Interaction of Non-ionic Hydrogels with Weak Aromatic Acids

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Summary: Measurements are reported of the swelling behaviour at 20 °C of poly (N isopropylacrylamide) (PNIPA) gels in aqueous solutions of two weak aromatic acids, phenol and resorcinol. For solute concentrations below 45 mmol/l the uptake of these solutions is similar. Due to selective solvation phenol exhibits an excess equilibrium concentration inside the gel of 5% over that in the surrounding bath, while for resorcinol, the excess is found to be 12%. At 50 mmol/l solute concentration, both systems display a volume transition accompanied by expulsion of the solvent. The solubility limits in water of these aromatic compounds, which are significantly different from each other (870 mmol/l and 9080 mmol/l respectively), are far above this critical concentration. In the collapsed condition the expelled liquid spreads on the surface of the phenol treated gel, while an ordered arrangement of separate droplets is generated in the case of resorcinol. In the latter case an acute contact angle was observed. It is also shown by acid-base titration that the PNIPA/water system may exhibit a slight ion exchanging character.

Keywords: collapse transition; elastic modulus; gel swelling; NIPA; phenol; resorcinol

Introduction

The volume transition exhibited by poly (N isopropylacrylamide) (PNIPA) gels in water has been extensively studied by various authors over the last couple of decades.[1,2] Murase et al.[3] were among the first to report the effects of aromatic compounds in the aqueous phase on this transition. In view of its possible applications to the treatment of waste water, in this paper we investigate the effects on the swelling properties of PNIPA gels due to the presence of two aromatic compounds, phenol and resorcinol, in the liquid phase.

Experimental

PNIPA gels were prepared from aqueous solutions of *N*–isopropyl–acrylamide (*NIPA*) (*Aldrich*) with *N,N'*–methylene–bisacrylamide (*BA*) (Aldrich) as a crosslinker, using 1,2-di-

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(dimethylamino)–ethane (*TEMED*) (*Aldrich*), ammonium-persulfate (*APS*) (*Aldrich*) by the regular radical polymerization process. Disks and cylinders were synthesized with a molar ratio [NIPA]/[BA] = 150. After polymerization the gels were removed from their moulds and washed in a large water bath of doubly distilled water for a week, changing the water daily.

The disks were cut out of a polymer film and dried over concentrated sulphuric acid. The 1 cm isometric cylinders were moulded directly and washed and dried in the same way. The monodisperse PNIPA latices were prepared according to the procedure of Wu et al.[4] The molar ratio of [NIPA]/[BA] was varied between 10 and 300.

Phenol (99.5 %) and resorcinol of high purity (99 %), both from MERCK, were used to prepare the aqueous solutions of the weak aromatic acids. Swelling was determined by weighing. The concentrations were derived from UV absorption measurements (Kontron Uvikon). For the sorption measurements the disks were equilibrated at 20.0 ± 0.2 °C for 48 hrs, determined from preliminary kinetic measurements.

The stress strain measurements were performed as described by Horkay and Zrínyi.[5] The dry cylindrical samples were immersed in the aqueous aromatic solutions for 8 days at 20.0 ±0.2 °C.

Automatic quasi-equilibrium acid-base titration was performed in a CO_2-free atmosphere using 0.01 M KNO_3 background electrolyte.[6] Solutions were prepared from fresh Millipore water. The initial pH was measured before the titration. The specific amount of net proton surface excess (Δn^{σ}, mmol/g), i.e. the difference between the surface excess amounts of H^+ (n^{σ}_{H+}) and OH^- (n^{σ}_{OH-}), was derived directly from the initial and equilibrium concentrations of the solute at each point of the titration.[7]

Results and Discussion

An important, albeit little known, property of PNIPA gels swollen in pure water is their response to pH, studied by acid-base titration, which measures the excess proton amount at the surface of the polymer.[8] Gel samples in the form of microbeads (of diameter 130 nm in the collapsed state) were washed exhaustively and titrated under carefully controlled conditions. The initial pH of the samples were between 6.7 and 7.3. The range of titration was limited between pH 3 and 11. The proton binding isotherms, i.e. the pH-dependence of the net proton surface excess amount ($\Delta n^{\sigma} = n^{\sigma}_{H+} - n^{\sigma}_{OH-}$, mmol/g) were calculated from the H^+/OH^- material balance. Positive values of net proton surface excess indicate acid consumption (proton binding) and negative ones mean consumption of base solution (release of protons or binding of hydroxyl ions).

