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A comparative study of polymer-dye interaction

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ABSTRACT: *The interaction between an anionic dye Methyl Orange and two poly cations namely, Poly (N-vinyl-4-methylpyridiniumiodide), (PC1) & Poly (vinylbenzyltriphenylphosphoniumchloride), (PC2) has been investigated by spectrophotometric method. The polymers are observed to induce metachromasy in the dye as evidenced from the considerable blue shift in the absorption maximum of the dye. The interaction constant and thermodynamic parameters of interaction have been determined by absorbance measurements at the metachromatic band. The effect of additives such as ionic salts, alcohols, urea and polyelectrolytes on the reversal of metachromasy has been studied and used to determine the stability of the metachromatic complex and to understand the nature of binding.*

Keywords*: methyl orange, polycations, metachromasy, stoichiometry, thermodynamic parameters*

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Introduction

The change in the absorption spectra of the dye when bound to a polyelectrolyte is termed as metachromasy. Metachromasia in the dye polymer interaction has been studied extensively since the discovery of this phenomenon in 1875 [1]. The concept of metachromasy suggests that a single individual compound is formed by the interaction of the dye and the chromotropic polymers. The investigations on the dye polymer complexation provide useful information about the nature and mechanism of binding process. Both polar and electrostatic interactions are involved in the binding of dye molecules on to the polymers [2-8]. Generally, a polyelectrolyte with relatively high charge density is found to be more efficient in inducing metachromasy. The interaction depends on the conformation of the dye and the polycations as well.

Methyl orange, an anionic dye has been used as a probe to study the mode and the extent of complex formation between small molecules, proteins and water-soluble polymers [9]. The binding of methyl orange and its homolog in aqueous solution has been studied by equilibrium dialysis method and the interaction constant and thermodynamic parameters of interaction has been evaluated and the significance of hydrophobic and electrostatic interaction accompanying the binding was also studied by Takagishi [10-12]. The interaction of methyl orange with dilute aqueous solution of ionone has also been reported [13]. The objective of the present study is to compare the binding affinities of methyl orange to the polycations mentioned in the previous studies and to determine the thermodynamic parameters of interaction. The stability of the metachromatic complex has been determined by studying the ease of reversal by using alcohols, namely methanol, ethanol and 2-Propanol as well by the addition of urea, sodium chloride, sodium lauryl sulphate and sodium carboxy methylcellulose.

Material and Methods

Materials

Methyl orange (MO), urea, sodium chloride, sodium lauryl sulphate, were purchased from Merck, and used without further purification. The solvents namely methanol, ethanol, 2-propanol (Merck) were distilled before use. The polycations poly(N-vinyl-4-methyl pyridiniumiodide) and poly(vinylbenzyltriphenylphosphoniumchloride) was a gift, the preparations of which are reported elsewhere [9]. The absorption spectra were recorded using a UV-2500 spectrophotometer.

Determination of stoichiometry of polymer-dye complex

Increasing amounts of polymer solution (0.0-9 mL, 1 x 10^{-3} mol.L^{-1}) were added to a fixed volume of dye solution (0.6 mL, 1 x 10^{-3} mol.L^{-1}) in different sets of experiments and the total volume was made up to 10 mL by adding distilled water in each case. The intensities were measured at 464 nm and at 378 nm in case of MO- PC1 and at 464 nm and 464 nm in case of MO-PC2 complex**.**

Study of reversal of metachromasy using polymer-dye complex

For measurements of the reversal of metachromasy, solutions containing polymer and dye in the ratio 1:2 in case of MO-PC1 and 1:3 in case of MO-PC2 were made containing different amount of alcohol. The total volume was maintained at 10mL in each case. The absorbances were measured at 378 nm and 464 nm in case of MO-PC1 complex and at 426 nm and 464 nm in the case of MO-PC2 complex.

