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5. Thermally induced intramolecular decarboxylation of coumarin-4-acetic acids were observed only when the acids were heated above their melting point¹. In the present investigation, thermal decarboxylation of the acids was not noticed when heated at 150°C at a pressure of 10⁻² torr. Hence the base catalyzed route alone was considered feasible.

POTENTIOMETRIC STUDIES ON MIXED-LIGAND BINUCLEAR COMPLEXES OF SOME TRANSITION METALS

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A review of the literature shows that mononuclear¹⁻³ mixed-ligand complexes of first row transition metals have been studied widely; however, scanty references are available on the study of formation of binuclear⁴⁻⁷ mixed-ligand complexes involving the above metal ions. The results of the studies on some binuclear mixed-ligand complexes of Cu(II), Ni(II), Zn(II) and Cd(II) formed by the simultaneous addition of the ligands EDTA and PDA to the metal ions have been reported in this communication.

Stock solutions of metal nitrates were prepared in double-distilled water and the metal contents of the solutions were estimated by standard methods⁸. The concentrations of all the solutions were checked potentiometrically. The pH-measurements were recorded with a Philips digital pH-meter having a working accuracy of ± 0.02 pH, using glass and calomel electrodes. The total volume (50 ml) and ionic strength ($\mu = 0.1, 0.2, 0.3$ M KNO₃) and the concentration of the metal and PDA (10×10^{-3} M), and EDTA (5×10^{-3} M) were kept constant at the beginning of each titration.

The dissociation constants of K₃EDTA ($pK_1 = 9.56$) and PDA ($pK_1' = 2.85$; $pK_2' = 5.09$)

were calculated by the method of Chaberck and Martell⁹ and the formation constants of the species 2 : 1 : 2 M (II) K₃EDTA-PDA using the expression of Gupta¹⁰.

Figure 1, curve b representing the titration of K₃EDTA exhibits no inflection indicating the non-labile nature of the remaining carboxy proton. Curve c depicting the titration of PDA exhibits inflection at $m = 1$ and $m = 2$ ($m =$ moles of base added per mole of metal ions or ligand) indicating the stepwise neutralization of the two carboxy protons of PDA.

Curve d representing the system 1 : 1 Cu(II)-K₃EDTA and curve e system 1 : 1 Cu(II)-PDA exhibit inflection at $m = 1$ and $m = 2$ which are attributed to the respective formation of 1 : 1 Cu(II)-K₃EDTA and Cu(II)-PDA binary species. An additional inflection at $m = 3$ in the case of 1 : 1 Cu(II)-PDA (curve e) may be attributed to the disproportionation of the initially formed 1 : 1 species, giving 1 : 2 Cu(II)-PDA species and metal hydroxide as may be clear by the following expression:

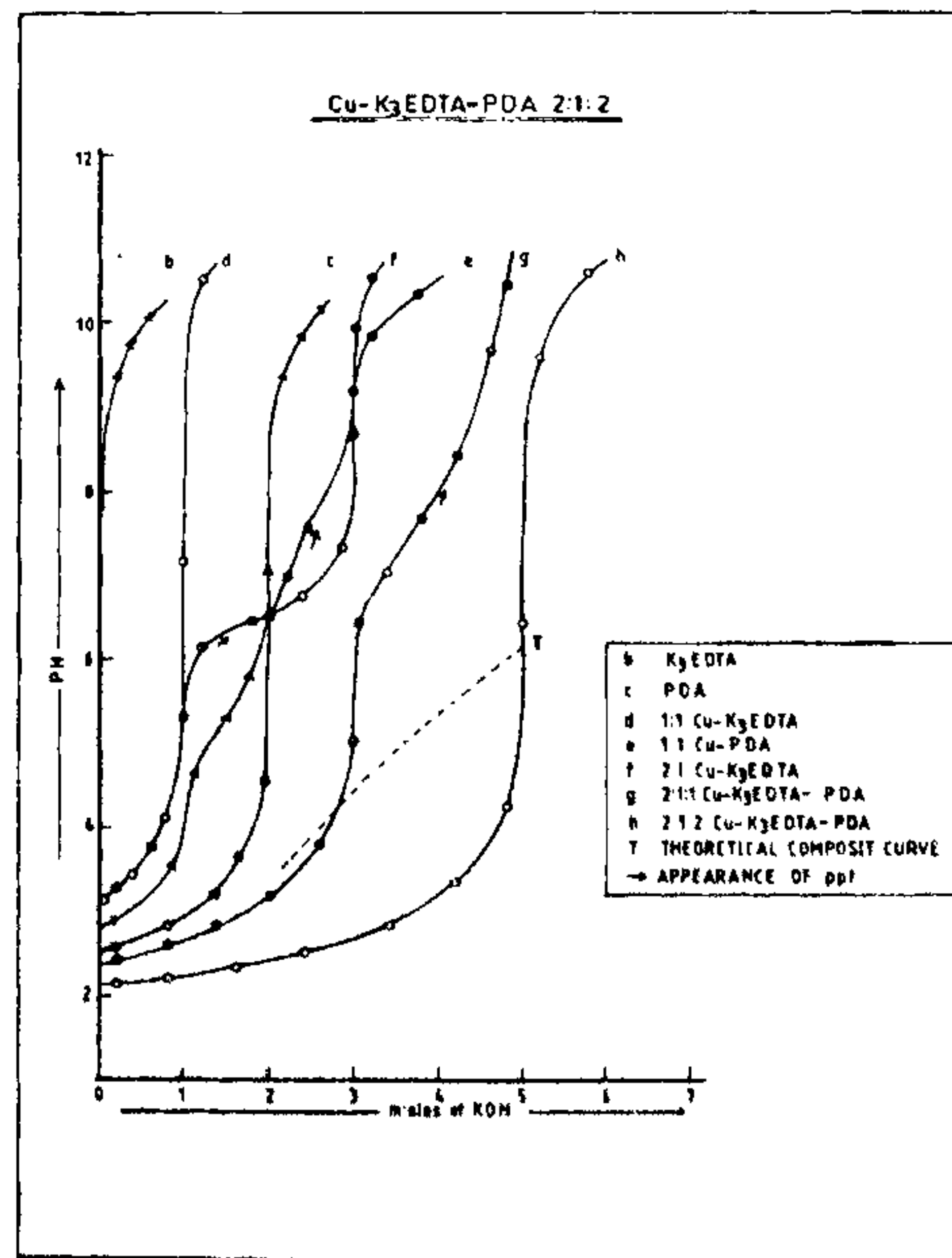
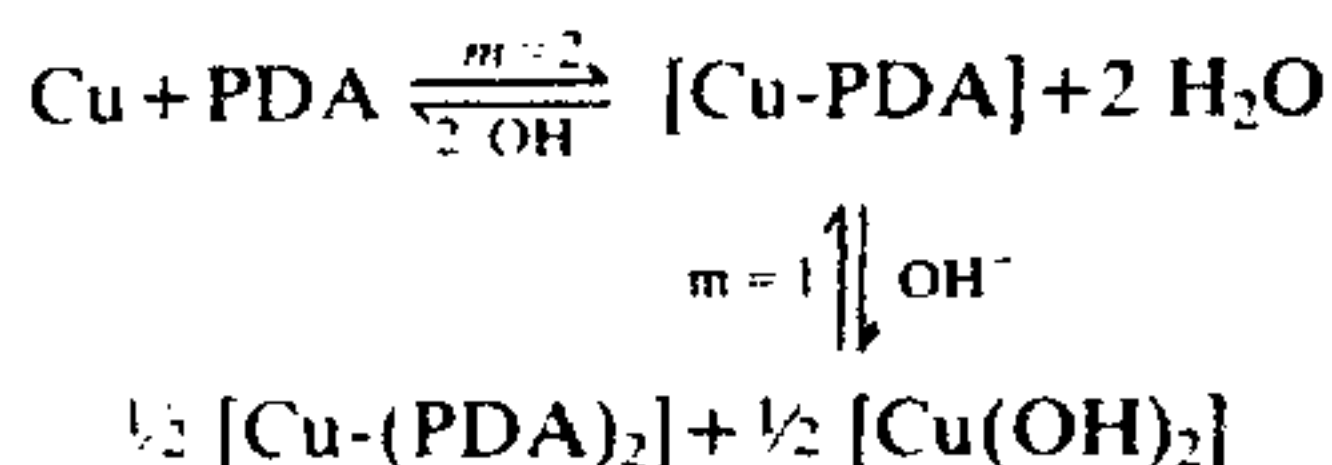


Figure 1. pH-titrations for the system: Cu(II)-EDTA-PDA; 2:1:2.



