Cloud point extraction (CPE)
Part I: Removal of Bromocresol green with neutral surfactant (TX100)

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ABSTRACT

A cloud-point extraction (CPE) process using the nonionic surfactant, Triton X-100, for the separation of bromocresol green (BCG) from aqueous solution is investigated using UV-vis spectrophotometer. The optimum extraction conditions viz. pH, dye and surfactant are arrived by OVAT (one variable at a time) procedure. The calibration model for variation of absorbance versus analyte is linear. Thermodynamic parameters (entropy, enthalpy and Gibb's free energy) are reported.

Keywords: Bromo cresol green (BCG), Cloud point extraction, Triton X-100, UV-vis spectra, calibration.

INTRODUCTION

Bromo cresol green (BCG) finds a pivotal role in textile industry. But, the dye is toxic at high concentrations and cause allergic reaction, respiratory cancer and skin disorder in humans. Cloud point extraction (CPE) technique has gained importance in this decade as a quantitative technique for the extraction of organic compounds [1-7] from aqueous solutions. The core of the method is based on the solubilization of analyte in the micellar [8] phase. More hydrophobic analytes show favorable distribution between the micellar and aqueous phases. The preconcentration factors are similar to distribution ratio in solvent extraction terminology [5]. The Higher numerical values of preconcentration factors in CPE add a new dimension in separation procedure over solid-phase extraction (SPE) and co precipitation. This is a green approach [1,9] and also simple as well as inexpensive. In this communication, we report the quantitative separation of BCG from aqueous solutions at micro level.

MATERIALS AND METHODS

Materials: Triton X-100 (Qualigens Analytical grade (Mumbai,India) was purified by heating for 3h at 70°C following the procedure of Kumar and Balasubrahmanium [10]. An aqueous solution of 0.1 mol/dm^3 TX-100 was prepared by dissolving 31.4 g in 500 Ll of standard volumetric flask. Bromocresol green sample from Fisher Scientific was used without further purification. A stock standard solution of BCG of 1.0 g dm$^{3-1}$ was prepared and the flask was wrapped with black paper to avoid photochemical effect. The

solutions for the current study were prepared by dilutions of the stock solution. Acetic acid, Sodium acetate, NaCl, Na_2SO_4, KH_2PO_4 and Na_2HPO_4 are of analytical grade from Merck India (Mumbai).

Method: In Carvalho's [11] procedure, the micelle and dye mixture under optimum conditions is heated and clouding/clearing temperatures are recorded. The average of these two temperatures (within an accuracy of $\pm 0.5^{o}C$) is called cloud point. This cloud point extraction experiment was carried out in a 10.0 ml centrifuge tube (with a screw cap) containing different amounts of TX-100 and BCG. The contents are sonicated for 2 minutes for thorough mixing. The solution is heated up to $80^{\circ}C$ in a thermostatic temperature bath for 20min. The turbid solution was centrifuged at 3500 rpm for 5 min followed by cooling for about 2 minutes. The two (surfactant rich (coacervate) and dilute) phases separate and their volumes were measured. Three replicate experiments were performed for assessing the precision. The concentrations of BCG in two phases were monitored in the visible region using PerkinElmer lamda-25 UV-Visible spectrophotometer.

Absorption Spectrum of BCG: The spectrum of aqueous BCG (Fig.1) in the visible region shows maximum extinction coefficient around 610 nm (Fig. 2). TX-100, the micelle, does not have any detectable influence on the absorption profile.
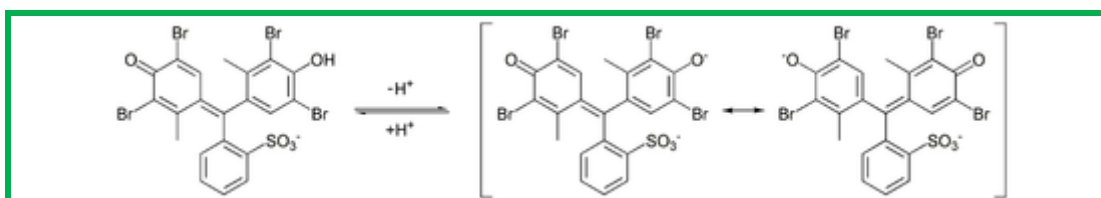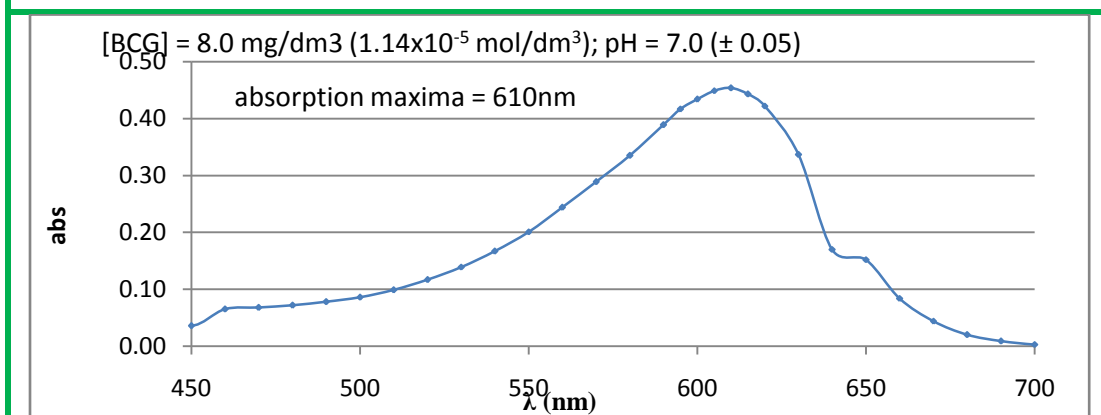

