CHAPTER V

APPLICATIONS OF THE MICROEMULSION SYSTEMS

This chapter is divided into two parts and comprises of details on applications of the microemulsion systems.

5.1 Solubilization of hydrophobic lysochrome organic dye

We have formulated a microemulsion system employing polar solvent/non-polar solvent/ non-ionic surfactants and the details of those systems have been elaborated in previous chapters. Herein, we used a variety of microemulsion systems to investigate the solubilization of Sudan Red G, a hydrophobic lysochrome azo dye. Sudan Red G, a water-insoluble lysochrome azo dye, was solubilized in the presence of two distinct surfactants, namely, conventional non-ionic surfactant Triton X-100 and sugar-based non-ionic surfactant PLANTACARE®810–UP, and the solubilisation was studied by carrying of UV-Visible spectroscopy measurements at a wavelength of 470 nm. The results obtained for the systems investigated by us indicate that upon increasing the concentration of both surfactants, the degree of solubilization of an otherwise water-insoluble dye increases significantly. The dye molecules are partitioned in the hydrophobic core of the self-assembled aggregates, according to our findings. The systems explored involved the solubilization of an otherwise water-insoluble dye using sugar-based non-ionic surfactants derived from a renewable natural source that are environmentally friendly, biocompatible, and biodegradable, as well as a greener option. This research provides a green alternative to the current solubilization procedures that are widely used in textiles and other associated industries such as imaging, displays, memory technologies, analytical chemistry, biological indicators, and so on.

5.1.1 Introduction

Solubilization is the spontaneous dissolution of insoluble materials into a solvent that produces a thermodynamically stable isotropic solution using surface-active agents (Dantas et al., 2013). There has been a growing interest in the application of different dyes due to their biodegradability and environmental friendliness (Zaib et al., 2013). It is well known that dyes have a number of advantages in terms of production and application (Paul et al., 2005; Tehrani-Bagha & Holmberg, 2013; Wormuth et al., 1990; Tehrani-Bagha et al., 2016; Dil et al., 2017).

Dyes are unsaturated organic compounds that absorb a portion of visible light and bind to textiles, paper, and other surfaces. The function of the dye in micellar surfactant systems and microemulsion systems has been extensively investigated by researchers as per the literature survey (Wormuth et al., 1990; Petcu et al., 2016; Dil et al., 2017; Friberg et al., 1992; Hosseinzadeh et al., 2008). All the dyes utilized for studies were insoluble in water. These water-insoluble dyes have a tendency to cause non-uniformity and uneven dyeing during the application procedure. As a result, the fact that microemulsion systems were used as solubilization media for such dyes in literature research (Paul et al., 2005) was fascinating. We have formulated and observed that microemulsions are single-phase, optically isotropic, and thermodynamically stable solution mixtures containing water and oil, as well as a suitable hydrophile–lipophile balance of a surfactant, as detailed in previous chapters. Depending on the phase that makes up the continuous phase, the microemulsion system is characterised as water-in-oil (w/o), oil-in-water (o/w), or bicontinuous microemulsion.

The oil-in-water (o/w) microemulsion phase has been discovered to be useful for the solubilization of pharmaceuticals of medicinal and cosmetic interest (Solans & Kunieda, 1996; Ali et al., 2020; Malmsten et al., 1999), as well as detergency, emulsion polymerization, increased oil recovery, drug delivery, and textile colouring (Hosseinzadeh et al., 2008; Solans & Kunieda, 1996; Ali et al., 2020; Shah et al., 2000; Nir et al., 2010; Noritomi et al., 2013; Aki et al., 2009; Schwarze et al., 2015). The microemulsion systems developed have also been reported in the literature to be employed as a media for solubilizing inkjet inks (Wormuth et al., 2003; Fite, 1995; Sporer et al., 1992) and as a carrier in low-temperature polyester dyeing (Fite, 1995). Previously, researchers looked into the ability of dye to be solubilized in micelles and vesicles (Takagishi, 1999; Mitchell & Ninham, 1981; Oakes et al., 2003), reverse micelles (Sawada et al., 2003; Maria Mihaly et al., 2003), microemulsion precursors, and microemulsion-based systems (Holmberg et al., 1994; Kumar & Mittal, 1999).

However, there was no clear evidence in the literature on how dyes get solubilized in o/w microemulsions. Furthermore, it was unclear whether the dye diffuses directly from the oil-swollen micelles to the substrate, or whether there is any breakdown of these micelles that releases the dye into the dye bath, allowing it to interact with the substrate later and carry out chemical and enzyme-catalysed reactions, as well as other applications (Sawada et al., 2003). Other important features of microemulsion systems are found in the textile industry, where they are utilised to dissolve both water and oil-soluble chemicals (Barni et al., 1991; Savarino et al., 1993). Thus, it can be inferred that, a microemulsion system plays a crucial role in the solubilization of a water-insoluble dye.

In general, dye is a coloured organic chemical that is used to permanently colour a substrate, such as fabric, paper, or plastic. As a result, it must be able to withstand external forces such as cleaning, rubbing, etc. The dye must possess particular groups that form bonds with the substrate to do this. In an aqueous solution, the dye has an affinity for the substrate to which it is applied. The surface and bulk properties of the fibre, the molecular structure of dyes, and the medium in which the dye molecules dissolve, all have a role in dye adsorption (de Castro Dantas et al., 2004).

