International Journal of Pharmaceutics, 5 (1980) 59–65

TEMPERATURE- AND CONCENTRATION-DEPENDENCE IN PSEUDOPLASTIC RHEOLOGICAL EQUATIONS FOR GUM GUAR SOLUTIONS

LOTFI BEN-KERROUR, D. DÛCHENE, F. PUISIEUX and J.T. CARSTENSEN *

Faculté de Pharmacie, Laboratoire Galénique, Université de Paris-Sud, 92290 Châtenay-Malabry (France)

(Received December 7th, 1979)
(Accepted January 9th, 1980)

SUMMARY

It is shown that for aqueous solutions of gum guar, the rheological relation is given by a power function. At infinite dilution the relationship approaches a Newtonian behavior. The temperature-dependence is elucidated and an overall equation, including concentration and temperature, is suggested. An internally consistent approach, considerably simpler than approaches previously reported in the literature is proposed and supported.

INTRODUCTION

Rheological behavior of polymer solutions is of pharmaceutical interest, both in the area of liquid dosage forms (syrups and suspensions) and in the area of solid (as granulation agents).

The viscosity of a liquid is usually obtained by subjecting it to a certain shear rate (ν, $\sec^{-1}$) and then measuring the shear stress (σ, dynes/cm^2). For a Newtonian liquid

$$\nu = (1/\eta)\sigma \tag{1}$$

Eqn. 1 defines the term viscosity, η (erg sec/cm). For non-Newtonian liquids (pseudoplastic liquids, plastic bodies and Bingham bodies), ν is not a linear function of σ, and hence a general viscosity per se is not defined. In this case an apparent viscosity, η', which is obviously not independent of σ, is defined as σ/ν.

The dependence of ν on σ has, for pseudoplastic liquids, been described as a power

---

* Present address and to whom enquiries should be addressed at: School of Pharmacy, University of Wisconsin, Madison, Wisc. 53706, U.S.A.

function (Scott Blair, 1967):

$$\nu = a \cdot \sigma^b \qquad (2)$$

or

$$\ln \nu = b \ln \sigma + \ln a \qquad (3)$$

Ostwald (1925, 1929) was the first to suggest this in a concise form. Maron and co-workers in a series of articles (Krieger and Maron, 1951; Maron, Madow and Krieger, 1951; Maron and Madow, 1953a and b; Maron and Fok, 1955; Maron and Levy-Pascal, 1955) investigated the apparent relative viscosity of latexes

$$\eta_r' = \eta'/\eta_0 \qquad (4)$$

where η_0 is the viscosity of the solvent. This was found to follow a power function in σ which follows from Eqns. 2 and 4:

$$\ln \eta_r = (1 - b) \ln \sigma - \ln a \qquad (5)$$

They denoted b, the non-Newtonian index, and found η_r' to be a function of concentration, x, by a modified Eiler equation (Eiler, 1941), viz:

$$\eta_r = (1 + \{q_1x/(1 - q_2x)\})^2 \qquad (6)$$

The dependence of η_r on absolute temperature (θ) is complicated:

$$\partial \ln \eta_r/\partial(1/\theta) = q_3\theta^2/(1 - q_4\theta) \qquad (7)$$

In Eqns. 6 and 7, the terms, q_i are substance-dependent constants. In an ongoing program on the rheological behavior of natural gums in these laboratories (e.g. Belloul, 1979) we have found relations of greater simplicity than those shown above, and it is the intention of this article to establish these simpler relations for one particular substance, gum guar.

MATERIALS AND METHODS

Solution of gum guar[1] were made in water containing 3.75% ethanol. The solutions were made by wetting the gum with ethanol, adding the water and agitating for 10 min with an agitator (Ultra-Turrax, type 45). The use of the small amount of alcohol facilitates the preparation, in that it eliminates lump formation, and in general, gives rise to replicability not possible without its use. The following concentrations, x (in per cent w/w) were prepared: 0.1, 0.2, 0.35, 0.5, 0.6, 0.75 and 1%. One hour after preparation,

---

[1] Laboratoire CECA, Usine de Baupte, 50500 Carentan, France.

