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Influence of poly(vinylpyrrolidone) on isotachophoretic separations of inorganic anions in aqueous electrolyte systems

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ABSTRACT

Poly(vinylpyrrolidone) (PVP), a water-soluble polymer, was investigated for the use in the isotachophoretic (ITP) separation of a group of eighteen inorganic anions. The polymer (added to the leading electrolyte) was found to influence selectively the effective mobilities of some of the anions. In some instances the resulting differences in these separation characteristics provided ITP separations otherwise impossible in aqueous electrolyte systems. These separations were often associated with changes in the migration orders of the separands (*e.g.*, chlorate and perchlorate; nitrate and sulphate; iodide, chloride and sulphate). The use of PVP in the ITP determination of iodide in mineral water was effective in achieving a complete resolution of this trace constituent from a large excess of matrix anions (chloride, sulphate). Consequently, a $5 \cdot 10^{-6}$ mol/l concentration of iodide could be detected and no sample preparation was needed.

INTRODUCTION

Capillary isotachophoresis (ITP) is a convenient alternative to the separation and determination of inorganic anions in various matrices (*e.g.*, refs. 1–8). Here, separations in aqueous electrolyte systems are preferred in spite of the fact that some organic solvents could provide better ITP differentiations of this group of anions [9,10]. This preference of the aqueous systems can probably be ascribed to limited solubilities of the zones forming constituents in organic solvents.

The ionic mobilities of many inorganic anions are close in aqueous solutions [11,12]. As the pK_a values of the corresponding acids are also low in water (*e.g.*, 11 and 12), there are limited possibilities for optimizing the ITP separations via differences in the ionic mobilities or via different pK_a values [9]. Complex equilibria provide one way to solve these problems [13,14]. In their use, however, disturbances due to precipitations of the separands can occur [10]. In some instances these ITP separands can be resolved when a counter-ionic constituent of appropriate charge number is employed in the leading electrolyte [2,15,16]. It was shown [17] that the effective mobilities of some inorganic anions are influenced in a differentiating manner via the formation of host–guest complexes with cyclodextrins.

It was reported recently [18] that poly(vinylpyrrolidone) (PVP) dissolved in water interacts differentially with halides. These findings, based on NMR measurements, led us to investigate the role of PVP in the ITP separations of a group of inorganic anions when water is used as a solvent. This paper presents the results from this investigation and also shows some practical aspects of the use of this polymer in analytical ITP.

EXPERIMENTAL

Instrumentation

A CS isotachophoretic analyser (VVZ PJT, Spišská Nová Ves, Czechoslovakia) was assembled in the column-coupling configuration of the separation

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unit [19,20] using modules provided by the manufacturer and a preseparation column (7 cm in length) made in this laboratory [20]. The analytical column was provided with an on-column UVD 1 spectrophotometric detector (VVZ PJT) and the detection was carried out at 254 nm.

Chemicals

Chemicals used for the preparation of the leading and terminating electrolyte solutions were obtained from Serva (Heidelberg, Germany), Sigma (St. Louis, MO, USA) and Lachema (Brno, Czechoslovakia). Some of them were purified by conventional methods. Hydroxyethylcellulose 4000 (HEC) obtained from Serva was purified on a mixed-bed ion exchanger (Amberlite MB-1; BDH, Poole, UK). It was used as an anticonvective additive [9] in the leading electrolyte.

PVP was obtained from Fluka (Buchs, Switzerland), Serva and Lachema. Aqueous solutions of the polymer (10%, w/v) were purified in the same way as HEC.

Water delivered by a Rodem-1 two-stage demineralization unit (OPP, Tišnov, Czechoslovakia) was further purified by circulation through laboratory-made polytetrafluoroethylene (PTFE) cartridges packed with Amberlite MB-1 (Serva). Freshly recirculated water was used for the preparation of the electrolyte solutions.

Samples of mineral water were kindly provided by Dr. K. Hyánková (Department of Ground Water, Komenský University, Bratislava, Czechoslovakia).

TABLE I

OPERATIONAL SYSTEMS

Parameter	Electrolyte[a]	
	Leading	Terminating
Anion	Cl^-	MES
Concentration (m*M*)	10	5
Counter ion	HIS	HIS
Anticonvective additive	HEC	–
Concentration (%, w/v)	0.2	–
pH	6.0	*ca.* 6.0
PVP (%, w/v)	0–10%	–

[a] MES = Morpholinoethanesulphonic acid; HIS = histidine; HEC = hydroxyethylcellulose.

RESULTS AND DISCUSSION

Influence of PVP on the effective mobilities of inorganic anions

The electrolyte systems used thoroughout are given in Table I. In experiments aimed at investigating the influence of PVP on the effective mobilities of the anions, the polymer was present in the leading electrolytes at 0–10% (w/v) concentrations. In preliminary experiments we found that PVP from various sources (see Experimental) and of various molecular weights (Fluka, types K30, K60 and K90) have the same influence on the effective mobilities of anions when present in the leading electrolytes at the same concentrations. Small differences were found in the relative step heights (R_{SH}) from the conductivity detector for the same concentrations of various PVP preparations and could be ascribed to different actual concentrations of the polymer rather than to differences, orginating *e.g.*, from their different molecular weights.

