Specific F− binding to phenyl ring of aromatic polymers

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ABSTRACT

Most of the hydrogels deswell more remarkably in F− containing solutions than in other monovalent anion containing solutions. However, significant deswelling followed by abnormal reswelling of polymer gel in KF solutions with increasing F− concentration was observed in a series of polymer gels consisted of phenyl rings, for instance, poly(styrene sulfonic acid) (PSSA), hydroxypropyl methylcellulose phthalate (HPMCP) and poly(4-vinyl phenol) (P4VPh) gel. Driving force of this phenomenon was studied to reveal the specific interactions involved in the aqueous systems of aromatic polymers. Elemental analysis and XPS results suggest that F− is embedded to the gel by the physical adsorption of KF, as well as the interactions between phenyl ring and F−. Further theoretical calculations revealed that the interaction may be (phenyl)CH$\cdots$F−(H$_2$O)$_n$ interaction, which is stronger than (phenyl)CH$\cdots$(H$_2$O)$_n$ hydrogen bond. This kind of interaction decreases with the increasing water number and it is invalid when the surrounding water number is more than 5 for the phenol–F−(H$_2$O)$_n$ system. Therefore, we conclude that F− could bind to phenyl ring via such (phenyl)CH$\cdots$F−(H$_2$O)$_n$ interaction in solutions with low hydrophilicity. The strong polarization effect of F− and (phenyl)CH$\cdots$F−(H$_2$O)$_n$ interaction are two important driving forces for the reswelling of gels.

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1. Introduction

Weak noncovalent interactions attract intensive interests in a wide range of fields such as self-assembly, supermolecules and bioscience. The presence of ions significantly influences the properties of polymers and biomaterials, for instance, the polymer cloud point, chromatographic selectivity, critical micelle concentration, protein solubility, folding and unfolding of DNA in aqueous solutions, interfere with the noncovalent interactions in these systems [1–3]. A classical theory, Hofmeister series, brought out one century ago to evaluate the ion effects on the protein solubility [4]. From then on, ion-specific effects were found to be ubiquitous in polymer/water systems and were investigated by means of theoretical calculations and a variety of experimental methods [3].

It is well known that π system plays significant role in the structure of biomaterials, such as protein and nucleic acid. Therefore, noncovalent interactions involved with phenyl ring and water play important role in determining the properties of biomaterials such as the structure of proteins, combination of DNA,

molecular recognition processes and so on [5,6]. Swelling study of polymer gels was found to be a simple and efficient method to study the ion-specific effects on polymers [7–13]. By swelling study, in addition with several instrumental analysis, a very stable hydration structure of phenol was revealed by investigation on the ion-effect of P4VPh gel [12,14]. In these studies, π–hydrogen bond, cation–π interaction and hydrophobic interaction were found to play significant roles on phase transition of P4VPh gel in the presence of different ion species and concentrations [15–18]. However, the interactions involved with phenyl rings is still far from fully elucidated.

F− and Li+, being small species which have strong hydration ability than other ions, is focused by scientists who work on theoretical computation of water/ion systems. In hydrated status, the radial distribution functions (RDFs) for the F−–H separations were close to zero so that the interaction between F− and adjacent water molecules was strong [19]. For hydrogel systems, hydrogen bond of water in the gel was strengthened by strongly hydrated cations and weakened in the presence of strong hydrated anions. Therefore, kosmotropic anions (e.g. F−) interact strongly with water to destroy the hydrogen-bonding between polymer gel and water, leading to a higher extent of gel deswelling. On the contrary, the strong interactions between chaotropic cations (e.g. Li+) will stabilized the hydrogen-bonding in gel–water system, leading to a lower extent of gel deswelling than in other univalent cations. Reswelling of the gel in concentrated LiCl solutions was even

occurred in several hydrogels, such as poly(vinyl alcohol) (PVA), poly(N-vinyl-2-pyrrolidone) (PVP), poly(allylamine) (PAlAm) gels [9,10]. In our previous work, similar effect concerning LiCl was observed in several aromatic polymer gels, i.e. PSSA, HPMCP and P4VPh gel. However, specific reswelling of the gels in concentrated KF solutions had never been reported by other researchers and the mechanism was not fully elucidated [20,21].

