Transformation of the rheological properties of a soya oil-in-water emulsion as a result of the addition of salt substitutes

SEPPO LAHTINEN

Department of Food Chemistry and Technology, University of Helsinki, SF-00710 HELSINKI, Finland

Abstract. The influences of 1.00 % wt/wt NaCl, Morton Lite Salt (50 % wt/wt NaCl and 50 % KCl) and Mineral Salt (65 % NaCl, 25 % KCl and 10 % $MgSO_4 \cdot 7H_2O$) on the rheological properties of an emulsion containing 1.0 % sodium alginate, 1.0 % acetylated distarch adipate, 68 % water and 30 % oil were compared at a pH value 4.5 by means of a coaxial cylinder viscometer. An empirical model composed of two exponential terms was used to describe the rheological behavior under a constant shear rate. The addition of any of the three salts increased the essential mechanical parameter values remarkably. The influences of Morton Lite Salt and Mineral Salt were quite similar and different from that of NaCl. When xanthan gum replaced sodium alginate in the emulsion, small decreases were observed in some of the parameter values owing to salt addition. No differences existed between the influences of salts in that case.

Index words: emulsions, rheological properties, sodium chloride, salt substitutes, alginates, xanthan gum

Introduction

Few systematical studies exist concerning the influences of inorganic salts on macromolecular compounds in an emulsion system. In general, stability, as well as rheological alterations, arise either because of the association of counterions with the polymer molecules or, partially, through influences on the structure and properties of the solvent (SABHARWAL and VAKALERIS 1972, VAKALERIS and SABHARWAL 1972, MITA et al. 1974, LATA et al. 1977, STONE and CAMPBELL 1980, VER-NON CARTER and SHERMAN 1980, 1981a, 1981b, RIVAS and SHERMAN 1983, 1984). Modification of stability or the rheological properties of some protein-stabilized emulsions is possible, by the substitution of other cations for sodium (LAHTINEN and PAALANEN 1982, LAHTINEN 1987). In this paper, the results arising from partial NaCl substitution in model emulsions containing starch and either sodium alginate or xanthan gum are presented.

Materials and methods

The roughened MV I P coaxial cylinder assembly of Haake Rotovisco RV3 viscometer was used in the measurements. The emulsion samples were prepared similarly and the start-shear experiment procedure was similar to that described earlier (LAHTINEN 1987). The shear rate $\dot{\gamma}$ was constant 4.68 s^{-1}, roughly corresponding to the stimuli associated with the sensory evaluation of textural properties of liquid foods (CUTLER et al. 1983, KIOSSEOGLOU and SHERMAN 1983). The measurement time was 5.0 minutes. Duplicate samples of each kind were prepared and three measurements were taken from each of them to obtain representative material for one-way analysis of variance and Tukey's test.

The empirical models (1) through (3) where G^* is the modulus of deformation over the linear part of the stress-time curve (LAHTINEN 1987), η_i is the empirical coefficient of the i:th exponential term and λ_i is the corresponding time constant were fitted to the data. Paired time (t) and shear stress (τ) values were collected for this purpose at intervals of two or ten seconds, depending on the rate of change of the shear stress. The same instants were used in every fitting. In practice, the values of G^* and τ' were first computed from the recorded curve. The standard error of estimate of τ $s_{\tau \cdot t}$ was then minimized with a computer to produce the parameter values in Eq. (2).