The influence of the polymer on the effective mobilities of the anions is clear from Fig. 1. Here, the leading ion (Cl^-) and acetate were taken as reference constituents (ref. 9, p. 307) as they exhibited minimum changes in their step heights with increasing concentration of PVP. It should be noted that the R_{SH} values in PVP containing leading electrolytes were not influenced on addition of HEC (to eliminate disturbances due to electroosmosis as PVP had only a limited capability in this respect). These findings suggest that the distributions of the anions between the soluble polymeric phases [21] did not play a significant role.

From the plots in Fig. 1, it is apparent that PVP retarded the anions in a differentiating manner. A rough classification of the effect of PVP on the effective mobilities leads to the following ordering: I^-, SCN^-, ClO_4^-, CrO_4^{2-} ≫ NO_3^-, ClO_3^-, NO_2^-, $P_2O_7^{4-}$, Br^-, $S_2O_3^{2-}$ ≫ Cl^-, SO_4^{2-}, PO_4^{3-}, SeO_3^{2-}, F^-, BrO_3^-, AsO_4^{3-}.

It is known that some organic anions interact with PVP. These interactions have been ascribed to hydrogen bonding, dipole–dipole (Van der Waals–Keesom) and dipole–induced dipole (Van der Vaals–Debye) forces and to hydrophobic effects [22]. Interactions of PVP with halogenides in aqueous solutions are explained via H_2O bridges between the polymer and the anions (the latter replace

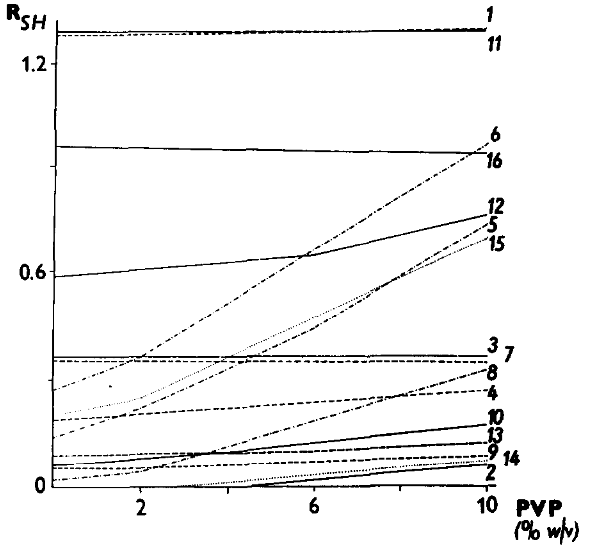

Fig. 1. Dependences of the effective mobilities (expressed in the R_{SH} units) of inorganic anions on the concentration of PVP in the leading electrolyte (for further details, see the text). 1 = AsO_4^{3-}; 2 = Br^-; 3 = BrO_3^-; 4 = ClO_3^-; 5 = ClO_3^-; 6 = CrO_4^{2-}; 7 = F^-; 8 = I^-; 9 = NO_2^-; 10 = NO_3^-; 11 = PO_4^{3-}; 12 = $P_2O_7^{4-}$; 13 = SO_4^{2-}; 14 = $S_2O_3^{2-}$; 15 = SCN^-; 16 = SeO_3^{2-}.

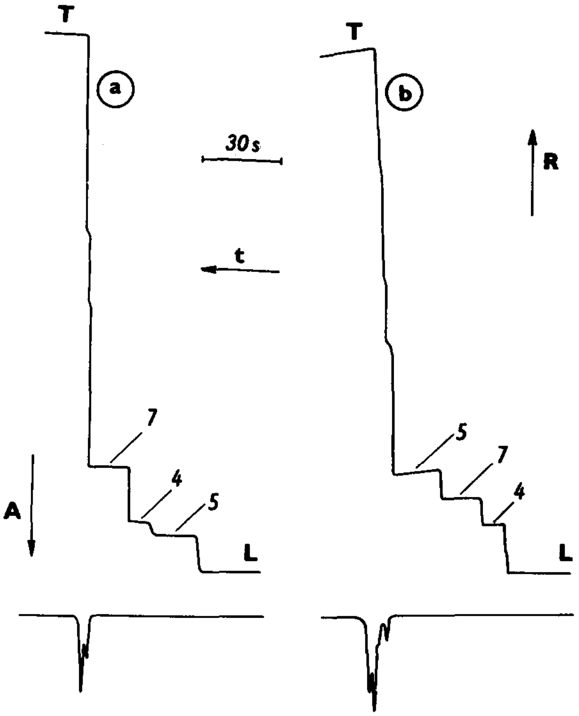

Fig. 2. Isotachopherograms from the separations of F^- (7), ClO_4^- (5) and ClO_3^- (4) by using leading electrolytes (a) without and (b) with PVP [6% (w/v) concentration]. Only the records from the analytical column are given. The driving current in the preseparation column was 250 μA and in the analytical column 50 μA. L, T = leading and terminating zones, respectively; *A*, *R*, *t* = increasing absorption, resistance and time, respectively.

