Effect of sodium salts on diffusion of poly(vinyl alcohol) in aqueous solutions

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A B S T R A C T
The Taylor dispersion technique has been used for measuring the tracer diffusion coefficients, $D_T$, for poly (vinyl alcohol) (PVA) in aqueous systems containing two specific electrolytes (i.e., NaCl and Na$_2$SO$_4$) at three different concentrations (0.0020, 0.050 and 0.10 mol dm$^{-3}$), and at 25 °C. The selection of these salts has been based on the Hofmeister series of cations and anions, which order the ions with respect to the behavior of some macroscopic properties (such as, surface tension) and that can be interpreted as an effect salting-out or salting-in, depending if the target ions are strongly (kosmotropic) or a weakly hydrated (chaotropic). In this work, we have been used the combination of two kosmotropic ions (Na$_2$SO$_4$) and another one with a kosmotropic cation and a chaotropic anion (NaCl).

These data, complemented by NMR measurements, permit us to have a better understanding about the effect of these sodium salts on transport and thermodynamic behaviour of PVA.

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1. Introduction

Poly(vinyl alcohol) (PVA) is a polymer of great interest because of its many desirable characteristics specifically for a wide range of applications, including pharmaceutical, biomedical, electrochemistry (for example, super-capacitors) [1], and sensors [2,3]. PVA has a relatively complete, there are PVA with different degrees of hydrolysis (Fig. 1b). For practical purposes, PVA is always a co-polymer of vinyl alcohol and vinyl acetate [4].

PVA is able to form hydrogels, being of particular interest for pharmaceutical and biomedical application. This comes out as a consequence of its non-toxic, non-carcinogenic and bio adhesive characteristics but also because their hydrogels show a high swelling degree and a rubbery and elastic nature [5]. These characteristics make this polymer appropriate for application such as drug delivery [6,7] and wound dressing [8].

Despite the hydrophilicity of PVA, it has been recently found that PVA either in gel or in aqueous solution act as an amphiphilic polymer. In fact, it has been observed that the solubility of a hydrophobic drug, simvastatin, is enhanced inside PVA gel matrix [9]. This occurs once the PVA adopt a conformational structure where the hydroxyl groups are directed away from the simvastatin, leaving the backbone structure free for hydrophobic interactions. Another interesting finding involves fluorene-based conjugated polyelectrolytes (CPEs) [10]. Conjugated polyelectrolytes tend to aggregate in water, which limits its electrical conductivity and photoluminescence for practical applications [11–13]. Surfactants and co-solvents can be efficiently used to promote the disaggregation of CPEs [10,14,15]. Knaapila et al. [16] have found that poly(vinyl alcohol), with a molecular weight around 30,000–40,000 g mol$^{-1}$ also leads to the breakup of CPE structure, highlighting the occurrence of hydrophobic interactions promoting the disaggregation process. Such interesting PVA behavior has motivated us to investigate its effect on the transport properties, by diffusion, of non-associated electrolytes. For that, we have used as reference the Hofmeister series [17,18] (Fig. 2). This series, proposed by Franz Hofmeister in 1888 [19] described the solubility of proteins in different electrolyte aqueous solutions. After that study, the series have been used to interpret the behavior and the effect of ions on the structure of water, and on the solubility of different macromolecules [20–22].
We proposed an experimental study of the binary diffusion for systems containing water and PVA over the concentration range from (0.001 to 0.227) mol dm\(^{-3}\), by using Taylor's dispersion technique at 25 °C. From these experimental diffusion results, the diffusion coefficient at infinitesimal concentration \(D_0\), the thermodynamic factors, \(F_T\), and the activity coefficients were estimated by using the Nernst and Onsager-Fuoss equations [23–25], respectively, permitting us to have a better understanding of its thermodynamics in aqueous solutions. These studies were complemented by structural information obtained from NMR spectroscopy.

