Polymer Bulletin 1, 115–120 (1978)

Polymer Bulletin

Two Component Hydrogels

2. Polymer- Polymer and Polymer-Solvent Interactions in a One Component Hydrogel – Experimental Verification –

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Summary

The equations of state for the ternary system water (1)- linear crosslinker (2)- one component gel (3) given in the previous paper are checked experimentally for polyethyleneoxide (PEO- linear) and polyvinylpyrrolidone (PVP- crosslinked). The interaction parameter χ_{12} has been found as independent of crosslinker length and crosslink density. χ_{23} and even more χ_{13} are dependent on the degree of crosslinking.

Introduction

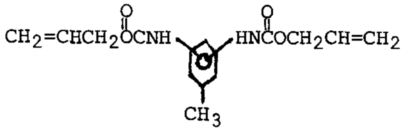
In our recent paper [1] the relationship

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

was developped describing the swelling behaviour of a one- component gel in an aqueous solution of a linear crosslinker. v_i are the solution phase and ϕ_i the gel phase volume fractions. This equation is totally independent of explicit contributions of the crosslink density. This will be checked in the following with the system PEO (linear) and PVP (crossl.)

Experimental

PVP networks were prepared by simultaneous copolymerization and crosslinking of N-Vinylpyrrolidone. The crosslinking agent used in the network preparations deserves some attention here as it is an analogue to those which are used in the preparation of our two- component gels. Two moles of allyl alcohol are reacted with one mol of 2,4- toluene- diisocyanate (2,4 TDI) to produce,



(I)

This diallylic compound is well adapted to our purposes due to its very small tendency to homopolymerize and its very high penchant to copolymerize with NVP to produce well defined networks. In experiments to be described in the third installment of this series of papers it was found that the reactivity ratios in the system NVP (1) and (I) (2) are $r_1 = 0.887$; $r_2 = 0$. In determining the interaction parameters for water- PEO-PVP, it is necessary to accept the "volumeless crosslink" [2] approximation in order to use the three component equations derived in the theoretical section. Hence, compound (I) represents our volumeless crosslink when compared with either the main chain length or the PEO used in our swelling measurements.

The NVP used was a fraction which boiled between 57- 58° C at 2 mm. Monomer (I) was prepared by dissolving 2 moles of allyl alcohol together with 1 mol of 2,4 TDI in 290 g CH_2Cl_2 and refluxing the mixture for three hours. The product is isolated by evaporation of the solvent, redissolved and recovered twice ($CH=CH_2$ calc. 18.61, found 18.00 %).

Networks were prepared by codissolving NVP, (I) and 0.8 % (based on monomer) of AIBN along with 10 % N- Methylpyrrolidone. These solutions were then injected into closed molds which consisted of two glossy mylar sheets separated by a silicone rubber gasket. The mylar sheets were backed by flat glass plates and the entire assembly was clamped together by strong spring binders. Polymerization at 60° C for two hours yielded polymer sheets (∿1 mm thick), which were demolded by immersing the sandwiches in Dry Ice/ methanol. The presence of N- Methylpyrrolidone aided this demolding process. The hydrogels were washed in water for 7 days,the water being changed twice daily. Three hydrogels were prepared in which the starting monomer compositions were 2.00 mole % monomer (I) (gel 1); 1.00 mole % (I) (gel 2); 0.50 mole % (I) (gel 3), respectively. The equilibrium swelling compositions for these materials in water at 25° C are:

Gel	Wt % Gel	ϕ_1	ϕ_3
1	18.62	0.8410	0.1590
2	14.82	0.8743	0.1257
3	10.55	0.9112	0.0888

M_n of PEO (Union Carbide Corp.) were determined by freezing point depression in aqueous solution and by OH- group titration when appropriate. ρ was given by the supplier.

PEO	ρ (g/ml)	M_n	$\bar{V}_{12}$
300	1.12	300	0.0675
600	1.12	615	0.0329
750	1.09	750	0.0262
1000	1.10	974	0.0203
2000	1.10	1903	0.0104

Equilibrium swelling measurements were performed at 25°C in aqueous solutions of PEO. The swollen gel is cut into conveniently sized rectangular pieces of 100-300 mg, blotted dry with tissue paper and weighed to an accuracy of 0.1 mg. The gel pieces are then placed into the PEO solutions and the vials are allowed to gently rotate at 25° C. Typically, the swelling equilibrium was established within 48 h for the lowest M_n PEO, within 72 h for the intermediate M_n PEO and within 96 h for the higher M_n PEO solutions. The hydrogels are then rinsed in fresh water, blotted dry and reweighed to determine the new equlibrium weight. The specimens are then dried at 60° C, under vacuum for 24 hours and weighed in the dry state.

