

Complex Formation of Sodium and Lithium Ions with Tropolone and Kojic Acid in Aqueous Solutions

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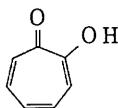
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Summary

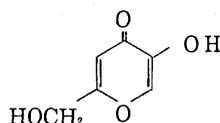
Complexation of sodium and lithium ions with tropolone and kojic acid (L) was studied in a 0.1 mol dm^{-3} tetraethylammonium perchlorate medium at 25°C by spectrophotometry. The formation constants were determined as: $K_{\text{NaL}} = 0.57 \pm 0.83$ and $K_{\text{LiL}} = 4.81 \pm 0.21$ for tropolone, and $K_{\text{NaL}} = 0.57 \pm 0.13$ and $K_{\text{LiL}} = 1.07 \pm 0.21$ for kojic acid, respectively, based on the concentration scale with estimated standard deviations (2σ).

Alkali metal ions play vitally important roles in a variety of biological systems [1,2], for example in transport phenomena. In most cases this type of activity is closely related to the complex formation of these ions with biological substances.

Although alkali metal ions combine rather strongly with certain ligands such as crown ethers and cryptand [1,3-5], they usually interact weakly with most of organic substances. This is why there have scarcely been quantitative studies on the complex formation of alkali metal ions with organic ligands.



tropolone



kojic acid

We found that alkali metal ions react with tropolone and kojic acid, both of which have carbonyl oxygen and hydroxyl oxygen atoms at the adjacent positions, though the former ligand has a seven-membered ring. These two ligands are coordinated to multivalent metal ions rather strongly [6,7], which implies chelation by the oxygen donor atoms, but any literature source on the complexation of alkali metal ions has not been available for these ligands. This fact motivated us to determine the equilibrium constants for alkali metal ions and these potential bidentate ligands, and we were especially encouraged by the successful application of spectroscopic measurements to the determination of their formation constants for *o*-phenylenediamine-*N,N,N',N'*-tetraacetate(PhDTA)[8].

Experimental Section

Reagents Tropolone (Aldrich) was recrystallized from petroleum ether and purified by sublimation. Kojic acid was recrystallized from water, and dissolved in double distilled water. Sodium and lithium perchlorates were prepared as described previously [9,10]. Tetraethylammonium perchlorate solution was prepared also as described elsewhere[8].

Equipments Measurements were carried out at $25 \pm 0.1^\circ\text{C}$ and at an ionic strength $I = 0.10 \text{ M}$ [11] (Et_4NClO_4). Electrochemical measurements were made by essentially the same method as stated in the previous report [8].

A ligand (say tropolone) solution (70 cm^3) was titrated with an alkali metal (say lithium) perchlorate solution that contained the ligand at the same concentration at the solution titrated in order to maintain the same ligand level. During the titration, differential absorbance was measured at 395 nm (lithium-tropolone), 399 nm (sodium-tropolone), 355 nm (lithium-kojic acid) or 315 nm (sodium-kojic acid) on a Shimadzu UV-265FW uv-visible spectrophotometer with a thermostated cell (light path=1 cm). All data were processed on an NEC PC98 personal computer.

Experimental Procedure A 0.01 M perchloric acid solution was chosen as a pH standard on the concentration scale (auto-protolysis constant $K_w = 1.22 \times 10^{-14} \text{ M}^2$ for the 0.10 M aqueous Et_4NClO_4 medium)[8].

A tropolone stock solution ($1.017 \times 10^{-3} \text{ M}$) was diluted to $5.085 \times 10^{-5} \text{ M}$ with double distilled water, and the final ionic strength and pH were adjusted to 0.1 M with Et_4NClO_4 and about 10 with Et_4NOH , respectively. A $1.060 \times 10^{-3} \text{ M}$ kojic acid stock solution $1.060 \times 10^{-3} \text{ M}$ kojic was diluted likewise, and the resultant ionic strength and pH were also adjusted to 0.1 M and about 10, respectively, in a similar way.

