European Polymer Journal Vol. 18, pp. 131 to 136, 1982
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0014-3057/82/020131-06$03.00/0
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RHEOLOGY OF CHLOROSULPHONATED POLYETHYLENE SOLUTIONS

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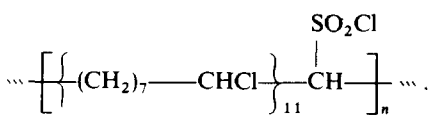
(*Received* 20 *May* 1981)

Abstract—The viscosity behaviour of chlorosulphonated polyethylene was studied as a function of shear rate, concentration and temperature in three aromatic solvents viz. benzene, toluene and xylene. The Carreau model was used to correlate the data. The time constant t_1 arising from the Carreau model was compared with the Bueche time constant λ_B; there appears to be good agreement between them especially at lower temperatures and higher concentrations. A unified curve based on plots of η/η_0 vs $\gamma\lambda_B$ correlated the data successfully. The temperaure dependence of the zero shear viscosity was studied. The apparent activation energy for viscous flow was linearly related to the polymer concentration.

BACKGROUND

Chlorosulphonated polyethylene [CSPE] is an important industrial elastomer. As an elastomer it has many potential applications due to its chemical resistance especially against ozone. Whenever chemical resistance is the primary requirement, then CSPE is normally dissolved in aromatic solvents and used as such in paints especially for surface coatings. The rheology of solutions of CSPE in aromatic solvents is therefore of obvious significance. It was considered desirable to study the viscosity behaviour of CSPE in such solvents, since there appeared to be no reports on this subject.

CSPE is modified polyethylene and various grades are manufactured. Depending upon the chlorine and sulphur contents as well as the base polyethylene used, the properties vary. The general structure of CSPE used by us had one chlorine atom per seven carbon atoms and one anchored sulphonyl chloride [—SO_2Cl] group per ninety carbon atoms of polyethylene back-bone chain. Thus, the structure appears as follows:



It was considered desirable to study the viscosity of CSPE solutions as a function of shear rate, temperature, concentration and also the nature of the aromatic solvent. Furthermore, it was also considered useful to correlate the data in terms of certain phenomenological rheological models.

EXPERIMENTAL

CSPE was prepared by a solution process using carbon tetrachloride as solvent and sulphurylchloride as chlorosulphonating agent. The base polymer was low density polyethylene [LDPE] viz. "Alkathene WRM-19" grade, with MFI of 20, procured from M/s. I.C.I. (India) Pvt. Ltd. The chlorine and sulphur contents of the product were 30 and 1.8% respectively by microanalysis.

The polymer solutions were prepared in benzene, toluene and *p*-xylene. The solution viscosities were measured in a Couette viscometer in the shear rate range 40–650 sec^{-1}. This rheometer was equipped with a thermostat which controlled the temperature within $\pm 0.1°$. The influence of shear rate, temperature, and concentration was studied for each solvent. The concentration of CSPE ranged from 6 to 10%. The data were taken in the temperature range 35–60° at increments of 5°. In all about 325 data points were generated.

RESULTS AND DISCUSSION

Influence of shear rate

Figures 1, 2 and 3 show the data for some selected range of variables in three solvents. It is seen that CSPE solutions in aromatic solvents are shear thinning in all the cases. The variation of viscosity with shear rate will be now analysed using phenomenological models.

Several rheological models are available, describing the viscosity behaviour of polymer solutions, polymer melts and suspensions as well as biological fluids [1]. Some of the models have theoretical foundations, but many of them lack the flexibility to fit viscosity data for a wide range of fluids and for a wide range of variables. Some of the models are empirical but correlate the viscosity data for various types of fluids through a small number of meaningful parameters.

We decided to fit the rheological data by using the Carreau model [2], which is given as:

$$\frac{\eta}{\eta_0} = \frac{1}{[1 + (t_1\dot{\gamma})^2]^S} \tag{1}$$

Here η is viscosity, η_0 is the zero shear viscosity and S is a dimensionless constant. This model is interesting, since it contains a time constant t_1 which is closely related to the elastic time constant for most polymeric materials (see for instance, Abdul Khalid *et al.* [3]). The procedure adopted to fit the model was basically

