

Polymer Aqueous Solutions as Quenching Media.

I. Polyvinylpyrrolidone

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SYNOPSIS

The cooling power of aqueous solutions of polyvinylpyrrolidone are studied with a silver standard sample by using two apparatuses quench with injection and quench with agitation. The dependences of the cooling rates at each temperature on polymer concentration and solution viscosity are established and empirical laws of variation are given.

INTRODUCTION

In order to confer to a metallic alloy some interesting mechanical properties, one proceeds to a heat treatment: Generally speaking, it is a set of heating and cooling. One stage of this treatment is very important and difficult to manage: the “quenching process.” It is established that when a metallic sample is quenched into a vaporizable liquid, there are three stages in the cooling process:

- (i) The first one is called film boiling; the liquid does not wet the hot metal, it is rapidly vaporized giving a blanket of vapor around the metallic sample and the cooling rate is rather weak.
- (ii) The second stage is called nucleate boiling, during which the heat transfer is very high because of the wetting of the hot surface by the liquid.
- (iii) The last stage takes place when the surface temperature of the metal becomes lower than the boiling point of the quenchant liquid. During this stage the cooling is much slower since it corresponds to the heat transfer by conduction and convection through the liquid.

The first stage can be modified or eliminated by some processes.¹⁻³

It is well known that mineral oils were and are the ideal quenchant media for steels because they present a stage of convection at high temperature (higher than that obtained with pure water) and allow the steel workpiece to cool down as slowly as possible in the neighborhood of the martensitic transformation temperature. (But the mineral oils present also some inconveniences, among which we could note their inflammability, their toxicity, and their aging.⁴⁻⁶)

A few years ago, some works showed that aqueous solutions of organic polymers can be used as quenchant media.^{7,8} The most popular polymers quenchants are polyalkyleneglycol, polyvinylpyrrolidone, and polyacrylate. They offer a number of advantages among which we could note:

- The possibility of regulating the cooling power for a given metallic alloy by changing one or more of the following parameters: agitation mode of the solution, nature and concentration of polymer and additives.⁷⁻⁹
- The environmental and economic advantages such as eliminating the quench oil fire hazard.

It is now interesting to be able to predict the cooling rate and the transition temperatures between the different stages from the polymer solution properties and the polymer characteristics. In this study we are going to try to correlate these properties with

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cooling rate and establish some empirical equations giving the cooling rate at given sample temperature as a function of solution viscosity, or concentration and polymer molecular weight. This approach should also permit to correct the aging effect on the cooling power of the solution.

EXPERIMENTAL

Characterization of the Samples

The samples of polyvinylpyrrolidone (PVP) have been furnished by BASF (FRG) and GAF (USA). The purity of the samples has been checked out by gas chromatography (Hewlett Packard 5880) from their aqueous solutions and no low molecular weight impurity was detected by this technique. We have used four samples of PVP: A, B, C, and D.

The weight average molecular weight was determined by light scattering measurements with a home built apparatus,⁹ (wave length = 6320 Å). The measurements of the refractive index increment were made with a Brice-Phoenix refractometer.

The viscosity measurements were made with an automatic capillary viscosimeter of high accuracy.¹⁰ The capillary diameter was 0.7 mm and the water flowing time was: 33.700 ± 0.001 s at 25°C. The apparatus was thermostated at $\pm 0.01^\circ\text{C}$.

The molecular weight distribution of the samples has been obtained by gel permeation chromatography (GPC) with an apparatus equipped with large columns from Pharmacia (700 mm length and 30 mm diameter) filled by a mixture of Sepharose C12B, C14B, and Sephacryl S300 gels. The eluent was water containing 0.1N NaCl and 400 ppm of NaN_3 as bacteriostatic. The calibration was made with commercial PEO standards.

Quenching Tests

The study was made with different concentrations for every polymer. The cooling power of the solutions was determined by using two apparatuses, I and II: They were equipped with a furnace and a thermostated bath of polymer solution (containing 11 at 25°C and 231 at 30°C for apparatuses I and II, respectively). The cooling curves were obtained by using a silver standard sample⁷ (16 mm in diameter and 48 mm high). A thermocouple 1 mm in diameter placed at the center of the silver sample allows us to follow the temperature as a function of time. The initial silver sample temperature was always 850°C.

In apparatus I, there is a system of injection of the solution in order to destabilize the film boiling by using an hypodermic needle, the end of it being

Table I Characteristics of the Polymer Samples

Polymer	$M_w \times 10^{-3}$	$(M_w * M_n)^{1/2} \times 10^{-5}$	$[\eta]_{25}$ (cm ³ g ⁻¹)
A	1700	7.0	172.00
B	1600	6.9	150.00
C	300	—	57.37
D	63	—	18.08

2 mm from the surface sample with an injection speed of 5 m s⁻¹. In apparatus II, the film boiling destabilization is obtained by agitation with a pump at different rates (in terms of fluid velocity). It was coupled with a microcomputer to follow the cooling power and to obtain the cooling rate curves ($-dT/dt$ vs. T) in less than a minute.

RESULTS

Characterization of the Polymers

In Table I, we have gathered the values of:

- Average molecular weight M_w deduced from light scattering measurements in water at 25°C.
- Intrinsic viscosity values measured in water at 25°C.

