

Studies of Equilibria Involving the Binary and Ternary Complexes of Aluminium with Eriochrome Cyanine R (ECR) and Cetylpyridinium Chloride (CP)

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ABSTRAK

Kertas ini membincangkan kajian stoikiometri kompleks binari (aluminium-ECR) dan ternari aluminium-ECR-CP) bgai aluminium. Kedua-dua kompleks didapati hadir dalam larutan dan berada dalam keseimbangan antara satu sama lain. Pemalar pembentukan, kadar tindak balas dan stoikiometri kedua-dua kompleks telah ditentukan dalam kajian ini dan mekanisme tindak balas yang mungkin bagi pembentukan kompleks ternari telah dicadangkan dalam kertas ini.

ABSTRACT

This paper is concerned with the study of stoichiometry of binary (aluminium-ECR) and ternary (aluminium-ECR-CP) complexes of aluminium. Both complexes are shown to be present in the solution and in equilibrium with each other. The formation constant, the reaction rate and the stoichiometry of both complexes have been evaluated and a possible reaction mechanism of the ternary complex formation is proposed in this paper.

Keywords: Eriochrome cyanine R, aluminium, ternary complex, binary complex and equilibrium

INTRODUCTION

Spectrophotometric methods for the determination of aluminium based on the binary complex formation with eriochrome cyanine R (ECR) has been reported to exhibit moderate sensitivity (Marczenko 1976). Introduction of a third component such as a long quaternary base (ionic surfactant) to this binary system leads to the formation of a ternary complex with advantageous properties. Spectrophotometric analysis for aluminium ions based on this ternary system is far more sensitive than the method based on a binary system.

To date, there is no comprehensive study reported in the literature concerning the stoichiometry of the binary and ternary systems, and also the equilibrium associated with these systems. This paper reports the results on the

study of the stoichiometry of the binary and ternary complexes of aluminium with ECR, as well as the stoichiometry of the intermediates of these complexes formed at sub-stoichiometric amounts of cationic surfactant. This study was carried out in order to fully understand the characteristic of the ternary complex since we are interested in using the system for the development of optical fibre aluminium sensor. Our work on the development of optical fibre aluminium sensor by using this system has already been published (Musa and Norleen 2002; Musa and Narayanaswamy 2002). This study is also carried out to deduce possible mechanisms for this ternary complex formation.

MATERIALS AND METHODS

Reagents

Aluminium standard solution of 2.0×10^{-4} M was prepared by dissolving 0.0237g of amount of hydrated aluminium potassium sulphate, $\text{Al}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ in deionised water and the solution was then diluted with deionised water to 250 mL. Aqueous solutions of 2.0×10^{-4} M ECR were prepared by dissolving required amounts of the reagent in deionised water and diluting it to 250 mL, to produce the 2×10^{-4} M solutions. A total weight of 0.0179 g cationic surfactant, cetyl-pyridinium chloride (CP) was dissolved in 250 mL deionised water to give CP standard solution of 2.0×10^{-4} M.

The ammonia-acetic acid buffer of pH 6.0 was prepared by mixing about 40 mL of 0.2 M ammonia solution with about 40 mL glacial acetic acid in deionised water. The pH value of this solution was adjusted to pH 6.0 using diluted ammonia solution or diluted glacial acetic acid solution, before dilution to 1 litre volume using deionised water.

Instrumentation

The absorbance of solutions was measured by using PERKIN-ELMER UV-Visible Spectrophotometer (λ V) and in all measurements, 1 cm cells were used. The pH measurements were carried out using an ECM 201 pH meter.

Procedures

Three methods have been used in this study to determine the stoichiometry of both binary and ternary complexes of the aluminium i.e. molar ratio method, continuous variation method (also known as Job's method) and slope ratio method. These are described below:

(i) Molar Ratio Method

In the molar ratio method, a series of solutions is prepared in which the analytical concentration of one reactant (usually the cation) is held constant while that of the other reactant varied (Skoog 1988). To determine the stoichiometric value of the reagent to the aluminium and that of the surfactant to the aluminium ion in the ternary complex, two approaches were used in this study. The first approach is where the concentration of the aluminium and the

reagent, as well as their molar ratio, were kept constant while the concentration of the surfactant was varied. In the second approach, the concentration of the aluminium and the surfactant, as well as their molar ratio, were kept constant while the concentration of the reagent was varied.

In the first approach, 1 mL of 2.0×10^{-4} M Al^{3+} solution and 5 mL 2.0×10^{-4} M of the reagent were used and added to a series of 25 mL volumetric flasks containing 2 mL buffer solution and different volumes of 2.0×10^{-4} M CP. All the solutions were then made to volume by using deionised water. In the second approach, 1 mL of 2.0×10^{-4} M Al^{3+} solution and 5 mL of 2.0×10^{-4} M CP were used. These solutions were added into a series of volumetric flasks containing 2 mL buffers and varied volumes of 2.0×10^{-4} M of the reagent. All the solutions were then made to 25 mL using deionised water before absorption measurements.

The same procedure was then applied to the binary complex but without surfactant added to the solution. In this case, the aluminium concentration was held constant and the reagent concentration varied.

