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Beneficiation of Solutes from Solvents: A Case of Oxalic Acid, Succinic Acid and Ethylenediaminetetraacetic Acid in Carbon Tetrachloride

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ABSTRACT

Background: This paper reports the beneficiation of Oxalic acid, Succinic acid and Ethylenediaminetetraacetic acid solutes from Carbon tetrachloride, Diethyl ether and n-Hexane solvents respectively. These solutes are the extracts obtained from the recovery from the binary immiscible solvents namely: Carbon tetrachloride-Water, Diethyl ether-Water and n-Hexane-Water that were used in accordance with the partition coefficient technique as reported by Onyeocha et. al. This technique was employed in the leaching of the specific solute from the contaminants. As described by Onyeocha et. al., the process was brought about by the diffusion equilibrium attained by the solute in the system i.e. the binary immiscible solvent(s) at a constant temperature and pressure. The spontaneous diffusion is the effect of the partition coefficient developed due to the different degrees of solubilities of the solute in the binary immiscible solvent. The partition coefficient technique is used for extraction, purification and concentration of solutes. Beneficiation is considered as the final process that brings the product (solute) to its most viable state.

Methods: The beneficiation methods that are proposed are physical methods. The properties of the solutes: Oxalic acid, Succinic acid and Ethylenediaminetetraacetic acid, and the properties of the solvents: Carbon tetrachloride, Diethyl ether, n-Hexane and Water are studied. The components of a mixture retain the individual physical properties that are associated with them. From the remarkable physical property of the solute and that of the solvent in which the solute is extracted, the best beneficiation method is proposed for the respective solute.

Results: The comparisons of the physical properties of the solutes and the solvents were made. From the analysis, Oxalic acid (anhydrous) has the melting point of 189 – 191°C and 101.5°C for the dihydrate while Carbon tetrachloride has freezing point of −22.92°C. Succinic acid has the melting point of 184 −190°C while Carbon tetrachloride has freezing point of −22.92°C. Ethylenediaminetetraacetic acid has melting point of 237°C while Carbon tetrachloride has freezing point of −22.92°C. Also, Succinic acid has melting point of 184 −190°C while Diethyl ether has melting point of −116.3°C and n-Hexane with the melting point of −96 to −94°C.

Conclusion: From the values of the freezing point and melting point of the solutes and the solvents, freezing, melting and filtration processes are recommended for the beneficiation of the listed solutes.

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Introduction

Beneficiation could be defined as any process that improves the economic value of the extract. [Beneficiation - Wikipedia] In the final stage of the extraction of solute(s) with a solvent by the partition coefficient technique, beneficiation involves removal of the solvent molecules from the solute crystals thereby producing pure solutes of the most viable nature. Consider the formation of solutions. In the dissolution of ionic compound in water, the polarity of water molecules gives the basis for the formation of ionic solution (aqueous solution). The slightly charged parts of water molecules attract the ions in the ionic compound and surround them to keep them separated from the other ions in solutions. The attraction between water molecules and the ions of the solute is strong enough to draw the ions away from the crystal surface and into the solution. These ions are described as being hydrated. The hydrated ions diffuse into the solution exposing the other solute ions to the attraction of the charged water molecules and consequent hydration [1-4]. The entire crystal gradually dissolves and hydrated ions become uniformly distributed in the solution.

Some ionic substances could form crystals that incorporate water molecules. These crystalline compounds are called hydrates. The

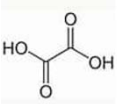
retain specific ratios of water molecules. A compound like oxalic acid forms a crystalline hydrate with the formula: $C_2H_2O_4.2H_2O$. Heating the crystals of a hydrate liberates the anhydrous salt. Ionic compounds are not soluble in nonpolar solvent such as: carbon tetrachloride, diethyl ether. The non-polar solvent molecules do not attract the ions of the crystal strongly enough to overcome the forces holding the crystals together. They differ in the bonding polarity and intermolecular forces. When oil and water are shaken together, oil droplets become dispersed in the water. When the shaking is stopped, the strong attraction of hydrogen bonding between the water molecules squeezes out the oil droplets, creating separate layers. Non-polar substances are soluble in non-polar liquids. The attractions between the non-polar molecules are London forces. London forces are weak forces. The intermolecular forces existing in the solutions of non-polar substances are similar to those in pure substances. The molecules could mix freely with one another [1-2].

