Ion-exchange Induced Change in the Structure and Osmotic Properties of Sodium Polyacrylate Hydrogels

Ferenc Horkay[1*], Peter J. Basser[1], Anne-Marie Hecht[2], Erik Geissler[2]

[1]Section on Tissue Biophysics and Biomimetics, Laboratory of Integrative and Medical Biophysics, NICHD, National Institutes of Health, 13 South Drive, Bethesda, MD 20892, USA

[2]Laboratoire de Spectrométrie Physique, Université Joseph Fourier de Grenoble CNRS UMR 5588, B.P. 87, 38402 St Martin d'Hères, FRANCE

SUMMARY: The swelling and volume transition of fully neutralized sodium polyacrylate gels were investigated in salt solutions using osmotic and small angle neutron scattering measurements. The volume transition was induced by monovalent/divalent cation exchange. The overall salt concentration and the ratio of monovalent to divalent cations were varied in the biologically significant range. The neutron scattering response of fully neutralized polyacrylate gels in the presence of excess salt is described by the sum of a dynamic and a static component. The thermal correlation length determined from the intensity of the dynamic component displays a maximum at the transition.

Introduction

Selective interactions between certain cations (e.g., calcium) and the anionic sites of biological polyelectrolytes play a significant role in important physiological functions such as nerve excitation, muscle contraction and cell locomotion. Investigation of the structure and thermodynamic properties of synthetic polyelectrolyte gels, as model systems, may contribute to a better understanding of metal ion - anionic site interactions in biological systems.(1)

Since the pioneering work of Tanaka(2) it is well known that under certain conditions polyelectrolyte gels undergo a discontinuous volume change. Although volume transitions have been reported for several different hydrogels containing charged monomers,(3-5) the nature of this transition is not fully understood. Previous polyelectrolyte gel studies were not performed under biologically relevant conditions (e.g., ionic strength, ionic composition). In this paper we combine osmotic and neutron scattering techniques to investigate the volume change induced by monovalent-divalent cation exchange in fully neutralized polyacrylic acid gels in the presence of excess salt.

CCC 1022-1360/00/$ 17.50+.50/0

Theory

The swelling pressure ω of a polyelectrolyte gel is[6)]

$$\omega = \Pi_{el} + \Pi_{mix} + \Pi_{ion} \tag{1}$$

where Π_{el}, Π_{mix}, and Π_{ion} are the elastic, mixing and ionic pressures, respectively. For networks made of flexible chains the elastic pressure, Π_{el}, is obtained from the theory of rubber elasticity.[7)] The resulting expression is

$$\Pi_{el} = -G = -G_0\varphi^{1/3} \tag{2}$$

where G is the shear modulus, G_0 is a constant (shear modulus of the dry network) and φ is the volume fraction of the polymer.

The osmotic mixing pressure, Π_{mix}, can be expressed by a Flory-Huggins type equation[6)]

$$\Pi_{mix} = -(RT/v_1)[\ln(1-\varphi) + \varphi + \chi_0\varphi^2 + \chi_1\varphi^3] \tag{3}$$

where v_1 is the molar volume of the solvent and χ_0 and χ_1 are constants.

In the presence of excess salt Π_{ion} does not contribute directly to the swelling pressure because Coulombic interactions between the charged monomers are screened.

For a gel made of flexible polymer chains the neutron scattering intensity can be described by a sum of dynamic and static components[8,9)]

$$I(q) = I_{dyn} + I_{stat} = \Delta\rho^2 \left[\frac{kT\varphi^2}{M_{os}} \frac{1}{1+q^2\xi^2} + \frac{8\pi\Xi^3\langle\delta\varphi^2\rangle}{(1+q^2\Xi^2)^2} \right] \tag{4}$$

where $\Delta\rho^2$ is a contrast factor, k is the Boltzmann constant, ξ and Ξ are respectively the thermodynamic and static correlation lengths, and q is the scattering vector. The first term in equation (4) describes the thermal concentration fluctuations the amplitude of which is governed by the longitudinal osmotic modulus M_{os} of the gel

$$\begin{aligned} M_{os} &= \varphi\partial\omega/\partial\varphi + (4/3)G \\ &= \varphi^2(RT/v_1)[1/(1-\varphi) - 2\chi_0 - 3\chi_1\varphi] + G_0\varphi^{1/3} \end{aligned} \tag{5}$$

The second term in equation (4) corresponds to static nonuniformities frozen-in by the cross-links.