The viscosity at zero shear rate of a polymer solution can be calculated by the following relationship as a function of the polymer concentration c_P :

$$\eta = \eta_0(1 + [\eta]c_P + k'[\eta]^2c_P^2 + \dots) \quad (1)$$

where η_0 is the solvent viscosity and k' is the Huggings constant, which reflects the first-order polymer-polymer interactions and depends on the thermodynamical quality of the solvent. $[\eta]$ is the intrinsic viscosity, which varies with molecular weight M_w according to the classical Mark-Houwink power law¹¹:

$$[\eta] = KM^a \quad (2)$$

Quenching Results

The ranges of concentration of the polymer solutions (c_P) were different according to molecular weight of the sample:

$$\text{polymer B: } 5 \leq c_P \leq 17.5 \text{ g L}^{-1}$$

$$\text{polymer C: } 12.5 \leq c_P \leq 50 \text{ g L}^{-1}$$

$$\text{polymer D: } 20 \leq c_P \leq 80 \text{ g L}^{-1}$$

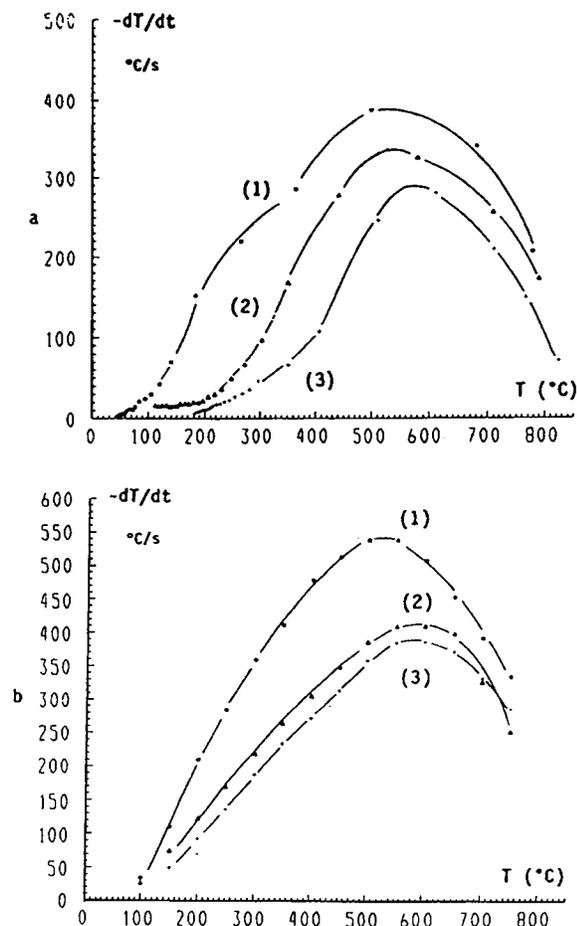


Figure 1 Cooling rate dependence on the polymer concentration for sample B: (a) tests by injection; $c_P = 6, 12,$ and 20 g L^{-1} for curves (1), (2), and (3), respectively; (b) tests by agitation; $c_P = 7.5, 12.5,$ and 17.5 g L^{-1} for curves (1), (2), and (3), respectively.

Effect of Polymer Concentration

We have reported in Figures 1 (a) and (b) some examples of cooling rate curves for injection (5 m s^{-1}) and agitation (0.4 m s^{-1}) as obtained with sample B. In both cases and in the whole temperature range, the cooling rate decreases as the concentration increases and the same observation was made with the other polymers.

This result is essentially interesting near 300°C because that temperature is within the martensitic transformation range for a great number of engineering steels. It is consistent with the previous observations of Hilder,⁸ who has only studied the variation of the cooling rate at its maximum and at 300°C with c_P .

The cooling rate decrease can be essentially explained by the increase of the solution viscosity when c_P increases through expression (1). It is also pos-

sible that, in the neighborhood of the hot silver sample, increasing the concentration will induce a growth of the local viscosity, which prevents the formation of solvent bubbles and their evacuation into the solution. Such a hypothesis has already been suggested by Moreaux et al.,⁷ who have systematically investigated the c_P dependence of θ_2 : transition temperature nucleate boiling-convection. The significant θ_2 increase that they have observed may be also attributed to a boiling hindrance enhanced by viscosity effect.

Effect of Polymer Molecular Weight

In order to evaluate the effect of polymer molecular weight, we have compared the cooling power of solutions of D and C at the same concentration $c_P = 25 \text{ g L}^{-1}$ and under the same test conditions (Fig. 2, curves 1 and 2). It is obvious that an increase of molecular weight induces a decrease of cooling rate. This is confirmed by the curve 3 of Figure 2, which corresponds to a sample B solution of lower concentration but higher molecular weight and shows a significant lowering of the cooling power.

This molecular weight effect can be easily understood from expressions (1) and (2), molecular weight having, in fact, an effect in the same sense as concentration.

