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Journal of Hazardous Materials B137 (2006) 827–835

Journal of Hazardous Materials

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Performance of TX-100 and TX-114 for the separation of chrysoidine dye using cloud point extraction

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Received 26 December 2005; received in revised form 1 March 2006; accepted 1 March 2006
Available online 5 April 2006

Abstract

Cloud point extraction (CPE) is carried out to extract chrysoidine dye from aqueous solution using two different non-ionic surfactants, TX-100 and TX-114. The effects of different operating parameters, e.g., concentrations of surfactant, dye and salt, temperature, pH on extraction of both dye and surfactant have been studied in detail. The extraction of dye increases with temperature, surfactant concentration and salt concentration. Various design parameters of a CPE process have been estimated by developing correlations for dye solubilization and fractional coacervate phase volume with the operating conditions. The equilibrium solubilization data at four different temperatures follow Langmuir type isotherm. A method is presented to calculate the feed surfactant concentration required for the removal of dyes up to a level of 3.82×10^{-6} M. The developed correlations may be useful to design a cloud point extractor of a desired efficiency.

Keywords: Chrysoidine; Solubilization; Cloud point extraction; Non-ionic surfactant; TX-100; TX-114; Coacervate phase; Langmuir isotherm

1. Introduction

Above the cloud point temperature, aqueous solution of a non-ionic surfactant separates into two phases, namely a surfactant rich phase, which has small volume compared to the solution and is called coacervate phase and the other is dilute bulk aqueous phase containing surfactant concentration slightly above the critical micelle concentration (CMC). The solute molecule present in aqueous solution of non-ionic surfactant is distributed between the two phases above the cloud point temperature [1]. The first applications of phase separation based on the cloud point phenomenon refer to the extraction of metal ions forming complexes sparingly soluble in water. The efficiency of the process depends on the hydrophobicity of the ligand and of the complex formed, on the apparent equilibrium constants in the micellar medium and on the formation kinetics of the complex and on the transference between the phases. This type of extraction by the cloud point method was initially described by Watanabe and Tanaka [2] for the preconcentration of Zn(II) using 1-(2-pyridylazo)napthol (PAN) as a ligand and PONPE as extractant. Later, this methodology was also applied to the determination of different metal ions in different types of samples. Another application of the CPE focuses on the isolation and purification of species of biological interest, mainly proteins. It is in this field of bioseparations that CPE currently finds one of its main use, as shown by the considerable volume of literature related to the extraction and purification of membrane proteins and other biomaterials [3,4]. The use of CPE for the extraction of organic compounds other than biomolecules is relatively recent [5]. CPE has been evaluated for the extraction of a series of chlorinated phenols from water [6]. Cloud point technique has been successfully employed for the preconcentration of polycyclic aromatic hydrocarbons [7–9], polychlorinated compound [6] and vitamins [5,10,11].

Dye containing waste stream is one of the major toxic industrial waste. Various types of dyes are used in the process industries like textile, pulp and paper, paints, etc. The effluents containing dyes are highly colored and cause water pollution. Chrysoidine is used as a dye for silk and cotton; in oils, fats and waxes for polishes, paper, leather, inks, wood and biological stains [12]. It is also used to dye maggots used as fishing bait. Several case reports and case–control studies sug-

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doi:10.1016/j.jhazmat.2006.03.003

gest an increased risk of bladder cancer in fishermen that used chrysoidine-dyed maggots as bait. Up to a three-fold excess risk for using bronze maggots for more than 5 years was reported in one case–control study [13].

Many investigators have studied different techniques for the removal of colored dye from wastewater, e.g., (a) different membrane separation processes like reverse osmosis (RO) [14], nanofiltration (NF) [15], micellar enhanced ultrafiltration (MEUF) [16,17] and membrane-wet oxidation [18]; (b) adsorption on to (i) agricultural solid waste [19], (ii) different bentonites [20], (iii) various types of activated carbon [21] and (iv) surfactant impregnated montmorillonite [22], etc.; (c) several oxidation processes [23]; (d) ozonations [24]. Cloud point extraction (CPE) may be an effective method for removing dye from aqueous solution [25,26].

In this study, cloud point extraction has been adopted to extract toxic chrysoidine dye. The effects of different operating parameters, e.g., concentration of the feed mixture (both dye and surfactant), pH, temperature and the presence of mono and divalent salt on the extraction of both the dye and surfactant have been studied in detail. The performance of two non-ionic surfactants is investigated to extract dye from synthetic dye solution. From the experimental data, a solubilization isotherm is developed to quantify the amount of dye solubilization. Correlations have also been developed to predict the fractional coacervate phase volume at optimum temperature and surfactant concentration. To meet the environmental standards and the economy of the CPE process, it is necessary to recover the surfactant from both the coacervate and aqueous phase. Solvent extraction process [25] may be applicable to separate surfactant both from the coacervate phase and the aqueous phase.

