extraction tower **202** through outlet **220**. In some embodiments, the outlet **220** can be in fluid communication with inlet **210** and the first organic phase can be recycled to the first extraction tower **202** for one or more extraction cycles. In some embodiments, the first aqueous phase can exit the first extraction tower **202** through outlet **225** and, from the first extraction tower, the first aqueous phase can be directed to the second extraction tower **204** via inlet **225** which can be the same as outlet **225**.
[0116] The second extraction towner can be in fluid communication with inlet **225**, inlet **230**, outlet **215**, and outlet **235**. In some embodiments, inlet **225** is the same as outlet **225** and the first aqueous phase from the first extraction tower **202** can enter the second extraction tower **204** through inlet **225**. In some embodiments, the organic solution enters the second extraction tower **204** through inlet **230**. In some embodiments, the second aqueous phase can exit the second extraction tower **204** through outlet **215** and, from the second extraction tower, the second aqueous phase can be directed to the first extraction tower **204** via inlet **215** which can be the same as outlet **215**. In some embodiments, the second organic phase can exit the second extraction tower **204** through outlet **235** and, from the second extraction towner **204**, the second organic phase can be directed to other unit operations (not shown) for further processing and/or storage. For example, in some embodiments, further processing of the second organic phase includes isolating or separating the one or more cycloalkanes from the organic solvent via evaporation, distillation, and other separation processes.
[0117] In one embodiment, the liquid-liquid extraction towner **200** includes a first extraction tower **202**, a second extraction tower **204** downstream from the first extraction towner **202**, and optionally one or more of the auxiliary components discussed above. The first extraction tower **202** can be in fluid communication with petroleum solution feed stream **210**, cucurbituril recycle stream **215**, organic raffinate stream **220**, and aqueous extract stream **225**. The second extraction tower **204** can be in fluid communication with aqueous extract stream **225**, organic solvent stream **230**, organic raffinate **235**, and cucurbituril recycle stream **215**. The petroleum feed stream **210** can include the petroleum solution. The cucurbituril recycle stream **215** can include the aqueous solution of cucurbituril and/or the second aqueous phase. The organic raffinate stream **220** can include the first organic phase. The aqueous extract stream **225** can include the first aqueous phase. The organic solvent stream **230** can include the organic solution. The organic raffinate **235** can include the second organic phase. The cucurbituril recycle stream **215** can include the second aqueous phase.
[0118] In another embodiment, the liquid-liquid extraction system can include a first extraction tower in fluid communication with a petroleum feed stream and an aqueous cucurbituril feed stream, wherein the petroleum feed stream includes at least one cycloalkane and one other hydrocarbon and wherein aqueous cucurbituril feed stream includes a cucurbituril macrocycle which is selective for the extraction of the cycloalkane; and a second extraction tower downstream from the first extraction tower, the second extraction tower in fluid communication with an aqueous extract stream from the first extraction tower and an organic solvent stream, wherein the aqueous extract stream includes the cycloalkane and cucurbituril macrocycle and wherein the organic solvent stream includes an organic solvent which is selective for the extraction of the cycloalkane.
[0119] CB[7] was dissolved in 300 mL of water to prepare a 5.0 mM CB[7] aqueous solution. Subsequently, 250 ml of Arabian crude oil sample was added to the aforementioned solution in the first extraction tower. After stirring and extraction for 30 min, the water phase was separated from the crude oil phase. The emulsified organic liquid in the water phase could be removed through filtration and stirred for 1 h. Then, 10 mL unemulsified water phase was extracted using CDCl3 for the NM R experiments, while the remaining water phase was extracted in the second extraction

tower using organic solvent like DCM, p-xylene, o-xylene, cyclooctane, or bromocyclohexane for back-extraction.

