THE HEAT CAPACITY OF WATER SWOLLEN POLY(2-HYDROXYETHYL ACRYLATE) ABOVE AND BELOW 0°C

Jan Biroš, Rattan Lal Madan* and Julius Pouchlý

Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, 162 06 Prague 6

Received April 23rd, 1979

Dedicated to Professor E. Hála on the occasion of his 60th birthday.

The heat capacities of water swollen poly(2-hydroxyethyl acrylate) were determined with a DSC-2 calorimeter in the range 220—350 K for concentrations between 0 and 1·95 g water per 1 g polymer. The results confirm conclusions obtained in a preceding paper for the system poly[2-(2-hydroxyethoxy)ethyl methacrylate]-water. At temperatures above 0°C the partial specific heat capacity of water in the polymer is independent of composition and equal to the specific heat capacity of pure liquid water. This indicates that water sorbed in the polymer is not strongly bound. Analysis of data on the heat capacity below 0°C has led to a conclusion that at a water content below 0·2 g/g or at temperatures 230 K and lower, the crystallization of water from the gel is inhibited by factors which make impossible the attainment of thermodynamic equilibrium. Non-freezing water should not be identified with "strongly bound" water.

The heat capacity of liquid water contains an unusually high configurational contribution, which reflects the heat instability of the structure of liquid water built up from hydrogen bonds. Hence, the determination of the partial specific heat capacity of water in solutions may lead to important conclusions concerning the structure and state of water in these systems. Many data have been obtained for dilute aqueous solutions of organic compounds. Recently, also mixtures with a lower water content have been studied: Measurements were carried out on polymers swollen in water, namely, on collagen[1,2] and poly[2-(2-hydroxyethoxy)ethyl methacrylate] (PHEOEMA)[3]. It was found that at usual temperatures the partial specific heat capacity of water in these systems is composition-independent and is approximately equal to[3], or even higher than[1], the heat capacity of pure liquid water. Similar results have been provided by measurements of mixtures of water with some non-electrolytes[4,5]. It follows therefrom that in the swollen polymer the structure of water is liquid-like, and the polymer does not contain any perceptible quantity of strongly bound immobilized water.

Such a conclusion is at variance with the existing interpretation of a phenomenon known as non-freezing of water in polymers. Calorimetric and volumetric measurements below 0°C have frequently demonstrated that part of water present in the polymer does not crystallize even at deep cooling (but it may be transformed into the glassy state[2,6]). It is assumed that this fraction

---

* Fellow of UNESCO Course in Macromolecular Chemistry, held in Prague 1978—1979; home address Government College Faridabad, India.

of water is so strongly bound on the polymer that it cannot be transformed into ice. In our earlier paper[3] we measured the heat capacities of water swollen PHEOEMA also at temperatures below 0°C. It was found that the degree of attainment of equilibrium in the crystallization and melting of water sorbed in the polymer considerably depends on the history of the samples and on the experimental procedure employed. Thermodynamic considerations and analysis of experimental data showed that the fraction of non-freezing water depends on many thermodynamic and non-equilibrium factors and cannot be a reliable guide for reaching conclusions on the state of water in polymers. We therefore recommended that measurements of heat capacities above 0°C should be given preference. A similar view has been adopted by Hoeve and coworkers[1,2].

In order to verify the correctness of our conclusions presented in the preceding paper, we carried out and interpreted the measurements of the heat capacity of water swollen poly(2-hydroxyethyl acrylate) (PHEA). Similar to PHEOEMA, this polymer is advantageous in that it has a comparatively low glass transition temperature, so that the measurements can be carried out under conditions of the viscoelastic behaviour of the system.

EXPERIMENTAL

Poly(2-hydroxyethyl acrylate) was prepared by radical polymerization[7]. The sample preparation and procedure employed were the same as in the preceding paper[3], only the output of the calorimeter was connected with a digital voltmeter (4 1/2 digit) and a punch-tape recording unit (Czechoslovak Academy of Sciences Development Works, Prague), and data obtained were treated with a programmable Wang 2200 computer.

RESULTS AND DISCUSSION

Glass transition of the polymer. Curves of the temperature dependence of heat capacity for the dry polymer and swollen polymer with the smallest amount of weighed water (Fig. 1) exhibit a region of a steep rise in heat capacity, undoubtedly due to the transition of PHEA from the glassy into the viscoelastic state. From the C_p curve of the dry polymer the glass transition temperature may be estimated as $T_g = 284$ K. The corresponding main transition temperature, determined by Kolařík[7] by dynamic-mechanical measurements, is $T_a = 282$ K at the frequency 1 Hz. Fig. 1 also shows distinctly that T_g of the polymer with the water content $Y_t = 0{\cdot}0915$ g/g is somewhat lower than 225 K, and thus beyond the range of our measurements; here one can identify a strong plastifying effect of water as a low-molecular weight diluent. For all the other samples (with a higher Y_t) the glass transition is obviously situated even lower.

