Viscosity measurements on nylon-6/ethyl alcohol solutions in presence of inorganic salts

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In this work shear viscosity data are reported for nylon-6/ethyl alcohol solutions in the presence of LiCl or $LiNO_3$ at different concentrations of nylon and salts up to the solubility. These data have been obtained mostly at 45°C; higher temperatures have been used in a few cases to avoid precipitation at short times. For comparison, some viscosity measurements have been performed on nylon-6/formic acid solutions also in presence of salts. The results seem to confirm interpretations already advanced by other authors both for the solubility and the solution properties of nylon-6 in the presence of similar salts.

INTRODUCTION

It is well known that nylons are insoluble in pure alcohols but they become soluble when in the presence of some inorganic salts (see, for example, Brandrup and Immergut[1]). Some specific works have appeared in the literature in connection with this effect. For instance, Petru *et al.*[2,3] have studied the effect of adding $CaCl_2$ on the solubility of ϵ-capralactam polymer in ethyl alcohol (EtOH) and methyl alcohol (MeOH). They observed that the quality of both the salt and the alcohols, and particularly the water content, plays a very important role in the solubility. The above authors explained the solubility through the formation of complexes which in their case, i.e. in presence of $CaCl_2$, could be similar to hydrites ($CaCl_2 \cdot 4ROH$). Such complexes should then be able to coordinate the nylon molecules partly destroying the pre-existing hydrogen bonds.

A similar interpretation in terms of adducts (or complexes) has also been advanced by Hamoud *et al.*[4] who have extensively studied[4–7] the optical activity of polyamides in alcoholic solutions in presence of $CaCl_2$. They were also able to obtain modified polyamides in the solid state by careful precipitation of the polymer from the $EtOH/CaCl_2$ solution. Direct evidence of the modifications due to the presence of the salt is given by their i.r. spectra which were affected at 3300, 1650 and 1250 cm^{-1}, i.e. in the regions corresponding to NH and CO stretching and NH bending[4], respectively.

In a related work, explicitly directed to the study of the effects of metal salts on the stress–cracking of nylon-6, Dunn and Sansom[8] also suggest that some inorganic chlorides destroy the intermolecular hydrogen bonding of the nylon by forming metal complexes with the amide carbonyl. In their study alcohol or water was necessary to transport the metal ion to the amide. Again the hypothesis is supported by experimental evidence, in this case through n.m.r. spectra.

In this work shear viscosity data are reported for nylon-6/EtOH solutions in presence of LiCl or $LiNO_3$ at different concentrations of nylon and salts up to the solubility. For comparison some viscosity measurements have been performed on nylon-6/HCOOH solutions also in presence of salts. The results seem to confirm the proposed interpretations both for the solubility and the solution properties of nylon-6 in presence of similar salts[9–12]. Before going into details of the work, the relevance that all such effects have in the polymer technology must be stressed. As far as the bulk properties are concerned, following the general idea of the salt–polyamide interactions and their influcence on such properties as melting temperature[9], crystallization kinetics[10], melt viscosity, etc.[11], very interesting results have already been obtained, largely increasing the elastic modulus of nylon-6 melt spun fibres[13]. For the solution properties on the other hand, beyond the clear consideration that it is possible in this way to avoid the use of the typical acid solvents of polyamides, the system alcohol/salt could be, for instance, the solvent in a wet spinning process for a polyamide with the same alcohol to be used as the coagulant agent. With regard to the previously quoted results[13], it could perhaps be possible to follow this alternate route towards high modulus fibres.

EXPERIMENTAL

Materials

The polymer employed in all experiments was an unfractionated sample of commercial nylon-6, manufactured by Montedison (Renyl BV). The sample had an intrinsic viscosity in *m*-cresol at 25°C of 1.45 dl/g, corresponding to a molecular weight of about 20 000[14,15].

Salts used were analytical grade LiCl and $LiNO_3$ (Carlo Erba RP products).