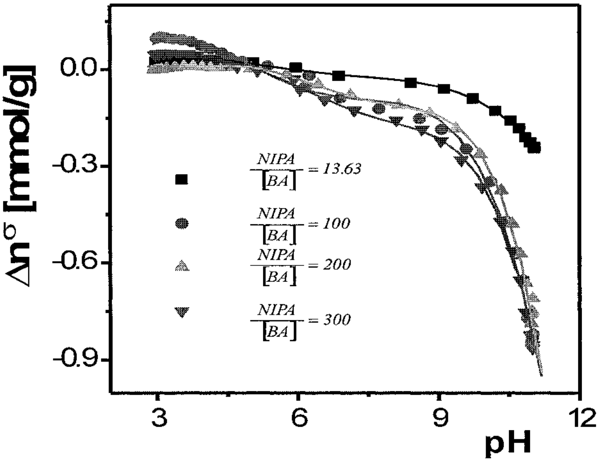
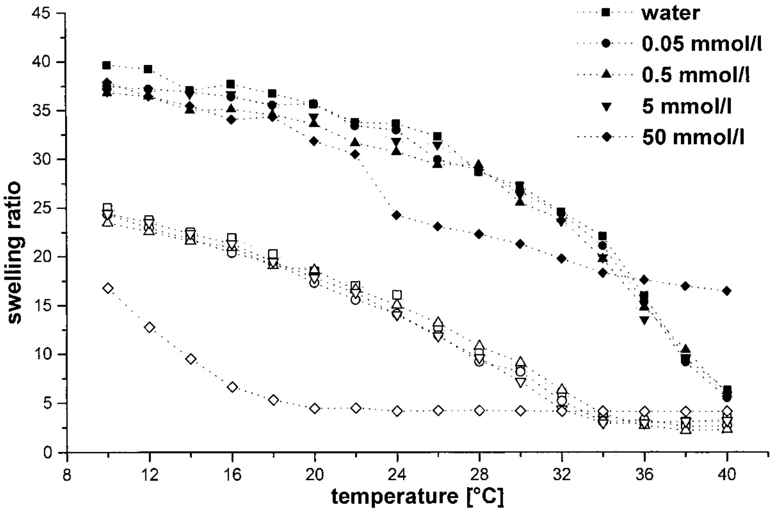


Fig. 1. Excess proton amount in PNIPA hydrogels for different cross-link densities.

The results of these measurements, shown in Figure 1 for a set of gels prepared at different cross-linking densities, indicate an isoelectric point at pH 5.2 – 6.2 with negative values of the excess proton amount above this value. The dissociation increases with increasing pH. Although this could conceivably be due to the presence of residual surfactant applied in the synthesis of the microgels in spite of the careful washing, it is more probably the result of a weak ion exchange character of the polymer gel.

The effect of different amounts of phenol and resorcinol in the surrounding aqueous bath is shown in Figure 2, where the degree of swelling is plotted as a function of temperature. These measurements were performed on samples with standard geometry (3 mm diameter disks of thickness 1 mm in the dry state). The temperature was changed by steps of 2 K, the samples being weighed each time after 25 min incubation. The curves in this figure show that both the swelling and deswelling properties are practically insensitive to the presence of either solute in concentrations below 50 mmol/l. For the 50 mmol/l concentration the response of the phenol containing sample with increasing temperature is much slower than that with resorcinol. The latter even reaches equilibrium by the end of the heating cycle. In the reverse direction the swelling response starts earlier in the system containing phenol.

a)



b)