A $1.386 \text{ mol kg}^{-1}$ lithium perchlorate stock solution was diluted to 0.9991 M for the tropolone system and to 1.408 M for the kojic system, and the pH of the solutions was adjusted to about 10. The diluted solutions contained respective ligands at the same concentrations as the ligand solutions titrated.

A $4.819 \text{ mol kg}^{-1}$ sodium perchlorate stock solution was diluted to 1.001 M for both ligand systems, and the pH and the ligand concentration of the resultant solutions were adjusted similarly.

Results and Discussion

As stated above, tropolone and kojic acid interact with lithium and sodium ions only very weakly, accordingly the potentiometric method is not applicable to obtain relevant formation constants. However, the spectra of the solution of either of these ligands were found to change appreciably, when an alkali metal ion was added. Spectral changes are illustrated in Fig. 1 for the tropolone-lithium ion system. Sodium ion caused similar but smaller spectral change.

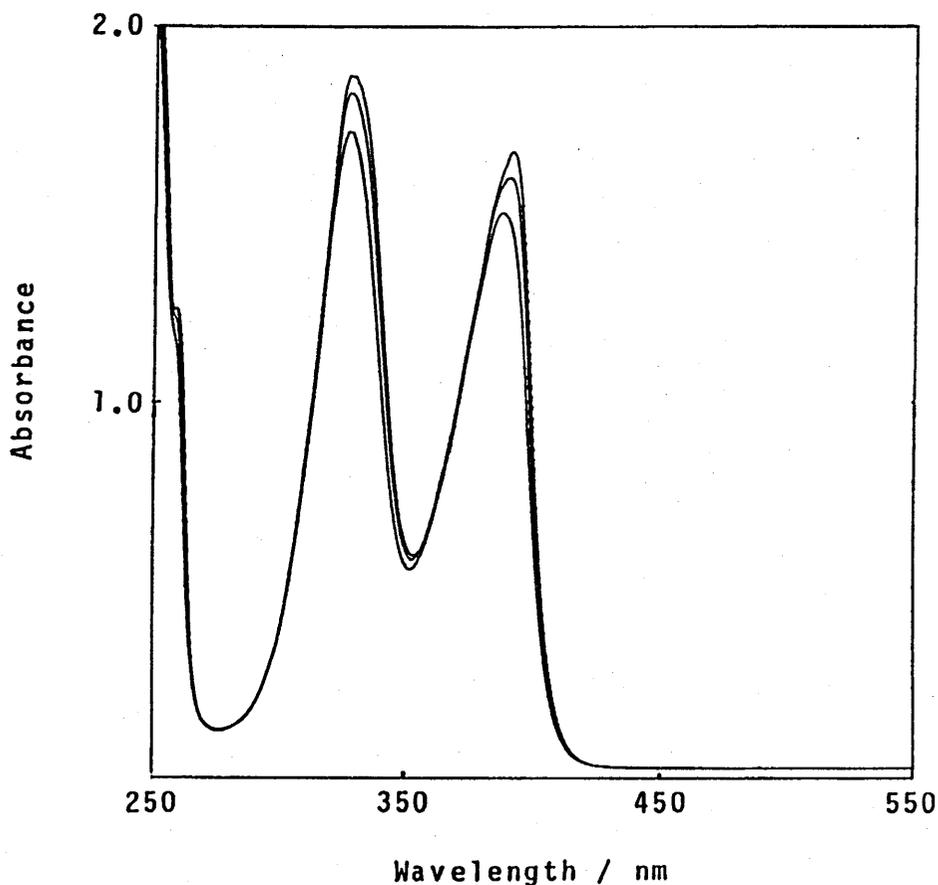


Fig. 1 Change in spectra of tropolone ($5.085 \times 10^{-5} \text{ M}$) on addition of a 0.9991 M lithium perchlorate solution at a pH of ca. 10. The spectral peak at 395 nm decreased with increasing concentration of lithium ion.

Let us consider the following complex formation;



where M denotes lithium or sodium ion, and L represents a ligand (tropolone or kojic acid anion). Since the protonation reaction is negligible at pH 10 for both the ligand and a complex ML ($pK_a = 6.69$ for tropolone [7], and 7.68 for kojic acid [6], respectively, at 25°C and 0.1 M), the formation of the metal complex ML should only be responsible for the spectral change observed.

