Pressure and Temperature Dependence of the Viscosity of Polymer Solutions in the Region of Phase Separation

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Received October 16, 1978

ABSTRACT: For the system *trans*-decahydronaphthalene/polystyrene (M = 110000) and the ranges of pressure, temperature, composition, and shear rate under investigation (1–1000 bar, 10–16 °C, 8–15 wt % polymer, and 20–320 s^{-1}), the viscosity coefficients η increase in a fairly exact exponential manner by roughly a factor of 6 per 1000 bar. Special attention was paid to the demixing conditions which manifest themselves in a sharp discontinuity of the ln η vs. p curves. The comparison of the obtained demixing data with the previously measured critical lines demonstrates that at elevated pressures the polymer solutions are stabilized by stirring, i.e., they demix at higher pressure (300 bar) or lower temperature (2 K). A molecular mechanism for this finding involving molecular interactions is put forward. For homogeneous solutions η increases exponentially with concentration. The interpretation of $\eta(p,T)$ with respect to the apparent volumes of activation, $V^{\ddagger}$, and the energies of activation, $E^{\ddagger}$, shows the following: (i) The hypothesis that the pressure dependence of η is essentially given by the pressure dependence of $E^{\ddagger}$ does not hold true for the present case and (ii) maximum in $V^{\ddagger}$ is found at the critical composition by analogy with the well-known maximum in $E^{\ddagger}$; the increase in $V^{\ddagger}$, associated with an approach of the critical point, is however much less pronounced than that of $E^{\ddagger}$.

The first attempts to investigate the influence of pressure on the viscosity of liquids date back to 1884, when Röntgen[1] studied the behavior of water. It was not until the pioneering work of Bridgman[2] that research in this field became somewhat more popular. But even then the number of papers dealing with the pressure influences on the viscosity remained low,[3] probably as a result of the great experimental difficulties. The cited investigations mainly deal with pure low molecular weight liquids, oils, and polymer melts. To the knowledge of the authors only two[4,5] not generally known works have so far been performed to study the influence of pressure on polymer solutions in the region of high dilution and none at moderate concentrations.

The present study was undertaken to extend already published[6] and current investigations concerning the influence of pressure on the thermodynamic properties of polymer solutions, in particular on their demixing, to the rheological consequences of hydrostatic pressure at moderate polymer concentrations. This seemed especially interesting since changes in the "free volume" of a liquid can be seen from its viscosity most easily; of all physicochemical properties the viscosity normally shows the highest dependence on pressure.

One question of the present work concerns the determination of the demixing conditions by the breakdown in viscosity upon the onset of phase separation[7] under pressure and the study of the excess viscosity[8–11] in the vicinity of the critical conditions as a result of fluctuations. The system under investigtion is *trans*-decahydronaphthalene/polystyrene, for which the thermodynamic data were already available.[6]

Experimental Section

Apparatus. The viscosity measurements under pressure were carried out with a modified Couette-type Haake viscometer which has a preselected speed of rotation. The equipment consists of a "Hochdruckmesseinrichtung 1000 bar", a "Grundgerät RV 2" (basic viscometer unit RV 2), a "Programmgeber 114" (programmer), and the measuring heads MK 125 and MK 50/500 (Haake-Messtechnik, Karlsruhe, BRD). With this apparatus the junction between the driving motor and the rotor, situated inside the pressure cell, is established by means of permanent magnets. The original autoclave, developed for flow operation and process control, was replaced by a special construction, which allows the reduction of the necessary amount of liquid from 570 to 110 mL and easy performance of discontinuous measurements. The main features of the entire apparatus can be seen from Figure 1.

Materials. Measurements were performed with a polymer sample of the nominal molecular weight 110000, for which the producer (Pressure Chem. Comp.) gives a value of less than 0.06 for the molecular non-uniformity $M_w/M_n - 1$. *trans*-Decahydronaphthalene (TD) was carefully redistilled in a silver-mantle column before use, but control measurements with the original product (zur Synthese, Merck-Schuchardt) did not show any differences. The liquid designated "200" from Haake was used for calibration purposes.

Procedure. The liquid under investigation is slowly pressed into the apparatus from below by means of a syringe as far as the buffer volume (Figure 1), carefully avoiding the formation of bubbles. The rest of the volume up to the pressure separator (the barrier against the oil of the pressure generator) can be filled with a proper liquid, normally with the solvent in order to spare material. Temperature variations could be kept below ±0.05 K and the pressure was read from a Heise gauge and from the signal of a pressure transducer (Fa. Burster, Gernsbach, Germany) with a reproducability of ±2 bar. The calibration of the pressure viscometer was performed by means of the standard liquid "200" supplied by Haake; in addition some data for the polymer solutions obtained with the pressure apparatus under atmospheric conditions were checked with the "Rotationsviskosimeter RV 2" and its attachments as described.[7] In all cases the deviations stayed below 0.5%.