We have investigated the solubilization of Sudan Red G, a water-insoluble lysochrome dye, in the microemulsion system. Sudan Red G is an odourless azo dye that is yellowish red in colour with a melting point of 225 °C. It can be used to colour fats, oils, and waxes, including the waxes used in turpentine-based polishes, because it is fat soluble. It is also used in polystyrene, cellulose, and synthetic lacquers. It can withstand temperatures of 100–110 °C. We prepared a microemulsion system with conventional non-ionic surfactant of polyoxyethylene type and a sugar-based non-ionic surfactant to explore the solubilization of Sudan Red G, a hydrophobic lysochrome dye (Solanki & Patil, 2021). The results obtained using conventional non-ionic surfactants as well as those using sugar-based surfactants for solubilization of the hydrophobic lysochrome dye, Sudan red G, have been compared in this chapter.

5.1.2 Materials and methods

The industrial-grade alkyl glucoside surfactant, PLANTACARE® 810 – UP, i.e., C_{8-10} fatty alkyl glucoside or UP-810 was received as a gift sample from BASF, Germany. The non-ionic surfactant Triton X-100 ($C_{14}H_{22}O(C_2H_4O)_n$, purity≥97.0%); the bile salt-based surfactants,

Sodium cholate hydrate ($C_{24}H_{39}NaO_5 \cdot xH_2O$, purity ≥97.0%) and Sodium deoxycholate ($C_{24}H_{39}NaO_4$, purity ≥97.0%) were procured from Sigma Aldrich, USA. A water-insoluble dye, Sudan Red dye, was procured from Alps Industries Ltd. All chemicals were used as received (Solanki & Patil, 2021).

5.1.3 Results and Discussion

Solubilization studies in non-ionic surfactant/[Bmim][PF6]/water microemulsion system.

The maximum solubility of Sudan Red dye in PLANTACARE®810–UP/[Bmim][PF_6]/H_2O and Triton X-100/[Bmim][PF_6]/H_2O microemulsion systems at varied mass fractions of surfactant (γ) was determined. Firstly, excess dye was added, the sample was sonicated for a few minutes, and the excess dye was allowed to settle for two days. The dye concentration was estimated by determining the visible absorbance spectrum at λ_{max}= 504 nm as illustrated in Figure 1, using a Perkin Elmer Lambda 35 UV–visible spectrophotometer after centrifuging and filtering the supernatant dye solution.

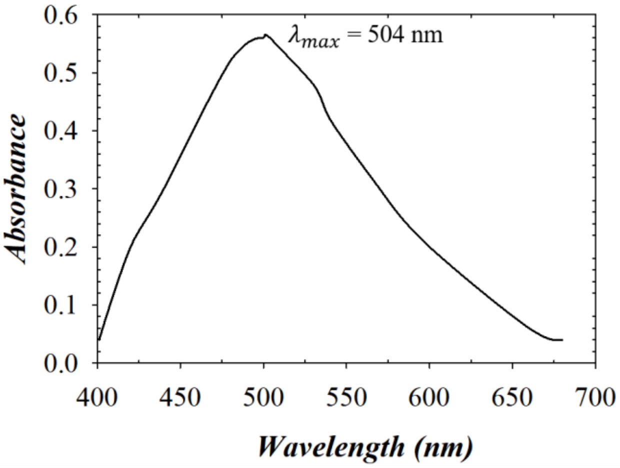

Figure 1. Absorption spectra of Sudan Red dye in hydrophobic ionic liquid/water microemulsion systems.

Sudan Red G, an otherwise water-insoluble lysochrome dye, was examined as a function of absorbance and surfactant concentration in a microemulsion system prepared with PLANTACARE®810–UP/[Bmim][PF_6]/H_2O and Triton X-100/[Bmim][PF_6]/H_2O. As illustrated in Figure 2, the absorbance was measured and the graph was plotted against the mass fraction of the surfactant (γ).

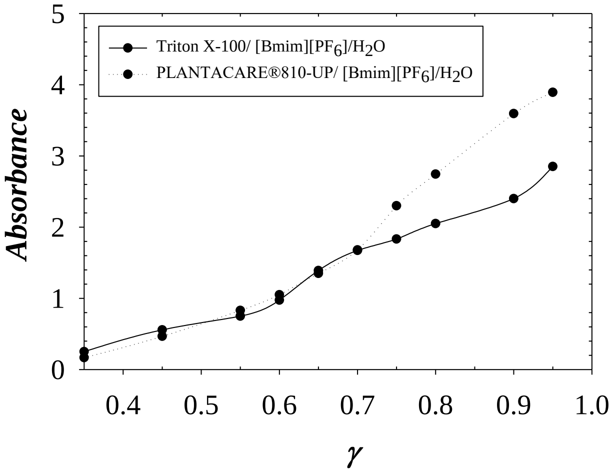

Figure 2. Graphical representation of Sudan Red dye in the Triton X-100/[Bmim][PF_6]/H_2O and PLANTACARE®810–UP/[Bmim][PF_6]/H_2O microemulsion systems as a function of absorbance and surfactant concentration (Solanki & Patil, 2021).

For both the microemulsion systems, PLANTACARE®810–UP/[Bmim][PF_6]/H_2O and Triton X-100/[Bmim][PF_6]/H_2O containing Sudan Red G dye, the absorbance intensity increases with the increase in surfactant mass fraction (γ). This effectively means that changing the γ values enhance dye solubilization. It is observed that non-polar, water-insoluble dyes are largely soluble in oil-swollen micelles, whereas water-soluble polar dyes are significantly soluble in the surfactant-rich interfacial region covering these micelles. The polarity of the oil component of the microemulsion system is said to affect the solubility of non-polar dyes.