Both polymer and salts were carefully dried before using: in fact, they were heated at 100°C under vacuum for at least 5 h and then stored in a desiccator. Anhydrous C_2H_5OH

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Table 1

Solvent	Salt (mol %)	Nylon (mol %)
Ethyl alcohol	LiCl 7.0	min
	LiCl 10.8	11
	LiCl 16.1	15
	$LiNO_3$ 5.6	min
	$LiNO_3$ 10.8	10
	$LiNO_3$ 16.1	25

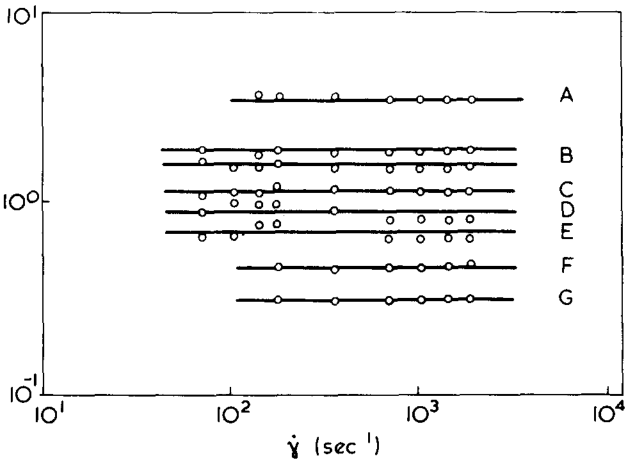

Figure 1 Viscosity vs. velocity gradient for nylon in EtOH/10.8% LiCl, $T = 45°C$. c(g/dl): A, 9.3; B, 8.4; C, 6.7; D, 5.9; E, 5.0; F, 4.2; G, 3.4

(99.5%) and HCOOH (85%), again manufactured by Carlo Erba, were used as solvents

Solution preparation and solubility

The salt/EtOH systems are the only ones for which detail is necessary. In all cases salt was dissolved in the alcohol and then the nylon solubilization was commenced. The solutions were always prepared at their boiling point in a flask immersed in a thermostatically controlled bath. Magnetic stirring was used in all cases and a condenser was mounted on the top of the flask to avoid solvent loss by evaporation. More details of the apparatus have been reported elsewhere[16]. Two different salt concentrations (the same for both salts, as molar percentages) have been used; the higher represents the solubility for LiCl in alcohol. For the chosen salt concentrations the nylon solubility was determined: small amounts of polymer were added to the solution and very long times (up to 16 h) were allowed for the solubilization because of the low rate of dissolution. The results are given in *Table 1*. In the same Table are also reported the minimum salt concentrations[2] which allow polymer solubilization.

Viscosity measurements

Different experimental techniques have been used at low and high polymer concentration. For up to 4% w/w concentrations, Ostwald type viscometers were used, with efflux times never lower than 200 sec. At the higher concentrations, cone and plate rotational viscometers were employed. In particular, a Shirley–Ferranti viscometer, equipped with the appropriate chamber to avoid solvent evaporation was used in the case of high volatility solvent (alcohol). A Weissenberg rheogoniometer was used in the case of low volatility solvent (HCOOH). The use of cone and plate viscometers was suggested by the expected change of apparent viscosity with the velocity gradient (i.e. the well known non-Newtonian behaviour) for the high concentration range.

For the alcoholic solutions the results, reported in *Figures 1–6* as log–log plots of viscosity, η, vs. velocity gradient, $\dot{\gamma}$, were mostly obtained at 45°C. Higher temperatures were used, when in the presence of $LiNO_3$, at concentrations close to the saturation because of the occurrence of precipitation in short times. The limiting values for low shear rates, η_0, could of course be evaluated in all cases. When different temperatures were employed extrapolation was made on Arrhenius plots.