Polymer solutions were measured in the concentration range 8–14 wt % polymer up to 1000 bar at several preselected temperatures. The shear rates ran from 20–320 s^{-1}; at lower values the reproducability would be too poor and at higher the magnetic clutch too weak. The subsistence of laminar flow conditions was corroborated theoretically[12,13] for all experiments. Since the volume between the buffer and the pressure separator was filled with pure solvent, the polymerconcentration was checked at the end of each run to make sure that no dilution had occurred; only in the case of the highest concentration did it fall by approximately 0.3 wt %, whereas in all other cases the dilution stayed well below 0.1%.

Results

In the experimentally accessible range of shear rates, only the immediate surrounding of the phase separation conditions showed some indications of flow anomalies (shear thickening,[7] cf. also Figure 12), whereas the solutions behaved strictly Newtonian elsewhere, as can be seen from Figure 2. The experimental results are summarized in Figures 3 and 4; their evaluation and discussion in the next

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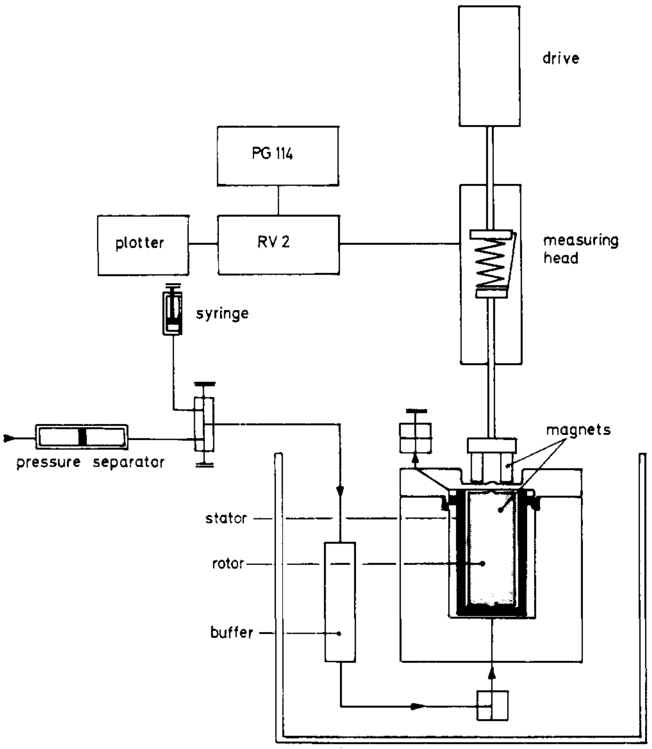

Figure 1. Schematic diagram of the pressure apparatus; modified Haake viscometer "Hochdruckmesseinrichtung 1000 bar".

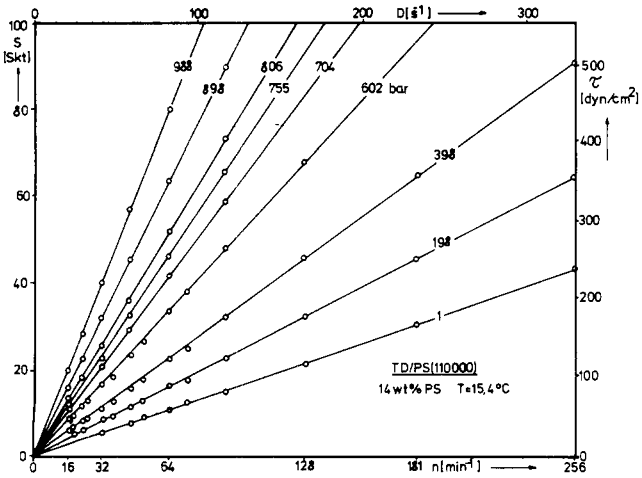

Figure 2. Shear stress, τ [dyn cm^{-2}] (Skt = scale reading, arbitrary units), as a function of shear rate, D [s^{-1}] (n = rpm of the rotor), for the system *trans*-decahydronaphthalene/polystyrene and the composition, temperature, and pressures indicated in the graph.

section will be performed in two parts: (i) the p, T, and c dependence of η for homogeneous conditions and (ii) the discontinuity in η when the solutions demix. A more detailed analysis of the two-phase region, like that performed in the previous work,[7] was dismissed in order to avoid laborious disassamblies of the apparatus which would become necessary if the phases seperated macroscopically. Especially at higher deviations from the homogeneous region, long-time shearing was avoided which means that the viscosity data obtained do not necessarily constitute steady-state values.