Results and Discussion

Since the hydrogels were placed into the PEO solutions in the swollen state the weight of dry gel is calculated from the known initial swollen weight and the amount of linear PEO absorbed is calculated from the difference between this value and the final dry weight. The control data presented in the Table were obtained by averaging the volume fractions of water and gel over five determinations for each gel in which the standard deviation was less than 0.5 %. The volume fractions were calculated for solution and gel phases at equilibrium taking into account all corrections including loss of linear polymer from solution to gel and exchange of solvent between solution and gel. Since the initial solution volume was more than ten times the initial gel volume the corrections are generally only in the order of 2- 5 %, but were, nevertheless, included in

Table A: Equilibrium conditions for the system water (1)- PEO (linear) (2)- PVP (crosslinked) (3)

PEO	300			600			750			1000			2000		
GEL	Sol V_2	Gel ϕ_2	ϕ_3	Sol V_2	Gel ϕ_2	ϕ_3	Sol V_2	Gel ϕ_2	ϕ_3	Sol V_2	Gel ϕ_2	ϕ_3	Sol V_2	Gel ϕ_2	ϕ_3
1	.0000	.0000	.1590	.0000	.0000	.1590	.0000	.0000	.1590	.0000	.0000	.1590	.0000	.0000	.1590
	.0442	.0242	.1587	.0429	.0177	.1645	.0457	.0059	.1689	.0455	.0139	.1682	.0455	-	-
	.0889	.0502	.1591	.0864	.0299	.1698	.0913	.0267	.1775	.0915	.0325	.1793	.0910	.0147	.1947
	.1332	.0763	.1607	.1301	.0591	.1763	.1369	.0545	.1887	.1374	.0517	.1914	.1367	.0261	.2191
	.1789	.1022	.1615	.1736	.0863	.1837	.1832	.0745	.1988	.1842	.0690	.2057	.1822	.0375	.2447
	.2255	.1357	.1629	.2190	.1083	.1915	.2303	.0957	.2107	.2312	.0887	.2177	.2280	.0472	.2755
2	.0000	.0000	.1257	.0000	.0000	.1257	.0000	.0000	.1257	.0000	.0000	.1257	.0000	.0000	.1257
	.0439	.0246	.1253	.0427	.0205	.1305	.0454	.0190	.1331	.0453	.0183	.1339	.0451	.0032	.1409
	.0880	.0582	.1264	.0859	.0418	.1372	.0913	.0406	.1410	.0910	.0379	.1437	.0904	.0197	.1602
	.1328	.0837	.1263	.1292	.0709	.1406	.1371	.0629	.1502	.1369	.0624	.1546	.1359	.0334	.1832
	.1768	.1172	.1281	.1732	.0981	.1462	.1833	.0881	.1592	.1833	.0862	.1649	.1817	.0466	.2045
	.2235	.1462	.1307	.2175	.1236	.1520	.2301	.1153	.1707	.2295	.1103	.1781	.2275	.0575	.2375
3	.0000	.0000	.0888	.0000	.0000	.0888	.0000	.0000	.0888	.0000	.0000	.0888	.0000	.0000	.0888
	.0441	.0318	.0883	.0422	.0283	.0921	.0447	.0267	.0936	.0447	.0259	.0958	.0447	.0169	.1026
	.0880	.0625	.0896	.0847	.0562	.0962	.0903	.0544	.1004	.0900	.0501	.1014	.0900	.0344	.1194
	.1328	.0968	.0901	.1291	.0826	.1040	.1344	.0820	.1073	.1353	.0790	.1112	.1349	.0543	.1383
	.1780	.1314	.0910	.1719	.1161	.1045	.1818	.1112	.1158	.1808	.1103	.1208	.1808	.0724	.1592
	.2236	.1669	.0916	.2148	.1429	.1073	.2274	.1394	.1246	.2262	.1340	.1277	.2273	.0858	.1806

