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Hydration–dehydration properties of methylcellulose and hydroxypropylmethylcellulose

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The degree and rates of hydration and dehydration of methylcellulose (MC) and hydroxypropylmethylcellulose (HPMC) play important roles in many commercial applications involving the use of these polymers. MC and HPMC are known to exhibit phase separation and associated gelation of aqueous solution which is caused by a decrease in stability in the hydrated polymer above the lower critical solution temperature. Hydration–dehydration phenomena of these solutions were studied using turbidimetric and microcalorimetric methods. The precipitation characteristics were observed by monitoring changes in percent light transmission with temperature. These measurements indicate a functional dependence of type and degree of substitution, molecular weight and uniformity of substitution. Scanning microcalorimetry experiments indicate that MC precipitates out of solution in a simple gelation process, while HPMC solutions exhibit broad peaks, which suggests molecular weight or branching effects. Heats of dehydration follow a linear relationship with total substitution. Hydration and rate of hydration can also be altered by controlled surface crosslinking and particle size. The importance of these hydration and rate of hydration phenomena in ceramic applications, as an example, will be illustrated.

INTRODUCTION

Cellulose, a natural carbohydrate that contains the basic repeating structure of anhydroglucose units, is a highly hydrophilic polymer having a HLB (hydrophilic lipophilic balance) number of 12.45, as calculated from the group contribution method (Davis & Rideal, 1969). However, because of its highly crystalline nature, cellulose is not soluble or swellable in water. In order to solubilize cellulose, various substitutions have been incorporated along the anhydroglucose backbone which help break down its crystallinity. Various commercial products such as methyl, hydroxypropyl, carboxymethyl and hydroxyethyl ethers of cellulose are sold under different trade names. METHOCEL® brand cellulose ethers (METHOCEL is the trademark of The Dow Chemical Company) are methylcelluloses or hydroxypropylmethylcelluloses with various molecular weight and substitution levels. Despite the fact that hydrophobic groups such as methyl or hydroxypropyl moieties are introduced at the cellulose backbone, the polymer retains enough hydrophilicity (with HLB varying from 10.0 to 11.25) to be highly water soluble. Introduction of these hydrophobic groups gives the polymer surface activity (as in polysoap) and unique hydration–dehydration characteristics.

The inverse solubility and gelation behavior of aqueous solutions of these polymers are well known (Sarkar, 1979). The swelling behavior of these polymers has also been reviewed recently (Doelker, 1990). This gelation process is associated with phase separation which is caused primarily by the hydrophobic bonding (Borchard, 1983) above a lower critical solution temperature (LCST). Depending on temperature and substitution values, these cellulose ethers will exist in a number of states as shown in Fig. 1. Solution calorimetry is a sensitive technique to measure the exothermic heat of hydration. However, detection of the endothermic heat of dehydration is most conveniently carried out using highly sensitive differential scanning calorimetry. This technique involves slow heating (1°C/min) of a dilute solution using a specially designed scanning microcalorimeter. The energetics are based on the following physical changes. In the solution state at lower temperatures, methylcellulose molecules are hydrated and there is little polymer–polymer interaction other than simple entanglement.

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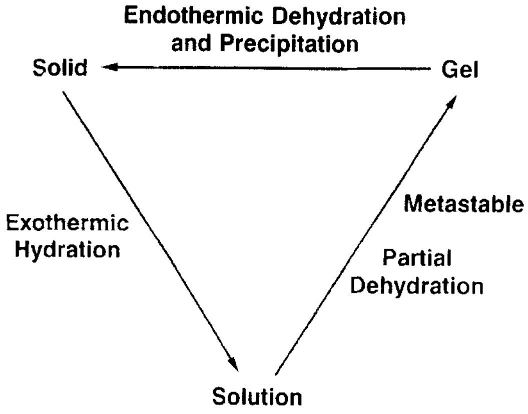

Fig. 1. Sol–gel transformation of aqueous solutions of methylcellulose and hydroxypropylmethylcellulose polymers.

As the temperature is increased, molecules absorb translational energy and gradually lose their water of hydration, resulting in lowering of viscosity. Eventually, a polymer–polymer association takes place, due to hydrophobic interactions, causing cloudiness in solution and an infinite network structure which results in a sharp rise in viscosity and turbidity as long as the concentration is relatively high. In addition, cooling reverses the process and the calorimeter can be used to test the thermodynamic reversibility. Previous workers have employed conventional DSCs to determine the effect of water on the gelation phenomena of xanthan and hyaluronic acid (Yoshida *et al.*, 1990). Use of a highly sensitive scanning microcalorimeter on dilute solutions of poly(*N*-isopropylacrylamide) has also been reported (Schild & Tirrell, 1990).

