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# The poly(vinyl alcohol)–borate system: influence of polyelectrolyte effects on phase diagrams

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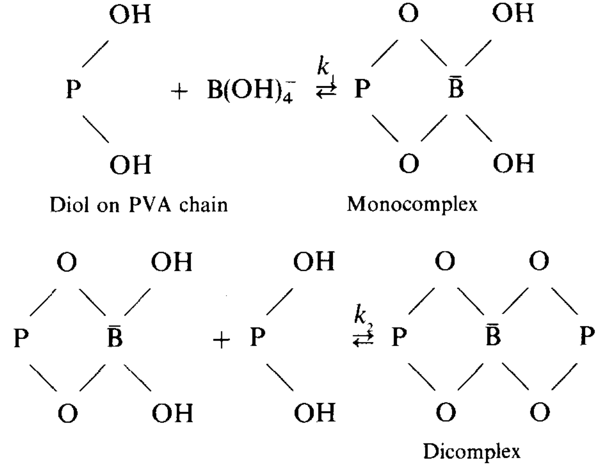
The formation of a reversible gel by complexation of borate ions with poly(vinyl alcohol) is described. The complexation induces electrostatic charges on the polymeric chains. We focus on the behaviour of the system when the charges are partially screened by a passive salt. In such a case, 're-entrant phases' can be observed; they result from a delicate balance between the electrostatic repulsions among charged complexes formed on the polymeric chain and the crosslinking induced by borate ions. We present here an interpretation of the phase transitions based on a thermodynamic approach.

**(Keywords: gel; poly(vinyl alcohol); borate ions)**

## INTRODUCTION

Hydrosoluble polymers that can form reversible gels by ion complexation have received much attention because these materials have attractive physicochemical properties and industrial interest. For example, polyhydroxy compounds and borate ions find applications in the oil industry as fracturing fluid[1]. Borate ions have long been known to form reversible complexes with poly(vinyl alcohol) (PVA)[2-4]. The complexation reaction can be described by



The formation constants for these two reactions are respectively $k_1$ for the formation of the monocomplexes and $k_2$ for the dicomplexes. The behaviour of the PVA–borate system has been reported by Keita and Ricard[5] in a previous paper and more recently by Kurokawa *et al.*[6]. The kinetics of complex formation between hydroxylated species and borate ions have been investigated using the temperature jump method[7-9]. It has been shown that the formation of the complex is fast, which is unusual in the domain of gels and complexing polymers. Indeed, the system described here is at equilibrium in a few minutes. Given a rest time of some hours for the samples, true thermodynamic equilibria are reached, and according to the conditions a sol, a physical gel or a demixed phase is obtained. A qualitative interpretation of this behaviour is given. A description of the zones where these three different situations are observed in a PVA–borate concentration diagram, or state diagram, is also given. This state diagram depends on temperature, ionic strength, and polymer and borate concentrations. In the absence of a passive salt, only gelation is observed; when there is an excess of passive salt, gelation and demixing can occur. We examine here the situation where the concentration of the added passive salt is not sufficient to screen the polyelectrolyte effect entirely.

In this article we first present state diagrams at a fixed salt concentration. The kinetics of diol–borate complex formation being fast, we propose a thermodynamic approach to describe the observed phenomena. Then we compare the theoretical variations in free borate ion concentrations needed for the onset of demixing of a semi-dilute poly(vinyl alcohol) solution with experimental results at different salt concentrations.

## EXPERIMENTAL

### *Materials*

PVA samples were supplied by Janssen Chimica and Rhône-Poulenc, respectively referenced J125 and R20/140 in this paper. They were purified by ultrafiltration and

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**Table 1** Polymer characteristics

| Sample | $\bar{M}_w$[a] | $\bar{M}_w/\bar{M}_n$ | Degree of hydrolysis | $C^{*b}$ (g l$^{-1}$) |
|---|---|---|---|---|
| R25/140 | 145000 | 1.6 | 88 | 12.5 |
| J125 | 160000 | 1.6 | 98 | 11.8 |

[a] Determined by size exclusion chromatography alongside low angle light scattering and differential refractometry

[b] Determined from viscometry or polymer concentration diagrams

freeze dried. *Table 1* gives the characteristics of these polymers. The OH and OAc sequence lengths determined by $^{13}$C n.m.r. for sample R were respectively 25 and 2. The degree of hydrolysis was not the same for the two samples, but this is not a determining parameter for the polymer behaviour in the presence of borate ions. Indeed, we checked that the same state diagram is obtained with different molecular weight samples and observed a slight shift of the homogeneous zone to higher polymer concentrations. Sodium chloride and borax (Prolabo) were used without further purification.

