Phase diagram of the system sodium alginate/water: A model for biofilms

W. Borchard [a,*], A. Kenning [a], A. Kapp [a], C. Mayer [b]

[a] *Institut für Chemie, Angewandte Physikalische Chemie, Universität Duisburg-Essen, Standort Duisburg, Lotharstr. 1, 47057 Duisburg, Germany*
[b] *Institut für Chemie, Physikalische Chemie, Universität Duisburg-Essen, Standort Duisburg, Lotharstr. 1, 47057 Duisburg, Germany*

Abstract

Sodium alginate is a polyelectrolyte consisting of the monomer units β-ᴅ-mannuronate and α-ʟ-guluronate. Mainly based on the theory of Khokhlow et al., the state diagram of the binary system alginate/water has been calculated using different sets of parameters like degree of ionization, degree of polymerization and interaction function. The calculations comprise miscibility gaps, liquidus curves, eutectic points and the behaviour at temperatures below the melting point of water. Also gel and swelling curves have been treated, where gels are physically crosslinked. The DSC diagram of a 0.5 by wt.% polymer sol shows a double melting peak, which is explained by a heterogeneity above $0\,^\circ\text{C}$. The crystallization of water seems to concentrate the gelled system irreversibly.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Sodium alginate; State diagram of polyelectrolyte/water; Eutectic temperature; Demixing; Freezing point depression; Swelling curve

1. Introduction

Sodium alginate which is the sodium salt of the alginic acid is a polyelectrolyte. It is a copolymer consisting of β-ᴅ-mannuronate (M) and its C-5 epimer α-ʟ-guluronate (G). For alginates from seaweeds the sequence of the units M and G is statistical as derived from the M and G content whereas the sequence of alginates from bacteria has been found to deviate from a statistical distribution mainly because GGG triades or G-blocks are missing [1]. Whereas algal alginates are free from acetyl groups, bacterial alginates are partly acetylated. The irregular structure of the copolymer is the reason, why the polyelectrolyte does not crystallize. In aqueous solutions at low pH there is no solubility of the copolymer. In the neutral range, the solubility is rather low (1–4%, w/w), only at high pH values the alginates can be dissolved due to dissociation of the carboxylic groups. In the phase diagram, copolymer/water a liquidus or solubility curve of the copolymer does not exist. Therefore, a limited "solubility" is provoked by other reasons.

For such a copolymer of relatively high molar mass of about 10^5–10^6 g/mol at very low water content we expect a glassy solidification. In the literature, it is reported that the low solubility of the alginates in water may be derived from the existence of a miscibility gap in the system alginate/water, which is complicated by the fact that a real separation into two liquid phases does not always occur [2]. At rather low polymer concentration in water the copolymer starts to gel, which is explained by the dominant influence of polymer–polymer interactions in regard to polymer–solvent interactions. Therefore, the presumably highly diluted phase seems to be dispersed in the gel without sedimentation in the gravitational or centrifugal field [3], which in former times was given the name coacervation by Bungenberg de Jong [4].

The inclusion of a dispersed phase in a gel phase does not necessarily mean that phase equilibria do not establish. In any case, the condition of heterogeneous equilibrium is supposed to be valid. This means that the chemical potentials of the coexisting species have to be the same in both phases although the mechanical equilibrium condition is possibly not fulfilled. Hence, it follows that the coexisting phases are not positioned in the gravitational or centrifugal field in the

---

* Corresponding author. Fax: +49 203 379 2110.
E-mail address: borchard@uni-duisburg.de (W. Borchard).

right way where the less dense phase has to be above the more dense [5].

The results of light scattering measurements show that in dilute aqueous alginate solutions of an ionic strength of 0.15 mol/L with copolymer concentrations below 0.5% (w/w) the second virial coefficients of the osmotic pressure are slightly negative and increase with increasing temperature for both types of algal and bacterial alginates [6]. The extrapolated Flory- or Θ-temperature for water/algal alginate is 168 °C whereas for bacterial alginate/water it is 194 °C.

Negative virial coefficients are also reported from light scattering experiments of aqueous algal alginates by Smidsrød and Haug [7] becoming positive in the dependence of the purification of the solutions by centrifugation at rather high ultracentrifugal accelerations.

With analytical ultracentrifugation, positive virial coefficients are obtained for highly diluted solutions of algal alginate below 0.25% (w/w). For bacterial alginates negative virial coefficients have been observed [8].