All these results are reported in *Figures 7* and *8* in the form of specific viscosity $\eta_{sp} = (\eta_0 - \eta_s)/\eta_s$ vs. nylon con-

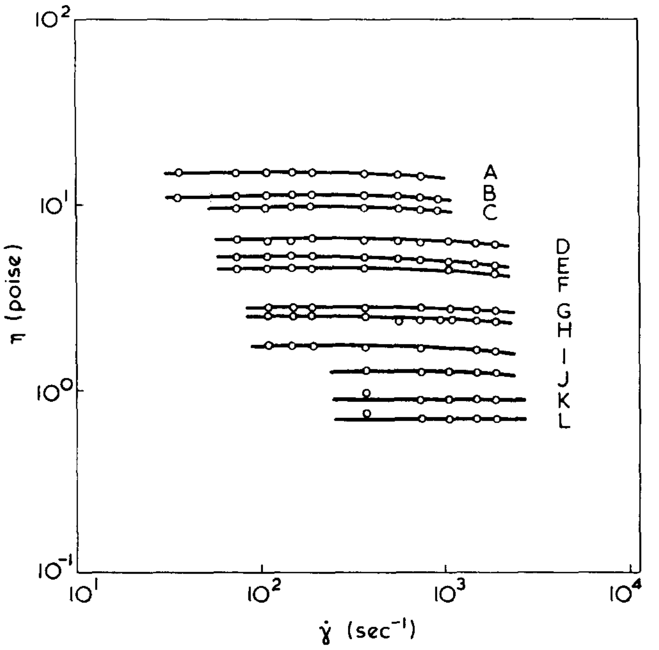

Figure 2 Viscosity vs. velocity gradient for nylon in EtOH/16.1% LiCl, $T = 45°C$. c(g/dl): A, 13.4; B, 12.5; C, 11.6; D, 10; E, 9.8; F, 8.8; G, 8.0; H, 7.1; I, 6.2; J, 5.3; K, 4.43; L, 3.54

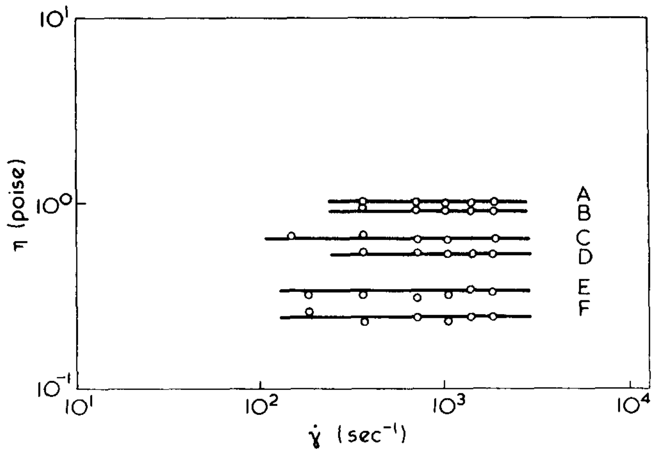

Figure 3 Viscosity vs. velocity gradient for nylon in EtOH/10.8% $LiNO_3$, $T = 45°C$. c(g/dl): A, 8.1; B, 7.2; C, 6.3; D, 5.4; E, 4.5; F, 3.6

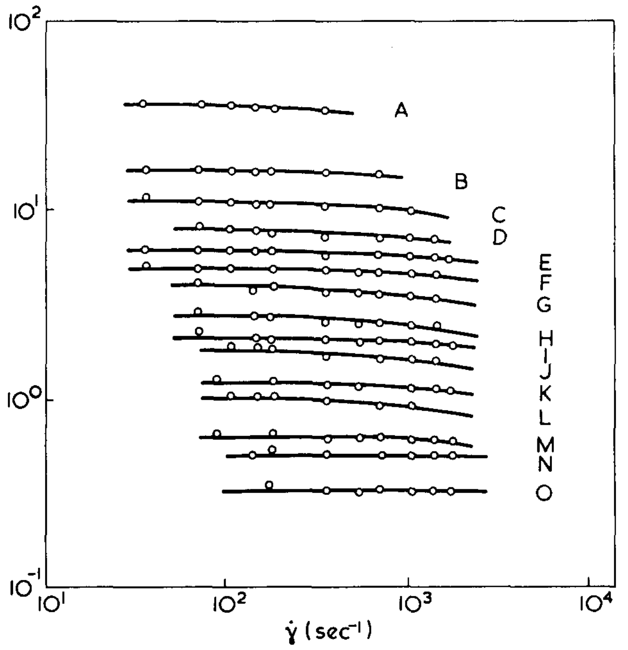

Figure 4 Viscosity vs. velocity gradient for nylon in EtOH/16.1% $LiNO_3$, T = 45°C. c(g/dl): A, 19.0; B, 16.1; C, 15.2; D, 14.2; E, 13.3; F, 12.3; G, 11.5; H, 10.4; I, 9.5; J, 8.5; K, 7.6; L, 6.6; M, 5.7; N, 4.7; O, 3.7

