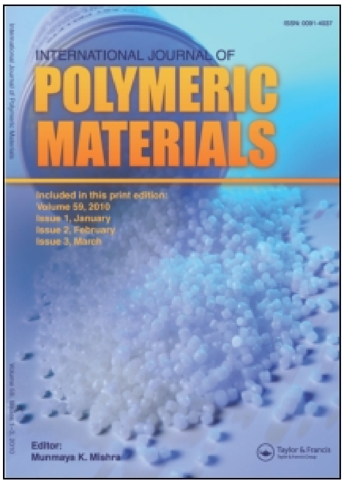

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Thermodynamic and Hydrodynamic Study of New Self-Crosslinking Gelatine

Zoica Cenuse[a]; Ilie Mandru[ab]
[a] Milligan and Higgins, Johnstown, NY, USA [b] University of Bucharest, Bucharest, Romania

To cite this Article Cenuse, Zoica and Mandru, Ilie(1998) 'Thermodynamic and Hydrodynamic Study of New Self-Crosslinking Gelatine', International Journal of Polymeric Materials, 40: 1, 127 — 132
To link to this Article: DOI: 10.1080/00914039808050149
URL: http://dx.doi.org/10.1080/00914039808050149

Intern. J. Polymeric Mater., 1998, Vol. 40, pp. 127–132
Reprints available directly from the publisher
Photocopying permitted by license only

Thermodynamic and Hydrodynamic Study of New Self-Crosslinking Gelatine

ZOICA CENUSE and ILIE MANDRU*

Milligan and Higgins, Johnstown, P.O. Box 506, NY 12095, USA

(Received 4 July 1997)

The thermodynamic and the hydrodynamic properties of the self-crosslinking gelatine with improved viscosity and gel strength were analysed in terms of the Flory-Huggins, Eyring and Mark-Houwnik equations.

The absolute, intrinsic viscosity and number average molecular weight, $\bar{M}$, were calculated at different temperatures. The ΔG, ΔH, and ΔS thermodynamic parameters were calculated from Eyring, Mark-Houwnik and Gibbs equation. The ΔG and ΔS values indicate the stability range of crosslinked gelatines when they are redisssolved in water.

Keywords: Thermodynamic properties of improved gelatine; hydrodynamic properties of crosslinking gelatine

1. INTRODUCTION

It is well known that a self-crosslinking gelatine has a large number of applications in paper industry, in pharmaceuticals and photographical field.

In our recent study [1], a crosslinking gelatine with improved viscosity and gel strength was prepared using a recently patented crosslinker [2]–a stabiliser formaldehyde donor.

In this study we report thermodynamic and hydrodynamic studies of above crosslinked gelatine and their water solutions.

*On Leave of Absence from the University of Bucharest, Bd. Carol I, No. 13, Bucharest, Romania.

2. MATERIALS AND METHODS

For the present study was used a Milligan and Higgins gelatine type B gelatine [1] crosslinked by M and H Hardener [2].

The viscosities of the crosslinked gelatine solutions were measured with 0.5 M NaCl solution (buffered at pH = 7.0) as the solvent medium. The Ubhelode viscometer gave a flow time for solvent at 25°C of 89 sec. The temperature of measurements was accurate within 0.1°C.

3. RESULTS AND DISCUSSIONS

The intrinsic viscosity $[\eta]$ has been determined using the Flory-Higgins equation:

$$\eta_{spec/c} = [\eta]^2 kc + [\eta] \tag{1}$$

where $\eta_{spec} = \eta/\eta_0 - 1$, η and η_0 are the viscosities of the crosslinked gelatines and solvent medium, respectively, c is the concentration of gelatines (g/dl) and k is Higgins constant.

The graph of $\eta_{spec/c}$ versus c is shown in Figure 1.

The intrinsic viscosity $[\eta]$ has been obtained from the intercept of the plot. The results are given in the Table I.

The molecular weight was calculated by the Mark Houwnik's equation [3]

$$\eta = k\bar{M}^{\alpha} \tag{2}$$

where $\bar{M}$ is number average molecular weight, k and α are coefficients. The k and α values for gelatines [3] are:

$$\eta = 1.1 \times 10^{-4} \bar{M}^{0.74} \tag{3}$$

The correlation between gel strength and numerical molecular weight is expressed by equation:

$$G = 1.4 \times 10^{-3} \bar{M} + 62.8 \tag{4}$$

and the graph is shown in Figure 2.

