



A STUDY OF THE BINDING OF ANIONIC MORDANT RED7 IN TWO DIFFERENT CATIONIC SOLUTIONS USING ABSORPTION SPECTROSCOPY

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ABSTRACT

The interactions of anionic dye, Mordant Red7 with two different cationic ligands (ethanol amine and tallow amine) were studied in acidic aqueous solution using UV-VIS absorption spectroscopy. The dye interacts strongly with oppositely charged ligands. The results have shown that the maximum absorbance of the dye decreased gradually after addition of opposite charge ligand, and also shows the emergence a new absorption band. The new peak was attributed to the formation of dye aggregation by intermolecular forces such as hydrophobic forces attraction, Van der Waals forces and hydrogen bonds. The binding constant (K) values of the dye to cationic ligands have been determined by means of Benesi-Hildebrand equation. The magnitude of K is large for tallow amine $43.05 \times 10^3 \text{ mol}^{-1} \text{ L}$ compared to ethanol amine $1.245 \text{ mol}^{-1} \text{ L}$. This is because; tallow amine able to self-assemble into micelles (surfactant) at a specific concentration called the critical micelle concentration (CMC), thereby, the dye binding to micelle of tallow amine surfactant. On the other hand "ethanol amine does not form micelles". The standard free energy change ΔG° for ethanol amine and tallow amine for the complexation process have also been determined.

Keywords: Anionic dye, Cationic ligand, Complex formation, Ligand-dye interaction, Stability constant, Spectrophotometry.

Contribution/ Originality

The interactions between dyes and ligands are an important in many industrial applications such as detergency, emulsion polymerization, enhanced oil recovery, drug delivery and textile dyeing and subjects of numerous investigations. The purpose is to define physical interactions and focusing on the influence of ligand structure on aggregation of dyes. However, until more recently, an understanding of the nature of molecular interactions between dyes in solution lacked much clarity. The main objective of this project was to study the effects of chemical structure and concentration of ligand (surfactant) on the solubilization and aggregation of dyes in aqueous solution. For this reason, the interactions of anionic Mordant Red7 with two different cationic

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solutions were investigated spectrophotometrically and optimization conditions of aggregations and calculate the binding constant and standard free energy.

1. INTRODUCTION

In the last few decades, many investigations have been made on the interactions between surfactants and water soluble dyes in order to acquire information about dye-surfactant associations [1-7]. The interactions between dyes and ligands are important in many industrial applications such as detergency, emulsion polymerization, enhanced oil recovery, drug delivery and textile dyeing [8-10] and subjects of numerous investigations [11-17]. The purpose of these investigations is to define the physical interactions and focusing on the influence of ligand structure on aggregation of dyes rather than other variables, e.g. ionic strength, solvent and temperature. The formation of aggregated dye molecules in aqueous solutions was first suggested to explain deviations of certain highly colored molecules from Beer's law [13]. It is known that dyes are amphiphiles, i.e. they have bulky non-ionic moieties attached to ionic head groups. Aggregation occurs in a stepwise manner, through dimers, then trimers, etc. by the stacking of flat molecules. A number of techniques have been used to study aggregation of dyes, such as light scattering, potentiometry, conductivity, colorimetry and UV-vis absorption spectroscopy which is among of the most widely used measurement method for studying in this area [18-20]. Thus, much attention has been given to spectrophotometric studies of monomer/dimer equilibria which rely on detection and identification of the individual species at the molecular level [21-25]. The strength of aggregation between two or more dye molecules depends upon a number of factors, i.e. structure of dye (dyes contain charge within the chromophore, so they tend to be more sensitive to environmental changes than dyes containing localized groups), solvent, temperature and interaction with ligand. However, more recently, an understanding of the nature of molecular interactions between dyes in solution lacked much clarity. Many experiments were done under different conditions (i.e. solvent, ionic strength, concentration) so that dimerisation or aggregation data could not be directly compared [1, 18, 19, 26]. The aggregated surfactants known as micelles are responsible for the solubilization of the hydrophobic substances in water [11]. Therefore, surfactants that start to aggregate into micelles at low concentrations, are good candidates for this purpose.