2. Experimental

2.1. Materials

Poly(vinyl alcohol), sodium chloride and sodium sulfate were supplied from Sigma-Aldrich and they were used as received (Table S1). For the NMR measurements, solutions were prepared with D\(_2\)O (Aldrich N0.99). The pH* values quoted is the direct pH-meter readings (room temperature) after standardization with aqueous (H\(_2\)O) buffers [26]. The solutions for the diffusion measurements were prepared using Millipore-Q water (specific resistance = 1.82 × 10\(^5\) Ω m, at 25 °C). All solutions were freshly prepared at 25 °C before each experiment.

2.2. NMR experiments

The \(^1\)H and \(^{23}\)Na NMR spectra were obtained using a Bruker Avance III HD 500 MHz NMR spectrometer. The methyl signal of tert-butyl alcohol was used as the internal reference for \(^1\)H (\(\delta \) 1.3) and the \(^{23}\)Na signal of a D\(_2\)O solution of NaCl 0.0089 mol kg\(^{-1}\) is used as the external reference for \(^{23}\)Na.

2.3. Dynamic light scattering measurements (DLS)

Hydrodynamic diameters of PVA solutions in water (\(c_1 = 5\) g dm\(^{-3}\)) and salts (\(c_2 = 0.02\) mol dm\(^{-3}\)) were determined by dynamic light scattering (DLS) on a Zetasizer Nano ZS90 instrument (Malvern Instruments, Malvern, UK) and expressed as intensity-weighted, z-average diameters (nm). Analyses were carried out on samples diluted in solutions of respective salts (NaCl, Na\(_2\)SO\(_4\)) at a scattering angle of 173°. Prior to measurements, all samples were filtered through a 0.45 μm syringe filter (Millipore, UK). The DLS measurements were performed at 25.0 ± 0.1 °C. Each sample was measured for four times and subsequently the mean and standard deviation were calculated.

2.4. Diffusion measurements

In last years, Taylor dispersion has become increasingly popular for measuring mutual diffusion coefficients (chemical interdiffusion) in liquids and in mixtures, permitting to obtain data with an inaccuracy of 1–2%. Having in mind this technique is well described in the literature [27–31], only a summary description of the procedure and equipment is here presented.

The usual procedure is to inject a small volume of solution containing solute at some concentration into a laminar carrier stream of different composition. As the injected sample flows through a long capillary tube with length and radius accurately measured, radial diffusion and convection along the tube axis shape the initial \(\delta\) concentration pulse into a Gaussian profile. Binary mutual diffusion coefficients (\(D\)) are calculated from the broadened distribution of the dispersed sample measured at the tube outlet (Eq. (1)). Extensions of this technique have been used to measure ternary and quaternary mutual diffusion.

Fig. 2. Typical ordering of Hofmeister ions series based on precipitation studies of solutions of typical and anionic proteins [18,19].

Fig. 1. Molecular structure of fully hydrolyzed (a) and partially hydrolyzed (b) PVA.
coefficients ($D_{ik}$) for multicomponent solutions [28]. These results include cross-coefficients $D_{ik}$ ($i \neq k$) describing the coupled fluxes of solutes driven by concentration gradients in other solutes.

In our work, a capillary tube of the length and radius of 3.0480 (±0.0001) cm and 0.03220 (±0.00003) cm, respectively, was used. The method for obtaining these accuracy values are described in the literature [30]. At the start of each run, a 6-port Teflon injection valve (Rheodyne, model 5020) was used to introduce 0.063 cm$^3$ of solution into the laminar carrier stream of slightly different composition. A flow rate of 0.23 cm$^3$ min$^{-1}$ (corresponding to 3.5 rotations per minute of the peristaltic pump head) has been used, and was controlled by a metering pump (Gilson model Minipuls 3) to give retention times of about 8 × 10$^3$ s. The dispersion tube and the injection valve were kept at 25.00 °C (±0.01 °C) in an air thermostat.

Dispersion of the injected samples was monitored using a differential refractometer (Waters model 2410) at the outlet of the dispersion tube. Detector voltages, $V(t)$, were measured at accurately 5 s intervals with a digital voltmeter (Agilent 34401 A) with an IEEE interface. An example of the dispersion profile of PVA/Na$_2$SO$_4$ standard experience is illustrated in Fig. S1 in Supplementary Information.