London Forces: Molecules are drawn together by intermolecular forces (van der Waals forces). All molecules interact by London force. London force is the only force that acts between non-polar molecules. Due to the swirling (movement) of the electron cloud around the atoms and molecules, instantaneous dipole moment is created between the species of the atoms. Electrons could pile up at one end of the molecule, leaving the nucleus at the other end partially exposed. One end of the molecule will have an instantaneous partial negative charge and the other end will have an instantaneous partial positive charge. The instantaneous partial charges on different molecules attract one another and the molecules stick together. London forces act between all types of molecules, polar and non-polar molecules.

Polar molecules have permanent partial charges in addition to the instantaneous partial charges that arise from the fluctuations in the electron clouds (London forces). There is the interaction of permanent dipole-dipole forces in addition to the London forces. The hydrogen bond forms when a hydrogen atom lies between two small but strongly electronegative atoms with lone pairs of electrons, specifically Nitrogen, Oxygen or Fluorine. London forces are the attractive forces that cause nonpolar substances to condense to liquids and to freeze into solids when the temperature is lowered sufficiently [2,3]. Because of the constant motion of the electrons, an atom or molecule can develop the temporary (instantaneous) dipole when its electrons are distributed unsymmetrically about the nucleus. [London Dispersion Forces (purdue.edu)]

Mixtures: A mixture is a form of matter that can be separated by making use of the physical properties of the components. Mixtures show the properties of the constituents. Because the components of the mixture retain their individual physical properties, the components can be separated by physical means. The methods of separation depend on differences in the physical property of the components. A mixture is a material made up of two or more different chemical substances which are not chemically bonded [2]. It is the physical combination of two or more substances in which the identities of the individual components are retained and are mixed in the form of solutions, suspensions and colloids. All mixtures can be separated by mechanical means such as: distillation, fractional distillation, electrolysis, chromatography, heat, filtration, ultra-filtration, freezing, freeze drying, gravitational sorting, centrifugation, etc. [Mixture - Wikipedia]

Freezing and Melting: Melting point is the temperature at which a solid changes into a liquid, freezing point is the temperature at which a liquid turns into a solid. The melting and freezing points change with pressure but generally, they are given at 1 atm. A pure substance has the same freezing and melting points but in practice, there is a small difference between these quantities. Mixtures of compounds such as petroleum, have ranges of melting and freezing points. In such a mixture, the initial melting point is close to the melting point of the lightest compound in the mixture while the initial freezing point is close to the freezing point (or melting point) of the heaviest compound in the mixture. Since the melting point increases with molecular weight, for petroleum mixtures, the initial freezing point is greater than the initial melting point. [freezing and melting point - Search (bing.com)] A liquid solidifies when its molecules have low energy such that they are unable to move past their neighbours. In solid, the molecules vibrate about their average positions but do not move from place to place. The freezing temperature changes slightly as the pressure is changed. The normal freezing point of a liquid is the temperature at which it freezes at 1 atm. Most liquids freeze at higher temperatures when subjected to pressure because the solid phase is denser with molecules packed more closely together than in the liquid phase and the pressure holds the molecules together. However, except at very high pressures, the effect of pressure is small. Iron melts at 1800 K under 1 atm and only a few degrees higher when the pressure is a thousand times as great. Water is an exception to the general rule. Water freezes at a lower temperature under pressure. Ice melts under pressure because water has a higher density than ice. Many of the hydrogen bonds in ice are broken when ice melts thereby allowing ice to shrink into a smaller volume [2].