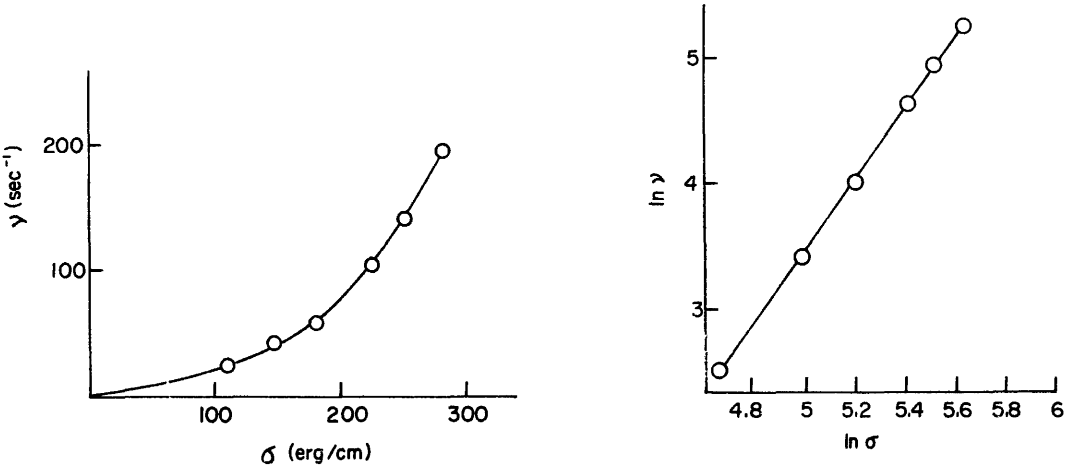

Fig. 1. A: rheogram of a 0.6% solution of gum guar in a 3.75% ethanolic solution in water. The curve is the average of the up and down curve. The hysteresis loop is practically non-existing, amounting to less than 0.5% difference. B: the data in Fig. 1A treated in log–log fashion.

the solutions were placed, at 25 ± 0.2°C, in the cell of a rotary viscometer (Rheomat 30[2]). The rheograms (ν as a function of σ) emerge as shown example-wise in Fig. 1A. The experiment was repeated on the same solution after 6 and 22 h without change in rheogram. The results in the following are averages of these 3 values, and in no case is the standard deviation more than 0.5% of the mean. The same procedure was then carried out at 4 other temperatures (30, 40, 50 and 60°C). It should be pointed out that the rheograms emerge as a *curve* and that for the numerical treatment, 6 selected points (the ν-values in Fig. 1A) were used. Only slight (less than 0.5%) hysterisis occurred.

DISCUSSION

It is seen in Fig. 1B, that the rheograms adhere well to Eqn. 3. Several objections have been raised in the past to this type of equation, on dimensional grounds (e.g. Reiner, 1960). However, by assigning the constant 'a' a dimension of $\text{cm}^{-b}\,\text{erg}^{b}\,\text{sec}$ obviously although not in a general sense, overcomes this type of objection. In the gum guar system, the values of 'a' and 'b' are concentration-dependent. As seen from Fig. 2, b regresses linearly on x, i.e.

$$b = \alpha_1 x + \beta_1 \qquad (8)$$

The data points for 5 temperatures are shown in Table 1. The data show that β_1 is about unity, so that as $x \to 0$, $b \to 1$, which is consistent with the Newtonian behavior of the solvent. (3.75% ethanol in water has a viscosity of 1.03 cps at 25°C and is Newtonian.)

The value of b varies with temperature (T°C). As seen from Table 1, β_1 is temperature-independent, so that the temperature-dependence of b is strictly tied to that of α_1. Fig. 3

---

[2] Contraves, A.G. Zurich, rep. J. Lamy et Cie., 63900 Galuire, France.

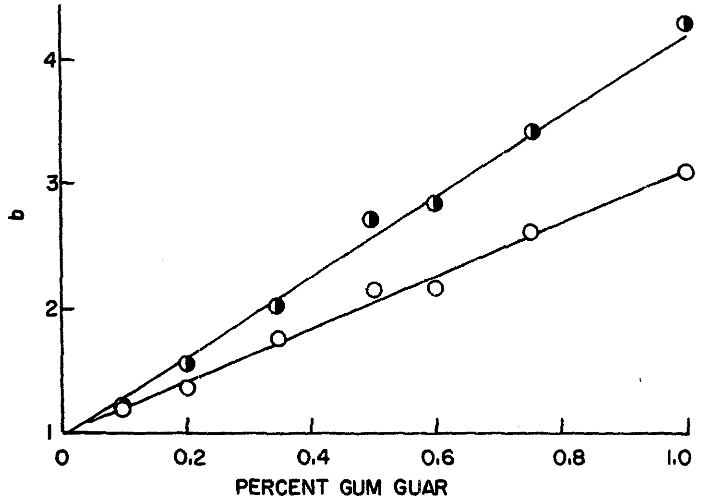

Fig. 2. The value of b in Eqn. 2 (i.e. the slopes of graphs as shown in Fig. 1B) as a function of x, the concentration of gum guar. Note that the ordinate starts with the value one. ◑, 25°C; ○, 60°C. The linear curve corresponds to Eqn. 8.