In this work, we investigated the swelling behavior of a series of polymer gels containing phenyl ring, for instance, PSSA, P4VPh and HPMCP gel, in KF solutions. Their swelling behavior in the solutions containing a small cation, i.e. Li$^+$, was also investigated for the purpose of comparison. Due to the complexity and importance of the interactions involved with phenyl ring and F$^-$ ion in the nature, we investigated this F$^-$–phenyl interactions qualitatively and quantitatively by experimental methods, such as swelling study, estimation of F$^-$ binding amount, XPS, NMR, and FT-IR. Moreover, this kind of special interaction has been further proved by computational investigations at a molecular level. Some of the experimental methods could not be applied to all the samples; however, all of the results support our proposal.

2. Results and discussion

2.1. Specific reswelling of aromatic polymer gels in KF solutions

F$^-$ is capable to have a strong binding to many ambient molecules due to its strong hydration ability. General polymer gels tend to deswell more remarkably in the presence of F$^-$ than in other univalent Hofmester anions [9,10]. However, in our recent studies, abnormal reswelling of polymer gels in concentrated F$^-$ solutions was observed in several aromatic polymer gels, i.e. PSSA, HPMCP and P4VPh gel. To elucidate this specific phenomenon, the swelling degrees of these gels in F$^-$ containing solutions are illustrated in Fig. 1. The data of Li$^+$ containing solutions are also shown for comparison. Cl$^-$ and K$^+$, ranking in the middle of Hofmeister series, were chosen as the counterion of Li$^+$ and F$^-$ due to their less significant effect on the volume transition of polymer gels than other ions.

In both KF and LiCl solutions, PSSA gels deswell followed by reswelling with increasing concentration. The deswelling of polymer gels in the presence of electrolyte ions is universal and is ascribed to the destruction of hydrogen-bonding by ions [9,10,15,20]. Both F$^-$ and Li$^+$ ions have strong hydration ability. However, F$^-$ plays a destabilization role on the hydrogen-bonding hydration while Li$^+$ plays a stabilization role [20]. Generally, the deswelling of hydrogels in F$^-$ solution is more significant than in other anion solutions, while that in Li$^+$ solutions is less significant than in other cations. The presence of cations will stabilize the hydrogen bond between polymer and water, therefore cations with strong hydration ability (e.g. Li$^+$) will lead to the reswelling of polymer gel. This stabilization effect has been observed and discussed in several aqueous polymer systems [9,10,20]. Briefly, when hydrated to cations such as Li$^+$, positive charge on the water hydrogen increase and negative charge on the water oxygen decrease, leading to an increase in the ability of electron-pair acceptance and a decrease in the ability of electron-pair donation of water [9]. Therefore, the affinity between hydrated water molecules and the –SO$_3^-$, –OH as well as –COOH will increase, which lead to the stabilization effect and the reswelling of these gels in concentrated LiCl solutions.

However, the reswelling of polymers in KF solutions observed in phenyl ring containing polymers, such as PSSA, P4VPh and HPMCP, remain to be a margin for investigation [1,20,21]. The phenomenon implies that F$^-$ could bind to phenyl ring through a specific interaction.
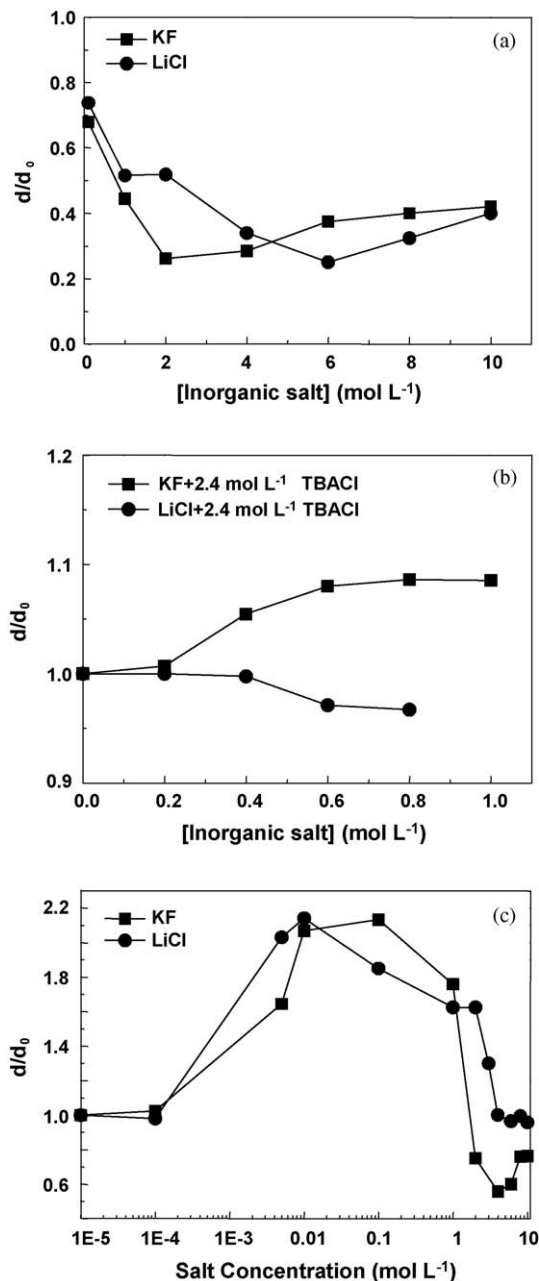

