Formation of Beryllium Chelates with O-Cresotic Acid: A Potentiometric and Conductometric Study

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With 5 Figures

Summary

The increase in hydrogen ion concentration of monosodium o-cresotate solution by the progressive addition of beryllium sulphate indicated the possibility of the formation of a complex and also the displacement of hydroxyl hydrogen of monosodium o-cresotate. In the mixtures of beryllium sulphate and monosodium o-cresotate mixed in 1:2 or more mole ratios, two colourless complexes are formed, one at about pH 5—25 containing beryllium and o-cresotate in 1:1 ratio and the other above pH 8.5 containing beryllium and o-cresotate in 1:2 ratio.

The specific conductivity curves obtained by the conductometric titrations of 1:1, 1:2 and 1:3, mole ratio mixtures of beryllium sulphate and monosodium o-cresotate by alkali, show definite break when one equivalent of alkali is added indicating the formation of only one 1:1 mole ratio complex of beryllium and o-cresotate.

Sebastian and collaborators[1]) have investigated beryllium complexes with benzoic, tri-carboxylic, citric, salicylic, phthallic and lactic acids. Further researches on beryllium chelates of salicylic acid and its derivatives have been made by Rosenheim and Lehmann[2]) for which they have shown that the anion is so stable that beryllium is not precipitated by ammonia and only slightly by sodium hydroxide. O-cresotic acid also serves as a good chelating agent. Tripathi and Prakash have investigated many chelate complexes of cresotic acid with the metals as Uranyl[3])[4]), Copper[5]), Iron[6]), Aluminium[7]) etc. which are reported to be quite stable.

[1]) Sebastian M. Tanatar and E. K. Kuruvaski, J. Russ. Phys. Chem. Soc. 39, 1630 (1907).

[2]) A. Rosenheim and F. Lehmann, Lieb. Ann. 440, 153 (1924).

[3]) S. C. Tripathi and S. Prakash, Z. physik. Chem. 208, 181 (1958).

[4]) S. C. Tripathi and S. Prakash, J. I. C. S., 35, 118 (1958).

[5]) S. C. Tripathi and S. Prakash, J. I. C. S. 35, 139 (1958).

[6]) S. C. Tripathi and S. Prakash, Z. physik. Chem. 209, 326 (1958).

[7]) S. C. Tripathi and S. Prakash, J. I. C. S. 35, 445 (1958).

MEEK and BANKS[8]) studied beryllium sulphosalicylate complex at pH 10.0 in ultraviolet region at 317 mμ using JOB's method[9]) of continuous variation and have shown that at the optimum pH range (9.0 to 11.0) only one complex is present in which the mole ratio of the acid to beryllium is 2:1.

Sulphosalicylate and mercurisulphosalicylate complexes of beryllium have been studied by SINGH[10]) with the help of physico-chemical methods.

Experimental

Standard solutions of beryllium sulphate were prepared by direct weighing of A.R.B.D.H. sample of $BeSO_4$. $4 H_2O$. Fresh solutions were always employed to avoid effects due to hydrolysis.

The monosodium salt of o-cresotic acid was prepared by the addition of equivalent amount of A.R.E. Merk sample of sodium bicarbonate in L.R.B.D.H. sample of o-cresotic acid. The mother liquor was evaporated to dryness on a waterbath. The crude sample of monosodium salt of o-cresotic acid was crystallised in absolute alcohol. White shining crystals obtained were dired in desiccator. Carbon, hydrogen and oxygen contents were determined by combustion.

Standard solutions of monosodium o-cresotate were prepared by direct weighing of the prepared sample.

Physico-chemical measurements

All the measurements were made at a constant temperature of 32 ± 0.1 °C. pH was measured by Leeds Northrups A. C. operated pH meter using glass and saturated calomel electrodes. The instrument was standardised with a standard buffer solution.

Electrical conductivity was measured by Leeds Northrups KOHLRAUSCH slide wire bridge with an A. C. operated audiofrequency oscillator in the circuit. The null point was detected by the head-phone supplied by the same manufacturers.

Study of the complex forming systems

To study the complex formation of beryllium with monosodium o-cresotates monovariant method was employed. To constant volumes of beryllium sulphate varying amounts of monosodium-o-cresotate were added. Thus a number of sets of mixtures containing beryllium sulphate and monosodium-o-cresotate in the ratios of 1:1, 1:2, 1:3 were prepared. To these mixtures varying amounts of standard solutions of caustic soda were added. The total volume of the mixtures were kept constant in all the cases. The sets were left for about twenty four hours to attain the equilibrium. For comparison beryllium sulphate and monosodium o-cresotate were titrated separately with alkali by potentiometric and conductometric methods, under similar conditions.