Binary diffusion coefficients of PVA in water and in aqueous solutions were calculated by fitting the dispersion equation

$$V(t) = V_0 + V_1 t + V_{\text{max}} \left( \frac{t_\text{R}}{t} \right)^{1/2} \exp \left[ -12 D \left( \frac{t}{t_\text{R}} \right)^2 / t^2 \right]$$

(1)

to the detector voltages. The additional fitting parameters were the mean sample retention time $t_\text{R}$, peak height $V_{\text{max}}$, baseline voltage $V_0$, and baseline slope $V_1$.

In addition, values of tracer diffusion coefficients, $D_T$, for PVA in aqueous solutions of sodium chloride and sodium sulfate were also measured. For these ternary systems, PVA(1)/NaCl(2) and PVA/(1)/Na$_2$SO$_4$(2), the following dispersion equation should be considered.

$$V(t) = V + V_1 t + V_{\text{max}} \frac{t_\text{R} (a + b \alpha_1) \sqrt{D_1 e^{-12D_1(t-t_\text{R})^2/t^2}} + (1 - a - b \alpha_1) \sqrt{D_2 e^{-12D_2(t-t_\text{R})^2/t^2}}}{(a + b \alpha_1) \sqrt{D_1} + (1 - a - b \alpha_1) \sqrt{D_2}}$$

(2)

However, considering that the concentration of the salt under study (component 2) is significantly higher than the concentration of PVA (component 1), ensuring the occurrence of tracer diffusion, and that the concentrations of NaCl (or Na$_2$SO$_4$) in the injection and carrier solutions are equal, the second term inside square brackets in Eq. (2) is null and, consequently, Eq. (2) becomes equal to the Eq. (1), being $D = D_{\text{tracer}}$ [32–34].

### 3. Results and discussion

#### 3.1. NMR experiments

As a first approach we aim to understand if the presence of ions, in particular sulfate and chloride, in solution would affect the structure of PVA. For that, we have obtained the $^1$H and $^{23}$Na NMR spectra of PVA in the presence of increasing concentrations of both NaCl and Na$_2$SO$_4$ salts. Figs. 3 and 4 and Figs. S2 and S3 (Supplementary Information) show the dependence of the $^{23}$Na and $^1$H chemical shifts as function of the concentration of the NaCl and Na$_2$SO$_4$ added to a solution of PVA 0.0089 mol kg$^{-1}$, respectively.

Although the $^{23}$Na NMR spectra show a noticeable shift to low frequencies in solutions of PVA/NaCl (Figs. 3 and PVA/Na$_2$SO$_4$ (Fig. S2), the corresponding $^1$H signals of PVA in the presence of increasing concentrations of both the salts are not affected, as is shown in Fig. 4 and Fig. S3. These observations can be regarded as an indication that the predominant interactions of both the salts, NaCl and Na$_2$SO$_4$, in solutions of PVA probably occur mostly with the solvent rather than with the polymeric chain, being the polymer conformations unaffected by the presence of the salts. Similar results we have previously obtained for the addition of NaCl to aqueous solutions of $\alpha$-aminoacids, including $\gamma$-aminobutyric acid (GABA), $\alpha$-amino pentanoic acid (DAPA) and $\varepsilon$-aminoehexanoic acid (EAHA) [35,36]. Moreover, the width of $^1$H and $^{23}$Na signals does not change significantly, which suggest that the viscosity of the solution of PVA is not substantially changed with the addition of salts to the solution.