$V_1 = 1 - V_2$ $\phi_1 = 1 - \phi_2 - \phi_3$

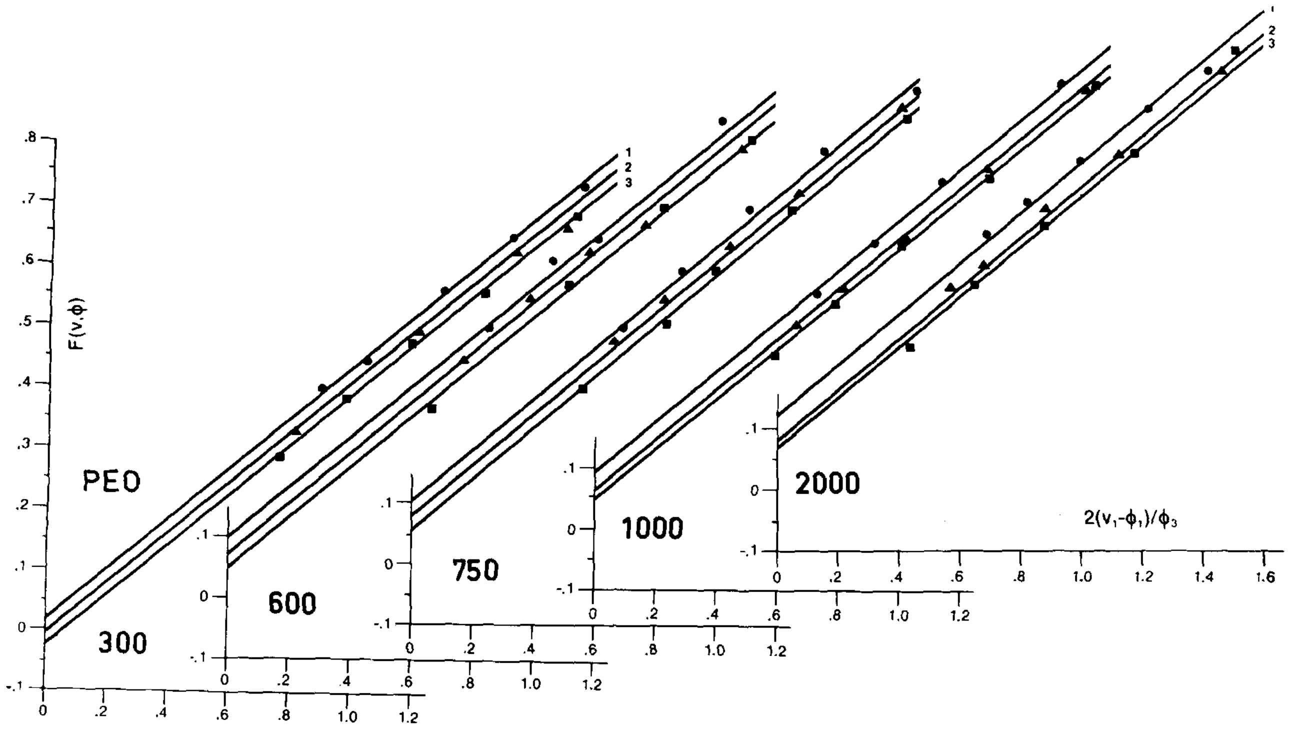


Figure 1: Plots suggested by equation (1) for the gels 1, 2 and 3 where the swelling study is for the system water - PEO and PVP. Starting monomer (I) compositions (mole %): 2.00 for gel 1, 1.00 for gel 2 and 0.50 for gel 3.

the calculations. In Table A we give the equilibrium volume fractions for the PEO linear polymers that penetrated the PVP gels. For $M_n > 2000$ the gels absorbed no appreciable amount of the linear polymer.

These data are fitted to equation (1) by a least squares method and average χ_{12} values for each PEO are tabulated (Avg. $\chi_{12} = 0.4189 \pm 0.0070$): We present the data as a plot of the left side of equation (1) vs. $2(v_1 - \phi_1)/\phi_3$ as illustrated in Figures 1. The curves are grouped with respect to M_n of the penetrant, PEO. In these figures all of the lines for each penetrant are drawn with the same slope. These results show, as should be the case, there is no dependence of χ_{12} on the cross link density of the gels. Moreover, the slopes for each penetrant used with each gel all fell in a very narrow range of values which fell well within the limits of experimental error. Hence, we have determined the value of χ_{12} to be 0.4189 irrespective of M_n of the PEO. This result is strong evidence that χ_{12} is independent of concentration over the concentration range and molecular weight range studied.