Curve f representing the titration of 2 : 1 Cu(II)-K₃EDTA exhibits an appreciable lowering in pH and an inflection at $m=1$ which may be attributed to the formation of 2 : 1 Cu(II)-K₃EDTA complex. An additional inflection at $m \approx 3$ (except in the system 2 : 1 [Zn(II)-K₃EDTA] may be attributed to the disproportionation of 2 : 1 Cu(II)-K₃EDTA complex into 1 : 1 Cu(II)-K₃EDTA with the precipitation of the half of the metal as metal hydroxide.

An inflection at $m \approx 5$ may be attributed to the disproportionation of the 2 : 1 Zn-EDTA into a stable 1 : 1 Zn-EDTA complex, the remaining half of the metal probably goes into the solution as ZnO_2^{2-} at the high pH range.

Curve g depicts the pH titration of the 2 : 1 : 1 Cu(II)-K₃EDTA-PDA system. Further lowering in pH and a single well-defined inflection at $m=3$ may be attributed to the formation of a soluble binuclear mixed-ligand species by the simultaneous addition of both the ligands to the metal ions.

In the mixed-ligand system 2 : 1 : 2 Cu(II)-K₃EDTA-PDA (curve h) the lowering in pH followed by a single sharp inflection at $m=5$ may be attributed to the simultaneous addition of both the ligands to the metal ion forming a 2 : 1 : 2 Cu(II)-K₃EDTA-PDA complex. This is further supported by the non-superimposable nature of the theoretical composite curve¹¹ with the experimental curve h (the curve¹¹ has been drawn by the addition of double the horizontal distances of curve c (PDA) with that of curve f for 2 : 1 Cu(II)-K₃EDTA).

The absence of heterogeneous phase during the titration of the system 2 : 1 : 2 Cu(II)-K₃EDTA-PDA and the constancy observed in the values of

formation constants (table 1) lend further support to the formation of the mixed-ligand binuclear species.

The thermodynamic stability constant ($\log k_0$) has been graphically found (figure 2) from the values of $\log k$ determined at various ionic concentrations: 0.1, 0.2 and 0.3 M (KNO₃). The magnitude of the negative values of ΔG° (table 1) is quite significant and lends support to the stability of the binuclear mixed-ligand complex formed. The stability of the complexes in terms of the metal ion is of the following order Cu(II) > Ni(II) > Zn(II) > Cd(II) which is in accordance with the Irving William Order¹².

The authors express their gratitude to Prof. J. P. Tandon, Rajasthan University, Jaipur for valuable suggestions.