Experimental

Polyacrylic acid gels were made by the free-radical copolymerization of partially neutralized acrylic acid and N,N'-methylenebis(acrylamide) in aqueous solution according to a method described previously.[10)] After gelation, the gel samples were fully neutralized, washed in deionized water and then swollen in salt solution. Swelling pressure measurements were carried out by equilibrating gels with aqueous solutions of poly(vinyl pyrrolidone) (molar mass: 29 kDa) of known osmotic pressure.[11,12)] A semipermeable membrane was used to prevent penetration of the polymer into the network. This procedure gives the dependence of ω upon the polymer volume fraction, φ, for each gel.

The shear moduli of the gels were determined from uniaxial compression measurements performed on cylindrical specimens using a TA.XT2I HR Texture Analyser (Stable Micro Systems, UK). The absence of volume change and barrel distortion was verified.

Small angle neutron scattering (SANS) measurements were carried out at the National Institute of Standards and Technology (NIST), Gaithersburg MD, on the NG3 instrument with an incident wavelength of 8 Å. Two sample-detector distances were used: 3 m and 13.1 m. Gel samples were swollen in D_2O. Corrections for incoherent background, detector response and cell window scattering were applied.[13)]

All experiments were carried out at 25 ± 0.1°C.

Results and Discussion

Fig. 1 shows the variation of the swelling degree of a fully neutralized sodium polyacrylate gel in different salt solutions. Increasing the salt concentration leads to gel contraction because ions screen the repulsive interactions between charged monomers. In solutions of alkali metal salts, the swelling degree, $1/\varphi$, decreases gradually. When divalent cations are added to the system, above a certain critical concentration a sudden volume change occurs. We note that in biological systems (e.g., in nerve membranes), under physiological conditions, volume changes were observed at a similar concentration and molar ratio of divalent to monovalent cations.[1,14)]

In Fig. 2 is shown the dependence of the shear modulus G upon the swelling degree $1/\varphi$ for a polyacrylate gel in different salt solutions. In solutions containing both NaCl and $CaCl_2$ (open symbols) G is a function of the swelling degree only, implying that Ca does not form strong bridges between the polymer chains, i.e., G_0 is constant. When $CoCl_2$ is added to a gel swollen in NaCl solution, however, *G* progressively increases with increasing Co concentration (filled symbols). This effect may be the consequence of complex formation between Co ions and the carboxylate groups of the polymer.

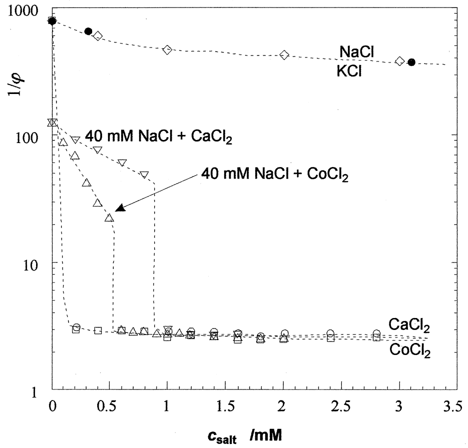

Fig. 1: Variation of the equilibrium swelling degree ($1/\varphi$) of sodium polyacrylate gels as a function of the salt concentration.