2. Experimental

2.1. Materials

Triton X-100 (*iso*-octyl phenoxy polyethoxy ethanol, molecular weight: 628, λ_{max}: 226 nm, supplied by Loba Chemie, Mumbai, India) and Triton X-114 (octyl phenol poly(ethylene glycol ether), molecular weight: 537, λ_{max}: 223 nm, supplied by Amresco, Solon, OH, USA) have been used as non-ionic surfactants. The critical micellar concentrations of TX-100 and TX-114 are 2.8×10^{-4} and 2.1×10^{-4} M [27], respectively. Cloud points of TX-100 and TX-114 in aqueous solution are 65 and 24 °C [28], respectively. Chrysoidine dye (molecular weight: 262.74, dye content: 97.5%, supplied by Loba Chemie) is used in this study. For all the experiments, surfactants and dye are used without further purification. The structure of the dye molecule in basic and in acidic medium is shown in Fig. 1a and b, respectively. The wavelength at which the maximum absorption occurs is 457 nm at acidic pH and 430 nm at basic pH.

2.2. Methods

Solutions (50 ml) are prepared by dissolving accurately weighed amount of surfactant and dye in distilled water at different concentrations. Each experiment is conducted using a 50 ml measuring cylinder containing different concentration of surfactants, dye and salt solution in a constant temperature bath (supplied by Testing Instruments Manufacturing Company Ltd., Kolkata, India) for 20 min. After complete phase separation, the measuring cylinder is removed from the temperature bath and cooled for 2 min. The volumes of the coacervate phase and concentration of dilute phase have been measured.

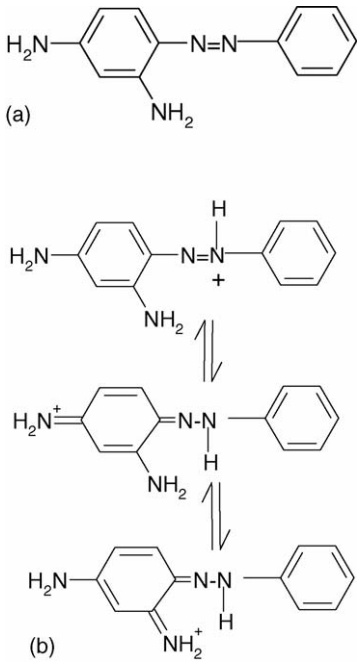

Fig. 1. (a) Structure of chrysoidine in basic pH. (b) Structure of chrysoidine in acidic pH.

2.3. Operating conditions

The concentrations of chrysoidine in the feed are 4.77×10^{-5}, 9.52×10^{-5}, 1.90×10^{-4}, 3.82×10^{-4} and 7.63×10^{-4} M. The concentrations of TX-100 and TX-114 in the feed are varied from 0.03 to 0.25 M. All the experiments have been conducted at four different temperatures (75, 80, 85 and 90 °C for TX-100 and 40, 45, 50 and 55 °C for TX-114). To observe the effect of salt on extraction of chrysoidine and surfactant, monovalent NaCl and divalent $CaCl_2$ are selected. The concentrations of salts (NaCl and $CaCl_2$) have been chosen as 0.05, 0.1, 0.2, 0.3 and 0.5 M. The pH values of the solutions are adjusted to 2.0, 3.5, 5.0, 6.5, 9.0, 11.0 and 12.0 by adding hydrochloric acid and sodium hydroxide as appropriate.

2.4. Analysis

The concentrations of dye and surfactants are determined by spectrophotometry (make: Thermo Spectronic, USA; model: GENESYS 2, Rochester, New York). Pure TX-100, TX-114 and chrysoidine solutions are initially calibrated separately for different concentrations in terms of absorbance units, which are recorded at the wavelength of 226, 223 and 457 nm, respectively, at which maximum absorption takes place. Standard technique

is used to find out the concentrations of both dye and surfactants [29].

3. Results and discussions

This section is divided into four parts. In first part, the effects of different factors (e.g., concentrations of non-ionic surfactants, dye and salt, temperature and pH of the solution) on the extent of extractions of both dye and surfactant and fractional coacervate phase volume have discussed. The nature of solubilization isotherm at different temperature has been presented in the second part. Variation of fractional coacervate phase volume with temperature is explained in part three. In the last part, a calculation procedure for the determination of surfactant requirement for the dye removal to a desired level is briefly discussed. The extent of extraction (E) and the fractional coacervate phase volume (F_c) are defined as,

$$\text{Extraction } (E) = \left(1 - \frac{C_d}{C_0}\right) \times 100$$

$$F_c = \frac{\text{volume of cocervate phase}}{\text{total volume of solution}}$$

where C_0 and C_d are the feed and dilute phase concentration, respectively.

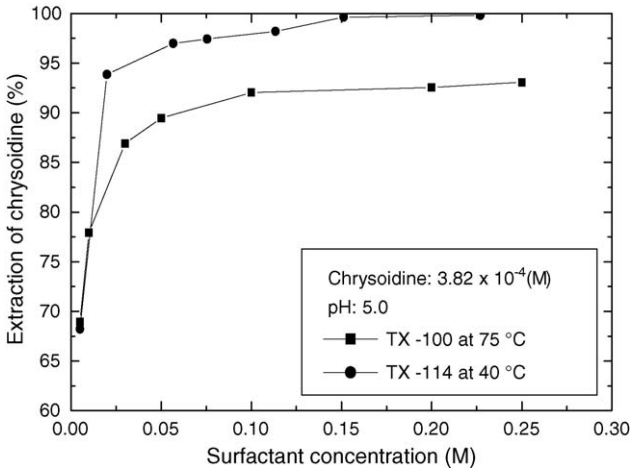

Fig. 2. Effect of surfactant concentration on extraction of dye.