$$\tau = G^*\dot{\gamma}t \qquad\qquad t \leq t' \qquad (1)$$

$$\tau - \tau' = \dot{\gamma}\sum_{i=1}^{n}\eta_i[1 - e^{(t'-t)/\lambda_i}] \quad t \geq t' \qquad (2)$$

$$t' = \frac{\tau'}{G^*\dot{\gamma}} \qquad\qquad\qquad (3)$$

The salt substitute mixtures were similar to Morton Lite Salt (50 % wt/wt NaCl and 50 % KCl) and Mineral Salt (65 % NaCl, 25 % KCl and 10 % $MgSO_4 \cdot 7H_2O$). The basic emulsion contained 1.0 % wt/wt sodium alginate (Manucol DH, Kelco International Ltd), 1.0 % acetylated distarch adipate (Instant Clearjel, Laing National Ltd), 68 % ion-exchanged water and 30 % soybean oil. The pH value of the basic emulsion was 4.5 and the salt concentration of the samples was 1.00 % wt/wt. The experiments were also accomplished with another emulsion that contained 0.5 % xanthan gum (Keltrol, Kelco Division of Merck, Inc.) and 0.5 % more water instead of the 1.0 % concentration of alginate. The same pH value and salt concentration as above were used in this latter type of emulsion.

In order to compare the influence of salts in an emulsion with that in water, apparent viscosities of either 1.4 % wt/wt sodium alginate or 1.4 % both alginate and starch were measured in ion-exchanged water once at shear rate values 37.44 s^{-1} and 26.44 s^{-1}, respectively. Measurements were taken from similar samples after the addition of 1.4 % wt/wt NaCl or Morton Lite Salt, too. The salt or polysaccharide concentration of 1.4 % approximately corresponded to those in the continuous phase of the emulsions. The MV I assembly that has smooth surfaces was used in these measurements. The samples were allowed to stand overnight before measurements were taken.

The ingredients sodium alginate and xanthan gum were used in the maximum concentrations allowed by the Finnish legislation. These ingredients were chosen because of their wide use in emulsions and because their polyionic nature makes them susceptible to the influences of salts. Acetylated distarch adipate was included for practical reasons for thickening and because it was observed to maintain its normal viscosity over the range of salt concentrations that was used. This ability was confirmed in preliminary experiments on its water dispersions by using starch in concentrations between 1.0 % and 3.0 %, and a NaCl concentration of 1.4 %. The pH value of these dispersion was 4.5, as it was in all experiments in this study.

Results and discussion

All the emulsion samples exhibited a behavior characteristic to viscoelastic mate-

Table 1. Means of the parameters describing the curves of the emulsion containing sodium alginate.

	G^* N/m^2	τ' N/m^2	η_1 $(N\ s)/m^2$	λ_1 s	η_2 $(N\ s)/m^2$	λ_2 s	$s_{r \cdot t}$ N/m^2
No salt	0.08	1.4	0.28	5.7	0.16	135	0.02
NaCl	0.30	8.5	0.79	3.9	0.14	4.5	0.07
Morton Salt	0.28	7.3	1.16	5.3	0.50	92	0.06
Mineral Salt	0.28	7.5	1.08	5.6	0.45	74	0.06
Least significant difference ($p \leq 0.05$)	0.03	1.4	0.23	1.3	0.09	46	

rials that do not show structural breakdown (ELLIOTT and GANZ 1971). A clear difference existed between the samples containing no added salt and the other samples in the emulsion that contained alginate, for the G^*, τ', η_1 and, in the case of the salt substitutes, η_2 values were clearly higher in the latter ones (Table 1). In addition, the influence of NaCl was distinctly different from that of the salt substitutes in this emulsion. In fact, only one exponential term would had been needed for the rheological characterization of the behavior obtained with NaCl instead of the two used (Table 1). Two exponential terms did not produce a lower standard error value than one term did. The first difference is important because it means that a structurizing mechanism associated with the behavior of starch and/or alginate molecules expressly at the oil-in-water interface governed the formation of the rheological properties. This becomes evident when we see that both the sodium alginate as such and in combination with the starch exhibited a slight decrease in apparent viscosity after the addition of 1.4 % of NaCl (Table 2). Such a decrease is a common property of many polysaccharides in water solution because of a reduction in the extent of hydration of their molecules (POMERANZ 1985). It has also been reported to occur in an emulsion stabilized by mesquite gum (VERNON CARTER and SHERMAN 1980). It is thus noteworthy that in the other emulsion that was otherwise similar but contained 0.5 % xanthan gum instead of alginate, small decreases were observed in some of the parameter values owing to salt addition (Table 3). However, no significant differences existed between the influences of salts in that case.

