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Phase diagram of borate – PVA system: Sol-gel transition and demixtion

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SUMMARY

We study the formation of reversible gels induced by addition of borax in aqueous poly(vinylalcohol). Under suitable conditions, sol, gel or demixed phase is observed. We present a qualitative interpretation of the phase diagrams. Important parameter for reversible gelation or demixing is the number of inter-polymer complexes which is governed by the complexation equilibrium.

INTRODUCTION

The large increase in the use of organic macromolecular gels is stimulated both by academic interest and applications in a broad range of industrial areas (food industry, cosmetics, optical lenses, pharmaceuticals, petroleum industry ; "superslurpers"...). For most of these uses, the gels are swollen in a "solvent", frequently water, and the concentration in active material is typically less than ten percent.

Such gels can be obtained by a chemical crosslinking between polymeric chains (chemical gels) or by inducing a temporary association between macromolecules (physical gels). In this last situation, a sol-gel transition may be obtained by changing temperature, pH, ionic strength etc... Several gelation mechanisms have been found : helix-coil transition (1) or even crystallite formation (2). Associations can also be due to hydrogen bonding, electrostatic or hydrophobic effects. A simple reversible cross-linking reaction may induce a physical gel. For instance, it is well known that poly(vinyl alcohol), PVA, reacts with borate ions and gives a gel (3). Contrary to a large number of physical gels, gels induced by complexation are generally clear and elastic.

The aim of this work is to describe the phase diagram (sol, uniform gel, demixed gel) observed for PVA/borax systems depending on temperature, ionic strength and, of course, polymer and borate concentrations.

We will discuss the importance of the complexation equilibrium which will enable us to give a qualitative interpretation of the phase diagrams in agreement with the results reported by Pezron and al. on galactomannam borate systems and with theoretical models (4) (13).

EXPERIMENTAL

Materials

PVA samples were supplied by JANSSEN CHIMICA and RHONE-POULENC. They are purified by ultrafiltration and freeze dried. The main characteristics of these polymers are given in Table 1 : Tacticity is

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*To whom offprint requests should be sent determined by 1H NMR, molecular weight by viscosimetry and multidetection steric exclusion chromatography. Sodium chloride and borax (which corresponds in fact to the borate-boric acid buffer (pKa = 9.2)) are used without further purification.

The desired amounts of PVA powder were dissolved in desionized water (Milli Q System of MILLIPORE) by heating. Absolute polymer concentrations were determined by total organic carbon analysis (DC80, DORHMANN/XERTEX).

Viscometry measurements were performed on a low-shear Contraves 30 rheometer.

Phase diagrams

5ml samples were prepared by mixing PVA, borax and sodium chloride solutions. After vigorous stirring, the system was kept at least 48h in a thermostated bath. It is difficult to distinguish precisely a sol and a reversible gel phase. Criterion has been chosen, a sample test tube kept in temperature regulated water bath, was turned upside down and if the meniscus holds, gel phase was obtained. The same result was found with laser beam : the speckle pattern visible at low scattering angle is observed on a screen. In the sol phase, the speckle pattern fluctuated randomly, in the gel phase the movement of the speckle was frozen. (5)

When precipitation occurs, first the gelled phase seems to be turbid, and solvent was expelled from the gel. After 48h, it was very easy to distinguish between a homogeneous phase sample and a demixed sample.

Table 1 : Polymer characteristics

Samples	Origin	Saponification degree % mole	meso diad % mole	$\overline{Mv}$
R 14/135	R-P	86.7	47.5	87000
R 20/140	R-P	87.6	52.7	155000
J 125	Janssen	97.9	48.6	173000

Samples	$\overline{Mw}$	I poly-dispersity	$[\eta]$ ml/g	C* g/l
R 14/135	73000	1.7	65.5	15.3
R 20/140	145000	1.6	91.6	12.5
J 125	160000	2.2	102.4	11.8

RESULTS

A crucial parameter for the gelation onset is the overlap concentration C* beyond which polymer- polymer entanglements became important. The overlap concentration was determined classically from the variation of the specific viscosity of polymer solutions versus the adimensional parameter $[\eta]C$ (6) ($[\eta]$, intrinsic viscosity, C polymer concentration).

