Optical Determination of Carboxylate Ions Utilizing Flocculation of Colloidal $Al(OH)_3$

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Synopsis. Flocculation of colloidal $Al(OH)_3$ occurs by adding a suitable amount of Congo Red, and the supernatant liquid become scolorless. When some carboxylate ions are present in this colloidal mixture, the quantity of $Al(OH)_3$ decreases because of the formation of complexes, and then excess Congo Red gives a red color to the supernatant liquid. The indirect determination of some kinds of carboxylate ions was carried out by applying the measurement of optical absorption to the supernatant fraction.

An empirical method of measurement of the degree of fatigue was developed by Takeya and Kawada,[1] as described below. A mixture of alkaline Congo Red solution, aluminium potassium sulfate solution, and a body fluid (a serum or urine) was allowed to stand. After centrifugation of the colloidal liquid, the supernatant fraction was determined spectrophotometrically. According to their report, the supernatant fraction became colorless when water was used in place of body fluid. The reason that the supernatant became deep or light in color was, they reported, that the body fluid worked as a protective colloid toward colloidal $Al(OH)_3$.

We considered that the body fluid did not act as a protective colloid, but that carboxylate ions contained in the body fluid functioned as masking agents of Al^{3+}. That is, in the absence of body fluid, $Al(OH)_3$ is flocculated by a suitable amount of pigment anion and the supernatant fraction becomes colorless. However, in the presence of the body fluid, $Al(OH)_3$ decreases, Al^{3+} is masked by carboxylate ions contained in body fluid, and then excess Congo Red which takes no part in flocculation gives a red color to the supernatant fraction.

On the assumption described above, it became possible to determine indirectly carboxylate ion in solution in the suitable concentration range by the measurement of optical absorption of the supernatant fraction of the colloidal mixture.

Experimental

Reagent and Procedure. Takeya and Kawada's method[1] was modified. Aqueous solutions of carboxylate ions, citrate (0.1—1.2 mg/ml), oxalate (0.2—3.2 mg/ml) and lactate (2—32 mg/ml) were used as test solutions; all of these were used as sodium salts.

An aqueous mixture of 1 ml of test solution (including incremental amounts of carboxylate ions), 2 ml of 1.63 mM of aluminium potassium salfate solution, 2 ml of 0.35 mM of Congo Red solution and 2 ml of 4.5 mM of sodium hydroxide solution was allowed to stand for 2 h at 20 °C. In this mixture the Al^{3+}/OH^- is 1/2.76. After centrifugation, the supernatant fraction was measured spectrophotometrically at 490 nm.

Results and Discussion

As shown in Figs. 1—4, the curves of optical absorbance *vs.* content of carboxylate ions are somewhat similar to pH titration curves. In the lower concentration range of test solution, the curves are flat. In that flat part, Congo Red anion is strongly adsorbed. In the higher concentration range of test solution, the curves also appear flat. In the latter, carboxylate ion acts as a masking agent for a large amount of Al^{3+}, and it becomes hard for flocculation of $Al(OH)_3$ to occur.

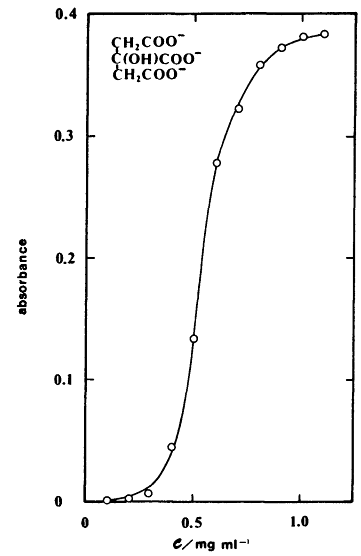

Fig. 1. Absorbance *vs.* content of citrate.

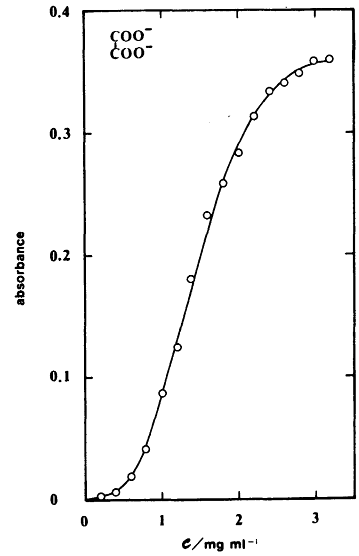

Fig. 2. Absorbance *vs.* content of oxalate.

As shown in Figs. 1—3, the more the number of COO− and of other anionic groups in a carboxylate ion increases, the larger the masking effect towards Al^{3+} becomes; that is, carboxylate ions can act as chelating agents to Al^{3+}. Mono-dentate ligands, such as acetate and hippurate, are not suitable for this experiment,

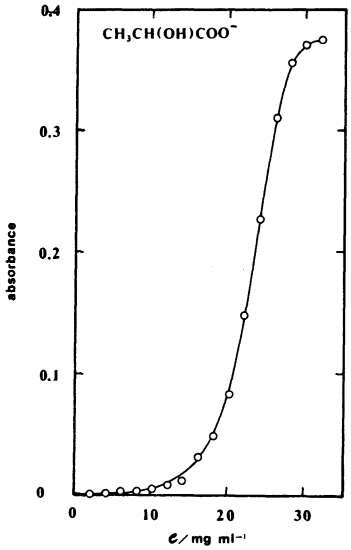

Fig. 3. Absorbance *vs.* content of lactate.

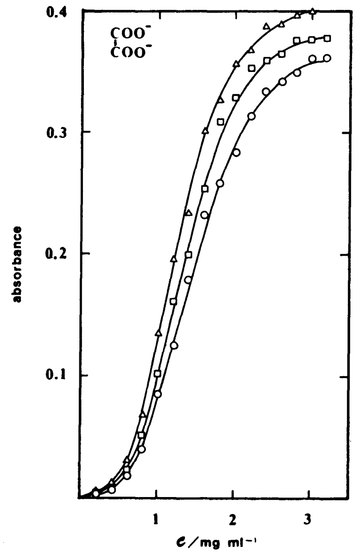

Fig. 4. The effect of temperature on absorbance. —△—: 10 °C, —○—: 20 °C, —□—: 30 °C.

because their masking abilities are very low.

The effect of temperature when oxalate is used as a sample is shown in Fig. 4. The slopes of the curves at lower (10 °C) and higher (30 °C) temperature become greater than that at the appropriate temperature (20 °C); this slope increase is not observed in the range 17—23 °C. At low temperature the formation of colloidal $Al(OH)_3$ is slow, while at high temperature its formation is fast, but the adsorption of pigment anion on the colloidal $Al(OH)_3$ occurs with difficulty. These tendencies are also observed for other carboxylate ions.

References

1) O. Takeya and T. Kawada, *Igaku To Seibutsugaku*, **4**, 230, 234, 244, (1943). Subsequently, more than 100 reports appeared which applied their method, *e.g.*, N. Matsumoto *Bull. Inst. Constit. Med., Kumamoto University*, **26**, 154 (1975); **29**, 429 (1979).