As a result, when the surfactant is added to water such that the concentration is greater than the critical micelle concentration (CMC), reverse micelles form, increasing the dye's solubility. From Figure 2 it can be inferred that the extent of solubilization of Sudan Red G was found to be greater in a microemulsion formulated with a sugar-based non-ionic surfactant compared to a microemulsion formulated with a conventional non-ionic surfactant, Triton X-100. When Triton X-100, a conventional non-ionic surfactant, is utilised in a microemulsion that is later used for solubilization, the maximum absorbance value increases from 0.503 nm to 1.390 nm. The absorbance value is much higher when PLANTACARE®810–UP, a sugar-based non-ionic surfactant, is used to formulate a microemulsion, ranging from 1.403 nm to 3.892 nm. This demonstrates that a sugar-based non-ionic surfactant is more effective than a conventional non-ionic surfactant at solubilizing Sudan Red Dye G.

The addition of the non-ionic surfactant to the W/IL reverse micelles increased the polarity of the W/IL microemulsion system, whereas the polarity of the IL pools remained constant as the IL pools formed, according to the UV-Visible absorbance spectra. The formation of ionic liquid microemulsions allows ionic liquids to dissolve a wide range of substances despite their restrictions. In almost all circumstances, dye solubility in microemulsions is significantly higher than in pure solvents. The major variable appears to be dye amphiphilicity, the more surfactant-like the dye gets, the more water-rich microemulsions it can dissolve.

5.1.4 Conclusions

The solubilization of an otherwise water-insoluble lysochrome dye, Sudan Red G is increased with an increase in surfactant mass fraction for the PLANTACARE® 810 – UP/[Bmim][PF_6]/H_2O ternary microemulsion system. The extent of solubilization of Sudan Red G was observed to be higher in a microemulsion formulated using sugar-based non-ionic surfactant as compared to that of the microemulsion system consisting of a conventional surfactant, Triton X-100. The principal site for polar dye solubilization, according to the findings, is the surfactant-rich interfacial region dividing the oil and water domains. Hence, it offers a green alternative to the existing processes of solubilization utilized widely in textile and other allied industries like imaging, displays, memory technologies, analytical chemistry, indicators for biological sciences, etc.

5.2 Extraction and efficient Recovery of metal ions

The recovery efficiency of heavy metal ions using a microemulsion has been examined. Water, organic solvent, and a sugar-based non-ionic surfactant were utilised to formulate the microemulsion system used in the extraction procedure. After the metal ions were recovered from the metal complex, the absorbance values of the metal ions were measured. The developed microemulsion system's phase behaviour was studied in depth. We have used industrial-grade sugar-based non-ionic surfactants in this study, which provide a greener alternative for the formulation of a microemulsion system due to their superior physicochemical qualities, non-toxicity, and biodegradability when compared to conventional nonionic surfactants. Furthermore, after the extraction of the metal salts, UV-Visible spectrophotometric investigations revealed that the absorbance increases with an increase in metal ion concentration in the aqueous phase and drops with an increase in potassium thiocyanate concentration in the aqueous phase. Moreover, it has been evaluated that a concentration of 4.0 mol/L potassium thiocyanate is the optimum concentration for recovering 0.05 mol/L cobalt and nickel salts efficiently. Inorganic chemicals, such as cobalt nitrate and nickel nitrate, were extracted with 94% and 97% efficiency, respectively. The present study is important from an economic as well as environmental standpoint as the extraction of the metal ions and the recovery of the same from aqueous as well as solid wastes are studied.

5.2.1 Introduction

Rapid industrialization expansion is one of the primary sources of heavy metal emission in today's day, resulting in considerable environmental damage (Zaib et al., 2013; Dantas et al., 2003). This is due to an increase in the demands of the global market. There are a number of industries, including: dyes, tanneries, paints, textiles, ceramics, and metallurgy are damaging water bodies and solid waste as a result of uncontrolled heavy metal disposal. Metal recycling can help to eliminate unnecessary risks to public health and the environment (Tao et al., 2006). Several reports in the literature cite the use of ion exchange, adsorption, reverse osmosis, membrane filtration, etc as effective methods for metal ion removal and effluent treatment (Zaib, Din, Sana, Manzar, & others, 2013; Dantas et al., 2003; Tao et al., 2006; Shen et al., 2016). Later on, the use of the microemulsion system was brought forward as an economical and contemporary method (Dantas et al., 2004; Mihaly,et al., 2010; Al-Ghouti et al., 2013; Vinhal & Cassella, 2019; Shang et al., 2012), when compared with other traditional methods which show less reactivity, fewer biodegradability, huge thermal, chemical as well as photolytic stability (Radi et al., 2016; Uddin, 2017; Fite et al., 2012; Ding et al., 2003; Lu & Xu, 2016; Ding et al., 2013; Mukherjee et al., 2016). Therefore, for the recovery of the metals from the aqueous phase, the microemulsion system in the oil continuous phase must be explored (Solanki & Patil, 2021).