Determination of thermodynamic parameters

The thermodynamic parameters were determined by measuring the absorbances of the pure dye solution at both 464 nm and at 378 nm in the case of MO-PC1 and at 464 nm and 426 nm in case of MO-PC2 in the temperature range (36-54 ^{0}C). The same experiment was repeated with solutions containing varying amounts of polymer at various polymer-dye ratios (2, 5, 10, and 20).

Results and Discussion

The absorption spectra of methyl orange at various concentrations are shown in Fig. 1**.** It shows a single band with absorption maximum at 464 nm indicating the presence of a monomeric dye species in the range of concentration studied. The spectral changes on the addition of increasing amount of PC1 and PC2 are shown in Fig. 2 and Fig. 3, respectively. The intensity of 464 nm decreases progressively upon addition of increasing amounts of polymer solution and the absorption maximum shifts to 378 nm in case of MO-PC1 and to 426 nm in case of MO-PC2. The blue shifted band is attributed to the stacking of the dye molecules on the polymer backbone this reflects high degree of co-operativity in binding [14].

Determination of stoichiometry

To determine the stoichiometry of the polymer-dye complex, a plot of $\mathbf{A_{378}/A_{464}}$ versus the polymer/dye ratio was made. A similar procedure was repeated for MO-PC2 complex also. On adding increasing amounts of PC1 &PC2 to MO it was found that the absorption at the monomeric band decreases gradually and a new band occurs at 378 nm in case of MO-PC1 and at 426 nm in case of MO-PC2 as shown in Fig. 4 and Fig. 5, respectively. The stoichiometry of MO-PC1 complex was found to be 2:1 whilst that of MO-PC2 was found to be 1:1. A 1:1 stoichiometry indicates that one dye cation is bound to each potential anionic site resulting in stacking conformation. Whereas in the case of MO-PC1 the binding is 2:1 that indicates that the binding is at alternate anionic site this is due to lesser overcrowding and more aggregation of the bound dyes. Similar results were observed in case of binding of pincyanol chloride with poly(methacrylic acid) and poly(styrene sulfonate) [15].

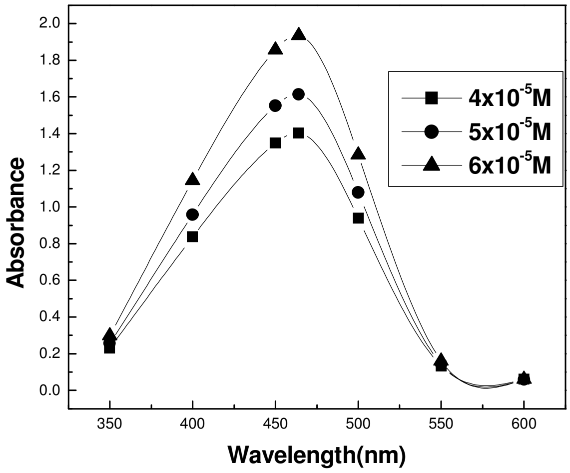

Figure 1. Absorption spectra of dye, MO.

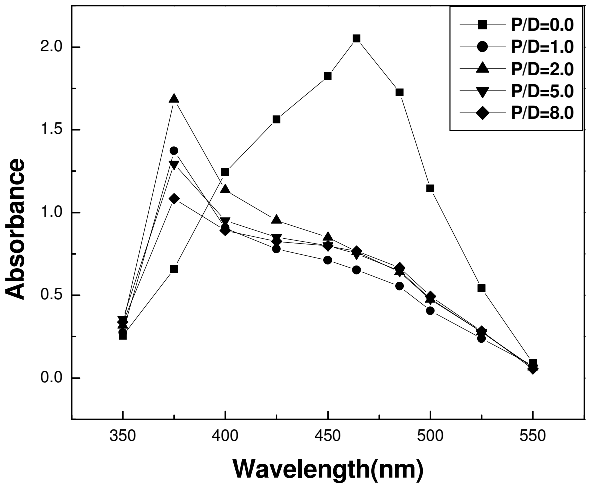

Figure 2. Absorption spectrum of MO-PC1 system at various P/D ratios.

