



Partitioning behavior of methylene blue in aqueous two phase systems

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ABSTRACT

Partitioning of methylene blue (MB) was studied in aqueous two phase systems (ATPS) prepared by mixing aqueous solutions of polymers or of a triblock copolymer with aqueous salt solutions. The partition coefficient (K) of MB in ATPS was investigated as a function of tie line length (TLL), electrolyte nature (Na_2SO_4 and Li_2SO_4), polymer molar mass, hydrophobicity of the polymers, and temperature. MB molecules concentrated preferentially in the top phase (the polymer rich phase). The partitioning behavior of MB was dependent on tie line length and polymer molar mass. It was observed that the MB partition coefficient is dependent on electrolyte nature, following the relative order $\text{Na}_2\text{SO}_4 > \text{Li}_2\text{SO}_4$. Values of K for MB decreased with increases in the hydrophobicity of the top phase. Higher temperatures facilitated the transfer of MB molecules to the top phase, indicating an endothermic process.

Keywords: aqueous two phase systems, methylene blue, partition coefficient.

INTRODUCTION

Aqueous two phase systems (ATPS) have been considered an attractive method to extract different compounds such as metals [1,2], biomolecules [3,4], and dyes [5-12]. ATPS can be formed by mixing aqueous solutions of water-soluble polymers (PEO is the polymer most commonly used) and salts in a specific concentration and temperature [13]. These systems are composed by two phases; one phase is rich in polymer (top phase), and other phase, the bottom phase, contains more salt. Nevertheless, water is the major component in both phases [13]. In comparison with traditional liquid-liquid extraction (water/organic solvent), the partitioning of the solutes in ATPS occurs between two non-miscible aqueous phases, which has evident environment benefits.

Methylene blue (MB) is a cationic dye widely used in the textile industry [14]. Depending on the type of contamination, MB can cause harmful effects such as vomiting, diarrhea, gastritis, mental confusion, and profuse sweating [15]. Therefore, many treatment processes have been developed for the removal of methylene blue from wastewater such as photocatalytic degradation [16], photo-Fenton processes [17], biodegradation [18], and adsorption processes [19,20]. However, there are no studies in the literature reporting the use of ATPS formed by polymers and sulfate salts as a possible method of extracting methylene blue from wastewater.

The aim of this work was to study the partition behavior of the cationic dye, methylene blue (MB), in aqueous two phase systems (ATPS) formed by polymers and sulfate salts. The influence of tie line length (TLL), electrolyte nature, polymer molar mass, hydrophobicity, and temperature on the partition coefficient of MB was investigated.

EXPERIMENTAL SECTION

Materials

Poly(ethylene oxide), PEO, with molar masses of 1500 and 6000 $\text{g}\cdot\text{mol}^{-1}$ was obtained from Vetec (Brazil). The Poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) copolymer, L64, with an average molar mass of 2900 $\text{g}\cdot\text{mol}^{-1}$, was purchased from Aldrich. The salts, Na_2SO_4 and $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$, were purchased from

Vetec (Brazil). Methylene Blue (MB) was acquired from Vetec (Brazil). The chemical structure of MB is illustrated in Figure 1. Distilled water was used in all of the experiments. All reagents were used as received.

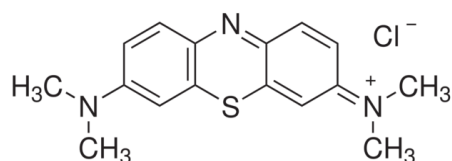


Figure 1. Schematic representation of the chemical structure of methylene blue

Partitioning experiments

The aqueous two phase systems (ATPS) were prepared by mixing aqueous solutions of polymers or a copolymer with aqueous salt solutions to obtain a total system composition in accordance with the corresponding phase diagram reported in the literature [21-23]. Four different compositions were chosen from each phase diagram. The prepared aqueous two phase systems were allowed to equilibrate at either 25 °C or 40 °C for 24 h in a thermostatic water bath (Tecnal, Brazil). After this time, the aliquots from the top and bottom phase were removed. A total of 2.5 g from each phase were mixed with 1.5 mg of methylene blue in a glass tube. These systems were continuously mixed and left in the thermostatic water bath at either 25 °C or 40 °C for 24 h.

2.3. Partition coefficient

The partition coefficient (K) of methylene blue (MB) between the two phases is defined as:

$$K_{MB} = \frac{A_T}{A_B}$$

where A_T and A_B are the absorbance of MB adjusted by the respective dilution factor in the top and bottom phases, respectively.