From the temperature dependence of the virial coefficients it may be derived that the miscibility gap in the system water/alginate in principal has an upper critical point, which is situated above the decomposition temperature. The reported Θ-temperatures are so high that in the thermodynamic modelling of the system the two branches of the miscibility gap (binodals) are assumed to be parallel to the temperature axis in the temperature range between 25 and 0 °C.

From the general form of miscibility gaps in polymer nonelectrolyte/solvent systems it is known that the critical points of demixing are shifted versus $x_2^* \rightarrow 0$, with increasing molar mass of the polymer, where x_2^* is the base molar fraction of the polymer [9]. Following the Flory–Huggins–Staverman–van Santen theory (FHSS-theory) [10–12] the asymmetric shape of the miscibility gap with respect to $x_2^* = 0.5$ or also the weight fraction of the polymer $w_1 = 0.5$ is an image of the different sizes of macromolecules and low molecular solvent molecules. Thus, it can be expected that the branch of the demixing curve, which represents the diluted phase, is very close and nearly parallel to the T-axis for $x_2^* \ll 1$ [13].

In polysaccharide systems, the existence of hydrophobic surfaces along the polymer chains has been mentioned [14] being the reason for a strong interaction of sugar moieties and thereby the tendency of aggregation of different carbohydrates which have been studied by many authors and different methods. The aggregation of macromolecules occurring already at extreme dilutions in water leads to gelation of the system, which is differentiated from the case of demixing. At polymer mass fractions w_2 below the critical for gelation, $w_2 < w_{2,\text{cr.}}$, aggregated macromolecules or polymer clusters are present. With increasing polymer content the effective radius of the clusters diverges at the gel point. Beyond the gel point there is the gel cluster including also smaller clusters. In the phase diagram there is a gel curve, which separates the phase areas of homogeneous solution and homogeneous gel. The gel curve describes a second-order transition between solution (sol) and gel [15–17] and is no curve of coexistence.

The aim of the present contribution is to calculate first the coexisting concentrations in the demixed water/alginate system at room temperature under the assumption that the polymer is a polyelectrolyte. In the following step, the liquidus curve of water will be described where below the melting point of pure water pure ice coexists with a diluted solution of the copolymer. At the invariant eutectic point three phases that is ice, dilute solution and concentrated gel-like solution are in equilibrium.

In the third part, it will be shown what happens if ice coexists with a physically gelated system.

Finally, we want to compare the expected behaviour of the system with some experimental results obtained by DSC-measurements.

2. Modelling the miscibility gap of the system alginate/water

Polyelectrolyte solutions consist of polyions with their counterions in water or fluids with high permittivity like water. Their unique properties depend on the ionic strength of the surrounding medium, the nature of added low molecular weight electrolyte (if present), the valency of the counterions [18] and mainly the degree of ionization [13]. In many papers, it has been stressed that in aqueous systems beside the long-range Coulomb-interactions all other short-range interactions, such as hydrogen bonding, hydrophobic interactions, etc., have to be considered.

Recently, the demixing of polyelectrolytes was treated by considering a copolymer with different types of monomer units A and B, where only the monomer unit B is allowed to be ionized completely or partially [13]. The ionization of, e.g. carboxylic COOH groups may be achieved by adding base leading to charged COO$^-$ groups in a chain with positively charged counterions. If the acid or COOH groups in the chain are partly neutralized, the counterions are freely moving along the chain and adjacent chains because the exchange of hydrogen and counterions is possible at any monomer unit bearing COOH or COO$^-$ groups. Therefore, the charge can migrate which leads to a translational entropy of migration (tr-mig). The effect vanishes if the fraction of monomer units x, which is the ratio of the number of monomer units B to the total number of chain units is equal to the actual degree of ionization i, e.g. $x = i$. Generally, $x \geq i$ holds, because the maximum ionization is reached if all ionizable groups are charged. The degree of ionization i is an independent variable characterizing the charge density of the polymer chains.

In comparison to uncharged polymer chains also, the contribution of the counterions has been calculated which are distributed over the total volume leading to the condition of electroneutrality in the total volume. This effect was named the translational entropy contribution (tr-en).

Both effects have an influence on the minimum of the free energy or free enthalpy and thereby on the solubility of the polymer also in case that phase separation or demixing