H_2O molecules in the secondary and tertiary hydration spheres of the polymer [18].

Sulphite was found to be unstable in electrolyte systems containing PVP (it was oxidized to sulphate during the ITP run). This behaviour, at least as far as the extent is concerned, was not observed, *e.g.*, for nitrite, thus inducating a certain selectivity of the effect of PVP.

Examples of ITP separations of inorganic anions in water–PVP systems

The plots in Fig. 1 indicate that PVP provides some pratical possibilities for optimizing the separations of inorganic anions unattainable by other means (*e.g.*, pH, complex formation, non-aqueous or mixed solvents). For example, the isotachopherograms in Fig. 2 show that PVP is responsible for an improved separation of chlorate and perchlorate. Here, the effect of polymer can be explained analogously as for halides [18].

A model mixture consisting of anions with very close ionic mobilities in aqueous electrolyte systems (Fig. 3a) could be separated on addition of the polymer (Fig. 3b). From the practical point of view, *e.g.*, a change of the migration order of sulphate and nitrate (Fig. 3b) is worthy of attention. Also, the considerable retardation of I^- relative to Cl^- may have practical analytical utility. A series of isotachopherograms obtained in the determination of I^- in mineral water is given in Fig. 4 as an example.

Here, the spike mode of analysis as introduced by Arlinger [23] was preferred as it provides low detection limits when employed in conjunction with a selective detection method and appropriately chosen spacing constituents [24]. We were able to detect with confidence I^- present in a sample at a concentration of less than $5 \cdot 10^{-7}$ mol/l (for a 30-μl sample injection). This suggests that in mineral water (ten-fold diluted samples were injected) we could detect I^- at a 0.5 ppm concentration while Cl^- was present in the sample at a 10^4–10^5-fold excess. It is obvious that a better choice of the detection wavelength can lead to a further improvement in the detection limits (a 10–100-fold decrease seems feasi-

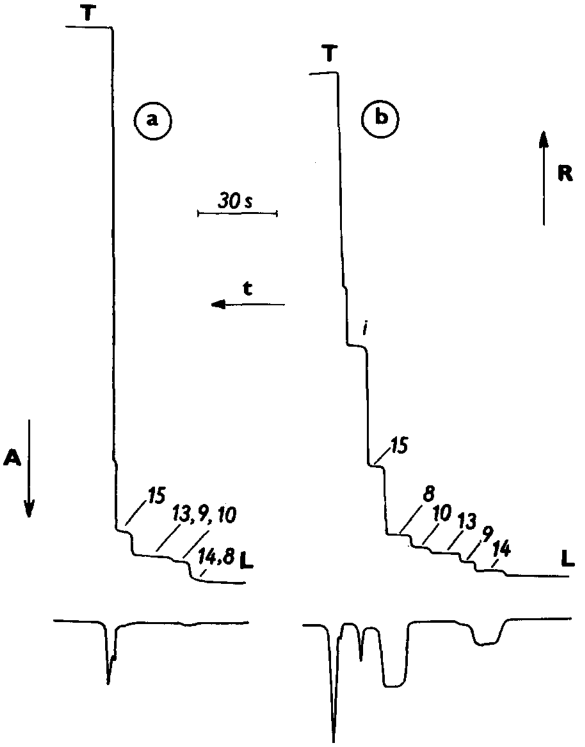

Fig. 3. Isotachopherograms from the separations of a model mixture of inorganic anions (a) without and (b) with the use of PVP [6% (w/v) concentration]. i = Impurities orginating from the electrolyte solutions. Driving currents and symbols as in Fig. 2; zone assignments as in Fig. 1.

ble) and thus to a dynamic range of determination unattainable in ITP by other means.

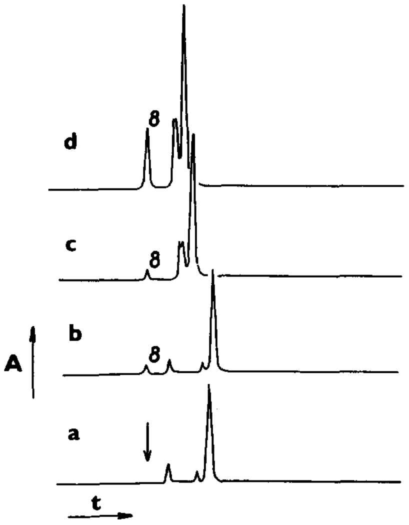

Fig. 4. Isotachopherograms from the determination of I^- (8) in mineral water samples. A 6% (w/v) concentration of PVP in the leading electrolyte was employed. Sulphate and fluoride, added to the samples at 10^{-4} mol/l I^-; concentrations, served as discrete spacers. (a) Blank experiment (only the spacers injected); (b) analysis of a model sample containing 10^{-6} mol/l I^-; (c,d) analysis of samples of mineral water (the samples were diluted 1:10 before the analysis). The arrow indicates the migration position of I^- in the blank experiment. Driving currents and symbols as in Fig. 2.

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