3.1. Factors influencing the extent of extraction

3.1.1. Extraction profile with surfactant concentration

Fig. 2 shows the effect of concentration of TX-100 and TX-114 on the extraction of chrysoidine at 75 and 40 °C, respectively, at a feed chrysoidine concentration of 3.82×10^{-4} M. It has been observed from the figure that for a chrysoidine concentration of 3.82×10^{-4} M, extraction of the dye increases sharply when TX-100 concentration increases from 0.005 to

Table 1
Fractional coacervate phase volume and surfactant extraction data for some selective conditions for CPE of chrysoidine using TX-100

Dye ($\times 10^5$ M)	TX-100 (M)	NaCl (M)	$CaCl_2$ (M)	Temperature (°C)	pH	Fractional coacervate volume	Surfactant extraction (%)
38.2	0.005	–	–	75	5.0	0.004	94.34
38.2	0.010	–	–	75	5.0	0.10	97.11
38.2	0.030	–	–	75	5.0	0.06	99.04
38.2	0.050	–	–	75	5.0	0.10	99.41
38.2	0.100	–	–	75	5.0	0.12	99.69
38.2	0.200	–	–	75	5.0	0.20	99.85
38.2	0.250	–	–	75	5.0	0.23	99.88
4.77	0.100	–	–	75	5.0	0.05	99.66
9.52	0.100	–	–	75	5.0	0.09	99.67
19.0	0.100	–	–	75	5.0	0.10	99.69
76.3	0.100	–	–	75	5.0	0.16	99.71
38.2	0.050	–	–	80	5.0	0.09	99.42
38.2	0.050	–	–	85	5.0	0.08	99.45
38.2	0.050	–	–	90	5.0	0.07	99.49
38.2	0.100	–	–	75	2.0	0.18	99.98
38.2	0.100	–	–	75	5.0	0.12	99.98
38.2	0.100	–	–	75	9.0	0.11	99.98
38.2	0.100	–	–	75	12.0	0.09	99.99
38.2	0.100	0.05	–	75	5.0	0.12	99.97
38.2	0.100	0.10	–	75	5.0	0.11	99.97
38.2	0.100	0.30	–	75	5.0	0.09	99.97
38.2	0.100	0.50	–	75	5.0	0.08	99.97
38.2	0.100	–	0.05	75	5.0	0.11	99.97
38.2	0.100	–	0.10	75	5.0	0.10	99.97
38.2	0.100	–	0.30	75	5.0	0.09	99.97
38.2	0.100	–	0.50	75	5.0	0.08	99.97

Table 2
Fractional coacervate phase volume and surfactant extraction data for some selective conditions for CPE of chrysoidine using TX-114

Dye ($\times 10^5$ M)	TX-114 (M)	NaCl (M)	$CaCl_2$ (M)	Temperature (°C)	pH	Fractional coacervate volume	Surfactant extraction (%)
38.2	0.0567	–	–	40	5.0	0.12	99.20
38.2	0.0756	–	–	40	5.0	0.13	99.62
38.2	0.1134	–	–	40	5.0	0.15	99.72
38.2	0.1512	–	–	40	5.0	0.18	99.75
38.2	0.2270	–	–	40	5.0	0.21	99.77
4.77	0.0756	–	–	55	5.0	0.06	99.31
9.52	0.0756	–	–	55	5.0	0.09	99.97
19.0	0.0756	–	–	55	5.0	0.11	99.52
38.2	0.0756	–	–	55	5.0	0.13	99.62
76.3	0.0756	–	–	55	5.0	0.17	99.81
76.3	0.0756	–	–	40	5.0	0.10	99.46
76.3	0.0756	–	–	45	5.0	0.12	99.56
76.3	0.0756	–	–	50	5.0	0.15	99.68
38.2	0.0756	–	–	40	2.0	0.19	99.53
38.2	0.0756	–	–	40	3.5	0.16	99.54
38.2	0.0756	–	–	40	5.0	0.13	99.62
38.2	0.0756	–	–	40	6.5	0.12	99.71
38.2	0.0756	–	–	40	9.0	0.10	99.66
38.2	0.0756	–	–	40	11.0	0.09	99.78
38.2	0.0756	–	–	40	12.0	0.08	99.80
38.2	0.0756	0.05	–	40	5.0	0.12	99.11
38.2	0.0756	0.10	–	40	5.0	0.11	99.13
38.2	0.0756	0.20	–	40	5.0	0.10	99.14
38.2	0.0756	0.30	–	40	5.0	0.09	99.15
38.2	0.0756	0.50	–	40	5.0	0.08	99.17
38.2	0.0756	–	0.05	40	5.0	0.11	99.45
38.2	0.0756	–	0.10	40	5.0	0.10	99.50
38.2	0.0756	–	0.20	40	5.0	0.09	99.55
38.2	0.0756	–	0.30	40	5.0	0.08	99.58
38.2	0.0756	–	0.50	40	5.0	0.07	99.60

0.1 M. Beyond 0.1 M, increase in extraction efficiency becomes gradual. Whereas, that for TX-114, beyond 0.15 M, the extraction efficiency is almost constant. It may also be observed from Fig. 2 that at a surfactant concentration of 0.15 M, dye extraction is about 92% when TX-100 is used. The extraction increases to about 99.6% when TX-114 is used at the same concentration level of dye and surfactant.