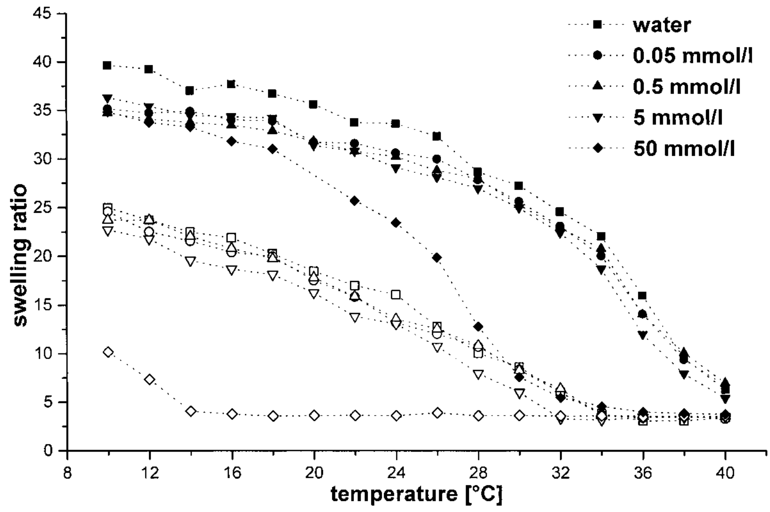


Fig. 2. Swelling ratio of PNIPA gels in aqueous solutions of a) phenol and b) resorcinol as a function of temperature. Solid and open symbols are increasing and decreasing temperature, respectively.

Uptake of the phenol and resorcinol solutions by the PNIPA gels is shown in Figure 3. This quantity was determined from UV measurements of the initial and final concentrations of the aromatic solute in the equilibrium solutions, combined with measurements of the mass balance. For equilibrium liquid concentrations smaller than 45 mmol/l in the surrounding bath, both phenol and resorcinol behave in a closely similar way. In this concentration range for phenol, the internal concentration of solute is 1.05 times greater than that in the surrounding bath, while for resorcinol the enhancement factor in the gel is 1.12. Above this limiting concentration, however, the responses are strongly different, in that the resorcinol system exhibits a maximum in its solvent uptake while phenol continues to rise, albeit at a lower rate. At equilibrium concentrations of the surrounding reservoir in excess of 50 mmol/l solvent is expelled from this system.

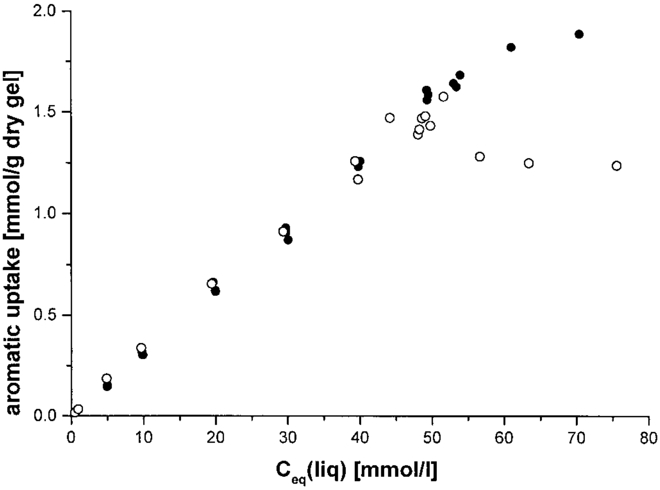


Fig. 3. Uptake of phenol (solid symbols) and resorcinol (open symbols) from their aqueous solutions at 20 °C by PNIPA gels.

Figure 4 shows the equilibrium swelling degree of the gel samples at 20 °C in aqueous solutions containing different amounts of phenol or resorcinol. It can be seen that at constant temperature a volume transition can be induced by the aromatic compounds. The concentration of the aromatic compounds where the collapse transition occurs in both cases is close to 50 mmol/l. This value lies well below the solubility limit in water both of phenol (870 mmol/l) and of resorcinol (9080 mmol/l).[9]

