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Water in Hydrogels. 3. Poly(hydroxyethyl methacrylate)/Saline Solution Systems

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ABSTRACT: High-resolution ^{23}Na NMR is used in conjunction with broad-line ^{1}H resonance and DSC to investigate the nature of water in poly(hydroxyethyl methacrylate) (PHEMA)/saline systems. The introduction of sodium ions into the hydrated polymer system increases the nonfreezable water content and depresses devitrification. The Na$^+$ ions also decrease water mobility below 250 K, confirming sodium as a water-coordinating ion. T_{2L} data indicate a low-temperature ($\approx$220 K) glass transition with T_g(heating) < T_g(cooling). A phase transition in hydrated PHEMA at $\approx$250 K is indicated. The behavior of the ^{23}Na line width and chemical shift are broadly consistent with similar studies in the literature that reveal the sensitivity of ^{23}Na to its local environment.

Introduction

Parts 1 and 2 of this study examined the role of water in poly(*N*-vinyl-2-pyrrolidinone/methyl methacrylate) copolymer (P(NVP/MMA)) and poly(hydroxyethyl methacrylate) (PHEMA), respectively.[1,2] The purpose of this paper is to extend the investigations on hydrated PHEMA to include PHEMA/saline systems. The incorporation of additional ions into the hydrated polymer exacerbates an already complex system but, nonetheless, poses some fundamental and challenging scientific questions. The motivation for this work rests on the use of PHEMA and similar polymers in the manufacture of soft contact lenses. Understanding the role of water in these polymer systems as it may relate to lens properties such as oxygen permeability and lens dehydration[3,4] is of interest in the development of new contact lens materials.

The earlier study exploited the combined techniques of low-resolution ^{1}H nuclear magnetic resonance (NMR) and differential scanning calorimetry (DSC) to delineate quantitatively different water types in the hydrated polymer. For PHEMA, the principal observation is the detection by NMR of glassy water ($T_g \approx 180$ K) and the subsequent freezing or devitrification of part of the water rendered mobile in a sample initially quenched to a temperature below T_g and then examined on the heating cycle.[1,2,5] The amount of freezable (normal or near normal) and nonfreezable (bound) water is determined. PHEMA is much less hydrophilic than PNVP/MMA but the relative fraction of water that is bound or nonfreezable in the saturated polymer is appreciably higher. Hysteresis effects are evidence that the fraction of nonfreezing water is controlled by a number of equilibrium and nonequilibrium factors, the latter being highly temperature and concentration dependent.[6]

The extent to which hysteresis associated with thermal history and nonequilibrium factors are present in systems containing Na ions is clearly evident in the DSC study by Hatakeyama and co-workers[7] on a water/sodium cellulose sulfate system. Upon quenching from the isotropic liquid to ca. 170 K, they deduce that a glassy state ensues which gives rise to four transitions: in order of increasing temperature there is a glass transition, cold crystallization, thawing, and a transition from a mesophase indicative of long-range order to the isotropic liquid state. Detection of the glassy state by DSC depended on water concentration and thermal history. Nonfreezable water was attributed to three water molecules strongly associated with the ionic groups and one molecule bonded to hydroxyl groups.

In this study on PHEMA/saline systems, DSC and ^{1}H NMR are further complemented with high-resolution ^{23}Na NMR. Many studies in the literature[8-18] attest to the sensitivity of ^{23}Na as a probe of the local environment. ^{23}Na has a quadrupole moment eQ whose interaction with local electric field gradients EFG = eq, defined in terms of the coupling constant $\chi_{Na} = e^2qQ/h$, dominates relaxation. Ideally, in solution under extreme narrowing conditions the quadrupole relaxation time T_q ($=T_1 = T_2$) is given by

$$T_q^{-1} = T_2^{-1} = \pi\Delta\nu = (2\pi^2/5)\chi_{Na}^{\ 2}\tau_c \tag{1}$$

$\Delta\nu$ is the line width, τ_c is a correlation time that characterizes fluctuations in the EFG, and a zero asymmetry parameter is assumed. It is evident that relaxation depends on the strength of the interaction defined by χ_{Na} and on τ_c. In aqueous solutions, changes in line width and chemical shift σ in large measure reflect changes in the bond between the Na$^+$ ion and water through ionic bonding, covalent bonding, or a change in the degree of hydration. Templeman and Van Geet[11] conclude that the presence of Cl$^-$ will not dominate relaxation even if it is occasionally in close contact with the Na$^+$ ion. Of course, it is doubtful if extreme narrowing conditions are strictly applicable in these systems[19-22] and interpretation is more complicated. Relaxation, for example, may well be nonexponential. Nor is any account taken of multiple-quantum transition.[22,23] In macromolecular systems, rapid exchange between relatively free and bound sites often occurs, and this situation is described by the expressions