[0120] FIG. **3** is a schematic diagram of a liquid-liquid extraction system in accordance with one or more embodiments of the present invention. In accordance with the process, CB[7] was dissolved in 300 ml of water to prepare a 5.0 mM CB[7] aqueous solution. Then 250 ml of petroleum solution (Arabian crude oil) was added to the aqueous solution in the first extraction tower. After stirring and extraction for 30 min, the water phase was separated from the crude oil phase. The emulsified organic liquid in the water phase could be removed through filtration and stirred for 1 h. Then, 10 mL unemulsified water phase was extracted using $CDCl_3$ for the NMR experiments, while the remaining water phase was extracted in the second extraction tower using organic solvent like DCM, p-xylene, o-xylene, cyclooctane, or bromocyclohexane for back-extraction. For nuclear magnetic resonance (NMR) experiments, $CDCl_3$ was used as the organic solvent for extraction. After extraction, the organic phase was separated from water phase, and the CB[7] aqueous solution was reused. The NMR and Gas chromatograph (GC) analysis showed the separation efficiency was 92.2% for ortho-xylene, 96.9% for ortho-dichlorobenzene, 96.7% for dibromobenzene, 96.8% for chlorotoluene in one extraction cycle. The aqueous CB[7] solution was able to separate these compounds without any loss in performance after recycling 5 times.

[0121] In some embodiments, a liquid-liquid extraction method is provided for separating and purifying various cyclohexanes using cucurbit[7]uril (CB[7]) aqueous solution. In some embodiments, the separation process achieves more than 93.9% specificity after one extraction cycle at ambient temperature and pressure, particularly achieving 60.3 mol % selectivity for cyclohexane, 16.5 mol % selectivity for methylcyclohexane, and 17.1 mol % for methylcyclopentane. Thermodynamic and kinetic analysis demonstrates that the cyclohexane, methylcyclohexane, and methylcyclopentane can exhibit a stronger binding ability and slower decomplexation constant rate than other hydrocarbons present in petroleum when hosted by CB[7]. Optimized host-guest models simulated by density-functional theory (DFT) calculation indicate that these cycloalkanes are good matches for the spherical interior cavity of CB[7], resulting in highly stable complexes. The method proceeded by a shape-induced separation based on host-guest chemistry with no energy costs, thereby improving the quality and lowering the costs of critical industrial separations.

[0122] The following Examples are intended to illustrate the above invention and should not be construed as to narrow its scope.

EXAMPLES

[0123] In the following examples, an aqueous solution CB[7] was employed as a liquid-liquid extraction solvent and used to separate several cyclohexanes from a petroleum solution. Results indicated that treatment of a crude oil sample with an equal volume of 5.0 mM CB[7] gave rise to the selective extraction of three simple hydrocarbons, CH, MCH, and MCP, in a 60.3:16.5:17.1 mol ratio. This process resulted in a respective 105-, 20-, and 46-fold increase compared to their initial low contents in the crude oil. Due to the distinct boiling points of these three compounds (b.p. 344.9 K for MCP, 353.9 K for CH, and 374.0 K for MCH), they can be easily separated through simple distillation. Additionally, the purity of CH was shown to be enhanced to 99.0% after five successive extractions.

[0124] Example 1. Liquid-liquid extraction experiments. CB[7] was dissolved in 300 ml of water to prepare a 5.0 mM CB[7] aqueous solution. Subsequently, 250 ml sample of petroleum solution (Arabian crude oil) was added to the aforementioned solution in the first extraction tower. After stirring and extraction for 30 min, the water phase was separated from the crude oil phase. The emulsified organic liquid in the water phase could be removed through filtration and stirred for 1 h. Then, 10 mL unemulsified water phase was extracted using CDCl.sub.3 for the NMR experiments, while the remaining water phase was extracted in the second extraction tower using organic solvent like DCM, p-xylene, o-xylene, cyclooctane, or bromocyclohexane for back-extraction.