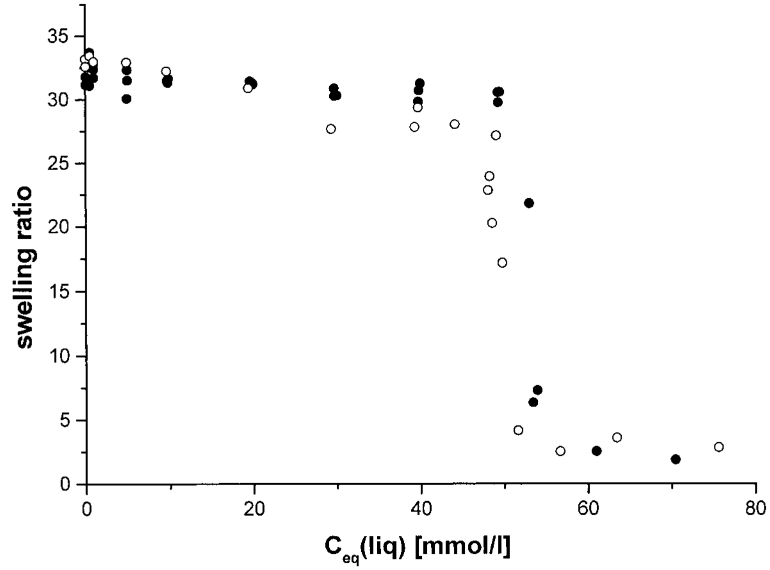


Fig. 4. Equilibrium swelling ratio (1/ϕ) of PNIPA gels at 20 °C in aqueous solutions of phenol (solid symbols) and resorcinol (open symbols).

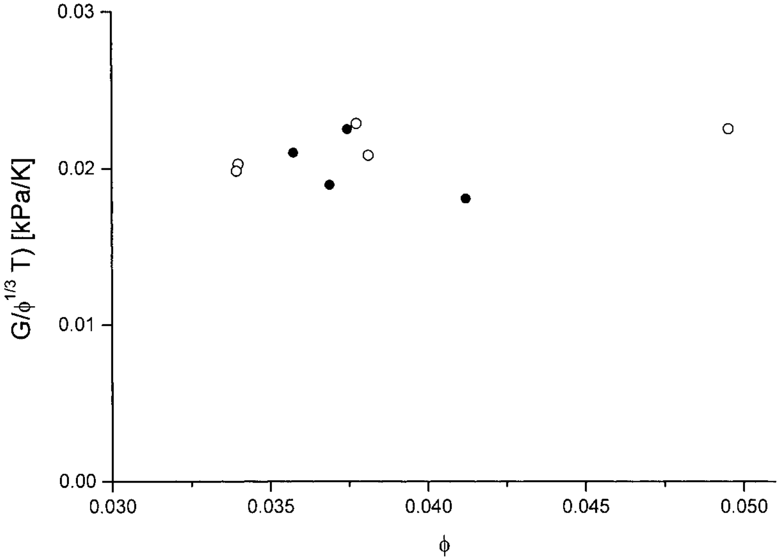
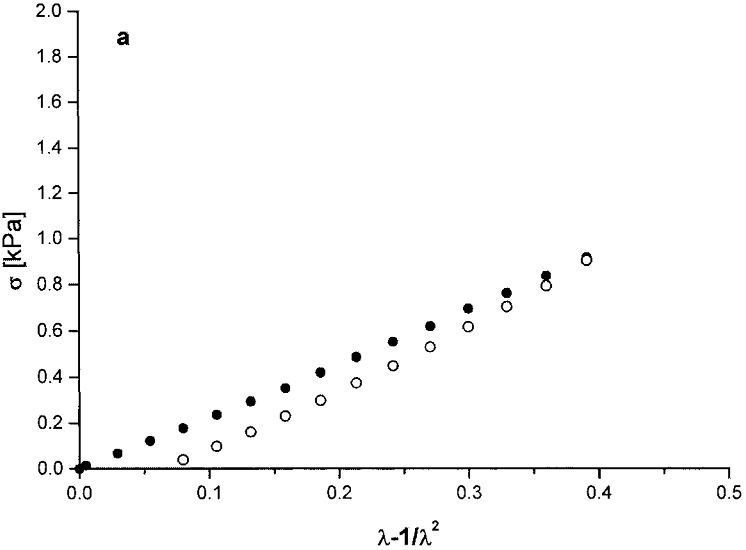


Fig. 5. Normalised shear elastic modulus of PNIPA gels swollen in aqueous solutions of phenol (solid symbols) and resorcinol (open symbols) at different concentrations.