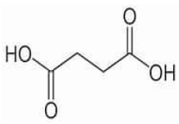


Oxalic Acid

Oxalic acid (Ethanedioic acid, HOOC-COOH) is a white crystalline solid. It becomes a colourless solution when dissolved in water. It has a density of 1.90 g cm^{-3} and a molecular weight of 90.03 g/mol. It has a melting point of 189 to 191°C. Oxalic acid is a dicarboxylic acid with the chemical formula $C_2H_2O_4$. It is called diprotic acid. It ionizes partially in aqueous solution. its conjugate base, known as oxalate ($C_2O_2^{-4}$), is a chelating agent for metal cations. Oxalic acid occurs as the dihydrate with the formula $C_2H_2O_4 \bullet 2H_2O$. [Oxalic acid - Wikipedia] It occurs as the potassium and calcium salts in nature. It is produced by the oxidation of carbohydrates. It can also be prepared in the laboratory by the oxidation of sucrose in the presence of nitric acid and a catalyst like vanadium pentoxide. [oxalic acid - Search (bing.com)] It is a reducing agent and it is used as a chelating agent with oxalate as its conjugate base. Oxalic acid is produced by the action of either hydrate of potash or of nitric acid on most organic compounds of natural occurrence. Oxalic acid is used in lanthanide chemistry as an important reagent. It is used in the manufacture of dye and in developing photographic film etc. Oxalic acid is a strong poison. The toxic symptoms from ingestion are many.

Table I: Properties of Oxalic Acid [Oxalic acid - Wikipedia]

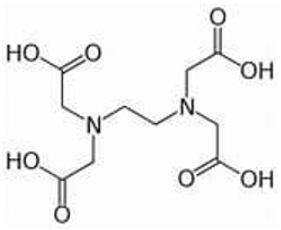
Molar mass	**90.034 g•mol^{-1} (anhydrous) 126.065 g•mol^{-1} (dihydrate)**
Density	1.90 g•cm^{-3} (anhydrous, at 17°C) 1.653 g•cm^{-3} (dihydrate)
Melting point	189 – 191°C (372 – 376°F; 462 - 464 K) 101.5°C (214.7°F; 374.6 K) dihydrate
Solubility in water	46.9 g/L (5°C), 57.2 (10°C), 75.5 (15°C), 95.5 (20°C), 118 (25°C), 139 (30°C), 178 (35°C), 217 (40°C), 261 (45°C), 315 (50°C), 376 (55°C), 426 (60°C), 548 (65°C)
Solubility	237 g/L (15°C) in ethanol 14 g/L (15°C) in diethyl ether
Vapour pressure	<0.001 mmHg (20°C)
Acidity (pKa)	1.25, 4.14
Magnetic susceptibility	−60.05•10^{-6} cm^3/mol
Heat capacity (C)	91.0 J•mol^{-1}•K^{-1}
Std molar entropy (S$^{\ominus}$298)	109.8 J•mol^{-1}•K^{-1}
Std enthalpy of formation ($\Delta_f H^{\ominus}_{298}$)	−829.9 kJ•mol^{-1}



Succinic Acid:
Succinic acid is a dicarboxylic acid with the chemical formula $(CH_2)_2(CO_2H)_2$.

Table II: Properties of Succinic Acid [Succinic Acid - Wikipedia]

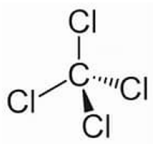
Molar mass	**118.088 g•mol^{-1}**
Density	1.56 g/cm^3
Melting point	184–190°C (363–374°F; 457–463 K)
Solubility in water	58 g/L (20°C) or 100 mg/mL
Boiling point	235°C (455°F; 508 K)
Solubility in Methanol	158 mg/mL
Solubility in Ethanol	54 mg/mL
Solubility in Acetone	27 mg/mL
Solubility in Glycerole	50 mg/mL
Acidity (p*K*a)	pK_{a1} =4.2 pK_{a2} = 5.6
Magnetic susceptibility	-57.9•10^{-6} cm^3/mol
Flash point	206°C (403°F; 479 K)



Ethylenediaminetetraace tic Acid (EDTA):
Ethylenediaminetetraacetic acid is an aminopolycarboxylic acid with the formula $[CH_2N(CH_2CO_2H)_2]_2$. This white, water-soluble solid is widely used to bind to iron (Fe^{2+}/Fe^{3+}) and calcium ions (Ca^{2+}). It binds these ions as a hexadentate ("six-toothed") chelating agent.