Phase diagrams

In water, only two phases were observed :a sol for solutions diluted in borax or PVA, homogeneous gel in a large range of concentrations (Fig. 1). For a given polymer concentration, the borax concentration at the threshold increases with temperature. Phase diagrams from different temperature and PVA molecular weight samples merge in a single diagram by plotting the free borate concentration against the reduced polymer concentration, C/C* (Fig.2).

In salt solution (0.25 Mole/l Na Cl), a third zone (demixed gel) appears if PVA and borax concentrations are large enough. For a given polymer concentration C (C>C*), the formation of an homogeneous gel is first observed by increasing the borate amount in the system . Above a critical concentration in borate, a kind of syneresis is observed : first the whole mixture becomes turbid, but progressively, a solution is expelled and the equilibrium is reached. Finally, a white dense gel phase and a sol are obtained. In dilute solution, the polymer chains precipitate slowly and then, after a very dense and turbid gel is formed surrounded by a diluted polymer sol.

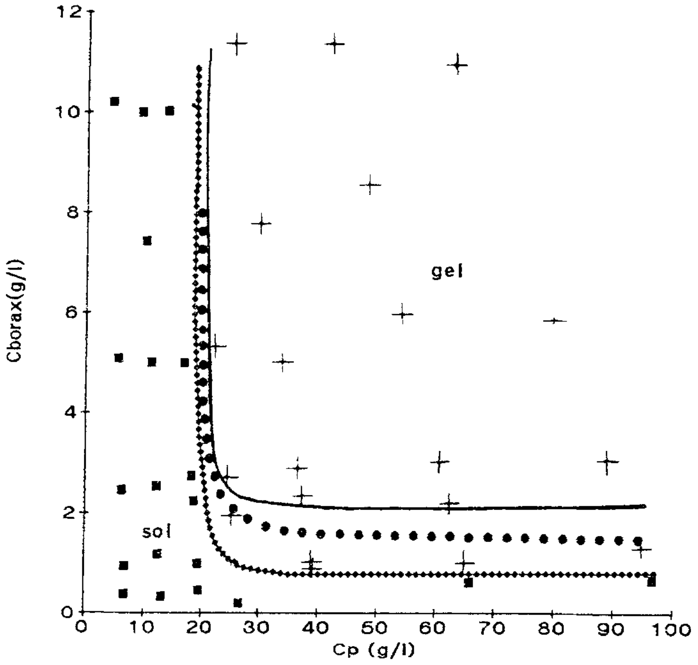


Fig. 1 : Phase diagram PVA (J 125) borax-water systems at various temperatures

——— t = 40°c ● ● ● ● t = 20°c ++++++ t = 9°c

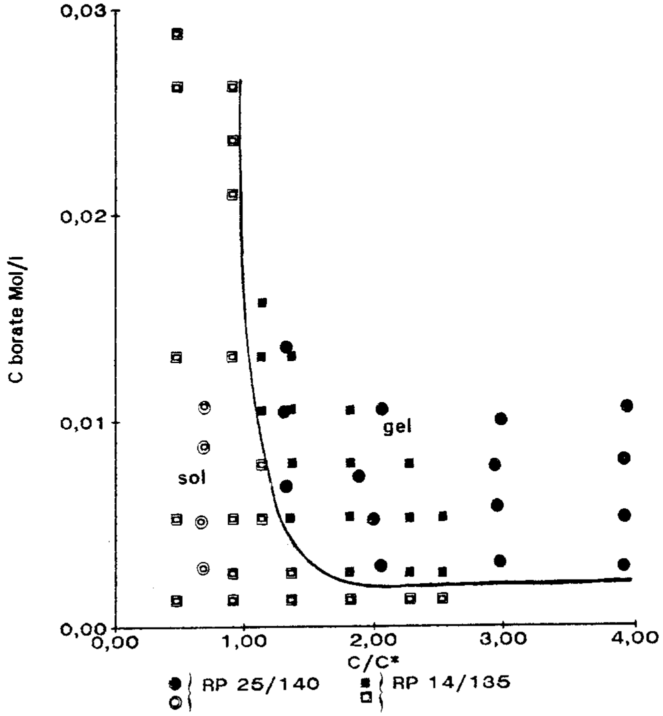


Fig. 2 : PVA-borax-water systems : sol-gel transition superposition for different polymer molecular weights.