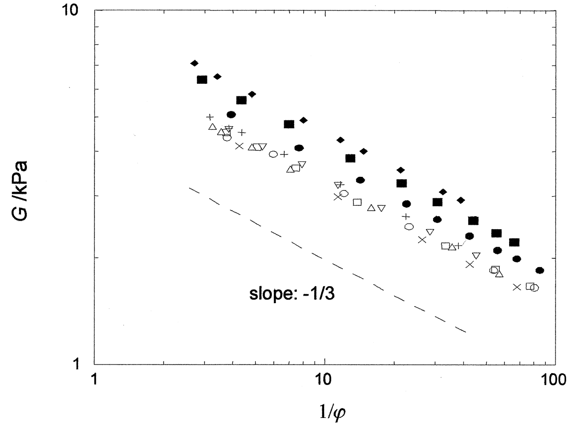

Fig. 2: Variation of the shear modulus *G* as a function of the swelling ratio $1/\varphi$. Open symbols: gels swollen in 40 mM NaCl solutions containing different amounts of $CaCl_2$ (0-0.8 mM). Closed symbols: gels in 40 mM NaCl solutions containing $CoCl_2$ (0.1-0.3 mM).

In Fig. 3 the variation of the swelling pressure is shown as a function of the polymer volume fraction for polyacrylate gels in salt solutions. The curves through the experimental points are the least-squares fits to equation (3). The values of χ_0 and χ_1 obtained from the fits are listed in Table 1. It is apparent that χ_0 varies little with the concentration of divalent cations, while χ_1 exhibits a jump-like increase in both systems.

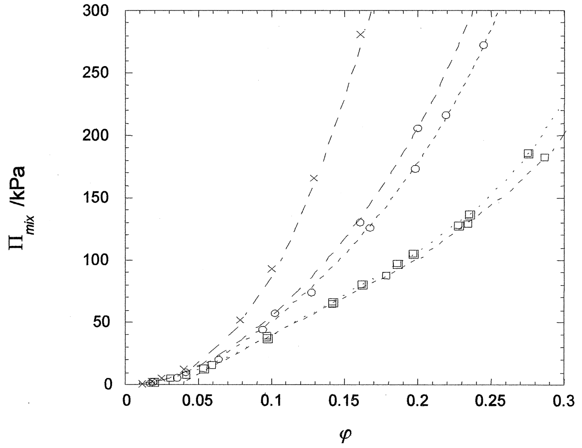

Fig. 3: Π_{mix} vs. φ curves for polyacrylate hydrogels in salt solutions. x 40 mM NaCl; o 40 mM NaCl + 0.2 mM $CaCl_2$; • 40 mM NaCl + 0.1 mM $CoCl_2$; □ 40 mM NaCl + 0.8 mM $CaCl_2$; ■ 40 mM NaCl + 0.3 mM $CoCl_2$.

Table 1: Values of χ_0 and χ_1 for polyacrylate hydrogels in equilibrium with salt solutions.

System	χ_0	χ_1
40 mM NaCl	0.448 ± 0.001	0.21 ± 0.01
40 mM NaCl + 0.2 mM $CaCl_2$	0.450 ± 0.001	0.45 ± 0.01
40 mM NaCl + 0.5 mM $CaCl_2$	0.453 ± 0.001	0.50 ± 0.01
40 mM NaCl + 0.8 mM $CaCl_2$	0.454 ± 0.001	0.53 ± 0.01
40 mM NaCl + 0.1 mM $CoCl_2$	0.452 ± 0.001	0.47 ± 0.01
40 mM NaCl + 0.2 mM $CoCl_2$	0.454 ± 0.002	0.50 ± 0.01
40 mM NaCl + 0.3 mM $CoCl_2$	0.455 ± 0.001	0.52 ± 0.01

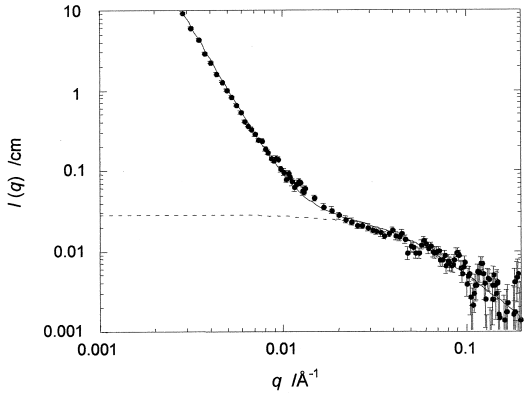

Fig. 4: Neutron scattering spectrum of a polyacrylate hydrogel. The continuous curve through the data points is the least squares fit to equation (4).