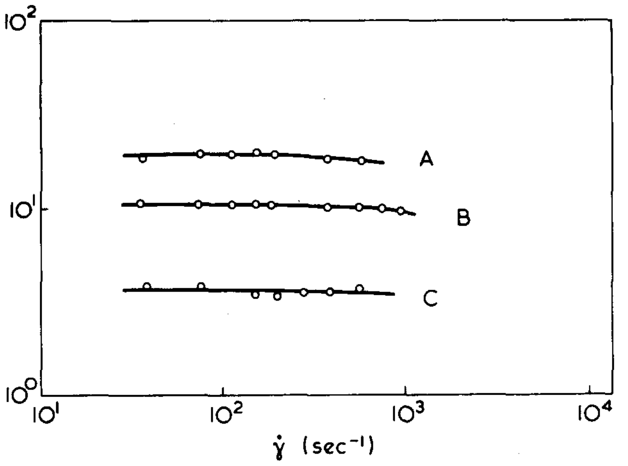

Figure 5 Viscosity vs. velocity gradient for nylon in EtOH/16.1% $LiNO_3$, T = 56°C. c(g/dl): A, 19; B, 16.1; C, 12.3

centration, where η_s is the solvent viscosity.

When formic acid was used as solvent the measurements were carried out at room temperature (~26°C). The results are reported in *Figures 9, 10* and *11* as η vs. $\dot{\gamma}$ and η_{sp} vs. c, respectively.

RESULTS AND DISCUSSION

Although the discussion which follows primarily concerns the viscosity results, a few comments with regard to the solubility are in order. As already noted in ref 2, there is a minimum value for the salt concentration above which the nylon becomes soluble. Such a value depends on the salt type (see *Table 1*). This suggests that the salt interacts first with the alcohol and then possibly with the polymer. As for the dependence of this action on the salt type, this implies dependence on the anion, although it is believed that the primary interaction is due to the Li^+.

Further increase in the salt concentration brings the polymer into solution: again differences are found in the action of different salts. It must be noted that the differences are in line with the ranking of the salts for their ability to bind to denatured biopolymers in water solutions[17–19].

As far as viscosity results are concerned, we shall first discuss the flow behaviour of the system LiCl/nylon/HCOOH in comparison with nylon/HCOOH. In this case, the formic acid being a solvent '*per se*', the LiCl should possibly affect only the polymer. The results in *Figure 11* show that add-

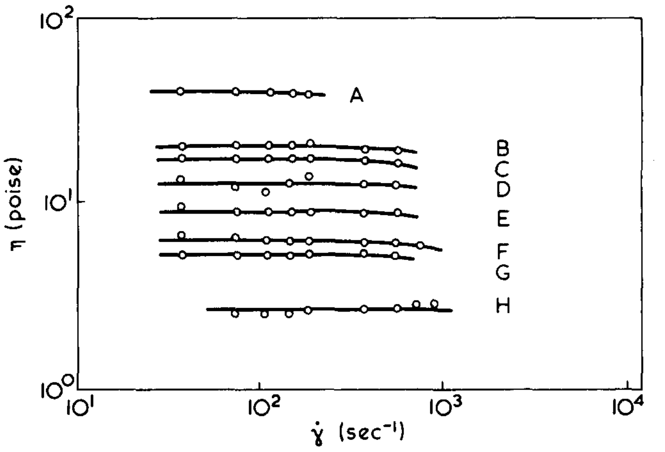

Figure 6 Viscosity vs. velocity gradient for nylon in EtOH/16.1% $LiNO_3$, T = 68°C. c(dl/g). A, 21.9; B, 20.0; C, 19.0; D, 17.1; E, 16.1; F, 15.2; G, 14.2; H, 12.3

