



Extraction of Kerogen from Oil Shale using Mixed Reversible Ionic Liquids

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Abstract--Numerous of the separation issue usually accompanying with traditional ionic liquids can solve with Reversible ionic liquids. It can be forth and reversed back between ionic and molecular forms empowering superficial separations by means of considerable changes in situ property. This leads to actually sustainable processes. A comprehension of the systems phase behavior gives frameworks into the ability of separation.

To our knowledge, the experimental information available in the literature for mixtures containing the pair Kerogen- Reversible Ionic Liquids (RevIL) is limited. Thus the objective of the current investigation is to produce data for Kerogen with different Reversible Ionic Liquids RevIL solvents to aid the extraction efficiency.

The samples of Oil Shale collected from real Iraqi sedimentary rock deposits. Four Reversible Ionic Liquids solvents 3-(triethoxysilyl)-propylammonium 3-(triethoxysilyl)-propyl carbamate (TESAC), (3-(tripropylsilyl)-propylammonium 3-(tripropylsilyl)propyl carbamate (TPSAC), 3-(trimethoxysilyl)-3-(trimethoxysilyl)-propyl propylammonium (TMSAC), carbamate 3-(triethylsilyl)propylammonium 3-(triethylsilyl)-propyl carbamate (TEtSAC)) are derived from carbon dioxide which reacts reversibly with silvlated amine molecular liquids to produce ionic liquids.

The efficiency of four Reversible Ionic Liquids (TEtSAC, TMSAC, TPSAC, and TESAC) and for mixed Reversible ionic liquid (Binary mixtures) as a selective solvent in the kerogen extraction from oil shale was investigated.

The extraction efficiency was found to be more dependent on the basicity strength of hydrogen bond of the RevIL. It was found that higher extraction efficiencies are accompanied with higher hydrogen bond basicity.

Four single RevILs and three binary mixtures (RevIL) to extract the Kerogen from oil shale is used, one mixed binary solvent (TESAC+TMSAC) has the highest distribution coefficient, extraction efficiency and selectivity and greatest variation between its density and boiling point and those of Kerogen is selected. Therefore it can be considered as an excellent extracting solvent for Kerogen from oil shale.

Keywords: Kerogen, Oil Shale, Reversible Ionic Liquids, Extraction.

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I. Introduction

Oil shale is one type of sedimentary rock when exposed to temperatures up to 500 °C by destructive distillations forms liquid oil-like hydrocarbons the method is called retorting. Oil shales is composite of three portions, kerogen which it waxy, organic solid substance insoluble inorganic solvents and CO₂ because of molecules of kerogen its size is large and can include vanadium, molybdenum, iron, and uranium, four types of kerogen depends on H/C ratios (hydrogen contents), bitumens which it soluble in CO₂, and inorganic matrix[1,2].

Because of alternative sources of energy must sophisticated and the world economy growth, It is indispensable to find new experiments and new solvents concerning the recover of Kerogen (unconventional resources), i.e., developing new economical technology to extract Kerogen from oil shale [3-5]. Presently, steam has been used to recover Kerogen from oil shale, the disadvantage of the process is generating big amounts of polluted wastewater and intensive of energy. The second method of recovery by using distillation with organic solvent, the disadvantage of this method is along with the solvent, low-end carbon fractions will be distilled from the Kerogen and its intensive of energy.Recently, new solvent separation technique (Switchable ionic liquids) the advantage of this method is environmentally friendly and efficient of energy, first, blending the Kerogen with molecular liquid permits oil's contaminants to filtrate. Second, when ionic liquid was formatted, phase separation established between the solvent and Kerogen phase. Final, the ionic liquid is return to its molecular liquid state and recycled [6-10].

The Reversible ionic liquids (RevIL) are arised from silylated amines. These configurations are illustrated in Fig. 1. At 1 atm, ionic liquids are formed from reaction of carbon dioxide (CO₂) with molecular liquids. Upon sparging N_2 with the ionic liquids or heating to release CO₂, it returns to molecular liquids form.[11-13].