At constant temperature and feed chrysoidine concentration, the fractional coacervate phase volume increases (as shown in Tables 1 and 2) with feed surfactant concentration. This is because of the fact that the concentration of surfactant in the coacervate phase remains nearly constant at constant temperature [1], and hence to maintain material balance, the coacervate phase volume increases. Therefore, there is more surfactant in micellar form present in the micellar rich phase (as volume of surfactant rich phase is more). This increases the extent of solubilization and also the extraction efficiency. However, beyond a surfactant concentration (0.1 M for TX-100 and 0.075 M for TX-114) the extraction becomes nearly constant. The surfactant partition coefficient (defined as the ratio of the concentration of surfactant in the coacervate phase to that in the dilute phase) remains almost constant with increasing surfactant concentration as shown in Fig. 3. As the partition coefficient remains unchanged, the distribution of the dye in these two phases remains almost constant. This is reflected in the near constant values of extraction in Fig. 2.

3.1.2. *Effects of initial dye concentration on extraction*

The effects of feed chrysoidine concentration on the dilute phase chrysoidine concentrations have been shown in Fig. 4. Surfactants used are 0.1 M of TX-100 and 0.075 M of TX-114 for the feed chrysoidine concentrations of 4.77×10^{-5}, 9.52×10^{-5}, 1.90×10^{-4}, 3.82×10^{-4} and 7.63×10^{-4} M. It has been observed from the figure that in both the cases, the dilute phase chrysoidine concentration increases sharply with

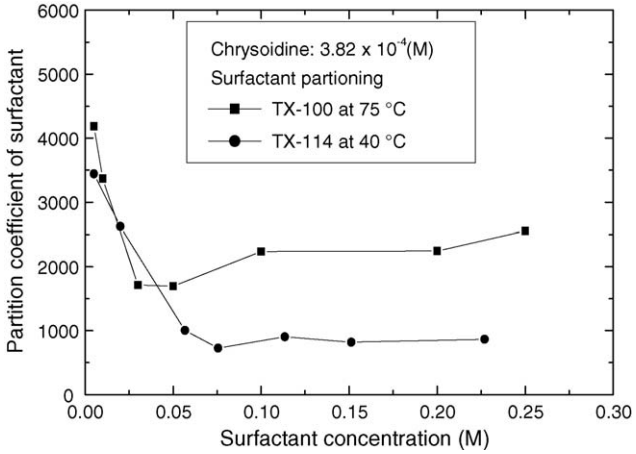

Fig. 3. Effect of surfactant concentration on the partition coefficient of surfactant.

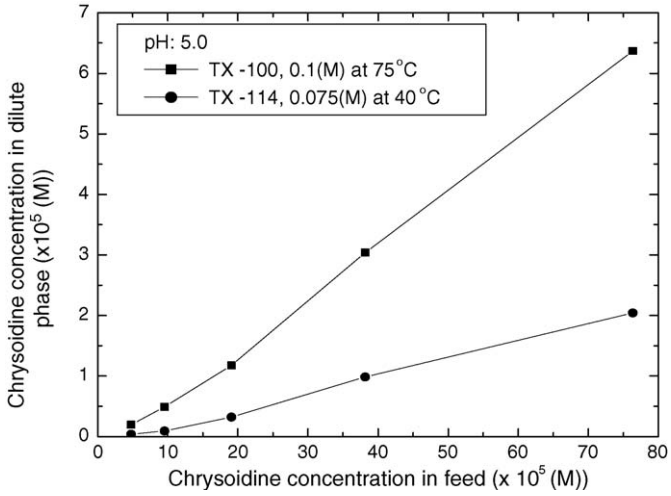

Fig. 4. Effect of feed dye concentration on the dilute phase dye concentration.

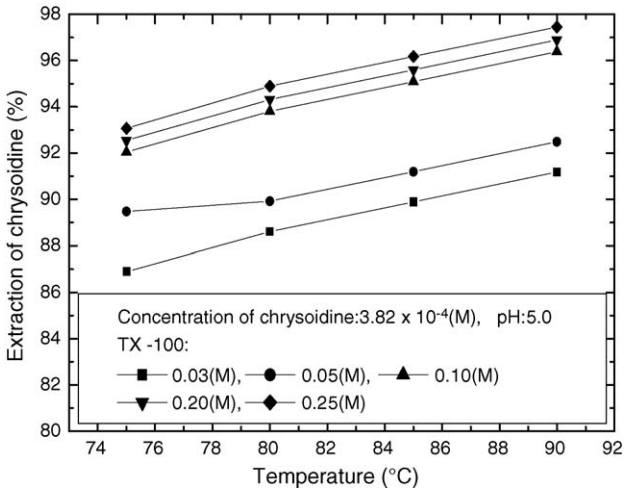

Fig. 5. Effect of temperature on the dye extraction at different TX-100 concentration and at a dye concentration of 3.82×10^{-4} M.

the feed chrysoidine concentration. From Fig. 4, it may also be observed that for a particular feed dye concentration, dilute phase dye concentration remains much higher when TX-100 is used. For example, for 3.82×10^{-4} M dye, about 92% of dye extraction is possible when 0.1 M of TX-100 is used at 75 °C. For the same dye concentration, 0.075 M of TX-114 at 40 °C increases the extraction up to about 97.5%.