Fig. 1. Effects of salt concentrations on the swelling degree of PSSA gel (a), P4VPh gel (b) and HPMCP gel (c) in aqueous solutions containing F$^-$ or K$^+$.

Note that the P4VPh gel does not show obviously volume transition even in concentrated inorganic salt solutions due to the very stable hydrogen-bonding hydrations to the phenol OH proton and to the phenol ring by anions and cations. Therefore, the reswelling of the gel was investigated in KF solutions containing 2.4 mol L^{-1} TBACl because volume transition of P4VPh gel can occur via specific interactions in this condition [15]. Due to the complexity of the solution composition, further quantitatively experiments such as total F$^-$ embedded amount and XPS were not performed.

When compared with Fig. 1(a)–(c), the reswelling of P4VPh and HPMCP gel in KF solutions were definitely, but less significant than that of PSSA gel. Implying that the interactions between F$^-$ and phenyl ring in these systems are weaker than those in PSSA system, and this assumption was proved by computational studies which will be illustrated in Table 3 and discussed in the following text.

Table 1
Total F$^-$ binding amount in PSSA gel estimated by mass and elemental analysis.

	Elemental analysis			F$^-$ binding (mass)	F$^-$ binding (elemental analysis)	H$_2$O/KF
	C (%)	H (%)	N (%)			
1 mol L^{-1} KF	17.42	4.14	0.28	4.8	6.3	21.4
2 mol L^{-1} KF	25.55	3.92	0.37	1.3	3.3	9.9
6 mol L^{-1} KF	9.86	2.38		13.3	13.6	4.2
10 mol L^{-1} KF	4.25	2.57		31.6	35.8	4.0

2.2. Total F$^-$ embedded amount

To study the F$^-$ binding to the polymer gels quantitatively, the total F$^-$ embedded amount of PSSA gel was determined. They were calculated from the C% of dry KF-embedded gel by elemental analysis and the weight change of the gel during the period of swelling, respectively, basing on an assumption that the composition of the dry gel was C$_8$H$_8$O$_3$S + xKF (Table 1). The F$^-$ embedded amount measured by both methods reached a minimum value in 2 mol L^{-1} KF solution, and mounted up when KF concentration further increased. Similar tendency was found in HPMCP gels. The total F$^-$ embedded amount of HPMCP gel in 1, 2, 4, 6, 8 mol L^{-1} KF solutions were determined to be 28.1, 9.1, 8.0, 16.1 and 28.9 mmol per gram dry gel, respectively. The F$^-$ embedded amount reached the minimum at 4 mol L^{-1} and increased dramatically after that. The antipolyelectrolyte swelling in the low salt concentration caused the large difference of swelling degrees between 1 and 2 mol L^{-1} KF, leading to a higher extent of gel shrinking and KF squeezing out.

These results implied that some F$^-$ ions were diffused into the gel matrix or physical adsorbed on gel surface, but were squeezed out with the solvent by the shrinking of gel. However, the embedded amount increased significantly after the swelling minimum, which suggests the existence of a specific interaction between F$^-$ and polymer in concentrated KF solution. Interestingly, although the C% decreased significantly when KF concentration was higher than 2 mol L^{-1}, the H% only decreased slightly. It can be interpreted by the strong hydration ability of SO$_3^-$ and F$^-$, which lead to the binding of H$_2$O to PSSA gel even in dry status [20]. Due to this deviation, the F$^-$ embedded amounts obtained from mass and elemental analysis were semi-quantitative. However, these results agree well with the swelling study, i.e. the F$^-$ embedded amount increased significantly after minimum when PSSA gel merely contains a little amount of water. The water molecules surrounding one monomer unit of PSSA was estimated to be 21.4, 9.9, 4.2 and 4.0 in 1, 2, 6 and 10 mol L^{-1} KF solution, which are even insufficient for the hydrophobic hydration so that the specific F$^-$ binding to PSSA should be ascribed to the F$^-$–phenyl ring interaction.