Discussion

$\eta(p,T,c)$ for the Homogeneous Region. In the case of Newtonian behavior, the following equation for the change in the viscosity coefficient η with the variables of state and with concentration c holds true:

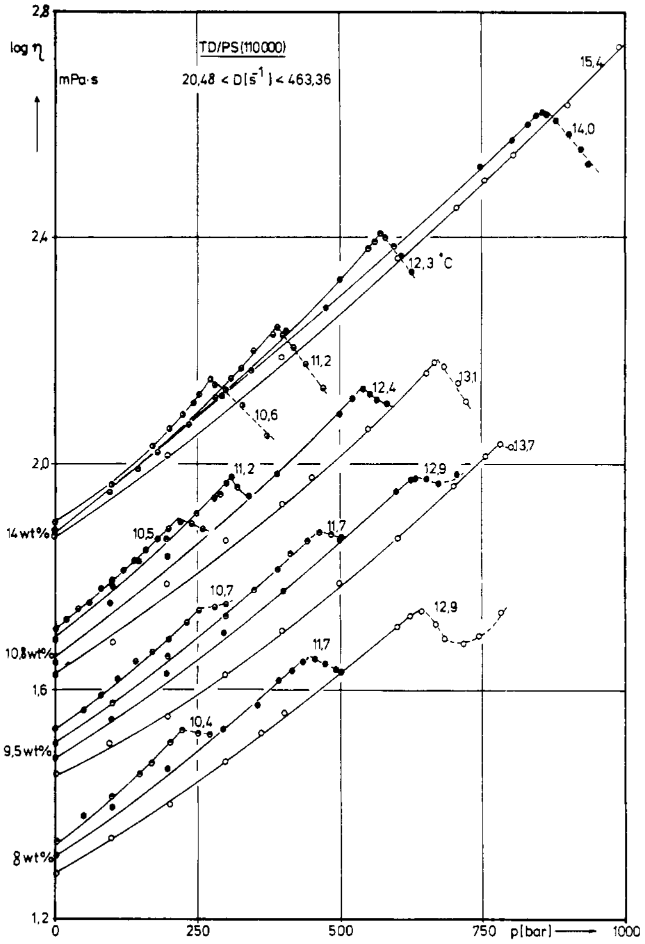

Figure 3. Pressure dependence of the viscosity coefficient η for the indicated temperatures and compositions.

$$d \ln \eta = \left(\frac{\partial \ln \eta}{\partial p}\right)_{T,c} dp + \left(\frac{\partial \ln \eta}{\partial T^{-1}}\right)_{p,c} dT^{-1} + \left(\frac{\partial \ln \eta}{\partial c}\right)_{p,T} dc \quad (1)$$

According to Bondi[17] and to de Guzman[15]

$$\left(\frac{\partial \ln \eta}{\partial p}\right)_{T,c} \equiv \frac{V^{*}}{RT} \text{ [bar}^{-1}] \quad (2)$$

and

$$\left(\frac{\partial \ln \eta}{\partial T^{-1}}\right)_{p,c} \equiv \frac{E^{*}}{R} \text{ [}K] \quad (3)$$

where V^* and E^* are the apparent volume and energy of activation for the viscous flow, respectively (apparent, since a possible T and p dependence of the pre-exponential factor in the corresponding kinetic equation[16] for η is ignored). A general interpretation of the third partial differential has not yet been given, but in the limiting case of infinite dilution and if the polymer concentration c is given in grams per milliliter, it is identical with the Staudinger index $[\eta]$:

$$\lim_{\substack{c \to 0 \\ D \to 0}} \left(\frac{\partial \ln \eta}{\partial c}\right)_{p,T} = [\eta] [\text{cm}^3 \text{ g}^{-1}] \quad (4)$$