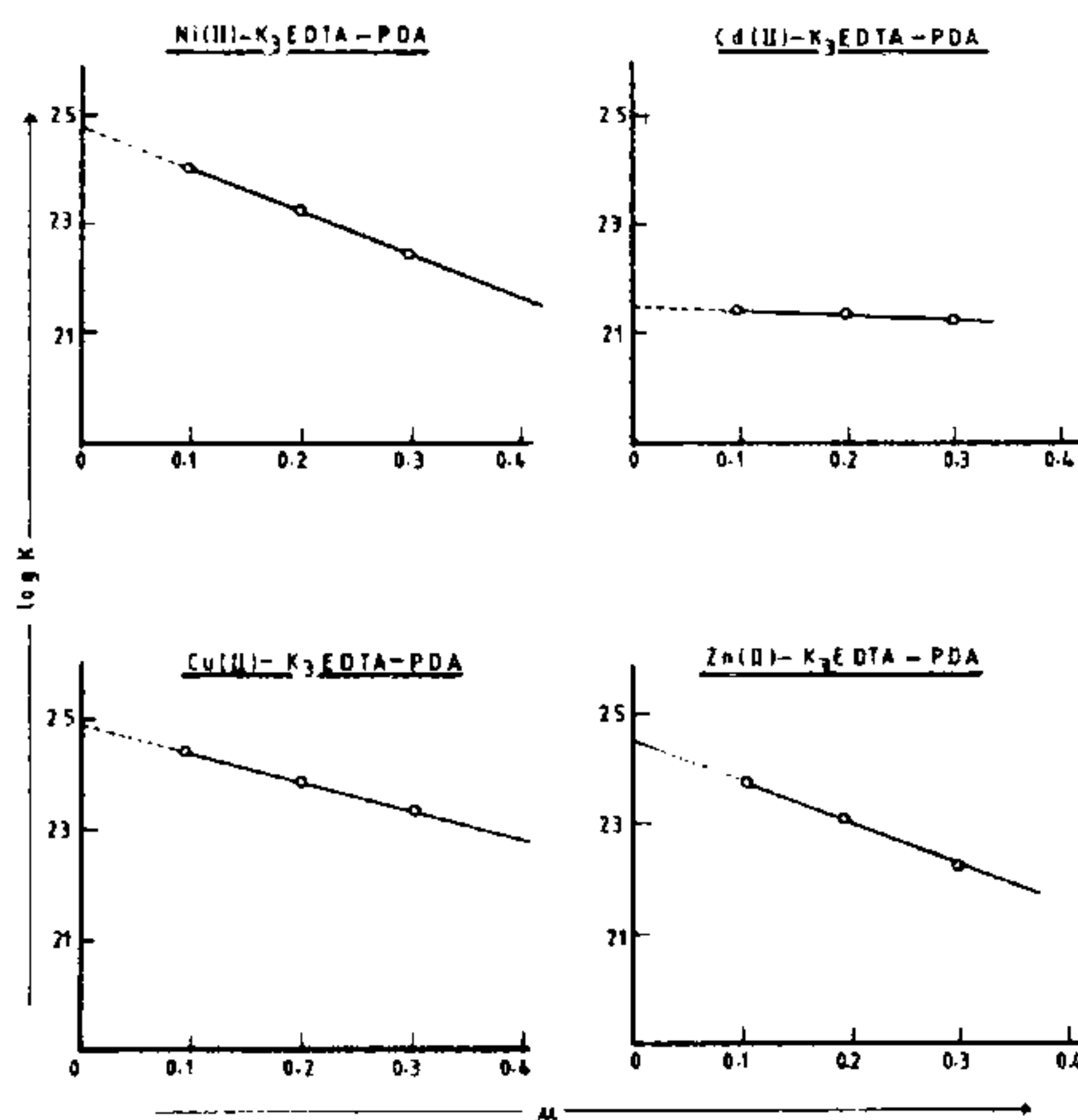


Figure 2. $\log k$ plotted against the respective ionic conc. (μ) to find out $\log k_0$.

Table 1 Graphically derived $\log k_0$ values for M_2LA_2 complexes and calculated values of ΔG°

System	$\log K_{M_2LA_2}$			$\log k_0$	ΔG° kcal/ mol/deg.
	0.1 M	0.2 M	0.3 M		
Cu(II)-EDTA-PDA	24.41 ± 0.15	23.68 ± 0.12	23.36 ± 0.16	24.90	-33.93
Ni(II)-EDTA-PDA	23.99 ± 0.18	23.30 ± 0.19	22.43 ± 0.19	24.80	-33.80
Zn(II)-EDTA-PDA	23.54 ± 0.19	23.20 ± 0.17	21.99 ± 0.16	24.50	-33.39
Cd(II)-EDTA-PDA	21.38 ± 0.12	21.33 ± 0.14	21.33 ± 0.17	21.52	-28.93

12 June 1985; Revised 20 May 1986

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Ca-RICH PYROXENES FROM THE CARBONATITE COMPLEX OF TIRUPPATTUR, TAMIL NADU

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IN order to study the change of composition of clinopyroxenes (cpx) during the course of magmatic differentiation, seven microprobe analyses of cpx from a series of alkaline rocks of the carbonatite complex of Tiruppattur¹ (N 12°15'–12°30' and E 78°25'–78°35') were carried out by using JXA 90 A (15 kV), computer-attached electron probe micro-analyzer, in the geochemical laboratory of Moscow State University, USSR. The chemical analyses (table 1) show that the cpx are calcium-rich and

straddle the $\text{CaMgSi}_2\text{O}_6$ - $\text{CaFeSi}_2\text{O}_6$ join. By using the bulk rock analyses of associated alkaline rocks, compositions of a few cpx were also determined by the method of Rittmann² and were plotted along with the compositions of cpx obtained by microprobe analyses. All cpx are distinctly Ca-rich and fall near the field of Ca-rich cpx demarcated by Eriksson³, similar to cpx from Palabora carbonatite complex of Africa³. The diagram (figure 1) showing diopside-hedenbergite-acmite components of the analyzed cpx exhibits marked iron enrichment at late stages of magmatic fractionations. During the course of magmatic crystallization, increasing trend of Ca and Fe with decreasing trend Na and $\text{Mg}/(\text{Mg}+\text{Fe})$ was noted (table 1). Further, table 1 indicates that the cpx from the ultramafics show increase of Al with decrease in Si, while the syenites exhibit a decreasing trend of Al with increasing content of Si. DI of these cpx ($100 \text{ Mg}/\text{Mg}+\text{Fe}$) indicate two separate trends, one for ultramafics and another for syenites.