$$\Delta\nu_{obs} = P_b\Delta\nu_b + P_f\Delta\nu_f \tag{2a}$$

$$\sigma_{obs} = P_b\sigma_b + P_f\sigma_f \tag{2b}$$

where the subscripts f and b denote respectively free and bound states. P signifies the mole fraction in each state and $P_b = 1 - P_f$. The use of these expressions in subsequent analysis gives useful insight into ^{23}Na behavior but only in a semiquantitative manner.

It is a central theme of this paper that consideration of collated information from a variety of experimental

Table I
Collated DSC Data for the Three Polymacon Hydrated Systems

	heating cycle			cooling cycle		
sample	W_0, wt %	ΔH, cal g^{-1}	goodness of fit	W_0, wt %	ΔH, cal g^{-1}	goodness of fit
water	25 ± 5	23 ± 1	0.97	25 ± 5	6 ± 0.1	0.98
buffered saline	27 ± 5	47 ± 2	0.98	30 ± 6	16 ± 0.4	0.98
	35 ± 7	55 ± 3	0.99			
2% NaCl	34 ± 7	48 ± 2	0.98	39 ± 8	33 ± 1	0.98
	35 ± 7	50 ± 2	0.99	40 ± 8	36 ± 1	0.98

Table II
Collated NMR Data for the Three Hydrated Polymacon Samples[a]

sample	soln wt %	I_1	I_2	I_3	I_1/I_3	I_2/I_3	$T_0(\uparrow)$, K	$T_0(\downarrow)$, K
water	53 ± 3	0.45	0.32	0.50	0.90 (48)	0.64 (34)	170	180
buffered saline	65 ± 2	0.38	0.33	0.58	0.66 (43)	0.57 (37)	170	175
2% NaCl	61 ± 5	0.34	0.30	0.60	0.57 (35)	0.50 (31)	170	180

[a] All data refer to the heating cycle. T_0 is the temperature at which I_L becomes nonzero ($T_0(\uparrow)$) or is reduced to zero ($T_0(\downarrow)$). I_1, I_2, and I_3 are respectively, the peak intensity of $I(T_{2L})$ in the vicinity of 220 K, the minimum value of $I(T_{2L})$ near 260 K, and the maximum recorded value at ambient temperatures. The numbers in parentheses represent the corresponding weight percent.

approaches—in this case, DSC, ^{1}H NMR, and ^{23}Na NMR—greatly facilitates an unraveling of the complexities of the saline-soaked PHEMA systems under investigation.

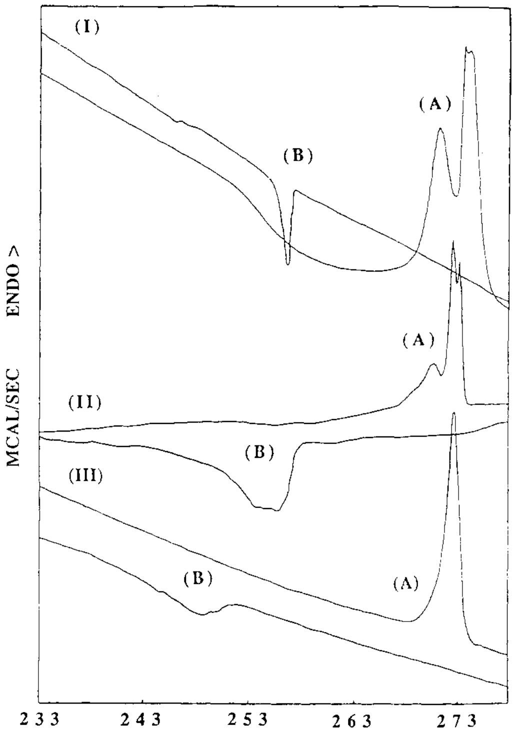

Figure 1. Typical DSC endotherms (A) and exotherms (B) for (I) S(43), (II) BS(42), and (III) SN(43).