EMPIRICAL MODELIZATION

We will try in a first step to modelize as well as possible the cooling behavior with empirical laws. The main purpose of such study is to adjust the

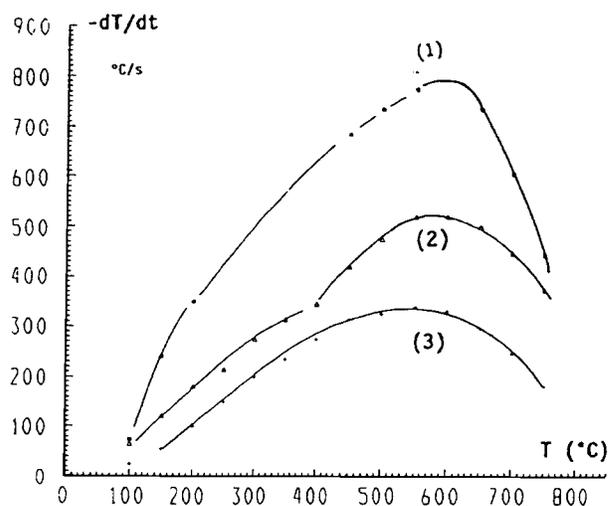


Figure 2 Variation of the cooling rate with the polymer molecular weight. Tests with agitation: (1) D, 25 g L^{-1} ; (2) C, 25 g L^{-1} ; (3) B, 13 g L^{-1} .

properties of a polymer solution for a desired cooling behavior.

From those results one can conclude that cooling power of a solution depends on the properties of polymer and solution. In order to predict cooling rate, some authors starting from experimental observations such as dependences of the cooling rate on concentration and molecular weight of polymer or viscosity of the solution have established some laws based on these parameters. Hilder⁸ gives an empirical relation predicting maximum cooling rate for PVP, poly(alkylene glycol) and polyacrylate solutions, where he introduces the bath temperature (T_B), the polymer concentration (C_P), and the fluid velocity (V):

$$CR_{\max} = \alpha' + \beta' C_P + \gamma' T_B + \delta' V \quad (3)$$

α' , β' , γ' , and δ' being constants. Unfortunately, such a relation does not take into account the polymer properties. We will determine an expression relating the solution and the polymer properties to the cooling rate, valid at least under our experimental conditions.

Cooling Rate and Polymer Concentration

Our empirical modelization is based upon the following observation: The logarithmic plot of $-dT/dt$ versus c_P at a given T is linear in the whole range of T . It follows that

$$\ln(-dT/dt) = A' \ln c_P + \ln B' \quad (4)$$

In Figures 3(a) and 3(b), we give some curves at 200, 400, and 600°C. We note that the coefficients A' and B' depend on the temperature and on the molecular weight of polymer. One finds again the fact that the lowest molecular weight means the highest the cooling rate. It is then obvious that c_P is not the good parameter.

Cooling Rate and Solution Viscosity

Another, easily available parameter is the global solution viscosity, which better takes into account the influence of molecular weight. In order to eliminate the molecular weight parameter, we have plotted in Figures 4(a) and 4(b)

$$\ln(-dT/dt) = A_1 \ln \eta + \ln B_1 \quad (5)$$

One can note that the discrepancies between the

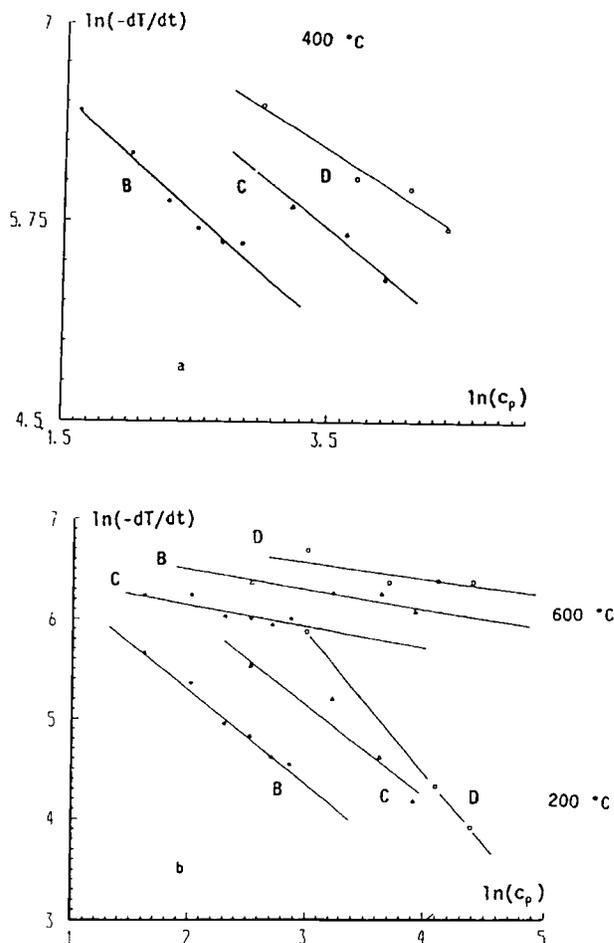


Figure 3 Cooling rate-polymer concentration relation for polymers B, C, and D (by agitation): (a) 400°C; (b) 200 and 600°C.

curves obtained for different molecular weights are significantly reduced. Nevertheless, this correction only based upon viscosity effect seems to be too important at low temperature and not sufficient at high temperature. The order of the curves is indeed inverted in Figure 4(b) at 200 and 600°C.

In a first stage, we have neglected the discrepancies between the results corresponding to different molecular weight and determined mean coefficients of expression (5) by a least square analysis method for the whole set of experimental points.

Examples of results are given in Figures 5(a) and 5(b). These curves show a rather good agreement between experimental and empirical curves. We can conclude the first time that a simple measurement of solution viscosity allows us to obtain an approximate cooling rate prediction and the viscosity is a much better parameter than concentration.