To obtain information on the variation of the microscopic length scales that control gel thermodynamics, SANS measurements were performed as a function of the calcium concentration. A typical SANS spectrum is shown in Fig. 4. The continuous line through the data points is the fit of equation (4), and the dashed line represents the thermodynamic component of the scattering signal (first term). The slope of the curve at low values of q is close to -4, characteristic of Porod scattering from smooth surfaces.[15)]

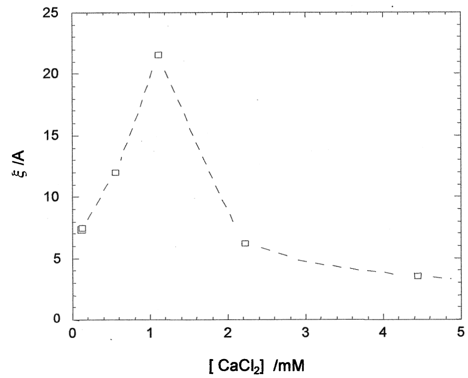

Fig. 5: Thermal correlation length ξ calculated from neutron scattering data as a function of calcium chloride concentration.

In Fig. 5 is plotted the thermal correlation length[16)], ξ, as a function of the calcium chloride concentration. ξ exhibits a maximum at the transition indicating that the spatial range of thermodynamic concentration fluctuations is significantly enhanced. This is the consequence of the reduction of the osmotic modulus at the critical point.

Conclusions

The addition of divalent cations to gels swollen in salt solutions significantly affects the mixing interaction term and leads to an abrupt volume transition. Combination of osmotic swelling pressure and SANS measurements provides consistent results on the thermodynamics of volume transition induced by monovalent-divalent cation exchange in sodium polyacrylate hydrogels. The scattering response of these gels can be described as a sum of dynamic and static terms. The thermal correlation length determined from the thermodynamic component of the SANS signal exhibits a maximum at the transition.

Acknowledgements

We acknowledge the support of the National Institute of Standards and Technology, U.S. Department of Commerce in providing the neutron research facilities used in this experiment. This work is based upon activities supported by the National Science Foundation under Agreement No. DMR-9423101. We are grateful to Dr. Boualem Hammouda for his invaluable help.

References

1. I.Tasaki, *Japan. J. Physiol.* **49**, 125 (1999)
2. T. Tanaka, *Phys.Rev.Lett.* **40**, 820 (1978)
3. J. Ricka and T.Tanaka, *Macromolecules* **17**, 2916 (1984); *Macromolecules* **18**, 83 (1985)
4. A. Suzuki and H. Suzuki, *J.Chem.Phys.* **103**, 4706 (1995)
5. S. Hirotsu, Y. Hirokawa and T. Tanaka, *J.Chem.Phys.* **87**, 1392 (1987)
6. P.J. Flory, "*Principles of Polymer Chemistry*", Cornell University, Ithaca, NY 1953
7. L.R.G. Treloar, "*The Physics of Rubber Elasticity*", Clarendon, Oxford 1976
8. S. Mallam, F. Horkay, A.-M. Hecht, A.R. Rennie and E. Geissler, *Macromolecules* **23**, 54 (1991)
9. F. Horkay, A.-M. Hecht, S. Mallam, E. Geissler and A.R. Rennie, *Macromolecules* **24**, 289 (1991)
10. F. Horkay, I. Tasaki and P.J. Basser, *Biomacromolecules* **1**, 8 (2000)
11. H. Vink, *Europ. Polym. J.* **7**, 141 (1971)
12. F. Horkay and M. Zrinyi, *Macromolecules* **15**, 81 (1982)
13. NIST Cold Neutron Research Facility. NG3 and NG7 30-meter SANS Instruments Data Acquisition Manual, January 1999.
14. I. Tasaki and P.M. Byrne, *Brain Res.* **475**, 1 (1988); *Biopolymers* **32**, 10 (1992); *Biopolymers* **34**, 20 (1994)
15. O. Glatter and O. Kratky, "*Small Angle X-ray Scattering*" Academic Press, London 1982.
16. P. G. de Gennes, "*Scaling Concepts in Polymer Physics*", Cornell: Ithaca, NY 1979.