Table III: Properties of Ethylenediaminetetraacetic Acid [Ethylenediaminetetraacetic acid - Wikipedia]

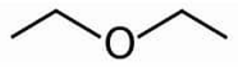
Molar mass	292.244 g•mol^{-1}
Density	0.860 g cm^{-3} (at 20°C)
Melting point	(237°C) 458.60°F
Acidity (p*K*a)	2.0, 2.7, 6.16, 10.26
Std enthalpy of combustion ($\Delta cH^{\ominus}298$)	−4461.7 to −4454.5 kJ mol^{-1}
Std enthalpy of formation ($\Delta_f H^{\ominus}298$)	−1765.4 to −1758.0 kJ mol^{-1}



Carbon Tetrachloride:
Carbon tetrachloride is an organic compound with the chemical formula CCl4. It is a colourless liquid with a "sweet" smell that can be detected at low levels. It is practically not flammable at lower temperatures.

Table IV: Properties of Carbon Tetrachloride [Carbon Tetrachloride - Wikipedia]

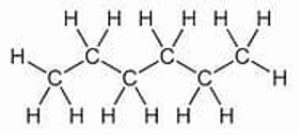
Molar mass	**153.81 g/mol**
Density	1.5867g•cm^{-3} (liquid) 1.831 g•cm^{-3} at −186°C (solid) 1.809 g•cm^{-3} at −80°C (solid)
Melting point	−22.92°C (−9.26°F; 250.23 K)
Solubility in water	0.097 g/100 mL (0°C) 0.081 g/100 mL (25°C)
Boiling point	76.72°C (170.10°F; 349.87 K)
Magnetic susceptibility	−66.60×10^{-6} cm^3/mol
Heat capacity (C)	132.6 J/mol•K
Std molar entropy (S$^{\ominus}$298)	214.39 J/mol•K
Std enthalpy of formation ($\Delta_f H^{\ominus}298$)	−95.6 kJ/mol
Gibbs free energy ($\Delta_f G^{\circ}$)	−87.34 kJ/mol



Diethyl Ether:
Diethyl ether is an organic compound with the formula $(C_2H_5)_2O$.

Table V: Properties of Diethyl Ether [Diethyl Ether - Wikipedia]

Molar mass	**74.123 g•mol^{-1}**
Density	0.7134 g/cm^3, liquid
Melting point	−116.3°C (−177.3°F; 156.8 K)
Solubility in water	6.05 g/100 mL
Boiling point	34.6°C (94.3°F; 307.8 K)
Magnetic susceptibility	−55.1•10^{-6} cm^3/mol
Heat capacity (C)	172.5 J/mol•K
Std molar entropy (S$^{\ominus}$298)	253.5 J/mol•K
Std enthalpy of formation ($\Delta_f H^{\ominus}$298)	−271.2 ± 1.9 kJ/mol
Std enthalpy of combustion ($\Delta_c H^{\ominus}$298)	−2732.1 ± 1.9 kJ/mol



n-Hexane:
Hexane is a significant constituent of gasoline. It is a colorless liquid, odorless when pure, and with boiling points approximately 69°C (156°F). It is widely used as a cheap, relatively safe, largely unreactive, and easily evaporated non- polar solvent. n-Hexane is an organic compound with the formula C_6H_{14}.