The absorbance of MB in both phases was determined by measuring the absorption at 665 nm in a Shimadzu UV-2600 spectrometer. Three experiments were performed in order to determine the average of the partition coefficient. The relative standard deviation of the partition coefficient was less than 10 %.

K of MB was determined for four different tie line lengths (TLL) for all of the ATPS, where TLL is:

$$TLL = \sqrt{(C_{\text{polymer}}^T - C_{\text{polymer}}^B)^2 + (C_{\text{salt}}^T - C_{\text{salt}}^B)^2}$$

C_{polymer} and C_{salt} are the polymer and salt concentrations in % (w/w), in the top (T) and bottom (B) phases of the ATPS used. TLL is a thermodynamic parameter that shows the difference between polymer and salt concentrations in the top and bottom phases of the ATPS.

RESULTS AND DISCUSSION

Influence of tie line length (TLL) and salt on the partitioning of methylene blue

The experimental partition coefficients of methylene blue as a function of TLL values of the ATPS formed by PEO1500/ $\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$ and PEO1500/ $\text{Li}_2\text{SO}_4/\text{H}_2\text{O}$ at 25 °C are presented in Figure 2. The results show that TLL values have a great effect on MB partitioning. With increases in the TLL of the ATPS, methylene blue preferentially partitions to the polymer rich phase, as showed by K values higher than 1. This behavior indicates the affinity of methylene blue to the top phase. Similar results were obtained for the partitioning of different dyes in aqueous two phase systems [5-12].

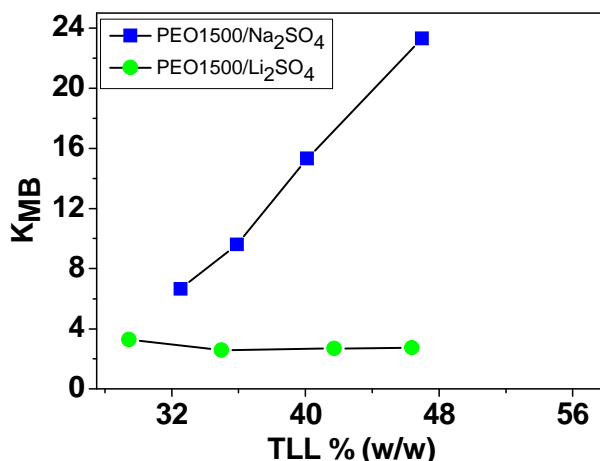


Figure 2. Partition coefficient of methylene blue as a function of TLL values of the ATPS formed by PEO1500/Na₂SO₄/H₂O and PEO1500/Li₂SO₄/H₂O at 25 °C

The effect of salt on the partitioning of methylene blue (MB) is shown in Figure 2. The relative order of the partition coefficient of MB is PEO1500/Na₂SO₄ > PEO1500/Li₂SO₄, indicating that sodium sulfate is more efficient in the partitioning of MB in the polymer rich phase than lithium sulfate. da Silva and Loh [24] showed that the PEO structure is more positively charged in ATPS formed with lithium than with sodium. Therefore, a higher rate of interaction between the cationic dye, methylene blue, and PEO1500-Na⁺ than in ATPS formed by PEO1500/Li₂SO₄.

The Gibbs standard energy change ($\Delta_r G^\circ$) was obtained to understand the influence of salt on the partition behavior of MB in the ATPS formed by PEO1500/Na₂SO₄ and PEO1500/Li₂SO₄ at 25 °C. The Gibbs standard energy change ($\Delta_r G^\circ$) was determined by following the thermodynamic relationship:

$$\Delta_r G^\circ = -RT \ln K_{MB}$$

where R is the universal gas constant, T is the absolute temperature, and K_{MB} is the dye partition coefficient.

$\Delta_r G^\circ$ is the change in the Gibbs energy of the system when 1 mol of MB is transferred from the bottom phase to the top phase. As can be observed in Figure 3, $\Delta_r G^\circ$ values are negative and show the spontaneous transfer of methylene blue to the polymer rich phase. Additionally, $\Delta_r G^\circ$ values are more negative in the ATPS composed by PEO1500/Na₂SO₄ than PEO1500/Li₂SO₄, demonstrating the greater preference of MB to the top phase of the ATPS formed by PEO1500/Na₂SO₄.