The aim of this work is to study the effects of chemical structure and concentration of ethanol amine and tallow amine on the solubilization and aggregation of dyes in aqueous solution. For this reason, the interactions of Mordant Red7 with these ligands were investigated spectrophotometrically, the optimization conditions of aggregations were determined, and the binding constant and standard free energy were calculated.

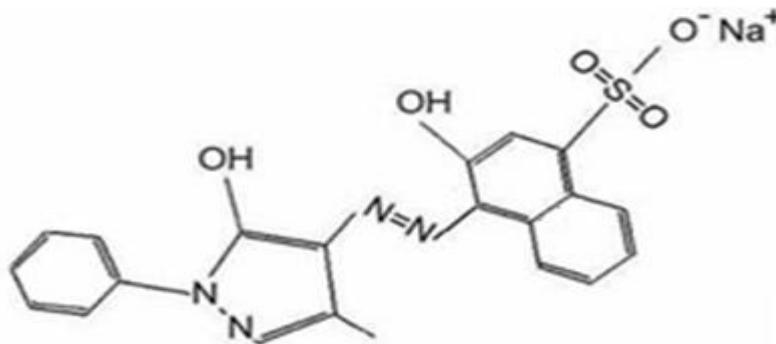


Fig-1. Structure of Mordant Red7

2. EXPERIMENTAL

2.1. Materials

High quality materials were used as received without further purification. Mordant Red7 (1-Naphthalenesulfonic acid, 4-[(4,5-dihydro-3-methyl-5-oxo-1-phenyl-1H-pyrazol-4-yl)azo]-3-hydroxy) shown in fig.1 was obtained from Hoechst. Mordant Red7 is a red powder blue, slightly soluble in water, ethanol and acetone; their solution was yellow-brown-red. The ligands used in this study were ethanol amine (C_2H_7ON) and tallow amine ($C_{19}H_{34}N$) which supplied by Surechem products Ltd. The purity of ligands was 99.5% and 99.0% respectively. Ultra-pure water was used for solution preparation.

2.2. Preparation of Dye and Ligand Solutions

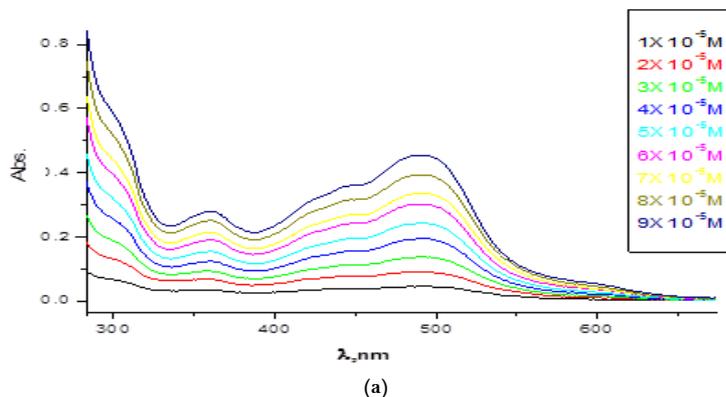
The concentration of dye was kept constant ($9.0 \times 10^{-5} M$) during the whole process. A series of different concentrations 1×10^{-4} to 3×10^{-2} M of acidic aqueous solutions (pH from 1.5 to 2) of specific ligands was added to the certain amount of the dye. The samples were shaken at room temperature and measured with UV-VIS spectrophotometer.

2.3. Spectrophotometric Measurements

The absorption spectra of dye solutions were recorded using single beam Biochrom Ltd, Cambridge CB4 of j England interfaced to a computer. The absorption spectra were obtained using 1.0 cm quartz cuvettes supplied by Starna. dye concentration ($9.0 \times 10^{-5} M$) exhibits absorbance maximum (λ_{max}) at 490 nm.