(D = shear rate). The question whether the above

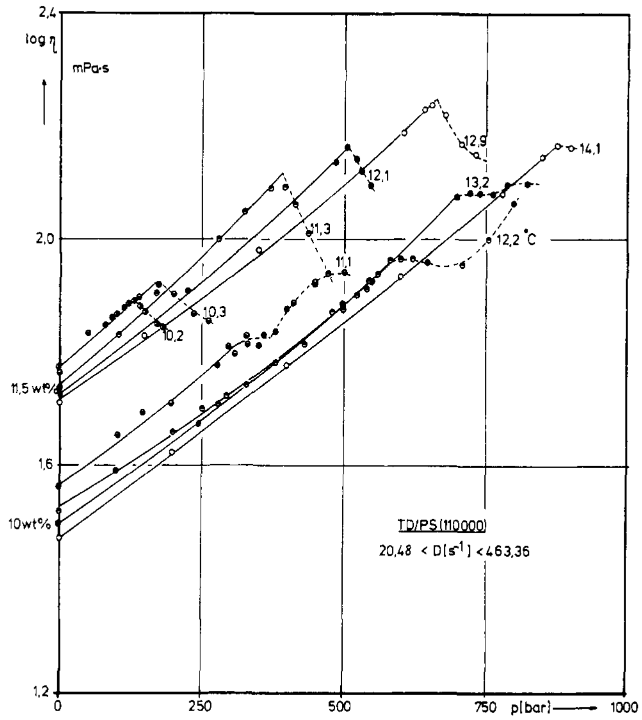

Figure 4. Pressure dependence of the viscosity coefficient η for the indicated temperatures and compositions.

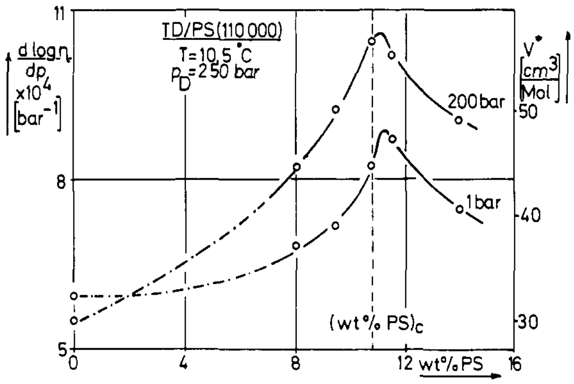

Figure 5. Concentration dependence of the apparent volume of activation, $V^{\ddagger}$ (eq 2), for 10.5 °C and the indicated pressures; p_D is the demixing pressure for the given temperature and the critical composition which is indicated by the dashed vertical line.

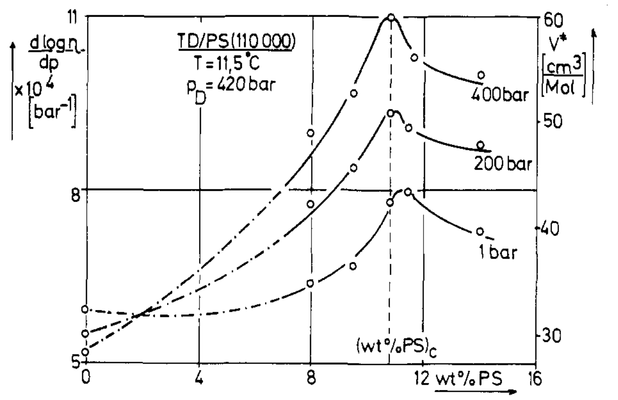

Figure 6. Same as Figure 5 but for 11.5 °C.

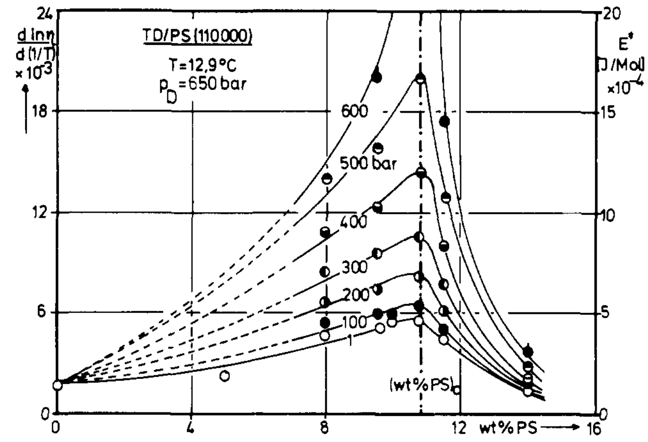

Figure 7. Concentration dependence of the apparent energy of activation, $E^{\ddagger}$ (eq 3), for 12.9 °C and the indicated pressures; p_D is the demixing pressure for the given temperature and the critical composition which is indicated by the dashed vertical line.

equation can be generalized, i.e., whether it is possible to interpret $(\partial \ln \eta/\partial c)_{p,T}$ as a measure for the hydrodynamic volume of the solute at arbitrary concentrations, is being studied. In the present work attention was focused on the viscosity in the vicinity of the demixing conditions in order to obtain information on the extra effects due to fluctuation.