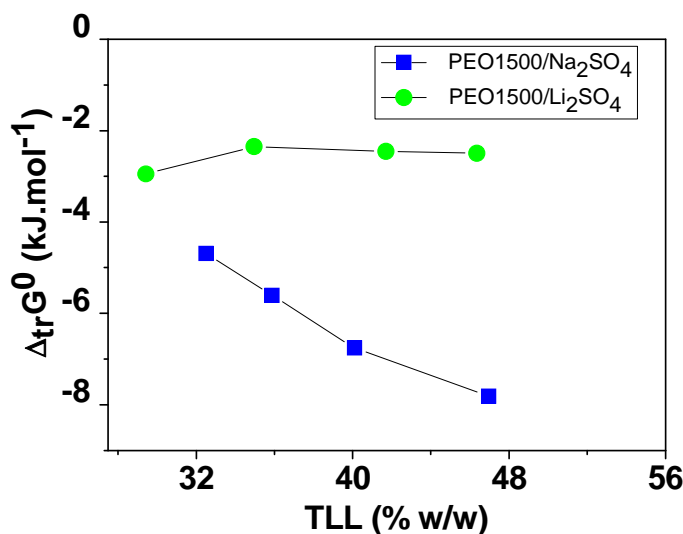


Figure 3. Values of Gibbs standard energy change of the transfer of methylene blue as a function of TLL values of the ATPS formed by PEO1500/Na₂SO₄/H₂O and PEO1500/Li₂SO₄/H₂O at 25 °C

Influence of PEO molar mass on the partitioning of methylene blue

Figure 4 shows the partition behavior of methylene blue (MB) in the aqueous two phase systems formed by PEO1500/ Na_2SO_4 and PEO6000/ Na_2SO_4 at 25 °C. The experimental results revealed that the partition coefficient of methylene blue is influenced by the molar mass of PEO. K_{MB} decreases with increases in PEO molar mass. A similar tendency was found in the partitioning of biomolecules in aqueous two phase systems [25]. This behavior can be explained as a reduction of the configurational entropy of the polymer rich phase as the PEO molar mass increases [26].

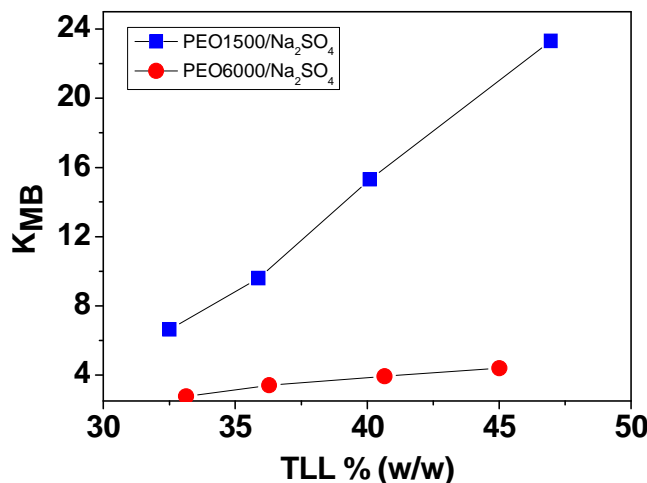


Figure 4. Effect of the molar mass of PEO on the partition coefficient of methylene blue

Influence of the hydrophobicity of polymers on the partitioning of methylene blue

In order to gain insight about the effect of hydrophobicity of macromolecule on partitioning behavior of methylene blue, ATPS formed by L64 copolymer and sodium salt was used. L64 is a triblock copolymer with the $(\text{EO})_{13} - (\text{PO})_{30} - (\text{EO})_{13}$ structure while EO is ethylene oxide and PO is propylene oxide. This type of triblock copolymer self-associates in aqueous solutions after increasing the temperature and/or concentration, forming micellar-like aggregates consisting of a core dominated by hydrophobic segment of PO surrounded by a corona of hydrophilic segment of EO [27]. Therefore, L64 is a polymer more hydrophobic than PEO.

Figure 5 shows the partition coefficient of methylene blue (K_{MB}) in the ATPS formed by PEO1500/ $\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$ and L64/ $\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$ at 25 °C. As can be observed, K_{MB} decreases with increases in the hydrophobicity of the polymer rich phase. The relative order of the partition coefficient is PEO1500 > L64. This behavior indicates that the presence of PO segments in the macromolecule structure reduces the interaction between methylene blue and the polymer. Consequently, a higher content of methylene blue molecules concentrate in the bottom phase of the ATPS formed by L64 than in the ATPS formed by PEO1500.

