the other hand, titration could be carried out at about 0.001*M* concentration as converted to the concentration of nonionics similary to the case of nonionics alone.

3) Other effects on the titration

The volume of barium chloride solution was fixed by the results of the determination of nonionics alone. Any other dyes useful for this titration could not be found.

The authers wish to express their thanks to Mr. S. Okuda and Sanyo Yushi CO. Ltd., for the gift of nonionics.

Summary

A volumetric determination of cationics and nonionics in mixtures was established with sodium tetraphenylborate as a titrant using Methyl Orange and Congo Red as indicators. For the determination of cationics, this method could be applied to a mixture of one mole of cationics and two moles of nonionics with an error of ±1%. For the determination of nonionics, this method could be applied to a mixture of one mole of nonionics and forty moles of cationics with an error of ±5%.

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35. Hiroshi Fujiwara, Takatsuka Yashiki, and Tokunosuke Kanzawa : Rheology of the Pharmaceutical Suspension. III. Effects of Some Additives on Viscous Behavior of Barium Sulfate-Water System.

(*Research Laboratories, Takeda Chemical Industries, Ltd.*[*1])

In the previous paper,[1] flow properties of barium sulfate suspensions in various concentrations were studied with rotational viscosimeter and it was clarified that the flow properties of the suspensions are classified into several types according to the concentration of barium sulfate, that is, Bingham flow, negative shear-rate thixotropy, and pseudoplastic flow.

In this paper, the effects of adding some high polymers such as sodium carboxymethylcellulose (Na-CMC), methylcellulose (MC), and polyvinylpyrrolidone (PVP) to the suspension in order to disperse the particles finely and to prevent the sedimentation were studied.

Experimental

1) Sample

$BaSO_4$: The same product as described in the previous paper.
Na-CMC : High type of Na-CMC (Hercules Co.).
MC : Marpolose M600 (Matsumoto Fat Co.).
PVP : NPK-30 (Wako Pure Chemicals Co.).

[*1] Juso-Nishino-cho, Higashiyodagawa-ku, Osaka (藤原 洋, 矢敷孝司, 神沢得之助).

1) H. Fujiwara, T. Yashiki, T. Kanzawa : Takeda Kenkyusho Nempo, **20**, 65 (1961).

2) Measurement of rheogram

A viscosimeter of Quette type "Universal Rheometer UH-1" (Shimadzu Co.) was used and shearing stress was measured as a function of the rate of shear (rheogram).

3) Measurement of the sedimentation volume

Fifty milliliters of 33% $BaSO_4$ suspension was poured into a 50 ml. graduated cylinder with a glass stopper, which was shaken vigorously for 2 min. The cylinder was kept in an isothermal bath at 30±0.1°. After equilibration, which was attained within 120 hr., the sedimentation volume was measured. Dividing the volume by the weight of $BaSO_4$ particles, specific sedimentation volume (ml./g.) was obtained.

4) Measurement of viscosity of a Na-CMC solution

Brookfield viscosimeter BL (Tokyo Keiki) was employed to measure the low viscosity of the Na-CMC solution.

Result and Discussion

The viscosity of the aqueous solution of Na-CMC varied with the time when it was sheared continuously, and this phenomenon was ascribed to the change of the aggregates of Na-CMC molecules by shearing force.[2] Therefore, in order to obtain a Na-CMC solution of constant viscosity, the solution was sheared with a high speed mixer until the solution showed equilibrium viscosity. As shown in Fig. 1, the viscosity of 0.3% Na-CMC solution decreases with a lapse of time, when the solution was sheared in the mixer. The viscosity decreases for 1.5 hours and then becomes constant.

To the Na-CMC solutions in various concentrations thus treated, barium sulfate was added and 50% suspension was prepared. The flow properties of the suspensions were measured (Fig. 2).