Pressure Dependence. Similar to the maxima in $E^{\ddagger}(c)$, known for low molecular weight liquids since the work of Friedländer[8] and studied for polymer solutions by Debye and co-workers,[9] maxima in $V^{\ddagger}(c)$ can be observed with the present upper critical solution pressures (Figures 5 and 6). These maxima stem from the enhancement of the normal increase of the viscosity with pressure by the dissipation of energy resulting from the vanishing concentration dependence of the chemical potential. Since samples of high molecular uniformity have been used, the maxima are found at the thermodynamic critical concentration (cf. ref 7).

The $V^{\ddagger}$ values for the pure solvent (taken from the literature[17]) decrease with increasing pressure, whereas they increase for the present polymer solutions and normally also for the melts of polystyrene.[18] At the intersection of the curves in Figures 5 and 6, the pressure dependence of log η can be taken to be linear. For low molecular weight liquids $V^{\ddagger}$ amounts to $^1/_3$ to $^1/_4$ of the molar volume;[19] in the present case of polymer solutions the increase of $V^{\ddagger}$ with concentration is less than expected from the large volume of the polymer and depends on the thermodynamic quality of the solvent. Measurements over larger temperature intervals with a different system have shown that $V^{\ddagger}$, i.e., the pressure dependence of η, achieves its minimum when the second osmotic virial coefficient reaches its maximum.[20,24]

Temperature Dependence. Figure 7 shows how the thermodynamic conditions prevailing in the surrounding of the critical point influence the temperature dependence of η at the indicated pressures. The data for the pure solvent have again been taken from the literature;[17,21] for control purposes the function $\eta(T,p)$ was also calculated by means of the relations given by Cogswell and McGowan;[22] the results turn out to be in good agreement with the experiments.

Under the assumption that the pre-exponential factor in the kinetic equation for the viscosity coefficient does not depend on T and p, the influence of pressure should solely be given by the pressure dependence of the activation energy:[23]

$$RT\left(\frac{\partial \ln \eta}{\partial p}\right)_{T,c} = V^{\ddagger} = \left(\frac{\partial E^{\ddagger}}{\partial p}\right)_{T,c} \qquad (5)$$

The above equation also results from the interpretation of $E^{\ddagger}$ as the work which must be done against the internal

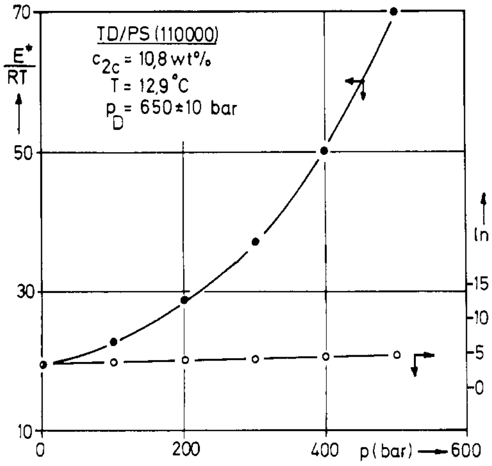

Figure 8. Test of the validity of eq 5 according to which the pressure dependence of ln η should be governed by the pressure dependence of the activation energy E^*.

pressure p_i plus the external pressure p in order to create a hole large enough for viscous flow[23]

$$E^* = \int_V^{V+V^*} (p_i + p)\,\mathrm{d}V \qquad (6)$$

if p_i can be considered to be independent of p and p to be negligible as compared with p_i (which should be a good approximation for the present p range). By means of the thermodynamic equation

$$p_i + p = \alpha T/\beta \qquad (7)$$

(α = thermal expansion coefficient, β = isothermal compressibility) it should be possible to estimate the influence of pressure on η from the knowledge of the volume properties of the particular liquid.

The evaluation of the experimental results with respect to the validity of eq 5 has demonstrated that this expression constitutes an acceptable approximation for the pure solvent (the increase in η amounts ca. 1% per 100 bar only, so that the points on the ordinate of Figure 7 practically coincide) and for good thermodynamic conditions.[24] Close to the phase separation conditions it is obviously in error, since E^* increases much more with pressure than ln η (cf. Figure 8), especially so as the critical conditions are approached. Moreover, it should be noted that the description of the viscosity as a function of the distance to the critical pressure ($p_c - p$) by analogy with the treatment of Debye[9] ($\eta(T - T_c)$) turns out to be impossible. A feasible explanation for this finding is given in the next section.

Concentration Dependence. The observed increase of η with polymer concentration is again[7] close to the simple Arrhenius type,[25] i.e., log η varies almost linearly with w_2 (wt % polymer) over wide ranges as can be seen from Figure 9. The insert in this graph demonstrates how the polymer concentration would have to be increased when the pressure is released to keep the viscosity constant.

