Interaction behavior of polion-counterion for sodium polystyrene sulfonate

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1. Data

The experimental specific conductance increases with the increase of concentration of NaPSS [2]. The experimental specific conductance data (Table 1) can be converted into equivalent conductance as the relation as

\[ A = 0.001 (\kappa - \kappa_0)/c \] (1)

where \( \kappa = \) Experimental specific conductance of the solution.

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Experimental specific conductance of the solvent.

L = Equivalent conductance of the system.

By using Table 1 and Eq. (1), the equivalent conductance data is calculated. The equivalent conductance graphs are fitted with the help of scaling theory [3]:

\[ L = f \left( \lambda_0^0 + \frac{F_0 e \zeta_0^2 \ln(\zeta_0/\varepsilon)}{3\pi \eta_0} \right) \]  

(2)

Table 1
Specific conductance, \( \kappa \) of sodium polystyrene sulphonate in water and methanol-water mixtures at 298.15 K

| Water | 0.1 v.f. of methanol | 0.2 v.f. of methanol |
|-------|---------------------|---------------------|
| c x 10^4 equiv.l^-1 | \( \kappa \) S/cm | c x 10^4 equiv.l^-1 | \( \kappa \) S/cm | c x 10^4 equiv.l^-1 | \( \kappa \) S/cm |
| 12.11 | 89.79 | 12.25 | 70.60 | 13.32 | 58.12 |
| 10.04 | 76.05 | 10.18 | 59.86 | 11.09 | 49.44 |
| 08.41 | 65.03 | 08.47 | 50.94 | 09.24 | 42.08 |
| 06.97 | 55.12 | 07.07 | 43.53 | 07.67 | 35.75 |
| 05.80 | 46.94 | 05.90 | 37.17 | 06.40 | 30.54 |
| 04.84 | 40.11 | 04.93 | 31.92 | 05.33 | 26.09 |
| 02.89 | 25.86 | 04.08 | 27.13 | 04.45 | 22.37 |
| 01.69 | 16.69 | 02.89 | 20.30 | 03.72 | 19.24 |
| 0.810 | 09.63 | 01.69 | 13.26 | 02.89 | 15.62 |
| 0.810 | 09.63 | 01.69 | 13.26 | 02.89 | 15.62 |
| 0.810 | 09.63 | 01.69 | 13.26 | 02.89 | 15.62 |
Here, $F = \text{Faraday number}$, $Z = \text{Counterion valence}$, $e = \text{Electronic charge}$, $\eta_0 = \text{Solvent viscosity coefficient}$, $\xi_o = \text{Correlation blob size}$ and $\xi_e = \text{Electrostatic blobs size}$.

The relation (2) is used to the calculated $A$ against $c$ data for NaPSS to evaluate $f$ which is a very important parameter for polyelectrolyte behavior. The experimental equivalent conductivity ($A$) against $(\sqrt{c})$ for NaPSS in water and methanol-water mixture are perfectly matched with the scaling theory (Fig. 1). From this Fig. 1, it is clear that the equivalent conductivities show the increase with decreasing concentration within the concentration range investigated here. The experimental equivalent conductivities for NaPSS in water, 0.1 v.f. of methanol and 0.2 v.f. of methanol at 298.15 K are reported in Table 1S.

Fig. 2 represents the plot of $f$ vs. $\sqrt{c}$ of NaPSS solutions. $f$ values increase slightly as the concentration of NaPSS increases at 298.15 K. Such trends were also observed in the literature [2]. When the concentration of NaPSS increases, the relative permittivity of the system increases because of ionic polarizability of NaPSS [4]. Mohanty and Zhao in the year 1998 mentioned in their work that the increment of the effective dielectric constant of the system was not fully figured out [5], but the experimentally there is the evidence of the increment for the effective dielectric constant on the system [4,6]. For NaPSS, especially, the frequency relied on dielectric constant is increased with the concentration of NaPSS [7]. Increment of dielectric constant ($\varepsilon$) of the system gives the reduction of Bjerrum length ($l_B = \frac{e^2}{\varepsilon K_B T}$). As $l_B$ settles the scale of the distance between the dissociated counterions on the poly-ion chain [4,8,9], there will be a small number of condensed counterions as the dielectric constant of the system rises. For charge density parameter, the structural value [10] for NaPSS in water was used ($\lambda = 2.83$ at 298.15 K).

The observed $f$ is reduced with the increment of methanol content of the mixture over the entire NaPSS concentration range investigated (Fig. 3). On increasing the methanol content, the dielectric constant of the system reduces at 298.15 K. Lower dielectric constant elevates higher counterion-binding and hence results in a lesser amount of uncondensed counterions in going water to 0.2 v. f.