The analytical ligand concentration, C_L , is equated as follows;

$$\begin{aligned} C_L &= [L] + [ML] \\ &= [L] (1 + K_{ML} [M]) \end{aligned} \quad (2)$$

The differential absorbance observed, ΔA , is the difference between the absorbance of the initial solution of a ligand alone, A_0 , and the absorbance after addition of metal ion, A. Thus,

$$\begin{aligned} \Delta A &= A_0 - A \\ &= \epsilon_L C_L - (\epsilon_L [L] + \epsilon_{ML} [ML]) \\ &= (\epsilon_L - \epsilon_{ML}) [ML] \\ &= \Delta \epsilon [ML] \end{aligned} \quad (3)$$

where ϵ_L and ϵ_{ML} are the molar extinction coefficients of a ligand and a metal complex ML, respectively. Substitution of eqns. 1 and 2 into eqn. 3 gives the following expression;

$$\begin{aligned} \Delta A &= \Delta \epsilon K_{ML} [M] [L] \\ &= \Delta \epsilon C_L / (1 + [M]) \end{aligned} \quad (4)$$

In Fig. 2 is illustrated a plot of differential absorbance against wave lengths, and in Fig. 3 a plot of ΔA at 395 nm as a function of the analytical concentration of lithium ion.

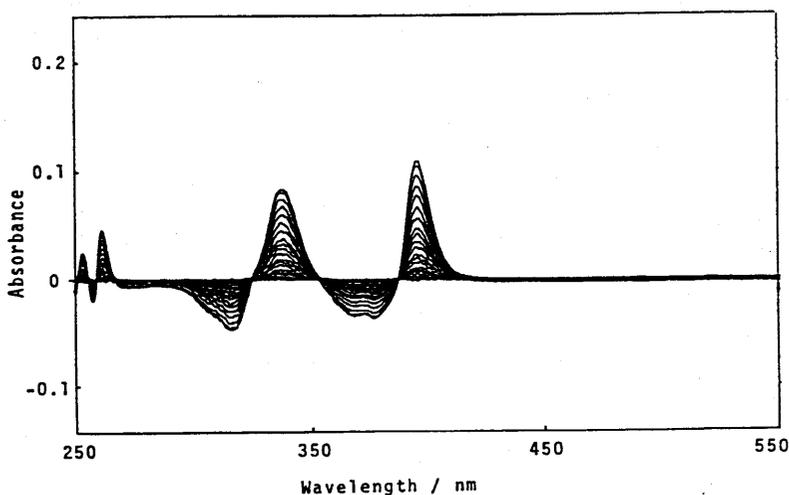


Fig. 2 Differential spectra of the tropolone-lithium ion solution under the same conditions as mentioned in Fig. 1.