Experimental Section

The procedures used to record and analyze T_2 (^{1}H) and DSC data are described fully in the earlier publications.[1,2] ^{23}Na spectra were recorded at a resonance frequency of 79.38 MHz on a Bruker MSL300 spectrometer with chemical shifts referenced to the ^{23}Na resonance peak for 0.1 M NaCl. No account was taken of susceptibility corrections, which, in any event, are expected to be less than 1 ppm.[11] The polymer, available commercially as Polymacon, contains small amounts of ethylene glycol dimethacrylate (0.4 wt %) and benzoin methyl ether (0.2 wt %). The following sample designations are used: S(*W*), as before, denotes *W* wt % water relative to the dry polymer, incorporated after polymerization; SN(*W*) denotes samples hydrated with 2 wt % NaCl solution; and BS(*W*) refers to samples hydrated with a buffered saline solution having the following formulation: NaCl (0.9 wt %), $NaH_2PO_4 \cdot H_2O$ (0.016 wt %), and anhydrous Na_2HPO_4 (0.066 wt %). This solution approximates the pH and osmolality of tears in the eye.

Results and Discussion

DSC Results. Representative endotherms and exotherms for PHEMA hydrated with water, buffered saline, and 2 wt % NaCl solutions are presented in Figure 1. The traces exemplify to varying degrees the principal features observed in the earlier study,[2] in particular, the exotherm on heating (devitrification) and structure of the endotherms and exotherms indicative of a distribution of freezing/thawing temperatures in the system. Note, however, that structure is much less pronounced in the endotherms for SN(*W*) and that the devitrification exotherm is significantly weaker in BS(*W*) samples and virtually absent in SN(*W*) samples.

Extensive measurements were carried out on the three hydrated systems as a function of solution content (Figure 2). Recall that the intercept on the *W* wt % axis represents the nonfreezable water and that the slope of the straight line denotes the associated heat of fusion/thawing. The extent to which the latter departs from the value for bulk water (79.6 cal g^{-1}) provides an indication of the degree of water dispersion in the system. The collated results are given in Table I. A number of general observations can be made at this juncture:

(i) The fact that $\Delta H_{\text{exo}} < \Delta H_{\text{endo}}$ is in accord with earlier observations.[1,2]

(ii) The introduction of NaCl produces a small but significant increase in the amount of nonfreezable water W_0 which is consistent with the notion that the Na$^+$ ion is a water structure forming ion in aqueous solution.[16]

(iii) Interestingly, the introduction of NaCl increases ΔH, indicating that the freezable water detected by DSC is somewhat more bulklike.

(iv) Devitrification is depressed with the addition of NaCl.

NMR T_2 (^{1}H) Results. The earlier study on water in hydrogels[1,2] confirmed the particular sensitivity of T_2 to different water motions and environments. T_2 versus temperature reveals the onset of molecular motion and hysteresis associated with increasing and decreasing temperature cycles, whereas T_2 component intensity data permit estimates of the relative amounts of distinguishably different types of water in the hydrogel. Data for BS(63) and SN(61) are presented respectively in Figures 3 and 4. Collated data for the three hydrated systems are furnished in Figures 5 and 6. The following observations can be drawn:

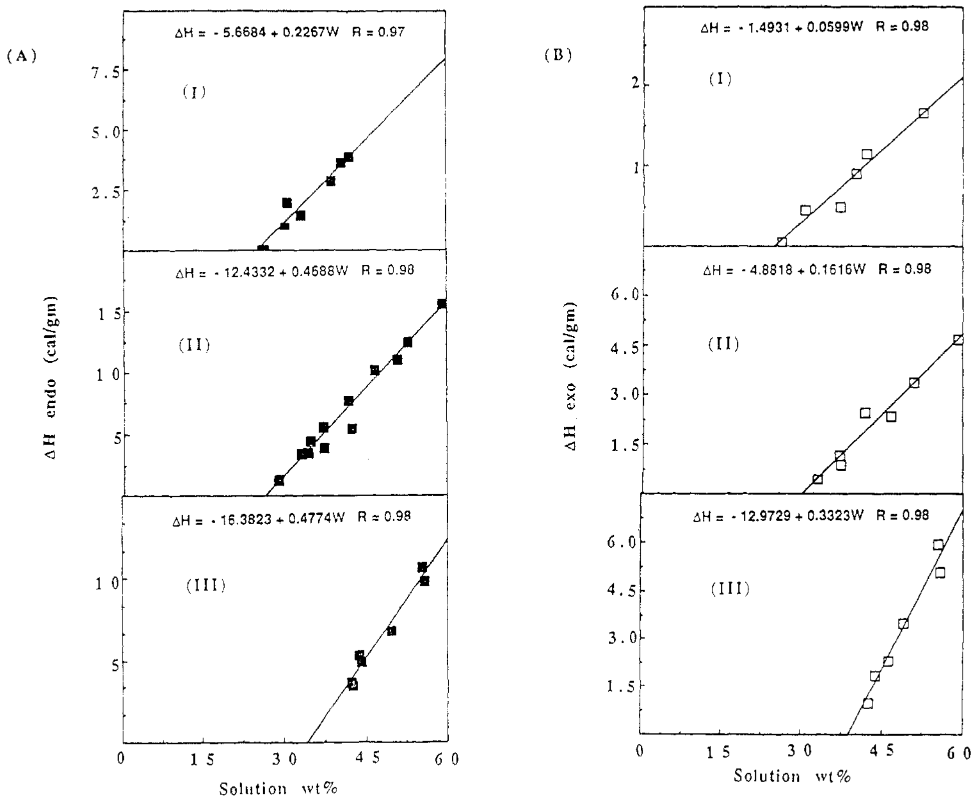

Figure 2. Change in enthalpy, ΔH, as a function of solution content for endothermic (A) and exothermic (B) hydrated Polymacon data. The regression fits to the data are as indicated: (I) S(W); (II) BS(W); (III) SN(W) samples.

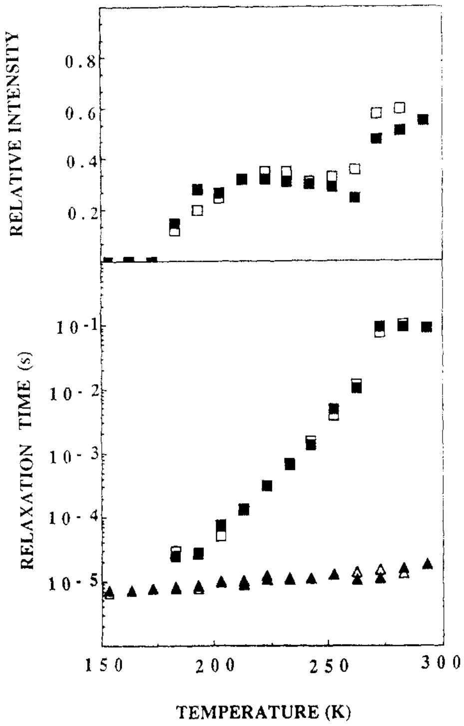

Figure 3. NMR T_2 and $I(T_{2L})$ vs temperature for BS(63). Filled points denote the heating cycle and unfilled points the cooling cycle.

(i) T_{2L} represents water behavior at low temperatures with perhaps an additional contribution from plasticized polymer at higher temperatures. In all cases mobility sets in at low temperatures reflecting glassy water passing through its glass transition. Note that motion sets in at a lower temperature on the heating cycle (after quenching from room temperature) than on the decreasing temperature cycle (stepped slow cooling). This implies that T_g(heating) < T_g(cooling).

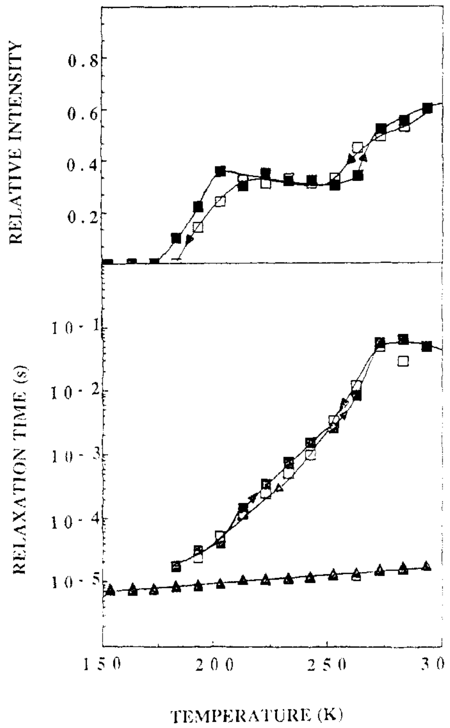

Figure 4. NMR T_2 and $I(T_{2L})$ vs temperature for SN(61). Filled points denote the heating cycle and unfilled points the cooling cycle.