[0125] Then, the extracted organic phase in the second extraction tower in the first (former) cycle was used as the sample solution for another extraction, wherein a new sample of 300 mL 5.0 mM CB[7] aqueous solution was added to further improve the purity of CH. In some examples, this procedure was repeated successively, with cycles are referred to as “successive extraction” herein.
[0126] This procedure was repeated under varying conditions to investigate the changes in separation performance. In some examples, extraction experiments according to this procedure were carried out by dissolving CB[7] in acidic (pH=1, HCl), basic (pH=14, NaOH), and high salinity (1 mol/L NaCI) aqueous solution, as well as sea water. This procedure was also repeated using CB[5], CB[6], and CB[8] as prepared in 4 M HCl solutions to increase their solubility.
[0127] Example 2. .sup.1H NMR analysis. The .sup.1H NMR spectra of sample solutions were recorded by 600 MHz BRUKER AVANCE III spectrometers using the deuterated solvent as the lock and the residual solvent as the internal reference. In the host-guest experiments, neat liquid hydrocarbons were added into CB[7] D.sub.2O solution (1.0-10.0 mM). The volume of CB[7] D.sub.2O solution was adjusted based on the integration of CB[7] and hydrocarbons to achieve the desired ratio of CB[7] and hydrocarbons. The following solutions were analyzed: petroleum solution (Arabian crude oil), water phase from the first extraction using CB[7], organic phase from the second extraction using CB[7], and pure cyclohexane, methylcyclohexane, and methylcyclopentane dissolved in CDCl.sub.3. FIG. **4** depicts the .sup.1H NMR spectra of the following four samples: i. petroleum solution (Arabian crude oil), ii. water phase from the first extraction, iii. organic phase from the second extraction, and pure cyclohexane, methylcyclohexane, and methylcyclopentane dissolved in CDCl.sub.3.
[0128] Example 3. GC-MS analysis. Gas chromatography-mass spectrometry (GC-MS) analysis was performed on the following solutions: petroleum (Arabian crude oil); water phase from the second extraction using CB[7]; standard samples of n-hexane, methylcyclopentane, benzene, cyclohexane, n-heptane, methylcyclohexane, and toluene; water phase from the second extraction using CB[7] at pH 14; water phase from the second extraction using CB[7] at pH 1; water phase from the second extraction using CB[7] in 1.0 M NaCl solution; water phase from the second extraction using CB[7] in a seawater solution; water phase from the second extraction using CB[5] in 4 M HCl solution; water phase from the second extraction using CB[6] in 4 M HCl solution; and water phase from the second extraction using CB[8] in 4 M HCl solution.
[0129] GC-MS analysis was performed using an Agilent 7890A gas chromatography machine with both flame ionization detector (FID) and quadrupole mass spectrometer (Agilent 5975 CM SD). Samples were injected into the split inlet with 10:1 split ratio under 250° C. The sample was further separated on a DB-1MS column (30 m×0.25 mm×0.25 μm). The oven was programmed at 35° C. with 10 min hold, ramped at 5° C. min-1 increments to 90° C. and then 30° C. min-1 increments to 280° C., the total run time was 27.3 min; injection temperature was 250° C.; detector temperature was 300° C. with hydrogen, air, and make-up flow-rates of 35, 300, and 30 mL min-1, respectively; the helium (carrier gas) flowrate was 1.2 mL min-1 and septum purge flow 3.0 mL min-1. The elutes were separated into 2 flows, for FID and MSD separately, after the column separation. The MSD peaks were used for structural elucidation by searching from NIST GC-MS database, and FID signals were used for quantitative analysis. Note: Due to a break in the DB-1M S column (30 m×0.25 mm×0.25 μm) during testing, the peak of CH in some GC-M S spectra has shifted from 4.6 min to 3.8 min. The peaks of other hydrocarbons have also shifted accordingly.
[0130] FIG. **5**A depicts three GC-MS spectra of a petroleum solution (labelled “Crude oil”), organic phase solution from the second extraction using CB[7] (labelled “After separation”), and standard samples of n-hexane, methylcyclopentane, benzene, cyclohexane, n-heptane, methylcyclohexane, and toluene. (labelled “Standard samples”). FIG. **5**B depicts an expanded view of the three GC-MS spectra of FIG. **5**A. FIG. **5**C depicts the GC-MS spectrum of water phase from the second extraction using CB[7] at pH 14. FIG. **5**D depicts the GC-MS spectrum of water phase from the second extraction using CB[7] at pH 1. FIG. **5**E depicts the GC-MS spectrum of water