TURBIDIMETRY

A simple way to monitor the hydration–dehydration phenomena of cellulose ethers in solution is to measure the transmission of light through a solution as a function of temperature. The experimental apparatus consists of an aluminium block which is heated by circulating constant temperature fluid through a copper tube wound around the block that holds a 1 cm light path through a 12 mm OD × 75 mm long tube. The aluminum block is bored horizontally so as to pass 800 nm infrared light through a 600 μm single fiber light guide, a collimator lens system, through the sample in the cell, and then to another collimator lens system followed by another 600 μm single fiber optical light guide which connects to a detector. The light source and the detector are contained in a fiber optics analog electronics box designed and fabricated in-house. A rubber septum is used on the glass tube to minimize solvent loss during heating.

A constant temperature circulating bath capable of temperature programming was used to program heating and cooling rates of the sample. An *x*-*y* recorder was used to record changes in % light transmission with temperature. Under normal operation, heating and cooling rates were controlled at 1°C/min. All the solutions were aged at 5°C in a refrigerator before running the test to ensure complete hydration.

Figures 2–5 show the precipitation and resolubilization curves for 0.5% solutions of several METHOCEL cellulose ether samples. They have 2% solution viscosity of about 4000 mPa.s at 20°C, and different DS (degree of methoxyl substitution) and MS (hydroxypropyl molar substitution) values. These are METHOCEL A4M (DS = 1.75, MS = 0), METHOCEL F4M (DS = 1.71, MS = 0.13), METHOCEL E4M (DS = 1.90, MS = 0.22) and METHOCEL K4M (DS = 1.36, MS = 0.23), respectively. These curves illustrate that upon heating to a characteristic incipient precipitation temperature (IPT), a sharp decrease in light transmission takes place. Cloud point (CP) is defined as the temperature at which light transmission

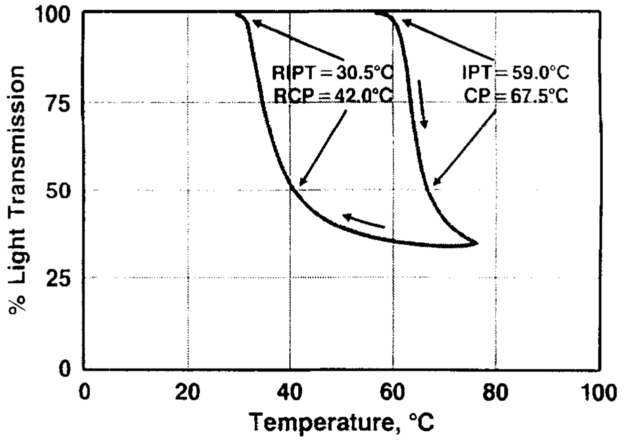

Fig. 2. Precipitation temperatures of 0.5% aqueous solution of a methylcellulose sample with methoxyl DS of 1.75.

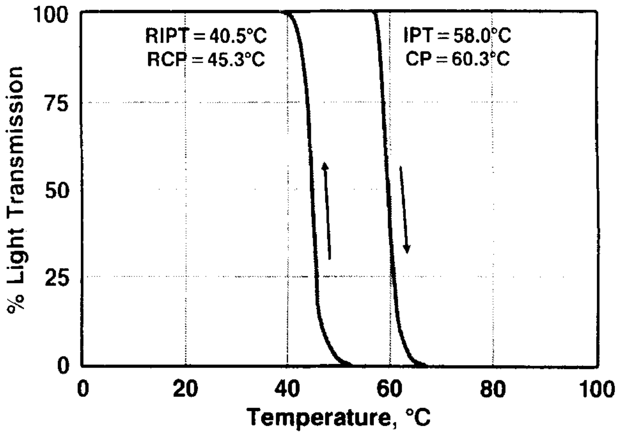

Fig. 3. Precipitation temperatures of 0.5% aqueous solution of a sample of hydroxypropylmethylcellulose with DS of 1.71 and MS of 0.13.

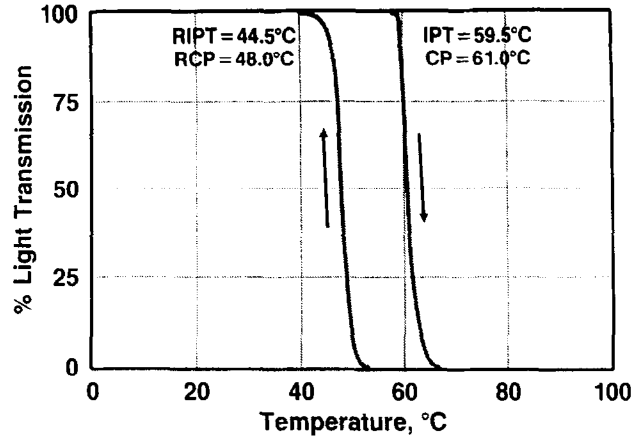

Fig. 4. Precipitation temperatures of 0.5% aqueous solution of a sample of hydroxypropylmethylcellulose with DS of 1.9 and MS of 0.22.