#### 3.2. Dynamic light scattering measurements (DLS)

DLS measurements showed that hydrodynamic diameter of PVA in water differed in comparison with PVA dissolved in used salt solutions (Table 1). The largest hydrodynamic diameter was found out for PVA dissolved in water (48.0 ± 6 nm). On the contrary, $z$-average diameters for PVA in NaCl were the smallest (37.0 ± 1 nm), PVA in the Na$_2$SO$_4$ solutions behaved differently, and its hydrodynamic diameters were larger (41.0 ± 5 nm) than that of NaCl (37.0 ± 1 nm). The reason of this behaviour could be seen in the different effect of the ion from the Hofmeister series on the PVA. Na$_2$SO$_4$ salt containing a kosmotropic cation and kosmotropic anion, whereas NaCl salt is a combination of a kosmotropic anion and chaotropic cation [37]. Additionally, differences in particle size were also observed in distribution curve. PVA in water showed the presence of trimodal distributions indicating the presence of a three particle population. Narrow bimodal distribution curve confirmed

![Fig. 3. $^{23}$Na NMR spectra of a D$_2$O solution of PVA 0.0089 mol kg$^{-1}$, at 25 °C as a function of increasing concentrations of NaCl: (a) 0.0089 mol kg$^{-1}$ alone (external reference) and (b) 0.0045 mol kg$^{-1}$; (c) 0.0089 mol kg$^{-1}$; (d) 0.0178 mol kg$^{-1}$; (e) 0.0445 mol kg$^{-1}$ and (f) 0.0890 mol kg$^{-1}$.

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Reference [32–34].
the presence of a two particle population in PVA dissolved in NaCl solution. Finally, PVA in the Na2SO4 solutions confirmed narrow trimodal distributions indicating the presence of a three particle population.

3.3. Analysis of diffusion coefficients data by using Hartley model

The experimental diffusion coefficients, $D$, of PVA in aqueous solutions in the absence and presence of the electrolytes are shown in Tables 2 and 3, respectively. For each system, the limiting diffusion coefficients in the absence and presence of the electrolytes are shown in

$$D_0 = \frac{1}{2} \left( \frac{D_1 + D_2}{2} \right)$$

and

$$D = D_0 \left( 1 + \frac{1}{2} \frac{\partial \ln \gamma}{\partial c} \right)$$

where $D_0$ and $D$ represent the diffusion coefficients of PVA at infinitesimal and finite concentrations, respectively; $D_1$ and $D_2$, the first and second-order electrophoretic terms [23–25], respectively; and $\gamma$, the mean molar activity coefficient of PVA entities. However, taking into account that the values found for the binary diffusion coefficients (Table 3) into the concentration range studied are fairly constant, the Eq. (5) can be simplified to Eq. (6), if assuming that the effect of the electrophoretic terms on the diffusion coefficient is considered negligible (or, in other words, $F_M = D_0^2$). That is,

$$D = D_0^2 \left( 1 + \frac{1}{2} \frac{\partial \ln \gamma}{\partial c} \right)$$

where $\gamma$ is the thermodynamic activity coefficient of the solute. On the other words, considering that the variation of diffusion coefficients for the concentration range studied is small, we assume that PVA, when diffusing in aqueous solutions, behaves as a nonelectrolyte. In those circumstances, and using our results (Table 3), the thermodynamic factor, $F_T$, values have been estimated at the concentrations studied (Table 4).

Fig. 4. $^1$H NMR spectra of a D2O solution of PVA 0.0089 mol kg$^{-1}$, at 25 °C as a function of increasing concentrations of NaCl: (a) 0, pH $^*$ 6.77, (b) 0.0045 mol kg$^{-1}$, (c) 0.0089 mol kg$^{-1}$, (d) 0.0178 mol kg$^{-1}$, (e) 0.0445 mol kg$^{-1}$ and (f) 0.0890 mol kg$^{-1}$.

Table 1

| Sample            | z-Average diameter/(nm) |
|-------------------|-------------------------|
| PVA water         | 48 ± 6                  |
| PVA NaCl          | 37 ± 1                  |
| PVA Na2SO4        | 41 ± 5                  |
Table 2
Binary diffusion coefficients of aqueous PVA solutions, at different concentrations \(c\), using water as a carrier flow, at 25 °C.

