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LIPOPHYLIC POLYSACCHARIDES

K. C. SYMES

Tate & Lyle Ltd, PO Box 68, Reading, Berkshire RG6 2BX, UK

Colloidal solutions are generally considered to be of two types: lyophilic or lyophobic, depending upon the affinity shown towards the solvent by the dispersed phase. Polysaccharides in aqueous solution are normally lyophilic (or, in this case, hydrophilic) colloids. However, in some instances, e.g. when the polysaccharide is highly substituted with certain substituents or it is rich in deoxy-sugars or can adopt a conformation in which predominantly apolar regions are presented, the macromolecules can display amphiphilic character with a resultant change in some solution properties.

The ability of xanthan to form highly viscous, pseudoplastic solutions which have a yield stress has been attributed partly to the rigidity of the molecules but also to the formation of macromolecular aggregates. Relatively little consideration has been given to the nature of the attractive forces causing self-association although Blackwell and his co-workers suggest it is a hydrogen bonding phenomenon (Southwick *et al.*, 1980). However, Smith *et al.* (1981) propose that it may be an entropy-driven process caused by alignment of apolar regions as depicted in Fig. 1. This conclusion stemmed from the observation that the atypical fractional change in viscosity of xanthan solutions on addition of salt was proportional to the degree of substitution with pyruvate. A critical level of substitution occurred when one in three side-chains carried the substituent ($x = 0{\cdot}3$), signifying that the distribution of pyruvate methyl groups along the helical axis at this point begins to favour self-association in more than one direction.

Other solution properties of polysaccharides which may be influenced by the existence of apolar regions are given in Table 1. Few systematic surveys of the surface activity of hydrocolloids have appeared, however, and data is lacking.

One new microbial gum, indican, from *Beijerinckia indica* ATCC 19361, displays a number of exceptional solution properties which may be due to the polysaccharide having structural features (unbranched, highly acetylated and containing the deoxy-

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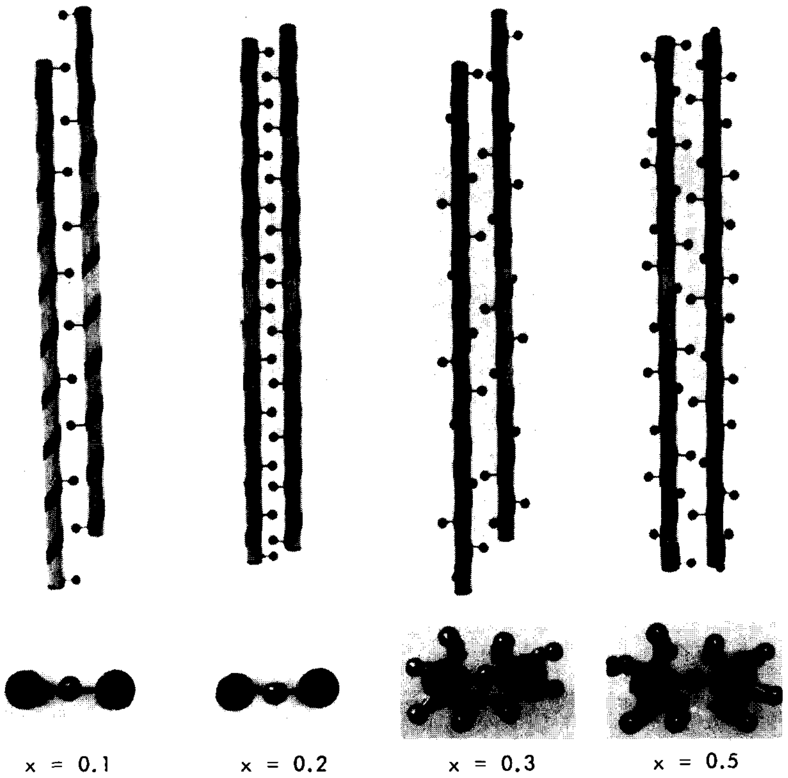

Fig. 1. Views of a xanthan model showing alignment of pyruvate methyl groups at varying levels of substitution assuming a regular distribution pattern.