The two-phase technique, i.e., water in oil microemulsion, is commonly used in recent studies due to its cost-effectiveness. Furthermore, it is very efficient and improves the potentiality of metal ion extraction from the microemulsion system, as well as the interfacial area of the W/O microemulsion phase, resulting in faster metal extraction (Beltrame et al., 2005; Steytler et al., 2001; Gao et al., 2012; Mihaly, Comanescu, et al., 2010). Different types of metallic cations, such as chromium (Dantas et al., 2001; Melo et al., 2015; Li et al., 2009), copper (Al-Ghouti et al., 2016), gold (Lu et al., 2011), lanthanide (Shan et al., 2005; Wang et al., 2012; Xia et al., 2008), and a few other metals (Steytler et al., 2016; Dantas et al., 2003; Kara et al., 2015), have been extracted in the literature by solubilizing the metals in the aqueous phase of the microemulsion system. The extraction and recovery of metal ions from the pseudo-phase ternary microemulsion system has been demonstrated in all of the above-mentioned studies. However, in this study, we have formulated a true ternary microemulsion system, and the results will be compared to those available in the literature.

The purpose of this research is to use industrial-grade sugar-based non-ionic surfactants to reduce the toxicity of microemulsion systems. In a recent study, the authors employed polyoxyethylene (4) lauryl ether (Brij30), i.e. (C_iE_j), as a nonionic surfactant for the purpose of extraction (Mihaly cet al., 2010). We have used alkyl polyglycosides or non-ionic sugar-based surfactants (C_nG_m) as a "greener alternative" to alkyl polyglycol ether (C_iE_j) surfactants in the current study to replace alkyl polyoxyethylene ether (C_iE_j) surfactants in the ternary microemulsion systems.

For the extraction of the metal ions, i.e., Cobalt and Nickel, a ternary microemulsion system comprising of sugar-based non-ionic surfactants that are ecologically benign, water as the polar phase, and ethyl acetate (EtOAc) as the organic phase was utilised. Furthermore, we conducted a thorough investigation of the phase studies of the microemulsion system, where fish-shaped diagrams were constructed and other phase diagram attributes were assessed. In addition, the microemulsion technique was used to recover cobalt and nickel ions efficiently. It was also looked at how to remove metal ions as efficiently as possible using the optimum amount of potassium thiocyanate (Solanki & Patil, 2021).

5.2.2 Material and methods

The non-ionic sugar-based industrial-grade surfactant, PLANTACARE® 810 – UP, i.e., C_{8-10} fatty alkyl glucoside was presented by BASF, Germany. The organic solvent, ethyl acetate [$CH_3COOC_2H_5$, purity 99%], the inorganic salt potassium thiocyanate [KSCN, purity 99%], the metal salts cobalt nitrate [$Co(NO_3)_2{\cdot}6H_2O$, purity 99%] and nickel nitrate [$Ni(NO_3)_2{\cdot}\ 6H_2O$, purity 99%] was procured from Sigma Aldrich, USA.

Phase studies of the ternary microemulsion system

The microemulsion was investigated using phase behaviour measurements. By passing "slices" through the phase prism at a 1:1 water to ethyl acetate (oil) ratio while altering the surfactant concentration (γ), the phase behaviour of a ternary microemulsion as a function of temperature and composition has been examined (Atkin & Warr, 2007; Solanki & Patil, 2021)).

To avoid loss of organic volatile solvents, microemulsion systems were made by weighing known amounts of water, ethyl acetate, and industrial-grade sugar-based non-ionic surfactant, PLANTACARE® 810 – UP in sealed glass stoppered test tubes. These test tubes were kept in a crystal-clear thermostat water bath (± 0.2 °C). The various phases corresponding to distinct phase areas were determined, namely 1∅ (one phase), 2∅ (lower two-phase) or water/oil droplet microemulsion, 2∅ (upper two-phase) or oil/water droplet microemulsion, and 3∅ (corresponding to three-phase regions).

These phase regions were designated by examining the phase boundaries over a temperature range of 32 to 60°C (Solanki & Patil, 2021).

While preparing the microemulsion system, the weight fraction of ionic liquid (α) is given by,

$$\alpha = \frac{m_{Oil\,(EtOAc)}}{m_{Oil\,(EtOAc)} + m_{H_2O}}$$

and as the weight fraction of surfactant (γ) in the total mixture,

$$\gamma = \frac{m_{surfactant}}{m_{Oil\,(EtOAc)} + m_{H_2O} + m_{surfactant}}$$

Studies on extraction of metal ions in the microemulsion system

In the present work, PLANTACARE®810–UP /EtOAc/H_2O was utilised to formulate a microemulsion system. A cobalt thiocyanate complex [$Co(SCN)_2^-$] was introduced to the microemulsion system to extract cobalt ions. 0.05 mol. L^{-1} cobalt nitrate hexahydrate [$Co(NO_3)_2 \cdot 6H_2O$] (dissolved in a unit volume of water) is added to 4.0 mol/L potassium thiocyanate (KSCN) to produce the cobalt thiocyanate complex [$Co(SCN)_2^-$] (dissolved in the unit volume of water).The function of potassium thiocyanate (KSCN) in this case is to form a complex with cobalt ions, i.e. it works as a complexing agent. We utilized an extensive experimental method of efficient recovery reported in the literature (Mihaly et al., 2011; Steytler et al., 2017; Shen et al., 2016; Petcu et al., 2016; Vinhal & Cassella, 2019; Guo et al., 2020).