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Fig. 1. scheme for Reversible Ionic Liquid solvent system

The objective of this research is to recover Kerogen from oil shale using different Reversible Ionic Liquids RevIL solvents. We present new experimental data for different systems including Kerogen + Reversible Ionic Liquids RevIL solvent. Different RevIL solvents were used, 3-(tripropylsilyl)-propylammonium 3-(tripropylsilyl)propyl carbamate (TPSAC), 3-(triethylsilyl)propylammonium 3-(triethylsilyl)-propyl carbamate (TEtSAC), 3-(trimethoxysilyl)-propylammonium 3-(trimethoxysilyl)-propyl carbamate (TMSAC), and 3-(triethoxysilyl)-propylammonium 3-(triethoxysilyl)-propyl carbamate (TESAC) created from the corresponding molecular liquid (precursors) (3-aminopropyl)-triethylsilane (TEtSA), (3aminopropyl)-trimethoxysilane (TMSA). (3aminopropyl)-tripropylsilane (TPSA), and (3aminopropyl)-triethoxysilane (TESA). There is no literature data to our knowledge on the binary mixture of Reversible Ionic Liquids RevIL solvent systems studied.

II. Experimental Section 2.1 Chemicals

In a nitrogen atmosphere closure the following chemicals were stockpiled: TESA, (3-aminopropyl)-triethoxysilane (Fluka, 97%); TMSA, (3-aminopropyl)-trimethoxysilane (Aldrich, 99+%); TEtSA, (3-aminopropyl)-triethylsilane (Aldrich, 98%); TPSA, (3-aminopropyl)-tripropylsilane (Aldrich, 99%).CO₂ was Supercritical Fluid Chromatography grade (99.999%) and extra purified to eliminate impurities and water trace through filter cartridge (Model 450B, Type 451 filter) and a Matheson gas purifier. The Oil Shale samples were collected from real Iraqi sedimentary rock deposits

2.2 Changes of Property

The reversible ionic liquids viscosities rely on molecular structure. Fig. 2 illustrates the reversible ionic liquids of TEtSAC, TPSAC, TMSAC, and TESAC. Viscosities measurements were done by using rheometer type Anton Paar (Physica MCR 301, Graz, Austria), and the behavior of Newtonian fluids were found for all liquids. The viscosities under 10 cP were found for every molecular liquids utilized; an extreme change in viscosity is noticed as the ionic liquid is created.



Fig. 2. Viscosity of the reversible ionic liquids

Polarity increased when molecular liquid reacted to form ionic liquid. The solvent polarity change used to increase separations as various organics are insoluble in the ionic liquid forms (heterogeneous mixture) but soluble in the molecular liquids forms (homogeneous mixture). Inverting temperature of Ionic liquid is the largest participant for lowering cost of process. The ionic liquids inverting temperatures investigated were: 150 °C for TPSAC,110 °C for TESAC, 146 °C for TEtSAC, and 145 °C for TMSAC.







Fig. 3. Process flow diagram for the recyclable extraction of Kerogen from Oil shale using reversible ionic liquids

2.3 Apparatus and Procedures

Reversible ionic liquids RevIL have capability to provide for effective separation of Kerogen from Oil Shale via filtration and then recycle of solvent upon splitting of Kerogen phase (phase of product) from the ionic liquids (phase of solvent). Fig. 3 shows flow diagram of a proposed process.

The property switch was a decisive asset in improving a designing for the Kerogen extraction from oil shale. At beginning oil shale was milled to approximately 0.2 mm of a particle size. No particle sizes larger 0.2 mm has been study yet. All the vessels of reaction loaded in a nitrogen filled closed chamber preserve at less than 10 ppm combined H_2O and O_2 .

Reaction of CO_2 bubbles through silvlated amines (Molecular precursors) at room temperature is exothermic, which proceeds within minutes until the reaction is completion.

Kerogen was miscible with similar volume of molecular liquid (TESA), while the RevIL counterpart (TESAC) was immiscible Kerogen. Sudden variation in polarity of solvent permitted to improve the strategy of extraction and solvent system recycle for superior efficiency of process and cost phase finally become lower.Product contamination with ionic liquid was noticed along three cycles and stayed through every cycle lower than 4 mol%. The proposed process was beneficial economically in contrast with Steam explosion route technology.

