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Research Note

Heat of wetting (hydration) of xanthan as determined by calorimetry

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The extracellular polysaccharide xanthan formed by fermentation of the bacteria *Xanthomonas campestris* has found widespread application in industry. In enhanced oil recovery xanthan is used for viscosity control due to its high salt tolerance. The solubility and dispersability of xanthan powders has been shown to vary widely. This has a large effect on the injectivity of the solution into petroleum reservoirs (Sandford *et al.*, 1981; Littmann, 1988; Kleinitz *et al.*, 1989). In order to gain a better understanding of the initial wetting and hydration of xanthan powders the heat evolved upon contact of xanthan powder and water has been investigated using a calorimetric technique. The aqueous phase was altered with regard to pH and NaCl content.

As wetting of a solid material is related to the surface forces between the solid and the liquid, the heat evolved upon wetting can be taken as a measure of the interaction between the solid and the liquid. This, in the present case, relates to the ability of the xanthan to disperse in the liquid.

MATERIALS

The commercial xanthan powder product from Kelco investigated has the following properties: molecular weight (SEC), $1{\cdot}05 \times 10^7$; pyruvate, 3·53%; acetate 4·88%. Elemental analysis of the sample indicated the presence of impurities containing nitrogen and sulfur. These comprised approximately 1% w/w. Cell residues could be observed in photomicrographs as reported elsewhere (Kulicke *et al.*, 1990). NaCl was of analytical grade from Merck. The pH was adjusted to 1·5, 2·5, 4·0 and 6·0 by addition of HCl. Salinity was altered by addition of NaCl: 0·1, 0·5 and 1·0 M NaCl solutions were investigated.

CALORIMETRY

The heat of wetting of xanthan powder by water was measured at 25·02°C using a LKB Bio Activity Monitor 2277 batch calorimeter. A known amount of xanthan (in general 22–27 mg ± 0·01) was placed in the calorimeter cell, covering the bottom of the sample cell. The sample cell was placed in the measuring cylinder. When thermal stability was obtained, the liquid (distilled water or brine) (1·7 ml) was added at a flow rate of 50 μl/min using an external peristaltic pump Pharmacia P-1. No stirring was applied to avoid heat contributions from changes in solution viscosity during the process. The flow rate was optimized to obtain a reproducible and 'simple' signal. In Fig. 1 the signal obtained under different conditions is given. The base line correction used in the evaluation of the integral heat is indicated as well, and is an approximation to the curve obtained when water is injected into the empty sample cell. Note the initial peak of curve 1a which is due to the flash evaporation of water as the first drop enters the cell. This signal is not assumed to occur when powder is present as there is an immediate contact between water and the xanthan powder. The fast flow rate (Fig. 1, curve c) was preferred to avoid the very complex curve obtained under slow injection conditions (Fig. 1, curve b). This complexity is assumed to be caused by differences in the time dependency of the different contributions to the integral heat evolved.

The method has previously been applied to measuring

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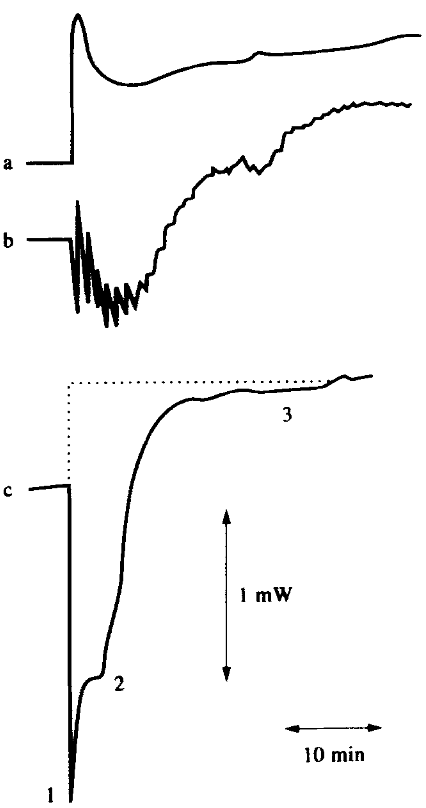

Fig. 1. Calorimetric signal under different conditions. (a) Injection of water, flow 50 μl/min, no xanthan. (b) Injection of water, flow 10 μl/min, 20·80 mg xanthan. (c) Injection of water, flow 50 μl/min, 19·20 mg xanthan. 1, 2 and 3 different stages of the wetting process.

the heat of immersion of different solids and determination of the surface areas of porous solids (Birdi *et al.*, 1991). The heat of wetting was calculated from the integral heat evolved during the process using the baseline correction described above. Areas were determined by the cut-and-weigh procedure. The standard deviation within each series was approximately 5% (see Table 1 below).

The samples were visually examined after each experiment. All showed the presence of non-hydrated material. The latter is the so called 'fish-eye' formation normally observed in xanthan solutions (Littmann, 1988). Hence the heats reported herein are relative, and will be affected by the presence of an unknown amount of non-wetted powder. The standard deviations, however, indicate that this amount of dry powder could be similar between runs.

Xanthan swells indefinitely like proteins when it is immersed in water, and eventually disperses completely upon high dilution. The polar groups are hydrated, and water is bound to the xanthan molecule by hydrogen bonds. In concentrated solutions, micro-gel structures and non-hydrated material is observed (i.e. Milas *et al.*, 1990).