The desired amounts of PVA powder were dissolved in deionized water (from the Milli Q system of Millipore) by heating. The actual polymer concentrations were determined by total organic carbon analysis (Dohrmann/Xertex DC 80).

### *Viscometry*

Viscosity measurements were performed on a low shear Contraves 30 rheometer.

### *State diagrams*

The 5 ml samples were prepared by mixing adequate amounts of poly(vinyl alcohol), borax and NaCl solutions. The systems were thoroughly stirred and then allowed to rest in a thermostatted bath for 48 h. The polymer concentration in the gel after demixing was determined as follows. The polymer concentration in the upper phase was obtained by total organic carbon analysis, then the polymer concentration in the gel was the difference between the overall polymer concentration and the polymer concentration in the sol, taking into account the densities of both phases. It may be difficult to distinguish between a sol and a reversible gel phase. We defined the gelation threshold as the point when the biggest temporarily crosslinked cluster occupied the whole vial volume. To determine this threshold approximately, two methods were used. In the first method, we measured the viscosity of the poly(vinyl alcohol)–borax–NaCl system and assumed that the gelation threshold had been reached when a drastic increase in viscosity was observed. The second method was inspired by the studies of Candau *et al.*[10] of an irreversible gelation transition and has been described before[11]. The speckled pattern from the sample when lighted by a laser beam and observed at low scattering angle fluctuates randomly in the sol phase, but no fluctuation is seen in the gel phase. Both methods give the same results.

## STATE DIAGRAM AT CONSTANT SALT CONCENTRATION

In previous work, Pezron and coworkers[11,12] investigated a similar system. They worked on galactomannan aqueous solutions containing borax and described the properties of such systems, in particular their state diagrams, according to a theoretical Flory-type model. Demixing results from the competition between the gain of energy when crosslinks are formed, the entropy decrease when the local monomer concentration increases and electrostatic repulsion between charged, complexed sites. Alternatively, the demixing results can be interpreted as changes in the equilibrium degree of the temporary network when crosslinking and repulsion between charges caused by complexation compete.

For the PVA–borate ion system Leibler *et al.*[13] discussed complexation equilibria, polyelectrolyte effects and reversible crosslinking. They showed that the dimensions of the individual polymer chains can be described by the elastic energy, the excluded volume effect and the electrostatic potential.

The state diagram of the PVA–borate system in 0.15 mol l$^{-1}$ NaCl aqueous solution is given in *Figure 1*. Four domains can be distinguished for a borate concentration lower than 0.1 mol l$^{-1}$ and a polymer concentration lower than 0.8 mol$^{-1}$ (i.e. moles of repeat unit per litre).

For low polymer and borate concentrations, the system is characterized by a sol. For a solution containing 0.8 mol l$^{-1}$ PVA and 0.15 mol l$^{-1}$ NaCl, the different situations encountered when the borate concentration is increased are described in *Figure 1*. The polymer concentration being higher than the overlap chain concentration $C^*$, the number of interchain contacts is much greater than one per macromolecule. So, when the borate concentration becomes adequate to ensure one intermolecular crosslink per chain, the onset of gelation occurs. The gel is then homogeneous because the mean distance $R_x$ between two dicomplexes is larger than the correlation length $\xi$ of the semidilute PVA solution. The gradual addition of borate makes $R_x$ decrease rapidly because the number of complexed sites increases. When $R_x$ becomes lower than $\xi$, demixing occurs and the gel does not fill the whole volume. Nevertheless, the gel