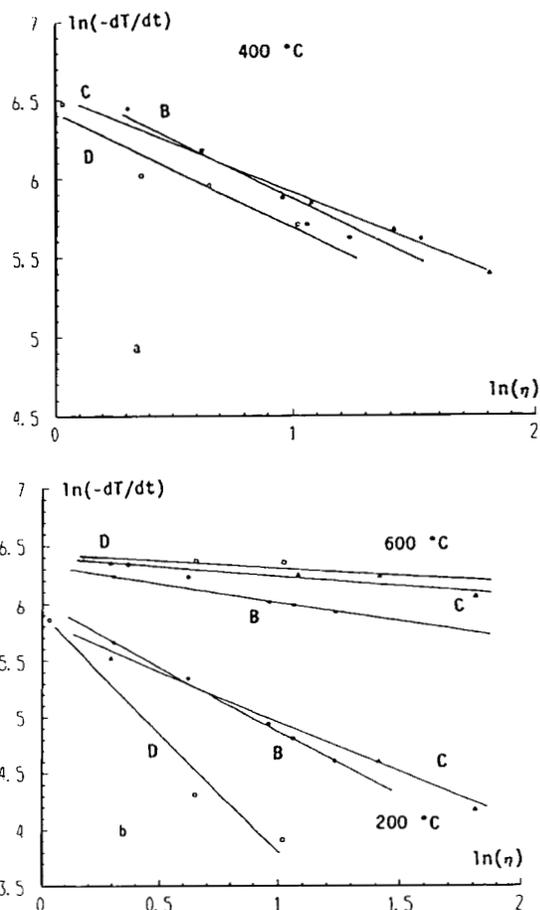


Figure 4 Cooling rate-solution viscosity relation for polymers B, C, and D (by agitation): (a) 400°C; (b) 200 and 600°C.

Precise Empirical Modelization

The viscosity correction has not allowed to superpose the cooling rate values well for the different polymer samples. In fact, it is well known that, in a heat transfer by convection, other parameters must be considered (thermal conductivity, specific heat, density, and dilatation coefficient). Moreover, if the presence of polymer constitutes an hindrance to the solvent boiling, the driving polymer properties for this phenomenon do not seem to be well known. We do not want to enter in theoretical considerations but only make our modelization precise to make it more useful from a practical point of view.

The analysis of the parameters A' and B' from relation (4) shows that these parameters depend on the polymer molecular weight and the curves converge around 400°C [see Figs. 6(a) and 6(b)]: The discrepancies are much more pronounced for $T \leq 400^\circ\text{C}$ than for $T > 400^\circ\text{C}$.

In Figures 7(a) and 7(b), we have plotted A' and $\ln B'$ as a function of $\ln(M_w)$. One can observe a linear dependence of those parameters on $\ln(M_w)$ at every temperature:

$$A' = H \ln(M_w) + G \quad (6)$$

$$\ln B' = F \ln(M_w) + E \quad (7)$$

The coefficients E , F , G , and H are only functions of T (°C). Relation (4) becomes

$$\ln(-dT/dt) = [H \ln(M_w) + G] \ln c_p + [F \ln(M_w) + E] \quad (8)$$

In Figures 8(a)-(d), we give the variations of those coefficients with temperature. These figures confirm the existence of a singular temperature close to 400°C. It is then necessary to separate the temper-

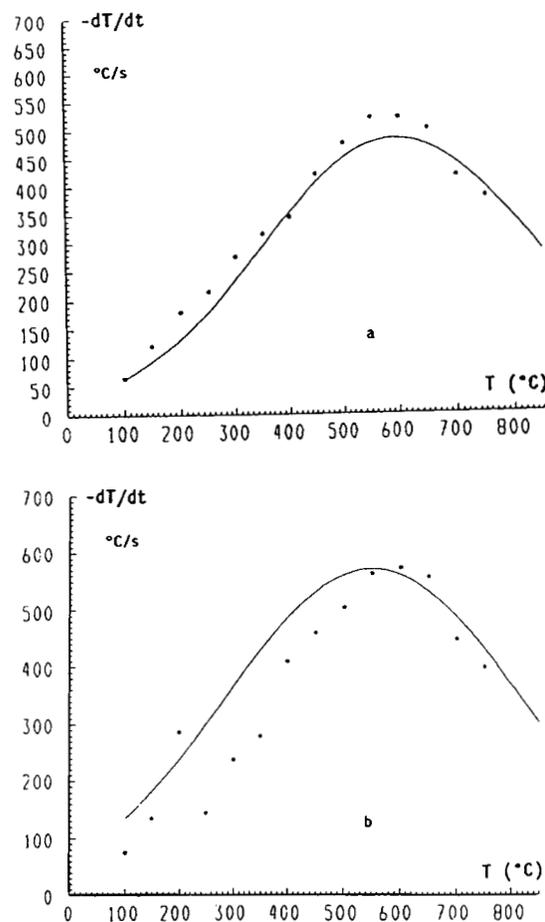


Figure 5 Experimental (*) and empirical (—) cooling rate curves obtained from relation (5); (a) polymer B, 25 g L⁻¹; (b) polymer D, 40 g L⁻¹.