(ii) Continuous Variation Method

In the method of continuous variation procedure, cation and reagent solutions of identical concentrations are mixed in such a way that the total volume and hence the total number of moles of reactants in each mixture is maintained at constant but the mole-ratio of reactants varies systematically (Skoog 1988).

For ternary complex, this method was applied for the determination of stoichiometry of aluminium to the reagent when the aluminium to CP ratio was held a constant. The aluminium, 2.0×10^{-4} M and the reagent 2.0×10^{-4} M solutions were then mixed in such a way that the total volume in each mixture was constant (6 mL) and the mole fraction of these reactants varied from 0.0 to 1.0. Two Job's plots with two different total volumes were needed in this study to enable the determination of the formation constant of the complex. Therefore, another set of solutions with total volume of 3 mL was also prepared in this study.

For binary complex, the same procedure was used but without the surfactant added to the solutions. Two sets of solutions with total volume of 3 mL and 6 mL were prepared, while the mole fractions of these reactants were varied from 0.0 to 1.0.

(iii) Slope Ratio Method

The slope ratio method is mainly used in the studies of weak complexes and requires that the formation of complex can be forced to completion with a large excess of either metal or reagent (4). Two sets of solutions were prepared. The first contained various amounts of metal ion each with the same large excess of ligand, while the second consisted of various amounts of reagent, each with the same quantity of large excess of metal.

For binary complex, the first set of solutions was prepared by adding 1 mL of 2.0×10^{-4} M aluminium to a series of 25 mL volumetric flasks containing 0

to 3 mL of 2.0×10^{-4} M of the reagent. The second set of solutions was simply prepared by adding 5 mL (2.0×10^{-4} M) of the reagent into a series of 25 mL volumetric flasks containing 0 to 3 mL of 2.0×10^{-4} M aluminium solution.

The same procedure was applied to ternary complex but in this case, the surfactant was added to the solution in such a way that the aluminium to CP ratio in both sets of solutions was held constant. In this experiment, two aluminium to CP ratios have been studied i.e. 1:3 and 1:6.

The stoichiometry of the binary and ternary complexes during the intermediate state from binary to ternary systems was determined by the three methods which have been mentioned earlier. The experimental procedures used were identical to that described above but the Al:CP ratios were held constant at 1:0.5; 1:1.0; 1:1.5; 1:2.0 and 1:2.5 for each of these.

An attempt was also made to determine the stoichiometry of the reagent to the surfactant in the absence and presence of aluminium. Since the complex of reagent-surfactant was very weak, the only method used in this study was the slope-ratio method.

In the absence of aluminium the first set of the solutions was prepared by adding 3 mL of 2.0×10^{-4} M into a series of solutions containing 0 to 3 mL of the reagent (2.0×10^{-4} M). The second set of solutions was prepared by addition of 3 mL of the reagent solution (2.0×10^{-4} M) into a series of solutions containing 0 to 3 mL of 2.0×10^{-4} M of CP solutions. In the presence of aluminium, the same procedures were applied but 1 mL of 2.0×10^{-4} M of aluminium solution is added into each set of the solutions.

RESULTS AND DISCUSSION

Absorption Spectra

Fig. 1 shows the effect of gradual addition of CP into the binary Al-ECR system. As can be seen from the spectra, addition of more CP will decrease the absorbance of the binary complex at 528 nm and increase the absorbance of the ternary complex at 606 nm. When the molar ratio of Al:CP reached 1:3, no absorption due to the binary complex at 528 nm was observed. The presence of a mixture of binary and ternary complex at low cationic surfactant concentration was also reported for Ga(III)-ECR-CTMA system (Marczenko and Kalowska 1979).

Stoichiometry of Binary Complex of Al-ECR

With binary complex, Al-ECR, all the methods used in this study revealed that the stoichiometry of this complex was 1:3. The graphs showing the stoichiometry of 1:3 for this complex are shown in *Figs. 2 to 4*. The stoichiometric ratio of 1:3 for binary complex of Al:ECR was also reported by Hill (1956).

Stoichiometry of Ternary Complexes of Al-CP-ECR

Figs. 5 to 7 show the graphs used to determine the stoichiometric ratio of Al:CP with the molar ratio of Al:ECR maintained a constant at 1:3. All these three methods gave identical results, i.e. the stoichiometric ratio of Al:CP as 1:3.

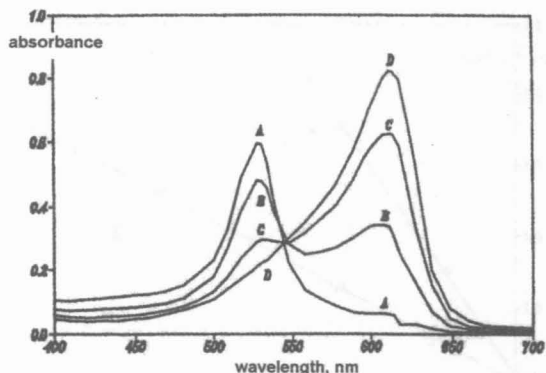


Fig. 1: The effect of addition of different amounts of CP into binary complex, Al-ECR. The molar ratios of Al:CP used 1:0 (A), 1:1.0 (B), 1:2.0 (C) and 1:3.0 (D)