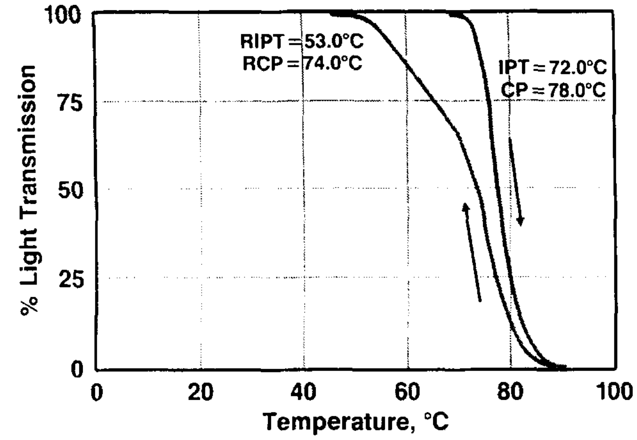

Fig. 5. Precipitation temperatures of 0.5% aqueous solution of a sample of hydroxypropylmethylcellulose with DS of 1.36 and MS of 0.23.

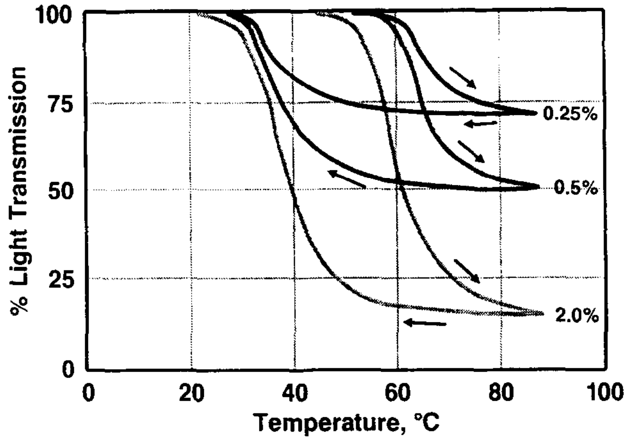

Fig. 6. Precipitation characteristics of a sample of methylcellulose with DS of 1.83 at different concentrations.

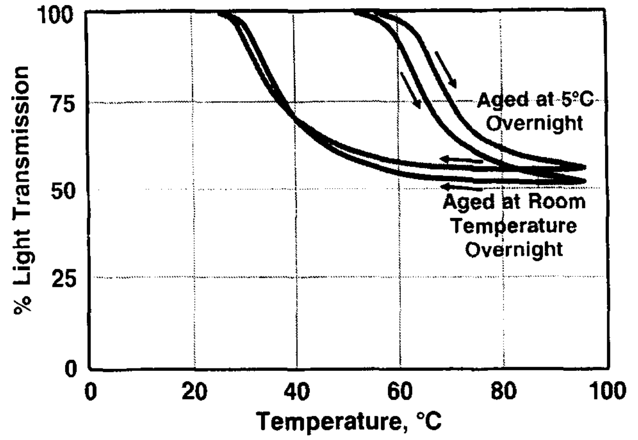

Fig. 7. Effect of ageing of an aqueous solution of methylcellulose on its precipitation temperatures.

reaches a 50% value. Light transmission finally levels off to an equilibrium value with nearly quantitative precipitation of the polymer. Upon cooling, we detected a large hysteresis, with the return cloud point (RCP) and return incipient precipitation temperature (RIPT) values considerably lower than CP and IPT, respectively. The values of IPT, CP, RCP, RIPT were found to be strongly influenced by the substitution, molecular weight and molecular weight distribution, etc. The standard deviation of these precipitation temperature values was ±2%.

As seen in Figs 2–5, methylcellulose polymer exhibits a large hysteresis and lower turbidity than the HPMC samples. There were also considerable differences in the precipitation characteristics among HPMC samples based on their substitution values. Figure 6 shows that the phase separation characteristics of these cellulose ethers are highly concentration dependent. Methylcellulose polymers are known to aggregate even at room temperature (Sarkar, 1979). This aggregation process can influence the dehydration–rehydration properties as shown in Fig. 7. The solution, aged at room temperature overnight, showed a shift to a lower CP. It should be noted that the two different METHOCEL A4M samples, as shown in Figs 2 and 7, show different precipitation (i.e. based on the final turbidity values) characteristics. Apparently, this can be attributed to the differences in substitution and the substitution distribution. The data in Table 1 show that the precipitation temperature values are not very sensitive to the heating and cooling rates. This suggests that the precipitation–resolubilization process is relatively fast.

It was observed that the METHOCEL cellulose ether sample, degraded to 15 mPa s grade product, showed a significantly lower CP. This is presumed to be the effect of aggregation phenomena discussed previously (Sarkar, 1979). Prud'homme believes (pers. commun.) that these processes are co-operative in nature because a binding site adjacent to an already hydrophobically bonded site is partially immobilized.