   [8]) H. V. MEEK and C. V. BANKS, J. Amer. chem. Soc. **73**, 4108 (1951).

   [9]) P. JOB, Ann. Physik (10) **9**, 113 (1928).

   [10]) R. S. SINGH, D. Phil. Thesis, 1956, Allahabad, India.

Discussion

In the graphs the abscissa represents the number of equivalents of alkali added per gram ion of hydrogen of the ligand while the ordinate represents the measurements of physical properties viz. pH and specific conductivity.

Figure 1 shows the changes in the hydrogen ion concentration of (0.05 M) monosodium o-cresotate solution by the addition of (0.05 M) beryllium sulphate. The pH of monosodium o-cresotate (6.75) falls when beryllium sulphate is added in varying quantities (figure 1, curve A). It is almost constant after pH 3.5 when about one equivalent of beryllium sulphate is added. Curve A' shows the pH of beryllium sulphate only at similar concentrations. The pH of the mixture (A) is lower that the pH of the metallic salt solution (A'). This fall of pH indicates clearly that some complex is formed in the system in which hydroxyl hydrogen is displaced.
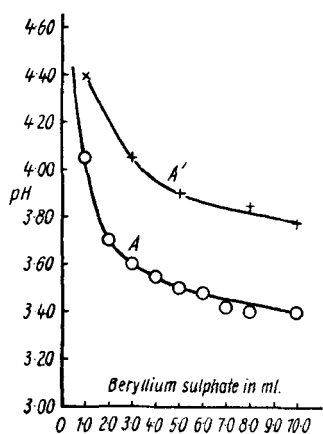

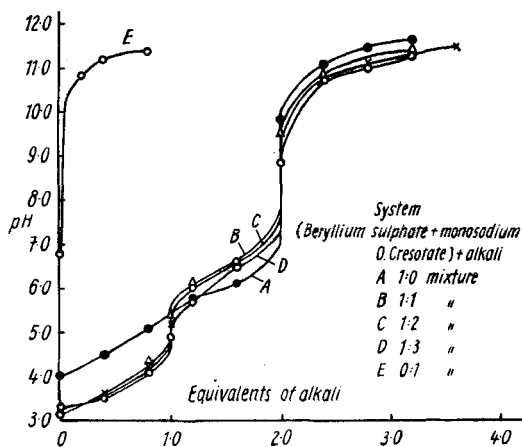Fig. 1   Fig. 2

Figure 2 shows the variation of hydrogen ion concentration with the progressive addition of alkali to the systems (i) (0.05 M) beryllium sulphate (curve A) and mixtures of (0.05 M) beryllium sulphate and (0.05 M) monosodium o-cresotate in the ratios of (ii) 1:1 (curve B) (iii) 1:2 (curve C), and (iv) 1:3 (curve D) while curve E shows the reaction of alkali on monosodium o-cresotate itself.
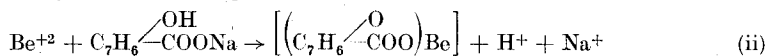
In the curve A (figure 2) the precipitation of beryllium hydroxide starts after the addition of one equivalent of alkali at about pH 5.2 and is complete after the addition of two equivalents of alkali at about

pH 9.5. The reaction may evidently be represented by the stoicheio-metric relation:

$$BeSO_4 + 2NaOH \rightarrow Be(OH)_2 + Na_2SO_4. \qquad (i)$$
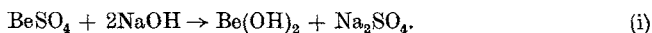
From the curve E (figure 2) it is evident that as the monosodium o-cresotate is a monosodium salt in which hydrogen ion of carboxyl group has been replaced by sodium and no liberation of hydrogen of hydroxyl group takes place by caustic soda. Addition of very little caustic soda shows steep rise in pH showing no free hydrogen ion present in the system.
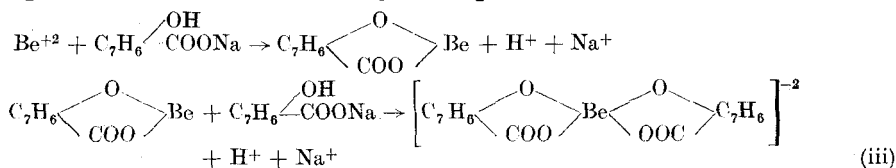
Curve B (figure 2) shows the tiration of hydrogen ion liberated by alkali in 1:1 mixtures of (0.05 M) beryllium sulphate and (0.05 M) mono-sodium o-cresotate. pH is plotted against the equivalents of alkali added in the mixtures. The white precipitate appeared in the 1:1 mixtures, dissolved by the gradual addition of caustic soda and again precipitation of metallic hydroxide starts in the system at about pH 6.5. The precipi-tation is complete after the addition of two equivalents of alkali at about pH 9.55. Out of the two inflections in the curve B (figure 2), the inflection at one equivalent of alkali shows the complex formation in 1:1 mole ratio with respect to beryllium and monosodium o-cresotate, and the other inflection at two equivalents of alkali shows the complete precipitation of beryllum hydroxide from the complex. It may be pre-sumed that during the complex formation hydroxyl hydrogen of mono-sodium o-cresotate is displaced and oxygen of hydroxyl and carboxyl groups of o-cresotate share in the complex formation. The reaction may be explained by the following equation:

$$Be^{+2} + C_7H_6{\overset{OH}{\underset{COONa}{\diagdown}}} \rightarrow \left[\left(C_7H_6{\overset{O}{\underset{COO}{\diagdown}}}\right)Be\right] + H^+ + Na^+ \qquad (ii)$$

The above 1:1 chelate is not stable in alkaline medium. As the acidity in the system decreases the complex starts braking at about pH 6.5 and after that complete precipitation of the complex takes place as metallic hydroxide.

In curves C and D (figure 2) the potentiometric titration values of 1:2 and 1:3 mixtures of (0.05 M) beryllium sulphate and (0.05 M) monosodium o-cresotate are represented graphically. The liberated hydrogen in the systems during the process of complex formation is titrated by alkali. In the 1:2 and 1:3 mixtures the initial pH of 1:1 mixture is lower than the initial pH of 1:1 and 1:3 mixtures. In the systems of both the mixtures there is no appearence of any precipitate of beryllium hydroxide even by the addition of excess of alkali. This clearly indicates that the chelate formed in the systems at higher pH is very stable and is different from that formed in 1:1 mixtures.

In both the curves C and D (figure 2) there are two inflections, one at one equivalent and the other at two equivalents of alkali added in the systems. This indicated the presence of two complexes. The stoicheiometric relation of the two complexes may be in 1:1 and 1:2 mole ratios with respect to beryllium and ó-cresotate. It can be inferred that in acidic medium at about pH 5.25 the complex of 1:1 mole ratio is formed and in alkaline medium at about pH 8.5 formation of another complex containing beryllium and o-cresotate in 1:2 ratio, takes place. The equation for the reaction may be represented in the following ways:

$$Be^{+2} + C_7H_6 \underset{COONa}{\overset{OH}{<}} \rightarrow C_7H_6 \underset{COO}{\overset{O}{<}} Be + H^+ + Na^+$$

$$C_7H_6 \underset{COO}{\overset{O}{<}} Be + C_7H_6 \underset{COONa}{\overset{OH}{-}} \rightarrow \left[C_7H_6 \underset{COO}{\overset{O}{<}} Be \underset{OOC}{\overset{O}{<}} C_7H_6 \right]^{-2}$$

$$+ H^+ + Na^+ \tag{iii}$$

The complex of 1:2 ratio is very stable and due to its strong stability there are no free beryllium ions in the systems to be precipitated as hydroxide.

Figure 3 represents the results of pH measurements with similar experiments as in figure 2 with one lower concentration (0.025 M) of the reactants. The curves A, B, C, D and E of figure 3 are of exactly
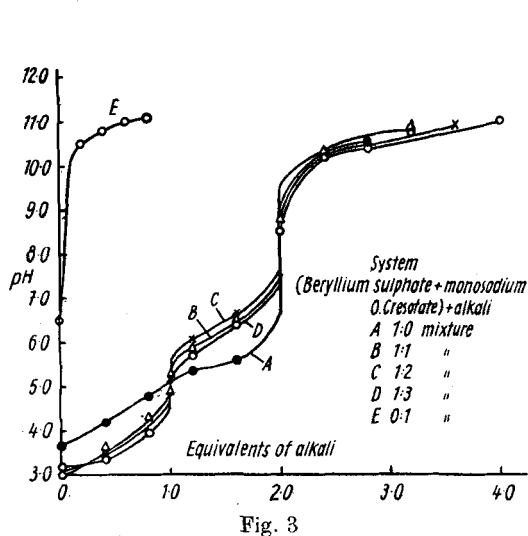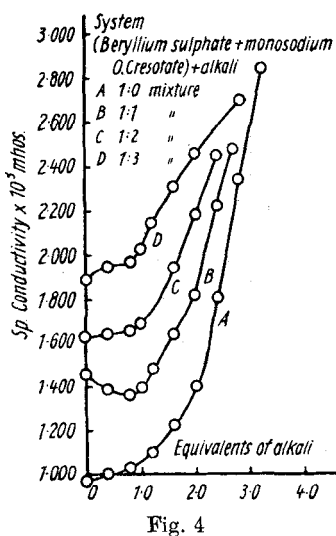

Fig. 3   Fig. 4

similar nature as figure 2 which lay sufficient evidence for the formation of two complexes of beryllium with monosodium o-cresotate containing beryllium and o-cresotate in 1:1 and 1:2 mole ratios in acidic and alkaline mediums respectively.