**Fig. 1.** Variation of $A$ with $\sqrt{c}$ of NaPSS in water (circles), 0.1 vol fraction (v.f.) of methanol (squares) and 0.2 v.f. of methanol (triangles) at 298.15 K. Calculated values from scaling concept: dashed lines.
of methanol. Such trends were also seen in the same systems of higher temperatures [11] Usually, is given by [12]:

\[ \Lambda = f(\lambda_0^c + \lambda_p) \]  

(3)

where \( \lambda_p, f \) symbols have usual meanings. \( \lambda_p \) can be calculated with the help of known values of \( \Lambda \) and \( f \). The \( \lambda_0^c \) values are taken from Table 2. The calculated values of \( \lambda_p \) are plotted with the square root of NaPSS concentration (Fig. 4).

The trends of the variation of \( \lambda_p \) with \( \sqrt{c} \) of NaPSS (Fig. 4) were matched with the experimental equivalent conductivity of NaPSS in water and methanol-water mixture (Fig. 1).

To discuss the spontaneity of the counter-ion condensation procedure, information on \( \Delta G_A^0 \) is necessary. For this aim, \( K_A \) for the binding of the counterions onto to polyionic sites known as the equilibrium constant for the reaction can be obtained as:

Free site + Na\(^{+} \leftrightarrow \) Combined site; has been estimated as a function of concentration from \( f \) taking the relation as:

Fig. 2. Variation of \( f \) with \( \sqrt{c} \) for NaPSS in water (triangles), 0.1 v. f. methanol (squares) and 0.2 v. f. methanol (circles).

Fig. 3. Variation of \( f \) with v. f. of methanol.
Table 2

Properties of water and methanol-water mixtures at 298.15 K and the corresponding \( \lambda_0^0 \) values of the Na ion with \( \xi \) calculated \( [\xi = \frac{e^2}{bK_B T}] \) with \( b = 2.52 \) Å and best-fitted \( \xi \).

| Calculated (\( \xi \)) (Å) | Best-fitted (\( \xi \)) (Å) | \( \eta_0 \)/mPa.s | \( r \) | \( \lambda_0^0 \)/S.cm².mol⁻¹ |
|---------------------------|---------------------------|----------------|--------|----------------------------|
| Water                     | 3.15                      | 3.52           | 0.8959 | 78.30                      | 50.10                      |
| 0.1 v.f. of methanol      | 3.29                      | 3.61           | 1.1441 | 75.09                      | 44.94                      |
| 0.2 v.f. of methanol      | 3.45                      | 3.74           | 1.4346 | 71.61                      | 36.78                      |
|                           |                           |                |        |                            |                            |

Here \( K_B \) = Boltzmann constant.

Fig. 4. Variation of \( \lambda_4 \) with \( \sqrt{c} \) for NaPSS in water (circles), 0.1 v.f. methanol (squares) and 0.2 v. f. methanol (triangles).

Fig. 5. Variation of \( \Delta G_A^0 \) with \( \sqrt{c} \) for NaPSS in water (circles), 0.1 v. f. methanol (squares) and 0.2 v. f. methanol (triangles).
\[
\ln K_A = \ln \left( \frac{1 - f}{f} \right) - \ln(fc) \tag{4}
\]

\[
\Delta G_A^0 \text{ can very easily obtain from:}
\]

\[
\Delta G_A^0 = -RT \ln K_A \tag{5}
\]

where \( R \) = gas constant and \( T \) = temperature.

Fig. 5 displays the variation of \( \Delta G_A^0 \) with \( \sqrt{c} \) of NaPSS in water and methanol-water mixtures. The negative \( \Delta G_A^0 \) values suggest that the counterion condensation process is not nonspontaneous for NaPSS system over the full range of concentration even though the process becomes less spontaneous as the concentration rises. More increase of methanol to the system makes the counterion condensation procedure less suitable.

The transference number of the polyion (\( T_P \)) has been calculated:

\[
T_P = \frac{\lambda_p}{A} \tag{6}
\]

where the symbols have the usual meanings.

In Fig. 6, we present the plot of \( T_P \sqrt{c} \) of NaPSS ion in water and 0.1 and 0.2 v. f. methanol-water mixture at 298.15 K. \( T_P \) is observed higher than 1 over the entire range of concentration in our study, and reduce with the increase of NaPSS concentration. The values of \( T_P \) were also higher than 1 for different aqueous polyelectrolyte solutions [13].

2. Experimental design, materials, and methods

Methanol was obtained from Merck, India. The purity of methanol is 99.0%. The binary mixture of water and methanol were made from 0.1 to 0.2 v. f. of methanol at 298.15 K constant temperature. Sodium polystyrene sulfonate (Sigma Aldrich, USA) of 70,000 g mol\(^{-1}\) with (1) a degree of sulfonation and (<1.2) a polydispersity index was purchased. The solution of sodium polystyrene sulfonate was made in triple distilled water and methanol-water mixture. The calibration of the conductivity cell was performed by 0.1 and 0.01 M KCl solutions [14]. The conductance was noted as described in the literature [1].

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Conflict of 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.dib.2019.104365.

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