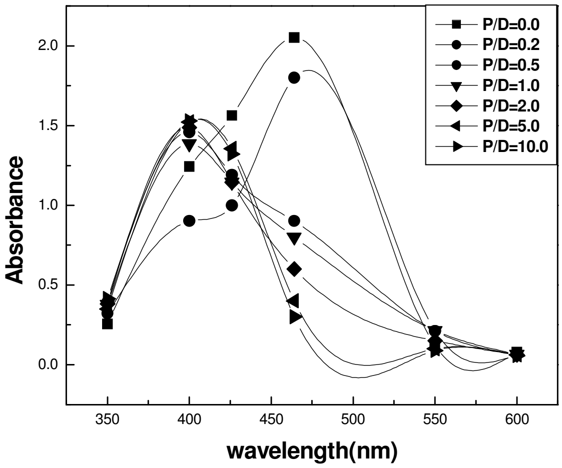

Figure 3. Absorption spectrum of MO-PC2 system at various P/D ratios.

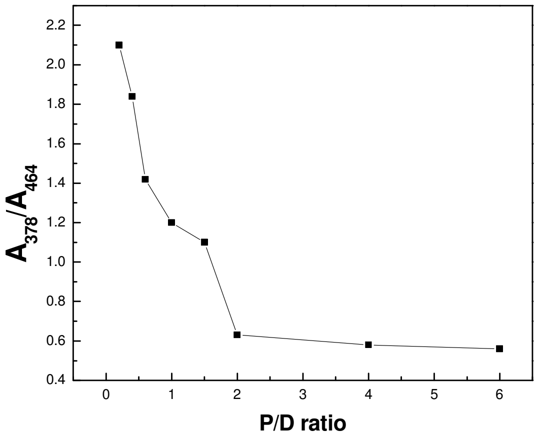

Figure 4. Stoichiometry of MO-PC1 complex.

Reversal of metachromasy

Effect of alcohols& urea

The metachromatic effect is presumably due to association of the dye molecules on binding with the polyanion, which may involve both electrostatic and hydrophobic interactions. The destruction of metachromatic effect may occur on addition of low molecular weight electrolytes and urea. The destruction of metachromasy by alcohol and urea is attributed to the involvement of hydrophobic bonding has already been established [16, 17]. The efficiency of alcohols in disrupting metachromasy were found to be in the order methanol < ethanol < 2-propanol, indicating that reversal becomes quicker with increasing hydrophobic character of the alcohols. The above facts are further established in the present system. In case of MO-PC1, 60% methanol, 50% ethanol and 40% 2-Propanol were sufficient to reverse metachromasy. Whilst in the case of MO-PC2, 40% methanol, 30% ethanol, 25% 2-Propanol were sufficient to reverse metachromasy. This indicates stronger stacking of the bound dyes in case of PC1 than in the case of PC2. This may be well interpreted in terms of the conformation of polycations PC1 and PC2 respectively. Thus PC1 has a more flexible conformation due to the greater involvement of hydrophobic forces between the bound dye molecules. The results are shown in Fig. 6 and Fig. 7, respectively. Takagishi et al. [18] reported that, on binding of butyl orange by bovine serum albumin, urea reduces the structure of the aqueous environment of the dye and the polycation to participate in the formation of hydrophobic interaction. The molar concentrations of urea needed for reversal of metachromasy were found to be 5 mol.L^{-1} in case of MO-PC1 complex and 4 mol.L^{-1} in the case of MO-PC2 complex. The results are shown in Fig. 8 and Fig.9, respectively.

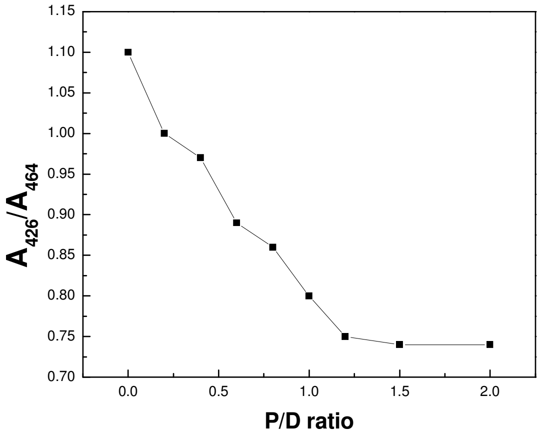

Figure 5 Stoichiometry of MO-PC2 complex.