phase from the second extraction using CB[7] in 1.0 M NaCl solution. FIG. **5**F depicts the GC-M S spectrum of water phase from the second extraction using CB[7] in a seawater solution. FIG. **5**G depicts the GC-M S spectrum of water phase from the second extraction using CB[5] in 4 M HCl solution. FIG. **5**H depicts the GC-M S spectrum of water phase from the second extraction using CB[6] in 4 M HCl solution. FIG. **5**I depicts the GC-MS spectrum of and water phase from the second extraction using CB[8] in 4 M HCl solution.

[0131] Example 4. Single crystal growth of host-guest complex samples. 20 mg of CB[7] was dissolved in 2 mL water. 100 uL of hydrocarbon was added and the mixture was vigorously shaken to make an emulsion. The resulting solution was slowly evaporated in oven at 85° C. To gain a deeper insight into the complexation of CH and CB[7], crystallization of the host-guest complex was achieved. Single crystal X-ray diffraction (SCXRD) analysis showed that CH@CB[7] crystallized with two types of 1:1 host-guest complexes in the asymmetric unit cell (see FIGS. **6**A-F). A close inspection of the crystal structure of CH@CB[7] revealed that one CH is lying flat and the other is tilted at a 62° angle within the cavity of CB[7]. Both the CH molecules are in an energy-minimum chair conformation and located in the hydrophobic cavity of CB[7]. Additionally, single crystals of host-guest complexes were obtained between CB[7] and other cyclic hydrocarbons, e.g. MCP@CB[7], MCH@CB[7], and cyclooctane@ CB[7]. In all of these single crystal structures, all the guest molecules occupy their lowest energy or near lowest energy conformation and are located in the cavity of CB[7].

[0132] The most significant driving force of CB[7] to bind guest molecule in water phase is the hydrophobic effect, which is reflected with the ability of removing high-energy water molecule from the cavity of CB[7]. Molecular dynamics (MD) simulations have revealed that CH can effectively remove all high-energy water molecules from the cavity of CB[7], whereas n-hexane and Ben exhibit partial removal capabilities. This discrepancy can be attributed to the spherical shape of cyclic hydrocarbons, which allows them to better fit within the spherical cavity of CB[7] compared to linear hydrocarbons and oblate aromatic hydrocarbons. These findings are consistent with binding constant measurements.

[0133] Example 5. Binding Constant Determination by Fluorescent experiments. Due to the extremely low water solubility of hydrocarbons, it is very challenging to obtain binding constants through direct host-guest complexation titration. In previous studies, researchers used a fluorescent dye displacement method to test the binding constant of hydrocarbons with CB[6] or CB[7] in an acidic solution (pH=3). They introduced hydrocarbon gas into a mixed solution of CB[n] and dye and then calculated the binding constant of hydrocarbon with CB[n] by monitoring the fluorescence changes of the system. This process has been by the procedure by utilizing Berberine Chloride (BC), a pH insensitive fluorescent dye known to have a strong binding affinity with CB[7].

[0134] Firstly, direct fluorescent titration at 298K was performed to retest the binding constant of BC and CB[7], producing a binding constant 2.3×10.sup.7 M.sup.−1 in H.sub.2O for a 1:1 host-guest binding mode. Subsequently, BC was mixed with hydrocarbon aqueous solutions and introduced concentrated CB[7] into the solution. The binding constants of CB[7] towards hydrocarbon were calculated by fitting the change of fluorescence emission intensity versus the concentration of CB[7] to a competitive binding model in Scientist™. Moreover, this method allows for the qualitative determination of the binding constant of hydrocarbon (HC) and CB[7] based on the shape of the curve. Specifically, if the binding constant of HC@CB[7] is higher than that of BC@CB[7], the curve will exhibit an “S” shape. Conversely, if the binding constant of HC@CB[7] is similar to that of BC@CB[7], the curve will be a polyline. Finally, if the binding constant of HC@CB[7] is lower than that of BC@CB[7], the curve will be a “C” shape.