Table 1. Precipitation temperatures of METHOCEL at different heating and cooling rates for different products and viscosities

Temperature		25–90°C Heating curve		Cooling curve	
Heating rate, °C/min	Cooling rate	IPT (°C at 98.6% trans)	CP (°C at 50% trans)	RIPT (°C at 98.6% trans)	RCP (°C at 50% trans)
0.5% METHOCEL A4M 87070201 A % OCH_3 = 1.85					
0.5	4.33	57.0	65.3	30.8	43.5
0.5	0.27	57.5	65.8	31.7	44.0
1.08	1.08	59.5	65.7	30.5	41.7
0.18	1.08	56.0	65.4	29.6	45.0
0.09	1.08	54.0	66.0	29.7	46.1
0.045	1.08	55.0	66.0	32.6	50.0
0.5% METHOCEL E4M 87101901E (DS = 1.92; MS = 0.21)					
0.5	2.17	55.4	57.0	39.8	43.3
0.5	1.08	55.6	57.0	42.5	45.6
0.5	0.54	55.2	56.8	46.1	42.7
0.5	0.135	55.8	57.3	47.5	44.0
0.5% METHOCEL A4M 91030911A (DS = 1.76)					
1.0	1.0	60.5	82.0	33.0	59.0
0.5% METHOCEL A4M 91030911A degraded to 15 cps product					
1.0	1.0	61.0	74.9	34.0	49.8

DIFFERENTIAL SCANNING MICROCALORIMETRY

A high sensitivity differential scanning microcalorimeter (Model MC-2D, MicroCal Inc.) was used to determine transition heats and temperatures associated with the dehydration of cellulose ethers in aqueous solution. The procedure is similar to that reported in the literature for dilute solutions of poly(*N*-isopropyl acrylamide) (Schild & Tirrell, 1990) except that an updated version of the equipment was used.

The scanning microcalorimeter utilizes two cells, sample and reference, of 1.2 ml, machined from titanium, and located in the geometric center of a vacuum adiabatic chamber. Chamber control consists of an aluminum shield which is dynamically controlled to match the temperature of the sample cell. When a temperature induced process takes place, a temperature difference is directed via a 100 junction wire-wound thermopile that provides an electrical signal to an amplifier and control unit which, in turn, modulates power into the sample cell to minimize the off-balance signal. The calorimeter thus records the difference in electric power, which is directly proportional to the difference in heat capacity between the sample and water filled reference cell. These devices respond to both endothermic and exothermic processes and accurately record changes in the apparent specific heat (ΔC_p) as a function of temperature.

The cells are totally filled with dilute solution, without headspace. Nitrogen gas pressure, *c.* 60 psig, is maintained on a common header external to the calorimeter. This design allows experimental data to be collected above the normal boiling point of the solvent. In general, the procedure was to prepare 0.5% aqueous solution of each cellulose ether. Each sample was vacuum degassed, back filled with argon, and stored under refrigeration at 5°C for at least 10–15 h before use. Loading of the solution was carried out using a syringe, taking care to avoid air bubbles. After loading and equilibrium, the instrument was set to record data every 0.2°C with a scan rate of 1°C/min. Prior to a series of runs, a baseline experiment was carried out by adding degassed water to each cell and scanning over the temperature range of interest. The calorimeter was judged to be operating satisfactorily when ΔC_p did not exceed 4 mcal/degree over the 25–110°C range. All data analyses, including statistics and graphics, were performed using the ORIGIN (ORIGIN is the trademark of the Microcal Inc.) software package (version 2.9) included with the calorimeter.

Figures 8–12 illustrate the thermal data for METHOCEL A4M, F4M, E4M, J5M and K4M samples, respectively. The plot for the dehydration of METHOCEL A4M indicated a single precipitation process with a two state sol–gel transition. Precipitation of these cellulose ethers with increasing temperature followed a normal process of molecular weight fractionation with high molecular weight species precipitating first. Compositional variation would also influence the width of the endotherm; however, at this time no suitable analytical technique exists to determine sequence distribution. T_m, thus reflects the precipitation temperature of mean molecular weight species.

In contrast, HPMC samples showed a more complicated curve illustrated by overlapping thermal transi-

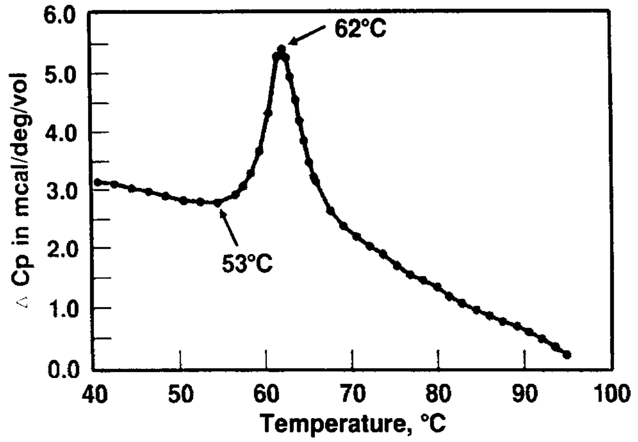

Fig. 8. DSC scan of 4.67 mg/ml aqueous solution of a METHOCEL A4M sample.