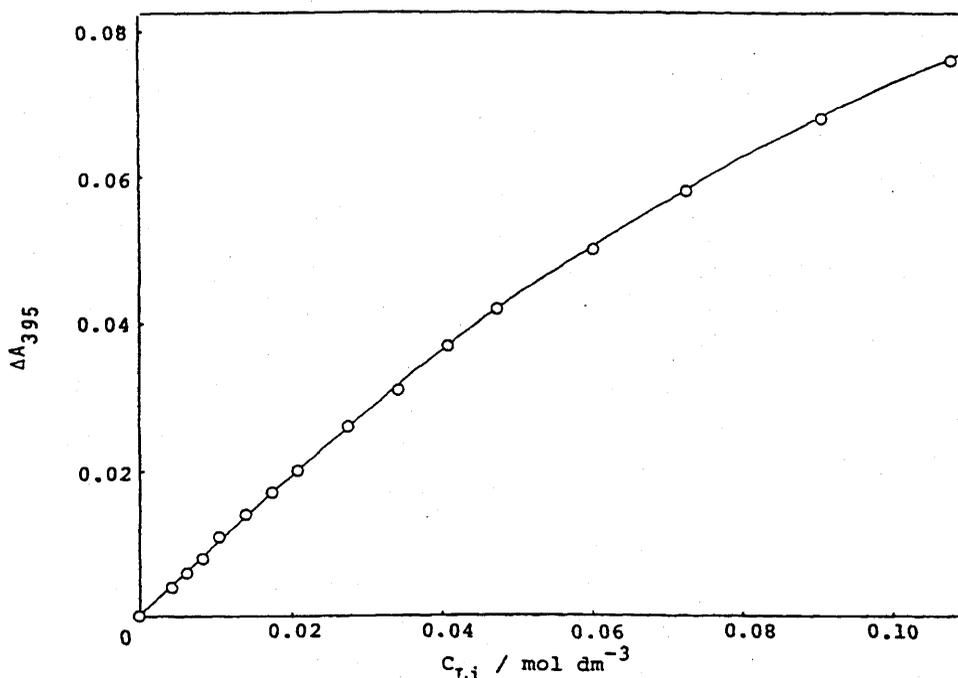


Fig. 3 Plot of the difference in absorbance at 395 nm, ΔA , against the analytical lithium concentration, C_{Li} , for the lithium tropolone system. The curve is drawn by use of the values of K_{ML} and $\Delta \epsilon$ obtained from this work.

When equating $k = \Delta \epsilon C_L$;

$$1/\Delta A = (1/K_{ML} [M] + 1)/k \quad (5)$$

As the first approximation, $[M]$ is nearly equal to the analytical concentration of metal ion, C_M . Indeed a straight line was obtained when plotting $1/\Delta A$ against $1/C_M$, which gave a slope $1/k K_{ML}$, and an intercept $1/k$.

In the case of the complexation of lithium ion with tropolone,

$$1/K_{ML} = 0.93, \text{ and } 1/K = 4.7 \quad (6)$$

Thus $K_{ML} = 5.1$ and $\Delta \epsilon = 4.2 \times 10^3$. These values may be used as initial values for further refinement of the constants. Data processing of all absorbance values led to more refined formation constants summarized in Table 1, based on the non-linear least squares method. It should, however, be mentioned that they are concentration constants rather than thermodynamic ones [12].

Quite the same procedure was applied successfully to the sodium system as well as kojic acid-alkali metal ion systems, and the constants thus obtained are summarized in Table 1, together with those for divalent metal ions.

Comparison of the formation constants permits us to realize great difference in constants between the alkali and the alkaline earth metal ions. It should be noted that the constants shown there are logarithmic for the latter. The difference, however, may not be surprising if we take into consideration the difference in charge.

Another salient feature is the effect of the ionic radius on complex formation, and lithium ion interacts always more strongly than sodium ion. This is also true for PhDTA, which is a potential hexadentate ligand ($\log K_{ML} = 1.99$ for Li^+ and 0.73 for Na^+)[8].

As evident from Table 1, any alkaline earth metal ion interacts more strongly with tropolone than with kojic acid, though proton bonds to these ligands in a reversed manner. Although such a general inclination is not found for the alkali metal complexes, we can readily point out the strong affinity of lithium ion to tropolone.

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- 11) Non-SI unit: $1M = 1 \text{ mol dm}^{-3}$.
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Table1. Formation Constants of Alkali Metal Complexes (K_{ML}) Compared with Those of Alkaline Earth Metal Complexes ($\log K_{ML}$)

metal ion	tropolone	kojic acid	ionic radius/Å
$K_{ML}^{a)}$ / mol ⁻¹ dm ³			
Li ⁺	4.81(21)	1.07(21)	0.60
Na ⁺	0.57(83)	0.57(13)	0.95
$\log (K_{ML} / \text{mol}^{-1}\text{dm}^3)$			
Be ²⁺	7.40 ^{b)}	0.31
Mg ²⁺	3.82 ^{b)}	3.0 ^{c)}	0.65
Ca ²⁺	3.06 ^{b)}	2.5 ^{c)}	0.99

a) This work (estimated standard deviations (2σ) are shown in parentheses for the least significant digit). b) Ref. 7 (25°C, 0.1 M (NaClO₄)). c) Martell, A. E.; Smith, R. M. "Critical Stability Constants", Vol. 3, Plenum, New York, 1977 (25°C, 0.1 M).