3. RESULTS AND DISCUSSION

3.1 UV-VIS Spectra of dye in the Presence of Ethanol Amine and Tallow Amine



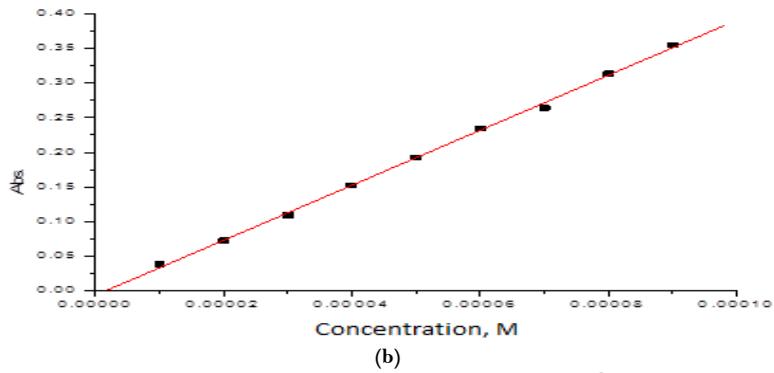


Fig-2.(a) UV-VIS spectra observed for different concentrations of dye in water at room temperature. (b) Beers law plot for dye in water at λ_{max} 490 nm

The concentrations of the dye ranging from 1×10^{-5} to $9 \times 10^{-5} \text{ mol L}^{-1}$ in aqueous solution exhibited an Absorbance maximum (λ_{max}) at $490.0 \pm 0.1 \text{ nm}$. The molar extinction coefficient of dye (ϵ_m) was calculated at 490.0 nm as $3971.67 \text{ molL}^{-1}\text{cm}^{-1}$ at 298K. An excellent correlation ($R = 0.9994$) indicated that the Beer-Lambert Law was obeyed in the dye concentrations ranges of interest which illustrated in fig 2b.

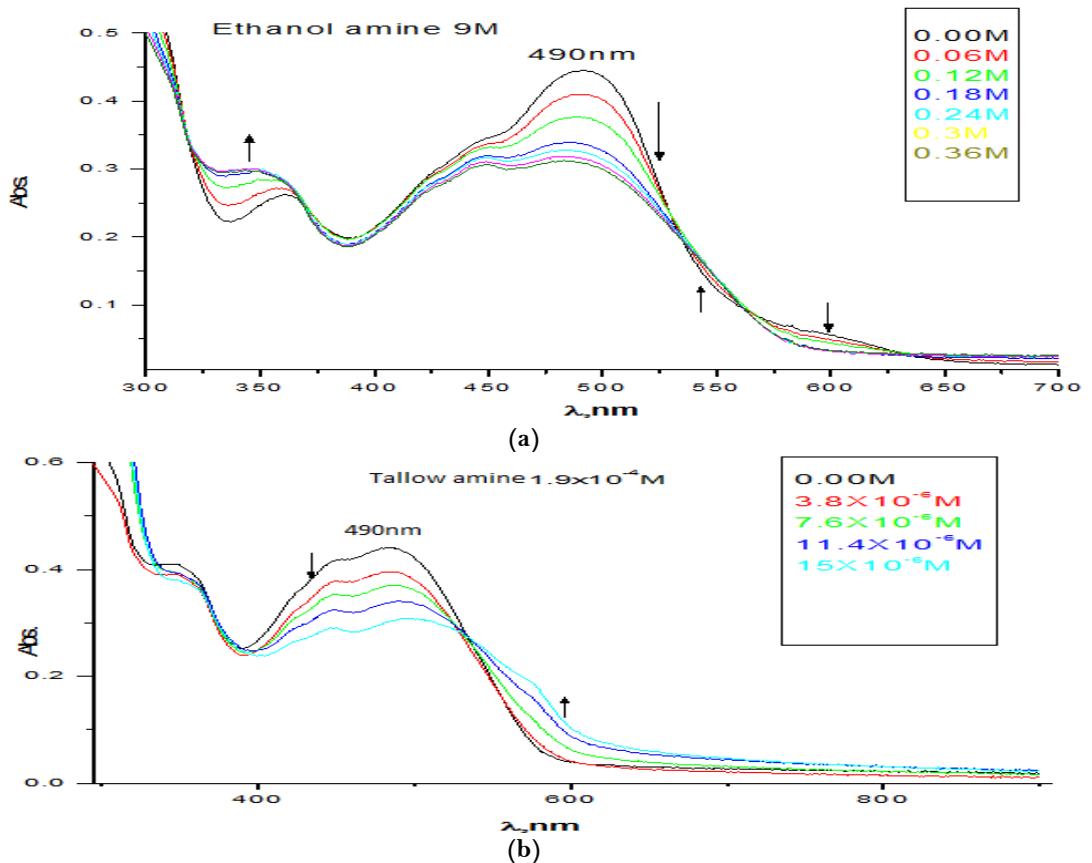


Fig-3. Visible absorbance spectra of dye ($9 \times 10^{-5} \text{ M}$) at various concentration of ethanol amine (a) and tallow amine (b) at 298nm