Effect of ionic strength

Tan et al. [19] have reported the disruption of metachromatic band with the variation of ionic strength. Sodium chloride of varied ionic strength was added to MO-PC1 and MO-PC2, and the absorbances were measured in the range 350-700 nm. In case of PC1 the monomeric band reappears at higher ionic strength (1 x 10^{-3} mol.L^{-1}) than compared to that of PC2 (1x10^{-4} mol.L^{-1}). In aqueous solutions the charged polymer molecule will be in the extended conformation due to the repulsion between the charged groups. On adding the dye the conformation of the polycation changes to a compact coil owing to dye binding, resulting from electrostatic interaction thus giving rise to metachromatic band. The concentration of sodium chloride required to reverse metachromasy was greater in case of MO-PC1 than in the case of MO-PC2. This indirectly indicates that MO-PC1 complex is more stable than MO-PC2 complex. The results are shown in Fig. 10 and Fig. 11, respectively.

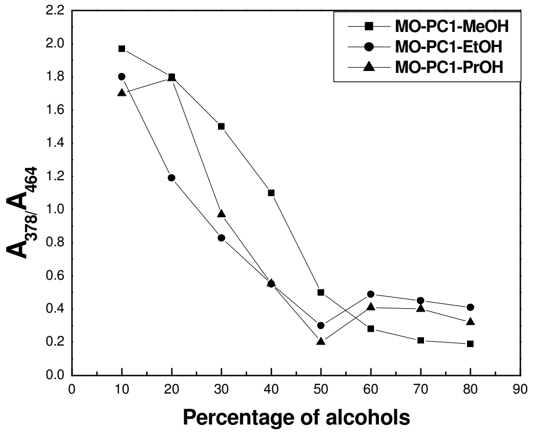

Figure 6. Effect of alcohols on reversal of metachromasy in MO-PC1 system.

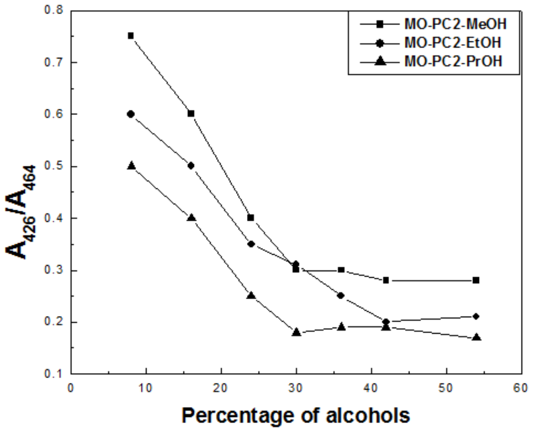

Figure 7. Effect of alcohols on reversal of metachromasy in MO-PC2 system.

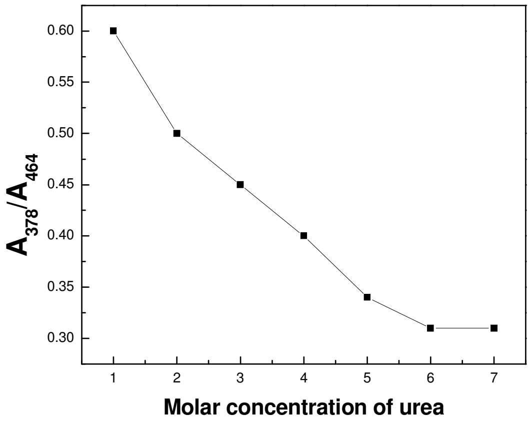

Figure 8. Effect of urea on reversal of metachromasy in MO-PC1system.