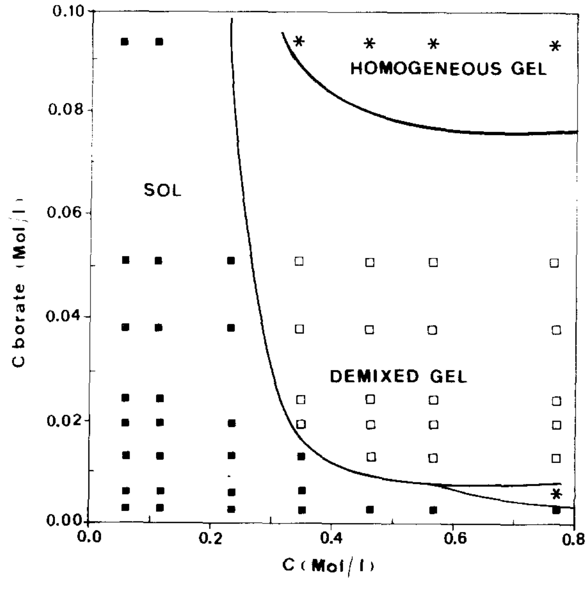

**Figure 1** Phase diagram of the PVA–borate system in 0.15 mol$^{-1}$ NaCl aqueous solution at 20°C (PVA R20/140): (■) sol; (□) demixed gel; (∗) homogeneous gel

expansion does not depend only on the number of crosslinks but also on the distance between the charged sites smeared on the chains: when the distance between two charged sites decreases and becomes comparable to the screening length (Debye length), which depends on the ionic strength, the ionic complexes repel, the gel swells and the system again becomes homogeneous for high borate concentrations.

The properties of such systems, in particular their state diagrams, have been described by Pezron *et al.* according to a theoretical Flory-type model for the borate–galactomannan system[11]. The volume of the gel results in the delicate balance between electrostatic repulsion and attraction through crosslinking.

## FREE ENERGY OF THE SYSTEM: PREDICTION OF A 'RE-ENTRANT PHASE'

A 're-entrant phase' is observed when borate ions are added to a solution of a polyhydroxy polymer. First, a homogeneous gel is formed. With further addition of borate, the gel will demix, then it will be homogeneous again and it will demix with an excess of borate. The 're-entrant phase' corresponds to a demixed gel–homogeneous gel transition.

'Re-entrant phases' have already been observed in galactomannan–borax systems (galactomannans are also polyhydroxy polymers) and described using a Flory-type approach[9,14]. We briefly sum up this approach which is limited by several assumptions: (1) the ion binding on the polyelectrolyte is neglected[12]; (2) the Donnan equilibrium term is not taken into account, which is reasonable; and (3) heterogeneous crosslinking, which is related to the polymer tacticity, is not taken into account. For solutions of rather low ionic strength, so that the polyelectrolyte effect is not entirely screened, the free energy of a semidilute polyol solution containing borate ion may be expressed as the sum of three terms: $F_{\mathrm{pol}}$, the free energy of a semidilute solution of neutral polymer; $F_{\mathrm{el}}$, the free energy which results from electrostatic repulsion; and $F_{\mathrm{comp}}$, the free energy for the formation of intermolecular dicomplexes. The last of these is proportional to the product of the number of dicomplexes and the energy ($kTE$) won by the formation of a dicomplex. So

$$F|_{\mathrm{volume\,unit}} = F|_{\mathrm{pol}} + F|_{\mathrm{compl}} + F|_{\mathrm{el}}$$

and

$$\frac{F|_{\mathrm{pol}}}{kT} = \frac{1}{2}v(1-f)C^2N_{\mathrm{A}}^2 + \frac{1}{6}w^2(1-f)^3C^3N_{\mathrm{A}}^3$$

where $v$, $w^2$, $(1-f)$ and $C$ represent, respectively, the excluded volume interaction parameter of the polymer, the third virial coefficient, the free site fraction and the polymer concentration in moles per unit volume of the polymer. $N_{\mathrm{A}}$ is the Avogadro constant. Also

