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# Two Component Hydrogels

## 1. Polymer- Polymer and Polymer- Solvent Interactions in a One Component Hydrogel – Theoretical Considerations –

**W. R. Good and H.-J. Cantow**

Institut für makromolekulare Chemie der Universität, 7800 Freiburg i. Br.,
Federal Republic of Germany

### Summary

This and the subsequent papers concern with two component hydrogels, consisting of a polymer backbone built up by one polymer component, which is crosslinked by bridges of another polymer with varying length. In order to understand the effects of the crosslinker chain length on the networks as a whole the thermodynamic interaction parameters for the system, with special reference to the swelling behaviour, have to be determined first. By adapting and extending Sakurada' s method the equations of state for the ternary system water-linear crosslinker- one component gel are developped first.

### Introduction

The work to be reported in this and subsequent papers was initiated to study the structural and physical properties of hydrophilic networks which are composed of two chemically different chains, both of which, in their linear forms, are water soluble. This new class of hydrogels is expected to exhibit unique physical properties which, hopefully, can be interpreted in terms of their structural characteristics and the interactions which exist between the two different polymeric components and the enclosed solvent, water. In this paper we will report the results of considerations aimed at elucidating the solvent- polymer and polymer- polymer interactions which should prevail in a binary network of the two polymer components.

At this point we wish to unambigously define a one component gel and a two component gel. The one component gel is a network in which the crosslink itself is sufficiently short as to neglect it as being a component of the gel. In effect, in a one component gel the crosslink is considered to be volumeless and of tetrafunctional nature.By contrast, a two component gel is one in which the crosslink is sufficiently long such that it plays an important role in affecting the physical properties of the system. In this case the actual crosslink points are trifunctional in nature.

The binary networks to be reported in the subsequent paper of this series consist of polyvinylpyrrolidone and polyethyleneoxide (PVP and PEO). From the standpoint of visualization, the PEO component serves as a long chain bridge or crosslink between the main chains of PVP. However, as the PEO component becomes longer and exists in higher concentrations the differentiation between main chain and crosslink becomes clouded since the crosslink length approaches the

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distance between branch points of the main chain. Hence, the network is best described as a cross-linked graft copolymer. In order to understand definitely the effects of crosslinker chain length on the networks as a whole it is necessary to first determine the thermodynamic interaction parameters for the system. Since we are paticularly interested in the effects with respect to swelling characteristics in water, it was also necessary to determine individual interaction parameters between the solvents and the two polymeric components. This is accomplished by adapting and extending a method first reported by Sakurada et al [1].

## Theory

Ternary phase relationships between one solvent and two linear polymers have been reported by several authors [2,3]. In addition, Krigbaum et al [4,5] have reported phase relationships for crosslinked polymers together with mixed solvents. Sakurada et al [1] have derived phase relationships for the system involving a crosslinked polymer, a linear polymer and one solvent. It is this general system we are concerned with in the present work and, using Flory- Huggins [2] formulation for thermodynamics of polymer solutions, we will develop the equations of state for this ternary system.

Consider the system: water (1), crosslinker component (linear) (2), and backbone polymer (crosslinked) (3). The total change in free energy upon bringing the crosslinked polymer into contact with a solution of the linear polymer may be expressed as

$$\Delta F = \Delta F_m + \Delta F_e \quad , \tag{1}$$

where $\Delta F_m$ is the free energy change on mixing and $\Delta F_e$ represents the elastic free energy of the network. For the present we will only be concerned with the free energy of mixing and will present the elastic component only in a formal way. Development of the elastic contribution will be done separately when we become concerned with its contribution on the total free energy change of the system. The free energy of mixing may be separated into its enthalpic and entropic components,

$$\begin{aligned} \Delta H_m &= kT \sum_{i<j} n_i \phi_j \chi_{ij} \\ \Delta S_m{*} &= -k \sum_{i=1}^{3} n_i \ln\phi_i \quad , \end{aligned} \tag{2}$$

where $\phi_i$ represents the volume fraction of the component i at equilibrium and $\chi_{ij}$ are the Flory- Huggins interaction parameters we seek. Since we have,

$$\chi_{ji} = \chi_{ij}\bar{V}_{ji} \quad , \tag{3}$$

where $\bar{V}_{ji} = \bar{V}_j/\bar{V}_i$ and represents the ratio of molar volumes of the jth and ith components, our problem reduces to one of finding the three interaction parameters, $\chi_{12}$, $\chi_{13}$ and $\chi_{23}$. The total free energy change is then written,

$$\Delta F = kT \left[\sum_{i<j}^{3} n_i \phi_j \chi_{ij} + \sum n_i \ln\phi_i\right] + \Delta F_e \quad . \tag{4}$$

The conditions for equilibrium in this three- component system are:

$$\mu_{1g} = \mu_{is} \qquad \mu_{2g} = \mu_{2s} \tag{5}$$

where chemical potentials are subscripted g for the gel phase and s for the external solution phase.