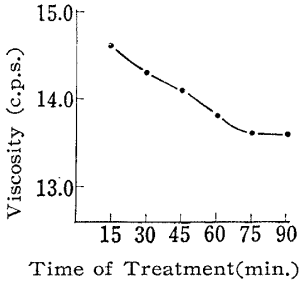

Fig. 1. Relationship between Shearing Time and Viscosity of 0.3% Sodium carboxymethylcellulose when Shearing is applied by Juice Mixer

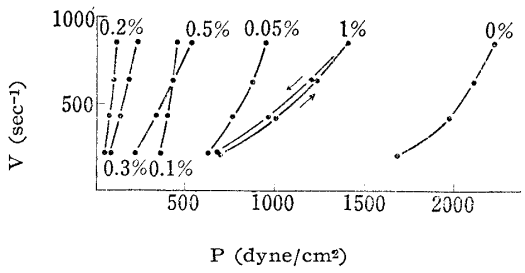

Fig. 2. Rheogram of 50% Barium Sulfate Suspension containing Na-CMC of Various Concentrations

As described in the previous paper, 50% aqueous suspension of barium sulfate showed Bingham flow. However, by the addition of Na-CMC the flow properties of the suspension were changed. The apparent viscosity of the suspension at maximum rate of shear (860 sec^{-1}) decreased progressively as the concentration of Na-CMC increased. At the concentration of 0.2% Na-CMC, the apparent viscosity became minimum and over 0.2% Na-CMC, it increased again.

As to yield values, an addition of Na-CMC also made it decrease in proportion to the concentration of Na-CMC added. The suspension showed Newtonian flow at 0.2% Na-CMC, pseudoplastic flow at higher concentration of Na-CMC and thixotropy at 1.0% Na-CMC. When MC or PVP was added to 50% barium sulfate suspension, on the other hand, such a marked effect by Na-CMC was not observed and these suspensions showed still Bingham flow (Figs. 3 and 4). Though a slight decrease of viscosity was recognized by the addition of 0.1% MC (Fig. 3), it is not so significant as it was found

2) E.H. de Butts, J.A. Hudy, H. Elliot : Ind. Eng. Chem., **49**, 94 (1957).

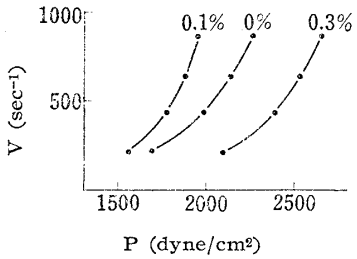

Fig. 3. Rheogram of 50% Barium Sulfate Suspension containing Methylcellulose in Various Concentrations

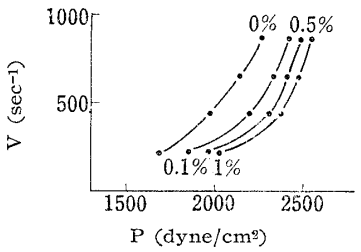

Fig. 4. Rheogram of 50% Barium Sulfate Suspension containing Polyvinylpyrrolidone in Various Concentrations

with Na-CMC and in the case of PVP a gradual increase of the apparent viscosity was observed with an increase of the concentration (Fig. 4).

It is clear from these observations that only an addition of a small amount of Na-CMC decreases both apparent viscosity and yield value of the barium sulfate suspension.

It is well known that more flocculated particles in a suspension settle to a larger volume than less flocculated ones and that a smaller volume is observed in the state of deflocculation.[3] Fig. 5 shows the relationship between specific sedimentation volume and the concentrations of high polymers.

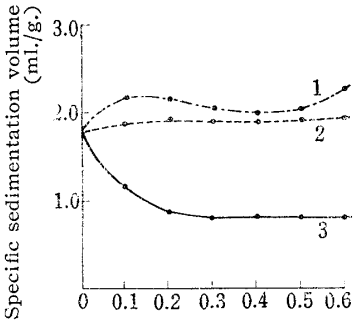

Fig. 5. Relationship between Specific Sedimentation Volume and the Concentration of Dispersing Agent

1. Methyl Cellulose.
2. Polyvinylpyrrolidone.
3. Sodium-Carboxymethylcellulose.

Though high specific sedimentation volume is observed without any higher polymer, the volume decreases markedly as the concentration of Na-CMC increases, and in a presence of more than 0.2% Na-CMC, the specific sedimentation volume becomes constant. The constant sedimentation volume is only 37% of the one measured without Na-CMC. At the concentration of 0.2% Na-CMC, and over, a constant sedimentation volume is observed, and so it is consistent well with the concentration at which Newtonian flow and the minimum viscosity is observable. By the addition of MC or PVP, however, only slight difference of the sedimentation volume is observed.