2.3. XPS analysis

To estimate the fraction of F$^-$ bound by specific F$^-$–phenyl interaction and free F$^-$ embedded by physical adsorption in total F$^-$ embedded amount, PSSA gel swelled to equilibrium in 2 and 6 mol L^{-1} KF solution was analyzed by XPS. Table 2 shows the binding energies and relatively amount of C 1s, F 1s and Fig. 2 shows their XPS spectra. The results of HPMCP gel are given in Table 3.

For original PSSA gel, the binding energy of all C 1s is 284.8 eV, which is typical for phenyl C and saturated C of alkyl ring. However, after treated by KF, C 1s can be divided into several statuses with binding energy in the range of 284.8–289.45 eV. In the case of 6 mol L^{-1} KF solution, 62% of C atom remain the binding energy of 284.8 eV and others change to the statuses with higher binding energy. The C 1s binding energy of semi-ionic C–F bond was

reported to be ca. 287 eV and that of covalent C–F bond is ca. 289–290 eV in fluorinated carbon materials [22]. The excitation of C 1s_a to higher energy statuses may be caused by the cation–π interaction between phenyl ring and K$^+$, as well as the interaction between PSSA and F$^-$. The C 1s with the binding energy of 286.27
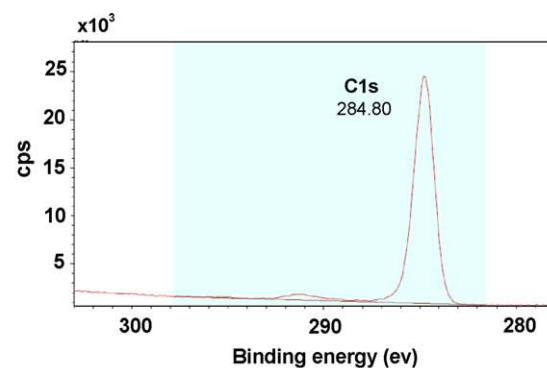
(a) C1s spectrum of pure PSSA gel
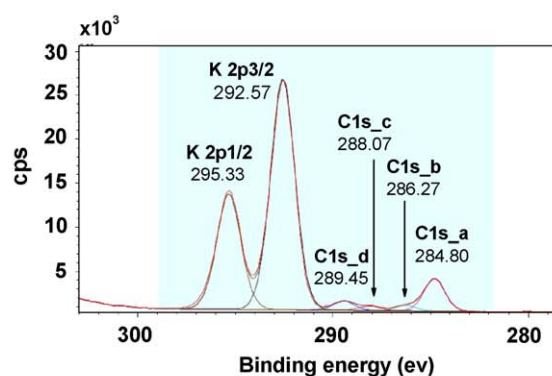
(b) C1s spectrum of PSSA-6 mol L^{-1} KF gel
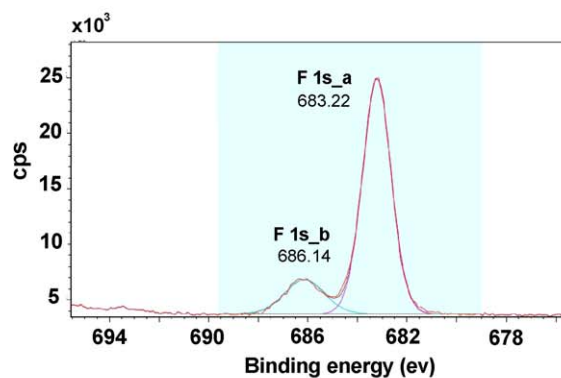
(c) F1s spectrum of PSSA-6 mol·L^{-1} KF gel

Fig. 2. C 1s and F 1s XPS spectra of PSSA gel before and after immersing in 6 mol L^{-1} KF solution. (a) C 1s spectrum of pure PSSA gel, (b) C 1s spectrum of PSSA-6 mol L^{-1} KF gel and (c) F 1s spectrum of PSSA-6 mol L^{-1} KF gel.

Table 2
C 1s and F 1s binding energies and relative amounts of C and F in PSSA gels.

