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Polyelectrolyte behaviour of poly(vinyl alcohol)-boric acid complexes

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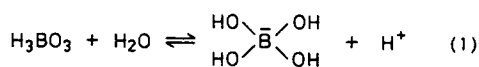
The polyelectrolyte behaviour of poly(vinyl alcohol)-boric acid complexes is investigated. A plateau is observed in the dependence of pK_a on the degree of neutralization, while the HENDERSON-HASSELBACH plots show two linear regions with different slope related to two different macroconformations. The complexes undergo a transition to an extended rigid conformation when neutralized in aqueous solution determined by decreased flexibility of the chain and charge acquisition.

Polyelektrolytisches Verhalten von Poly(vinylalkohol)-Borsäure-Komplexen

Das polyelektrolytische Verhalten von Poly(vinylalkohol)-Borsäure-Komplexen wurde untersucht. In Abhängigkeit des pK_a -Wertes vom Neutralisierungsgrad wurde ein Plateau gefunden, während in der HENDERSON-HASSELBACH-Darstellung zwei lineare Bereiche mit unterschiedlicher Steigung auftraten, die zu zwei verschiedenen Makrokonformationen gehören. Bei der Neutralisierung in wässriger Lösung erfolgt, bedingt durch die verringerte Biegsamkeit der Ketten und die Ladungsaufnahme, ein Übergang der Komplexe in die starre, gestreckte Kettige Konformation.

1. Introduction

It is well known that the viscosity of poly(vinyl alcohol) (PVAL) solutions increases and that the solutions gelatinize, when certain low-molecular substances are introduced. Borax is one of the most familiar additives. Boric acid can be considered as Lewis acid, the dissociation of which takes place with the attachment of one water molecule (Scheme 1) [1].

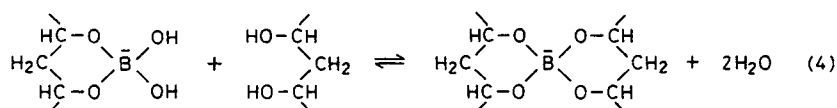
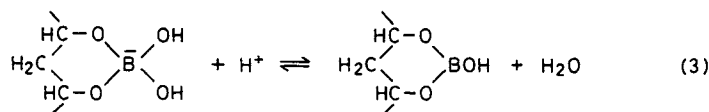
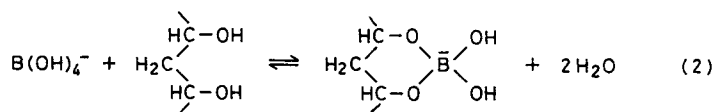


Scheme 1

The formation of complexes of polyvalent alcohols (containing hydroxyl groups in 1,2- and 1,3-positions) with boric acid can be presented by the Scheme 2 [2]. In an acid medium (eq. (1)) the equilibrium is drawn to the left. On alkali titration the equilibrium is in fact practically drawn to the right. This brings about the formation of complexes according to equations (2) and (4).

In analogy to the reactions of low-molecular polyvalent alcohols DEUEL and NEUKOM [3] admit that the boric acid forms with PVAL a monodiol (1:1), while with borax didiol (2:1) complexes are formed, which provide crosslinking. This determines the gelatinization of the solutions in an alkaline medium.

SAITO et al. [4] studied the complex formation of PVAL by applying the method of equilibrium dialysis. Only part of the



Scheme 2

boric acid is linked and the type of linkage is monodiol eq. (3). The ^{11}B -NMR study of the reaction of PVAL with boric acid at $\text{pH} = 5$ and 11 shows that the reaction product is a monodiol complex [5]. The gel obtained on neutralization of PVAL-boric acid complexes is heterogeneous [6].

In the present work the polyelectrolyte behaviour of PVAL-boric acid complexes is studied.

2. Experimental

PVAL of molecular weight 50000 and residual acetate groups of 1.5% is used. The polymer is completely saponified, purified by dialysis, reprecipitated with methanol-acetone (1:1) and dried i.vac.

The polymer solutions of concentration 0.13% at different molar ratios are titrated under nitrogen at 298 K and ionic strength 0.02 and 0.10 (KCl). Laboratory digital pH-meter Radelkis OP 211/1 with calomel and glass electrodes is used. 0.1 N KOH, free from carbonates, is used as titrant.