$$\frac{F|_{\mathrm{comp}}}{kT} = -k_2f(1-f)C^2N_{\mathrm{A}}E$$

where $k_2$ is the formation constant of the dicomplex, and the concentration of these dicomplexes $[\mathrm{BP}_2^-]$ is given by

$$[\mathrm{BP}_2^-] = k_2f(1-f)C^2$$

which corresponds to the reaction of a singly complexed site with a free site on a polymeric chain. In addition

$$\frac{F|_{\mathrm{el}}}{kT} = \frac{1}{2I}f^2C^2N_{\mathrm{A}}$$

where $I$ is the ionic strength. The fraction of complexed sites $f$ is directly linked to the complexation equilibria. When monocomplexes ($\mathrm{BP}^-$) and dicomplexes ($\mathrm{BP}_2^-$) are formed on a polymeric chain, it can be seen[11] that the number of borate units involved in the complexation is proportional to the free borate concentration $[\mathrm{B}^-]$ and the uncomplexed polymer unit concentration $[\mathrm{P}]$

$$[\mathrm{BP}^-] + [\mathrm{BP}_2^-] = \tilde{K}[B^-][P]$$

where $\tilde{K}$ is a global complexation constant, the value of which depends on the ionic strength of the medium[12]. The limit value at very high ionic strength is given the symbol $\tilde{K}_0$.

Since $[\mathrm{P}] = (1-f)\mathrm{C}$ and $[\mathrm{BP}^-] + [\mathrm{BP}_2^-] = f\mathrm{C}$

$$f = \frac{\tilde{K}|[\mathrm{B}^-]|}{1+\tilde{K}|[\mathrm{B}^-]|}$$

and

$$\frac{F}{kT} = \frac{1}{2}v(1-f)^2C^2N_{\mathrm{A}}^2 + \frac{1}{6}w^2(1-f)^3C^3N_{\mathrm{A}}^3 - k_2f(1-f)C^2N_{\mathrm{A}}E + \frac{N_{\mathrm{A}}}{2I}f^2C^2 \qquad (1)$$

The $C^3$ term can be neglected in a first approach. Assuming that the borate ion and salt concentrations ($[\mathrm{B}^-]$ and $C_{\mathrm{s}}$, respectively) are the same in all phases, we can assume that the variables $C$, $[\mathrm{B}^-]$ and $C_{\mathrm{s}}$ are independent. Gel demixing is obtained when the second derivative of the free energy with respect to polymer concentration is equal to 0. Thus, the following relationship can be derived

$$\frac{1}{2}v(1-f)^2N_{\mathrm{A}} - k_2f(1-f)E + \frac{1}{2I}f^2 = 0 \qquad (2)$$

For any ionic strength and $[\mathrm{B}^-]$ value, $\tilde{K}$ can be estimated[9] and then $f$ (equation (1)). The $f$ value is then introduced into equation (2) and by iteration the root which verifies the equation is found. This corresponds to the demix fraction $f_{\mathrm{dem}}$. From this value, $[\mathrm{B}^-]_{\mathrm{dem}}$ is calculated. For each ionic strength and passive salt concentration, $[\mathrm{B}^-]_{\mathrm{dem}}$ is obtained. For each ionic strength and passive salt concentration, $[\mathrm{B}^-]_{\mathrm{dem}}$ and other concentrations in demixing conditions can then be estimated.

This model predicts a 're-entrant phase' for very low salt concentrations; that is, for a salt concentration low enough so that the polyelectrolyte effect is no longer neglected. In this situation three gel transitions, homogeneous to demixed, are expected when the borate concentration is increased.

## 'RE-ENTRANT PHASES': EXPERIMENTAL RESULTS AND COMPARISON WITH THEORETICAL PREDICTIONS

The state diagram for the PVA–borate system at constant temperature and polymer concentration ($T = 20°C$, $C = 0.91\ \mathrm{mol\,l^{-1}}$) is given in *Figure 2*, where the borate concentration is shown *versus* the salt concentration.