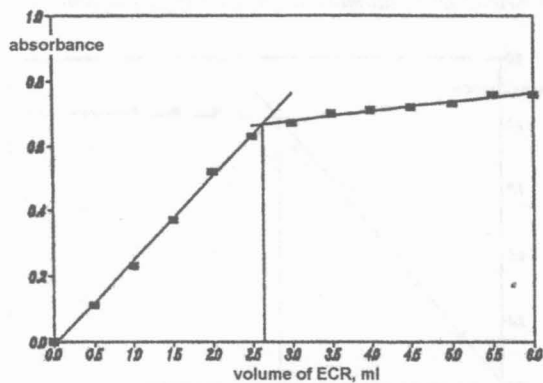


Fig. 2: Graph for stoichiometry determination of binary complex, Al-ECR by means of molar ratio method

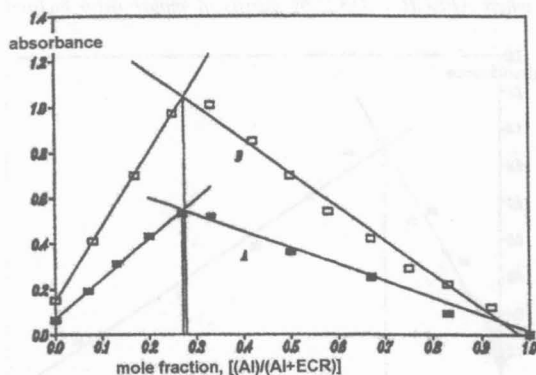


Fig. 3: Job's plots for stoichiometry determination of binary complex, Al-ECR by means of continuous variation method, when the total volume was maintained at 3 mL (A) and 6 mL (B)

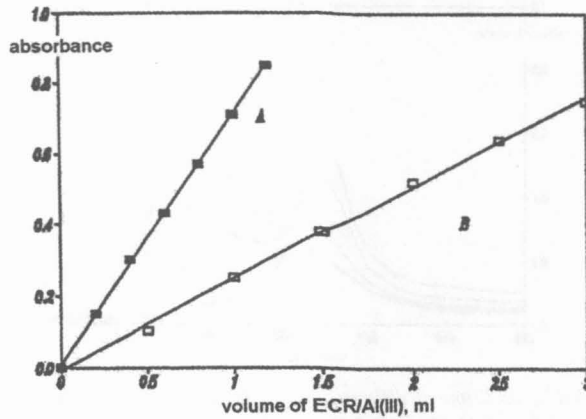


Fig. 4: Graph for stoichiometry determination of binary complex, Al-ECR by means of slope ratio method when aluminium (A) and ECR (B) concentration varies

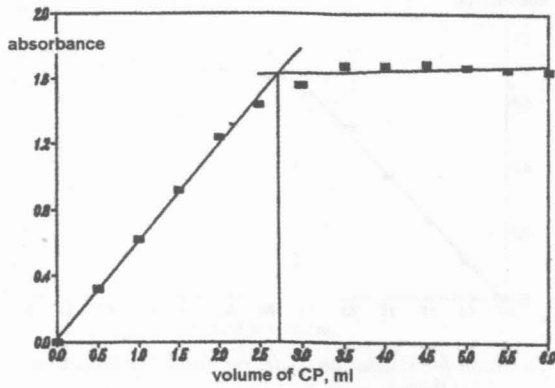


Fig. 5: Graph for stoichiometry ratio determination of Al:CP in the ternary complex, when Al:ECR = 1:3.0 by means of molar ratio method

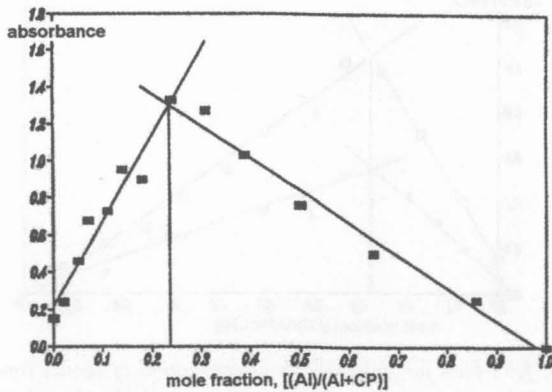


Fig. 6: Job's plot for stoichiometry ratio determination of Al:CP in the ternary complex, when Al:ECR = 1:3.0 by means of continuous variation

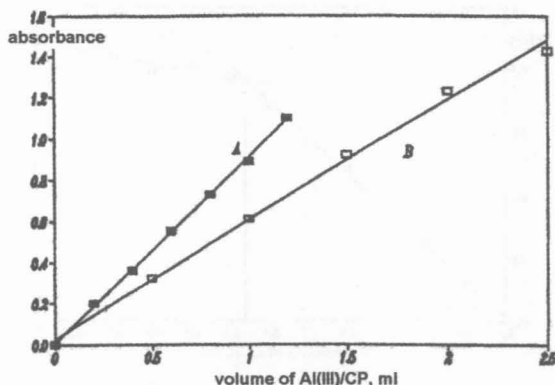


Fig. 7: Graphs for stoichiometry ratio determination of Al:CP in the ternary complex by means of slope ratio method, when aluminium (A) and CP (B) concentration varies. Aluminium concentration of 4.0×10^{-4} M was used