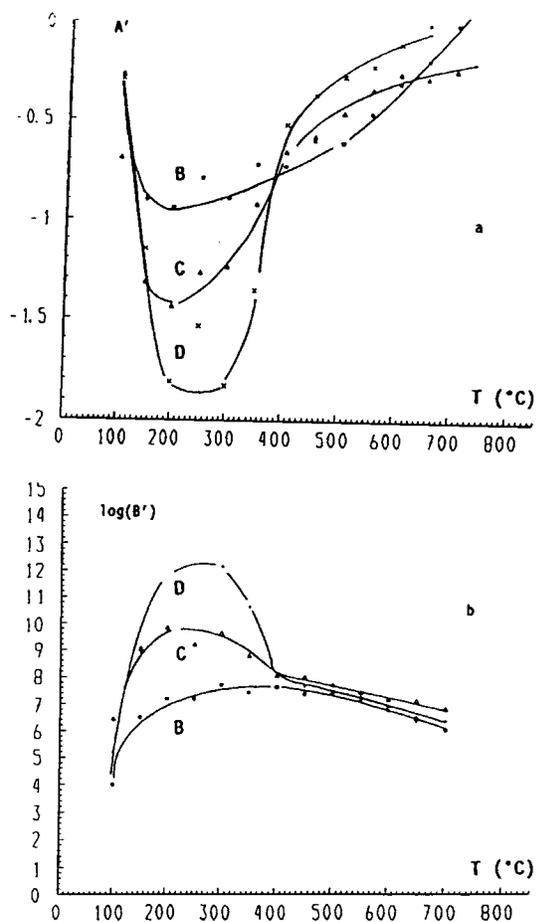


Figure 6 Parameter A' (a) and parameter B' (b) from relation (4) versus temperature.

ature range into two domains ($T < 400^\circ\text{C}$ and $T > 400^\circ\text{C}$).

The adjustments of results of Figures 8(a)–(d) in polynomial functions by the least square analysis method have led to the following expressions:

$$E(T) = \alpha_1 T^2 + \beta_1 T + \gamma_1 \quad (9)$$

$$F(T) = \alpha_2 T^2 + \beta_2 T + \gamma_2 \quad (10)$$

$$G(T) = \alpha_3 T^2 + \beta_3 T + \gamma_3 \quad (11)$$

$$H(T) = \alpha_4 T^2 + \beta_4 T + \gamma_4 \quad (12)$$

From relations (9)–(12), one can write the empirical expression of the cooling rate:

$$\begin{aligned} -dT/dt = \exp\{ T^2[\alpha_1 + \alpha_2 \ln(M_w) + \alpha_3 \ln C_p \\ + \alpha_4 \ln C_p \ln(M_w)] + T[\beta_1 + \beta_2 \ln(M_w) \\ + \beta_3 \ln C_p + \beta_4 \ln C_p \ln(M_w)] + [\gamma_1 + \gamma_2 \ln(M_w) \end{aligned}$$

$$\begin{aligned} + \gamma_3 \ln C_p + \gamma_4 \ln C_p \ln(M_w)] \} \\ -dT/dt = \exp(T^2 U + TV + X') \quad (13) \end{aligned}$$

In relation (13), U , V , and X are functions of M_w and C_p and contain four terms: The first term is independent of M_w and C_p , the second one depends only on M_w , the third one depends only on C_p , and the last one varies with M_w and C_p .

Numerical Application

The different coefficients of the relations (9)–(12) are reported in Tables II and III. The empirical equation (13) allows us to reproduce the cooling rate curves as shown by examples of Figure 9.

DISCUSSION

In the precedent part we have only considered the cooling rate which is a practical parameter but on a

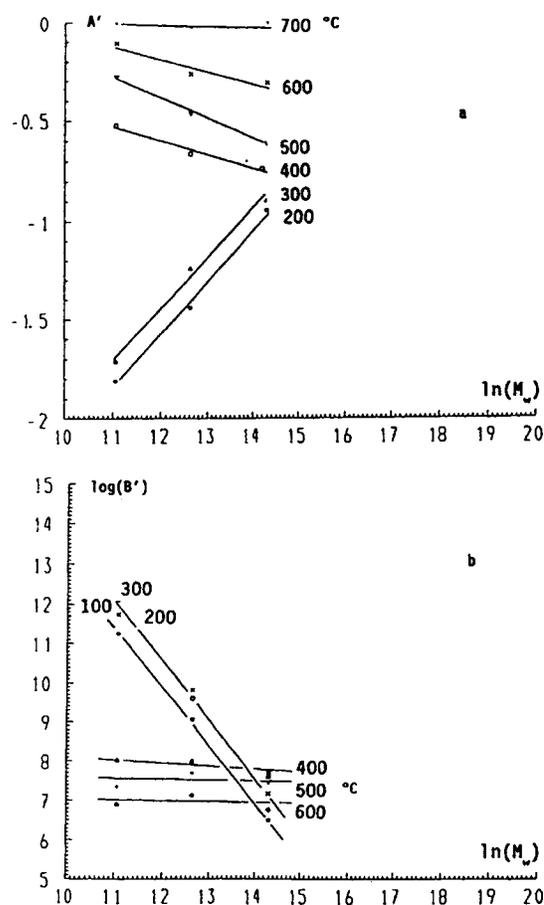


Figure 7 Dependences of parameters A' (a) and parameter B' (b) on polymer molecular weight at different temperatures.