[0135] FIG. **7** illustrates a graph showing the results of fluorescence titration while adding CB[7] to the mixture of CH and BC. The graph displays a typical S-shaped curve, indicating that the complexation constant is greater than that of BC with CB[7]. After calculation, the binding

constant of CH@CB[7] was determined to be 2.5×10.sup.9 M.sup.−1.
[0136] FIG. **8** displays a chart showing results of other fluorescence titration using C5-C8 hydrocarbons with CB[7], wherein binding constants are expressed as Log(K.sub.a) and hydrocarbons are graphically depicted and arranged by molecular weight. The results suggest that cyclic hydrocarbons have stronger binding affinity with CB[7] than other branched, linear, and aromatic hydrocarbons. This observation can most probably be ascribed to the shape of cyclic hydrocarbons, which fitted better within the spherical cavity of CB[7].
[0137] FIG. **9**A illustrates a 3-dimensional chart showing binding constants of CB[7] with different hydrocarbons multiplied by water solubility against number of carbon molecules contained therein, wherein a-h differentiate hydrocarbons with shared number of carbon molecules. Likewise, FIG. **9**B illustrates a 3-dimensional chart showing binding constants of CB[7] with different hydrocarbons multiplied by water solubility and hydrocarbon content in petroleum solutions/crude oil against number of carbon molecules contained therein, wherein a-h differentiate hydrocarbons with shared number of carbon molecules. Notably, these figures show cyclohexane having the highest calculated value, with methylcyclohexane and methylcyclopentane close behind in both. These results clearly help explain why CB[7] can be utilized to selectively separate cyclic hydrocarbons, especially cyclohexane, methylcyclohexane, and methylcyclopentane from petroleum solutions/crude oil.

Claims

1. A method of separating cycloalkanes comprising: contacting a petroleum solution including one or more cycloalkanes with an aqueous solution including a cucurbituril macrocycle to produce a first aqueous phase and a first organic phase, wherein the cucurbituril macrocycle is selective for extraction of at least one of the one or more cycloalkanes.
2. The method according to claim 1, wherein the one or more cycloalkanes includes one or more of cyclohexane, methylcyclohexane, and methylcyclopentane.
3. The method according to claim 1, wherein the petroleum solution further contains one or more of linear hydrocarbons, branched hydrocarbons, and aromatic hydrocarbons and wherein the cucurbituril macrocycle is selective for the extraction of at least one of the one or more cycloalkanes over the one or more of linear hydrocarbons, branched hydrocarbons, and aromatic hydrocarbons.
4. The method according to claim 1, wherein the cucurbituril macrocycle has the following chemical structure: ##STR00005## wherein: a.sup.1 indicates a point of attachment to b.sup.1; a.sup.2 indicates a point of attachment to b.sup.2; n is 1-20; X is O, S, or NH; and R.sup.1 and R.sup.2 are independently selected from the group consisting of hydrogen, H, optionally substituted C.sub.1-C.sub.30 alkyl group; optionally substituted C.sub.2-C.sub.30 alkenyl group; optionally substituted C.sub.2-C.sub.30 alkynyl group; optionally substituted C.sub.2-C.sub.30 carbonylalkyl group; optionally substituted C.sub.1-C.sub.30 thioalkyl group; optionally substituted C.sub.1-C.sub.30 alkylthiol group; optionally substituted C.sub.1-C.sub.30 hydroxyalkyl group; optionally substituted C.sub.1-C.sub.30 alkylsilyl group; optionally substituted C.sub.1-C.sub.30 aminoalkyl group; optionally substituted C.sub.1-C.sub.30 aminoalkylthioalkyl group; optionally substituted C.sub.5-C.sub.30 cycloalkyl group; optionally substituted C.sub.2-C.sub.30 heterocycloalkyl group; optionally substituted C.sub.6-C.sub.30 aryl group; optionally substituted C.sub.6-C.sub.30 arylalkyl group; optionally substituted C.sub.4-C.sub.30 heteroaryl group; and optionally substituted C.sub.4-C.sub.30 heteroarylalkyl group.
5. The method according to claim 4, wherein n is 7.
6. The method according to claim 4, wherein n is 6.
7. The method according to claim 4, wherein n is 7.
8. The method according to claim 4, wherein X is 0.