The visible absorption spectra of mixed solution of a fixed concentration of dye at $9 \times 10^{-5} \text{ mol L}^{-1}$ for several ethanol amine concentrations ranging from 0.06 to 0.36 mol L^{-1} , and tallow amine

from 3.8×10^{-6} to 1.52×10^{-5} mol L⁻¹ in aqueous media at 298 K are illustrated in fig 3a and 3b. As ethanol amine and tallow amine concentrations increased the dye absorbance at (λ_{\max}) 490 ± 0.1 nm. diminished and then the absorbance reached a minimum at 0.36 mol L⁻¹ of ethanol amine and 1.52×10^{-5} mol L⁻¹ of tallow amine. In fig. 3a, as can be seen, the new peak was formed at 330 nm and increased gradually after addition of ethanol amine. The increasing absorbance can be assumed to some sort of association or complex formation between dye and ethanol amine [14-19]. The complex formation of the dye–ligand is a consequence of mutual influences of electrostatic and hydrophobic interactions. In the present case, the formation of ion pair (dye–ligand) reduced the electrostatic interaction between anionic dye molecules and thus enhanced aggregation of dyes by London dispersion and hydrophobic forces [20]. An enhancement in the absorbance with spectral shift was observed due to addition of ethanol amine because of the amphipathic nature of dye and presence of aromatic moiety, it is a tendency to aggregate in aqueous media, especially at higher concentration of polar ligand. After the aggregates became evident, the ligand was added to the dye solution in increments until no further growth in the spectra. As more dye molecules are binding with ligands the aqueous solution becomes more hydrophobic environment, the maximum absorbance shifted a lower wavelength in its absorption maxima. The decreases in λ_{\max} and increasing absorbance values of new peak can be attributed to some sort of association exhibited many isopiestic points which prove the equilibrium between aggregated and free dyes in aqueous solution.

Tallow amine ligand can play as surfactant and form aggregation in certain concentration known as CMC because it has long-chain molecules and the presence of both hydrophobic and hydrophilic groups within the same molecule. The surfactant aggregates known as micelles which are responsible for the solubilization of the dyes. Because the concentration of Tallow amine used is higher than CMC concentration [17], the micelles will be formed immediately after first addition. The changes in spectrum of the dye in aqueous solution produced upon addition of tallow amine in acidic media are illustrated in Fig.3b. There is loss in absorbance peak of dye (490nm) together with the simultaneous appearance of a new absorption peak in the spectrum at (590nm). The presence of isosbestic point indicates equilibrium between two different species free dyes in solution and species binding with tallow amine ligand, i.e. there is equilibrium between (ligand–dye) and free dye in bulk solution [1, 20]. The new peak formed is a clear indication for the incorporation of dye with cationic micelles and increased with increasing hydrophobicity of surfactants. However, the observed subsequent increase of new absorption is attributed to the presence of aggregated dyes in micelles. Going from aqueous solution to the more hydrophobic micellar environment, the maximum absorbance of dye shifted a higher wavelength in its absorption maxima. Furthermore, it not only shows that the aqueous spectrum becomes successively replaced by a micellar spectrum, but also that a micellar concentration is reached where there are no further spectral changes, i.e. incorporation into the micelle reaches completion.