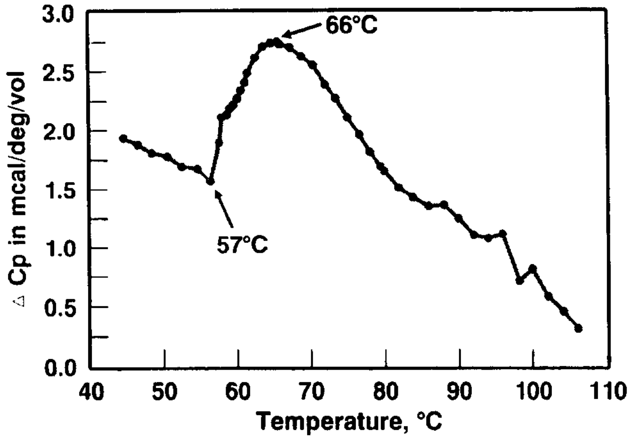

Fig. 9. DSC scan of 5.0 mg/ml aqueous solution of a METHOCEL F4M sample.

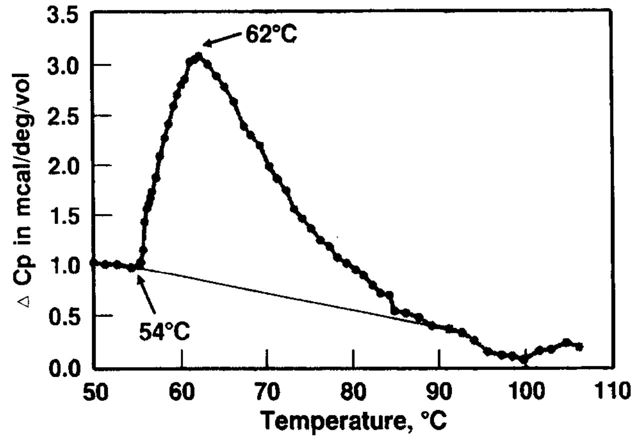

Fig. 10. DSC scan of 4.79 mg/ml aqueous solution of a METHOCEL E4M sample.

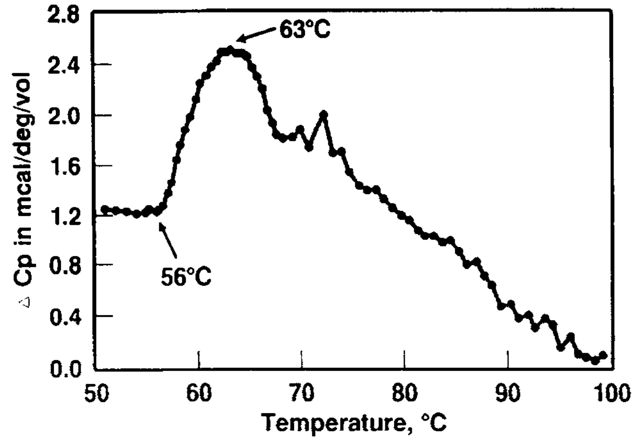

Fig. 11. DSC scan of 4.62 mg/ml aqueous solution of a METHOCEL J5M sample.

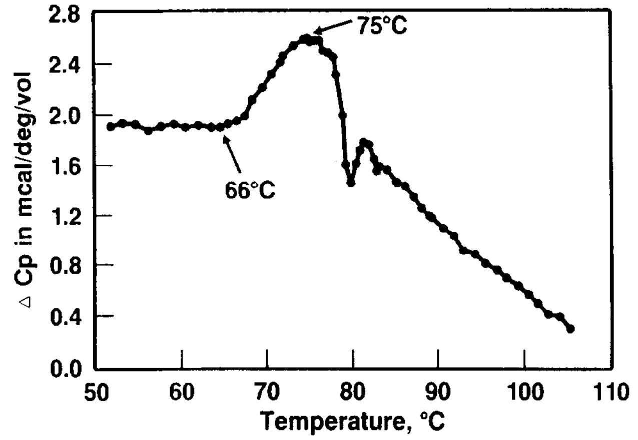

Fig. 12. DSC scan of 4.98 mg/ml aqueous solution of a METHOCEL K4M sample.

tion. In the case of METHOCEL K4M, we saw a broad endotherm centering at 75°C followed by a small transition at 81°C. This may suggest a phase separation, according to molecular weight distribution, with overlapping peaks due to short hydroxypropyl chain branching. This pattern was more pronounced in the METHOCEL J5M sample with high hydroxypropyl substitution. Here the peaks exhibited greater overlap and the precipitation did not appear to be complete until nearly 90°C. These observations are consistent with other recent work (Schild & Tirrell, 1990).

Overall, we found the following order of enthalpy of dehydration: K4M < F4M < A4M < J5M < E4M. The energy requirement of E4M was approximately three times that of K4M. In an effort to correlate thermal data with structure, we tabulated the different property information in Table 2. From these data, it was found that the only correlating pair was the measured heat of dehydration (kcal/repeating unit) with (DS + MS) as shown in Fig. 13. This analysis showed a linear trend with a correlation coefficient (R^2) of 0.98 by least squares fit. The x axis intercept at $\Delta H = 0$ gave a (DS + MS) = 1.335 and indicated that below this value the enthalpy changed sign in the precipitation process. This suggests the minimum degree of

Table 2. Thermal data — METHOCEL cellulose ethers

Type	2% Visc	DS	NS	MW(ru)	DS+MS	TM, °C	Q/M,cal/g	ΔH,kcal/ru
A4M	4515	1.84		187.8	1.84	62.0	4.04	0.758
J5M	4738	1.37	0.71	220.8	2.08	63.8	3.77	0.832
E4M	5213	1.88	0.25	202.9	2.13	62.0	5.14	1.043
F4M	5048	1.71	0.17	194.6	1.94	68.1	3.77	0.734
K4M	4847	1.45	0.23	195.7	1.68	75.0	1.87	0.366

ΔH = 1.248(MS + DS) − 1.666. (MS + DS) = 1.335 at ΔH = 0 ru. repeating unit.