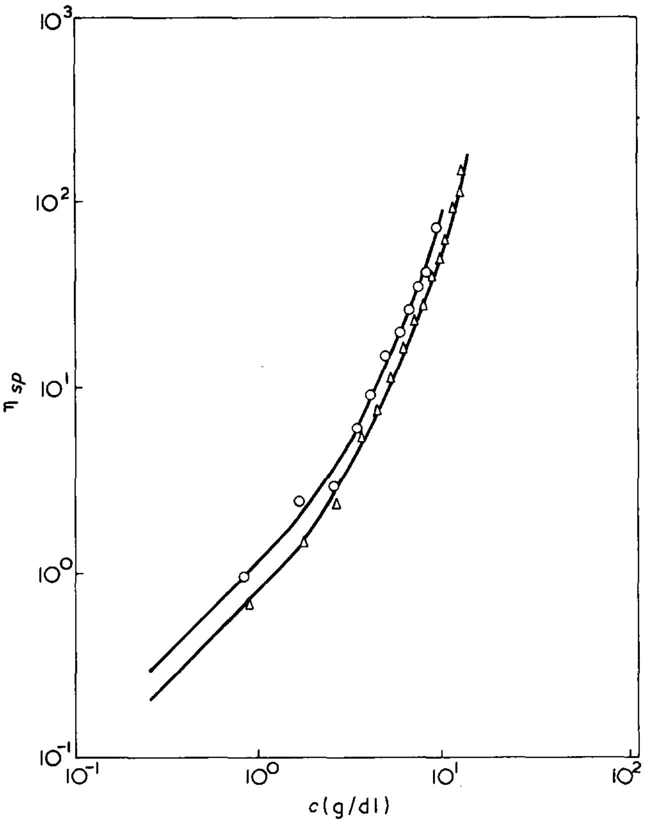

Figure 7 Specific viscosity vs. concentration for nylon in EtOH/10.8% LiCl (△) and EtOH/16.1% LiCl (○), T = 45°C

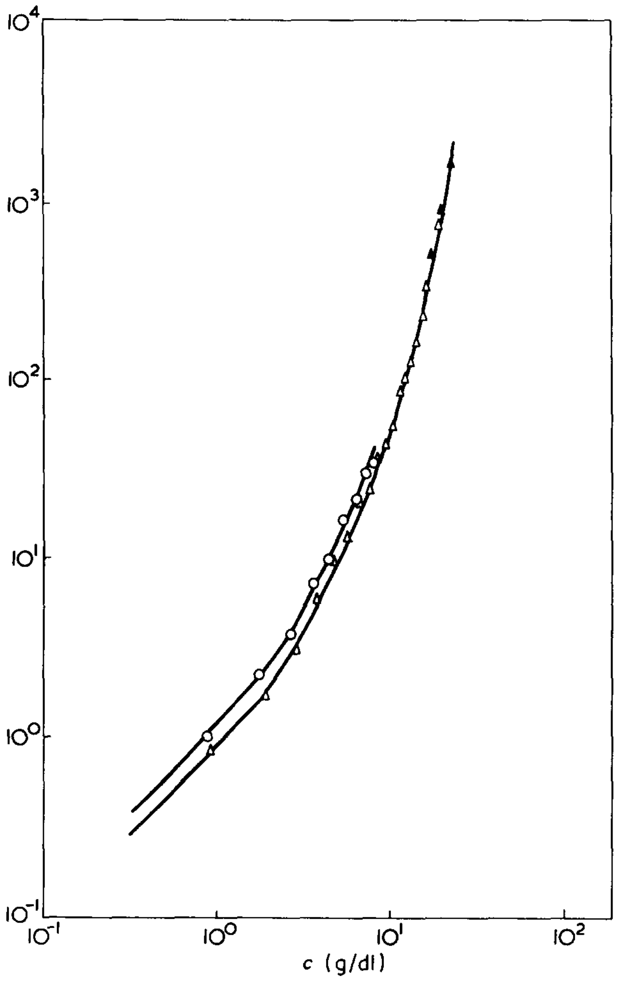

Figure 8 Specific viscosity vs. concentration for nylon in EtOH/10.8% $LiNO_3$ (△) and EtOH/16.1% $LiNO_3$ (○), $T = 45°C$. (▲), correspond to data obtained at different temperatures and extrapolated on Arrhenius plots