The entire contents of the glass test tube were vigorously shaken for around 20-30 minutes before being allowed to rest at room temperature for 12 hours to achieve equilibrium. As a result, two distinct phases emerged, with the microemulsion occupying the upper phase and the aqueous phase occupying the lower phase, which is consistent with those reported by Cadar et al. (2017). Due to the extraction of cobalt ions in the top phase, which is the microemulsion, the upper phase is highly coloured, whilst the aqueous phase is colourless. After reaching equilibrium, the two distinct phases, the coloured upper phase microemulsion and the colourless bottom aqueous phase, were collected separately in a vial using syringes.

Furthermore, the nickel ions were extracted in the same manner as the cobalt ions. We employed 0.05 mol/L nickel nitrate hexahydrate [$Ni\ (NO_3)_2 \cdot 6H_2O$] (dissolved in a unit volume of water) and 4 mol/L potassium thiocyanate (KSCN) (dissolved in a unit volume of water) to form nickel thiocyanate complex [$Ni\ (SCN)_2^-$]. The nickel ions are removed in the upper microemulsion phase, resulting in a brightly coloured upper phase.

UV-Visible Spectrophotometry measurements.

As the two phases were divided into two vials, the lower colourless aqueous phase received 0.1 mol/L potassium thiocyanate (KSCN) to ensure that all of the metal ions were extracted in the microemulsion system. Using a Perkin Elmer Lambda 35 UV–visible spectrophotometer, the absorbance maximum (λ_{max}) for the metals ions in the microemulsion system was determined to be λ_{max} = 622 nm for cobalt ions and λ_{max} = 593 nm for nickel ions.

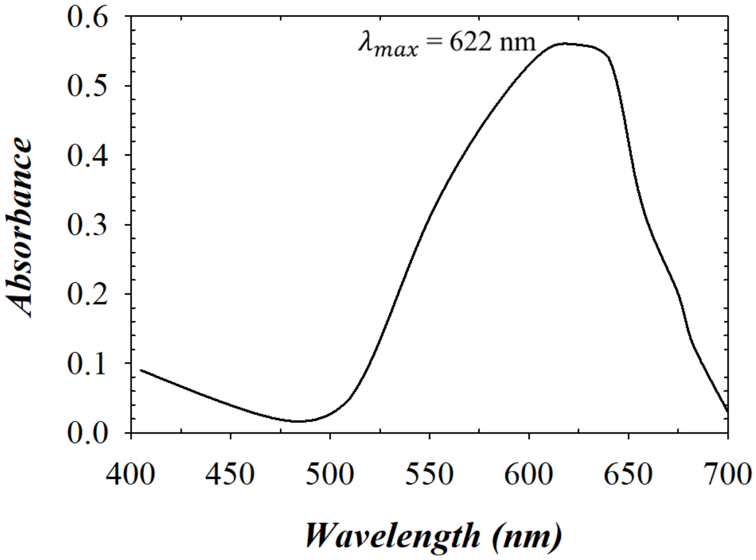

Figure 1. Absorption spectra of aqueous phases after cobalt ions recovery with potassium thiocyanate for PLANTACARE®810–UP/EtOAc/ [$Co(SCN)_2^-$]/ H_2O microemulsion systems.

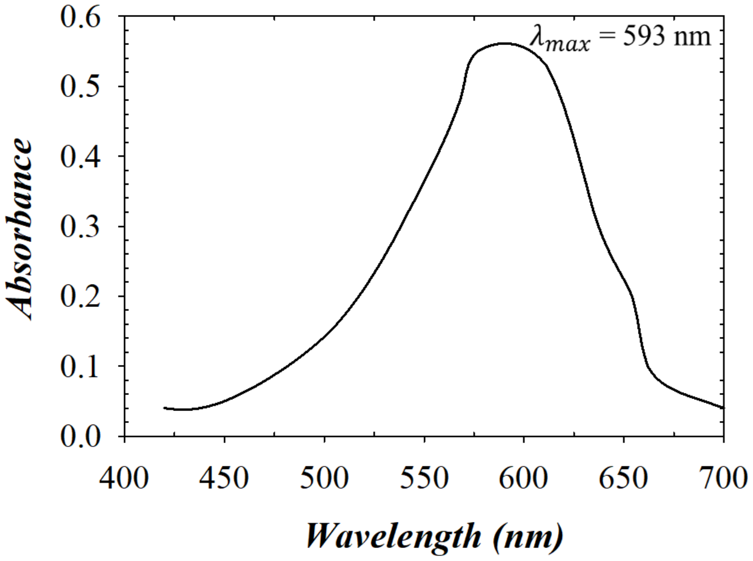

Figure 2. Absorption spectra of aqueous phases after cobalt ions recovery with potassium thiocyanate for PLANTACARE®810–UP/EtOAc/ [$Ni(SCN)_2^-$]/ H_2O microemulsion systems.

Recovery Efficiency.

The recovery efficiency (E %) for both metal ions (cobalt and nickel ions) was computed using the equation,

$$Efficiency\ (E\ \%) = \frac{C_{in} - C_{fin}}{C_{in}} \times 100$$

Here, C_{in} denotes the initial concentration of metal ions (cobalt and nickel ions) in an aqueous solution, whereas C_{fin} denotes the final concentration of metal ions (cobalt and nickel ions) following metal ion recovery.