| \(c/(\text{g dm}^{-3})\) | \(c_{\text{m}}/(\text{mol dm}^{-3})^a\) | \(D/(10^{-9} \text{ m}^2 \text{ s}^{-1})\) |
|---------------------------|---------------------------------|-----------------------------|
| 1.0                       | 0.0227                          | 0.240                       |
| 1.5                       | 0.0341                          | 0.236                       |
| 2.0                       | 0.0455                          | 0.235                       |
| 3.0                       | 0.0682                          | 0.229                       |
| 5.00                      | 0.1136                          | 0.223                       |
| 10.0                      | 0.2273                          | 0.205                       |

\[ a \] \(c_m = \frac{c}{M} \), where \(c_m\) and \(M\) represent the monomer concentration PVA and its monomer molar mass (\(M = 44 \text{ g mol}^{-1}\)), respectively.

Table 3
Binary diffusion coefficients of PVA measured from PVA solutions at different concentrations, \(c^a\) at 25 °C.

| \(c/(\text{g dm}^{-3})\) | \(c_{\text{m}}/(\text{mol dm}^{-3})^b\) | \(D/(10^{-9} \text{ m}^2 \text{ s}^{-1})\) |
|---------------------------|---------------------------------|-----------------------------|
| 2.5                       | 0.0568                          | 0.239                       |
| 5.0                       | 0.1136                          | 0.228                       |
| 7.5                       | 0.1704                          | 0.221                       |
| 10.0                      | 0.2273                          | 0.210                       |

\[ a \] These experiments were carried out by using PVA carrier solutions of concentration \(c/(\text{g dm}^{-3})\), and the injected solutions \((c + \Delta c)\) differed in general, by 7.5 g/L or less.

\[ b \] \(c_m = \frac{c}{M} \), where \(c_m\) and \(M\) represent the monomer concentration and the monomer molar mass (\(M = 44 \text{ g mol}^{-1}\)) of PVA, respectively.

Having estimated \(B\) value from the linear relationship fitted to our diffusion coefficients \((B = -0.665 \text{ dm}^3 \text{ mol}^{-1})\) and the Eq. (10), the values for the activity coefficient, in the concentration range studied, were computed and collected in Table 4. From the analysis of this table, it can be seen that the gradient of the free energy or thermodynamic factor \((F_I)\), as well as the activity coefficient \((\gamma)\) of PVA, decreases when its concentration increases, leading us to conclude that the interactions PVA and water molecules are responsible by a transport of an appreciable fraction of larger aggregates, having a lower mobility than the non hydrated PVA. The gain hydration water from PVA macromolecules will lead to large resistance to motion through the liquid and, consequently, a lower diffusion coefficient.

3.4. Effect of electrolytes on tracer diffusion of poly(vinyl alcohol) in aqueous solutions

Tables 5 and 6 show our experimental values of \(D\) for PVA measured at tracer concentrations in aqueous solutions of sodium chloride and sodium sulfate, respectively, at different concentrations (that is, \(c = 0.02, 0.05\) and \(0.10 \text{ mol dm}^{-3}\)).

From Tables 5 and 6, it can be observed that the tracer diffusion coefficients of PVA decrease as its concentration increases, independently of the concentration of electrolyte.

However, in aqueous solutions containing NaCl (or Na2SO4), the deviations between the tracer diffusion coefficient values \((D_{\text{tracer}})\) in these supporting electrolytes and the limiting diffusion coefficients of the PVA in water \((D^0)\), at the same temperature and at infinitesimal concentration of PVA \((c \rightarrow 0)\), are positive (i.e., \(\Delta D^0/D^0\) = 8% and 69%, for NaCl and Na2SO4, respectively).

The increase in the \(D^0\) values for both aqueous systems containing these salts when compared with \(D^0\) value in water, as well as the gradient of chemical potential, indicates the presence of salting-out effects (Tables 2,3). In fact, previous diffusion studies involving interactions between ions and macromolecules, such as proteins [24], show that sulfate ion is a strongly hydrated ion, known as water structure maker; consequently, its presence will not favor interactions between PVA and water molecules. PVA-PVA interactions thus become stronger than the water–PVA interactions and the PVA molecules may associate by hydrogen bonds interactions. It is also worth noticing that the positive deviation for \(\Delta D^0/D^0\) can be explained by the non-neglecting role of sodium ions as a water structure-making. Thus, as a consequence of predominant electrolyte–water interactions, the PVA conformations remain unaffected, as it was discussed in the previous section.