Figs. 8 to 10, on the other hand, show the graphs used to determine the stoichiometric ratio of Al:ECR when the molar ratio of Al:CP was kept constant at 1:3. The results were similar to that obtained for Al:CP with a stoichiometric ratio of Al:ECR of 1:3. Therefore the stoichiometry of the ternary complex, Al-ECR-CP determined by the three methods is 1:3:3 (aluminium to eriochrome cyanine R to cetylpyridinium chloride). This result confirms the belief that a stoichiometric complex is formed at low cationic surfactant concentration (Marczenko and Jarosz 1982). It was previously indicated that the presence of micelles is necessary in the ternary complex formation (Bailey *et al.* 1968). This is based on the observation that no colour change was noticed when quaternary ammonium salts such as tetraethyl- and tetrabutylammonium bromide were used instead of cationic surfactants. Since these compounds are not surfactants, they do not produce micelles. Klopf and Cook (1984) point out however, that in most systems it has not been established whether surfactant monomer or micellar interaction are responsible for sensitisation of the complex. In some systems, both phenomena can be involved. By using spectrophotometric and amperometric titration, it has been shown later that at low concentration of surfactant (below c.m.c.) stoichiometric ternary complexes which contain a few molecules of cationic surfactants are formed (Marczenko and Kalowska 1981). These include ternary complexes such as Fe(III)-ferron (Goto *et al.* 1982), Be(II)-ECR (Marczenko and Kalowska 1978), Tin(IV)-catecol violet (Bailey *et al.* 1968), Mo(II)-catecol violet (Bailey *et al.* 1968) and UO(II)-CAS in the presence of CTMA ion. The stoichiometric ratio of Al(III)-ECR-CP of 1:3:3 found in this study seems to agree with the observation above on the point that the favourable effects of cationic surfactants on complexation reactions are not solely due to the unusual environment on the surface of surfactant micelles as what it was previously believed (Goto *et al.* 1982). For Gd(III)-CAS-CP system, there was evidence that the sensitisation of the complex is due to monomer interaction (Klopf and Cook 1984). At this point however, the colour intensity

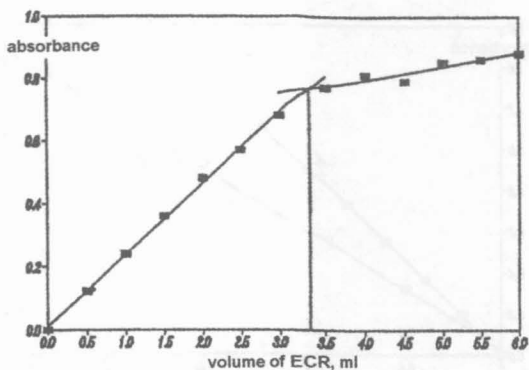


Fig. 8: Graph for stoichiometry ratio determination of Al:ECR in the ternary complex, when Al:CP = 1:3.0 by means of molar ratio method

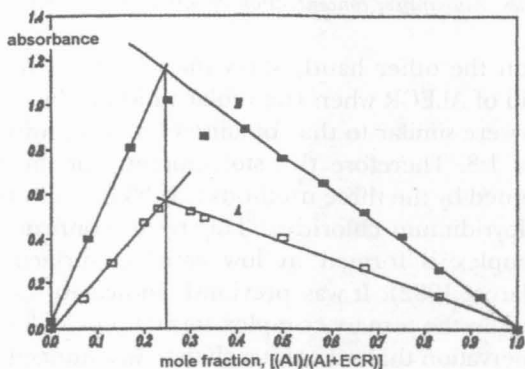


Fig. 9: Job's plot for stoichiometry ratio determination of Al:ECR in the ternary complex, when Al:CP = 1:3.0, by means of continuous variation. Total volume was maintained at 3 mL (A) and 6 mL (B)

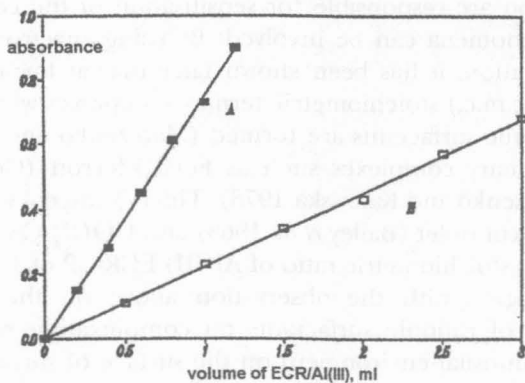


Fig. 10: Graph for stoichiometry ratio determination of Al:ECR in the ternary complex, when Al:CP = 1:3.0, by means of slope ratio method, when aluminium (A) and ECR (B) concentration varies

is not at its maximum since as found in this study, the colour intensity of the complex increases as the concentration of the surfactant increases. Though the Al-ECR-CP system has been used for aluminium determination, no result on the stoichiometry of this complex was reported (Marczenko and Jarosz 1982).

An attempt was made in this study to determine the stoichiometric ratio of Al:ECR in the ternary complex with the molar ratio of Al:CP kept a constant but at a higher value than 1:3. With an Al:CP molar ratio of 1:6, the results obtained are shown in Figs. 11 to 13 from which it can be deduced that the stoichiometric ratio of Al:ECR was still 1:3.