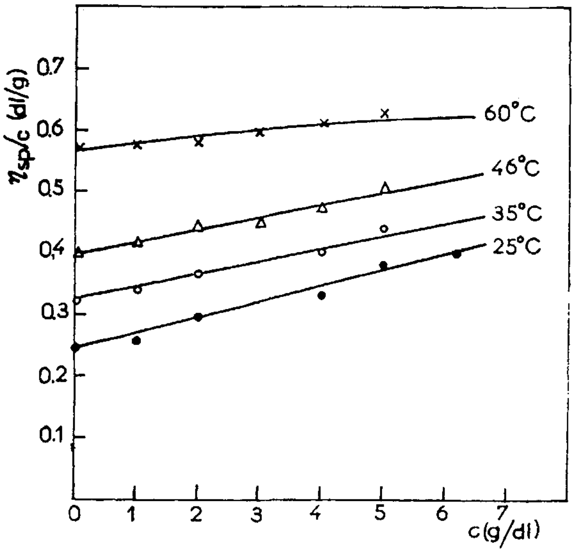

FIGURE 1 Graph of $\eta_{spec/c}$ versus c using Flory-Higgins equation for a type B crosslinked gelatine.

TABLE I Intrinsic viscosity $[\eta]$, average molecular weight $\bar{M}$ for type B crosslinked gelatine [1] and gel strength, G

t (°C)	$[\eta]$ (dl/g)	$\bar{M}$ (g)	G
25	0.243	39,050	82
35	0.335	51,000	140
45	0.440	73,730	160
60	0.565	103,371	210

It is well known that the molecular weight of gelatines decreases with the increase in temperature. The molecular weight of type B crosslinked gelatine increases with the increase of the temperature, as is shown in Figure 1.

But the molecular weight is dropping on time [1] if gelatine is redissolved.

The enthalpy of activation, ΔH, was calculated using the Eyring equation [4].

$$\lg\eta = \left\{\lg\left(\frac{hN}{V} - \frac{\Delta S^*}{2.303R}\right)\right\} + \frac{\Delta H^*}{2.303R}\frac{1}{T} \qquad (5)$$

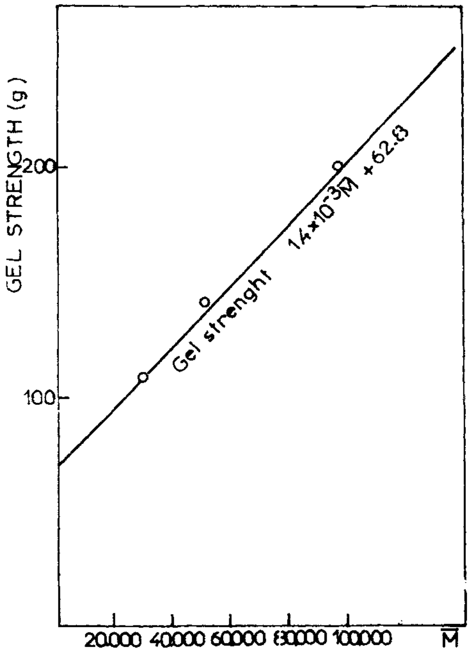

FIGURE 2 The plot of gel strength versus $\bar{M}$ for a type B crosslinked gelatine.

where η is the absolute viscosity, h is the Planck's constant, N, Avogadro's number, V molar volume of the solvent medium, R the universal gas constant and T is the absolute temperature.

The plot of the log η versus $1/T$ is shown Figure 3.

The calculated ΔH values from the slope are recorded in Table II.

The Gibbs' free energy of activation has been calculated by the following equation:

$$\Delta G = R + \ln(\eta V/hN) \tag{6}$$

where the symbols have usual significance [4].

From the equation

$$\Delta G = \Delta H - T\Delta S \tag{7}$$

the entropy ΔS was calculated.

The ΔG and ΔS values are also given in Table II.