	Pure PSSA gel		PSSA gel-2 mol L^{-1} KF		PSSA gel-6 mol L^{-1} KF	
	Binding energy (eV)	Concentration (mol%)	Binding energy (eV)	Concentration (mol%)	Binding energy (eV)	Concentration (mol%)
C (total)		69.84		51.74		22.62
C 1s_a	284.80	69.84	284.80	47.01	284.80	14.13
C 1s_b			286.30	3.39	286.27	2.41
C 1s_c			287.78	1.34	288.07	1.99
C 1s_d					289.45	4.09
F (total)				12.96		25.4
F 1s_a			684.00	4.12	683.22	21.09
F 1s_b			686.41	8.84	686.14	4.31

Table 3
C 1s and F 1s binding energies and relative amounts of C and F in HPMCP gels.

	HPMCP-H gel		HPMCP-H gel-2 mol L^{-1} KF		HPMCP-H gel-6 mol L^{-1} KF	
	Binding energy (eV)	Concentration (mol%)	Binding energy (eV)	Concentration (mol%)	Binding energy (eV)	Concentration (mol%)
C (total)		69.36		64.64		40.03
C 1s_a	282.44	25.75	282.24	31.25	284.80	19.67
C 1s_b	283.92	33.87	283.83	26.21	286.30	14.49
C 1s_c	285.33	4.69	285.33	5.20	287.67	4.08
C 1s_d	286.62	5.05	286.42	1.98	288.82	1.79
F (total)				3.98		15.97
F 1s_a			681.28	1.16	683.21	15.37
F 1s_b			683.71	2.82	685.79	0.60

and 288.07 eV is assumed to be excited by the interaction between C atom of PSSA and F$^-$, with similar bond strength as that of semi-ionic C–F bond. The C 1s with the binding energy of 289.45 is even as high as that of covalent C–F bond.

On the other hand, F$^-$ exists in two modes: binding energy 683.22 eV (83%) and 686.14 eV (17%). Those at 683.22 eV can be ascribed to the physical adsorption of KF, while those at 686.14 eV should be ascribed to the interaction between C atom and F$^-$. The

reported F$^-$ binding energy of KF crystal is 683.6 eV, while that of semi-ionic C–F bond is 685.6 eV and covalent C–F bond is 687.3 eV [22,23]. Hence, the binding energy of excited F 1s_b (686.14 eV) implies that the interactions for C atom and F$^-$ should be stronger than the semi-ionic C–F bond and weaker than the covalent C–F bond.

In the case of 2 mol L^{-1} KF solution, similar bond energy of each elements were detected. However, the composition of excited C

(A) phenol-(H$_2$O)$_4$

(AA) Benzenesulfonate-(H$_2$O)$_4$

(B) phenol-F$^-$(H$_2$O)$_4$
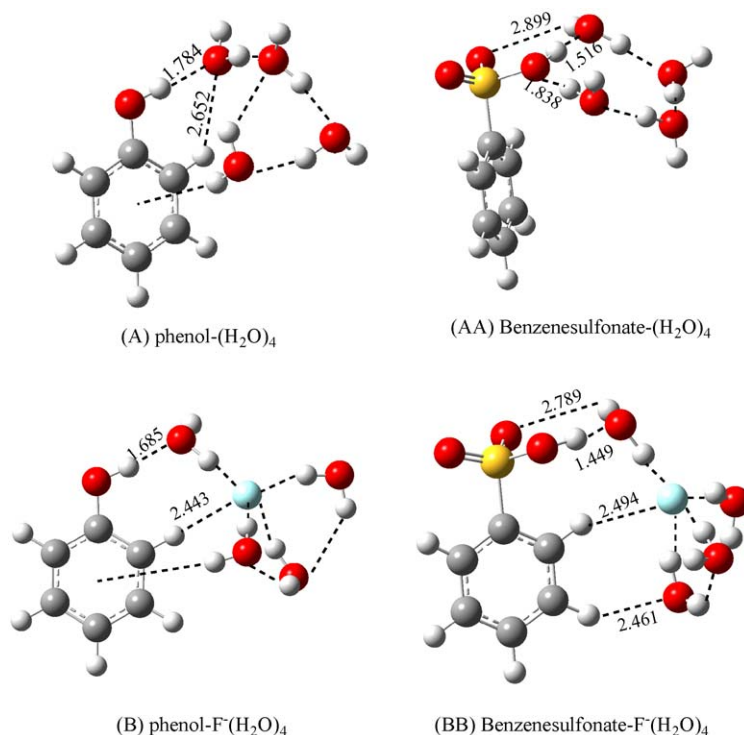
(BB) Benzenesulfonate-F$^-$(H$_2$O)$_4$