2.5 Proposed Process Scale-Up

The TESA (molecular liquid) was mixed with Oil shale and sand was separated off. The Oil shale composition was supposed to be 20 wt.% hydrocarbons and the residue Oil shale. The mass ratio of mixture Kerogen to TESA is 50:50 which feeding to the first conversion reactor. to begin the forward reaction in the the reactor. stoichiometrically CO₂ was added. The exit streams temperature of the exothermic forward reaction was 42 °C, and 100% completion was set out to the forward conversion. In a decantation step using a splitter, 4 mol.% was taken of the ionic liquid along with the product (Kerogen); the residual ionic liquid feed enter to a second conversion reactor supposed to be Kerogen free. From experimental findings, the reverse reaction temperature occurs at 110 °C.At this step, in the mixer (Oil shale / molecular liquid), TESA were recycled back and reused and CO₂ leaves. TESA and Kerogen has been three times recycled to improve separation capability quantify of the proposed process. Fifty-eight million barrels per year produced of Kerogen which is typical to refinery of great capacity. Hence, the proposed process (solvent technology) notably low expensive than the steam explosion route

III. Results and Discussion

3.2 Determination of Extraction Efficiency

Fifty weight percent of Kerogen was added into TESA to produce homogeneous system. Filtration is necessary at this point eliminate sand, salts and any contaminants. After bubbling CO_2 till the exothermic reaction was completed, the homogeneous phase becomesviscous more, an indication of theformation of the ionic liquid. To accelerate the solution separation between the ionic liquid phase (polar) and Kerogen phase (non-polar), the centrifuge has been used. The necessity of the centrifuge step, because of the high values viscosities of system Kerogen- ionic liquid and to analogous densities between the ionic liquid and the Kerogen.







Fig.4. Extraction Efficiency of Kerogen using different RevILs as single solvent

Three times the cycle was repeated by reintroducing Kerogen. Three times was repeated the recycle experiment, and three runs averaged values of separation efficiency were reported.

Kerogen extraction efficiency is determined by the concentration of kerogen in each phase. The extraction efficiency is calculated using Eq.(1):

Extraction Efficiency % =
$$\frac{C_i - C_{f,i}}{C_i} \times 100$$
 (1)

Where:

 C_i = Initial concentration. $C_{f,t}$ = feed samples Concentration with time [14].

3.3 Influence of various kinds of Reversible Ionic Liquids

The influence of various Reversible Ionic Liquids RevIL as solvent in both conditions (binary and single mixture) was studied. There were various factors influence efficiency of extraction such asviscosity, polarity of solvent and other physical properties of the solvent influence on the extractant efficiencies. The properties of solvent of RevIL are determined fundamentally by the charges on the anions (the degree of localization), beside the salt ability to act as hydrogen bond acceptor and/or donor. Furthermore, the major factors that effect on the RevIL physical properties are ability of H- bonding; the anions charge distributions and interactions of dispersive.

3.3.1 Influence of Single RevIL on the Efficiency of Extraction

The RevIL TESAC, TMSAC, TEtSAC and TPSAC were used as solvents. Fig. 4 illustrates that efficiency of extraction of kerogen was in the following arrangement:

The efficiency of extraction was dependent on the hydrogen bond basicity strength of the RevIL. It was found that higherefficiencies of extraction areaccompanied with higher hydrogen bond basicity.

3.3.2 Influence of Binary Mixture RevIL on the Extraction Efficiency

The efficiency of extraction of kerogen using Binary Mixture RevIL is shown in Fig. 5. There is no data were published to our knowledge on Binary Mixture RevIL systems. The extraction efficiency is strongly influenced by the hydrogen bond basicity strength of the ILs. Fig. 5, shows that the extraction efficiency in Binary Mixture RevIL was higher than Single RevIL since hydrogen bonding between ILs and Kerogen molecular joins single anion in the case of Single RevIL while in binary mixture RevIL joins two anions.







Fig.5. Extraction Efficiency of Kerogen using different RevILs as binary mixture

Higher distribution ratios are experimenting with longer length of alkyl chain on the cation of the RevIL. The efficiency of extraction of Kerogen using binary mixture RevILs is varied in following arrangement:

TESAC+TMSAC > TESAC+TEtSAC > TESAC+TPSAC.