Stoichiometry of Binary and Ternary Complexes of Al-ECR in Binary-Ternary Transition

As shown in Fig. 1, addition of CP into the binary system at a concentration below the stoichiometric amount will be insufficient to completely transform

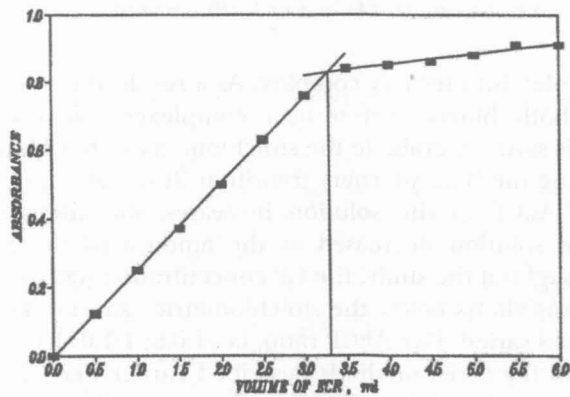


Fig. 11: Graph for stoichiometry ratio determination of Al:ECR in the ternary complex, when Al:CP = 1:6.0, by means of molar ratio method

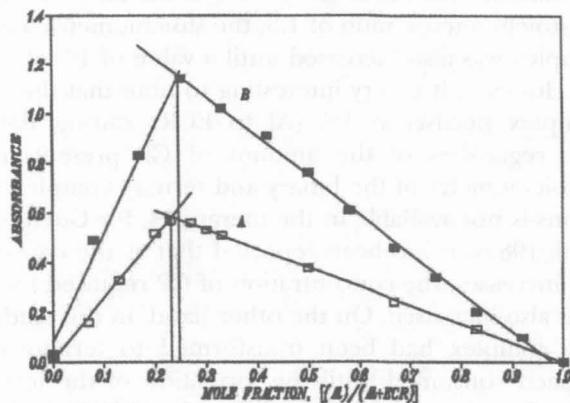


Fig. 12: Job's plot for stoichiometry ratio determination of Al:ECR in the ternary complex, when Al:CP = 1:6.0, by means of continuous variation. Total volume was maintained at 3 mL (A) and 6 mL (B)

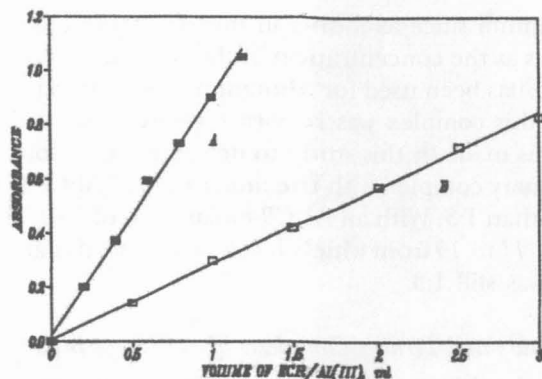


Fig. 13: Graph for stoichiometry ratio determination of Al:ECR in the ternary complex, when Al:CP = 1:6.0, by means of slope ratio method, when aluminium (A) and ECR (B) concentration varies

the binary complex into ternary complex. As a result, the solution will contain a mixture of both binary and ternary complexes. This condition will be exploited in this study to evaluate the stoichiometry of both binary and ternary complexes during the binary-ternary transition. It was also observed that as the molar ratio of Al:CP in the solution increases, the amount of the binary complex in the solution decreased as the amount of the ternary complex increased. Throughout the study, the CP concentration was such that the molar ratio of Al:CP was always below the stoichiometric ratio i.e. 1:3 while the ECR concentration was varied. Five Al:CP ratio, i.e. 1:0.5; 1:1.0; 1:1.5; 1:2.0 and 1:2.5, were chosen and the three methods described earlier were used to determine the stoichiometric ratio of the Al:ECR in these complexes.

Table 1 summarises the results obtained for the stoichiometric ratios determination of Al:ECR in both binary and ternary complexes when CP was gradually added to the solution. This result shows that as the Al:CP ratio increased and approached its stoichiometric ratio of 1:3, the stoichiometric ratio of Al:ECR in the ternary complex was also increased until a value of 1:3 of Al:ECR ratio has been achieved. However, it is very interesting to note that the stoichiometry of the binary complex persists at 1:3 (Al to ECR) during the binary-ternary transition state, regardless of the amount of CP present in the solution. Although the stoichiometry of the binary and ternary complexes in the binary-ternary transitions is not available in the literatures, for Gd(III)-CAS-CP system (Klopf and Cook 1984), it has been reported that as the concentration of the binary complex increases, the concentration of CP required for sensitisation of the complex was also increased. On the other hand, in this study we found that as more binary complex had been transformed to ternary complex, more surfactant has been consumed until the formation of the ternary complex is completed. Therefore, it can be inferred that for Gd(III)-CAS-CP system, the increases in CP concentration are necessary since more binary complex is available in the solution to be transformed to a ternary complex.