TABLE 1
Some Solution Properties which may be used to Characterise Lipophilic Behaviour

	Lipophilic characteristics			
Lipid binding	*Surfactancy*	*Apolar association*	*Solvent solubility*	
Starch/oleate	$\gamma \downarrow$	Viscosity versus conc.	*Examples*	*% MeOH*
Cyclodextrin	$\gamma_i \downarrow$	Viscosity versus salt conc.	Alginate	50
Mycobacteria, PS/palmitate	O/W surface films	Viscosity versus *T*, °C	XG	66*
			HPG	80
S. cerivisiae, mannan/sterol	HLB	Liquid crystals	Idemitsu	90*
			Indican	100*
			HPC	100
	Flocculation	Yield stress/gelation	* Yield stress	

Beijerinckia indica ATCC 19361 (syn. *B. lacticogenes*)	2	1→3 Glc
	1	1→4 Man
	1–2	1→4 Rha
	1	Acid
	15%	Acetyl, linear
Beijerinckia indica ATCC 9039 (syn. *Azotobacter indicum*)	1	Glc
	1	Heptose
	1	L-Gul A
	20%	Acetyl, linear
Beijerinckia mobilis NCIB 9879 (syn. *B. indica*)	1	Glc
	1	Heptose
	3	L-Gul A
	Acetyl, pyruvate, branched	
Azotobacter indicus var *myxogenes* ATCC 21423 (syn. *B. indica*)	73%	Glc
	16%	Rha
	11%	Uronic acid
	10%	Acetyl

Fig. 2. Compositions of the repeating units of some *Beijerinckia indica* spp.

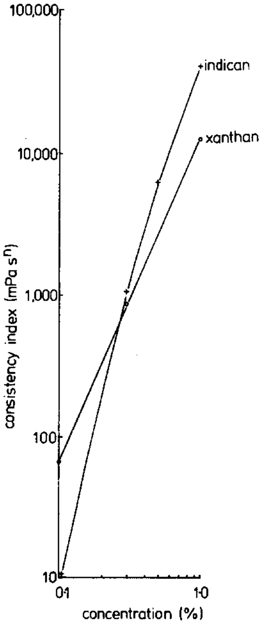

Fig. 3. Relationship of solution viscosity to gum concentration.

sugar rhamnose; Fig. 2) which promote apolar self-association. Thus indican solution viscosity shows an extremely high concentration dependence (Fig. 3) and, at concentrations above 0·5% w/v, solutions develop high yield stresses (Fig. 4). These gelatinous solutions are thixotropic as shown by the pronounced hysteresis in the shear rate/shear stress curves (Fig. 5). Moreover this behaviour is evident in solvents other than water, such as neat methanol or ethylene glycol. Suspensions of solids in alcohols gelled with indican have the important advantages, compared with dry powders, in their ease of transport and rapid dispersion or dissolution (Fig. 6).

Surface and interfacial tensions (γ and γ_i respectively) are lowered by indican over a prolonged period (Fig. 7) but this alone probably does not account for its highly effective oil/water (O/W) emulsion stabilising activity. Emulsion stability seems to

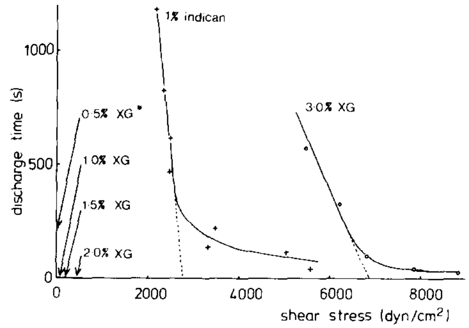

Fig. 4. Measurement of the yield stress of 1% aqueous indican by use of the gun rheometer. (0·5–2·0% Xanthan results from Sheth (1976).)

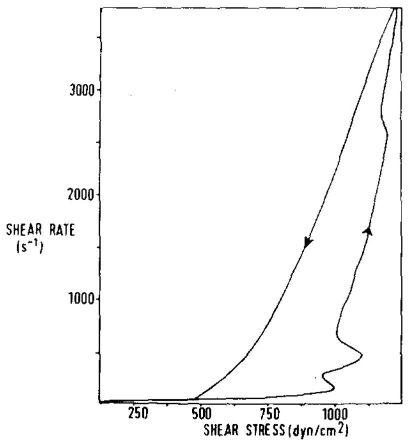

Fig. 5. Rheogram of 1% aqueous indican.