The entities of PVA offer less frictional resistance to motion through the liquid and, consequently, the diffusion coefficient of this aqueous system becomes higher.

These facts are also supported by the analysis of hydrodynamic radii of PVA, as seen by DLS, in the presence of NaCl and Na2SO4 solutions when compared with those obtained in the absence of salt (Table 1). Such values clearly suggest that the presence of NaCl and Na2SO4 does not favor the interactions between PVA and water molecules leading to lower radii and consequently higher diffusion coefficients.

4. Conclusions

The mutual diffusion coefficients for PVA in water, and in aqueous solutions without and with sodium chloride and sodium sulfate at 25 °C were measured.

In view of obtaining higher diffusion coefficients values in solutions containing these salts and in trace concentrations of PVA, when compared with those obtained in the absence of these same salts, we can conclude that the diffusion of this polymer in aqueous solutions is strongly affected by the presence of these electrolytes as a result of the salting-out effect, being more favorable at high salt concentrations and at infinitesimal concentration of PVA. The presence of both salts does not favor the interactions PVA and water molecules, and
correspondingly, the polymer conformations unaffected by their presence. These facts are also supported by NMR spectroscopy and DLS measurements.

Diffusion coefficients measured for aqueous solutions of systems containing PVA and salts provide transport data necessary to model the diffusion in pharmaceutical and engineering applications.

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### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2020.112728.

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### Table 5

| \( c_1/(\text{mol dm}^{-3}) \) | \( D_{\text{Tracer}}/(10^{-9} \text{ m}^2 \text{s}^{-1}) \) (\( C_2 = 0.02 \text{ mol dm}^{-3} \)) | \( D_{\text{Tracer}}/(10^{-9} \text{ m}^2 \text{s}^{-1}) \) (\( C_2 = 0.05 \text{ mol dm}^{-3} \)) | \( D_{\text{Tracer}}/(10^{-9} \text{ m}^2 \text{s}^{-1}) \) (\( C_2 = 0.10 \text{ mol dm}^{-3} \)) |
|----------------|-------------------------------|-------------------------------|-------------------------------|
| 0.0455         | 0.266                         | 0.265                         | 0.255                         |
| 0.1136         | 0.224                         | 0.215                         | 0.246                         |
| 0.2273         | 0.228                         | 0.233                         | 0.225                         |

\( \Delta D_{\text{Tracer}} = \frac{D_{\text{Tracer}}(C_2) - D_{\text{tracer}}(C_0)}{C_2 - C_0} \)

### Table 6

| \( c_1/(\text{mol dm}^{-3}) \) | \( D_{\text{Tracer}}/(10^{-9} \text{ m}^2 \text{s}^{-1}) \) (\( C_2 = 0.02 \text{ mol dm}^{-3} \)) | \( D_{\text{Tracer}}/(10^{-9} \text{ m}^2 \text{s}^{-1}) \) (\( C_2 = 0.05 \text{ mol dm}^{-3} \)) | \( D_{\text{Tracer}}/(10^{-9} \text{ m}^2 \text{s}^{-1}) \) (\( C_2 = 0.10 \text{ mol dm}^{-3} \)) |
|----------------|-------------------------------|-------------------------------|-------------------------------|
| 0.0455         | 0.300                         | 0.285                         | 0.380                         |
| 0.1136         | 0.280                         | 0.239                         | 0.340                         |
| 0.2273         | 0.233                         | 0.200                         | 0.270                         |

\( \Delta D_{\text{Tracer}} = \frac{D_{\text{Tracer}}(C_2) - D_{\text{tracer}}(C_0)}{C_2 - C_0} \)

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\( \Delta D_{\text{Tracer}} = \frac{D_{\text{Tracer}}(C_2) - D_{\text{tracer}}(C_0)}{C_2 - C_0} \)