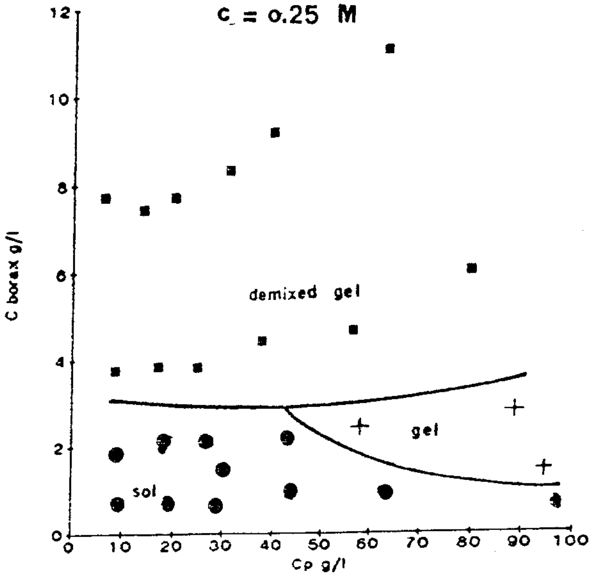
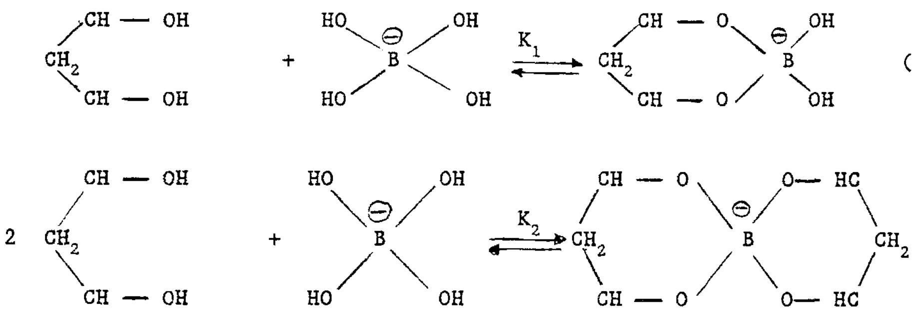


Fig. 3 : PVA (J 125) borax-saline solution systems at 20°c

DISCUSSION

Gel formation

The most important parameter for both gelation and demixing is the number of crosslinks formed in the system. PVA-borax interaction leads to charged monodiol borate complexes and didiol borate complexes (II) which play the role of tie points for the physical network. The reactions are schematized below :



(I)

(II)

SINTON reported that only mesodiads are complexable .^{11}B NMR measurements lead to the equilibrium constants K_1 , K_2 in dilute solution. In fact, it is very difficult to determine the interpolymer dicomplexation, because the signal becomes very broad when the viscosity of the sample increases and that the signal results from the sum of interchain and intrachain dicomplexes. Nevertheless, for a fixed polymer concentration, the crosslink concentration must stay proportional to the free borate concentration . Moreover, the tie points are proportional to the intercontact polymer in semidilute solution and scale like $C^3 /^3 \; ^{-1}$ where ν is the swelling exponent relating the gyration radius and the chain molecular weight (ν=3/5 for a good solvent). The number of crosslinks depends on temperature by the enthalpy of dicomplexes formation. The total number of crosslinks is related to the product of three probabilities ; interchain contact, borate on the site for dicomplexes formation, temperature sufficiently low to form a dicomplex. (see ref. 4).

$$Nt \approx \left| B^- \right| \times C^{3\nu/3\nu-1} \exp^{-\Delta H_2 /RT} \qquad [1]$$

Gelation is reached for one crosslink per chain. Dividing the number of crosslinks by the number of chains in solution, we find :

$$p = \text{total crosslink number per chain} \approx M \left|B^-\right| C^{1/(1-3\nu)} \exp^{-\Delta H_2/RT} \qquad [2]$$