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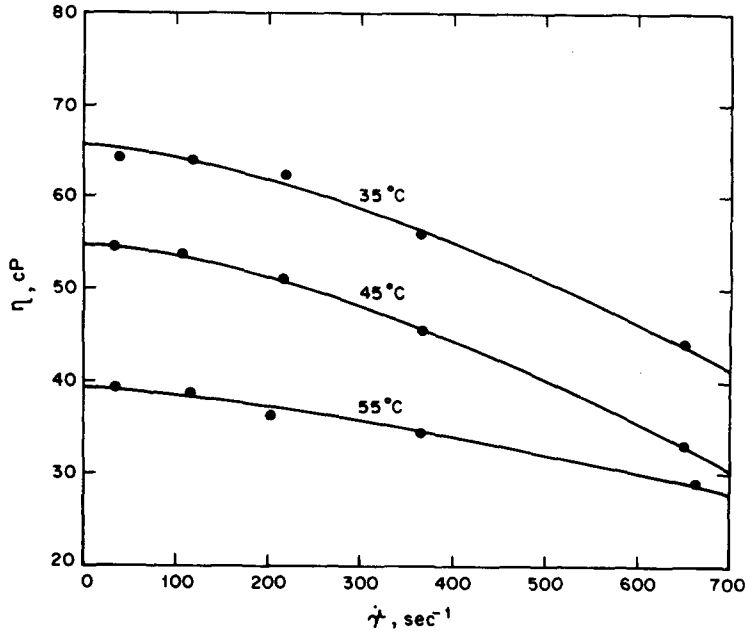

Fig. 1. Solution viscosity of CSPE in benzene (concentration = 10 g/100 ml).

the same as that used by Carreau *et al.* [4] involving a nonlinear regression method using Morequeardt modification [5]. The criterion for parameter value selection was such that the following quantity was kept minimum:

$$\Delta = \sum_{i=1}^{N} W_i(Y_i^E - {}_0Y_i^C)^2 . \qquad (2)$$

Here N is the number of data points, W_i is the weight associated with each datum given by $W_i = [1/Y_i^E]^2$ and Y_i^E and Y_i^C represent respectively the experimental and calculated values of the dependent variables.

Table 1 shows the values of model parameters viz. η_0, t_1 and S obtained by the above procedure. The variance values show that the model fitted the data very well. It may be noted that S is related to the conventional power law index for Ostwald–de Waele fluids by the relation $n = 1 - 2S$. It can thus be seen that the range of n values for the data reported is 0.7–1. This implies that the fluids are mildly pseudoplastic.

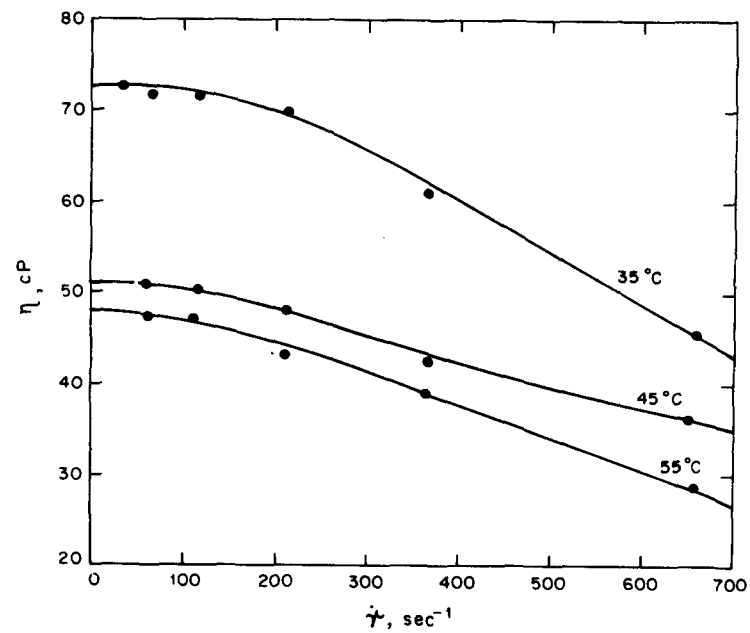

Fig. 2. Solution viscosity of CSPE in toluene (concentration = 10 g/100 ml).

