

Effect of Addition of Sodium Salts to Salicylic Acid-Cetrimide System

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Abstract □ The viscosity of salicylic acid-cetrimide systems was altered in the presence of sodium salts. The viscosity variation was associated with the degree of salicylic acid saturation of the surfactant solution and apparently not with the pH of the system. The increase in viscosity was probably due to formation of sodium salicylate by a reaction of the sodium additive with the acid and the interaction of this salicylate with the free cetrimide molecules in the system. The decrease in viscosity was attributed to the non-availability of these surfactant molecules.

Keyphrases □ Salicylic acid-cetrimide systems—effect of sodium salts on viscosity □ Cetrimide-salicylic acid systems—effect of sodium salts on viscosity □ Sodium salts—effect on viscosity of salicylic acid-cetrimide systems □ Viscosity, salicylic acid-cetrimide systems—effect of sodium salts

In past studies, additives of various types such as polar and nonpolar solvents (1) and surfactants that are anionic (2), cationic, and nonionic (3) were added to salicylic acid-cetrimide systems similar to those in the present investigation and the resulting change in viscosity was measured. This change was found to differ with the type of additive. As a continuation of these studies of viscosity response to additives, the effect of aqueous solutions of electrolytes that are mainly alkaline in reaction on the macromolecules formed by the interaction of salicylic acid with cetrimide (4) was investigated. Sodium salts of carboxylic and phosphoric acids as well as sodium carbonate were used.

EXPERIMENTAL

Materials—Cetrimide BP¹ and recrystallized salicylic acid, m.p. 158–159°, were the same as those described previously (1). The following were used: sodium citrate²; sodium tartrate³; sodium acetate³; sodium pyrophosphate⁴; sodium phosphate, dibasic⁴;

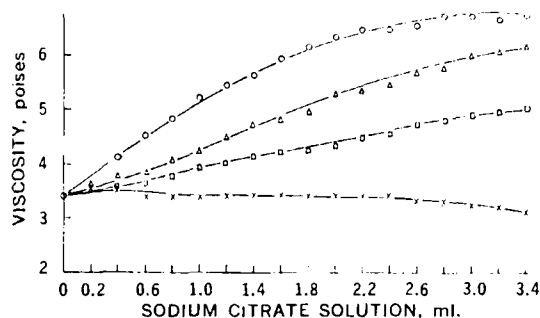


Figure 1—Effect of sodium citrate solutions of varying concentration on the viscosity of systems containing 1.4% salicylic acid and 5% cetrimide (50 g.) at 25°. Key (sodium citrate, % w/v): ○, 10; △, 6; □, 4; and ×, 1. Shear rate = 78.56 sec.⁻¹.

¹ Glovers Chemicals Ltd., Leeds 12, England.
² May and Baker, Dagenham, England.
³ British Drug Houses, Ltd., England.
⁴ E. Merck, Darmstadt, Germany.

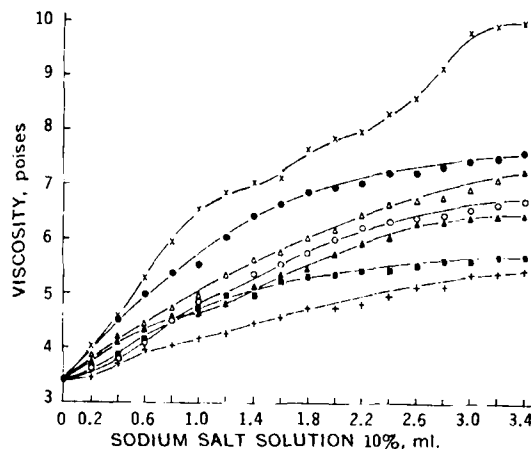


Figure 2 Viscosity increase due to addition of sodium salt solutions (10% w/v) to systems containing 1.4% salicylic acid and 5% cetrimide (50 g.) at 25°. Key: △, sodium phosphate, dibasic; +, sodium phosphate, monobasic; ×, sodium carbonate; ○, sodium tartrate; ▲, sodium acetate; ●, sodium phosphate, tribasic; and ■, sodium pyrophosphate. Shear rate = 78.56 sec.⁻¹.

sodium phosphate, tribasic⁴; sodium phosphate, monobasic⁴; and sodium carbonate⁴.