ing the salt largely decreases the specific viscosity of the solution in the low range of concentration. This, in the usual interpretation of viscosity in dilute solutions[20], corresponds to a greater coiling of the macromolecule, that is, a smaller end-to-end distance for the polymer in the presence of salt. This should imply intramolecular interactions due to the salt, which is in line with previous results[2,4,9–12]. When polymer concentration increases it is possible that LiCl also favours intermolecular interactions: again this can be seen from the results of *Figure 11*, where the break-point in the slope of the curves (i.e. the point beyond which solutions can no longer be considered dilute) in the case of added salt occurs at a smaller value of concentration. This is also confirmed by some of the data in *Figures 9* and *10* where, at the highest concentrations investigated, non-Newtonian behaviour occurs as it occurs at lower $\dot{\gamma}$ values in presence of salt, again indicating the occurrence of intermolecular interactions for this case. Of course these interactions occur together with the usual physical interactions well known as entanglements. A similar result was also observed in a study of the flow behaviour of molten nylon in presence of salts[11].

With regard to the results obtained with alcoholic solutions, no direct comparison is, of course, possible. The observations are therefore limited to the viscosity dependence upon salt concentration at the same polymer concentration. *Figures 7* and *8* show that in the dilute region lower viscosities correspond to higher salt concentrations. Thus it is confirmed that the salts produce smaller end-to-end distances for the coiled molecule. However, going towards the higher polymer concentrations, where the slope of curves in log–log plots becomes much larger than unity, the differences become smaller, due to the intermolecular interactions which may be increased by the salt. Finally, with reference to the dependence of the specific viscosity values upon the type of salt, we observe that $LiNO_3$ produces lower values than LiCl. This is in line with the previously reported results for the solubility and the already quoted interpretations. In particular, all the results presented here may be qualitatively

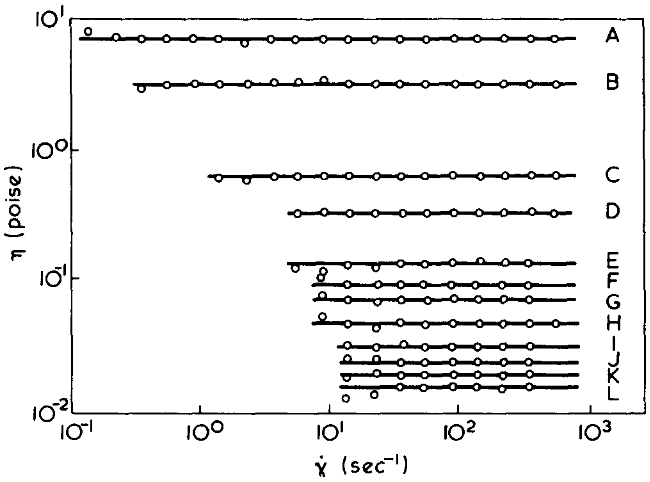

Figure 9 Viscosity vs. velocity gradient for nylon in HCOOH, $T = 26°C$. c(g/dl): A, 2.3; B, 1.73; C, 1.17; D, 0.94; E, 0.56; F, 0.46; G, 0.34; H, 0.23; I, 0.12; J, 0.06; K, 0.03; L, 0.00