From these observations, the following explanation can be made. Flocculated barium sulfate particles in the suspension are covered with Na-CMC and the particles are made more hydrophilic or finely dispersed. When 0.2% Na-CMC is added to the barium sulfate suspension, entire surface of the particles is covered with Na-CMC, thus yield value disappears, and the minimum viscosity is observed. Further addition of Na-CMC increases only the concentration in equilibrium solution and the flow properties of such suspensions become similar to the properties of concentrated Na-CMC solution gradually. Thixotropy which is observable at the addition of 1.0% Na-CMC to the suspension is due to the property of 1.0% Na-CMC solution.

3) C.R. Bloomquist, R.S. Shutt : Ind. Eng. Chem., 32, 827 (1946).

The cause of the covering of Na-CMC over barium sulfate-particles, carboxyl groups of Na-CMC may take part in the adsorption process, because the addition of MC or PVP has not significant effects on the viscosity and the specific sedimentation volume.

Summary

To investigate the effects of some high polymers on dispersion of barium sulfate particles, rheograms and sedimentation volumes of the suspensions containing sodium carboxymethylcellulose (Na-CMC), methylcellulose (MC) and polyvinylpyrrolidone (PVP) were measured. By the addition of Na-CMC to the suspension, a marked decrease of yield value and apparent viscosity were observed, though MC and PVP increase the apparent viscosity of the suspension. By the addition of 0.2% Na-CMC, the minimum viscosity in Newtonian flow was observed and further addition of Na-CMC increased the apparent viscosity again in pseudoplastic flow. The concentration (0.2% Na-CMC) was consistent well with the one at which the lowest sedimentation volume was attained. MC or PVP did not change the sedimentation volume of the suspension significantly. As the cause of good dispersion of the suspension in the case of Na-CMC, its adsorption on barium sulfate particles was assumed.

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36. Hiroshi Fujiwara, Takatsuka Yashiki, and Tokunosuke Kanzawa : Rheology of the Pharmaceutical Suspension. IV. Adsorption of Sodium Carboxymethylcellulose on Barium Sulfate Particles in Aqueous Suspension.

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In the previous paper,[1] it was observed that the viscosity of barium sulfate suspension decreased by an addition of sodium carboxymethylcellulose (Na-CMC). This phenomenon might be caused by the adsorption of Na-CMC on barium sulfate particles in the suspension. This assumption was ascertained in this paper by determining the amount of adsorbed Na-CMC by the colorimetric method and from the adsorption isotherms obtained it became clear that the adsorption is of Langmuir type.

Experimental

1) Sample
$BaSO_4$: The same product as described previously. Na-CMC : Low, medium and high type Na-CMC (Hercules Co.). This classification is made according to the degree of polimerization of Na-CMC.
2) Determination of the amount of Na-CMC adsorbed.
Several methods were developed by Corner,[2] Houghton,[3] Nile[4] and Szalkowski[5] for

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*1 Juso, Higashiyodogawa-ku, Osaka (藤原 洋, 矢敷孝司, 神沢得之助).
1) H. Fujiwara, T. Yashiki, T. Kanzawa : This Bulletin, **11**, 198 (1963).
2) A. Z. Conner, R. W. Eyler : Anal. Chem., **22**, 1129 (1950).
3) B. Houghton : J. Soc. Chem. Ind. (London), **60**, 254 (1941).
4) Nile : Anal. Chem., **21**, 950 (1949); **23**, 1792 (1951).
5) C. R. Szalkowski, W. G. Marder : J. Am. Pharm. Assoc., **44**, 533 (1955).