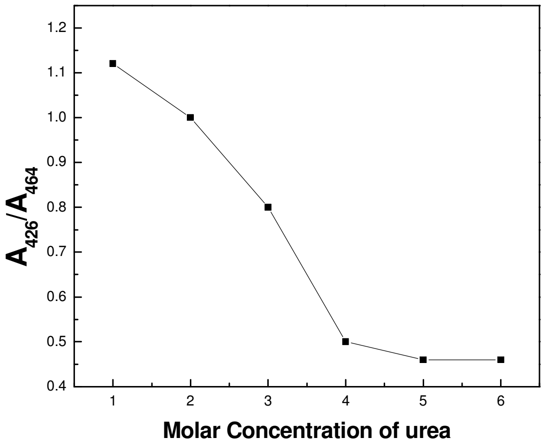

Figure 9. Effect of urea on reversal of metachromasy in MO-PC2 system.

Effect of surfactants

On adding increasing amounts of sodium lauryl sulphate to MO-PC1 and MO-PC2 complex it was found that the monomeric band gained intensity. The concentrations of sodium lauryl sulphate required to reverse metachromasy was found to be 1 x 10^{-4} mol.L^{-1} in the case of MO-PC1 and 1 x 10^{-5} mol.L^{-1} in the case of MO-PC2. This is due to the formation of micelles by the surfactants in aqueous solutions. The effects of surfactants have been reported in literature [20] .The results are shown in Fig. 12. The results match with those reported in the literature [21]. Similar results are obtained for reversal of metachromasy also using sodium carboxymethylcellulose.

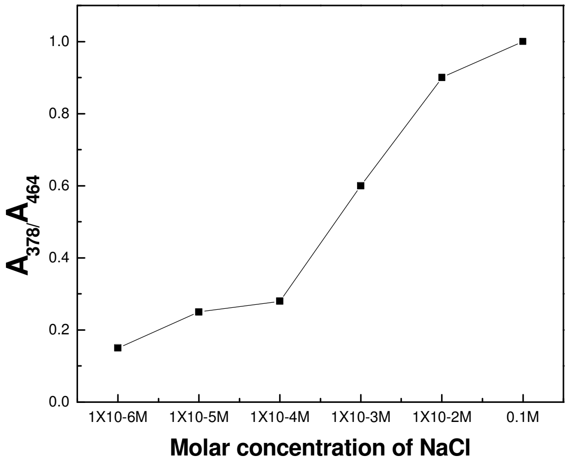

Figure 10. Effect of Sodium chloride on reversal of metachromasy in MO-PC1.

Effect of nature of the quarternising side chains:

In addition to coulombic forces, the non-ionic interactions between the dye molecules and the polymer side-chains contribute towards the binding mechanism. The effect of alkyl and aryl side chains on the dye binding characteristics of the quarternised poly-2-vinyl and poly-4-vinyl pyridine derivatives have already been reported [22]. This is further confirmed from interaction constants which are greater for the poly(*N*-vinyl-4-methyl pyridinium iodide), (PC1) than for poly(vinylbenzyltriphenylphosphonium chloride) (PC2) which could be due to the lesser steric hindrance offered by the methyl groups. A similar effect of an increase in the interaction energy between the dye and the polymer due to the intercalation of the dye and the polymer has been reported for methyl orange and poly(3-benzyl-1-vinylimidazolium bromide) [3].

Determination of interaction parameters

In order to determine the thermodynamic parameters of interaction between the dye and the polymer, absorbance (A) of the MO-PC1 complex was measured at 378 nm and that of MO-PC2 complex was measured at 426 nm using different sets of solutions containing varying amounts of polymer solution (C_S) in a fixed volume of dye solution (C_D). The plots of $C_D.C_S/$ $(A-A_O)$ against C_s for MO-PC1 and MO-PC2 systems at different temperatures are shown in Fig. 13 and Fig. 14, respectively. The absorbance measurements were carried out at four different temperatures. Absorbance results were treated using Rose-Drago eqn [23]: $C_D.Cs/(A-A_0) = 1/K_cL\ (\varepsilon_{ds}- \varepsilon_d) + Cs/L\ (\varepsilon_{ds}- \varepsilon_d)$. C_D refers to the initial molar concentration of the dye and C_S refers to the molar concentration of the polymer. The value of K_c was obtained from the slope and intercept of the plot of $C_DCs/$ $(A-A_0)$ against C_S. In each case the thermodynamic parameters of interaction such as ΔH shown in Fig. 15, ΔG and ΔS shown in Fig. 16 were also calculated. The thermodynamic parameters for MO-PC1 and MO-PC2 are given in Table.1.