The carbonatite complex comprises a sequence of zoned co-magmatic members of alkali syenites, ultramafics and carbonatites in two adjacent independent structural basins designated as Sevvattur and Jogipatti basins. The host rocks of cpx indicate two separate trends of evolutions⁴:

1. Biotite-oligoclase → pyroxenite → biotite pyroxenite → apatite-magnetite-orthoclase-biotite pyroxenite

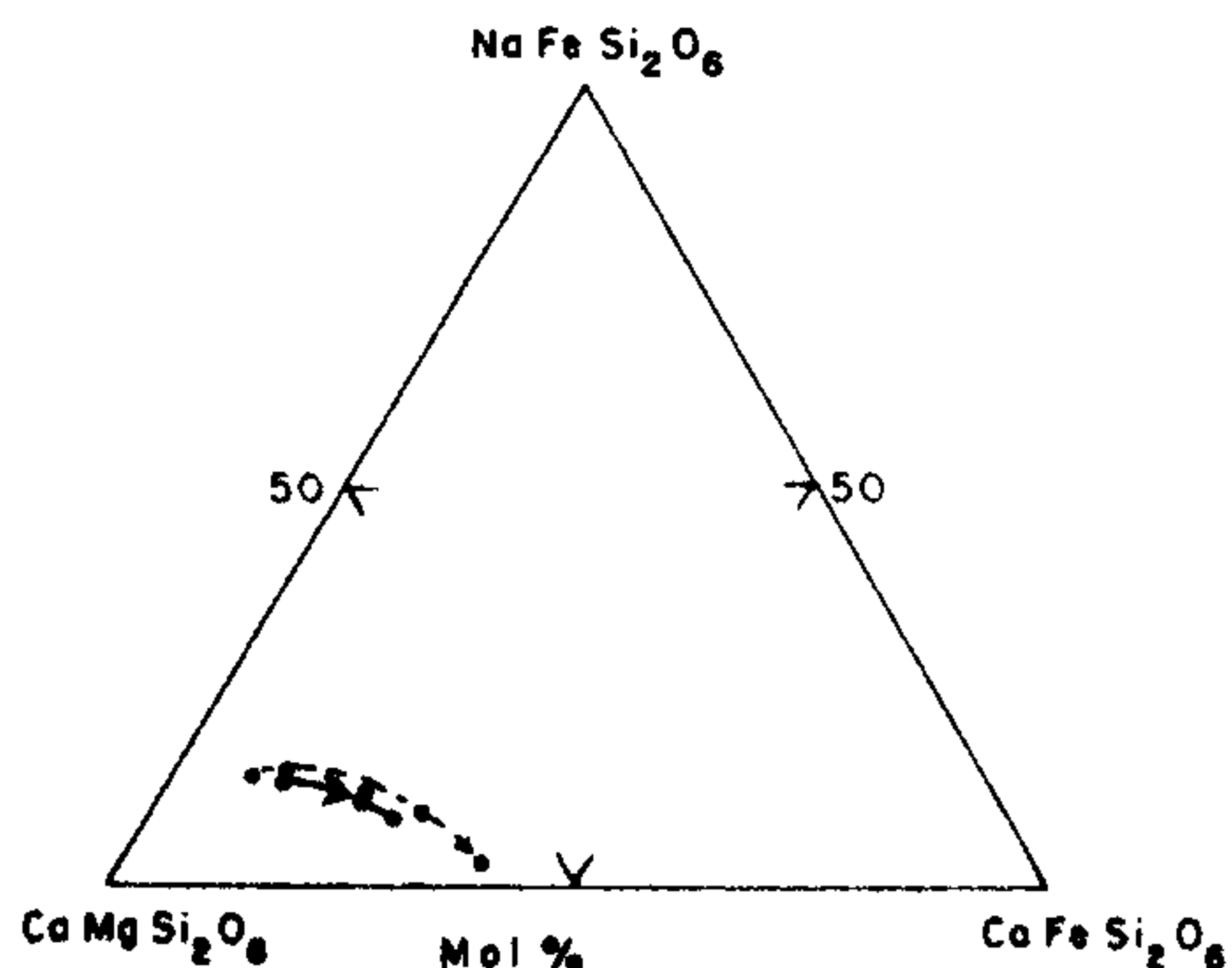


Figure 1. Crystallization trends of iron enrichment in calcium-rich pyroxenes from alkaline rocks of Tiruppattur (trend of pyroxenes from ultramafic rocks---; from syenites —).