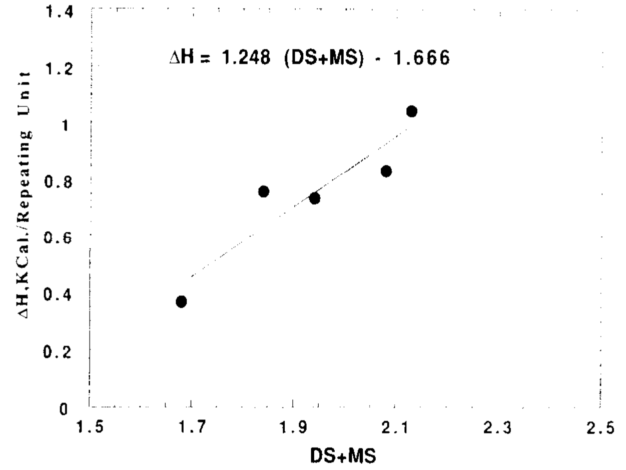

Fig. 13. Heat of dehydration of METHOCEL cellulose ether products as a function of the total molar substitution.

substitution (methylhydroxypropyl) needed for obtaining water solubility of these cellulose ethers under the current manufacturing process conditions. Extrapolation of the line to (DS + MS) = 0 gave a $\Delta H = -1.67$ kcal/(repeating unit) which represents the heat of precipitation of pure unsubstituted cellulose. The precipitation process was spontaneous at temperatures equal to or greater than the melting point, T_m. Conversely, cooling below IPT reversed the process. The gelled state can be thought of as a metastable state leading to the formation of the pure solid which would have the highest degree of order (Tanford, 1980). The plot of ΔH vs (DS + MS) indicated an increased water structure breakage around the polymer due to increased hydrophobic bonding with increased total degree of substitution. METHOCEL K4M, having the least total degree of substitution also had the lowest heat of dehydration in the series.

RATE OF HYDRATION FROM SOLUTION CALORIMETRY

The rate of solubilization of METHOCEL cellulose ethers plays a very important role in many applications, such as pharmaceutical controlled and/or sustained release tablets, spray plaster (both gypsum and cement based), ceramic processing, etc. It is apparent that the rate of hydration will depend on both chemical factors, such as degree and type of substitution, distribution of substituent groups, molecular weight distribution, etc., and physical factors such as particle size, particle size distribution, extent of surface treatment and surface crosslinking. In most cases, the initial uptake of water by methylcellulose is fast, then becomes diffusion controlled by the formation of a gel layer around a particle. For this reason conventional techniques developed for food products (Pilosof *et al.*, 1985) cannot be used. As an alternative we measured rates of hydration using a solution calorimeter. In this method, a 250 mg tablet of cellulose ether was prepared in a pellet press and placed in distilled water at 37°C in a Tronac solution calorimeter (Model 458) to make a final solution concentration of 1%. The exothermic heat of solution was then measured as a function of time.

Figure 14 illustrates the heat evolution with time for different METHOCEL cellulose ether samples. These data do not adequately reflect the true process rates since the total number of moles of polymer participating were not analytically defined. In an effort to correct this, we divided the apparent heat values in Fig. 14 by the respective heats of dehydration (calories/repeating unit) from the DSC experiments. Figure 15 depicts the normalized data and reflects the amounts of cellulose ethers dissolving as a function of time. The relative order of the hydration or solution rates of different

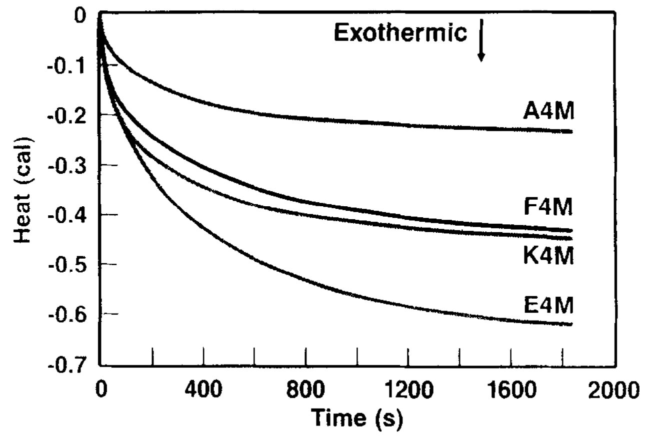

Fig. 14. Heats of solution of different METHOCEL cellulose ether pellets at 37°C to make a final solution concentration of 1%.