Two things attract attention: first, the missing critical "hump" which was encountered[7] when the critical conditions were approached under atmospheric pressure by reducing $T - T_c$ instead of the present isothermal variation of p (this finding may mean that the additional dissipation of energy by fluctuation is increasingly hindered by the growing pressure); second, a chance for the determination of the Staudinger index at higher pressures from the present viscosity measurements with relatively concentrated solutions, if the data (including that of the pure solvent) really fall on a straight line.

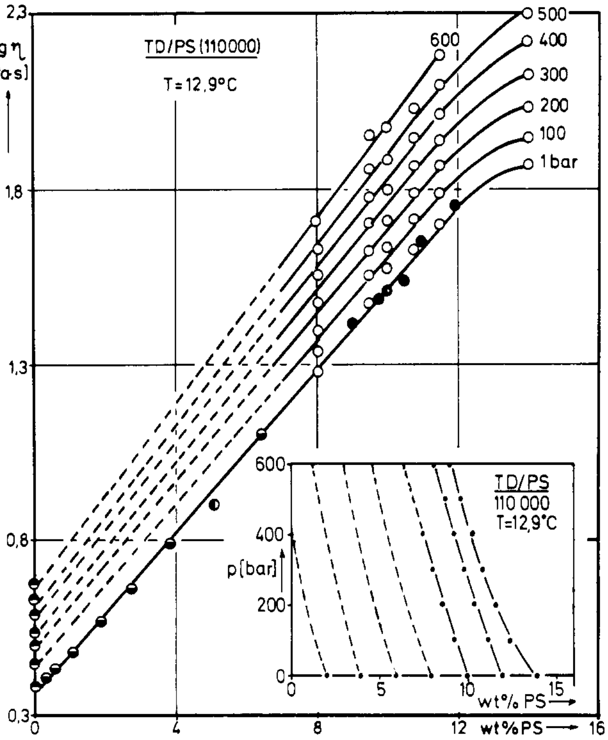

Figure 9. Concentration dependence of log η for 12.9 °C and the indicated pressures; the insert demonstrates how the polymer content of the solution must be increased when the pressure is released in order to keep the viscosity constant.

In order to clarify the latter point the results for atmospheric pressure, which cover the entire concentration range, are evaluated with respect to $[\eta]$ according to some common extrapolation procedures.[26] Among the three possibilities shown in Figure 10, the Arrhenius plot turns out to be the most apt. The independence of $[\ln \eta/\eta_0]/c$ on ln η/η_0 expected from the linear variation of log η vs. w_2 (Figure 9) is however only substantiated for the higher polymer concentrations, whereas a slight deviation from the linearity at the decisive lower concentrations makes a reliable determination of $[\eta]$ from the present data impossible.

The Discontinuity in $\eta(p)$ and the Phase Separation. From the breakdown in the viscosity shown in Figures 3 and 4, a demixing surface (demixing pressure as a function of polymer concentration and temperature) can be constructed by analogy with the determination of the isobaric demixing curves already described.[7] The projection of the thus obtained isopleths into the p,T plane is shown in Figure 11, together with part of the critical line[6] resulting from turbidity measurements. The fact that the points for the different concentrations nearly coincide on the dynamic curve is in accord with the results of comparable equilibrium experiments.[27] More surprising are the discrepancies between the two curves, which show up when the pressure is increased, since they imply that the polymer is kept in solution by stirring up to nearly 300 bar higher or 2 K lower than at rest.

This finding is not due to polymer degradation, which according to experience[28] could take place under the present thermodynamic conditions, since GPC diagrams are identical before and after the experiments. Naturally the dynamic curve should be shifted toward the static curve when the shear rate is reduced until the two lines eventually coincide. At higher pressures the corresponding extrapolation turns out, however, to be impossible with the present viscometer, as can be seen from Figure 12. It is