In figure 4 the results of the specific conductivity study of beryllium o-cresotate complex are represented graphically. Curve A shows the conductometric titration of (0.05 M) beryllium sulphate and caustic soda. The specific conductivity is plotted against the equivalents of alkali added in beryllium sulphate solution. From the examination of the curve it is seen that there is a definite break in the curve, when two equivalents of alkali are added. It shows that two equivalents of alkali are required for complete precipitation of beryllium hydroxide equation (i).

In the conductometric titration of monsodium o-cresotate with alkali there is steady increase in specific conductivity and due to the continuous increase in specific conductivity a straight line is obtained.

Conductometric titration has also been made with (0.05 M) caustic soda and 1:1, 1:2, and 1:3 mixtures of (0.05 M) beryllium sulphate and (0.05 M) monosodium o-cresotate. In the begining, there is slight increase in sp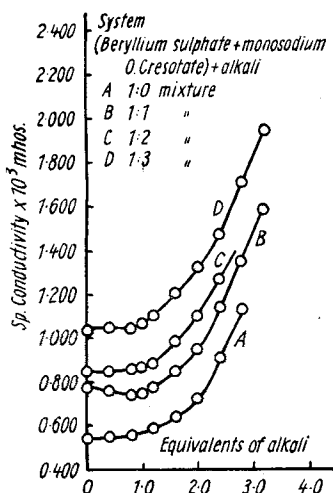ecific condu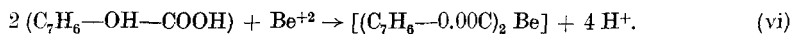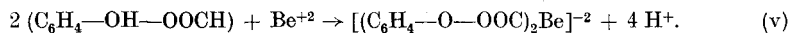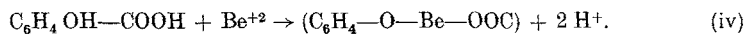ctivity by the addition of alkali, but after the addition of one equivalent of alkali there is sharp rise in specific conductivity showing a definite break at one equivalent of alkali. This shows the formation of a 1:1 mole ratio complex of beryllium and o-cresotate. The reaction can be represented by the equation (ii). From the specific conductivity study no indication for the formation of a complex containing beryllium and o-cresotate in 1:2 ratio is obtained.

Fig. 5

The results of specific conductivity measurements with similar experiments as in figure 4 with a lower concentration (0.025 M) of the reactants, are plotted graphically in figure 5. All the curves A, B, C, D give the same inference as shown by the curves of figures 3. It also shows the formation of only one complex of beryllium and o-cresotate containing the reactants in 1:1 ratio and no indication of 1:2 mole ratio complex is obtained.

JONES and coworkers (loc. cit.) and ASMUSSEN et al (loc. cit.) have shown that beryllium forms two types of complexes with salicylic acid, one containing beryllium and salicylate in 1:1 ratio, and the other, in 1:2 ratio, is formed when two or more moles of salicylate are added to beryllium. The coordination takes place between the oxygen atoms of hydroxyl and carboxyl groups. ROSENHEIM et al (loc. cit.) have also

shown that beryllium forms a 1:2 complex with salicylic acid and its derivatives. Beryllium of the complex is not precipitated by strong ammonia and very slightly by sodium hydroxide solution. Their composition can be represented by the following equations:

$$C_6H_4\,OH\text{---}COOH + Be^{+2} \rightarrow (C_6H_4\text{---}O\text{---}Be\text{---}OOC) + 2\,H^+. \tag{iv}$$

$$2\,(C_6H_4\text{---}OH\text{---}OOCH) + Be^{+2} \rightarrow [(C_6H_4\text{---}O\text{---}OOC)_2Be]^{-2} + 4\,H^+. \tag{v}$$

$$2\,(C_7H_6\text{---}OH\text{---}COOH) + Be^{+2} \rightarrow [(C_7H_6\text{---}O.OC)_2\,Be] + 4\,H^+. \tag{vi}$$

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