Fig. 3. Optimized geometries of benzene sulfonic acid and phenol systems. The important hydrogen-bonding distances are shown in Å.
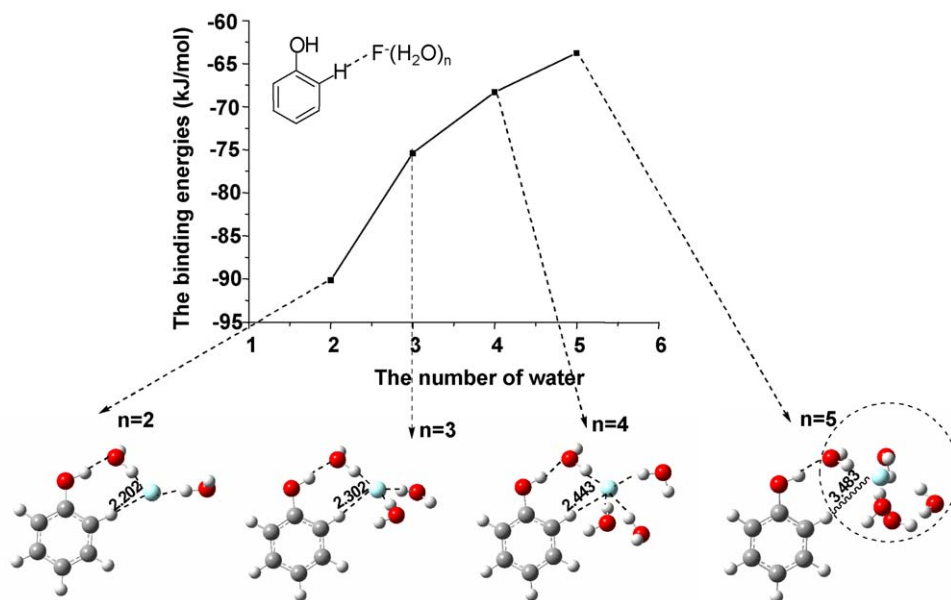
Fig. 4. The binding energies (in kJ mol^{-1}) and optimized geometries (the distance of H$\cdots$F$^-$ is shown in Å) in phenol systems with different numbers of water molecules.

atom was lower than that in 6 mol L^{-1} KF solution, which agrees with the swelling study that the F$^-$–phenyl interaction is stronger in more concentrated KF solutions.

In the case of HPMCP gel, the excitation of C 1s and F 1s was also occurred. However, in terms of lower binding energies and lower fraction of excited C 1s and F 1s atoms, the F$^-$ binding ability is weaker in HPMCP systems than in PSSA ones, especially in 2 mol L^{-1} KF solutions. It implies that the F$^-$ embedded to HPMCP gels before 2 mol L^{-1} primarily caused by the physical adsorption.

Due to the drying process of the gel sample for XPS analysis, the comparison of binding energy cannot be directly applied to the aqueous systems. However, we can safely divide the F$^-$ embedded to the aromatic polymer gels into two groups: one is embedded by physical adsorption and the other is bound by the F$^-$–phenyl interaction.

2.4. Computational results

To better elucidate the F$^-$–phenyl interaction based on the experimental observation, we herein show the computational results. Firstly, the geometries and BSSE-corrected interaction energies of the phenol with F$^-$(H$_2$O)$_n$ (n = 2–5) have been computed and shown in Fig. 3. Obviously, the total binding energy between phenol and F$^-$(H$_2$O)$_n$ decreases and the distance of (phenol)CH$\cdots$F$^-$ increases with the increasing water molecules. Especially, the (phenol)CH$\cdots$F$^-$ interaction disappears when the number of water molecules is 5, which can be demonstrated by the (phenol)CH$\cdots$F$^-$ distance of 3.483 Å. These results demonstrate that there is a certain interaction between (phenol)CH and F$^-$ in the limited amount of water molecules, and support the experimental results that aromatic polymer gels can reswell in concentrated KF solution.