PEO	$\bar{V}_{12}$	χ_{12}
300	.0675	.4160
600	.0315	.4143
750	.0263	.4157
1000	.0203	.4282
2000	.0104	.4205

Although we observe the slopes to be independent of penetrant M_n and gel crosslink density, it is obvious that the intercepts of these curves are dependent on both gel crosslink density and molecular weight of component 2. Although SAKURADA et al [2] state that the linear relationship should be independent of the M_n of component 2 it is clearly seen that the intercept from equation (1) is explicitly dependent on $\bar{V}_{12}$, the ratio of solvent to linear polymer molar volume. It should be noted that these authors used linear polymers of much higher molecular weight than in the present study. Hence, $\bar{V}_{12}\chi_{23}$ becomes negligible as compared to $(\chi_{13} - \chi_{12})$ if χ_{23} is not too large. However, in our case $\bar{V}_{12}\chi_{23}$ is not negligible and must be taken into account. If we call the intercepts from Figures 1 I, we may write,

$$I = (\chi_{13} - \chi_{12}) - \bar{V}_{12}\chi_{23} \,, \qquad (2)$$

were χ_{12} represents the slopes of these lines. Then, rearranging and solving explicitly for $(I + \chi_{12})$ we have

$$I + \chi_{12} = \chi_{13} - \left(\frac{\chi_{23}}{\chi_{12}}\right) \chi_{12}\bar{V}_{12} \,, \qquad (3)$$

where we have normalized χ_{23} with respect to χ_{12} in order to use the values of χ_{12} for each PEO molecular weight rather than the average value. In the foregoing table we have presented the χ_{12}values for each linear polymer used in the swelling studies and in Figure 2 we have plotted the left side of equation (3) vs. $\chi_{12}\bar{V}_{12}$ for each hydrogel studied. If χ_{23} is independent of crosslink density than all these points should fall on the same straight line having slope of $-(\chi_{23}/\chi_{12})$ and intercept of χ_{13}. If χ_{23} is

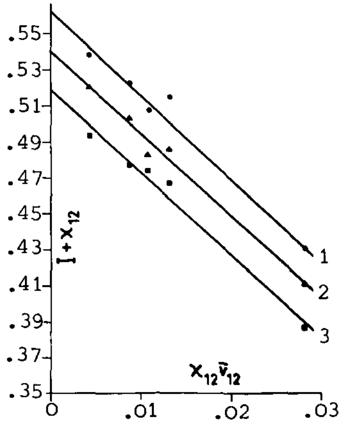


Figure 2: Dependence of the intercept from figs. 1 on $\bar{V}_{12}$ for PVP gels 1, 2, 3. Slopes yield χ_{23} and intercepts give χ_{13}.

dependent on crosslink density but independent of molecular weight of the penetrant we should obtain a family of straight lines all having different slopes and intercepts of χ_{13} characteristic for the gel crosslink density. It is also conceivable that χ_{23} is dependent on both M_n of component 2 and crosslink density of the gel. It is apparent from Figure 2 that χ_{23} is at least dependent on crosslink density as the date points definitely are grouped with respect to gel crosslink density. For penetrant molecular weights >300 we have a fairly good linear correlation. Hence, as may be expected, χ_{23} exhibits behavior which supports the idea that the polymer- polymer interaction can be characterized as a structural unit phenomenon which is implied in its definition in the FLORY- HUGGINS theory. Most importantly, we see that χ_{13} is quite strongly dependent on crosslink density. This is a crucial point, as it is common practice among workers in the field to assume that the solvent- polymer interaction parameter is independent of crosslink density. This approximation may be valid, but our data indicate it to be valid only for very lightly crosslinked gels. In the table we tabulate the set of interaction parameters found for the three PVP gels and five linear polyethylene glycol polymers used in this study. The χ_{13} values reported are extrapolated from the data of Figure 2.

Gel	$\overline{\chi}_{12}$	$\chi_{13}{}^{+}$	$\chi_{23}{}^{*}$
1	.4189	.5631	1.931
2	.4189	.5412	1.934
3	.4189	.5196	1.913

+ Extrapolated
* For PEO $M_n > 600$

Conclusion

By using the ternary phase relationship for a solvent, crosslinked polymer and linear polymer and extending the treatment first introduced by SAKURADA et al it is possible to determine the FLORY- HUGGINS interaction parameters for the three- component system Water, PEO (linear), and PVP (crosslinked). Moreover, this treatment indicates that the degree of crosslinking in the network polymer is reflected in the value of the interaction parameters associated with the network chains; implying an entropic contribution on the interaction parameter exists.

The interaction parameters for H_2O- PVP (χ_{13}), H_2O- PEO (χ_{12}) and PVP-PEO (χ_{23}) are important for us in the development of the thermodynamic equations of state for the two- component gels in which the PEO component is no longer merely a swelling agent but rather a part of the network itself. The correlation between the systems studied here and the two- component networks may well be heavily dependent on our understanding of the interactions elucidated in this paper.

We have to thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

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Received August 2, 1978