Fig. 1: Structure of BCG dye

[BCG] = 8.0 mg/dm3 (1.14×10^{-5} mol/dm^3); pH = 7.0 ($\pm$ 0.05)

absorption maxima = 610nm

Fig. 2: Spectra of BCG

Univariate experimental design for optimum operating conditions: Each of the influencing factors viz. concentrations of buffer, BCG, surfactant, electrolytes, phase volume ratio on CPE, pre concentration factor, partition coefficient were varied to arrive at optimum extraction conditions.

RESULTS AND DISCUSSION

The optimum conditions for maximum extraction of BCG from OVAT experiments are in (Tables 1 to 6).

Table 1:Effect of pH on extraction efficiency and distribution coefficient (K_d)

$[BCG]_{initial}$ = 1.28×10^{-4} mol/dm^3; [TX-100] = 4.0×10^{-2} mol/dm^3; Temp = 80 ± 0.1 $^\circ$C

pH (± 0.05)	$10^4[BCG]_{mic}$ mol/dm^3	$10^6[BCG]_{dil}$ mol/dm^3	Efficiency (η %)	K_d
2.0	7.23	2.88	93.63	250.79
4.0	6.67	2.24	95.06	297.40
6.0	7.30	2.40	94.68	304.00
7.0	7.43	1.12	97.52	662.86
8.0	6.95	2.24	95.05	310.20

Table 2:Effect of [TX-100] on extraction efficiency

$[BCG]_{initial}$= 4.29×10^{-5} mol/dm^3 ; Temp= $80 \pm 0.1$$^\circ$C

$10^2[TX\text{-}100]$ mol/dm^3	$10^4[BCG]_{mic}$ mol/dm^3	$10^5[BCG]_{dil}$ mol/dm^3	Phase volume ratio R_v (%)	Pre conc. factor f_c	Efficiency (% η)	K_d
2.0	2.88	3.62	2.56	40.00	16.47	7.96
3.0	3.36	2.59	5.26	20.00	40.73	12.96
4.0	3.62	2.26	6.10	17.39	49.73	16.04
5.0	3.64	1.62	7.53	14.29	65.31	22.49
6.0	3.68	1.33	10.20	10.81	71.80	22.94

Table 3: Effect of BCG on extraction efficiency
[TX-100] = 4.0×10^{-2} mol/dm^3; Temp = 80 ± 0.1 $^\circ$C

$10^5[BCG]_{int}$ mol/dm^3	$10^4[BCG]_{mic}$ mol/dm^3	$10^5[BCG]_{dil}$ mol/dm^3	Efficiency (% η)
1.43	1.38	0.69	54.97
2.86	3.60	1.38	54.85
4.29	4.43	2.21	51.57
5.72	6.22	3.22	47.80
7.15	8.17	4.29	44.17
8.58	8.71	5.51	39.96

Table 4:Effect of [salt] on extraction efficiency

Temp = $80 \pm 0.1$$^\circ$C; $[BCG]_{initial}$ = 4.29×10^{-5} mol/dm^3; [TX-100] = 4.0×10^{-2} mol/dm^3

10^2 [Electrolyte] Mol dm^{-3}	Efficiency (% η)			
	NaCl	Na$_2$SO$_4$	Na$_2$HPO$_4$	KCl
2.5	69.74	90.47	82.71	80.66
5.0	75.66	92.24	88.74	81.45
7.5	77.48	94.00	88.77	82.14
10.0	79.19	96.82	88.36	83.17
12.5	80.95	95.76	86.59	86.19
15.0	82.71	95.036	78.01	87.91

Table 5: Effect of Temperature on extraction efficiency		
Factors	Temp ($\pm 0.1°C$)	Efficiency (η %)
pH : 6.0($\pm$0.05)	70	83.89
[BCG]$_{initial}$: 1.72x10^{-4}mol/dm^3	80	86.63
	90	88.80
[TX-100] : 4.0x10^{-2}mol/dm^3		

Table 6: Thermodynamic parameters pH = 6.0($\pm$0.05); [BCG]$_{initial}$ = 1.72x10^{-4}mol/dm^3; [TX-100] = 4.0x10^{-2}mol/dm^3			
Temp ($\pm 0.1°C$)	-ΔG (KJ/mole)	ΔS (KJ/mole/K)	ΔH (KJ/mole)
70	12.61		
80	13.68	0.11	22.98
90	14.74		

Calibration model of dye using CPE: The linear least squares analysis of concentration of BCG in the range 0.5-8.0 mg/dm^3 against absorbance follows a linear pattern without any intercept on y axis.