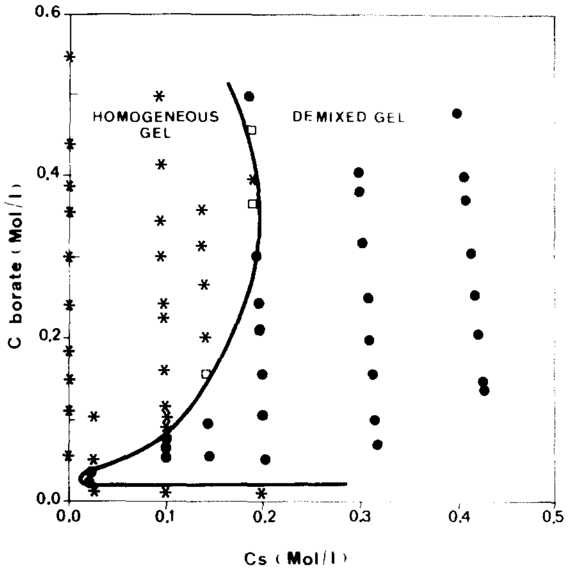

**Figure 2** Phase diagram for PVA–borate solutions at a constant polymer concentration ($C = 0.91\,\mathrm{mol\,l^{-1}}$) and 20°C (PVA J125) for various NaCl concentrations: (∗) homogeneous gel; (□) opaque gel; (●) demixed gel

When the borate concentration is increased, a homogeneous gel is obtained. Then, a demixing threshold is reached when more borate is added; beyond this, an opaque gel and a low viscosity sol coexist. As the model presented in the previous section predicts it, if the salt concentration is not too high, the electrostatic repulsions between the complexes bound to the chains are no longer screened and the demixed gel tends to expand. With a further addition of borate, which induces an increase in the number of charges on the chains, the demixed system can again become homogeneous. Thus, the gel fills the whole sample volume.

Without a passive salt, the transition homogeneous gel–demixed gel ('re-entrant phase'), which is expected from theoretical data for a high borate concentration, is never observed because the solubility limit of borate has been reached. *Figure 3* gives our experimental results and the data calculated from equation (2). The parameters $E$ and $\tilde{K}_0$ were estimated experimentally and $k_2$ chosen for the best experimental fit. This value is in the region of the corresponding association constant when homologous small molecules are involved[9]. Ths values of the parameters are $k_2 = 0.35\,\mathrm{mol^{-1}\,l}$, $E = \Delta G/RT = 3.1$, $\tilde{K}_0 = 40\,\mathrm{mol^{-1}\,l}$ and $v = (7 \times 10^{-10})^3\,\mathrm{m^3}$. $\tilde{K}_0$ is the complexation constant in the absence of electrostatic effects (in a large excess of passive salt). There is good agreement between experimental data and theory.

The variation of the 're-entrant phase' with temperature is shown in *Figure 4.* The homogeneous gel domain increases with temperature. The maximum concentration corresponds to the limit of the polyelectrolyte effect and increases with temperature: at 2°C it is only $0.13\,\mathrm{mol\,l^{-1}}$, while at 20°C it is slightly above $0.2\,\mathrm{mol\,l^{-1}}$. The results can be predicted qualitatively by taking into account the variations in $k_2$, $\tilde{K}$ and $E$ with temperature.

## VARIATION OF THE POLYMER CONCENTRATION IN THE DEMIXING ZONE OF THE 'RE-ENTRANT PHASE'

The osmotic pressure $\Pi$ in the gel can be expressed simply as

$$\Pi = C\frac{\partial F}{\partial C} = \left[v(1-f)^2C^2N_A + \frac{1}{2}w^2(1-f)^3C^3N_A^2 - 2k_2f(1-f)C^2E + \frac{f^2C^2}{I}\right]RT \qquad (3)$$

When demixing occurs, the demixed gel is in equilibrium with the sol. The polymer concentration in the gel is calculated under the assumption that the polymer concentration in the surrounding solution is low and that there is no osmotic pressure difference between the two phases ($\pi = 0$). The solution to equation (3) can be calculated for each borate concentration. The variation of the polymer concentration in the more concentrated phase *versus* the borate concentration is shown in *Figure 5*. Experimentally, the polymer concentration in the gel, after the onset of demixing, is calculated as the difference between the total polymer concentration and the polymer concentration in the sol (determined by total organic carbon analysis), taking into account the density of each phase.