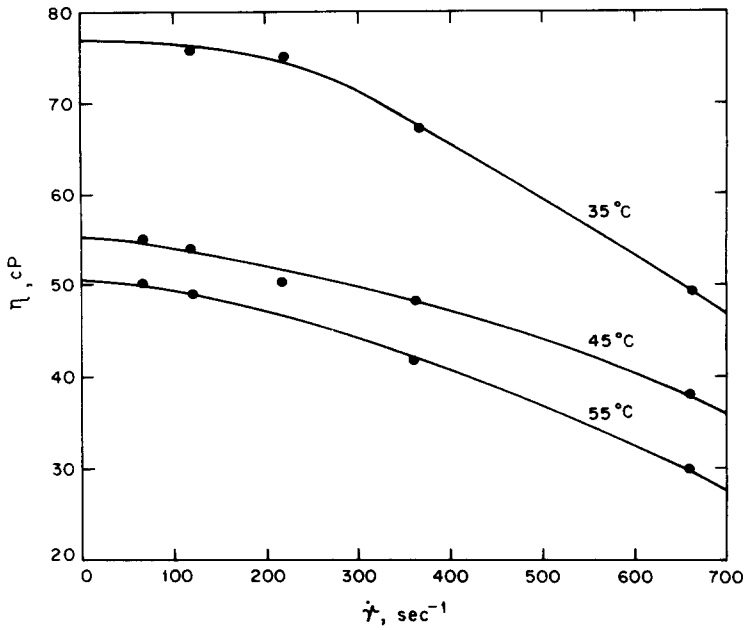

Fig. 3. Solution of CSPE in xylene (concentration = 10 g/100 ml).

The time constnat t_1 was found to be of the order of 10^{-3} sec. The time constant obtained from the fit of Carreau model will be compared with the time constant obtained by the relation given by Bueche [6], which is as follows:

$$\lambda_B = \frac{12(\eta_0 - \eta_s)\bar{M}_v}{\pi^2 CRT}. \quad (3)$$

Here η_0 is the zero shear viscosity, η_S is the solvent viscosity, $\bar{M}_v$ is the viscosity average molecular weight, C is the concentration in g/100 ml, R the gas constant and T the temperature. The values of the Bueche time constants have been tabulated in Table 1 for various concentrations and temperatures and compared with the time constants t_1 emerging from the Carreau model. It is seen that there is a fair agreement between the two time constants, especially at lower temperatures and higher concentrations.

A general functional relationship of the following type can be used to correlate the viscosity data:

$$\frac{\eta}{\eta_0} = f(\dot{\gamma}\lambda_B). \quad (4)$$

Figures 4 and 5 show the shear rate dependent solution viscosities plotted as a function of reduced shear rate ($\dot{\gamma}\lambda_B$) according to Eq (4). There is a very good correlation, when the data are plotted in this manner. There was a considerable overlap and therefore all the points have not been shown.

The advantage of such a correlation is that the curve is unique for each solvent and therefore, with limited information about the dependence on concentration and temperature, extension to any other value of concentration and temperature could be made.

Influence of temperature

The influence of temperature on viscosity was studied; in particular, η_0 was studied as a function of temperature. There appear to be two prevalent approaches concerning the correlation of temperature effect. Many workers (see, for instance, the recent work of Ansorena *et al.* [7]) have shown that the viscosity of dilute polymer solutions varies with temperature according to an Arrhenius type law,

$$\eta_0 = A \exp(q/RT). \quad (5)$$

Table 1. Estimated parameters in Carreau Model for CSPE solutions

Sample no.	Solvent	Temp. (°C)	Conc. (g/100 ml)	η_0 (cp)	S	$t_1 \times 10^3$ (sec)	$\lambda_B \times 10^3$ (sec)	Variance $\times 10^3$
1	Benzene	35	10	66.0	0.1427	1.32	1.06	8.9
2	Benzene	55	10	43.5	0.0890	1.12	0.66	11.2
3	Benzene	35	8	47.5	0.1266	1.28	0.89	10.1
4	Benzene	55	8	27.5	0.0861	1.13	0.52	17.2
5	Toluene	35	10	72.5	0.1439	1.34	1.20	1.6
6	Toluene	55	10	46.5	0.0921	1.15	0.72	8.2
7	Toluene	35	8	49.0	0.1086	1.24	0.93	8.3
8	Toluene	55	8	30.0	0.0540	0.86	0.49	9.2
9	*p*-Xylene	35	10	77.5	0.1458	1.43	1.35	1.6
10	*p*-Xylene	55	10	51.0	0.1016	1.24	0.75	5.8
11	*p*-Xylene	35	8	57.5	0.1418	1.29	0.96	8.5
12	*p*-Xylene	55	8	46.0	0.0900	1.15	0.69	9.8