As in Tables 1 and 2, the fractional coacervate phase volume increases with feed dye concentration at constant temperature, surfactant concentration and pH. It is well known that compounds, like, urea, formamide, etc., increase CMC of the non-ionic surfactants in the aqueous solution because of their disruption of the water structure [27]. This may increase the hydration of the hydrophilic group of the surfactant [27]. In the present study, the chrysoidine dye has similar active functional group of urea. Therefore, it may be assumed that in presence of dye (at constant surfactant concentration), CMC of the non-ionic surfactant increases. This implies that the number concentration of the micelles decreases with dye concentration. Therefore, increasing feed dye concentration only results in an increase of unsolubilized dye that will be increasing its concentration in the dilute phase and hence reduces the extraction efficiency. The presence of dye increases the CMC that results in lesser number of micelle and hence a lowering of the volume. But this decrease is more than offset by the hydrating effect of the dye resulting in the formation of larger molecules. The effective volume thus shows a small increase with the chrysoidine concentration.

3.1.3. *Effects of temperature on extraction*

The effects of temperature on the efficiency of chrysoidine extraction are shown in Fig. 5 for an initial chrysoidine concentration of 3.82×10^{-4} M at 0.03, 0.05, 0.10, 0.20 and 0.25 M of TX-100. It is clear from the figure that the extraction of chrysoidine increases with temperature and TX-100 concentration. It may be observed that the extraction of chrysoidine (for 3.82×10^{-4} M of feed dye and 0.25 M of TX-100) increases from about 93 to 97.5%, when the temperature increases from 75 to 90 °C. The variation of chrysoidine extraction with temperature using TX-114 at different feed dye concentration is shown in Fig. 6. Same trend of dye extraction with temperature has been observed when TX-114 is used instead of TX-100. It may be noted that for TX-114, the extraction of dye is marginally improved with temperature. The extraction (for 3.82×10^{-4} M of feed dye and 0.075 M of TX-114) increases marginally from about 97.5 to only 98%, when the temperature increases from 40 to 55 °C. Therefore, the extraction should be carried out at an operating temperature of 40 °C for TX-114.

At higher temperature, CMC of non-ionic surfactants decreases [30]. Moreover, non-ionic surfactants appear relatively more hydrophobic at higher temperatures, due to an equilibrium shift that favors dehydration of the ether oxygens [31]. This leads to an increase in the number concentration of micelles. Therefore, the solubilization capability of the micellar solution increases with temperature leading to an increase in the dye extraction. It is also evident from Table 1 that the volume of coacervate phase decreases with temperature. For example, at 3.82×10^{-4} M of dye and 0.05 M of TX-100, fractional volume of coacervate phase decreases from 0.10 to 0.07 when temperature is raised from 75 to 90 °C. At an elevated temperature,

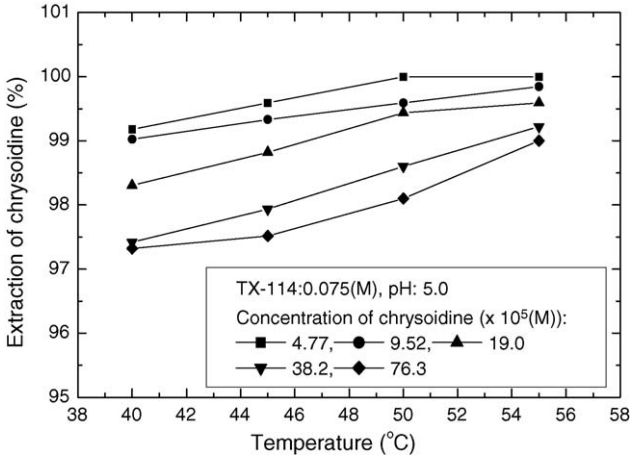

Fig. 6. Effect of temperature on the dye extraction at different dye concentration and at a TX-114 concentration of 0.075 M.

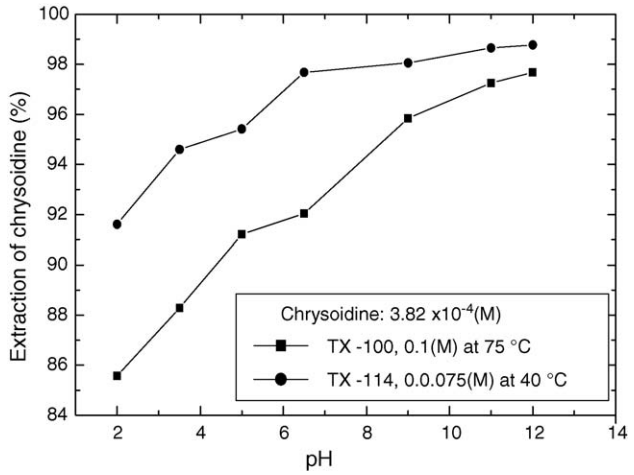

Fig. 7. Effect of pH on extraction of dye using TX-100 and TX-114.