TABLE 1
Stoichiometric ratios of Al:ECR in the binary and ternary complexes determined by the methods of slope ratio, molar ratio and continuous variation

Al:CP ratio	1:0.5	1:1.0	1:1.5	1:2.0	1:2.5
molar-ratio method:					
(i) binary	1:3.1	1:3.3	1:3.3	1:3.4	-
(ii) ternary	1:0.8	1:1.3	1:1.6	1:2.2	1:2.6
continuous variation method:					
(i) binary	1:2.5	1:2.9	1:3.3	1:3.1	1:3.2
(ii) ternary	1:0.6	1:1.1	1:1.3	1:2.0	1:2.6
slope-ratio method:					
(i) binary	1:3.1	1:3.4	1:3.3	1:3.3	-
(ii) ternary	1:1.1	1:1.9	1:1.8	1:2.3	1:2.6

Stoichiometry of the Reagent to the Surfactant, ECR-CP in Absence and Presence of Aluminium

In this section, the study is aimed at investigating the stoichiometry of any ECR-CP complex both in the presence and absence of aluminium in the solution. The result from this study would clarify how aluminium ions play a role in determining the stoichiometry value of the ECR-CP complex.

Fig. 14 shows the spectra of CP and ECR alone as well as that of the weak complex, ECR-CP at 480 nm. The addition of CP to ECR has a very small effect on the spectrum of the ECR and it has a very low contrast since the difference between the λ_{max} in their absorption spectra, $\Delta\lambda$ is only 30 nm. The same observation has been reported by Klopff and Cook (1984) for interactions between CAS and CP. This complex is so weak that attempts to use molar ratio method and continuous variation method to determine its stoichiometry were unsuccessful. The slope ratio method is the only method that could be used for the determination of the ECR-CP stoichiometry.

Fig. 15 (A) shows the graphs for the determination of the stoichiometry of ECR-CP in the absence of aluminium. The slope-ratio of these graphs showed that the stoichiometry of ECR-CP is 1:4. This result was rather unexpected, since the stoichiometry of the ternary complex of 1:3:3 suggests that the stoichiometry for ECR:CP should be 1:1 and not 1:4. However, this result suggested that aluminium ions might play a role in producing the ratio of 1:3:3 (therefore ECR:CP = 1:1) in the ternary complex. Quaternary bases were reported to form a kind of ion associate through dissociated or nearly dissociated sulphonic, carboxyl and hydroxyl groups of the triphenylmethane reagents (Savvin *et al.* 1978; Chernova 1977). On observation of the structure of ECR molecule, it can be noted that it has four functional groups with which the CP could be associated. Therefore, in the absence of aluminium in the solution, CP could be possibly associated with all of these functional groups and hence produce the stoichiometry of 1:4 for ECR:CP.

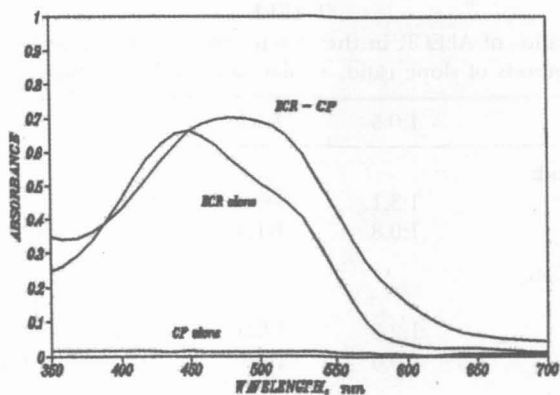
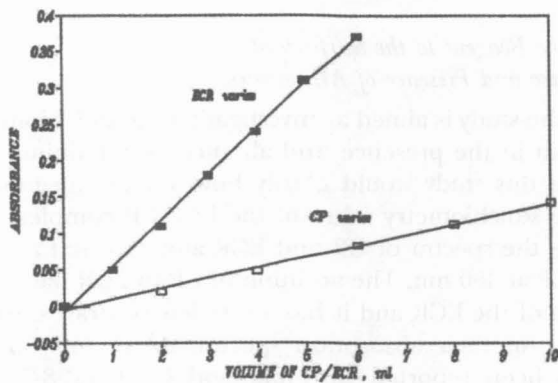
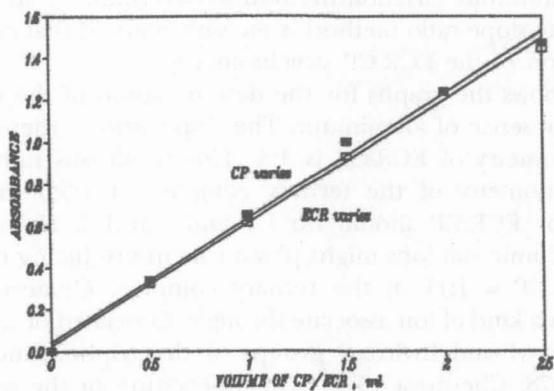


Fig. 14: Absorption spectra of CP, ECR and ECR-CP complex. CP = 10.0 mL, ECR = 10.0 mL of 2.0×10^{-4} M concentration



(A)