a
σ [kPa]
2.0
1.8
1.6
1.4
1.2
1.0
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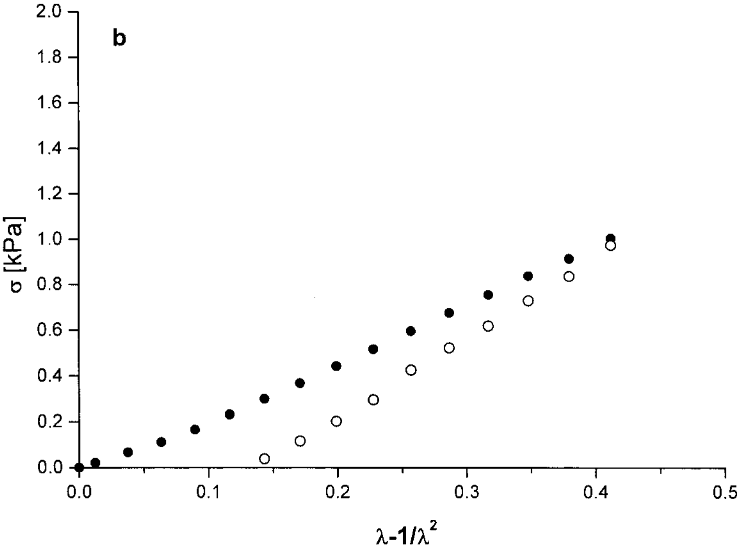
b
σ [kPa]
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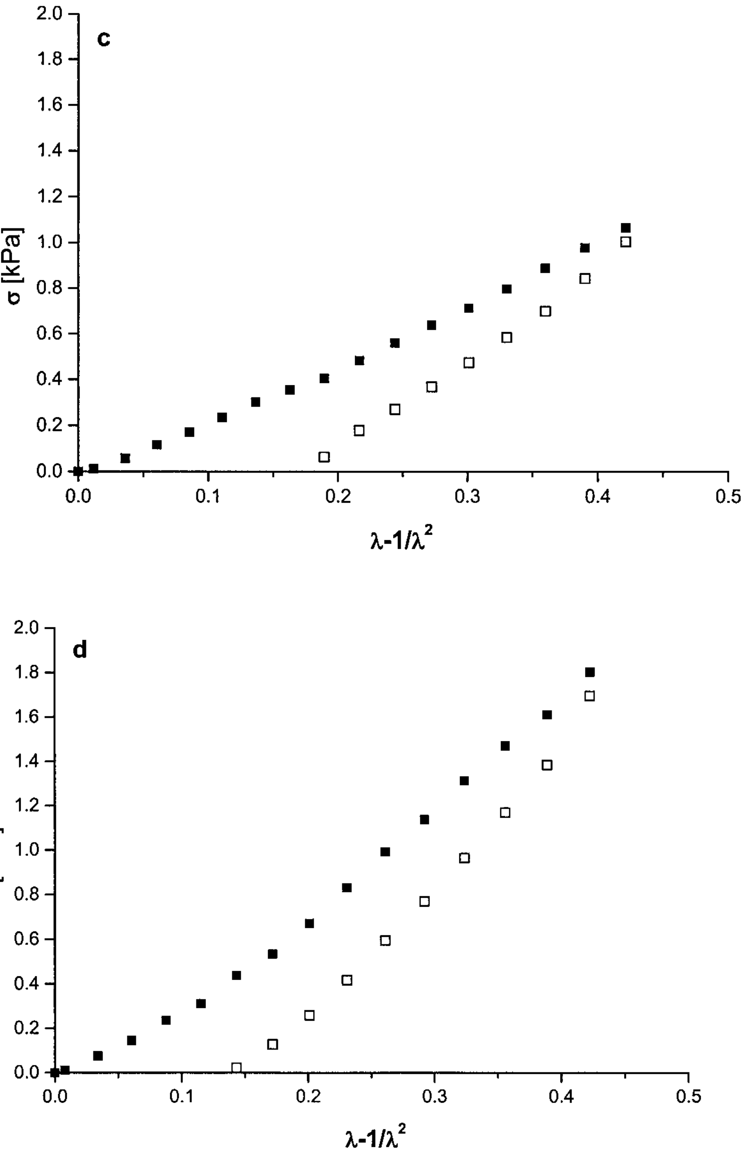

Fig. 6. Stress-strain curves for PNIPA gels swollen to equilibrium in aqueous solutions containing a) 40 mmol/l phenol, b) 50 mmol/l phenol, c) 40 mmol/l resorcinol, d) 50 mmol/l resorcinol, at 20 °C. The curve of increasing stress (solid symbols) lies above that of decreasing stress (open symbols) owing to the loss of solvent during compression.