In addition, we have investigated the phenol and benzenesulfonate with (H$_2$O)$_4$ and F$^-$(H$_2$O)$_4$, respectively. The optimized geometries are shown in Fig. 4, together with important hydrogen-bonding distances. Table 4 summarizes the calculated binding energies and important hydrogen-bonding distances in the four systems. The interaction energy for phenol–(H$_2$O)$_4$, benzenesulfonate–(H$_2$O)$_4$, phenol–F$^-$(H$_2$O)$_4$ and the benzenesulfonate–F$^-$(H$_2$O)$_4$ was calculated to be -14.5, -44.7, -68.3 and -103.1 kJ mol^{-1},

respectively. Among them, the (phenyl)CH$\cdots$F$^-$(H$_2$O)$_4$ interactions were found to be the strongest. The strong interaction can also be demonstrated by the hydrogen-bonding distances ($r_{CH\cdots F^-}$ equals 2.443 Å in phenol–F$^-$(H$_2$O)$_4$ system and $r_{CH\cdots F^-}$ is 2.494 Å in benzenesulfonate–F$^-$(H$_2$O)$_4$ system). In addition, the polarization effect of F$^-$ makes the hydrated water molecules have strong interaction with the OH group in phenol and benzenesulfonate. At the same time, the hydrogen-bonding interaction of F$^-$(H$_2$O)$_4$ cluster with benzenesulfonate is much stronger than with phenol. These DFT calculated results give support to the experimental observation that there is powerful hydrogen-bonding interaction such as (phenyl)CH$\cdots$F$^-$(H$_2$O)$_4$ in our investigated systems.

Thus, the observed reswelling of aromatic polymer gels in higher concentrated KF solutions may be ascribed to two factors: one is the stabilization of hydrogen-bonding between polarized water molecules and the OH group, and the other is the strong (phenyl)CH$\cdots$F$^-$ interaction. The strong interactions make the hydrated anions accessible to the "hydrophobic" part.

Generally, hydrophobic hydration is destabilized upon approach of strongly hydrated ions and the hydrophobic bond is favorable to inducing salting-out effects such as gel collapse. However, in the present case, the interaction between F$^-$ anion and benzenesulfonate is so strong that phenyl ring is not repulsive but attractive to the hydrated F$^-$ ion. Therefore, the typical salting-out effects by F$^-$ anion through destabilization of hydrophobic hydration would be well diminished. The strong polarization effect of F$^-$ and (phenyl)CH$\cdots$F$^-$ interaction are two important ingredients for the reswelling of gels.

Table 4
The binding energies and bond length of gel-model hydrogen bond.

	Bond energy (kJ mol^{-1})	(Gel-model) OH$\cdots$O(H$_2$O) bond length (Å)	(Gel-model) CH$\cdots$F$^-$ bond length (Å)
Phenol–(H$_2$O)$_4$	-14.5	1.784	–
Phenol–F$^-$(H$_2$O)$_4$	-68.3	1.685	2.443
Benzenesulfonate–(H$_2$O)$_4$	-44.7	1.516	–
Benzenesulfonate–F$^-$(H$_2$O)$_4$	-103.1	1.449	2.494

3. Conclusion

Aromatic polymer gels, such as PSSA, HPMCP and P4VPh gels, are capable to swell in KF solutions with certain concentrations, which are very special cases for polymer gels. The reswelling of these gels in concentrated KF solutions ($>2 \text{ mol L}^{-1}$) suggest that F^- could bind phenyl ring through a specific interaction, which is favored with the limited amount of water. The total F^- embedded amount of PSSA gel increases significantly after the swelling minimum (i.e. in 2 mol L^{-1} KF solution), which can be ascribed to the physical adsorption of KF, as well as the interaction between phenyl ring and F^-. Further theoretical calculations support the experimental results and demonstrate that the interaction is the (phenyl)CH$\cdots F^-(H_2O)_n$ interaction. The strong polarization effect of F^- and the (phenyl)CH$\cdots F^-$ interaction are two crucial factors for the reswelling of the gels.

4. Experimental

4.1. Materials

Sodium styrene sulfonate (SSS) was purchased from Tokyo Kasei Co. Ltd. Methyl N,N-bis-acrylamide (MBA) obtained from Beijing Chemical Co. Ltd. was used as crosslinker. P4VPh (Mw 22000) were purchased from Polyscience Inc. Ethylene glycol diglycidyl ether (EGDGE, 50% solution) was obtained from Aldrich Chemical Co. Ltd. and used as a crosslinker of P4VPh. HPMCP-55 with phthalyl content of 33% was ACROS organic reagent. MBA was used as crosslinker of HPMCP. Other chemicals were Analytical Reagents products of Beijing Chemical Co. Ltd.