(ii) T_{2L} tends to be longer on the decreasing temperature cycle down to ca. 250 K, which is symptomatic of supercooling in keeping with the conclusions of DSC. $I(T_{2L})$ is correspondingly greater in this temperature regime. Hysteresis is not observed in the T_2 data for BS(63) but is revealed in $I(T_{2L})$. The data for SN(61) are especially interesting in the manner that both T_{2L} and its intensity are greater on the cooling cycle down to ca. 250 K as

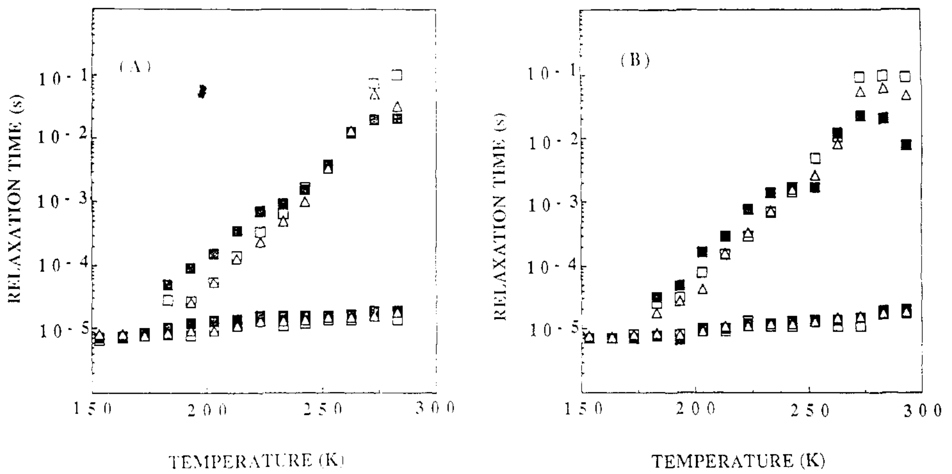

Figure 5. Composite plot of NMR T_2 vs temperature for the three saturated Polymacon systems. (A) Cooling cycle; (B) heating cycle. (□) BS(63); (■) S(53); (△) SN(61).

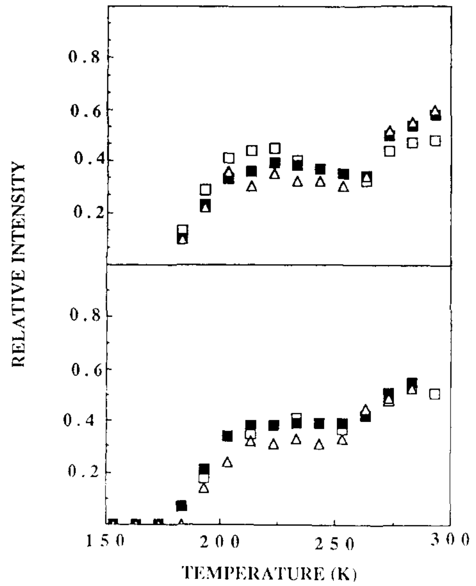

Figure 6. Component T_{2L} intensity data for the three saturated Polymacon systems. (A) Cooling cycle; (B) heating cycle. (□) S(53); (■) BS(65); (△) SN(61).

expected but then fall below the magnitude observed on the heating cycle between 250 K and ca. 215 K. Recall that the exotherm for this system occurs in the vicinity of 250 K.

(iii) Considering the collated data in Figure 5, it is clear that the mobility achieved in the water hydrated system S(50) is appreciably greater than in BS(63) or SN(61) for temperatures below ca. 250 K.

(iv) The tendency for T_{2L} in S(53) to decrease with temperature above ambient indicates chemical exchange between heterogeneous sites as described by Resing.[24] This of course implies that the water phase has not yet reached its truly isotropic state within the temperature range of these measurements.