Partial specific heat capacity of water above 273 K. If the heat capacity C_t related to 1 g of dry polymer is plotted as an isothermal dependence on the water content Y_t (in grams per one gram of dry polymer), the slope gives the partial specific heat capacity of water for the given Y_t. For PHEA at temperatures above the melting point of ice this dependence may be expressed by means of linear relations (where C_t is given in J g^{-1} K^{-1}):

$$C_t = 1{\cdot}87 + 4{\cdot}13 Y_t\,, \quad 300\ \mathrm{K}\,; \tag{1}$$

$$C_t = 1{\cdot}96 + 4{\cdot}19 Y_t\,, \quad 320\ \mathrm{K}\,; \tag{1'}$$

$$C_t = 2{\cdot}09 + 4{\cdot}23 Y_t\,, \quad 350\ \mathrm{K}\,; \tag{1''}$$

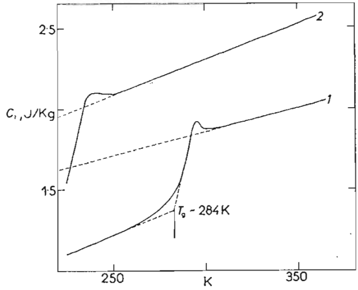

FIG. 1

Temperature Dependence of Heat Capacity in the Glass Transition Region
1 Pure PHEA, *2* water swollen PHEA, $Y_t = 0{\cdot}0915$ g/g.

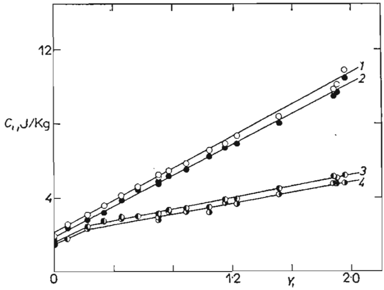

FIG. 2

Isothermal Dependence of Heat Capacity C_t on Water Content Y_t (in g/g of polymer)
Temperature T in K: *1* 350, *2* 300, *3* 230, *4* 225.

(Fig. 2). Hence, at a given temperature the partial specific heat capacity of water in swollen PHEA is independent of gel composition, approaching the specific heat capacity of liquid water, which according to our measurements is $4{\cdot}28\ \mathrm{J\,g^{-1}\,K^{-1}}$ in the given temperature range. It is known that liquid water has a heat capacity about twice as high as ice. This finding is generally explained through the low heat stability of hydrogen bonds in liquid water compared with bonds in ice; the difference $C_p(1) - C_p(s)$, called the configurational contribution, represents energy consumed by the decomposition or deformation of hydrogen bonds during heating of liquid water. An assumption is justified that in the mixed phase any form of strongly bound water (water immobilized by strong hydrogen bonds or dipole forces) has a heat capacity corresponding only to the sum of contributions of vibrations of vibrational modes of the thermal motion, and thus roughly the same as the heat capacity of ice. If, however, the heat capacity of water in PHEA resembles that of liquid water, its structure or bonds with polar groups of the polymer are thermally labile, similar to the structure of hydrogen bonds in liquid water; hence, in this case water cannot be strongly bound.

The dependence of melting point on composition. The decrease in the melting point of the solvent ΔT_f is known to be due to a decrease in its thermodynamic activity in the mixed phase. Consequently, using the equilibrium decrease in the melting point, it is possible to calculate the activity of water in a mixture which is in equilibrium with the crystalline solvent. In our preceding paper[3] we used this procedure to transform the dependence of ΔT_f on composition into a nonisothermal dependence of activity on composition, which could be compared with the sorption isotherm of water in the polymer. For the system PHEA–water the sorption isotherms are not available, but the activity may at least be calculated from measured ΔT_f values. For this purpose again Eq. (*I-7*)*) was used, derived assuming a linear dependence of $C_p(1) - C_p(s)$ on temperature. Fig. 3 then shows depression of the melting point and the equilibrium activity (a) as a function of composition. The nonisothermal dependence of activity thus obtained may be expressed in terms of the empirical equation

$$Y = \frac{1{\cdot}330 \,.\, 10^{-3}}{1 - 1{\cdot}9283a + 0{\cdot}9289a^2}\,. \qquad (2)$$