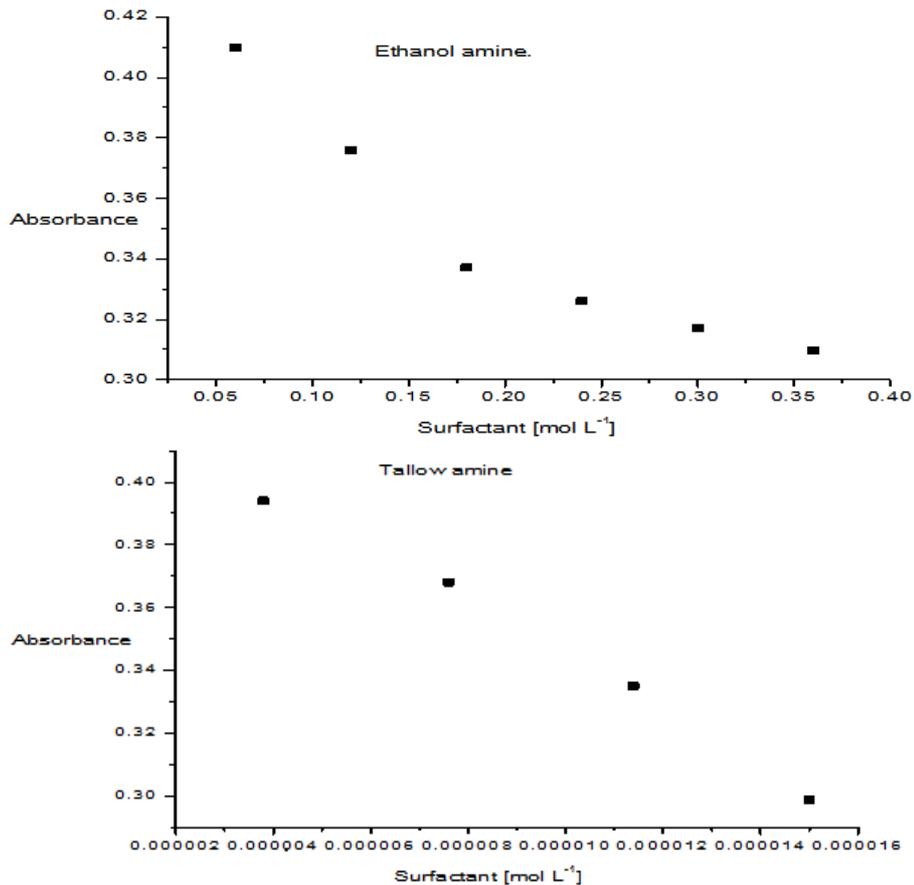


Fig-4. The absorbance change of 9×10^{-5} mol L⁻¹ dye with the different concentrations of ethanol amine and with the concentrations of tallow amine in presence of the dye

The absorbance change of 9×10^{-5} mol L⁻¹ dye with the different concentrations of ethanol amine and with the concentrations of tallow amine are shown in Fig 4. In presence of ethanol amine, the absorbance of dye initially decreased exponentially with increasing the surfactant concentrations and reached a minimum value [19]. In Fig.4b, the linear decreases of absorbance of dye at 490 nm after tallow amine cationic surfactant concentration added and it is clear that the changes that occur do so above its CMC. Above the CMC, the amount of monomer of dye decreases linearly with the increase in surfactant concentration is regarded to be caused by the incorporation of dye molecules to micelles. Consequently, the changes are attributed to solubilization of free dye in cationic surfactants micelle. It is demonstrated that the location of a dye in a surfactant micelle can be assessed from the absorption spectrum of the dye-containing micellar solution.

3.2. Determination of Binding Constant

The spectrophotometric data were employed to calculate the binding constant of dye-surfactant. The equilibrium of the dye (D) and ligand molecule (M) can be assumed to follow as:



Where D, M, DM and K_b represent the dye, ligand molecule, dye-ligand associate and binding constant (K_b) respectively. The binding constant, K_b , and molar extinction coefficient ϵ_m can be determined using the Benesi-Hildebrand Equation [26] which is valid for high surfactant concentration [1, 3] in the following modified form:

$$\frac{D}{\Delta A} = \frac{1}{(\epsilon_m - \epsilon_0)} + \frac{1}{K_b(\epsilon_m - \epsilon_0)C_m}$$

Where ϵ_0 is the molar extinction coefficient of the D_1 , ϵ_m is the molar extinction coefficient of D_1 fully bound to micelles, C_m is the micellized surfactant concentration is equal to total surfactant concentration minus CMC, K_b is the binding constant, D_1 is the total concentration of D_1 , $\Delta A = A - A_0$ is the difference between the absorbance of D_1 in the presence and absence of surfactant.

The plot of $D/\Delta A$ against $1/C_m$ was found to be linear in all cases as shown in Fig 5. The values of K_b and ϵ_m were calculated respectively from the slope and the intercept.