The ionic liquid overall ability to form with a solute molecule a hydrogen bond comes from an adversary relationship between its constituent ions. The cations and anions interactions too complex in ILs; they include not only van der Waals interactions but also dipole-dipole derived interactions and other Coulombic interactions. Although, The factual reason for this observation stays indistinct.

IV. Conclusions

Numerous of the separation problems associated with traditional ionic liquids can be solve with Reversible ionic liquids. The unparalleled switchable capability of RevIL systems permit into a single unit operation for coupling separations and reactions as described for Kerogen extract from oil shale (recyclable solvent). The separation and recycle are viable due to the change in solvent properties change, as the non-ionic liquid is converted to ionic liquid.

Contamination less than 4 mol. % for Kerogen recovery from oil shale was found in product stream using RevIL solvents. There is a great earning and a strong amelioration over existing technologies when scale-up the process. Four single RevILs, three binary mixture RevILs to extract the Kerogen from oil shale, mixed binary solvent (TESAC+TMSAC) shows highest distribution coefficient and selectivity, and extraction efficiency. The greatest variations between its density and boiling point and those of Kerogen make there an excellent solvent for extracting Kerogen from oil shale.

References

[1] M.D.Fenton, H.Henning, R.L.Ryden, *Oil Shale, Tar Sands and Related Materials*. Washington, D.C.: American Chemical Society;1981.

[2] T.F.Yen,G.V.Chilingarian,*Oil Shale*. Amsterdam: Elsevier;1976.

[3] E.Knaus, J.Killen, K.Biglarbigi, Crawford Peter, *An Overview of Oil Shale Resource. In Oil Shale: A Solution to the Liquid Fuel Dilemma*: American Chemical Society; 2010.

[4] K.Urov, A.Sumberg, "Characteristics of oil shale-like rock of known deposit and outcrops" Monograph. Oil Shale; vol.16, No. 3, 1999.

[5] P.L.Russell, *Oil Shales of the world. Their origin, occurrence and exploitation*, Pergamon Press; 1990.

[6] A.K.Burnham, *In Composition, Geochemistry and Conversion of Oil Shales. Snape*, C. ed.: Kluwer Academic, Dordrecht, 1995.

[7] T.Yamada, P.Lukac, M.George, R.Weiss "Reversible, room-temperature ionic liquids. Amidinium carbamates derived from amidines and aliphatic primary amines with





carbon dioxide". Chem Mater Commun: vol. 19. No 1,2007, pp. 967–969

[8] L.A.Blanchard, D.Hancu, E.J.Beekman, J.F.Brennecke,"Ionic Iiquid/CO₂ biphasic systems: New media for green processing", Nature, vol.399, No. 1, 1999, pp. 28-29.

[9] V.Blasucci, R.Hart, V.Llopis-Mestre, D.Hahne, M.Burlager, H.Huttenhower, B.Thio, C.L.Liotta, C. A.Eckert,"Single component, reversible ionic liquids for energy applications", Fuel, vol. 89, No. 1, 2010, pp. 1315– 1319.

[10] L.A.Blanchard, J. Brennecke,"Recovery of organic products from ionic liquids using supercritical carbon dioxide", Ind.Egn.Chem.Res., vol. 40, No. 1, 2001, pp. 287-292.

[11] V.M.Blasucci, R.Hart, P.Pollet, C.L.Liotta, C. A.Eckert,"Reversible ionic liquids designed for facile separations", Fluid Phase Equilibria, vol.294, No. 1, 2010, pp. 1-6.

[12] M.Freemantle, "Designer solvents - Ionic liquids may boost clean technology development", Chern. Eng. News, vol. 76, No. 1, 1998, pp. 32-37.

[13] P.G.Jessop, D.J.Heldebrant, L.Xiaowant, C.A.Eckert, C.L.Liotta, "Reversible nonpolar to polar solvent", Nature, vol. 436, No. 1, 2005, pp. 1102-1109.

[14] K.F.Chasib, "Study on the effect of adding co-solvent (n-alkoxyethanol) to sulfolane on the toluene extraction", Scientia Iranica. Transaction C, Chemistry and Chemical Engineering, vol. 20, No. 6, 2013, pp. 1899-1911.



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