International Journal of Pharmaceutics, 9 (1981) 315–319
Elsevier/North-Holland Biomedical Press

Effect of surfactants on the flocculation of magnesium carbonate suspensions by xanthan gum

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(Received February 23rd, 1981
(Revised version July 21st, 1981)
(Accepted July 23rd, 1981)

Summary

Magnesium carbonate suspensions were deflocculated by the anionic surfactant, docusate sodium. Sedimentation volume of the flocculated systems and the docusate sodium concentration needed for deflocculation were related to the particle size and specific area of the two types of magnesium carbonate. The concentration of xanthan gum required to induce flocculation was related to the surfactant concentration because of competitive adsorption at the particle–medium interface. A non-ionic surfactant, polysorbate 40, had no effect on flocculation state of the suspensions.

Introduction

Aqueous magnesium carbonate dispersions, though flocculated in the absence of any additive, became more highly flocculated in the presence of xanthan gum (Tempio and Zatz, 1980). Based on adsorption and zeta potential measurements, flocculation was ascribed to a mechanism in which polymer molecules acted as links between particles (Tempio and Zatz, 1981). This mechanism requires simultaneous adsorption of a single polymer molecule to two or more particles. Other molecules with attraction for the magnesium carbonate surface might be expected to modify the adsorption of xanthan gum and, consequently, alter its effect on suspension flocculation. Two surfactants, an anionic and a non-ionic agent, were employed in this study to evaluate their influence on suspension properties.

Experimental

The solids used in this study, light magnesium carbonate[1] and heavy magnesium carbonate[2], were used as received. Surfactants included an anionic material, docusate sodium[3], and a non-ionic agent, polysorbate 40[4]. Xanthan gum[5] was food grade. Suspensions were prepared with distilled water, and contained 0.1% methylparaben and 0.02% propylparaben as preservatives.

Suspensions were prepared by dispersing the solid in a concentrated solution of the surfactant (or in water if no surfactant was present) with a double-bladed mixer[6]. The xanthan gum, if present, was added as a 1% water solution and mixing was continued for 3–5 min. The suspension was transferred to a graduated cylinder, made up to volume with distilled water, and then transferred back to the beaker for a final period of mixing. Sedimentation volume was measured as described earlier (Tempio and Zatz, 1980).

Particle size distributions of the two types of magnesium carbonate dispersed in water were measured with an automated device that utilizes an optical sensor[7]. Each particle in a dilute suspension that flows through a narrow tube momentarily interrupts a continuous collimated light beam. Instrument response is proportional to the projected area of each particle. A built-in microprocessor calculates the distribution. In most cases, 10,000 particles were sized as the basis for the calculated distribution.

Results and Discussion

Particle size distributions for heavy and light magnesium carbonate are shown in Fig. 1. The heavy material contains a higher percentage of larger particles (median diameter = 4.3 μm) than does light magnesium carbonate, with a median diameter of 3.3 μm. A third curve in Fig. 1 shows the distribution for a suspension of heavy magnesium carbonate containing xanthan gum. As with previously reported results for suspensions in a 0.9% sodium chloride medium (Tempio and Zatz, 1980), the distribution was shifted to the right, indicating an increase in particle size. The median particle diameter rose to 5.4 μm in the presence of xanthan gum.

The effect of docusate sodium concentration on suspension volume of 5% magnesium carbonate suspensions is shown in Fig. 2. The sedimentation volume of the heavy magnesium carbonate suspension remained essentially constant until the docusate sodium concentration exceeded 0.15%. Sedimentation volume dropped and

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[1] Fisher Scientific, Fairlawn, N.J.

[2] Amend Drug and Chemical, Irvington, N.J.

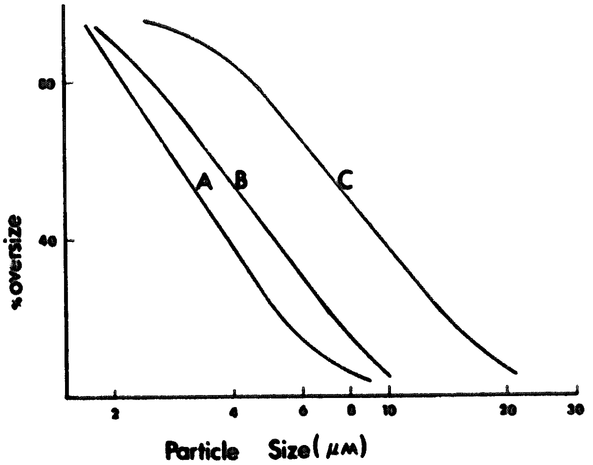
[3] Aerosal OT, American Cyanamid, Pearl River, N.Y.