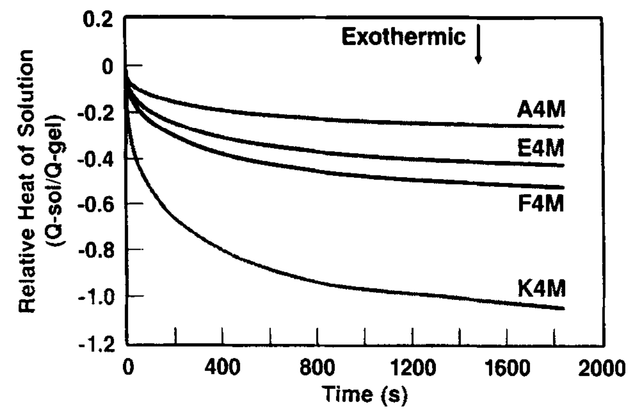

Fig. 15. Normalized heats of solution of different METHOCEL cellulose ether pellets at 37°C.

METHOCEL cellulose ethers was found to be: K4M < F4M < E4M < A4M.

HYDRATION PHENOMENA IN CERAMIC APPLICATION

Among many other uses of METHOCEL cellulose ethers, their use in ceramic processing (Sarkar & Greminger, 1983) will be shown as an example of where they impart plasticity and green strength. The rate of plasticization of a ceramic mix was evaluated according to a previously published experimental procedure (Schuetz, 1986). Here we used a Haake Torque Rheometer (Rheocorder). For this experiment 487.5 g of alumina powder (Alcoa A16 S6) and 12.5 g of METHOCEL cellulose ether powder were dry-blended for 1 min by tumbling in a plastic bag. Approximately half of this mixture was added to a Haake Rheocorder head and the torque rheometer started at 40 r.p.m. All the water (145.1 g) was then added (to give total solid concentration of 77.5%) and the recorder zero time noted. The remainder of the solid mixture was quickly added and the data collected for approximately 10 min or until torque levelled off.

Figure 16 shows the torque vs time curves for different METHOCEL cellulose ethers at 25°C. Initially, torque increased very sharply until it reached a maximum, indicating hydration and plasticization. After this, as the mix became increasingly plastic, torque decreased and eventually levelled off, indicating equilibrium plasticization. The initial phase of the curve is extremely important in many extrusion operations. The time of plasticization (or rate of hydration) will be greatly influenced by particle size, type and degree of substitution, distribution of substituent, molecular weight and temperature. When the mix is heated beyond the equilibrium time there is a gradual increase in torque as the solution begins to dehydrate and gel. The torque value reaches a peak followed by a sharp decrease as the gel structure begins to break up due to precipitation of the cellulose ether. The mix is adhesive in nature below the gel point and cohesive above the gel point.

Figures 17 and 18 show further elucidation of this rate for hydration/plasticization phenomena for different METHOCEL cellulose ethers at 40°C and 55°C, respectively. METHOCEL A4M, F4M and K4M samples exhibited CP and gelation temperatures in increasing order and gel strengths in decreasing order (Sarkar, 1979). Also, it is known that both gelation temperature and gel strength increase with concentration, which is reflected in these hydration tests. The actual concentration of METHOCEL cellulose ether based on water in these tests was 8.61%, at which point these samples may be gelling at temperatures much lower than the gelation temperatures normally quoted for a 2% solution. In all of these experiments, the torque rose quickly reflecting hydration of cellulose

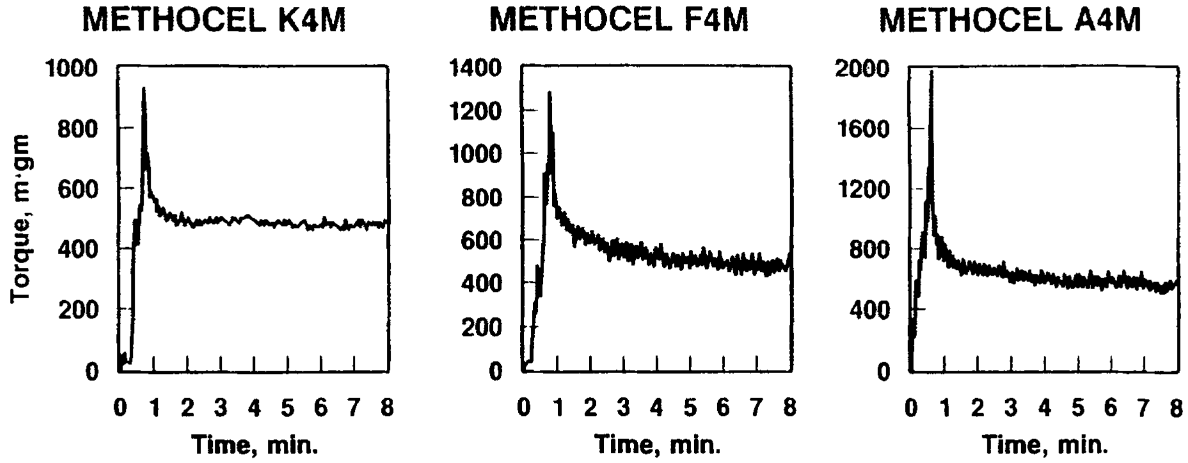

Fig. 16. Hydration of ceramic mixtures composed of 75.5% alumina, 22.5% water and 2% different types of METHOCEL cellulose ethers at 25°C.