5.2.3 Results and discussion

Phase behaviour studies in water/ethyl acetate/ non-ionic sugar-based surfactant ternary microemulsion system

Cadar et. al. (2017) developed a pseudo ternary microemulsion system and carried out extractions, however the concentration of the surfactant at which microemulsion forms, as well as the phase studies, were not investigated (Cadar et al., 2017). However, in this study, we investigated the phase of the microemulsion system and determined the $\overline{X}$ value, which is defined as the smallest weight fraction of surfactant required to dissolve the two immiscible liquids at which the microemulsion (one-phase system) develops.

Figure 3 represents the fish-shaped diagram that was obtained by plotting *T/°C* (Temperature) against γ (mass fraction of surfactant) for formulated microemulsion system using PLANTACARE® 810 – UP/EtOAc/H_2O. The vertical sections through the phase prisms for the non-ionic sugar-based surfactants were shown at equal masses of ethyl acetate and water, and the $\overline{X}$ value of the microemulsion system was found to be $\overline{X} = 0.48$. The characteristic parameters of the above ternary microemulsion systems are also investigated and summarised in Table 1, where $\emptyset$ is ratio water/oil (1:1); γ_0 and T_0 are co-ordinates of the fish head; $\overline{\gamma}$, $\overline{T}$ are co-ordinates of the fishtail and finally, $\Delta\gamma$, ΔT is the maximum extension of surfactant concentration and temperature of the 3-phase body (Solanki & Patil, 2021).

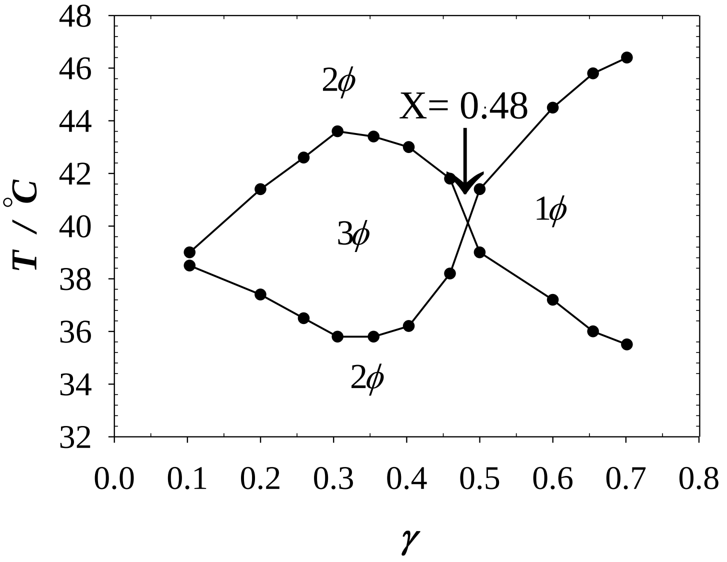

Figure 3. Fish-shaped phase diagram obtained by taking a vertical section through the phase prism for equal masses of water: Oil (Ethyl acetate) (1:1), showing One phase (1∅), upper two-phase (2∅) (Water/Oil droplet μE), lower two-phase (2∅) (Oil/Water droplet μE) and three phases (3∅) regions respectively. *T/°C* is the Temperature and 'γ' is the weight fraction of surfactant, PLANTACARE® 810 – UP in the total mixture (Solanki & Patil, 2021).

Table 1. Characteristic parameters of the constructed Phase diagrams

Microemulsion System	∅	γ_0	T_0/°C	$\bar{\gamma}$	$\bar{T}$/°C	$\Delta\gamma$	ΔT/°C
PLANTACARE® 810 – UP/ EtOAc/ H_2O	0.5	0.1	38.2	0.48	40.0	0.38	0.8

The ratio of water: oil (1:1) ∅ ; coordinates of fish head γ_0, T_0; coordinates of fishtail $\bar{\gamma}$, $\bar{T}$; maximum extension of surfactant concentration and temperature of the 3-phase body $\Delta\gamma$, ΔT.

Effect of increasing the potassium thiocyanate concentration on metal recovery efficiency.

To investigate the effect of potassium thiocyanate concentration on the transfer of cobalt ions from the aqueous phase to the microemulsion phase, we prepared KSCN solutions with various concentrations ranging from 0.5 to 10 mol/L and determined the absorbance spectra with a Perkin–Elmer Lamda 35 UV-Visible spectrophotometer. The cobalt nitrate content was kept constant at 0.05 mol/L in this experiment.

Figure 4 shows the absorbance spectra of the aqueous phase after extraction of the cobalt ions using KSCN 0.1 mol/L. The maximum absorbance values for the microemulsion system PLANTACARE® 810 – UP/EtOAc / [Co(SCN)$_2^-$]/ H_2O have been seen to decrease as the potassium thiocyanate content is increased (KSCN). Cadar et al. (2017) have reported similar findings, using sodium thiocyanate and a nonionic surfactant of the C_iE_j type. More precisely, it has been observed that using 4.0 mol/L potassium thiocyanate (KSCN) concentration in the initial composition, all the cobalt ions were extracted from the aqueous phase.