The heat effect, ΔH, measured is made up of different contributions such as: heat of wetting, heat of swelling or gelation, heat of solution, and heat of dilution. All these contributions are exothermal. Other effects such as dissociation of COO^-, Na^+ at the pyruvate will also give a heat contribution. The total signal measured also contains an endothermal contribution from the heat of evaporation of water entering the cell. The latter is, however, taken into account by the baseline correction. In Fig. 1 (curve c) a typical heat signal is given. As the different processes have different kinetics the time dependence will be different. This is seen in the shape of the recorded signal. Three different stages of wetting were observed (1) initial wetting; (2) wetting of less accessible powder; and (3) final slow wetting or gel formation and equilibrium evaporation of water, the latter leading to the endothermal baseline shift. The fish-eye formation and hence slow wetting and hydration also affects the magnitude of the heat evolved. The exothermal heat of dissolution of many compounds is known to be very complex and even for simple synthetic macromolecules the occurrence of exothermal heat of dissolution is not easy to interpret (Morawetz, 1975).

In order to investigate the performance of the method used the heat evolved during the hydration and dissolution of the protein bovine serum albumin (BSA) was determined. With BSA no fish-eye formation was seen. A linear relation through the origin between the mass (12–27 mg) of BSA and the heat evolved upon wetting ΔQ was found giving ΔH = 58·06 J/g BSA in distilled water. The standard deviation of the 7 measurements was 3·01 J/g which is in agreement with the measurement on xanthan given below.

In Table 1 the measured heats of wetting of the xanthan powder and standard deviations are given. In Fig. 2 the relation between ΔH and pH is presented for four different NaCl concentrations when the pH was adjusted. The heat measured in distilled water without adjusting the pH is somewhat different as pH will change on dissolution of xanthan. The general trend seen is that ΔH increases with increasing pH at constant ionic strength. Statistically there is a significance at the 95% confidence level for the increase of ΔH with increasing pH between 1·5 and 6. In distilled water

Table 1. Heat of wetting of xanthan powder as a function of salinity and pH

		Salinity NaCl		
	Dist	0·1 M	0·5 M	1·0 M
pH	Heat of wetting (J/g)			
1·5	46·6 (1·7)	44·6 (3·0)	44·0 (3·6)	45·5 (2·6)
2·5	43·0 (3·6)	47·9 (5·9)	52·5 (2·4)	48·6 (1·2)
4·0	52·1 (2·1)	49·8 (4·8)	50·6 (2·5)	53·9 (0·7)
6·0	52·3 (2·2	54·4 (0·8)	54·7 (0·7)	56·7 (2·5)
No pH adjustment	54·5 (2·8)	48·5 (4·6)	50·8 (5·3)	55·2 (3·2)

Standard deviation indicated in parentheses.

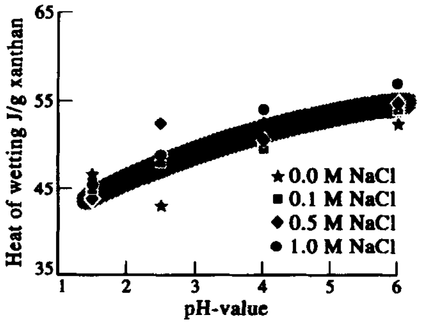

Fig. 2. Heat of wetting of xanthan powder at 25·02°C as a function of pH and salinity of aqueous solution.

($I = 0$) this trend is apparently different as a minimum is seen at pH = 2·5. This difference can be the result of ion-exchange effects, which are reduced when the solution salinity is increased and the pH adjusted. The overall trend is a small increase in the magnitude of ΔH with increasing salinity.

When pH increases the degree of dissociation of carboxylic acid groups reduces to zero, and the heat contribution decreases. Above pK_a (*ca.* pH 4·7 determined by hydrogen titration) the contribution is zero (Morawetz, 1975). For the average heat of wetting in a Fig. 2 the magnitude of $d\Delta H/dpH$ is seen to decrease as pH increases. This could be assumed to be rooted in a decrease in dissociation, but as the xanthan is supplied as a sodium salt hydration of this may be of more importance. Any definite conclusion is, however, speculative due to the complex nature of the process and the unknown magnitudes of the various heat contributions.

The findings presented here may explain the general experience that the swelling of the xanthan polymer is more effective in fresh water with a low pH (Littmann, 1988). From the thermodynamics of solutions we know that an increased exothermal enthalpy indicates a decrease in solubility if no large changes in entropy are encountered. Hence as either pH or salinity increases, the solubility or ease of swelling is decreased reflected in the increase in heat signal. The effect of pH is found to be more pronounced than that of NaCl.

The xanthan used here may also be obtained with an added dispersing agent which by visual examination in test tubes leads to a faster wetting and dispersion of the xanthan. However, injectivity tests in sandpacks of this product dissolved in water at pH 5 show that the actual injectivity (ease of injection as given by the resistance towards injection) decreases relative to the use of 'pure' xanthan. This was reflected in the heat of wetting in distilled water of xanthan–dispersant product being some 17% larger than the heat of wetting of xanthan alone.

In conclusion, the calorimetric method applied herein may be used to indicate small but significant variations in the initial solubility/dispersability of xanthan powder and other similar products, although the heat signal measured is not well defined in terms of the different contributions. Hence the method may find application in product screening.

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