(v) The collated intensity data in Figure 6 and in Table II are revealing in a number of respects. First, the amount of glassy water rendered mobile (I_1/I_3) at ca. 220 K is greatest for the water hydrated sample S(50). The observed intensity indicates that the bulk of the water is tightly bound in S(53), whereas the proportions of tightly bound water in BS(63) and SN(61) are appreciably lower. Second, the difference between I_1/I_3 and I_2/I_3 representing the extent of devitrification progressively decreases for samples S(50), BS(63), and SN(61) in keeping with the conclusions of DSC. Unlike the relative amounts of tightly bound water (I_1/I_3), the amount of water that survives the devitrification process and remains mobile at ca. 255 K (I_2/I_3) is essentially the same for all three hydrated systems. Recall that W_0 from the endothermic data is of the same order of magnitude and changes only modestly with the introduction of Na^+ ions.

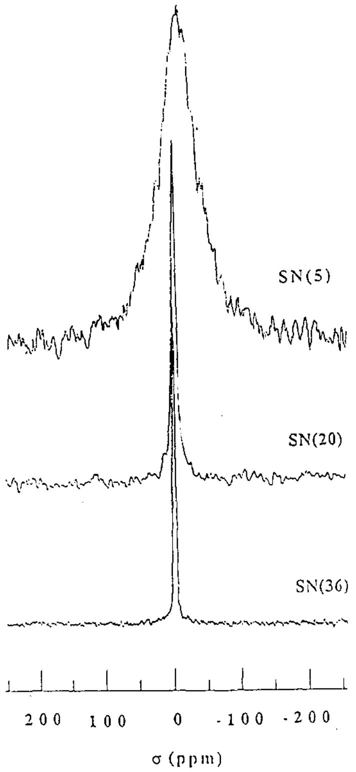

Figure 7. ^{23}Na resonance lines at 293 K for SN(5), SN(20), and SN(36).

^{23}Na NMR Results. The preliminary discussions in the Introduction noted the sensitivity of ^{23}Na to its immediate environment by virtue of quadrupolar interactions with the local EFG. Line-width and chemical shift data were recorded over a wide range of solution contents and a modest range of temperatures (293–313 K). It was considered unwise to exceed 313 K lest water is driven off. As is typical for Na in aqueous solution, a single symmetrical line is observed (Figure 7). The way in which $\Delta\nu$ and σ respond to decreasing levels of hydration (Figure 8) is broadly consistent with the general pattern observed in similar studies.[10,12,16,17] At high water contents the Na^+ ion is fully hydrated and experiences a reasonably

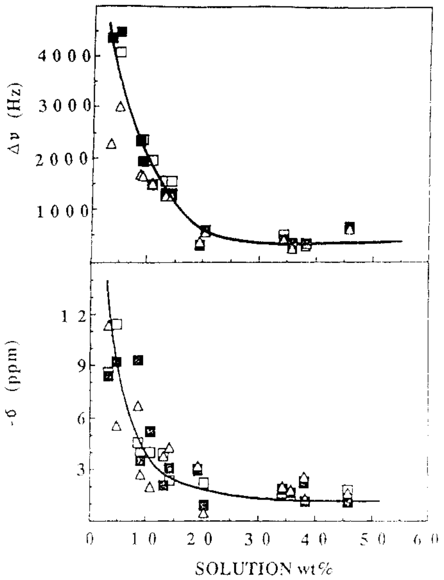

Figure 8. ^{23}Na line width at half-height ($\Delta\nu$) and chemical shift (σ) as a function of solution weight percent in SN(W) samples. (□) 293 K; (■) 303 K; (△) 313 K.

symmetric EFG (eq is small) with the result that line widths are small and chemical shifts are modest. Note, however, that the line widths in the most heavily hydrated samples are still appreciably greater than $\Delta\nu$ for concentrated aqueous electrolytes of comparable salt concentration. This indicates that the Na$^+$ ion still senses the polymer matrix even in the heavily hydrated state. As expected, the line width and chemical shift decrease with increasing temperature. As the water content decreases, broadening sets in fairly abruptly in the vicinity of ca. 25 wt % solution, which, interestingly, is close to the nonfreezable water content W_0 determined by DSC (Table I). As the solution content decreases, eq and τ_c increase.