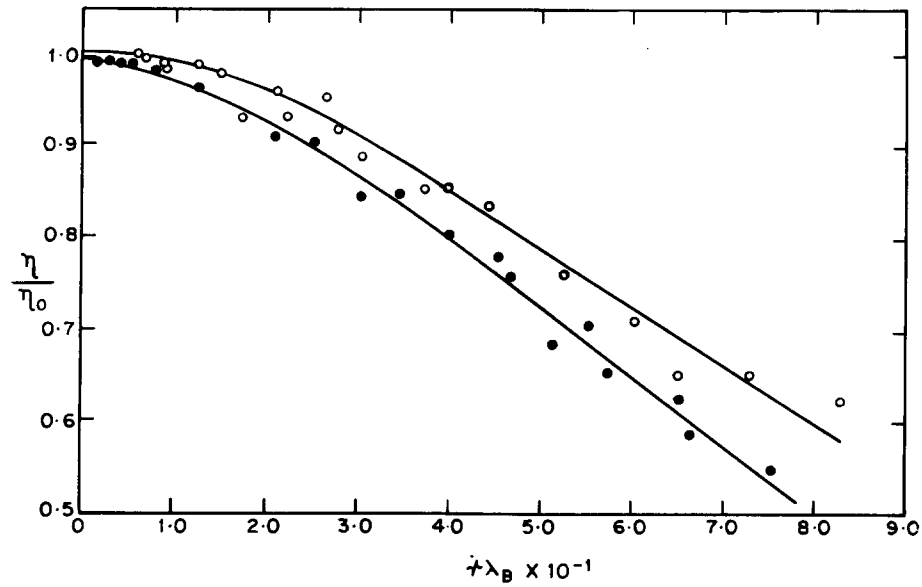

Fig. 4. CSPE solution viscosity as a function of reduced shear-rate (●) benzene; (○) toluene.

Here η_0 is the zero shear viscosity of the solution, q is the apparent activation energy for viscous flow and A is a pre-exponential factor.

Recently free volume theories have been increasingly used for correlating the viscous behaviour of polymer solutions and melts [8–12]. In this approach the viscosity of polymer solutions and melts is given as:

$$\eta_0 = KC^aM^b \exp(B/f). \quad (6)$$

Here K is a constant characteristic of the polymer, C is the concentration (or the density in the case of melts), M is the molecular weight and f the free volume fraction at the relevant temperature and pressures. We have a = b = 1 for dilute polymer solutions. Further, for melts and concentrated solutions, we have b = 3.4. It is usually assumed that B = 1. The free volume is usually interpreted as being given by the difference between the total volume and the volume occupied by the molecules. This approach has been successfully used to explain the nonlinear viscoelasticity of polymeric solutions. In such an approach, the dependence of viscosity upon temperature is predicted by assuming an appropriate variation of free volume with temperature.

We will use Eqn (5) to represent the viscous behaviour of CSPE solutions. The apparent activation energy of viscous flow is a function of the nature of polymer, the solvent, the concentration and the molecular weight of the polymer. One could postulate linear dependence of the apparent activation energy on the concentration [13]. Thus we have the follow-