[4] Tween 40, ICI Americas, Wilmington, DE.

[5] Keltrol, Kelco Co., San Diego, CA.

[6] Counter-rotating mixer, Brookfield Engineering, Stoughton, MA.

[7] HIAC PA-720, HIAC Instruments, Montclair, CA.



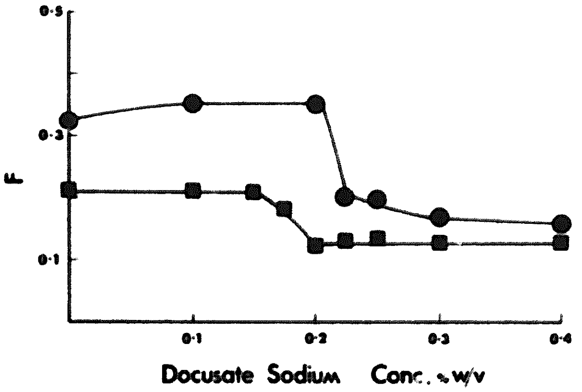


Fig. 1. Particle size distribution of magnesium carbonate suspended in water. A: light magnesium carbonate. B: heavy magnesium carbonate. C: heavy magnesium carbonate containing 1 part xanthan gum/50 parts solid.

Fig. 2. Effect of docusate sodium on sedimentation volume of 5% magnesium carbonate suspensions. ●, light magnesium carbonate; ■, heavy magnesium carbonate.

reached a value that was essentially constant at docusate sodium concentrations of 0.2% and above. The suspension, which was flocculated in the absence of the surfactant (Tempio and Zatz, 1980) became deflocculated when the concentration of docusate sodium exceeded a critical value. The deflocculated suspensions were caked and could not be resuspended with prolonged vigorous shaking while the flocculated suspensions were easily resuspendible.

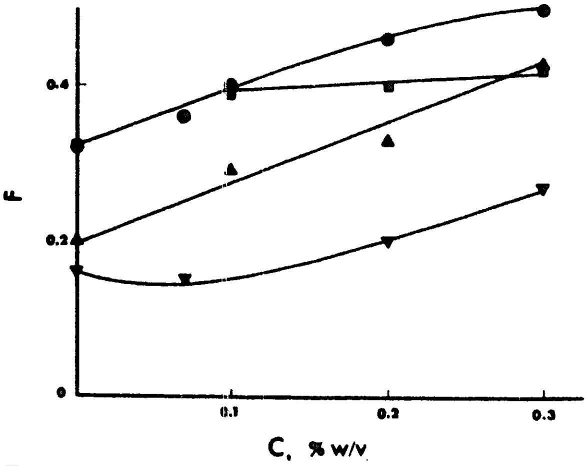
The change in suspension properties can be explained as a consequence of the alteration of the character of the particle surface. Adsorption of the surfactant caused the particles to acquire a negative charge which was sufficient to induce the primary particles making up the flocs to separate. Presumably, a concentration of about 0.2% docusate sodium was necessary for adsorption of sufficient surfactant molecules to generate the necessary repulsive interparticulate potential.

The pattern with light magnesium carbonate was similar (Fig. 2) although the values of sedimentation volume differed from those for the heavy material. The flocculated suspensions of light magnesium carbonate (those containing 0–0.2% docusate sodium) had higher values of sedimentation volume than did flocculated suspensions of heavy magnesium carbonate. This can be explained in terms of the difference in particle size between the two materials. Although both sets of suspensions contained the same mass of magnesium carbonate, there was a larger number of particles in the suspensions containing light magnesium carbonate because of its smaller particle size. It was possible to arrange those particles into a more voluminous, open framework than with a smaller number of larger particles. This effect of particle size was also observed in flocculated benzocaine suspensions (Liao and Zatz, 1980a and b).

A second difference between the curves in Fig. 2 is the concentration of docusate sodium at which deflocculation becomes essentially complete. This concentration was somewhat higher in light magnesium carbonate suspensions because the solid particles had a higher total surface area than that of an equal mass of heavy magnesium carbonate. A higher concentration of the surfactant was thus required to allow adsorption of sufficient surfactant to cause deflocculation.