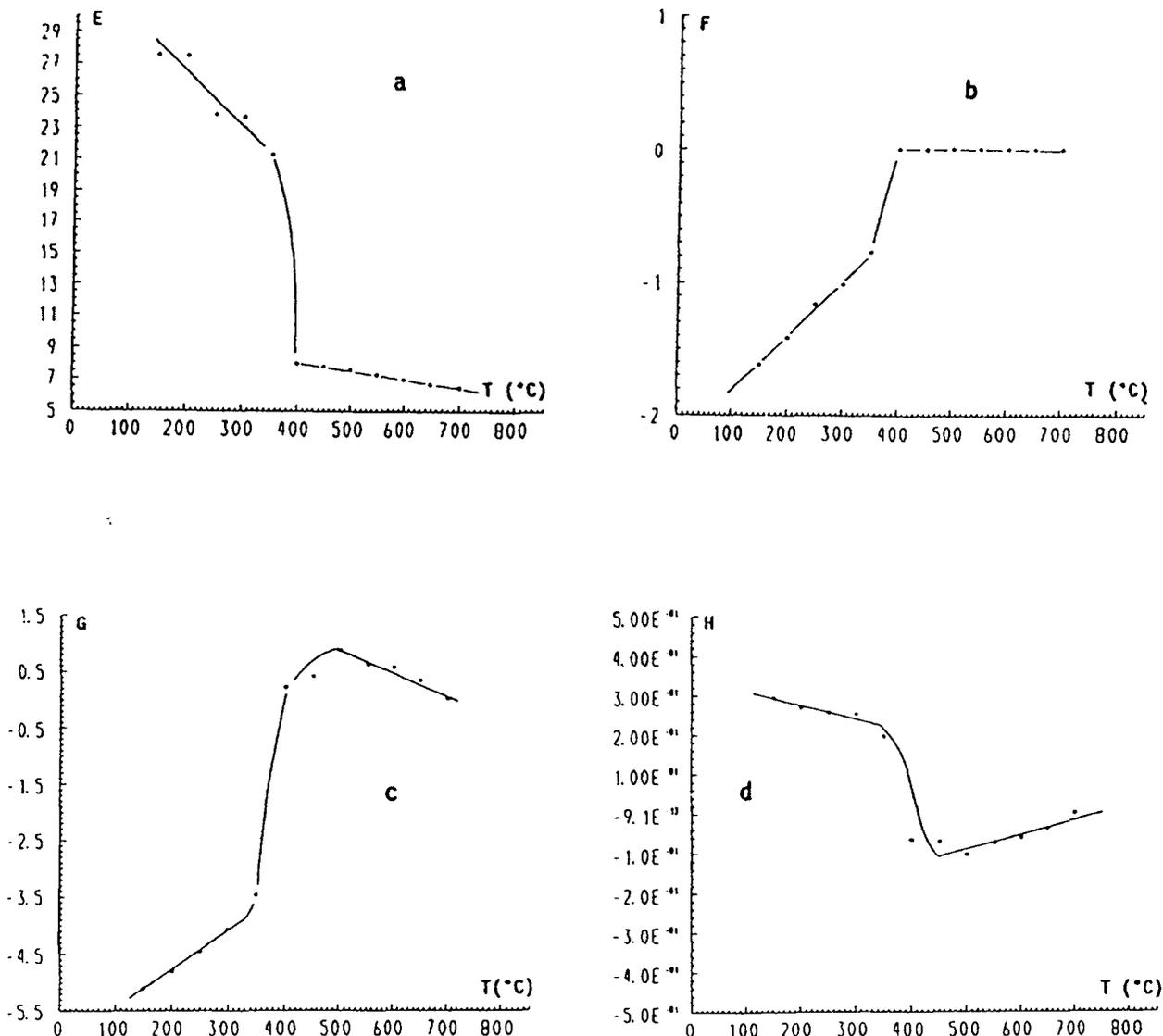


Figure 8 Dependences of parameters *E* (a), *F* (b), *G* (c), and *H* (d) from relations (9)–(12) on temperature.

more fundamental point of view the results must be analyzed in terms of heat transfer and compared with some well-known empirical equations.

A simple calculation of the Reynolds number *Re*

shows that our quench tests in apparatus II were performed in a regime of laminar flow. In the hypothesis of a heat transfer by forced convection, for a cylinder whose axis is in the direction of the liquid

Table II Values of Coefficients α , β , and γ for $T < 400^\circ\text{C}$

	$\alpha \times 10^6$	$\beta \times 10^6$	$\gamma \times 10^6$
E	-661.485	343402.208	-17681054.497
F	39.870	-20520.797	1295039.752
G	162.567	-86033.233	6601425.792
H	-9.604	5190.646	-432583.010

Table III Values of Coefficients α , β , and γ for $T > 400^\circ\text{C}$

	$\alpha \times 10^6$	$\beta \times 10^6$	$\gamma \times 10^6$
E	20.369	-32640.185	19226619.586
F	-2.122	2729.748	-875810.100
G	-21.480	23821.999	-5906882.848
H	1.657	-1686.717	344910.679