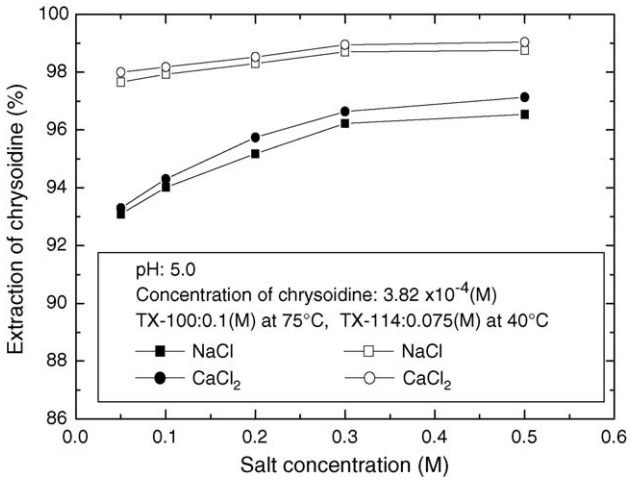

Fig. 8. Effect of NaCl and $CaCl_2$ concentration on extraction of chrysoidine.

the interaction among the TX-100 micelles increases leading to dehydration from the external layers of micelles resulting into a decrease in volume of coacervate phase [31].

3.1.4. Effects of pH on extraction

The effects of the pH of the solution on the extent of chrysoidine extraction are shown in Fig. 7 for 3.82×10^{-4} M of feed chrysoidine using 0.1 M of TX-100 and 0.075 M of TX-114 at 75 and 40 °C, respectively. Extraction of chrysoidine is less in acidic pH and increases with pH. p*K* value of the present dye is found to be around 6.0. At lower pH (less than p*K* value), the dye is protonated, as shown in Fig. 1 and its ionic characteristics increase leading to less solubilization of the dye in the hydrophobic micelles. At higher pH (above p*K* value), the dye is deprotonated and it behaves like a hydrophobic molecule and easily gets solubilized in the micelles. Therefore, dye solubilization is more at basic pH leading to an increase in the dye extraction and lower fractional coacervate phase volume (Tables 1 and 2).

3.1.5. Effects of salt concentration on extraction

Fig. 8 shows the variation of extraction efficiency with salt (NaCl and $CaCl_2$) concentration. The surfactants used are TX-114 at 40 °C and TX-100 at 75 °C. It may be observed from the figure that the extraction of chrysoidine increases from about 93 to 97% when concentration of $CaCl_2$ increases from 0.05 to 0.5 M at a fixed initial dye concentration (3.82×10^{-4} M in this case) and TX-100 concentration of 0.1 M. Beyond 0.3 M the increase in efficiency becomes gradual. Same trend of chrysoidine extraction has been observed with NaCl. The trend with TX-114 is similar. It is well known that due to its salting-out effect, salts decrease the cloud point of the surfactant and it promotes the dehydration of the ethoxy groups on the outer surface of the micelles [2]. For example, cloud point temperature of TX-100 decreases from 63 to 54 °C when the concentration of sodium chloride increases from 0.05 to 0.5 M; for the same variation of concentration of calcium chloride, cloud point decreases from 62 to 53 °C. Similarly, cloud point temperature of TX-114 decreases from 22.5 to 18 °C for the above variation of NaCl concentration and it is from 22 to 17 °C for the same concentration variation of $CaCl_2$. Therefore, addition of NaCl increases phase separation enhancing the micellar concentration in the coacervate phase, leading to solubilization of more dye. The fractional coacervate phase volume also decreases with salt concentration. Due to salting-out effect, more water goes to the dilute phase, decreasing the volume of the coacervate phase. It is clear from Fig. 8 that the salting-out effect is more pronounced for divalent calcium chloride compared to monovalent sodium chloride.

3.2. Solubilization isotherm

In order to determine dye solubilization capacity of TX-100 and TX-114 at different temperatures, the experimental data are used to calculate the solubilization isotherms. These isotherm data are the basic requirements for the design of CPE system.

Figs. 9 and 10 show the isotherms at different temperatures, for chrysoidine–TX-100 and chrysoidine–TX-114 system, respectively. The Langmuir type adsorption isotherm is successfully used in describing many adsorption processes. The

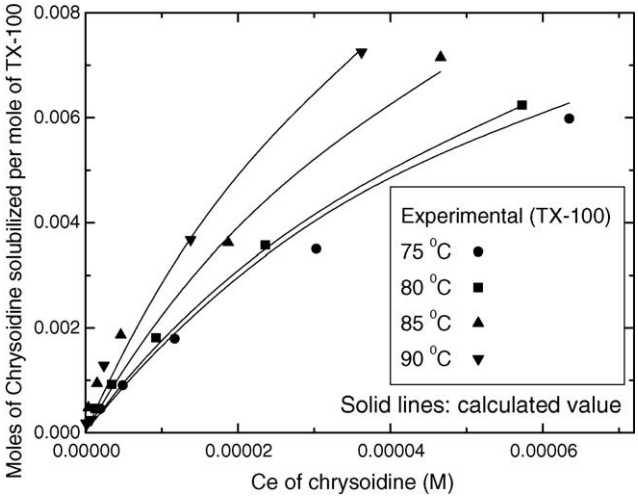

Fig. 9. Solubilization isotherm for chrysoidine at different temperature using TX-100.