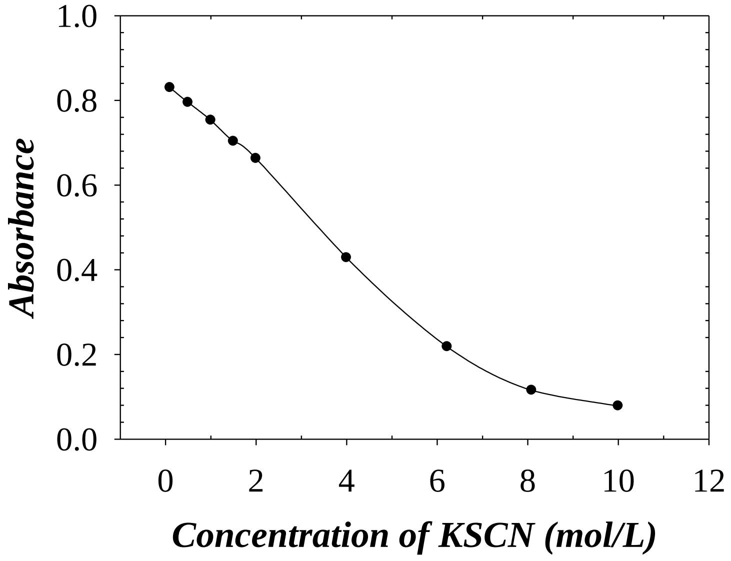

Figure 4. Variation in maximum absorbance values of the aqueous phase treated with different concentrations of potassium thiocyanate (KSCN) after the extraction of 0.05 mol/L cobalt nitrate [Co $(NO_3)_2 \cdot 6H_2O$] in the case of PLANTACARE® 810 – UP/ EtOAc/ Co $(SCN)_2^-/H_2O$ microemulsion system. (λ_{max} = 622 nm)

Therefore, by calculating the recovery efficiency, it has been observed that increasing the concentration of the potassium thiocyanate (KSCN) from 0.5 to 10.0 mol/L results in an increasing trend for the best recovery of the cobalt ions yielding 97 % from the formulated microemulsion system. Hence, it is observed that there is a rise in the recovery effectiveness of cobalt ions salt from 75% (at 0.5 mol/L KSCN) to 97% (at 4.0 mol/L KSCN).

Figure 5 illustrates the graphical representation of absorbance against potassium thiocyanate (KSCN) concentration of the lower aqueous phase treated with KSCN 0.1 mol/L after the removal of the nickel ions in the case of PLANTACARE® 810 – UP/EtOAc /[Ni $(SCN)_2^-$]/water microemulsion system. Here, similar observations were obtained that on the increasing concentration of potassium thiocyanate, there is a decrease in the maximum absorbance values of the nickel ions which suggests that there is a good amount of recovery of the nickel ions where the yield was found to be in the range of 93.9 % (~94 %)from the formulated microemulsion system.

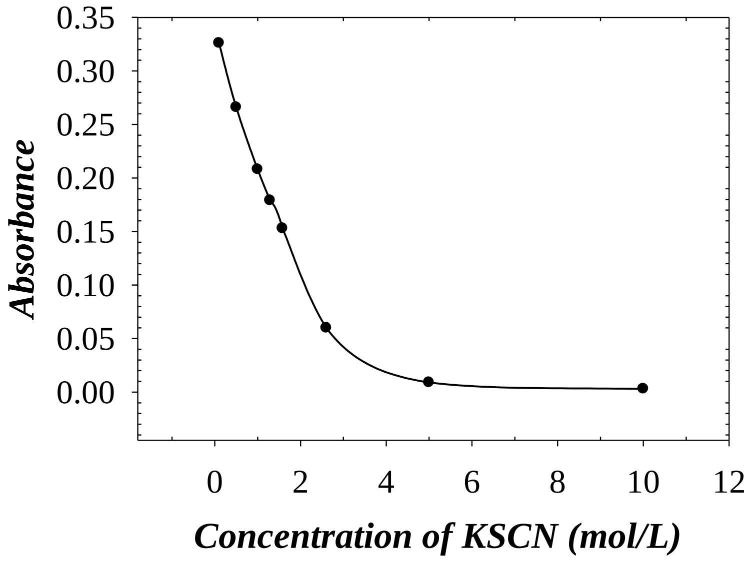

Figure 5. Variation in maximum absorbance values of the aqueous phase treated with different concentrations of potassium thiocyanate (KSCN) after the extraction of 0.05 mol/L nickel nitrate [Ni $(NO_3)_2 \cdot 6H_2O$] in the case of PLANTACARE® 810 – UP / EtOAc/ Ni $(SCN)_2^-$/ H_2O microemulsion system. (λ_{max} =593 nm).

Hence, it is inferred that the potassium thiocyanate (KSCN) salt utilised here functions as a complexing agent for both cobalt and nickel ions, forming Co $(SCN)_2^-$ and Ni $(SCN)_2^-$ in a microemulsion system. In other words, the potassium thiocyanate (KSCN) concentration influences the transfer of cobalt and the nickel ions from the aqueous phase into the microemulsion phase (Cadar et al., 2017).

Effect of increasing the metal salts concentration on its recovery efficiency.

To study the maximal concentration of cobalt and nickel ions that are to be recovered using 4.0 mol/L concentration of KSCN, different solutions (5 each) of cobalt nitrate hexahydrate [Co $(NO_3)_2 \cdot 6H_2O$] and nickel nitrate hexahydrate [Ni $(NO_3)_2 \cdot 6H_2O$] with dissimilar values of concentrations ranging from 0.05 mol/L to 0.15 mol/L were prepared.

Figure 6 illustrates the variation in the absorbance of an aqueous phase after treatment with KSCN 0.1 mol/L and the recovery of various concentrations of cobalt ions, while Figure 7 represents the absorbance spectra for the aqueous phase that is been treated with KSCN 0.1 mol/L after the recovery of different concentrations of nickel ions.