Results for two different salt concentrations ($C_s = 0.07$ and $0.1\,\mathrm{mol\,l^{-1}}$) are given in *Figures 6* and *7*. For a given total borate concentration, represented on the $y$ axis, the $C/C_0$ ratio is plotted on the $x$ axis, where $C$ is the polymer concentration in the phase of interest and $C_0$ is the total polymer concentration. When this ratio is equal to 1, there is only one phase – the homogeneous gel. When two phases exist, the polymer concentration in the sol is low and $C/C_0$ is less than 1. Conversely, in the collapsed gel, which is polymer-rich, this ratio is larger than 1.

Closed diagrams have been obtained in the first demixing zone of the 're-entrant phase'. At constant temperature, the area of the closed zone decreases with increasing salt concentration because the difference between the limits of the demixing zone is reduced as the salt concentration increases (*Figure 2*). As the temperature

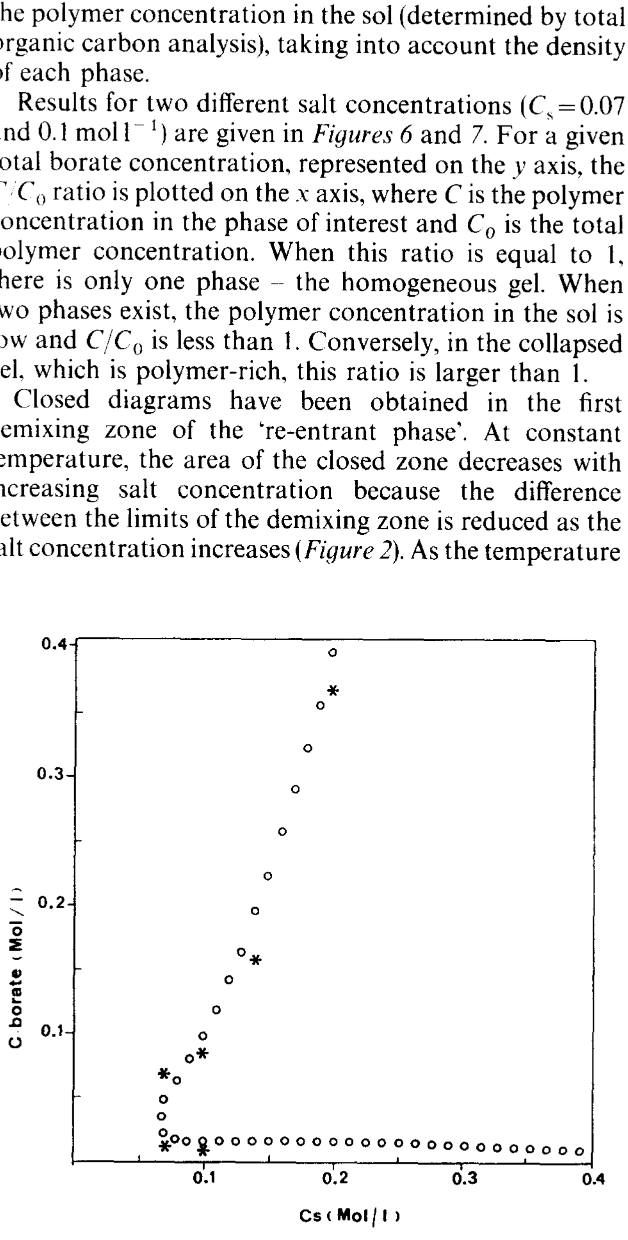

**Figure 3** Variation with NaCl concentration of the borate concentration at the onset of demixing at a constant polymer concentration ($C = 1\,\mathrm{mol\,l^{-1}}$) and 20°C ($k_2 = 0.35\,\mathrm{mol^{-1}\,l}$, $E = \Delta G/R\bar{T} = 3.1$, $\tilde{K}_0 = 40\,\mathrm{mol^{-1}\,l}$ and $v = (7 \times 10^{-10})^3\,\mathrm{m^3}$): (○) data calculated from equation (2); (∗) experimental data