Table 2. Influence of salts on apparent viscosities of the polysaccharides in water.

Salt type	Apparent viscosity $\times 10^3$	
	Alginate $(N\ s)/m^2$	Alginate & starch $(N\ s)/m^2$
No salt	15.3	54.8
NaCl	14.5	47.4
Morton Salt	—	48.5

Table 3. Means of the parameters describing the curves of the emulsion containing xanthan gum.

	G^* N/m^2	τ' N/m^2	η_1 $(N\ s)/m^2$	λ_1 s	η_2 $(N\ s)/m^2$	λ_2 s	$s_{r \cdot t}$ N/m^2
No salt	0.17	5.5	0.85	5.3	0.38	100	0.05
NaCl	0.15	3.8	0.73	5.8	0.35	37	0.05
Morton Salt	0.17	3.8	0.70	5.2	0.38	37	0.04
Mineral Salt	0.17	3.6	0.82	5.5	0.36	35	0.04
Least significant difference ($p \leq 0.05$)	n.s.	0.7	0.14	n.s.	n.s.	37	

n.s. — not significant.

There was no difference between the influences of the salt substitutes in the emulsion that contained alginate (Table 1). This fact, as well as their different influence in this emulsion when compared with that of NaCl, is best explained by the more difficult association of sodium and magnesium in relation to potassium ions with the polymer molecules. The potassium ion with its smallest hydration radius is able to approach most closely the negative site attachment on a macromolecule. Hence, it will be held most strongly according to Coulomb law. This property probably led to alterations in the physical structure of the emulsion, perhaps through the medium of multiplied interfacial formation of hydrogen bonds between adjacent drops covered by the hydrocolloid film (VERNON CARTER and SHER-

MAN 1981b). The influence of magnesium and sulphate ions was small because of their large size and low concentration.

It is possible that the somewhat smaller reducing influence of the salt substitutes on the extent of hydration of macromolecules played a role in the formation of the difference between NaCl and the salt substitutes, too. This influence originates from the lower total amount of ions in the salt substitutes compared with that in equal masses of NaCl. However, the increase in apparent viscosity of the alginate-starch dispersion was negligible after the addition of 1.4 % Morton Lite Salt instead of NaCl (Table 2). It remains to be seen whether such difference has an importance in this type of emulsions. The above results do not support it.

References

CUTLER, A.N., MORRIS, E.R. & TAYLOR, L.J. 1983. Oral perception of viscosity in fluid foods and model systems. J. Texture Studies 14: 377—395.

ELLIOTT, J.H. & GANZ, A.J. 1971. Modification of food characteristics with cellulose hydrocolloids. I. Rheological characterization of an organoleptic property (unctuousness). J. Texture Studies 2: 220—229.

KIOSSEOGLOU, V.D. & SHERMAN, P. 1983. The rheological conditions associated with judgement of pourability and spreadability of salad dressings. J. Texture Studies 14: 277—282.

LAHTINEN, S. 1987. A dynamic analysis model for stress decay in emulsions under steady shear rate. Accepted for publication in Lebensmittelwissenschaft und -Technologie.

— & PAALANEN, L. 1982. Effect of three-component dietary salts on the coalescence of protein stabilized emulsions. Finn. Chem. Lett. 1982, 1—2: 22—24.

LATA, P., SHARMA, M.K. & JAIN, S.P. 1977. Electrolyte flocculation of haemoglobin-stabilized toluene/water emulsion. Indian J. Chem., Sect. A 15: 958—961.

MITA, T., IGUCHI, E., YAMADA, K., MATSUMOTO, S. & YONEZAWA, D. 1974. Dispersion state of protein-stabilized emulsions. II. Effect of sodium chloride on stability of oil-in-water systems. J. Texture Studies 5: 89—96.