The dependence of heat capacity on temperature below 273 K. According to the Gibbs phase rule, the heterogeneous system ice–water swollen polymer has two degrees of freedom. Hence, at a given pressure the phase equilibrium is described by

$$Y = Y_{eq}(T)\,, \qquad (3)$$

---

* Equations from the preceding paper[3] are given with their original number and preceded by *I*.

which gives the temperature dependence of composition of the swollen gel in equilibrium with ice. Thus, in the phase diagram Y *vs* T the heterogeneous system in equilibrium moves along a line independent of its total composition Y_t. If the system is heated, ice melts gradually up to T_f, when the last parts of ice melt down, and consequently $Y = Y_t$. Hence,

$$Y_t = Y_{eq}(T_f)\,. \tag{4}$$

In the measured dependence of heat capacity on temperature melting is reflected in an accelerated increase of heat capacity, which ends at $T = T_f$, when the measured heat capacity suddenly drops to $C_p(l)$. As has been derived[3] (Eq. (*I-12*)), at the equilibrium melting the dependence $C_t(T)$ is given by

$$C_t = Y\bar{c}_1 + \bar{c}_2 + (Y_t - Y)\,c_s + \phi(T)\,, \quad T \leqq T_f \tag{5}$$

$$C_t = Y_t\bar{c}_1 + \bar{c}_2\,, \quad T \geqq T_f, \tag{5'}$$

where $\bar{c}_1$, $\bar{c}_2$ are partial specific heat capacities of water and of the polymer in the mixed phase, and c_s is the specific heat capacity of ice; the term $\phi(T)$ corresponds to the peak on the curve and represents the contribution of melting, which at equilibrium is a function of temperature only.

In Eq. (*5*) all terms with the exception of one are independent of Y_t. If, consequently, $(C_t - Y_t c_s)$ is plotted against T, the ascending parts of the curves must be superimposed for various Y_t, failing which the system is not at equilibrium. In the preceding

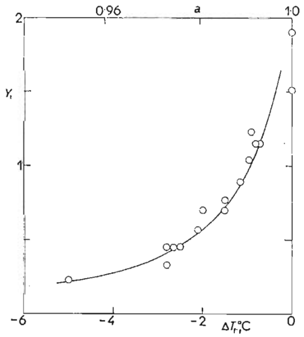

FIG. 3

Dependence of the Water Concentration Y_t on Depression of the Melting Point ΔT_f and on Activity a for the System PHEA–Water paper[3] it was found that the crystallization and melting of H_2O in PHEOEMA proceed very little or not at all for $Y_t \leqq 0{\cdot}4$; by employing the procedure just described, it was proved that the cause lies in the non-establishment of phase equilibrium in cooling and heating, probably due to the considerable slowing-down of diffusion. Also, our results with PHEA indicate that $(C_t - Y_t c_s)$ is a function of both T and Y_t. This is documented by Fig. 4, in which Y_t is plotted on the x-axis for the sake of clarity, while T is the parameter of the curves. In this plot at the state of equilibrium a series of horizontal half-straight lines should be obtained, the ordinate of which increases with increasing temperature; the half-straight line for T is defined only for $Y_t \geqq Y_{eq}(T)$. In the plot in Fig. 4 the lines are horizontal only at a higher water content; for $Y_t < 1$ the dependence decreases, because the degree of attainment of equilibrium gradually decreases. Similarly to PHEOEMA, we may therefore infer that the "non-freezing" of water in concentrated PHEA gels is due to retardation effects; in this case however the degree of attainment of equilibrium decreases more gradually with decreasing water content. As is shown in the following paragraph, the horizontal course of the line for 230 K is probably due to the fact that at any concentration the phase transformation of water does not take place to any considerable extent.

The isothermal dependence of heat capacity on composition below 273 K. As has been shown[3], Eqs (*5*) and (*5'*) may be rewritten so as to adequately describe the isothermal dependence of heat capacity on the water content Y_t (Eq. (*I-26*)). Assuming

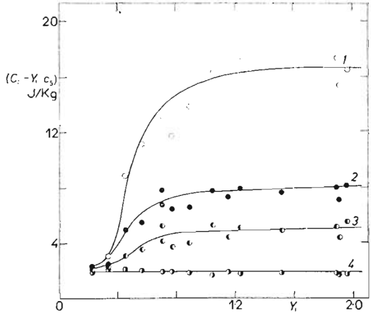

FIG. 4

Test of Thermodynamic Equilibrium in the System PHEA–Water: Dependence of $(C_t - Y_t c_s)$ on Water Content Y_t

Temperature T in K: *1* 270, *2* 265, *3* 260, *4* 230.