There are a number of possible scenarios to account for the observed dependence of $\Delta\nu$ and σ on W. For example, depletion of the hydration shell will induce distortion in the local Na$^+$ environment with a concomitant increase in broadening. It is entirely possible too that electrostatic interactions between Na$^+$ and fixed sites in the polymer are favored at low water contents which will generate appreciable electric field gradients due to the distortion of the Na electronic environment upon binding. τ_c will also increase. More generally, one can envisage a situation where some of the Na$^+$ ions may be involved in binding to fixed sites while others are relatively free, as described by eq 2. The relaxation rate in the bound state is significantly greater than in the free state. Chemical shifts respond in like manner. The states are presumed to be in equilibrium through rapid exchange except perhaps at low water concentrations. As the water content continues to decrease past the 25–30 wt % level, the sodium environment becomes increasingly distorted, leading to further increases for the bound values of both $\Delta\nu$ and σ. Therefore, the dramatic increases in the observed values for these parameters seen in Figure 8 are due to the fact that in eq 2, both P_b and $\Delta\nu_b$ (and σ_b) are increasing.

Intercomparison of Data. It is evident from the foregoing that $W \approx 30 \pm 5$ wt % is common to a number of experimental observations: it denotes the amount of nonfreezable water detected by DSC (Table I); it represents the amount of mobile water that survives devitrification or, in the parlance of Hatakeyama and co-workers,[7] cold crystallization; and it broadly signifies the water content where abrupt changes in ^{23}Na line width and chemical shift occur. It can be reasonably concluded from these observations that the tenacity for PHEMA to form $W_0 = 30 \pm 5$ wt % tightly bound water is high. When the water content approaches this level, the tendency is to deplete the hydration shell around the Na$^+$ ion or indeed to induce the ion to form a complex with the tightly bound water/polymer system. It is the water *in excess* of this tightly bound water, however, that demonstrates the most interesting characteristics and is particularly sensitive to the environment. When no sodium is present, this excess water appears bound to the hydrophilic moieties of the polymer/water matrix and becomes mobile at temperatures in the 220 K region. Once sufficient mobility is achieved, the water can undergo devitrification and refreeze. When sodium is present, however, there is a greater propensity for this water to hydrate the sodium ions and therefore participate in enhanced supercooling. Devitrification is significantly decreased. This would rationalize the observed depression of I_1/I_3 with the addition of Na$^+$ ions. It would, additionally, provide a plausible explanation for the more bulklike behavior detected in DSC data, that is, a higher ΔH and the absence of structure on the endotherms for SN(W) samples. From these observations, the strength of water interaction with system sites is expected to be (in decreasing order) tightly bound polymer > sodium ion hydration > loosely bound polymer. As water is added to the system, all the binding sites will be filled before any significant bulklike water is observed.

The second recurring parameter is the temperature 250 ± 5 K. It denotes the completion of the devitrification process and is precisely the temperature where Hatakeyama and co-workers[7] observed two simultaneous cold crystallization processes in their isothermal DSC data on hydrated sodium cellulose sulfate; it defines the temperature region where the DSC exotherm is detected in SN(W) samples; and it represents the temperature at which the observed hysteresis in T_{2L} for SN(61) inverts. Clearly, this temperature defines a phase transition in hydrated PHEMA, as it does in hydrated sodium cellulose sulfate.

Turning to the observation of different T_g values on the heating and cooling cycles, clearly there are different water structures induced by quenching and by slow cooling. It is intuitively sensible for the quenched sample to manifest a lower T_g (on the NMR frequency scale) since one would expect a more disordered structure to be created in rapid cooling of the highly mobile water that exists at ambient temperatures. Above the glass transition it is again reasonable to observe a higher T_{2L} in SN(61) over the heating cycle, at least up to 250 K. The observed inversion of hysteresis at this temperature arises principally from supercooling on the cooling cycle.

In summary, the addition of saline to the PHEMA/water system described in part 2 of this study did produce a complex system. However, with the addition of ^{23}Na NMR and careful examination of both the thermal and proton data, useful insight into the way in which water behaves in PHEMA hydrated with saline ensued. While not affecting the tightly bound water associated with the polymer, the sodium did affect the more loosely bound water which proved to be extremely sensitive to its temperature and physical environment. Examination of other polymer systems hydrated with saline should prove interesting. As noted earlier, the motivation for this work is the understanding of the role of water as it may relate to contact lens properties. Of primary importance is the dehydration of the lens and the subsequent potential to cause desiccation of the cells on the surface of the cornea. Since water bound to a polymer system or ionic moiety is expected to be less susceptibile to evaporation, it is of interest to quantitate the bound water and compare this value to clinical data.[4] Similar studies on other contact lens polymer systems would further define the relationship.

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