POMERANZ, Y. 1985. Functional Properties of Food Components. p. 96. Academic Press, Inc., Orlando.

RIVAS, H.J. & SHERMAN, P. 1983. Soy and meat proteins as food emulsion stabilizers. 2. Influence of emulsifi-

cation temperature, NaCl and methanol on the viscoelastic properties of corn oil-in-water emulsions incorporating acid precipitated soy protein. J. Texture Studies 14: 267—275.

— & SHERMAN, P. 1984. Soy and meat proteins as food emulsion stabilizers. 4. The stability and interfacial rheology of o/w emulsions stabilized by soy and meat protein fractions. Colloids Surf. 11: 155—171.

SABHARWAL, K. & VAKALERIS, D.G. 1972. Stability of fluid food emulsions. I. Effects of emulsifiers, electrolytes and sodium caseinate. J. Dairy Sci. 55: 277—282.

STONE, M.B. & CAMPBELL, A.M. 1980. Emulsification in systems containing soy protein isolates, salt and starch. J. Food Sci. 45: 1713—1716.

VAKALERIS, D.G. & SABHARWAL, K. 1972. Stability of fluid food emulsions. II. Interacting effect of electrolytes, sodium caseinate and emulsifiers. J. Dairy Sci. 55: 283—288.

VERNON CARTER, E.J. & SHERMAN, P. 1980. Rheological properties and applications of mesquite tree (Prosopis juliflora) gum. 2. Rheological properties and stability of o/w emulsions containing mesquite gum. J. Texture Studies 11: 351—365.

— & SHERMAN, P. 1981a. Rheological properties and applications of mesquite tree (Prosopis juliflora) gum. 3. The influence of mesquite gum on the interfacial tension between oil and water. J. Disp. Sci. Technol. 2: 381—397.

— & SHERMAN, P. 1981b. Rheological properties and applications of mesquite tree *(Prosopis juliflora)* gum. 4. Rheological properties of mesquite gum films at the oil-in-water interface. J. Disp. Sci. Technol. 2: 399—413.

SELOSTUS

Erään soijaöljy vedessä -emulsion reologisten ominaisuuksien muuttuminen NaCl:n korvaavien suolojen lisäyksen seurauksena

Seppo Lahtinen

Helsingin yliopisto, Elintarvikekemian ja -teknologian laitos, 00710 Helsinki

NaCl:n, Mortonsuolan (Morton Lite Salt) ja Mineraalisuolan 1.00 p-% pitoisuuden vaikutuksia 1.0 % natriumalginaattia, 1.0 % asetyloitua ditärkkelysadipaattia, 68 % vettä ja 30 % öljyä sisältäneen emulsion reologisiin ominaisuuksiin verrattiin koaksiaalisylinteriviskometrin avulla pH:ssa 4.5. Mortonsuola sisältää 50 p-% NaCl:a ja 50 % KCl:a ja Mineraalisuola vastaavasti 65 % NaCl:a, 25 % KCl:a ja 10 % $MgSO_4 \cdot 7H_2O$:a. Kahdesta eksponentiaalisesta termistä koostettua empiiristä mallia käytettiin kuvaamaan emulsion reologista käyttäytymistä vakion leikkausnopeuden alaisena. Mallin keskeisten mekaanisten parametrien arvot kasvoivat huomattavasti lisättäessä mitä tahansa kyseisistä kolmesta suolasta emulsioon. Mortonsuolan ja Mineraalisuolan vaikutukset olivat keskenään varsin samanlaiset, ja ne poikkesivat NaCl:n vaikutuksesta. Kun natriumalginaatti korvattiin ksantaanikumilla, emulsion joidenkin parametrien arvojen havaittiin hieman pienenevän suolan lisäyksen seurauksena. Suolojen vaikutusten välillä ei siinä tapauksessa ollut eroja.