We call $|B|g$ the threshold concentration above which gelation takes place.

$$|B|g \approx M^{-1} \; C^{-1/(1-3\nu)} \; \exp^{\Delta H_2/RT} \qquad [3]$$

An estimation of the enthalpy of formation ΔH_2 have been made by plotting $|B|g$ as a function of 1/T (fig 4). The straight line, with a negative slope, indicates that complexation reactions are exothermic. The corresponding enthalpy in good agreement with data reported by other authors (Table 2). It is very difficult to determine the concentration dependance as function of polymer concentration (expected law in $C^{-1/(1-3\nu)}$) because we got a poor precision on $|B|g$ measurements.

The threshold borate concentration decreases for a given polymer concentration when the polymer molecular weight increases as it is expected from relation [3]. Data from several PVA samples of different molecular weight can be superposed to obtain a master curve giving the variation of the free borate concentration versus the reduced concentration of polymer in agreement with the Pezron's results for the galactoman/borax system.

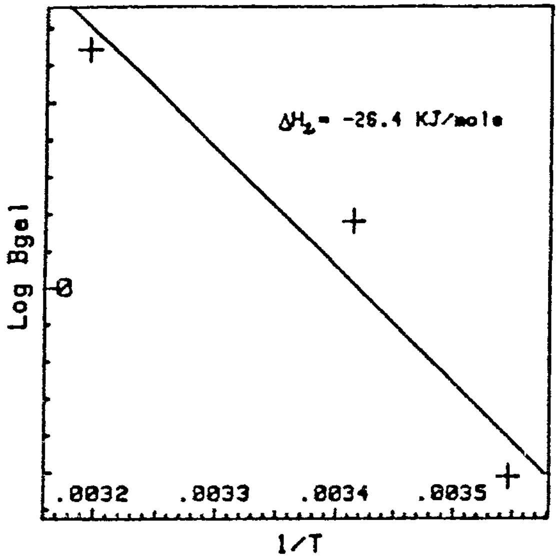


Fig. 4 : Variation of ln B_{gel} versus $1/_T$

Table 2 : Enthalpy values of dicomplex formation

authors	H kJ/mole	Ref	exp. techn.
Sinton	-34.7	10	B NMR
Shultz	-25.08	11	Elasticity
Shibayama	-20.9 to -33.4	12	Tg measurement
this work	-26.3		

Demixing

The crosslink number stays small and the average length between network tie points is estimated to be long enough to expect a swollen state for the chain between crosslinks. The salt screens the electrostatic repulsion and more dicomplexes can be formed in saline solution. Complexation induces more correlation between monomers and Rx (the end to end distance between two tie points) must be lower than ξ (the correlation length in semidiluted solution) :

$$\xi = C^{-\nu/(3\nu-1)}$$

For a sufficiently high borate concentration, the number of dicomplexes is higher than the natural interpolymer contacts, in that case the system demixes equalazing the number of dicomplexe and the natural interchain contacts. This situation is similar to a chemical gel at the swelling equilibrium (C* Theorem) (7). The PVA concentration when demixtion occurs is :

$$C \approx (M/p)^{1-3\nu} \qquad [4]$$

We call $|B|$ dem this critical concentration.
By combining [4] et [2], we find :

$$|B| \text{ dem} \approx \exp + \left(\frac{\Delta H_2}{RT} \right) \qquad [5]$$

In semi-dilute solution $|B|$dem seems to be only dependent on temperature and with the previous value $|B|$dem must increase with temperature. In dilute solution, the situation is not so clear, the excluded volume interactions are not screened like in semidilute solution. $|B|$dem is a complicated function of molecular weight and polymer concentration.

These results are in good agreement with previously data reported on galactomanan-borate system (4), (13)

This data treatment can be generalized to other systems of chains reticulated by a complexing ion agent like polyacrylamide - Cr^{3+} (8) or acrylic acid-acrylamide copolymers-Al^{+3}. All the phase diagrams are superposable by the plotting crosslink number against the reduced concentration C/C^{*}.

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