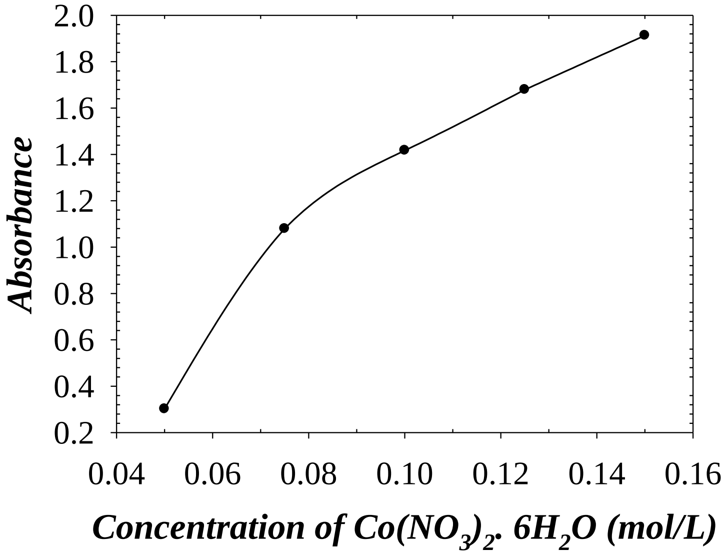

Figure 6. Variation in maximum absorbance values of the aqueous phase treated with 0.01 mol/L potassium thiocyanate (KSCN) after recovery of different cobalt nitrate [Co $(NO_3)_2{\cdot}6H_2O$] concentration using 4 mol/L potassium thiocyanate (KSCN) in the case of PLANTACARE® 810 –UP /EtOAc/Co $(SCN)_2^-$/ H_2O microemulsion system. (λ_{max} = 622 nm)

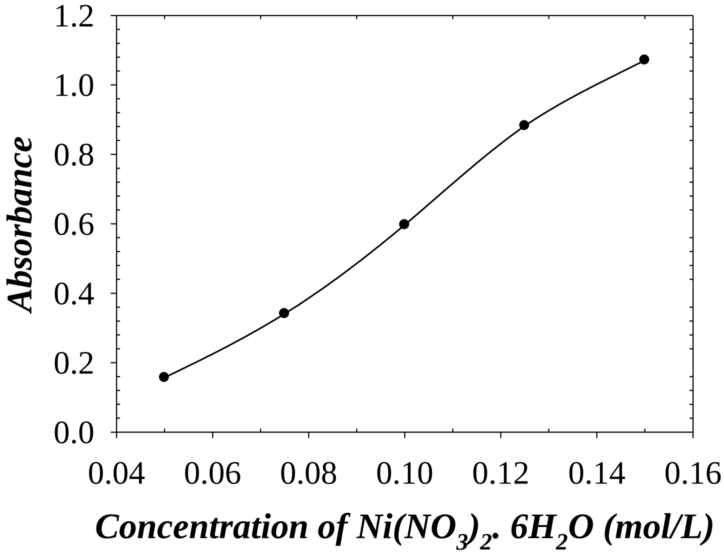

Figure 7. Variation in maximum absorbance values of the aqueous phase treated with 0.01 mol/L potassium thiocyanate (KSCN) after recovery of different nickel nitrate [$Ni(NO_3)_2 \cdot 6H_2O$] concentration using 4 mol/L potassium thiocyanate (KSCN) in the case of PLANTACARE® 810 – UP / EtOAc/ $Ni(SCN)_2^-$ / water microemulsion system. (λ_{max} = 593 nm)

The results obtained reveal that as the concentration of metal salts increases, the absorbance values of the metal salts (cobalt and nickel) also increase. In addition to this, to reformulate the above process, the recovery efficiency of metal ions (cobalt and nickel) from aqueous media was calculated. In the present study, it has been observed that on increasing the cobalt nitrate concentration from 0.050 to 0.100 mol/L or similarly increasing nickel nitrate concentration from 0.050 to 0.100 mol/L, there is no significant decrease in recovery efficiency. However, it has been observed that when the metal ion concentrations are higher than 0.100 mol/L, it shows better efficiency in the formulated ternary microemulsion system consisting of PLANTACARE® 810- UP /EtOAc/[$Co(SCN)_2^-$].

5.2.4 Conclusions

The phase behaviour of ternary microemulsion system consisting of PLANTACARE®810–UP/EtOAc/H_2O was investigated. The $\overline{X}$ is found to be 0.48 and hence, is used to study the recovery of cobalt as well as nickel ions from a synthetic aqueous solution. Moreover, it has also been observed that by making use of potassium thiocyanate (KSCN) having 4.0 mol/L concentration, we achieve the optimal results relating to the recovery of cobalt ions as well as the nickel ions (where the concentration of the cobalt ion and nickel ion is 0.05 mol/L).

Furthermore, it has been observed that there is no significant decrease in the recovery efficiency till 0.10 mol/L of metal salt concentration while keeping the KSCN concentration constant (4.0 mol/L) and keeping the concentration of the cobalt salt and nickel salt in the increased range of 0.05 - 0.15 mol/L. Hence, in this study, we were able to recover 93.9% (~94 %) of the nickel ions and 97% of the cobalt ions from the formulated microemulsion system. As a result, our investigation is an attempt to lessen the aftereffects on public health and the environment by extracting metal ions from various other industrial effluents and wastes. These findings can help overcome the lack of metals in the industrial region where they have been employed as raw materials.