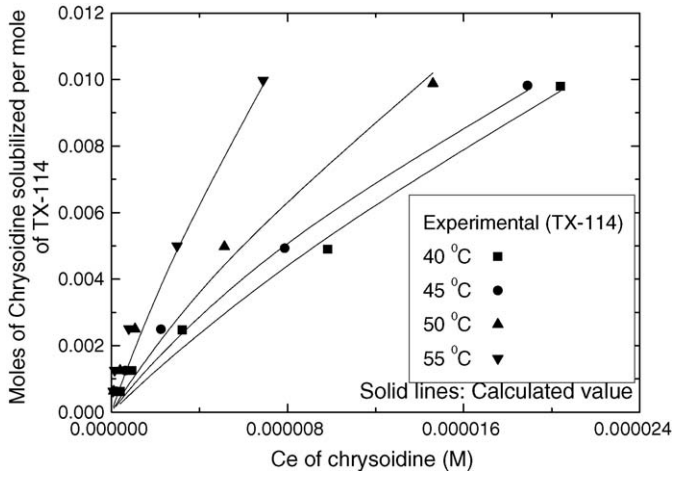

Fig. 10. Solubilization isotherm for chrysoidine at different temperature using TX-114.

same model has been used to explain the solubilization of dye molecule in both TX-100 and TX-114. Eq. (1) gives the expression of the well-known Langmuir model.

$$q_e = \frac{mnC_e}{1 + nC_e} \tag{1}$$

where q_e is the moles of dye solubilized per mole of surfactant. C_e is the dilute phase equilibrium concentration of the dye. The constant m and n are the Langmuir constants signifying the solubilization capacity and energy of solubilization, respectively [32].

Values of m and n for each operating temperatures are evaluated by regression analysis using the experimental data. The variations of m and n with temperature are fitted to a quadratic model. The expressions of m and n as function of temperature are given below:

For chrysoidine–TX-100 system:

$$m = 2.4 \times 10^{-1} - 5.9 \times 10^{-3}T + 3.7 \times 10^{-5}T^2 \quad (r^2 = 0.99) \tag{2}$$

$$n = -5.1 \times 10^4 + 1.3 \times 10^3 T - 5.9T^2 \quad (r^2 = 0.99) \tag{3}$$

For chrysoidine–TX-114 system:

$$m = 4.7 \times 10^{-1} - 1.9 \times 10^{-2}T + 2.1 \times 10^{-4}T^2 \quad (r^2 = 0.99) \tag{4}$$

$$n = -1.6 \times 10^5 + 5.90 \times 10^3 T - 37.4T^2 \quad (r^2 = 0.99) \tag{5}$$

where T is the temperature in °C.

3.3. Variation of fractional coacervate phase volume

In order to calculate the performance of a CPE process, the variation of the fractional coacervate phase volume with concentration of the feed surfactant and the operating temperature needs to be studied. In this regard, the following correlation for the fractional coacervate phase volume with the feed surfactant concentration is proposed:

$$F_c = aC_s^b \tag{6}$$

where F_c is the fractional coacervate volume and C_s is the molar concentration of the feed surfactant solution. As mentioned in the experimental section, a wide range of feed surfactant concentration and dye concentration is used in the experiments at various operating temperatures. F_c is thereby correlated with C_s using Eq. (6). For fixed feed dye concentration, the parameters a and b vary linearly with temperature and can be expressed as follows:

$$a = P + QT \tag{7}$$

$$b = R + ST \tag{8}$$

The parameters P, Q, R and S are evaluated for various feed chrysoidine concentrations. The value of Q varies from −0.04 to −0.06 for chrysoidine–TX-100 and −0.09 to −0.13 for chrysoidine–TX-114 system. Therefore, an average value of Q is considered for further calculations for both the cases. They are −0.05 for chrysoidine–TX-100 and −0.11 for chrysoidine–TX-114 system. The variation of S for both the system remains within 0.08–0.10. For both the cases, the average value of S considered is 0.09. Variations of P and R for the two dyes are expressed by the following correlation with feed dye concentration.

For chrysoidine–TX-100 system:

$$P = 5.9 - 2. \times 10^2 C_0 - 1.9 \times 10^{-8}\frac{1}{C_0^2} \quad (r^2 = 0.99) \tag{9}$$

$$R = 3.9 \times 10^{-1} + 6.9C_0 + 4.0 \times 10^{-9}\frac{1}{C_0^2} \quad (r^2 = 0.99) \tag{10}$$

For chrysoidine–TX-114 system:

$$P = 9.4 - 8.0 \times 10^3 C_0 + 1.8 \times 10^{-8}\frac{1}{C_0^2} \quad (r^2 = 0.99) \tag{11}$$

$$R = 4.2 \times 10^{-1} - 2.4 \times 10^3 C_0 + 2.2 \times 10^{-9}\frac{1}{C_0^2} \quad (r^2 = 0.97). \tag{12}$$

3.4. Determination of surfactant requirement for the removal of dye to a desired level without using salts

Using the developed correlations (Eqs. (1)–(5) and Eqs. (7)–(12)), a calculation procedure is outlined to determine the amount of surfactant required for the removal of dye up to a desired level. The solublization isotherm is defined as,

$$q_e = \frac{\text{models of dye solubilized}}{\text{moles of TX} - 100\,\text{used}} = \frac{A}{X} \tag{13}$$

where A is the moles of dye solubilized in the micelles and X is the moles of TX-100 used in the feed.