Measurement of Viscosity at 25°—The method described earlier (1) was adopted⁵.

Measurement of pH—This was determined using a pH meter⁶.

RESULTS AND DISCUSSION

Figure 1 shows the change in viscosity of salicylic acid-cetrimide systems with the addition of sodium citrate solutions of different concentrations. The viscosity increased in the presence of the sodium additive, the increase being higher with a greater volume of the salt solution. However, with a low concentration, a slight decrease in viscosity was noted. A similar rise in viscosity was found with

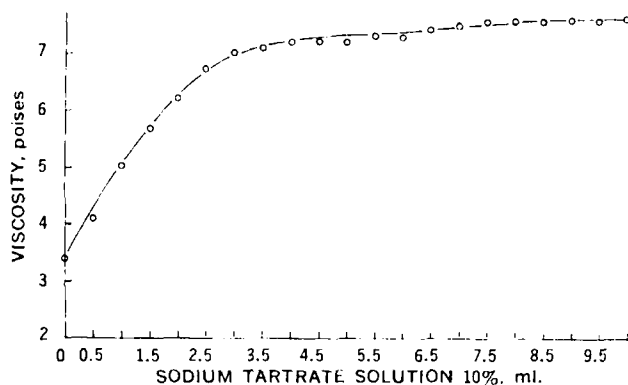


Figure 3—Effect of increasing the volume of sodium tartrate solution on the viscosity of systems containing 1.4% salicylic acid and 5% cetrimide (50 g.) at 25°. Shear rate = 78.56 sec.⁻¹.

⁵ A portable Ferranti viscometer, model VL, was used in this study.
⁶ Beckman pH expandometer.

Table I—pH of System Containing 5% Cetrimide and 1.4% Salicylic Acid (50 g.) to Which Sodium Salt Solutions Were Added

| Salt Solution, 10% w/v | Volume of Sodium Salt Solution, ml. | | | | | | | | | |
|-----------------------------|-------------------------------------|------|------|------|------|------|------|------|------|------|
| | 0 | 0.4 | 0.8 | 1.2 | 1.6 | 2.0 | 2.4 | 2.8 | 3.2 | 3.4 |
| Sodium citrate | 2.45 | 2.45 | 2.5 | 2.55 | 2.55 | 2.65 | 2.85 | 2.95 | 3.1 | 3.2 |
| Sodium tartrate | | 2.45 | 2.45 | 2.5 | 2.55 | 2.6 | 2.7 | 2.85 | 3.05 | 3.1 |
| Sodium acetate | | 2.45 | 2.5 | 2.5 | 2.6 | 2.6 | 2.65 | 2.85 | 3.05 | 3.1 |
| Sodium phosphate, dibasic | | 2.45 | 2.45 | 2.45 | 2.55 | 2.65 | 2.7 | 2.7 | 2.75 | 2.75 |
| Sodium phosphate, monobasic | | 2.45 | 2.45 | 2.5 | 2.5 | 2.5 | 2.55 | 2.55 | 2.6 | 2.6 |
| Sodium phosphate, tribasic | | 2.5 | 2.55 | 2.65 | 2.7 | 2.85 | 2.9 | 3.05 | 3.1 | 3.15 |
| Sodium pyrophosphate | | 2.45 | 2.5 | 2.55 | 2.6 | 2.65 | 2.7 | 2.7 | 2.75 | 2.8 |

Table II—Variation of pH of Salicylic Acid-Cetrimide System (50 g.) Containing 5% Cetrimide and Varying Concentration of Acid by Addition of Sodium Carbonate Solution, 10% w/v