Measurements of the elastic modulus in compression were also made for the same gels containing varying amounts of phenol and resorcinol. For all samples, the initial slopes of the stress-strain curves yielded the same value of the shear modulus G, after correction for the concentration according to the standard relation.[10]

$$G = nRT\phi^{1/3} \qquad (1)$$

Here, R is the gas constant, T the absolute temperature, n the number of elastically active chains per unit volume and ϕ is the polymer volume fraction. Figure 5 shows that the quantity $G/\phi^{1/3}T$ is a constant, independent of the concentration of phenol or resorcinol in the contacting solution. This result confirms that these solutes introduce no strong complexes that act as additional effective cross-links in the polymer network. While the stress-strain curves are reversible for low solute concentrations, this is no longer true for gels equilibrated with solutions of initial concentration of more than 30 mmol/l, either of phenol or of resorcinol.

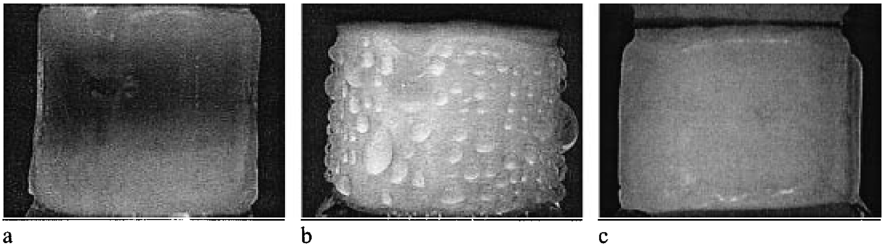

Fig. 7. Appearance of isometric cylindrical PNIPA gels during compression at 20 °C a) sample equilibrated with 40 mmol/l resorcinol, initial phase; b) same sample at maximum compression; c) sample equilibrated with 40 mmol/l phenol solution at maximum compression.

The responses, shown in Figure 6, correspond to solvent being expelled from the gel specimens during compression. This phenomenon is accompanied by the appearance of strong opalescence, which spreads throughout the sample upon application of stress. As the strain ($\lambda-1/\lambda^2$) increases, solvent is expelled to the wall of the gel. A striking difference in behaviour is observed, however, between the phenol containing samples and those containing resorcinol. In the former case the solvent wets the outer surface of the cylinder and runs down the outside. In the resorcinol system, the outside of the gel becomes decorated with beads of free solvent as well as blisters (see Figure 7), which essentially remain in the same position throughout the compression stage. The beads exhibit a contact angle of approximately 50° on the gel surface, indicative of a more repulsive interaction between gel and solvent than in the case of phenol. The remarkable columnar arrangement of solvent beads that can be seen in the figure appears to be unrelated to surface defects on these specimens. This pattern has probably a similar origin as the modulation effects that are sometimes observed in swelling and desswelling gels.[11,12]

Conclusions

Measurements of the swelling behaviour at 20 °C of PNIPA in aqueous solutions of two weak aromatic acids, phenol and resorcinol are reported. The uptake of these solutions is similar for solute concentrations below 45 mmol/l. Phenol exhibits an excess equilibrium concentration inside the gel of 5% over that in the surrounding bath, while for resorcinol, the excess is 12%. At solute concentration 50 mmol/l, both systems display a volume transition accompanied by expulsion of the solvent. The solubility limits in water of these aromatic compounds, which are significantly different (870 mmol/l and 9080 mmol/l respectively), are far above this critical concentration. In the collapsed condition the expelled liquid spreads on the surface of the phenol treated gel, while, in the case of resorcinol, an ordered columnar arrangement of distinct droplets develops on the cylinder surface. The contact angle of the droplets is approximately 50°.

Acknowledgement

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