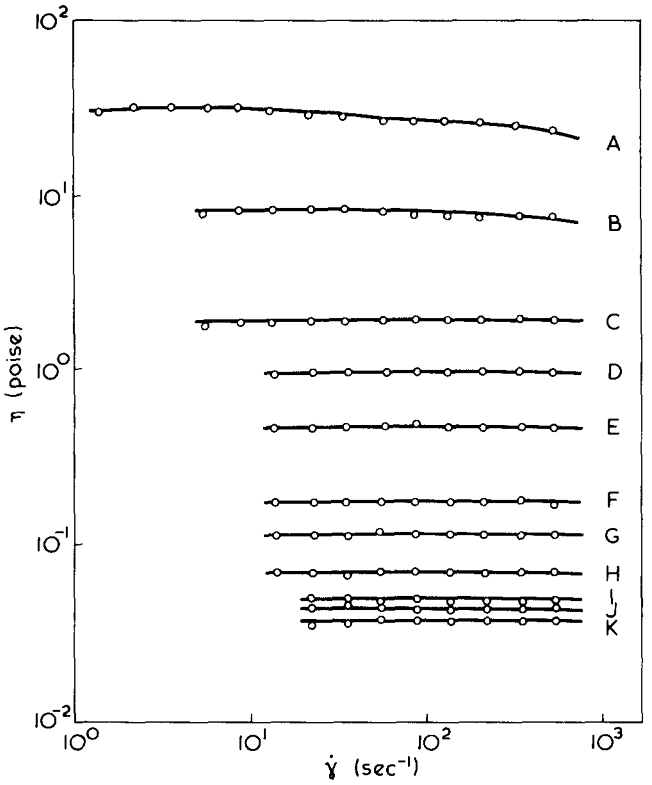

Figure 10 Viscosity vs. velocity gradient for nylon in HCOOH/10% LiCl, $T = 26°C$. c(g/dl): A, 2.4; B, 1.8; C, 1.2; D, 1.0; E, 0.6; F, 0.37; G, 0.28; H, 0.12; I, 0.062; J, 0.031; K, 0.000

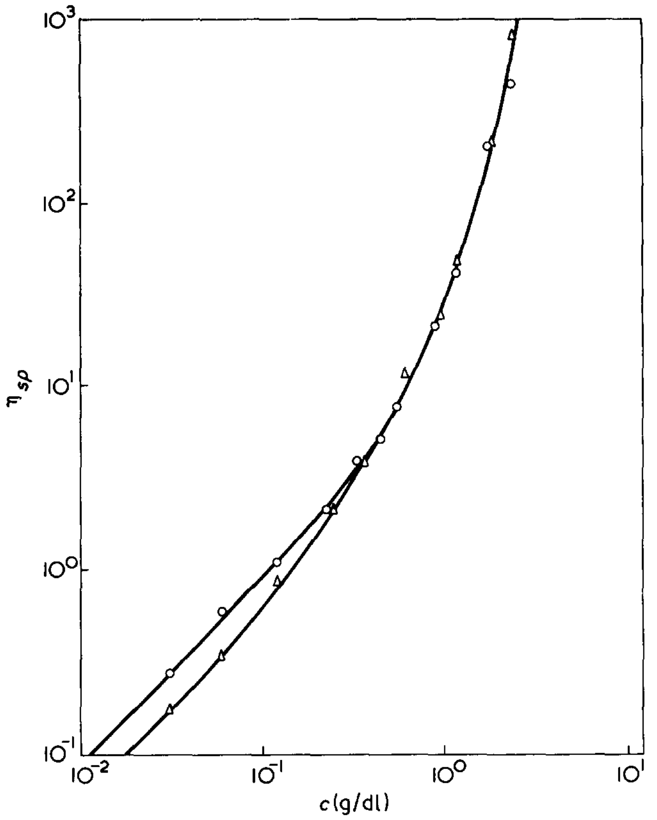

Figure 11 Specific viscosity vs. concentration for nylon in HCOOH (△) and HCOOH/10% LiCl (○), T = 26°C

understood according to the Dunn and Sansom hypothesis[8]. Complex structures should be formed with the intermolecular hydrogen bonds typical of bulk nylons substituted by hydrogen bonds tying the solvent (alcohol in this case) to the carbonyl group of the nylon. Also, according to ref 8, the slight difference in the η_{sp} values when the two different salts are employed is acceptable, due to the different solvation of the metal ion in the two cases. In fact a higher charge density on Li exists when in presence of $LiNO_3$ with respect to LiCl: thus $LiNO_3$ acts as a stronger proton donor.

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