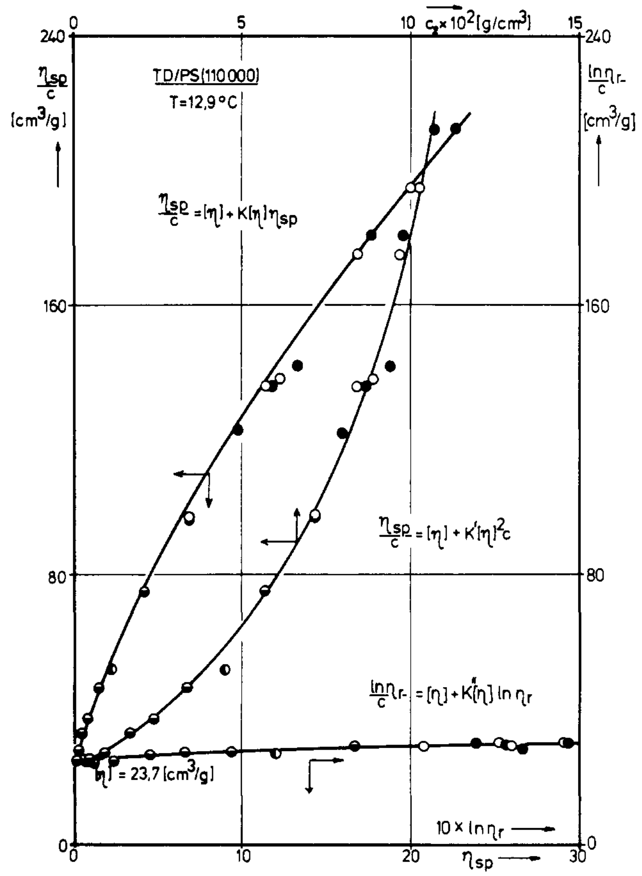

Figure 10. Various extrapolation procedures for the determination of the Staudinger index, [η] (cf. text), at 12.9 °C and atmospheric pressure.

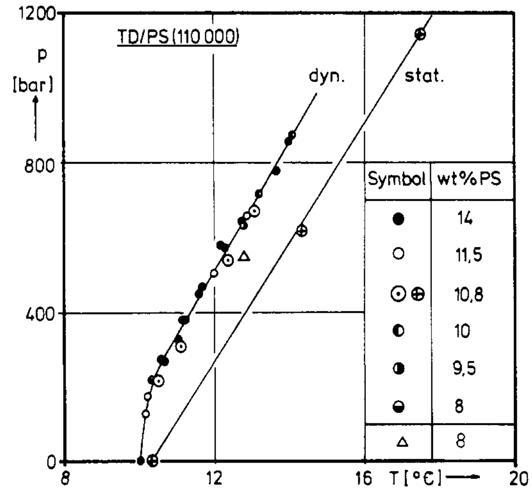

Figure 11. Comparison of the viscometric demixing data (dyn) with the critical line obtained from equilibrium measurements[6] (stat). Under the conditions given by the triangle the system demixes upon standing, although homogeneous when stirred.

only at near-atmospheric conditions, where the influence of stirring already begins to vanish, that the stabilizing effect of shearing can directly be followed by the dependence of the demixing pressure on the velocity gradient (Figure 13).

The theoretical interpretation of these findings seems difficult especially in the light of reports on opposite effects of shearing on the solubility of polymers.[29] To rule out pressure influences, which might overcompensate the effects of flow in the cited experiments (solutions of polystyrene in di(2-ethylhexyl) phthalate have been forced through a capillary), viscosity measurements of the present type were performed with the above system. They substantiate[24] the reported deterioration of the solvent power. From the current information[24,30] on the shear influences it must however be concluded that the improvement of the thermodynamic quality is by far the more common effect.

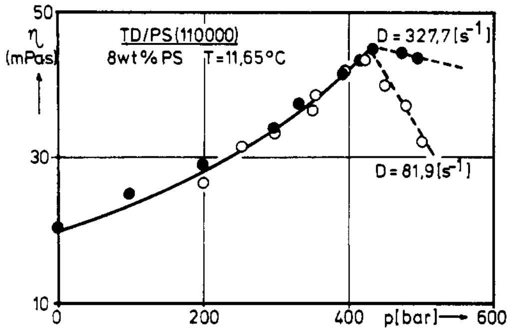

Figure 12. Pressure dependence of η in the region of demixing at various shear rates for a temperature at which the static and the dynamic curves run practically parallel (Figure 11).

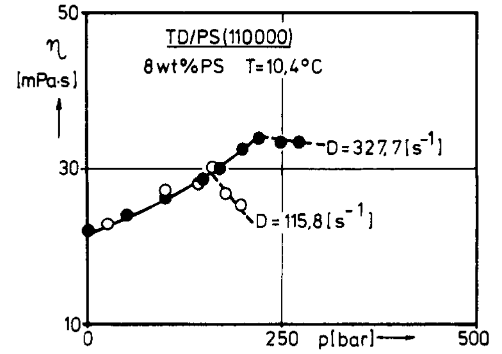

Figure 13. Pressure dependence of η in the region of demixing at various shear rates at a temperature at which the dynamic curve approaches the static one when the pressure is released.