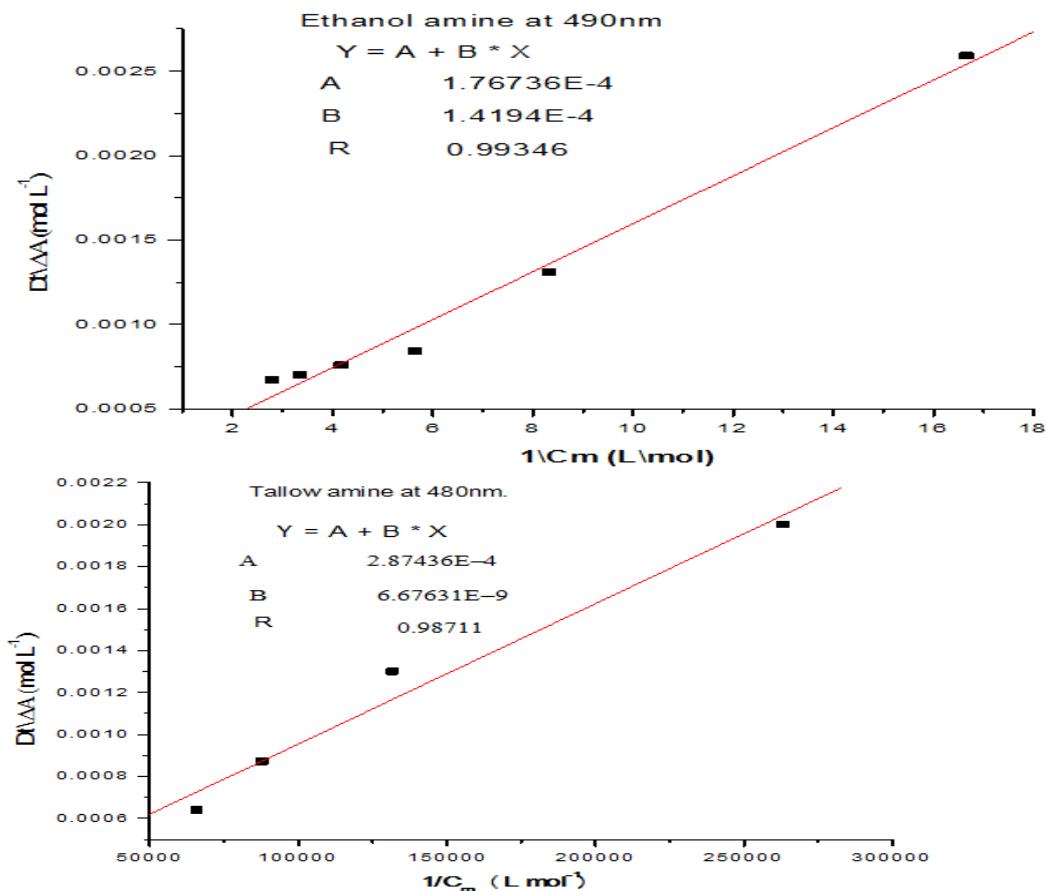


Fig-5. The plot of $D/\Delta A$ against $1/C_m$ for the ethanol amine and tallow amine

The standard free energy change ΔG^0 can be calculated from the values of K_b , as follows [27]: $\Delta G^0 = -RT \ln K_b$, where R is the universal gas constant and T is the room temperature. ΔG^0 , which is an indication of the tendency of the binding of D_1 to cationic ligand.

Table-1. Standard free energy change and binding constant values for the interaction of D₁ with cationic ligands.

Ligands	Ethanol amine	Tallow amine
ΔG° (KJ mol ⁻¹)	-0.543	-26.41
K_c (mol ⁻¹ L)	1.245	43.05x10 ³

4. CONCLUSION

Spectrophotometric methods were used to investigate the interaction between the anionic dye and two cationic surfactants. The spontaneity of the ion pair formation process was confirmed by the Gibb's free energy values, determined by spectrophotometric measurement method and using the Benesi–Hildebrand equation. The spectrophotometric study was confirmed that electrostatic interaction between dye and surfactant as well as dissolution of the aggregates both depends strongly on surfactant's concentration. The recovery of the dye from dye–surfactant ion pair was made through the addition of two opposite charged surfactants and the phenomenon was manifested itself due to the restoration of the initial visible absorption band. The formation constant (K) has been determined using the Benesi–Hildebrand equation. The magnitudes of (K) are comparable to those of some recently reported.

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