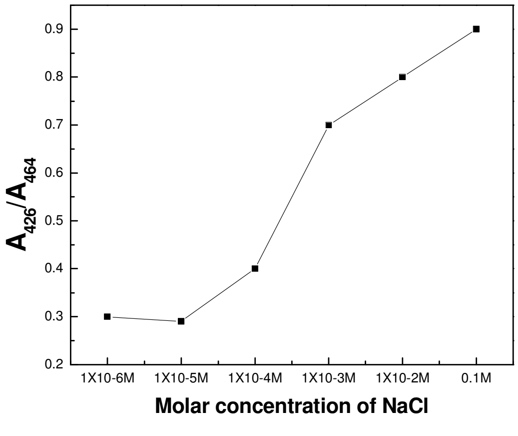

Figure 11. Effect of sodium chloride on reversal of metachromasy in MO-PC2 system.

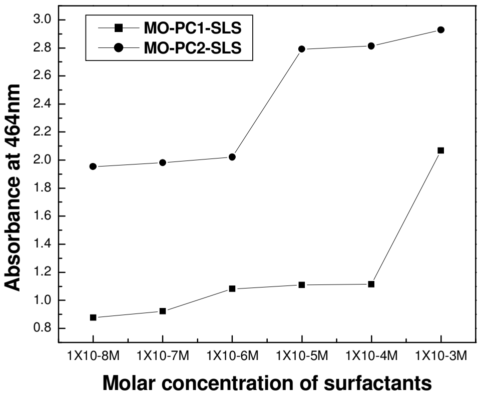

Figure 12. Effect of sodium lauryl sulphate on reversal of metachromasy MO-PC1 and MO-PC2 system.

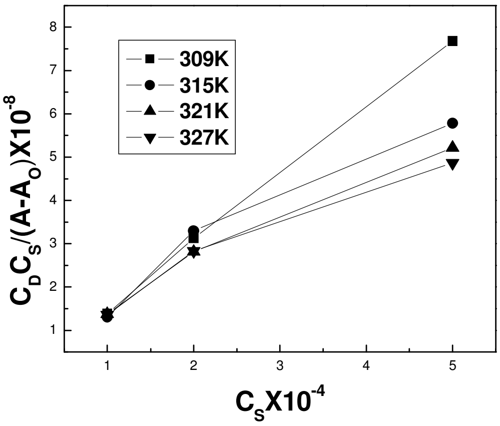

Figure 13. Plots of $C_D{\cdot}C_S/(A-A_O)$ against Cs for MO-PC1 system.

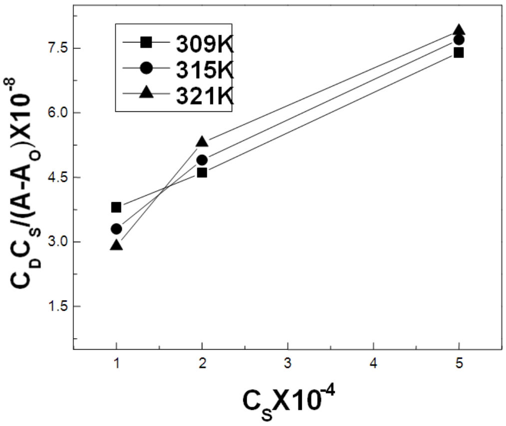

Figure 14. Plots of $C_D{\cdot}C_S/(A-A_O)$ against Cs for MO-PC2 system.