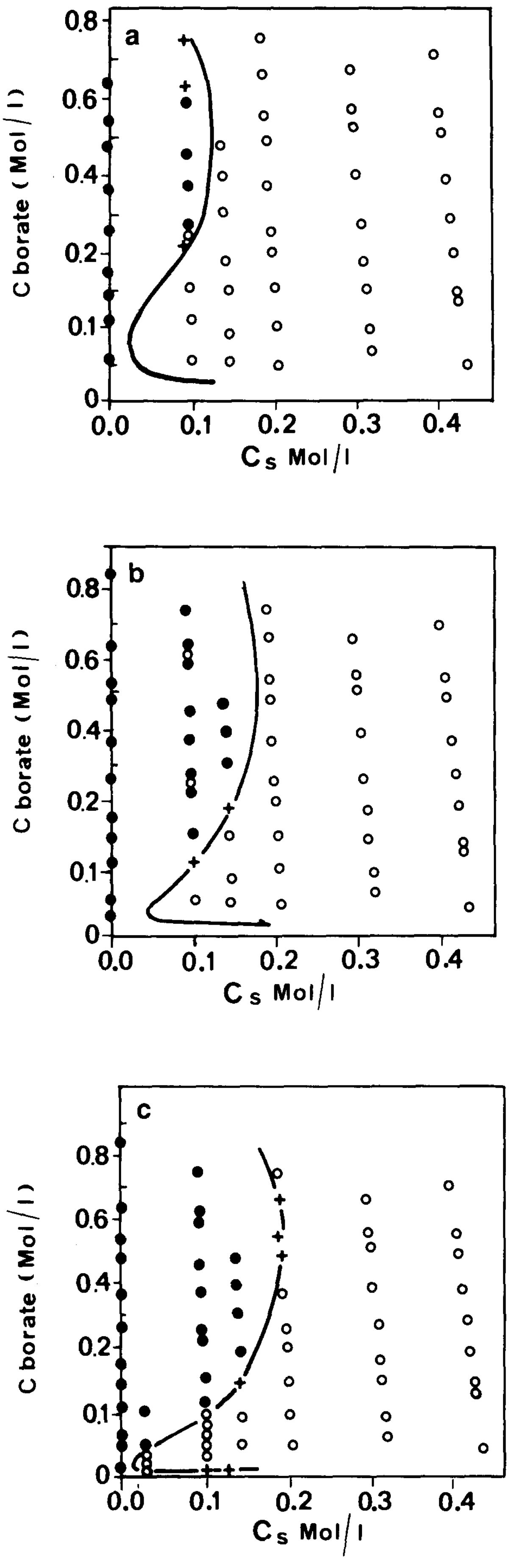

Figure 4 Influence of temperature on the 're-entrant phase' domain: (a) 2°C; (b) 10°C; (c) 20°C. (●) Homogeneous gel; (+) opaque gel; (○) demixed gel

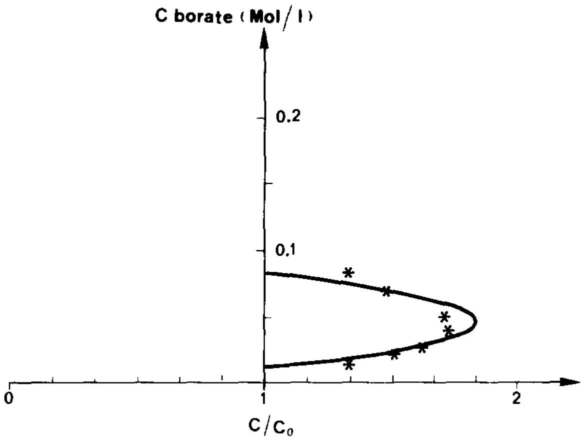

Figure 5 Prediction of the variation in polymer concentration in the demixed phase with borate concentration in the solution at a constant salt concentration ($C_s = 0.1\,\mathrm{mol\,l^{-1}}$), where $C/C_0$ is the ratio of the polymer concentration in the gel phase to the initial polymer concentration: (∗) experimental data; (——) theoretical curve derived from equation (3)