| 5% Cetrimide with: | Volume of Sodium Carbonate, 10% w/v, ml. | | | | | | | | | | | | | |
|---------------------|--|------|------|------|------|------|------|------|-----|------|------|------|------|------|
| | 0.4 | 0.8 | 1.2 | 1.6 | 2.0 | 2.2 | 2.4 | 2.6 | 2.8 | 3.0 | 3.2 | 3.4 | 3.6 | 3.8 |
| 1.2% Salicylic acid | 2.45 | 2.6 | 2.75 | 3.1 | 3.55 | 3.6 | 3.65 | 4.1 | 4.5 | 5.1 | 5.85 | 6.65 | 7.4 | 8.1 |
| 1.4% Salicylic acid | 2.45 | 2.6 | 2.75 | 3.0 | 3.25 | 3.35 | 3.45 | 3.65 | 3.9 | 4.35 | 4.75 | 5.45 | 6.15 | 6.95 |
| 1.6% Salicylic acid | 2.5 | 2.6 | 2.75 | 2.95 | 3.2 | 3.3 | 3.4 | 3.65 | 3.9 | 4.35 | 4.4 | 4.6 | 5.1 | 5.6 |
| 1.7% Salicylic acid | 2.45 | 2.55 | 2.7 | 2.9 | 3.1 | 3.2 | 3.25 | 3.35 | 3.6 | 3.85 | 4.05 | 4.35 | 4.8 | 5.35 |
| 1.8% Salicylic acid | 2.45 | 2.55 | 2.65 | 2.8 | 2.95 | 3.05 | 3.25 | 3.4 | 3.5 | 3.65 | 3.9 | 4.15 | 4.6 | 5.1 |

sodium acetate, sodium tartrate, sodium carbonate, and various sodium phosphates (Fig. 2). Increasing the total volume of sodium tartrate solution incorporated beyond the amount shown in Fig. 2 did not result in any further change, and the viscosity remained constant (Fig. 3). This situation also applied to the other sodium salts mentioned previously.

Sodium carbonate demonstrated the most marked viscosity effect (Fig. 2). This effect was found to be dependent on the amounts of salicylic acid and cetrimide present in the system, *i.e.*, the degree of saturation of the system. In related dispersions without additives, it was shown that, on the whole, maximum viscosity was attained at or near saturation (4). The viscosity behavior of systems consisting of the surfactant and such quantities of salicylic acid so as to produce undersaturated and oversaturated dispersions, when sodium carbonate solutions were added, was different in each type of system (Fig. 4). Where the salicylic acid concentration was less than that required for saturation, the viscosity alteration resembled that described previously. However, when the acid content exceeded what was necessary for saturation, there was a decrease or a small increase initially; subsequently, a reduction occurred, followed by a marked increase in viscosity. With sodium phosphate, dibasic, and sodium citrate solutions (Fig. 5), there was only a viscosity decrease in such systems and a rise in viscosity in those that were not saturated. The other sodium salts used also exhibited the same effect. The difference in behavior could be attributed to the fact that sodium carbonate is a strong alkali. This was supported by a similar viscosity variation observed when the sodium hydroxide solution was incorporated into identical systems.

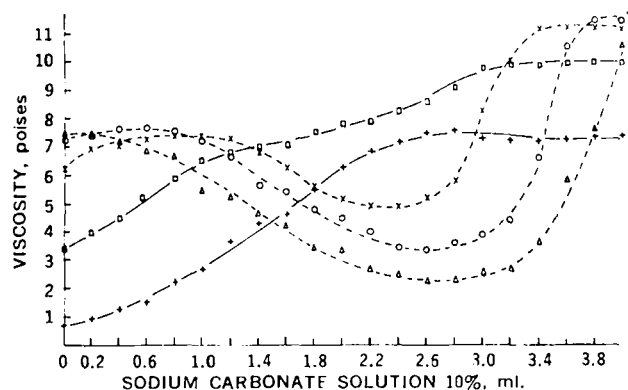


Figure 4—Relationship between viscosity change and saturation of salicylic acid-cetrimide system (50 g.) in the presence of sodium carbonate solution (10% w/v) at 25°. Key (salicylic acid, % w/v): +, 1.2; □, 1.4; ×, 1.6; ○, 1.7; △, 1.8; —, —, undersaturated; and - - -, oversaturated. Cetrimide = 5% w/v. Shear rate = 78.56 sec.⁻¹.

In the presence of sodium salts, the pH values obtained differed from one additive to another and with varying volumes of the same salt solution (Table I). Compared to the effect of sodium carbonate in the corresponding system (Table II), the pH variation (2.45 to 6.95) of the latter was very marked. The pH of the systems in Table I is strongly acidic, although the additive solutions are alkaline in reaction (Table III), with the exception of sodium phosphate, monobasic. In those systems containing different amounts of salicylic acid, the increase was greater with undersaturated than with oversaturated systems (Table II). This is due to the lower concentration of salicylic acid in the former case. A comparison of the change in viscosity (Fig. 4) with those of pH (Table II) showed that pH increased with the sodium carbonate solution added, irrespective of whether there was an increase or a decrease in viscosity. This suggested that the alteration in viscosity was not associated directly with the pH of the system concerned.