The working hypothesis for the explanation of the experimental results is the following: The shear forces will disrupt energetically favorable contacts, i.e., intersegmental contacts of the polymer or contacts between a polymer segment and a particular site of a larger solvent molecule. The consequences of such a rearrangement in a solution on its stability depend on the particular situation, on the predominance of either entropy or enthalpy effects. In the more common case of shear dissolving it is expected that the rupture of intermolecular contacts between segments is accompanied by a much larger increase in entropy than in enthalpy as a result of the gain in molecular mobility. Indications which support this conjecture are the increase in the hydrodynamic volume (shear thickening) and the results of X-ray investigations with streaming polymer solutions,[31] which were interpreted by the assumption that the polymer coils rotate as individuals and thus create approximately uniform distances between their centers of mass.

In the case of shear demixing the explanation could lie in the extremely large and viscous solvent. If the preferential solvation of the polymer segments by the phenyl groups were broken up by the drag on the bulky alcohol groups of the phthalate, the solution would demix for energetic reasons despite a certain gain in entropy.

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Cooperative Binding and Diffusion of Cyclodextrins in Aqueous Polymer Solutions

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Received January 16, 1979

ABSTRACT: Cooperative binding of α- and β-cyclodextrin to poly(methacrylic acid), sodium poly(styrene sulfonate), and poly(methylbenzyldiallylammonium chloride-SO_2) was discussed in terms of the variations of the differential diffusion coefficients of the cyclodextrins in the aqueous polymer solutions. Incorporation of McGhee and von Hippel's theory with the diffusion equation has given the number of consecutive residues covered by a bound cyclodextrin, the intrinsic binding constant, and the cooperative parameter for the systems investigated.

Diffusion of a small molecule in polymer solution may be suppressed for two reasons: one is the obstruction by the polymer of the diffusing path of the molecule[1] and the other is the immobilization of the molecule by a specific interaction with the polymer.[2] If the former is properly taken into account, the diffusion behavior of the molecule may be interpreted in terms of the interaction or be correlated with the binding isotherm to the polymer. From this point of view, we have discussed the diffusion of cyclodextrins (CD) in aqueous solutions of poly(methacrylic acid) (PMA), sodium poly(styrene sulfonate) (NaPSS), and their copolymers;[2] the decreases of the integral diffusion coefficients of CD's with the polymer concentration were explained by assuming the complex formation between a CD and a residue in the polymer.

β-CD, for instance, comprising seven glucopyranose rings, has the molecular weight of 1135 daltons. Therefore, it would be rather realistic to imagine that a CD molecule covers n consecutive residues in a polymer upon the complex formation. In the course of a continuing study of CD–polymer systems, it was found that β-CD induces PMA to give circular dichroism centered at 218 nm. The spectral change with CD concentration could not be explained by the 1:1 complex assumption. These facts prompted us to examine in more detail the diffusion behaviors of CD's in aqueous polymer solutions. The present paper reports the differential diffusion coefficient (D) of α- and β-CD in aqueous PMA, NaPSS, and poly(methylbenzyldiallylammonium chloride-SO_2) (BACS) solutions; the variations of D with CD or polymer concentration are explained by employing McGhee and von Hippel's model of cooperative ligand binding to homogeneous polymers.[3]

The variation of D of α-CD in PMA solution is shown in Figures 1A and 1B, where linear diminutions with the CD or PMA concentration are found. These are caused either by the decreased activity of the CD or by the increased obstruction by the polymer with their concentrations; eq 1 gives the relation empirically,

$$D_r = D_0(1 - 0.026c_p) - 1.09 \times 10^{-7}c_{CD} \qquad (1)$$

where D_0 (3.20×10^{-6} cm^2/s for α-CD) is D of α-CD at infinite dilution in the absence of polymer and c denotes the concentration in g/100 mL. Assuming the obstructive effect of a polymer to be the same for α- and β-CD, D_r of β-CD in the absence of any interaction with the polymer may be represented by the same equation by substituting 3.06×10^{-6} for D_0.[4] Figures 2A and 2B show that eq 1 holds for the α-CD–NaPSS system with the same coefficients. We assume that D_r of CD's in BACS solution for hypothetical noninteracting diffusion can be calculated by eq 1, too. For all systems, experiments were done under the conditions $c_p < 5.7$ and $c_{CD} < 1.4$.

β-CD in PMA and NaPSS solution interacts with the polymers and gives D dependent on both the CD and the polymer concentration. Figures 1C and 2C show D/D_r, the diffusion ratio, of β-CD against CD concentration, where characteristic S-shaped variations for the lower polymer concentration cases are found. This fact suggests intuitively that, with the CD concentration, the binding of β-CD

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