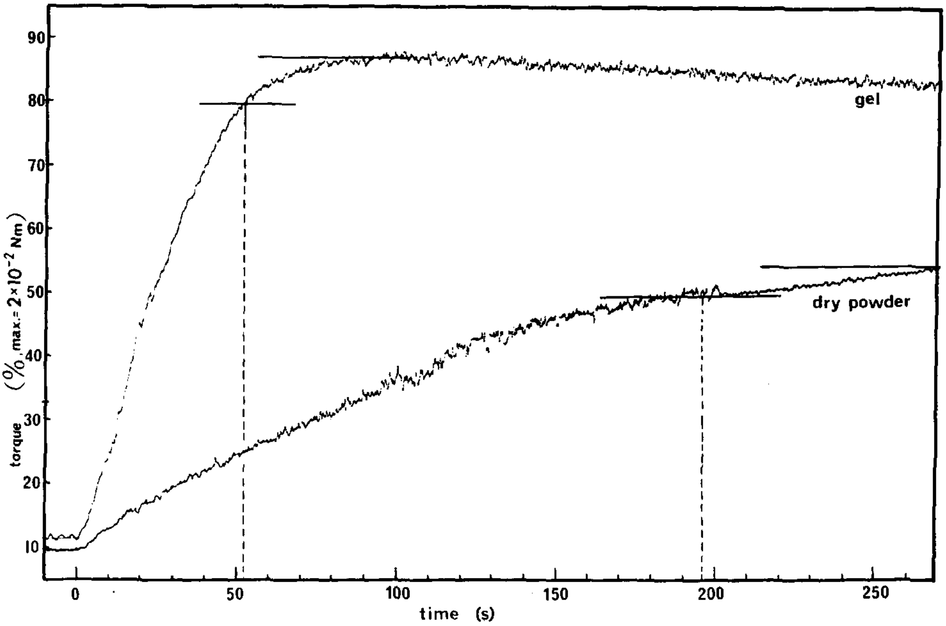

Fig. 6. Solution rates (as recorded by the torque on the stirrer) for xanthan in 3% NaCl solution added either as a dry powder or as a 20% solids suspension in methanol/ethanol (50:50) gelled with 0·25% indican.

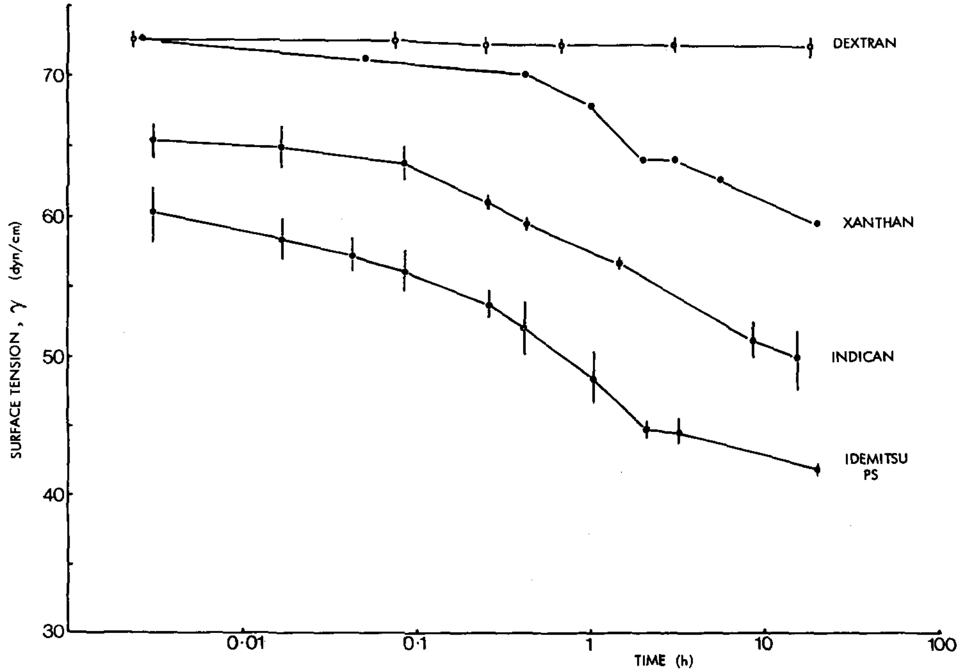

Fig. 7. Surface tension (by the Wilhelmy plate method) versus time for 0·1% polysaccharides in water. (Idemitsu PS, polysaccharide from *Arthrobacter carbazolum*.)

depend mainly on adsorption and formation of interfacial films. Certain gums (xanthan in particular) act as secondary stabilisers exerting their effect in the main by increasing the aqueous phase viscosity. The stability of indican stabilised emulsions, some of which are demonstrably more stable than those containing xanthan, can be explained by the former's ability to thicken and gel the aqueous phase whilst at the same time forming a protective interfacial film.

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