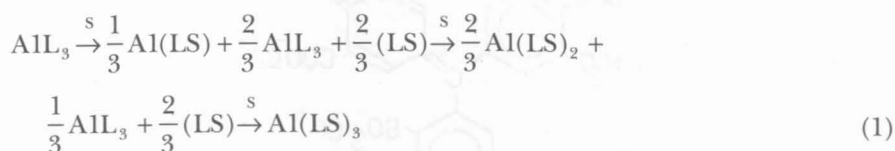
(B)

Fig. 15: Graphs for stoichiometry determination of ECR-CP complex in absence (A) and presence (B) of aluminium by method of slope ratio

Fig. 15 (B) shows the graphs for stoichiometry determination of ECR-CP in the presence of aluminium. The slope-ratio of these graphs showed that in the presence of aluminium the stoichiometry of ECR:CP is 1:1. This result suggests that the degree of the association between CP and the four functional groups in the ECR molecule in the presence and absence of aluminium in the solution, is not the same. As the aluminium ion approaches the ECR molecule, only one of these ion associations persist while the others dissociate to form a binding with the aluminium ion.

Proposal of a Reaction Mechanism for Al-ECR System

It is now established that the stoichiometry of the binary complex of Al-ECR is 1:3 while in the ternary complex of Al-ECR-CP, the stoichiometry is 1:3:3. In its binary-ternary transition state the stoichiometry of the binary complex persists at 1:3, while for the ternary complex, it increased gradually until the stoichiometry reached the value of 1:3:3. Fig. 16 shows the plots of Al:CP ratio versus Al:ECR ratio in the binary and ternary complexes based on the average values of the results shown in Table 1. This result suggested that the complexes will follow the sequence below:



where L = reagent

S = cationic surfactant

Other than binary complex, Eqn. (1) showed that before the ternary complex formation completed, the solution will also contain ECR-CP complex. The presence of ternary complex together with reagent-cationic surfactant complex in the solution was postulated by Wakamatsu and Otomo (1975) for Fe(III)-(2-bromo-4,5-dihydroxyazobenzene-4'-sulfonate)-CP system.

In the absence of aluminium, the preceding sections shows that the CP will be associated with all the functional groups available in the ECR molecule and will give stoichiometric ratio of 1:4 for ECR-CP complex. The structure of the ECR-CP complex could be as shown in Fig. 17.

The π -electron system in the sulphonic acid group of the ECR molecule is isolated from the rest of the conjugation system of the molecule (Marczenko and Kalowska 1981), therefore this explained why the association of this group with CP is "immune" to the presence of aluminium than the others. When aluminium ion approaches the ECR-CP complex, the repulsion between the aluminium and the CP which have the same positive charge, is believed to cause the dissociation of the CP-functional group other than the sulphonic acid group, in order to form a binding between the aluminium and these function

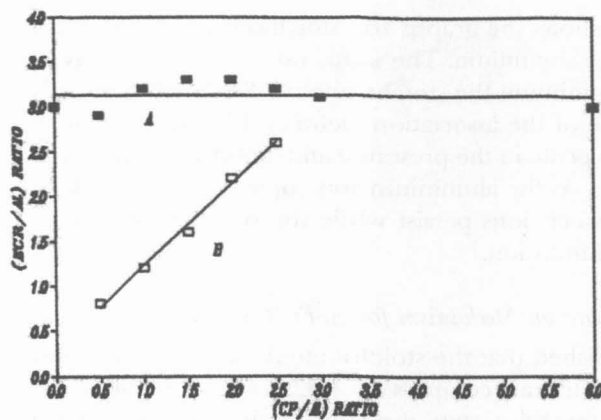


Fig. 16: Plots of ECR:Al ratio versus CP:Al ratio in the binary (A) and ternary complexes (B)

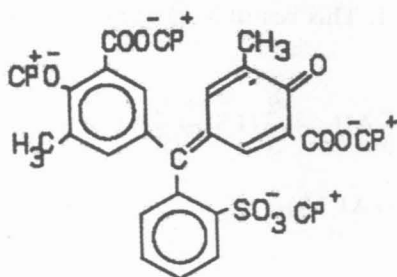


Fig. 17: Proposed structure of ECR-CP complex without the presence of aluminium in the solutions

groups. The possible structure of the ternary Al-ECR-CP complex based on these observations could be written as shown in Fig. 18.

By looking to the proposed structure of the Al-ECR-CP complex, it could be understood that the sensitisation of the binary complex by the CP could be in two ways:

- (i) Stabilising the negatively charged metal complex through electrostatic interaction between the negatively charged complex and the positively charged CP.
- (ii) The formation of a tautomer structure which further stabilised the complex.

While the first phenomena has also been suggested for other systems such as Gd(III)-CAS-CP (Klopf and Cook 1984) and niobium-morin-CTMA (Sanz-Medel and Alonso 1984), the second phenomena has never been reported in the literature and is a very interesting subject to pursue.