Differentiation of equation (4) with respect to the appropriate $n_i$ gives,

$$\ln a_{1g} = \ln \phi_1 + (1-\phi_1) - \overline{V}_{12}\phi_2 - \overline{V}_{13}\phi_3 + (\chi_{12}\phi_2 + \chi_{13}\phi_3)(\phi_2 + \phi_3) - \chi_{23}\overline{V}_{12}\phi_2\phi_3 + N \frac{\delta}{\delta n_1}(\Delta F_e) \tag{6}$$

$$\ln a_{2g} = \ln \phi_2 + (1-\phi_2) - \phi_1\overline{V}_{21} - \phi_3\overline{V}_{23} + (\chi_{21}\phi_1 + \chi_{23}\phi_3)(\phi_1 + \phi_3) - \chi_{13}\overline{V}_{21}\phi_1\phi_3 + N \frac{\delta}{\delta n_2}(\Delta F_e) \tag{7}$$

where we have converted chemical potentials to activities. According to Flory [2], the free energy of elasticity is given by:

$$F_e = \frac{KT\upsilon_e}{2}\left[3\alpha_s^2 - 3 - \ln \alpha_s^3\right] \quad , \tag{8}$$

where $\upsilon_e$ is the number of elastically effective chains and $\alpha_s$ is the linear deformation factor. Without making any assumptions as to the validity of the bracketed expression in equation (8) we may write,

$$(\mu_{ig} - \mu^o_{ig})_e = N \frac{\delta(\Delta F_e)}{\delta\alpha_s}\frac{\delta\alpha}{\delta n_i} = N \frac{\delta(\Delta F_e)}{\delta n_i} \tag{9}$$

and since, by definition,

$$\alpha_s^3 = 1/\phi_3 = (V_o + n_1\overline{V}_i/N + n_2\overline{V}_2/N)/V_o \quad , \tag{10}$$

the linear deformation factor may be expressed as a linear combination of factors in $n_1$ and $n_2$. Therefore,

$$\frac{\delta\alpha_s}{\delta n_1} = \overline{V}_1/3\alpha_s^2 V_o N \qquad \frac{\delta\alpha_s}{\delta n_2} = \overline{V}_2/3\alpha^2 V_o N \quad , \tag{11}$$

where N is Avogadro's number and $V_o$ is the volume of the unswollen network. Substituting into equation (9) we have,

$$N \frac{\delta(\Delta F_e)}{\delta n_1} = \frac{\overline{V}_1}{3\alpha_s^2 V_o}\frac{\delta(\Delta F_e)}{\delta\alpha_s} \tag{12}$$

$$N \frac{\delta(\Delta F_e)}{\delta n_2} \quad \frac{\overline{V}_2}{3\alpha_s^2 V_o}\frac{\delta(\Delta F_e)}{\delta\alpha_s} \quad . \tag{13}$$

Hence, we have expressed the change in elastic free energy for equations (6) and (7) in terms of a single common variable, the linear deformation factor. If we now rearrange equations (6) and (7) according to Sakurada et al [1] and substitute (12) and (13) for the differentials, the activity relations for the ternary phase read,

$$\ln a_{1g} = \ln \phi_1 + (1-\overline{V}_{12})\phi_2 + (1-\overline{V}_{13})\phi_3 + \chi_{12}\phi_2^2 + \chi_{13}\phi_3^2$$

$$+ (\chi_{12} + \chi_{13} - \bar{V}_{12}\chi_{23})\phi_2\phi_3 + \frac{\bar{V}_1}{3\alpha_s^2 v_o}\left[\frac{\delta}{\delta\alpha_s}(\Delta F_e)\right] \qquad (14)$$

$$\ln a_{2g} = \ln \phi_2 + (1-\bar{V}_{21})\phi_1 + (1-\bar{V}_{23})\phi_3 + \chi_{21}\phi_1^2 + \chi_{23}\phi_3^2$$

$$+ (\chi_{21} + \chi_{23} - \bar{V}_{21}\chi_{13})\phi_1\phi_3 + \frac{\bar{V}_2}{3\alpha_s^2 v_o}\left[\frac{\delta}{\delta\alpha_s}(\Delta F_e)\right] \qquad (15)$$

From equations (14) and (15) it can be seen that any dependence of $a_{1g}$ or $a_{2g}$ on the nature of the elastic free energy change with the linear deformation factor can be eliminated by solving these two equations simultaneously.

In the external solution phase in which the linear polymer is dissolved in the solvent we write the classical Flory- Huggins activity equations

$$\begin{aligned} \ln a_{1s} &= \ln v_1 + (1-\bar{V}_{12})v_2 + \chi_{12}v_2^2 \\ \ln a_{2s} &= \ln v_2 + (1-\bar{V}_{21})v_1 + \chi_{21}v_1^2 \end{aligned} \qquad (16)$$

where $v_i$ is used to distinguish solution phase volume fraction from gel phase volume fraction, $\phi_i$. Using equation (3) and combining equations (14), (15) and (16) according to the equilibrium conditions from equations (5) we obtain the relationship,

$$\frac{1}{\phi_3}\ \ln(v_1/\phi_1)\ - \bar{V}_{12}\ln(v_2/\phi_2)\ = 2\chi_{12}\frac{(v_1-\phi_1)}{\phi_3} + (\chi_{13}-\chi_{12}-\bar{V}_{12}\chi_{23}) \qquad (17)$$

If the left side of equation (17) be plotted vs. $2(v_1-\phi_1)/\phi_3$ a straight line results, the slope of which is $\chi_{12}$ and the intercept of which is $(\chi_{13}-\chi_{12}-\bar{V}_{12}\chi_{23})$. Obviously, the linear relationship will only hold if $\chi_{12}$ is concentration- independent. It is interesting to note that even though Sakurada et al used an incorrect form for the elastic contribution to the total free energy, their equation (6) is correct. In addition, most authors discard $\bar{V}_{12}$ and $\bar{V}_{23}$ from equation (14) as being negligible. If, however, they are carried through the derivation, upon combining equations (14), (15) and (16) these terms combine to be eliminated in any case. In short, equation (17) is totally independent of explicit contributions from the crosslink density. In a subsequent paper these expectations will be tested experimentally.

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