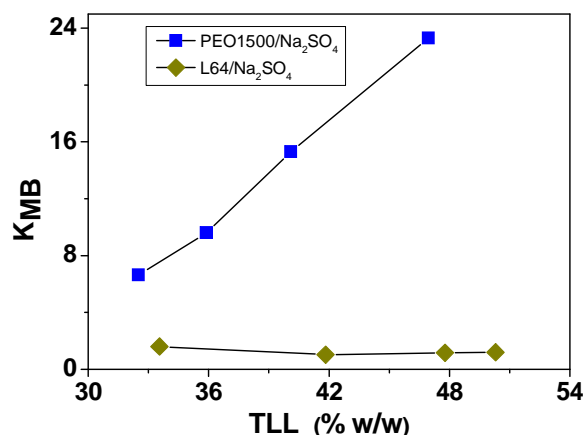


Figure 5. Effect of the hydrophobicity of the polymers on the partition coefficient of methylene blue as a function of TLL values of the ATPS formed by PEO1500/ $\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$ and L64/ $\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$ at 25 °C

Influence of temperature on the partitioning of methylene blue

Figure 6 shows the effect of temperature on the partitioning of methylene blue in the ATPS composed by PEO1500/ Na_2SO_4 / H_2O . As can be observed, K_{MB} values change markedly when the temperature is increased from 25 to 40 °C. A higher temperature leads to an increase in K_{MB} , indicating that the partitioning of MB is endothermic. This aqueous two phase system allows for a wide temperature range for the partition/extraction of methylene blue.

On the basis of the obtained results, thermodynamic parameters have been evaluated for the partitioning of MB in ATPS. The Gibbs free energy change of transfer $\Delta_{\text{tr}}G^\circ$ can be divided into two parts: (1) the enthalpy change ($\Delta_{\text{tr}}H^\circ$) and (2) the entropy change ($\Delta_{\text{tr}}S^\circ$). As defined by the classic thermodynamic relationship, $\Delta_{\text{tr}}G^\circ = \Delta_{\text{tr}}H^\circ - T\Delta_{\text{tr}}S^\circ$. Considering that $\Delta_{\text{tr}}G^\circ$ values are negative (Figure 3) and $\Delta_{\text{tr}}H^\circ > 0$ for the MB partition in the ATPS formed by PEO1500/ Na_2SO_4 / H_2O , it's possible to suggest that entropic factors lead to the preferential distribution of MB to the polymer rich phase in this ATPS.

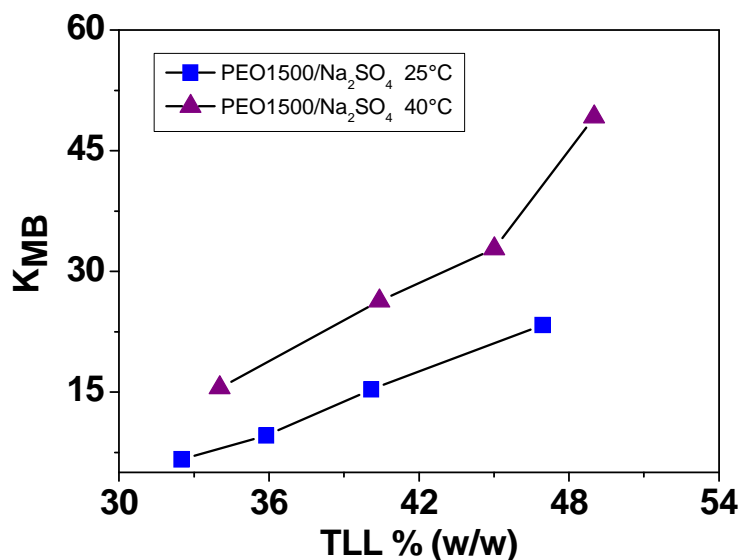


Figure 6. Effect of temperature on the partition coefficient of methylene blue as a function of TLL values of the ATPS formed by PEO1500/ Na_2SO_4 / H_2O

CONCLUSION

The partitioning behavior of methylene blue in ATPS composed by PEO/sulfate salt/ H_2O can be controlled by an adequate selection of the properties of the system. The experimental data demonstrated that MB molecules concentrated preferentially in the polymer rich phase. Additionally, it was verified that MB partitioning can be influenced by several factors, such as the TLL, the type of sulfate salt, the molar mass of PEO, the hydrophobicity of the polymer, and temperature.

This work has shown that aqueous two phase systems formed by PEO/ Na_2SO_4 / H_2O can be successfully used for the partition/extraction of methylene blue.

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