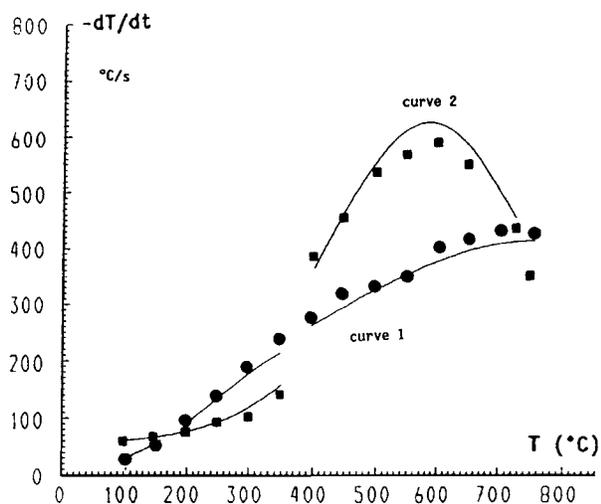


Figure 9 Experimental (*) and calculated (—) cooling rate curves for polymer B (17.5 g L⁻¹) solution (curve 1) and polymer D (60 g L⁻¹) solution (curve 2).

moving, it is well known that the Nusselt number varies with solution viscosity as¹²

$$Nu \propto \eta^{-1/6} \tag{14}$$

The heat flux Φ can be evaluated from the cooling rate curves and one can obtain a number Nu' proportional to Nu . (We do not know the heat transfer coefficient.)

Then in the hypothesis of forced convection, one expects that Nu' varies as $\eta^{-1/6}$ independently of molecular weight of the polymer sample and temperature. Figure 10, which corresponds to sample B, shows that such characteristics are never obtained whatever the temperature range is. On the other hand, the discrepancies between the predicted value of the exponent of relation (14) and the experimental ones are much pronounced for sample D than for sample B, and this is specially true for $T < 400^\circ\text{C}$ (Fig. 11).

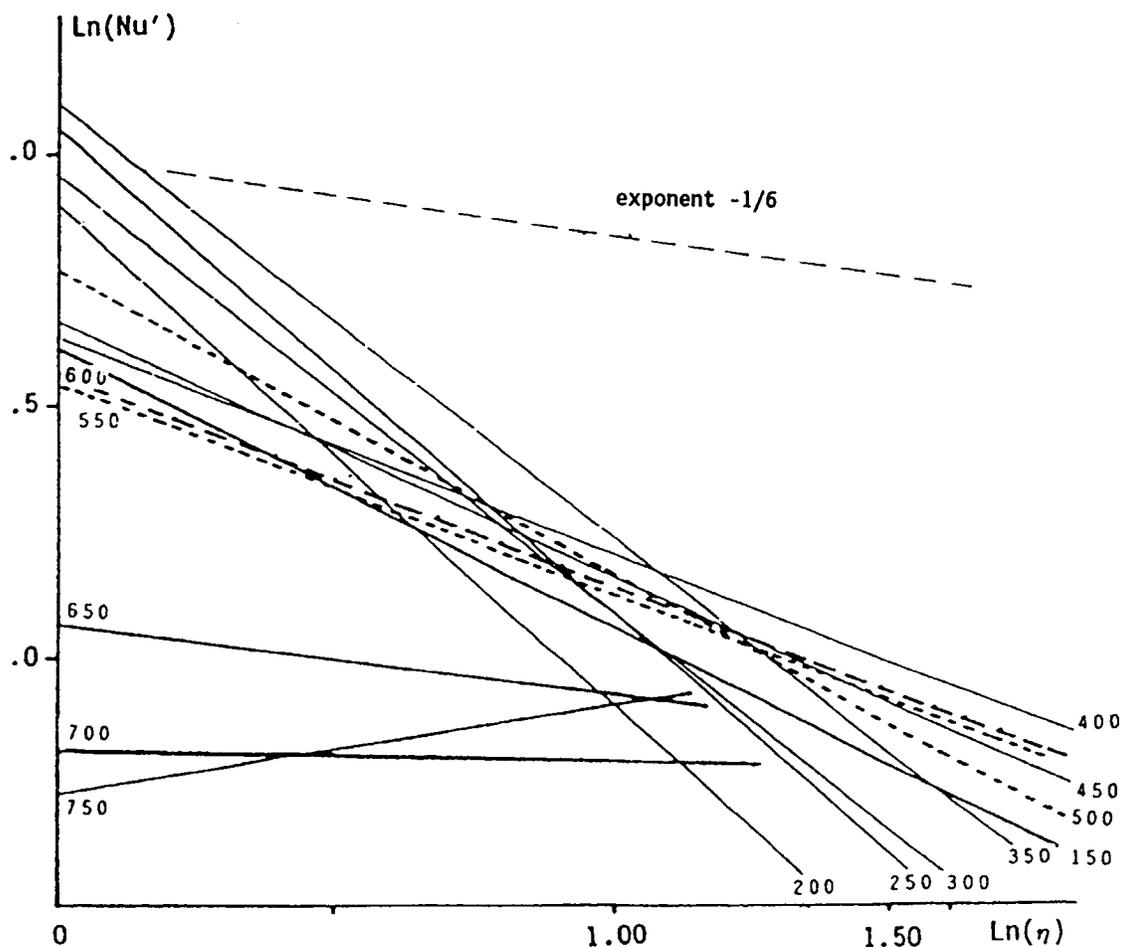


Figure 10 Logarithmic plot of Nu' versus η for polymer B solutions at different temperatures.