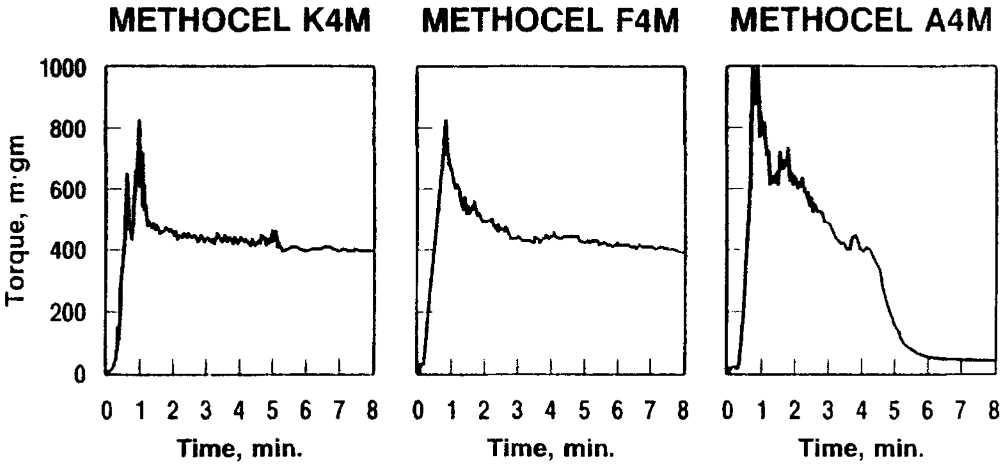

Fig. 17. Hydration of ceramic mixtures composed of 75.5% alumina, 22.5% water and 2% different types of METHOCEL cellulose ethers at 40°C.

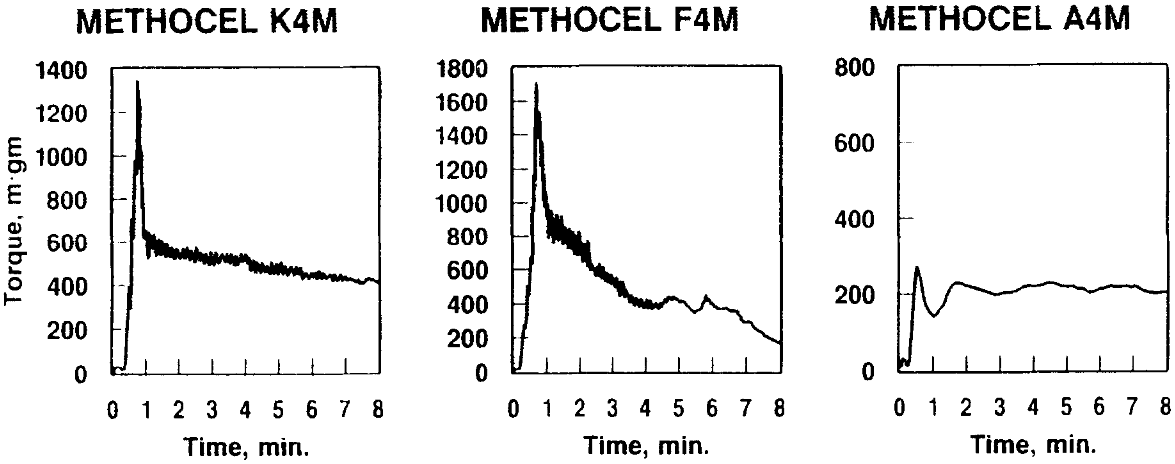

Fig. 18. Hydration of ceramic mixtures composed of 75.5% alumina, 22.5% water and 2% different types of METHOCEL cellulose ethers at 55°C.

ether molecules, decreased as the mixture became increasingly plastic, and finally levelled off to a value reflecting the viscosity of these polymers in water.

As seen in Figure 16, the maximum torque at 25°C increased in the order of K4M < F4M < A4M, reflecting increasing gel strength. The final torque was similar, reflecting the fact that they all have the same viscosity (and molecular weight) and complete solubilization of METHOCEL cellulose ether molecules. At 40°C, METHOCEL A4M does not hydrate properly, rather hydrated polymer gels out, resulting in mixture separation and adhesion to the rotor, which lowers the final torque value. On the other hand, METHOCEL F4M and K4M behave normally. At 55°C, there is no hydration of METHOCEL A4M. METHOCEL F4M now shows behavior similar to that shown by A4M at 40°C, reflecting proximity to the gelation temperature. METHOCEL K4M behaved normally, indicating a temperature below the gelation temperature of METHOCEL K4M. From a practical point of view, these findings are important in selecting cellulose ether types based on the temperature of operation.

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