9. The method according to claim 4, wherein R.sup.1 and R.sup.2 are H.
10. The method according to claim 1, wherein contacting the petroleum solution with the aqueous solution causes at least a portion of the at least one of the one or more cycloalkanes to be transferred from the petroleum solution to the aqueous solution.
11. The method according to claim 10, wherein the portion of the at least one of the one or more cycloalkanes is transferred from the petroleum to the aqueous solution through formation of a host-guest complex comprising a host and a guest and wherein the cucurbituril macrocycle is the host and the portion of the at least one of the one or more cycloalkanes is the guest.
12. The method according to claim 11, wherein the first aqueous phase includes the host-guest complex; and wherein the first organic phase includes the petroleum solution, the petroleum having a reduced concentration of the at least one of the one or more cycloalkanes.
13. The method according to claim 12, further comprising recovering at least a portion of the at least one of the one or more cycloalkanes from the first aqueous phase using an organic solution to produce a second aqueous phase and a second organic phase.
14. The method according to claim 13, wherein the second aqueous phase includes at least a portion of the cucurbituril macrocycle from the first aqueous phase, and wherein the second organic phase includes the portion of the at least one of the one or more cycloalkanes recovered from the first aqueous phase.
15. The method according to claim 14, further comprising recycling the second aqueous phase for use in one or more separation cycles.
16. A liquid-liquid extraction solvent comprising: an aqueous solution of a cucurbituril macrocycle, wherein the cucurbituril macrocycle is selective for the extraction of at least one cycloalkane and wherein the cucurbituril has the following chemical structure: ##STR00006## wherein: a.sup.1 indicates a point of attachment to b.sup.1; a.sup.2 indicates a point of attachment to b.sup.2; n is 1-20; X is O, S, or NH; and R.sup.1 and R.sup.2 are independently selected from the group consisting of hydrogen, H, optionally substituted C.sub.1-C.sub.30 alkyl group; optionally substituted C.sub.2-C.sub.30 alkenyl group; optionally substituted C.sub.2-C.sub.30 alkynyl group; optionally substituted C.sub.2-C.sub.30 carbonylalkyl group; optionally substituted C.sub.1-C.sub.30 thioalkyl group; optionally substituted C.sub.1-C.sub.30 alkylthiol group; optionally substituted C.sub.1-C.sub.30 hydroxyalkyl group; optionally substituted C.sub.1-C.sub.30 alkylsilyl group; optionally substituted C.sub.1-C.sub.30 aminoalkyl group; optionally substituted C.sub.1-C.sub.30 aminoalkylthioalkyl group; optionally substituted C.sub.5-C.sub.30 cycloalkyl group; optionally substituted C.sub.2-C.sub.30 heterocycloalkyl group; optionally substituted C.sub.6-C.sub.30 aryl group; optionally substituted C.sub.6-C.sub.30 arylalkyl group; optionally substituted C.sub.4-C.sub.30 heteroaryl group; and optionally substituted C.sub.4-C.sub.30 heteroarylalkyl group.
17. The solvent according to claim 16, wherein n is 7.
18. The solvent according to claim 16, wherein X is 0.
19. The solvent according to claim 16, wherein R.sup.1 and R.sup.2 are H.