A previous report (4) showed that salicylic acid interacts with cetrimide, resulting in the formation of a viscous product. In the current study, unsaturated systems contained insufficient salicylic acid to interact with all of the surfactant molecules, leaving free

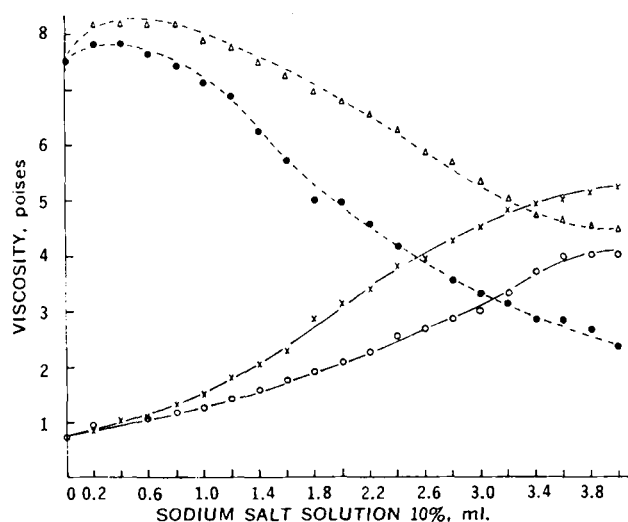


Figure 5—Change in viscosity of salicylic acid-cetrimide systems (50 g.) that are oversaturated (salicylic acid 1.8% and cetrimide 5%) and undersaturated (salicylic acid 1.2% and cetrimide 5%) on addition of sodium citrate and sodium phosphate, dibasic, solutions (10% w/v) at 25°. Key: - - -, oversaturated; ●, sodium citrate; △, sodium phosphate, dibasic; —, —, undersaturated; ×, sodium citrate; and ○, sodium phosphate, dibasic. Shear rate = 78.56 sec.⁻¹.

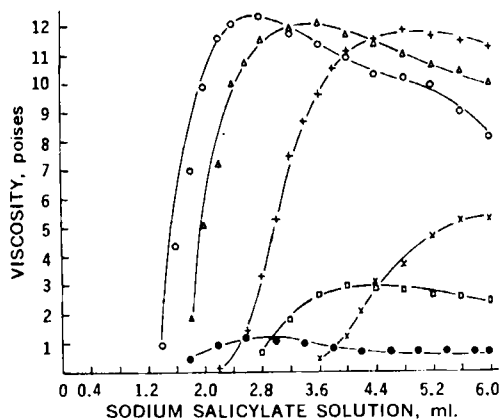


Figure 6—Viscosity variation of a fixed concentration of cetrimide (5% w/v) with varying sodium salicylate solutions and a fixed concentration of sodium salicylate solution (10% w/v) with varying amounts of cetrimide at 25°. Key (sodium salicylate, % w/v): ○, 40; △, 30; and +, 20. Key (cetrimide, % w/v): ●, 1.0; □, 2.0; and ×, 3.0. Shear rate = 78.56 sec.⁻¹.

cetrimide molecules for possible reaction with the added sodium salt. However, it was found that the addition of sodium salts to cetrimide in the absence of salicylic acid produced no effect on the viscosity of the solution. Therefore, it is not likely that the observed increase in viscosity is brought about by a simple reaction involving only surfactant molecules and the sodium salt.

The increase in viscosity may be due to a reaction between the sodium additive and the salicylic acid, with the tendency to form sodium salicylate. This sodium salicylate will interact with the free cetrimide molecules in unsaturated systems to give rise to the high viscosity values determined, in the same manner as was found when sodium salicylate solutions were allowed to interact with the surfactant solution without the acid (Fig. 6). Variation of the sodium salicylate or cetrimide concentration in the interaction between these two compounds resulted in a viscosity increase followed by a decrease as the volume of sodium salicylate solution became larger. When the cetrimide concentration was increased to 5% to correspond with that used in the systems studied so far, no increase in viscosity was recorded even after 4 ml. of sodium salicylate solution was incorporated. This is because, with a greater amount of surfactant, more sodium salicylate is required to effect a change in viscosity, as can be seen in the viscosity behavior of the 5% cetrimide solution when different quantities of sodium salicylate were added (Fig. 6).