Moles of dye solubilized can be obtained from mass balance,

$$A = V_0 C_0 - V_d C_e \quad (14)$$

where V_0 and V_d are the volume of the feed solution and that of the dilute phase after CPE. C_0 and C_e are the molar dye concentration in the feed and that remaining in the dilute phase after CPE. Hence, C_e is the desired concentration level of the dye for which the CPE is to be performed. In terms of fractional coacervate phase volume (F_c), Eq. (14) can be written as,

$$A = V_0[C_0 - C_e(1 - F_c)] \quad (15)$$

Using Eqs. (6), (13) and (15), the moles of surfactant required can be expressed as,

$$X = \frac{V_0}{q_e}[C_0 - C_e(1 - aC_s^b)] \quad (16)$$

If C_s is the concentration of surfactant initially in the feed, X in Eq. (16) can be expressed as,

$$X = C_s V_0 \quad (17)$$

Equating Eqs. (16) and (17), the following governing equation of C_s is obtained:

$$C_s = \frac{1}{q_e}[C_0 - C_e(1 - aC_s^b)] \quad (18)$$

Expressing q_e in terms of C_e from Eq. (1), the expression of C_s is obtained as,

$$C_s = \frac{(1 + nC_e)[C_0 - C_e(1 - aC_s^b)]}{mnC_e} \quad (19)$$

With the knowledge of feed dye concentration (C_0), the desired level of dye concentration in the dilute phase (C_e), isotherm constants m, n and design parameters a, b, Eq. (19) can be solved by trial and error to obtain C_s. Solving Eq. (19) using some typical temperature conditions and fixing the desired concentration level of dye in the dilute phase as 3.82×10^{-6} M, the surfactant concentrations required for various feed dye concentrations are calculated and plotted in Fig. 11 for both chrysoidine–TX-100 and chrysoidine–TX-114 systems, respectively. It may be observed from the figure that the required surfactant concentration increases with feed dye concentration and is less at higher temperature. Higher operating temperature requires higher energy input to the system. Therefore, there exists a trade off between the feed surfactant dose and the operating temperature with respect to the feed dye concentration to affect a desired level of dye removal.

4. Conclusions

Cloud point extraction is successfully used to remove toxic color chrysoidine dye using TX-100 and TX-114 as non-ionic surfactants. The effects of pH, temperature, concentrations of salts, surfactants and dye on the extraction of dye have been studied in detail. The extraction efficiency increases with temperature, surfactant and salt concentration. It is observed that for 3.82×10^{-4} M of chrysoidine, the optimum TX-114 concentration is about 0.15 M for 99% of dye extraction at 40 °C, whereas for TX-100, it is about 0.1 M for 92% extraction at 75 °C. For TX-100, the chrysoidine extraction increases significantly with temperature (from 75 to 90 °C). For TX-114, the extraction increases marginally with temperature (from 40 to 55 °C). This shows that TX-114 performs much better than TX-100 from the viewpoint of energy consumption. The optimum operating pH for both the surfactants is about 9.0. The addition of electrolytes enhances the extraction of chrysoidine. Chrysoidine extraction is more in the presence of calcium chloride compared to sodium chloride. The optimum salt concentration is found to be about 0.3 M. Solubilization isotherms are developed from the CPE data of chrysoidine. Temperature dependency of the constants of the isotherms is also evaluated. From the experimental results, a correlation has been developed to quantify the variation of fractional coacervate phase volume at different operating conditions. An approach to design a cloud point extractor has been proposed to estimate the surfactant required for a known temperature, initial and desired dye concentration.

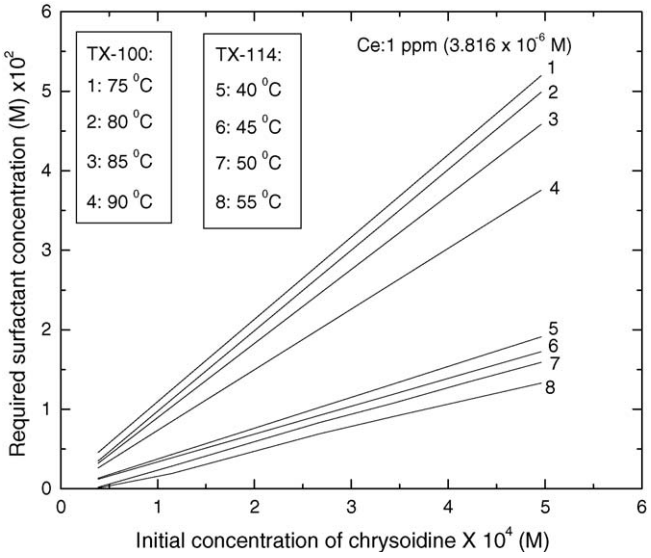

Fig. 11. Variation of the requirement of TX-100 and TX-114 concentration for different initial chrysoidine concentration at different temperatures to bring down its dilute phase concentration to 3.82×10^{-6} M.

Acknowledgements

This work is partially supported by a grant from the Ministry of human Resource Development (Scheme no. F. 27-1/2004.TS.V), New Delhi, Government of India. Any opinions, findings and conclusions expressed in this paper are those of the authors and do not necessarily reflect the views of MHRD.

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