4.2. Gel preparation

The preparation of PSSA, HPMCP and P4VPh gels were described in our previous works. Briefly, PSSA were prepared by 8 kGy γ irradiation of 20 wt% sodium styrene sulfonate with 5 mol% of MBA as crosslinker. Cylinder gels were obtained by setting capillary ($d = 1.0 \pm 0.1$ mm) into the solutions. The cylinder gels were immersed in deionized water until equilibrium swelling and then the gels were ion-exchanged from Na-type to H-type by 0.1 mol L^{-1} HCl. The water content, gel fraction and original diameters (d_0) of PSSA gels were determined to be 98.5%, 83% and 2.760 mm, respectively [21].

The preparation procedure of P4VPh gel is: an adequate amount of the polymer was dissolved in 1 M NaOH aqueous solution to prepare 22 wt% P4VPh solution. Then, EGDGE was added into the P4VPh solution. The amount of EGDGE was set to 5 mol% of phenol hydroxyl groups of P4VPh used. The crosslinking reaction was performed in a glass capillary (0.690 mm) at 25 °C for 24 h. Cylinder-type P4VPh gel samples prepared as above were immersed in water for 10 days to remove low molecular weight substances and non-crosslinked polymer, and finally equilibrium swelling in water was established prior to use. The water content, gel fraction and original diameters (d_0) of P4VPh gels were determined to be 97.3%, 89% and 0.860 mm, respectively [15,16].

The preparation procedure of HPMCP gel is: 20 wt% HPMCP was dissolved in 5% Na_2CO_3 with MBA as crosslinker (5 mol% of HPMCP). After stirred and placed overnight, the solutions was filled into glass tube and mixed by a centrifugal mixer with a speed of 2000 rev/min for 10 min to make homogeneous solutions. Capillaries with diameter of 1.0 ± 0.1 mm was set into the solution. Thus prepared samples were irradiated by γ-ray with 80 kGy at a dose rate of 50 Gy min^{-1} using ^{60}Co resource of Peking University. The cylinder gels were immersed in deionized water until equilibrium swelling and then the gels were ion-exchanged from Na-type to H-type by 0.1 mol L^{-1} HCl. The water content, gel fraction and original

diameters (d_0) of HPMCP gels were determined to be 96.1%, 69% and 0.90 mm, respectively [21].

4.3. Swelling degree

Cylinder-type swollen PSSA gels were immersed in 10 mL of solutions until the equilibrium of swelling was reached, i.e. the diameter of gel keep constant. The diameters of the gels before and after swelling were determined by a microscope (20×) and referred as d_0 and d, respectively. The swelling degree was defined as d/d_0.

4.4. X-ray photoelectron spectroscopy (XPS)

PSSA gel swollen in 2 and 6 mol L^{-1} KF solution was lyophilized before XPS analysis. The XPS data were taken on an AXIS-Ultra instrument from Kratos Analytical (UK) using monochromatic Al Kα radiation (225 W, 15 mA, 15 kV) and low-energy electron flooding for charge compensation. To compensate for surface charges effects, binding energies were calibrated using C 1s hydrocarbon peak at 284.80 eV. The data were converted into VAMAS file format and imported into CasaXPS software package for manipulation and curve-fitting.

4.5. Total F^- embedded amount

Gels equilibrated in deionized water were immersed in KF solution with different concentrations until equilibrium swelling was obtained. The KF-embedded gels were removed from the solution, wiping off excess surface solution and then dried to constant weight. The N, C and H compositions of thus prepared gel were measured by a VARIO EL elemental analyzer (Elementar, Germany). The total F^- binding amount was estimated from the results of mass, and elemental analyses based on the assumption that the composition of KF-embedded gels were PSSA + xKF, and x represents the number of F^- embedded to one monomer unit of PSSA.

4.6. Computational methodology

To explore the abnormal reswelling of gels in high concentrated KF solution, some calculations were carried out with the Gaussian 03 program [24]. Geometry optimization was performed by using density functional theory (B3LYP) method [25,26] with 6-311++G(d,p) basis set. All optimized geometries were verified by the vibrational analysis. According to the counterpoise (CP) calculations [27], the basis set superposition error (BSSE)-corrected interaction energies between (ion)–water clusters and organic molecules have been obtained.

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