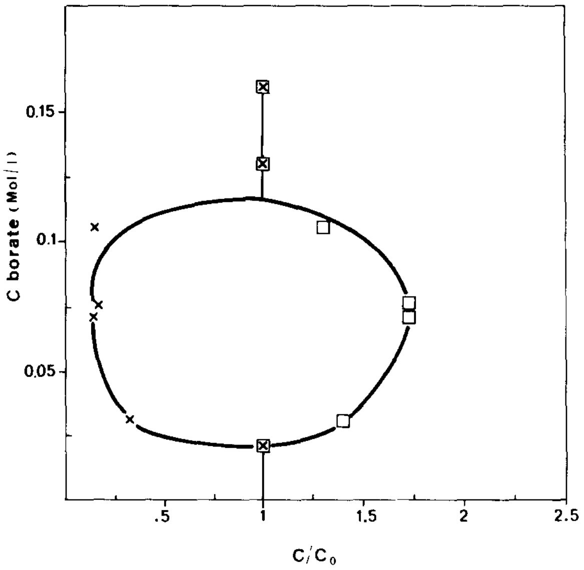

Figure 6 Variation in polymer concentration in the demixed gel phase with borate concentration in the solution at a constant salt concentration ($C_s = 0.07\,\mathrm{mol\,l^{-1}}$) and 20°C, where $C/C_0$ is the ratio of the polymer concentration in the gel phase to the initial polymer concentration: (×) polymer concentration in the sol; (□) polymer concentration in the gel

increases from 20 to 32°C (*Figure 7*), this closed domain decreases according to the variation of the demixing curves with temperature. Indeed, the range of borate concentrations for which the demixed gel exists decreases as the temperature increases (*Figure 4*). These results are in agreement with the theoretical predictions when $\tilde{K}$, $k_2$ and $E$ are varied to calculate the polymer concentrations at other temperatures from equations (1) and (3).

## CONCLUSION

In the semidilute regime, when the charges induced by borate complexation with PVA are not completely screened by the addition of a passive salt, a polyelectrolyte effect can induce a 're-entrant phase': the homogeneous gel can shrink when borate is added, leading to the onset of demixing. Then, the addition of more borate

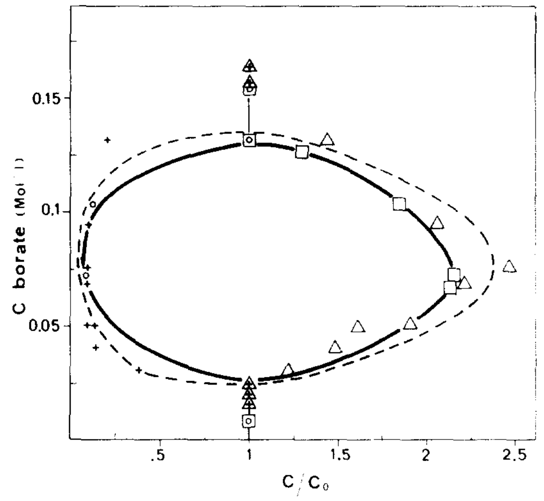

**Figure 7** Variations in polymer concentration $C$ in the demixed gel phase and in the sol phase with borate concentration in the solution for a total polymer concentration $C_0$ and a constant salt concentration ($C_s = 0.1\ \mathrm{mol\,l^{-1}}$): (+) polymer concentration in the sol (20°C); (△) polymer concentration in the gel (20°C); (○) polymer concentration in the sol (32°C); (□) polymer concentration in the gel (32°C). The lines are for guidance only

ions can again yield a homogeneous gel. The PVA–borate systems which can form reversible gels depend on many parameters. It is difficult to take into account all of these parameters, and we have proposed a mean-field theory using reasonable assumptions. Indeed, the experimental results are nicely described by a Flory-type approach expressing the competition between Coulombic repulsions among borate macrocomplexes and crosslinking induced by dicomplexes.

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