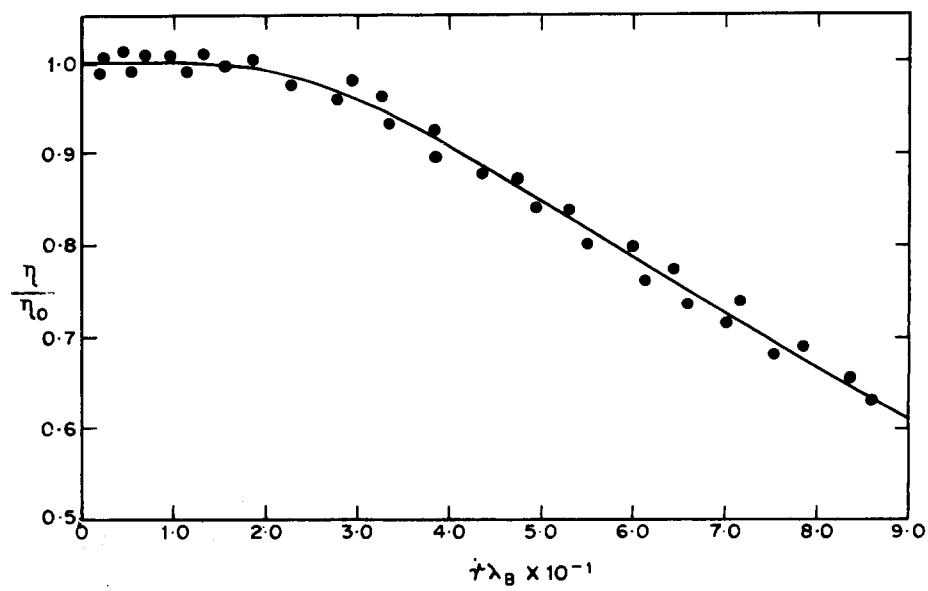

Fig. 5. CSPE solution viscosity as a function of reduced shear-rate for xylene solutions.

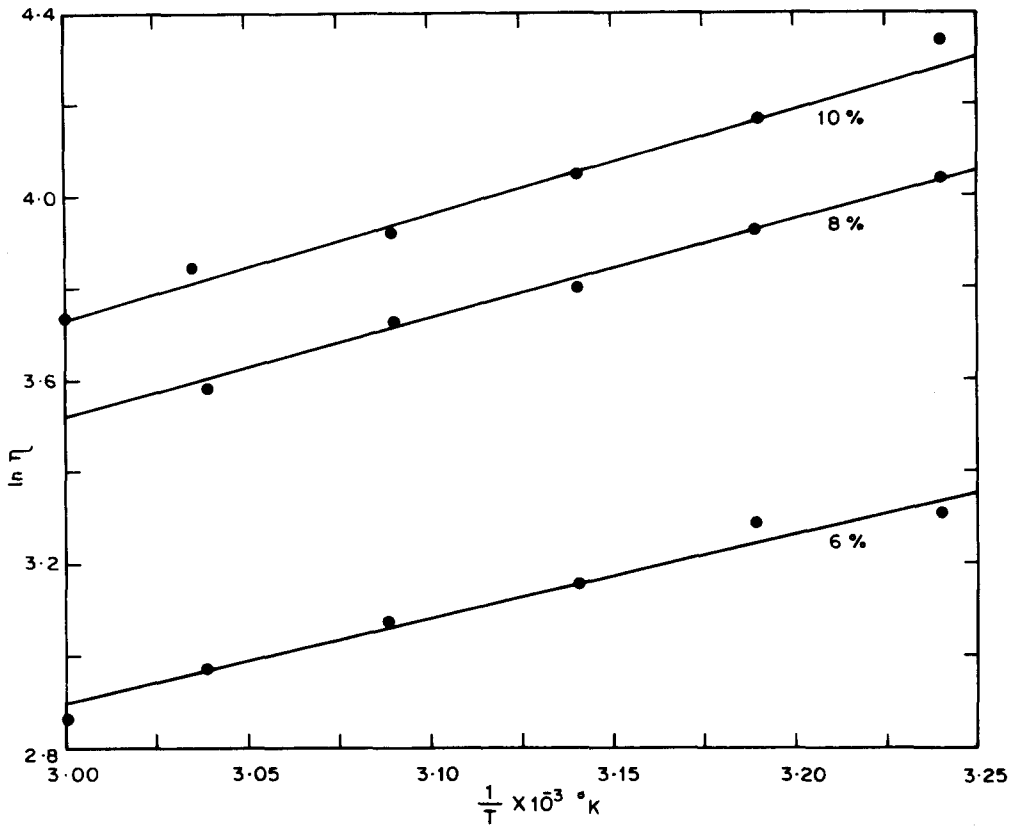

Fig. 6. Temperature dependence of viscosity for CSPE solutions in xylene.