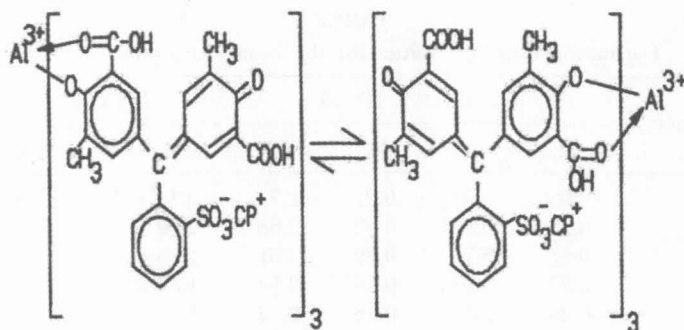


Fig. 18: Proposed structure of the ternary complex, Al-ECR-CP

Formation Constant of Aluminium Complexes with ECR

In this study, the formation constant of the binary and ternary complexes were determined from Job's plots by using the method described by Kirkbright *et al.* (1965). The following equations were used for the formation constant calculation:

$$K = x / (M - x)(L - 3x)^3 \quad (2)$$

$$x = 1/A \left[0.79 \left[-G + \sqrt{(G^2 + 4H^3)} \right]^{1/3} - 1.26H / \left[-G + \sqrt{(G^2 + 4H^3)} \right]^{1/3} \right] \quad (3)$$

where K = Formation constant

x = Some point on the curve corresponding to a certain concentration of the complex

M,L = The concentration of Al(M) and ECR(L) in the first Job's plot if no reaction had taken place between them.

M',L' = The concentration of Al(M') and ECR(L') in the second Job's plot if no reaction had taken place between them.

$$A = 27 (L' + M' - L - M) \quad (4)$$

$$H = AC - B^2 \quad (5)$$

$$G = A^2D - 3ABC + 2B^3 \quad (6)$$

where B = $9 (L^2 + 3LM - L'^2 - 3L'M')$

C = $(L'^3 + 9L'^2M' - L^3 - 9L^2M)$

D = $ML^3 - M'L'^3$

Substitution of x in the expression for K, provides the numerical values for the formation constant of binary and the ternary complexes as shown in Tables 2 to 4.

The results from these tables showed that the values of the formation constant for binary and ternary complexes are of the same order. This indicates

TABLE 2
Formation constant values for the binary complex, Al-ECR

Absorbance	mL of 2.0×10^{-4} M				K calculated from	
	M	L	M'	L'	1st Job's plot	2nd Job's plot
0.20	0.09	5.91	0.22	2.78	2.14×10^{11}	1.43×10^{11}
0.25	0.18	5.82	0.32	2.68	2.02×10^{11}	1.36×10^{11}
0.30	0.28	5.72	0.39	2.61	1.93×10^{11}	1.31×10^{11}
0.35	0.37	5.63	0.46	2.54	1.83×10^{11}	1.26×10^{11}
0.40	0.46	5.54	0.56	2.44	1.74×10^{11}	1.20×10^{11}
0.45	0.55	5.45	0.63	2.37	1.66×10^{11}	1.16×10^{11}
0.50	0.64	5.36	0.71	2.29	1.62×10^{11}	1.13×10^{11}
0.55	0.73	5.27	0.80	2.20	1.55×10^{11}	1.09×10^{11}

$$K_{\text{average}} = 1.53 \pm 0.34 \times 10^{11} \text{ M}^{-3}$$

TABLE 3
Formation constant values for the ternary complex, Al-ECR-CP when
Al:CP constant at 1:3

Absorbance	mL of 2.0×10^{-4} M				K Calculated From	
	M	L	M'	L'	1st Job's Plot	2nd Job's Plot
0.10	0.13	2.87	0.09	5.91	1.39×10^{11}	2.06×10^{11}
0.20	0.26	2.74	0.22	5.78	1.31×10^{11}	1.93×10^{11}
0.30	0.39	2.61	0.35	5.65	1.24×10^{11}	1.82×10^{11}
0.40	0.52	2.48	0.49	5.51	1.18×10^{11}	1.71×10^{11}
0.50	0.65	2.35	0.62	5.38	1.13×10^{11}	1.62×10^{11}

$$K_{\text{average}} = 1.54 \pm 0.33 \times 10^{11} \text{ M}^{-3}$$

TABLE 4
Formation constant values for the ternary complex Al-ECR-CP when
Al:CP constant at 1:6

Absorbance	mL of 2.0×10^{-4} M				K Calculated From	
	M	L	M'	L'	1st Job's Plot	2nd Job's Plot
0.10	0.10	2.90	0.07	5.93	1.39×10^{11}	2.08×10^{11}
0.20	0.22	2.78	0.19	5.81	1.33×10^{11}	1.97×10^{11}
0.30	0.34	2.66	0.31	5.69	1.27×10^{11}	1.86×10^{11}
0.40	0.46	2.54	0.43	5.57	1.21×10^{11}	1.76×10^{11}
0.50	0.58	2.42	0.55	5.45	1.16×10^{11}	1.67×10^{11}

$$K_{\text{average}} = 1.57 \pm 0.34 \times 10^{11} \text{ M}^{-3}$$

that the surfactant molecules are not predominantly involved in the complex formation between aluminium and ECR. As mentioned earlier in the preceding section, the π -electron system of the sulphonic group at which CP is associated with, is isolated from the rest of the ECR molecule. This could explain why CP remains inactive during the ternary complex formation. For the same reason, Marczenko and Kalowska (1981) explained that in triphenylmethane reagents, the associates of surfactant formed through the sulphonic groups do not affect the colour of the metal complex.

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