These experiments were repeated with suspensions containing low concentrations of xanthan gum. Suspensions with xanthan gum concentrations greater than 0.2% settled very slowly. They had to be left undisturbed for periods up to 6 months to permit determination of sedimentation volume values. The results are plotted in Figs. 3 and 4. In suspensions containing no docusate sodium, sedimentation volumes were raised by the inclusion of xanthan gum as a result of enhancement of flocculation by the polymer, although, with the heavy magnesium carbonate (Fig. 4) there was a decrease in sedimentation volume when the gum concentration was raised above 0.2%. This behavior is often observed when polymer flocculation takes place. It is due to adsorption of excess gum by a small proportion of the suspended particles (Slater and Kitchener, 1966). Flocculation by the gum also took place in suspensions containing docusate sodium (Figs. 3 and 4). The concentration of gum required to achieve a given degree of flocculation was directly related to the docusate sodium concentration.

The antagonism in action between docusate sodium and xanthan gum can be explained on the basis of the polymer-bridging model proposed earlier (Tempio and Zatz, 1980, 1981). Both the polymer and the surfactant are anionic materials while the solid surface is positively charged (Tempio and Zatz, 1981). Adsorption of the surfactant is required for deflocculation; flocculation enhancement by xanthan gum is also predicated on adsorption. Because both the polymer and the surfactant are



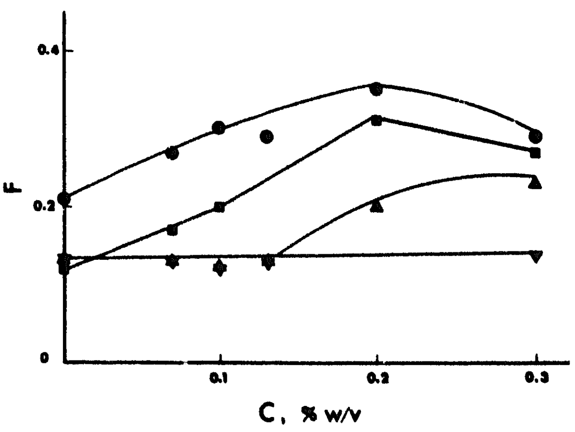


Fig. 3. Effect of xanthan gum concentration on sedimentation volume of 5% light magnesium carbonate suspensions. ●, no docusate sodium; ■, 0.2% docusate sodium; ▲, 0.25% docusate sodium; ▼, 0.3% docusate sodium.

Fig. 4. Effect of xanthan gum concentration on sedimentation volume of 5% heavy magnesium carbonate suspensions. ●, no docusate sodium; ■, 0.2% docusate sodium; ▲, 0.25% docusate sodium; ▼, 0.3% docusate sodium.

attracted to the particle–medium interface, the flocculation state of magnesium carbonate suspensions depends on which of the two materials succeeds in the competition. The driving force for adsorption is related to concentration in the suspension medium. Thus, if the concentration of docusate sodium is sufficiently greater than that of xanthan gum, surfactant adsorption dominates and the suspensions are deflocculated. On the other hand, if the ratio of polymer to surfactant concentration is sufficiently large, polymer adsorption dominates and the suspensions are flocculated.

Polysorbate 40 did not exhibit a tendency to deflocculate magnesium carbonate suspensions. In suspensions containing 0.067% xanthan gum, there was a slight rise in sedimentation volume when polysorbate 40 was present, but no substantial change in flocculation behavior was evident. Apparently the non-ionic surfactant was not attracted to the particle surface and did not materially influence the xanthan gum adsorption.

These results suggest a general approach to flocculation control in suspensions of positively charged solids containing xanthan gum. It is possible for suspensions to be too highly flocculated, leading to an unsightly appearance because of excessively large particles or even gel formation. In this instance, the addition of an anionic surface-active substance that can effectively compete with xanthan gum for the particle surface can antagonize the tendency toward flocculation. By balancing the concentration of gum and anionic additive, the system may be guided toward a mildly flocculated state which resists caking without disturbing suspension appearance. On the other hand, if it is necessary to add other materials to the formulation and no change in flocculation state is desired, a non-ionic material would be preferred. Thus, by proper choice of additives, control of final flocculation state may be achieved.

Acknowledgements

This work was supported by a grant from The Kelco Company.

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