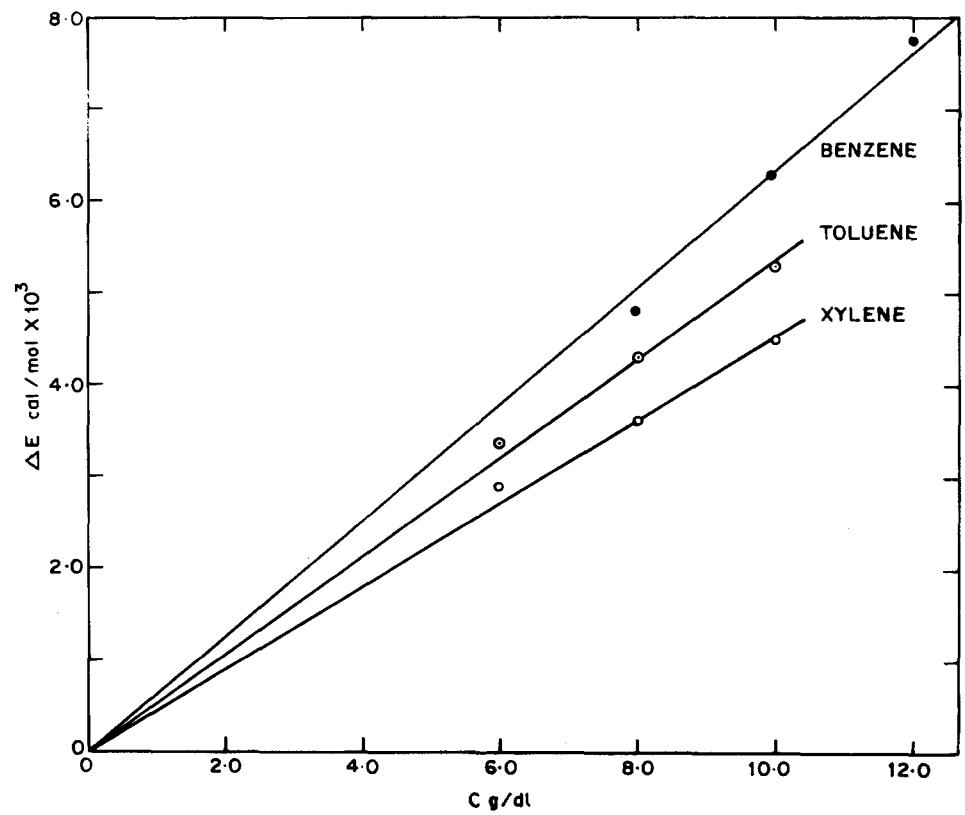

Fig. 7. Dependence of apparent activation energy on concentration for CSPE solutions in (●) benzene; (⊙) toluene; and (○) xylene.

ing equation:

$$q = q_0 + K_c C \tag{6}$$

q_0 being the activation energy of viscous flow for pure solvent and K_c is a coefficient depending on molecular weight of polymer.

We computed the activation energy of viscous flow for the solvents from the viscosity–temperature data for the solvents concerned, as reported in the literature [14]. Figure 6 shows some typical plots of ln η_0 vs $1/T$ for CSPE solutions in xylene. Activation energy of viscous flow was calculated from such plots. It was found that the activation energy of viscous flow increased with increasing concentration. Figure 7 shows a linear plot of this activation energy vs concentration. Aelenei and Schneider [13] studied the viscosity temperature relationships for poly(vinyl chloride) in tetrahydrofuran and found a similar dependence.

CONCLUDING REMARKS

It is useful to consider the significance of the present results in the context of literature data on other polymer solutions. As remarked earlier, Carreau *et al.* [4], have correlated data for a number of polymeric and non-polymeric fluids by using Eq (1). The data fits are excellent for a variety of systems. Among the previous efforts to obtain a universal correlation shown in Eqn (4), the work by Chitrangad *et al.* [16] may be mentioned, wherein rheology of a variety of polymers dissolved in aromatic solvents was studied. They showed that Eqn (4) could fit in a range of $\dot{\gamma}\lambda_B$ extending from 10^{-2} to 10^3. Therefore there appears to be considerable merit in using such plots for diverse systems.

The correlation for activation energy used here [Eqn (6)] has also been used by Ansorena *et al.* [7] for dilute polybutadiene solutions and by Aelenei and Schneider [13] for PVC–tetrahydrofuran solutions. These authors were additionally successful in obtaining a correlation of the parameters appearing in Eqn (5) with molecular parameters. Due to incomplete information, it has not been possible to establish such a comprehensive relationship in this work.

We have presented experimental data on the viscosity behaviour of CSPE solutions for conditions likely to be important industrially. It might be mentioned that the viscosity behaviour will refer to the paint base and not to the final product. Various aspects of pertinent rheological characteristics for coating applications have been summarised elegantly by Kornum [15] who showed that the viscosity characteristics play a vital role in the applications as well as the production of paint bases.

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