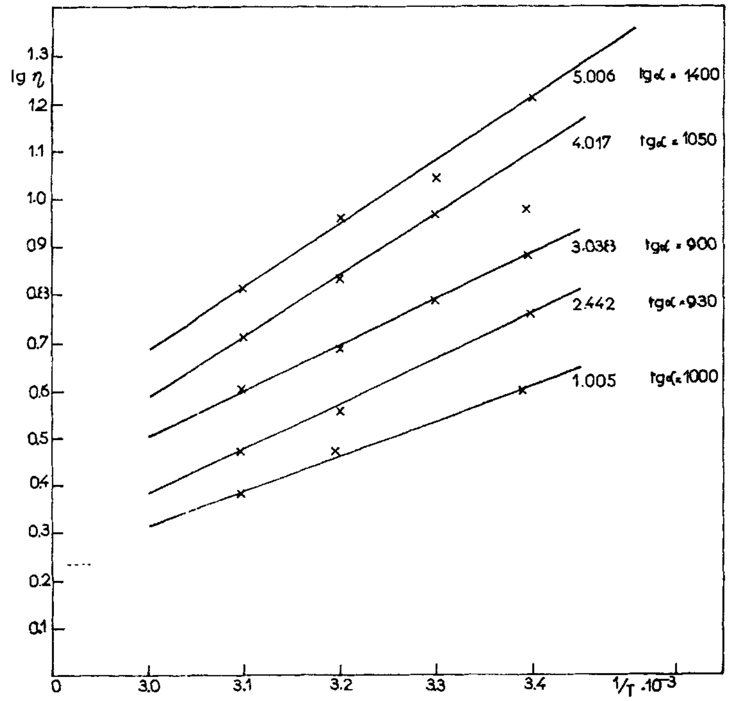

FIGURE 3 The plot of lg η versus $1/T$ according with Eyring equation.

In this regard we would like to say that it is possible to calculate the value of ΔS from the intercept of the plot of lg η against $1/T$ using equation (5), but the intercept is not sufficiently sharp and is better to avoid such calculations.

4. CONCLUSIONS

It can be seen from Table II, over the entire temperature range of the study, ΔG decreased with increase in temperature, but increased with the amount of crosslinked gelatine.

The decreasing of ΔG indicates that the stability of crosslinked gelatine decreases with the increase in temperature when it is redissolved in water.

TABLE II Thermodynamic parameters of crosslinked gelatine type B

Concentration (g/dl)	*T (K)*	*η (CP)*	*ΔG (KJ/mol)*	*ΔH (KJ/mol)*	*ΔS (J/mol, K)*
1.005	295	4.0	11.31		52.55
	303	3.5	11.27	26.805	51.27
	313	3.0	11.25		49.69
	323	2.5	11.11		48.58
2.442	295	9.0	12.75		24.92
	303	5.0	12.17		26.18
	313	3.7	11.79	20.104	26.56
	323	3.0	11.61		26.29
3.038	295	6.25	23.69		
	303	6.2	12.77		14.92
	313	5.0	12.57	19.23	14.42
	323	4.0	12.38		15.01
4.017	295	16,850	26.01		
	303	9.4	13.68	17.81	13.63
	313	6.8	13.37		14.18
	323	5.2	13.08		14.64
5.006	295	177,500	37.55		
	303	11.0	15.32	19.15	−6.53
	313	9.3	15.39		−7.15
	323	6.6	14.97		−6.19

ΔG and ΔS present a small variation with temperature for the same concentration of the crosslinked gelatine.

The ΔH value is more or less constant in entire range of concentration and temperature.

The ΔG, ΔH and ΔS parameters for water are 9.15 KJ/mol, 15.01 KJ/mol and 17.05 J/mol, K respectively.

In this regard, the bigger values of ΔS indicate stability of formed crosslinked gelatine (1.005 and 2.442 (g/dl)) while at concentrations of 3.038, 4.017 and 5.006 stability of crosslinked gelatine decreases dramatically.

References

[1] Cenuse, Z. and Mandru, I. (1997). *Intern. J. Polymeric Mater.*, **49**(1−2), 1.
[2] Kormanek, R. and Mandru, I. (1993). May 18th, *US Patent*, **5**, 210, 982.
[3] Veis, I. (1959). The Molecular Chemistry of Gelatine, Academic Press, New York.
[4] Eyring, V. (1980). Rheology of Polymers, Ch. **2**, p. 106, Mir Publishers, Moscow.