3. Results and discussion

Potentiometric titration of solutions with molar ratios boric acid : PVAL in the range 0.05 to 0.25 as well as in the presence of mannite as a complexing agent have been carried out. As the complexes are very weak acids, the equivalent point is determined using the method of INGMAN and STILL [7]. The experimental data are treated using nomographical scales [8]. The function of INGMAN F' is linear only in the case of the molar ratio 0.05 (Fig. 1). Two linear regions are observed at molar ratios in the range of 0.10 to 0.25.

One of the curves of the potentiometric titration is presented on Fig. 2. All curves obtained are of the form characteristic for very weak acids; most of the experimental points are of pH values above 8.

The polyelectrolytic behaviour is studied using the equation of HENDERSON-HASSELBACH:

$$\text{pH} = \text{pK} - \lg \frac{1 - \alpha}{\alpha} \quad (1)$$

$$\text{where } K = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad \alpha = \frac{[\text{A}^-]}{[\text{HA}] + [\text{A}^-]}$$

The pK of the polymer acids depends on the degree of neutralization [9]. The variation of pK with α is determined by the electrostatic and conformational free energy [10, 11]:

$$\text{pK}_a = \text{pH} + \lg \frac{1 - \alpha}{\alpha} = \text{pK}_0 + \frac{0.434}{RT} \frac{\partial G_{el}}{\partial Z} \quad (2)$$

Some dependences of pK on the degree of neutralization are presented on Fig. 3. $\text{pK}_0 = 8.8$ (ionic strength 0.10, molar ratios in the range 0.05 to 0.25) is determined by extrapolating the curves. At molar ratios 0.10 to 0.25 two regions are observed — one of linear increase of pK and a plateau. These curves differ from the known curves for poly(methacrylic acid) [9, 10, 12], where a third region, i.e. a new linear increase of pK , is observed. At the same time they are similar to the curves obtained on titration of phenol and of amino groups in the side chain of serum albumin [13]. These dependences together with the results of the hydrodynamic investigation are interpreted as being determined by the disentanglement of the macromolecules [9].

Viscosimetric investigations of aqueous solutions of PVAL-borax complexes have been carried out by MURA-

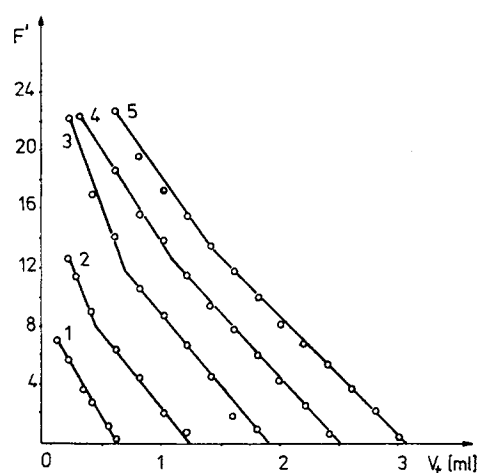


Fig. 1. INGMAN functions for H_3BO_3 -PVAL complexes. Molar ratios: 1 — 0.05; 2 — 0.10; 3 — 0.15; 4 — 0.20; 5 — 0.25

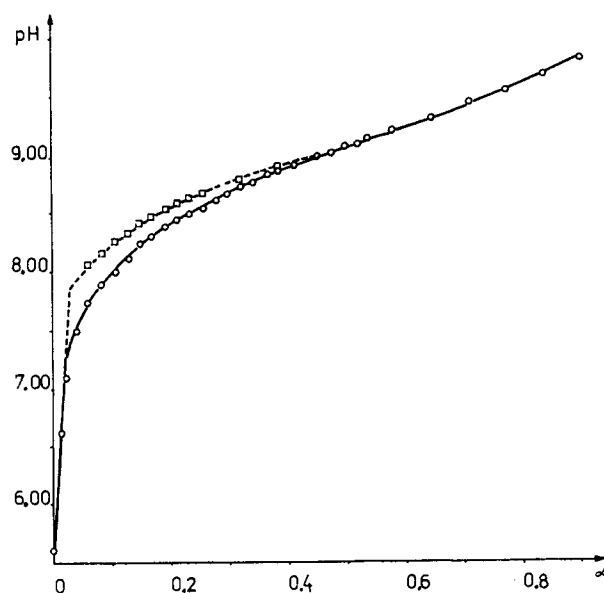


Fig. 2. Potentiometric titration curve for the H_3BO_3 -PVAL complex of molar ratio 0.25

KAMI et al. [14]. They observed linear dependences of the reduced viscosity on the concentration and found considerable increase of the intrinsic viscosity and the expansion factor on the increase of the molar ratio of borax/PVAL.