$\bar{c}_1$, $\bar{c}_2$ concentration-independent, this dependence (as can be seen also from the original equations (*5*), (*5'*)) consists of two linear intercepts; for $Y_t < Y_{eq}(T)$ the slope is equal to $\bar{c}_1$, *i.e.* to the partial specific heat capacity of water in the polymer, while for $Y_t > Y_{eq}(T)$ the slope is given by the heat capacity of ice. Moreover, at $Y_t = Y_{eq}(T)$ the dependence should exhibit a discontinuous contribution equal to $\phi(T)$. In the region of lower water content only the swollen polymer exists, while in the region above the singular point the swollen polymer coexists with ice. Fig. 2 shows that at 225 K and 230 K the break on the curves appears at $Y = 0{\cdot}23$ to $0{\cdot}25$. On the other hand, one can see in Fig. 3 that this Y_t has corresponding melting points 268–269 K, so that at 225 K under equilibrium conditions the break should appear at a much lower water content (extrapolation in Fig. 3 to $T = -43°\text{C}$ leads to a preliminary estimate that the break occurs for Y_t at the order of magnitude 10^{-2}). Hence, the concentration range from $Y_t = 0$ to $Y_t = 0{\cdot}23$, in which the system cannot contain ice, is much wider than it would correspond to equilibrium conditions. In the breaking point the line does not exhibit any distinct discontinuous jump, from which it is deduced that for $Y_t > 0{\cdot}23$ at 230 K ice melts, if at all, only to a scarcely perceptible degree (theoretical calculation based on data in Fig. 3 leads to an estimate of $\phi\,(230\text{ K}) \approx 0{\cdot}1$ J/gK). Conclusions reached in this paper are again very similar to those obtained for PHEOEMA in the preceding paper.

In order to prevent complications caused by the glassy state of the polymer at $Y_t = 0$ and $Y_t = 0{\cdot}09$, the heat capacities obtained by extrapolation of the C_t – temperature dependence for a viscoelastic polymer (Fig. 1) were plotted for these concentrations in Fig. 2.

Area below the melting peak. The area below the peak A defined by Eq. (*I-15*) has also been calculated using our data for the heat capacities of water swollen PHEA. Hence, $r = A/q_f$ has been calculated, q_f being the heat of melting of pure water in such an amount in which the latter is contained in the gel. The ratio is lower than unity and decreases with decreasing water content:

Y_t	1·23	1·04	0·89	0·56	0·33	0·17
r	0·81	0·82	0·80	0·74	0·23	0

In the literature, r is frequently regarded as the fraction of water which freezes after cooling of the system; $(1 - r)$ is regarded as being identical with the fraction of strongly bound water. As demonstrated by Eq. (*I-16*), however, thermodynamics does not interpret A as the heat of melting of ice yielding pure water, but as the sum of this quantity and the heat of mixing of liquid water with the polymer, the second term being usually negative. In addition, uncertainty involved in the determination of the temperature of "onset of melting" may result in the calculated A being smaller than the real total heat effect; finally, as has been shown by us, non-freezing of one part of water is caused by the non-establishment of equilibrium at lower T and Y;

the origin of retardation factors underlying this phenomenon should in our view be looked for rather in the high viscosity of the concentrated system at lower T than in the strong bond between water and polymer at the usual temperature.

CONCLUSION

Results described in this paper support our conclusions reached in the preceding paper[3]: The state and structure of water in swollen hydrophilic polymers are suitably investigated by measuring heat capacities above the melting point of ice and under conditions where the system behaves viscoelastically. Such measurements performed on PHEA allow us to conclude that in this polymer too the binding of water molecules is not much stronger than an average interaction between molecules of liquid water.

The authors are indebted to Dr J. Kolařík, Dr J. Kopeček and Dr J. Vacik from this Institute, for the samples and to Miss H. Vodičková for careful technical assistance.

REFERENCES

1. Hoeve C. A. J., Kakivaya S. R.: J. Phys. Chem. *80*, 745 (1976).
2. Hoeve C. A. J., Tata A. S.: J. Phys. Chem. *82*, 1660 (1978).
3. Pouchlý J., Biroš J., Beneš S.: Makromol. Chem. *180*, 745 (1979).
4. De Visser C., Perron G., Desnoyers J. E.; Can. J. Chem. *55*, 856 (1977).
5. Roux G., Perron G., Desnoyers J. E.: J. Phys. Chem. *82*, 966 (1978).
6. Franks F., Asquith M. H., Hammond C. C., Le B. Skaer H., Echlin P.: J. Microscopy *110*, 223 (1977).
7. Kolařík J., Vacík J., Kopeček J.: Int. J. Polym. Mater. *3*, 259 (1975).

Translated by L. Kopecká.