The viscosity reduction occurring in oversaturated dispersions could be caused by a change in the salicylic acid concentration due to a removal of the excess acid brought about by a reaction of the latter with the sodium additive. But since most surfactant in the system would have interacted with the acid, no increase in viscosity

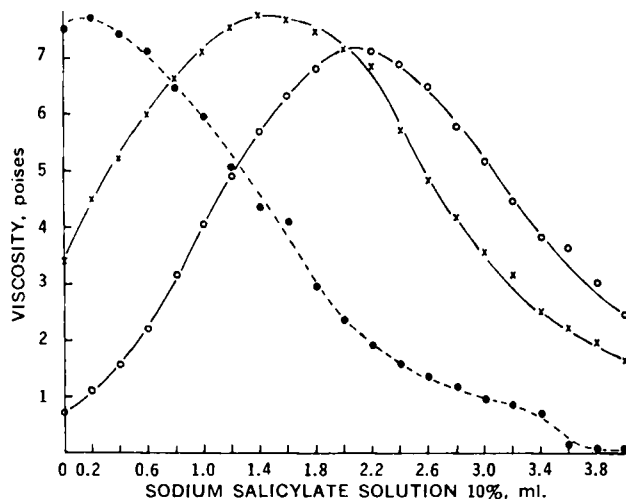


Figure 7—Viscosity behavior of systems (50 g.) containing 5% cetrimide and different quantities of salicylic acid in the presence of sodium salicylate at 25°. Key (salicylic acid, % w/v): ●, 1.8; ×, 1.4; ○, 1.2; —, undersaturated; and - - -, oversaturated. Shear rate = 78.56 sec.⁻¹.

resulted. Further evidence in support of these suggestions can be obtained from the results shown in Fig. 7. In undersaturated systems, the viscosity increased in a similar manner to that due to the addition of sodium salts (Figs. 1 and 2). However, after reaching a maximum, the viscosity decreased. This reduction could be attributed to a loss of free cetrimide molecules from the system because of the interaction with sodium salicylate. In oversaturated dispersions, only a lowering in viscosity was produced, as was stated earlier in relation to sodium citrate and sodium phosphate, dibasic (Fig. 5), since surfactant molecules were not available for the interaction with sodium salicylate.

In the case where the sodium additive is a strong alkali, such as sodium carbonate, the pattern of viscosity response varied with the volume of sodium carbonate solution added (Fig. 4). When adequate solution of the alkali was included, the amount of salicylic acid remaining would no longer be in excess of that essential for saturating the cetrimide solution and hence the system was not likely to be oversaturated anymore. Subsequent additions of sodium carbonate solution, therefore, increased the viscosity in accordance with that which occurred in the undersaturated systems. With the other sodium salts used, even when the total volume of the additive solution was increased to 8 ml., no subsequent increase in viscosity was produced after a prior decrease in viscosity.

The findings of this study suggest that viscosity variation of salicylic acid-cetrimide systems in the presence of some sodium salts depends on the availability of free cetrimide molecules and the interaction of the resultant sodium salicylate with these surfactant molecules. It did not seem to be governed by pH.

Table III—pH of Solutions of Sodium Salts

| Salt Solution | pH |
|----------------------------------|-------|
| Sodium citrate 1% | 8.55 |
| Sodium citrate 4% | 8.6 |
| Sodium citrate 6% | 8.65 |
| Sodium citrate 10% | 8.75 |
| Sodium tartrate 10% | 8.0 |
| Sodium acetate 10% | 8.6 |
| Sodium pyrophosphate 10% | 10.5 |
| Sodium phosphate, tribasic, 10% | 11.95 |
| Sodium phosphate, dibasic, 10% | 9.45 |
| Sodium phosphate, monobasic, 10% | 4.9 |
| Sodium carbonate 10% | 10.75 |

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ACKNOWLEDGMENTS AND ADDRESSES

Received February 7, 1973, from the *School of Pharmacy, University of Singapore, Sepoy Lines, Singapore 3*.
Accepted for publication June 15, 1973.