The charge of the dye does not influence the extraction efficiency. It is a di-anion around a pH of 6.5, as pKa values are 5.87 and 6.58. Our experimental result of increasing efficiency of extraction up to pH 8.0 is in conformity with decrease in cloud point. But, greater efficiency at pH> 8.0 is due to increased electrolyte concentration. In the concentration range of BCG in the present study, there is no significant change in extraction efficiency. This is attributed to unaltered cloud point with increasing concentration of dye. An increase in efficiency (Fig. 3) and pre-concentration (Fig. 4) factor of extraction with increasing surfactant concentration has been observed. The extraction of BCG with TX-100 is a cumulative effect of hydrophobic interactions between BCG and micelles in the solution. Purkait [12-15] reported that surfactant concentration as well as solubilized dye in the micellar phase increases to maintain the mass balance.

It has been shown that the presence of electrolyte changes the cloud point (CP) by different mechanisms [16]. Sodium chloride, a salting out electrolyte, decreases the cloud point temperature. It can promote the dehydration of ethoxy groups on the outer surface of the micelles. It results in enhancing the miceller concentration leading to solubilisation of more dye and consequently more extraction [17]. Thus, there is reduction in the time required for phase separation. A lower salt concentration gives a smaller pre concentration factor, due to the larger volume in the surfactant-rich phase [18]. The ability of salts to enhance extraction efficiency of the dye is in the order Na$_2$HPO$_4$ > Na$_2$SO$_4$ > NaCl > NaI (Fig.5). At higher temperature, the non-ionic surfactant becomes more hydrophobic, as CMC decreases [20]. The range of preconcentration factors reported in the literature [19,20] is between 10 and 100 (Fig. 6). But, CPE method gives a better preconcentration factor compared to conventional solvent extraction methods.
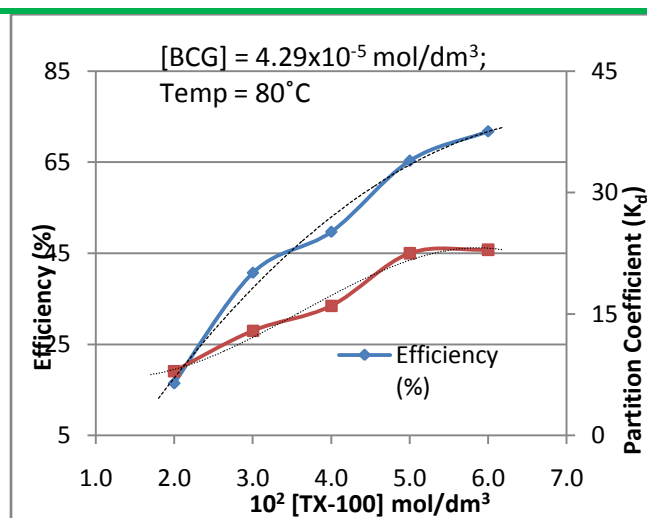
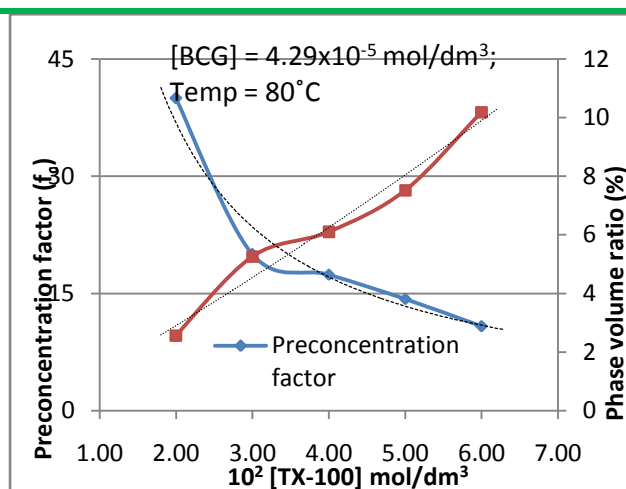Figure 3 Effect of [TX-100] on extraction efficiency and distribution coefficient

Figure 4 Effect of [TX-100] on pre-concentration factor and phase volume ratio

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