TABLE I

LEAST-SQUARES VALUES FOR PARAMETERS IN EQN. 8 AND 11. GUM GUAR SOLUTIONS IN WATER AT VARIOUS TEMPERATURES

T (°C)	ln a			b		
	α_2	β_2	r_2^2	α_1	β_1	r_1^2
25	−28.11	5.36	0.99	3.24	0.991	0.99
30	−27.43	5.93	0.99	3.16	0.910	0.98
40	−23.81	5.26	0.99	2.66	0.997	0.97
50	−21.73	5.80	0.99	2.34	0.934	0.98
60	−19.67	5.34	0.99	2.07	1.009	0.96

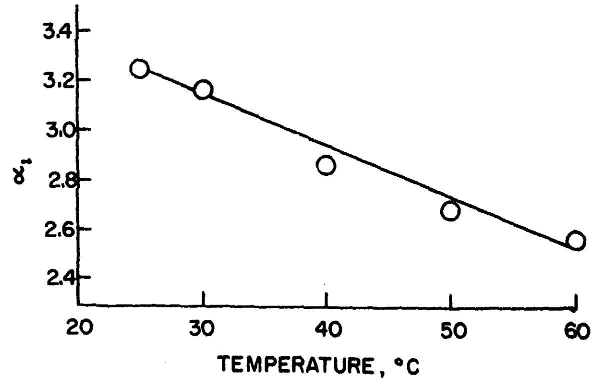

Fig. 3. The dependence of α_1 (from Eqn. 8, i.e. the slopes of plots as those depicted in Fig. 2). on temperature. The plot corresponds to Eqn. 9.

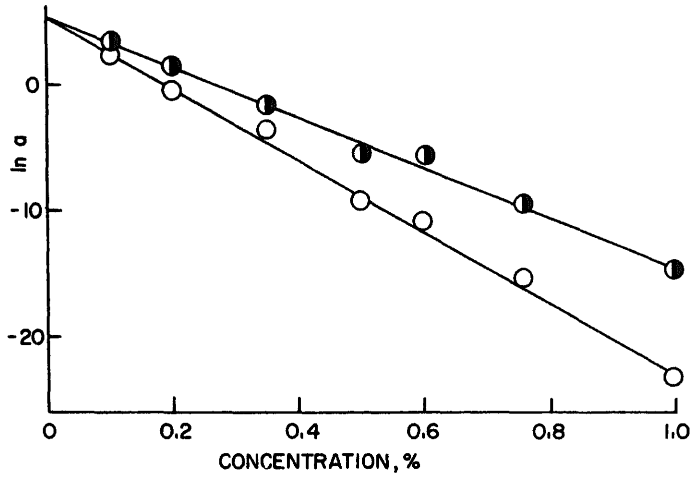

Fig. 4. ln a (a being the slopes from Fig. 1B) as a function of concentration, x. The data show adherance to Eqn. 11. ◑, 60°C; ○, 25°C.

shows α_1 from gum guar as a function of T. It is seen that it follows a linear equation well ($r^2 = 0.98$):

$$\alpha_1 = -0.0352T + 4.141 \tag{9}$$

Hence, one may write for gum guar:

$$b = (4.14T - 0.035)x + 1 \tag{10}$$

The value of a also varies with concentration, but, as shown in Fig. 4 this dependence is semi-logarithmic:

$$\ln a = \alpha_2 x + \beta_2 \tag{11}$$

ln a varies with temperature and again the intersection β_2 is virtually temperature-independent (Table 1). This value is $\beta_2 = 5.54 \pm 0.3$ ($n = 5$). As $x \to 0$, $\ln a \to 5.54$. The viscosity (η_i dyne cm^{-2} sec) at infinite dilution will approach a value not that of the solvent but one corresponding to the intrinsic viscosity. In the case cited here, $\ln a = 5.54$ at infinite dilution so that $a = 255$, i.e. $\eta_i = 1/255 = 0.04$ poise. If the value of the viscosity of the solvent is taken as 0.01 poise, then the intrinsic viscosity (η_i) is given by:

$$\eta_i = \lim_{x \to 0} [(\eta/\eta_0) - 1] = 3 \tag{12}$$

As seen in Fig. 5, the relation between α_2 and T is linear and given by:

$$\alpha_2 = 0.25T - 34.45 \tag{13}$$

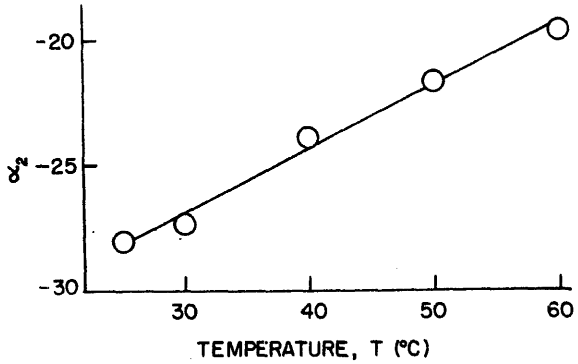

Fig. 5. Effect of temperature (T°C) on the value of α_2, (α_2 being the slopes from Fig. 4 and Eqn 11). The data show adherance to Eqn. 13.

It is therefore possible to write:

$$\ln a = (0.25T - 34.45)x + 5.54 \qquad (14)$$

This now allows the rheogram to be formulated in a general statement of the type of Eqn. 3, i.e.

$$\ln \nu = [(4.14T - 0.035)x + 1.0] \cdot \ln \sigma + [(0.25T - 34.45)x + 5.54)] \qquad (15)$$

It should finally be mentioned (Van Wazer, 1963, Zettlemoyer et al., 1960), that the power equation (Eqn. 2) holds up to a certain shear stress, above which Newtonian behavior sets in. This point, of course, is the intersection between the power parabola of Eqn. 2 and the straight line of Eqn. 1.

REFERENCES

Lylia Belloul, Thèse, Docteur es-Sciences Pharmaceutiques (Diplome d'Etat), Université de Paris-Sud, 1979, Etude rhéologique des solutions d'un polyélectrolyte: la gomme arabique. pp. 1–224.

Eilers, H., Die Viscosität von Emulsionen hochviskoser Stoffe als Funktion der Konzentration. Kolloid-Z., 97 (1941) 313–321.

Krieger, I.M. and Maron, S.H., Rheology of synthetic Latex, I – test of some flow equations. J. Coll. Sci., 6 (1951) 528–538.

Maron, S.H., Madow, B.P. and Krieger, I.M., Rheology of synthetic Latex, II – concentration dependence of flow in type V-GR-2 Latex. J. Coll. Sci., 6 (1951) 584–591.

Maron, S.H. and Madow, B.P., Rheology of synthetic Latex III – concentration dependence of flow in type III GR-S Latex. J. Coll. Sci., 8 (1953) 130–136.

Maron, S.H. and Fok, S.M., Rheology of synthetic Latex V – flow behavior of low temperature GR-S Latex. J. Coll. Sci., 10 (1955) 482–493.

Maron, S.H. and Levy-Pascal, A.E., Rheology of synthetic Latex VI – flow behavior of neoprene Latex. J. Coll. Sci., 10 (1955) 494–503.

Ostwald, W., Ueber die Geschwindigkeitsfuncktion der Viskosität disperser Systeme, Kolloid-Z., 36 (1925) 99–117.

Ostwald, W., Ueber die rechnerische Darstellung der Strucktürgebietes der Viskosität. Kolloid-Z., 47 (1929) 176–187.

Reiner, M., Deformation, strain and flow. An introduction to rheology, Interscience, N.Y., 1960, second ed. pp. 94–131.

Scott Blair, G.W., Elementary Rheology, Academic Press, N.Y., 1969, pp. 53–55.

Zettlemoyer, A.C. and Myers, R.R., In Eirich, F.R. (Ed.), Rheology, Academic Press, 1960, pp. 165–166.

Van Vazer, J.R., Lyons, J.W., Kim, K.Y. and Colwell, R.E., Viscosity and flow measurements – a laboratory handbook of rheology, Interscience, N.Y., 1963, pp. 15–17.