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Abstract

Full Text

CHEMISTRY

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OBTAINING AND STUDYING THE PHYSICO-CHEMICAL PROPERTIES OF FRACTIONS OF CARBOXYMETHYLCELLULOSE

(Presented by Academician A. V. Topchiev, 3 VII 1958)

In recent years, the water-soluble sodium salt of the carboxymethyl ether of cellulose (carboxymethylcellulose—CMC) has found broad practical application.

CMC is used in various branches of technology as a stabilizer, emulsifier, adhesive agent, active additive to synthetic detergents, and for many other purposes^(1,2).

Carboxymethylcellulose is a complex polydisperse product consisting of various fractions, which differ from one another in chemical composition⁽³⁾ and physicochemical properties, and it can be obtained with different values of the degree of etherification and polymerization.

Therefore not every grade of CMC meets the requirements of its intended purpose. Of the entire variety of possible CMC compounds, only some prove suitable for practical application in one or another field of technology. The choice of the most effective grade of CMC in each individual case is decided experimentally, since up to the present time no relationship has been established between the chemical composition of CMC samples, their physicochemical properties, and their behavior in the process of practical use.

In addition, CMC samples almost always contain a certain amount of sparingly soluble swelling fibers of the so-called gel-like phase. The content of the latter may have a substantial influence on the properties of carboxymethylcellulose solutions.

According to Djurig and Bander⁽⁴⁾, two types of CMC with identical average values of the degree of substitution and degree of polymerization, but with different contents of the gel-like phase, had entirely different rheological properties.

In connection with the above, the task set in the present work was to study the fractional composition of carboxymethylcellulose, the physicochemical properties of the fractions, and the influence of individual fractions on the behavior of CMC in the process of its practical use.

Four CMC samples were selected as the object of investigation. Of these, the first is a grade of CMC currently used for stabilizing clay solutions in drilling (2,5); the second is used for stabilizing silicate-salt solutions when drilling wells in zones of easily water-flooded and collapsing soft rocks (2), and also as an adhesive agent (6); the third is a German product of the VHR grade, which is also used in a number of countries for stabilizing flushing solutions when drilling oil wells; and the fourth is a specially obtained low-viscosity CMC preparation.

Fractionation of the samples was carried out as follows. To a 5-6% aqueous solution of the technical product, slowly, with vigorous stirring, ...

with stirring, at room temperature, a precipitant—acetone or methanol—was added until a persistent suspension appeared. The precipitated fraction was separated from the mother liquor by filtration on a Büchner funnel or by centrifugation in an ultracentrifuge at 20,000 rpm, and was then purified from sodium chloride and caustic soda by extraction with methanol.

In an analogous manner, the subsequent fractions were isolated from the mother liquor.

Along with fractionation by the method of precipitation with alcohol, all samples, except the last, were separated into gel-like and sol-like phases by centrifuging 2-3.5% aqueous solutions of technical CMC products in an ultracentrifuge. The resulting gel-like and sol-like phases were treated with methanol or acetone and purified from alkali and sodium chloride. Some of them were subjected to fractionation by precipitation according to the procedure described above. The yield of a fraction was determined as a percentage of the total weight of all fractions of the given sample. In the fractions obtained, the degree of polymerization was determined by Burchard's method (7), and the degree of substitution by iodometric determination of copper in the copper salt of carboxymethylcellulose.

The viscosity of the CMC fractions obtained was studied, as was their stabilizing action on suspensions of askangel bentonite clay.

Preliminary investigations established that the viscosity of aqueous CMC solutions with a concentration of 0.1% and higher does not obey Newton's law. Therefore, in the present work dilute solutions (0.05%) were studied; in these, as our determinations showed, the viscosity anomaly is practically absent. Viscosity was determined with a Pinkevich viscometer at $20 \pm 0.02^\circ$.

The stabilizing action of the CMC fractions was determined by filtration analysis with a pressure drop of 1 atm. Five-percent clay solutions were used, with 10% NaCl added as a coagulant and 0.75% CMC fraction added as a stabilizer.

The amount of filtrate that passed through a paper filter of area 60 cm² in 30 min was measured.

The results obtained are given in Table 1.

As is evident from these data, the fractionation technique used makes it possible to reveal the heterogeneity of CMC with respect to both indices—both the degree

of polymerization and the degree of etherification. At the same time, a regular change is observed in the properties of the fractions arranged in the order of their isolation: fractions with a lower degree of polymerization are characterized by a higher degree of etherification, as was shown for all the samples studied.

At the same time, study of CMC fractions obtained by the precipitation method showed that they are also not equivalent in their stabilizing ability. The third fraction, obtained from sample No. 1 and characterized by a low value of the degree of polymerization, gives the greatest water loss.

This investigation also shows that the gel-like phase isolated from CMC is characterized by a low stabilizing ability. This is especially evident in samples Nos. 2 and 3, where the water loss reaches 26 and 51 ml, whereas the sol-like phase of the same samples makes it possible to reduce filtration to 10 and 5 ml.

These data allow the conclusion to be drawn that, in addition to the degree of polymerization and etherification, which determine the effectiveness of the stabilizing ability of CMC preparations (², ⁵), the content of gel-like phase in them must also be taken into account.

The ratio of gel-like and sol-like phases in the product is important not only when CMC is used as a stabilizer for clay solutions, but also for other practical purposes, in particular when CMC is used as an adhesive agent.

Table 1

Sample No.	Fraction	Fraction yield, wt. %	Viscosity of 0.05% solutions, centipoise	Degree of polymerization	Degree of etherification	Water loss, ml
1	Initial sample		2.4	354	85.1	5.5
1	I fraction	49.8	2.9	417	80.7	4.1
1	II fraction	32.5	2.5	391	83.6	3.9
1	III fraction	17.7	1.3	197	90.5	7.4
1	Gel-forming phase	5.0	3.6	518	76.0	7.4
1	Sol-forming phase	95.0	2.4	375	84.1	3.9
1	I fraction	56.1	2.5	404	80.6	4.0

Sample No.	Fraction	Fraction yield, wt. %	Viscosity of 0.05% solutions, centipoise	Degree of polymerization	Degree of etherification	Water loss, ml
1	II fraction	43.9	2.3	342	86.0	3.9
2	Initial sample		3.2	500	63.8	11.7
2	Gel-forming phase	19.30	7.1	635	58.9	26.0
2	Sol-forming phase	80.70	2.0	276	66.3	9.9
2	I fraction	66.50	2.0	280	64.9	10.1
2	II fraction	33.50	1.8	253	68.1	8.7
3	Initial sample				79.3	5.0
3	Gel-forming phase	24.6				51.2
3	Sol-forming phase	75.4	4.2	547	84.1	4.8
3	I fraction	29.55	4.3	585	78.2	5.2
3	II fraction	70.45	3.6	512	91.9	4.3
4	Initial sample		—	83	84.2	—
4	I fraction	82.9	—	92	76.2	—
4	II fraction	3.2	—	55	85.7	—
4	III fraction	4.5	—	54	85.7	—
4	IV fraction	5.2	—	44	102.5	—

However, in this case, as we have shown experimentally by studying the fractions of sample No. 2, the gel-forming phase proves to be the most effective.

The comparative study we have carried out of the degree of homogeneity of CMC and of the properties of its individual fractions makes it possible to outline ways of developing the most effective grades of CMC, suited to their intended purpose.

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Note: Figure translations are in progress. See original paper for figures.

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