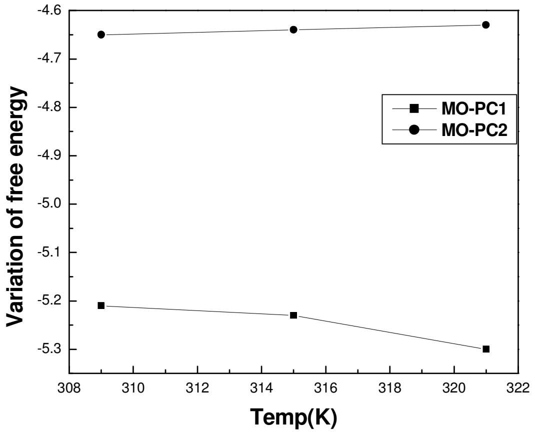

Figure 15. Variation of free energy for MO-PC1 and MO-PC2 systems.

Table 1. Thermodynamic Parameters for interaction of MO-PC1 and MO-PC2.

Temp (K)	**$Kc x 10^3 dm^3 mol^{-1a}$**		**$\Delta G Kcal. mol^{-1b}$**		**$\Delta H Kcal.mol^{-1c}$**		**ΔS cal. $mol^{-1}K^{-1d}$**	
	PC1	**PC2**	**PC1**	**PC2**	**PC1**	**PC2**	**PC1**	**PC2**
300	4.866	1.964	-5.532	-5.15	-2.306	-4.319	-4.827	-6.666
309	4.308	1.666	-5.33	-4.726				
315	4.266	1.58	-5.060	-4.423				
321	3.162	1.33	-4.948	-4.32				

a) Calculated from Fig. 13 and Fig. 14 according to Rose-Drago equation
b) Calculated from the thermodynamic equation $\Delta G = -RT\ln Kc$.
c) Calculated graphically by plotting lnKc against 1/T according to van't Hoff equation, $\ln Kc = -\Delta H/RT + C$.
d) Calculated from the thermodynamic expression $\Delta G = \Delta H - T\Delta S$.

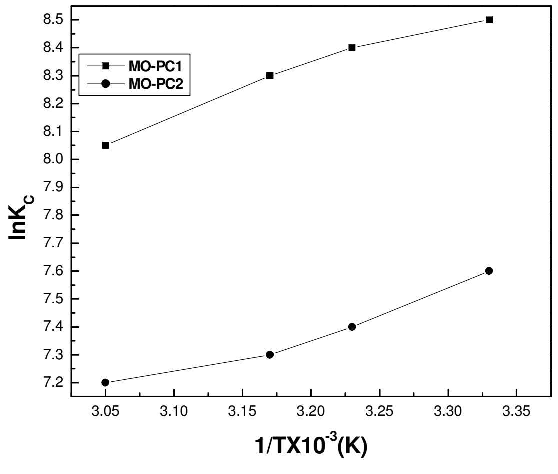

Figure 16. van't Hoff plot for MO-PC1 and MO-PC2 systems.

Conclusions

The polymers poly(*N*-vinyl-4-methylpyridiniumiodide) (PC1) and poly(vinylbenzyltriphenylphosphonium chloride) (PC2) induced metachromasy in the dye MO. The monomeric band occurs at 464 nm while the metachromatic band occurred at 378 nm in the case of MO-PC1 and at 426 nm in the case of MO-PC2. The spectral shifts in the case of MO-PC1 (86 nm) than in the case of MO-PC2 (36 nm) indicates that dye binding is stronger in the case of MO-PC1 than in the case of MO-PC2. These results are further confirmed by the reversal studies using alcohols, urea, sodium chloride and surfactants. The thermodynamic parameters further confirm the above fact. It is thus evident from the above studies that both electrostatic and non-ionic forces contribute towards the binding process and that the binding of PC1 with the dye ion is stronger than that between MO-PC2.Cooperativity in binding is observed to occur due to neighbor interactions among the bound dye molecules at lower P/D ratios leading to stacking. The stacking tendency is enhanced by the easy availability and close proximity of the charged sites.

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