The potentiometric titration curves with a plateau (Fig. 3) as well as the increase of the expansion parameter found by MURAKAMI et al. can be connected with the disentanglement of the macromolecule of PVAL. The latter is a result of the decrease of the flexibility because of the formation of cyclic complexes on the basic chain and the acquisition of a charge on their neutralization. At molar ratios of 0.10 to 0.25 both linear regions of a different slope in HENDERSON-HASSELBACH plots (Fig. 4) refer to two different macroconformations. To the same molar ratios correspond two linear regions in the plot of the INGMAN function (Fig. 1). The dependences referring to a molar ratio of 0.05 which are of linear character (Figures 1, 3 and 4) are the only exception. Gelatinization of

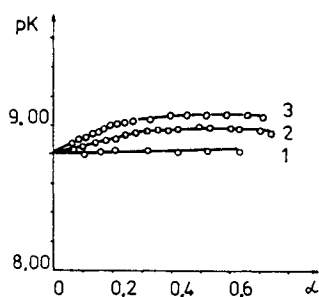


Fig. 3. Variation of pK with the degree of neutralization α . Molar ratios: 1 - 0.05; 2 - 0.15; 3 - 0.25

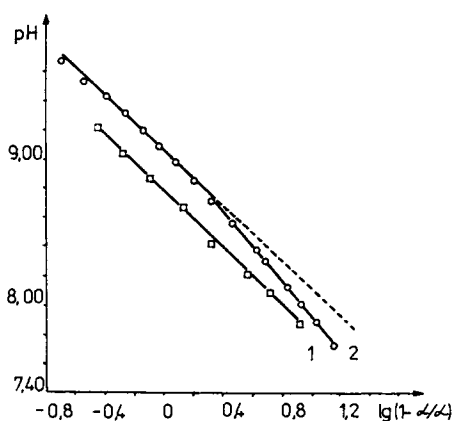


Fig. 4. HENDERSON-HASSELBACH plot for H_3BO_3 -PVAL complex of molar ratio 0.25

the solutions does not take place [6] at the same molar ratio and the neutralization of the complexes.

The lack of a range of pK increase following the plateau (Fig. 3), the high values of the expansion factor ($\alpha = 1.22$) as well as the lack of a polyelectrolyte effect show that the conformation approaching a rod-like structure is the most probable. At such conformation the groups with a charge in the polymer chain are separated and do not practically interact. The hypermolecular structures observed in electron microscopic investigations show as well that this conformation is the most probable. The solutions of PVAL are microheterogeneous and have a globular structure. Rod like structures with a length of 0.3 to 0.4 μm [6] appear on partial neutralization.

The variation of the free energy of the conformational transition (for a monomer unit of the polyelectrolyte) can be determined by the following equations [10, 11]

$$\Delta G_c = 2.303RT \int_0^1 (pK_a - pK_b) d\alpha \quad (3)$$

$$\Delta G_c = 2.303RT \int_0^1 (pH_a - pH_b) d\alpha \quad (4)$$

as the area between the experimental curve of pK_a (or pH_a) and the extrapolated curve of pK_b (or pH_b) at a high degree of

neutralization. The hypothetical values of pH depending on the degree of neutralization are determined by extrapolation (Fig. 4), and they are pointed out on Figure 2.

Table 1 shows the obtained values of $-\Delta G_c$. The values of the variation of free energy of conformational transition thus determined grow linearly with the decrease of the molar ratio. This is characteristic for copolymers, as the pK refers only to the monomer units with a group taking part in the neutralization. The values of the product $-\Delta G_c \cdot m$ (m - molar ratio) refer to both monomer units [15]. The product $-\Delta G_c \cdot 2m$ does not change essentially in the case of PVAL complexes of the studied molar ratios. These values are lower than those of the variation of free energy for conformational transition of poly(methacrylic acid) which is 427 J/mol ($I = 0.10$) [12].

Table 1. Values of $-\Delta G_c$ for different molar ratios m of H_3BO_3 : PVAL

Molar ratio H_3BO_3 : PVAL	Molar ratio of linked H_3BO_3 : PVAL	$-\Delta G_c$ J/mol	$-\Delta G_c \cdot 2m$ J/mol
0.150	0.130	1479	384
0.200	0.173	1176	407
0.250	0.211	749	316

From these results follows the conclusion that poly(vinyl alcohol)-boric acid complexes in aqueous solutions undergo a transition to an extended rigid conformation because of the decreased flexibility of the macromolecules connected with the formation of cyclic complexes and charge acquisition.

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