Table VI: Properties of n-Hexane [Hexane - Wikipedia]

Molar mass	**86.178 g•mol^{-1}**
Density	0.6606 g mL^{-1}
Melting point	−96 to −94°C; −141 to −137°F; 177 to 179 K
Solubility in water	9.5 mg L^{-1}
Boiling point	68.5 to 69.1°C; 155.2 to 156.3°F; 341.6 to 342.2 K
Magnetic susceptibility	−74.6•10^{-6} cm^3/mol
Heat capacity (C)	265.2 J K^{-1} mol^{-1}
Std molar entropy (S$^{\ominus}$298)	296.06 J K^{-1} mol^{-1}
Std enthalpy of formation ($\Delta_f H^{\ominus}$298)	−199.4–−198.0 kJ mol^{-1}
Std enthalpy of combustion ($\Delta_c H^{\ominus}$298)	−4180–−4140 kJ mol^{-1}

Background of the Study: Following the presentation on "EXPLORING NEW IDEAS; PERSONAL CARE AND CHALLENGES FOR PUBLIC HEALTH AND COVID-19 CRISIS" and the recommendation for the extraction of Oxalic acid, Succinic acid and Ethylenediaminetetraacetic acid from effluents and sewage disposals using binary immiscible solvent, for the sustainability of the environment, this write-up explores the physical methods for the beneficiation of these organic compounds from the dissolving solvents.

Statement of the Problem: The use of binary immiscible solvent in Partition coefficient technique leads to the control of the ramifications of polluting substances from the environment to give the clean and green habitat. These polluting substances are potent chemical substances with good health and strong economic values when they are used under control. Therefore, there is the need to restore the recovered solutes to their best viable states.

Justification of the Study: Onyeocha et. al. has recommended Carbon tetrachloride-water with the partition coefficient of 0.07383 for Oxalic acid, as good binary solvent for the extraction of Oxalic acid from contaminants. This result shows that Carbon tetrachloride is a good solvent for the leaching of Oxalic acid from contaminants. The final stage of the beneficiation process requires the separation of the extracted Oxalic acid from the dissolving solvent (Carbon tetrachloride). This analysis is reviewed also for Succinic and and Ethylenediaminetetraacetic acid.

Objective of the Study: The properties of Oxalic acid, Succinic acid and Ethylenediaminetetraacetic acid, and the properties of the corresponding solvents: Carbon tetrachloride, Diethyl ether and n-Hexane are studied to bring out the remarkable physical property that will enable the separation of the solute from the solvent. From the outstanding physical property chosen, a good separation method is devised for the solute.

Scope of Study: This proposal/principle could be applied for the beneficiation of organic compounds from their dissolving solvents. Mixtures of organic compounds in solvents are governed by London forces which are similar to the forces that are holding the pure compounds in their pure states. The separation of organic compound from the dissolving solvents therefore requires the application of the physical properties in the separation method.

Methods: The physical properties of both the solute and the solvent are compared. The separation method is devised. Some of the physical methods of separation are: distillation, fractional distillation, electrolysis, chromatography, heat, filtration, ultra-filtration, freezing, freeze drying, gravitational sorting, centrifugation etc.

Result: Table VII: Comparisons of the physical properties of the solutes and the solvents

Properties	**Oxalic acid**	**Succinic acid**	**EDTA**	**Carbon tetrachloride**	**Diethyl ether**	**n-Hexane**
Molar mass	90.034 g•mol^{-1}	118.088 g•mol^{-1}	292.244 g•mol^{-1}	153.81 g/mol	74.123 g•mol^{-1}	86.178 g•mol^{-1}
Density	1.90 g/cm^3 (at 17°C)	1.56 g/cm^3	0.860 g cm^{-3} (at 20°C)	1.5867g•cm^{-3} (liquid)	0.7134 g/cm^3, liquid	0.6606 g mL^{-1}
Melting point	189 – 191°C	184–190°C	237°C	−22.92°C	−116.3°C	−96 to −94°C

Conclusion
From the values of the freezing point and melting point of the solutes and the solvents, freezing, melting and filtration processes are recommended for the beneficiation of the listed solutes.

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