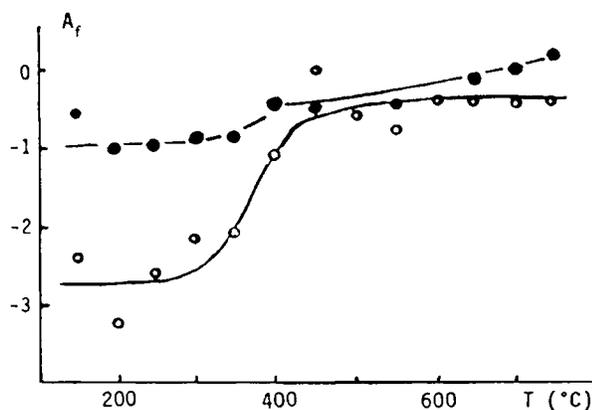


Figure 11 Exponent of relation (14) versus temperature for samples B (●) and D (○).

We can try to discuss different possible explanations of such behavior:

- (i) We have neglected the variations of solution density with concentration, but it is easy to show that such an effect is negligible in the concentration range used.
- (ii) Relation (14) is only valid in the case where the polymer solutions can be considered as Newtonian fluids. It is well known that solutions of high molecular weight polymers are no more Newtonian. The divergence from Newtonian behavior generally occurs for $M > 10^6$ if shear rate is lower than 1000 s^{-1} . The molecular weight of sample B does not reach this limit.

We will propose another explanation based on

- (i) A first remark: We have tried to compare isoviscous solutions in these set of experiments and this implies that the concentration range for sample B finishes where it begins for sample D whose solutions are characterized by high polymer content.
- (ii) Two further experimental observations:
 - When the metallic workpiece is taken from the quenching bath just after its quenching, it is generally coated by a thin layer of very viscous polymer solution.
 - We have followed some quenching tests by rapid video and observed that during the boiling stage there is not only appearance of vapor bubbles but also formation

of some white particles in the next vicinity of the metallic piece.

Our explanation is then based on the fact that the boiling induces a strong and brutal dehydration of polymer and the formation of a dense phase which remains adsorbed on the metallic piece acting as a thermal resistance. The fact that a polymer deposit is visible at the end of the quenching when $T < 100^\circ\text{C}$ shows that it is normal that it modifies the heat transfer in the convection stage and contributes to the decrease of heat flux, which is normally expected to only depend on the viscosity. Its influence in the stage of boiling is perhaps less important since its formation cannot be instantaneous. Such an effect is expected to be more pronounced when the concentration is higher since the condensed phase will be also more concentrated. This could well explain why sample D used in more concentrated solution differs from the two other polymers. In fact, this explanation has already been invoked in the case of polymer solutions which present an inverse demixing behavior (phase separation by heating).

CONCLUSION

In this paper we discuss results of a set of experimental quenching tests performed on polyvinylpyrrolidone aqueous solutions. We have particularly focused our attention on the influence of polymer molecular weight and concentration. In a first step, we have numerically analyzed our results and obtain empirical laws giving the cooling rate as a function of temperature and solution viscosity or concentration and molecular weight of the polymer.

In a second part we have compared the observed behaviors with those which can be predicted for a heat transfer in a simple forced convection regime. High discrepancies have been found even at low temperature where this behavior is the most probable. The exponent absolute value of the law of variation of the Nusselt number as a function of solution viscosity is much higher and this discrepancy apparently increases by decreasing molecular weight. We suggest that this is not directly due to molecular weight but to an additional concentration effect and to the thermal resistance role played by a deposit of polymer on the metallic sample.

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REFERENCES

1. J. C. Chevrier, F. Moreaux, and G. Beck, *Int. J. Heat Mass Transfer*, **15**, 1631 (1972).
2. F. Moreaux and G. Beck, *Mem. Sci. Rev. Met.*, **68**(4), 285 (1970).
3. G. Flament, F. Moreaux, and M. Martin, *Lett. Heat Mass Transfer*, **6**, 205 (1979).
4. C. Dumont, F. Moreaux, A. Simon, and G. Beck, *Trait. Therm.*, **94**, 81 (1975); **95**, 67 (1975).
5. B. Cortinchi, F. Moreaux, and G. Beck, *Entropie*, **85**, 55 (1979).
6. F. Moreaux, A. Simon, and G. Beck, *Heat Treat.*, **1**, 50 (1980).
7. F. Moreaux, J. M. Naud, G. Beck, and J. Olivier, *Heat Treat.*, **84**, *Lond. Proc.*, **18**, 1 (1984).
8. N. A. Hilder, *Heat Treat. Metals*, **2**, 31 (1987).
9. R. Libeyre, D. Sarazin, and J. François, *Polym. Bull. (Berlin)*, **4**, 53 (1981).
10. P. Gramain and R. Libeyre, *J. Appl. Polym. Sci.*, **14**, 383 (1970).
11. P. J. Flory, *Principles of Polymer Chemistry*, 10th printing, Cornell University Press, Ithaca, NY, 1978.
12. P. Avenas, J. F. Agassant, and J. Ph. Sergent, *La Mise en Forme des Matières Plastiques—Approche Thermomécanique*, ed. Tec. Doc. Lavoisier, Paris, 1982, pp. 111–162.

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