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Viscometric Determination of Thermodynamic Demixing Data for Polymer Solutions†

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ABSTRACT: Viscosity coefficients η were determined for the two systems cyclohexane/polystyrene (M = 390 000) and *trans*-decahydronaphthalene/polystyrene (M = 110 000) both of which exhibit upper critical solutions temperatures. Measurements were performed in the concentration range 3 to 15 wt % polymer and at shear rates from 40 to 1400 s^{-1}. Plots of η vs. T fall into two parts separated by a sharp discontinuity, which coincides with the visually determined cloud points within ±0.1 K. On evaluation of the homogeneous part of the different isopleths, a minimum in the apparent activation energy of flow is found at half the critical composition, in addition to the well-known maximum at the consolute point. Within the two-phase region reproducible measurements can be performed down to a few degrees below the demixing temperature. The amount of breakdown of the viscosity upon entry into the two-phase region is highly concentration dependent. It is most pronounced for the critical composition, and thus constitutes a new method for determination of critical conditions. Plots of log η vs. wt % polymer are practically linear sufficiently far from the critical temperature. Additional contributions in the neighborhood of the critical composition appear when the critical temperature is approached.

A great number of physical properties of binary liquid mixtures show certain peculiarities near their consolute point. Among them are: heat capacity,[1] ultrasonic absorption,[2] light scattering,[3] sedimentation,[4] and viscosity.[5–7] The present work evolved from our measurements on the excess viscosity of polymer solutions exhibiting both upper and lower critical solution temperatures.[8] In the course of this investigation we have observed a rapid breakdown of the viscosity of the homogeneous polymer solutions when the low-temperature demixing sets in. It was therefore near at hand to check whether this effect could be utilized to determine demixing temperatures. Such a method would be of particular interest for systems for which a visual determination of the cloud-point temperature is impossible (i.e., isorefractive components, colored solutions, or systems enclosed in windowless cells). Two further goals of the present investigation were the extension of the viscosity measurements into the two-phase region and the examination of the existence of viscometric critical concentrations[9] in the solutions under consideration.

Experimental Section

Apparatus. Viscosity measurements were carried out on the "Rotationsviskosimeter RV 2″ and its attachments as supplied by Haake Messtechnik OHG, using the sensor system NV (cup and bell shaped rotor). By means of the measuring heads MK 50 and MK 500, differing in their maximum torque, viscosity coefficients can be measured in the range from 5 to 10^5 mPa s, the shear rate D running from 10 to 5400 s^{-1}.

Materials. Two samples of polystyrene with the nominal molecular weights 110 000 and 390 000, obtained from the Pressure Chemical Co., were investigated. The values 0.06 and 0.1, respectively, are given by the producers for the molecular nonuniformity $((M_w/M_n) - 1)$. Cyclohexane (p.a.) and *trans*-decahydronaphthaline (zur Synthese) were obtained from E. Merck, Darmstadt. The former solvent was used without further treatment, whereas the latter was carefully redistilled in a silver-mantel column.

Viscosity Measurements. The solvent/polymer systems were kept at 40 to 50 °C for 1 week and were stirred from time to time in order to guarantee thermodynamic equilibrium. Viscosity measurements were then carried out at various temperatures, which have been reached by slowly cooling the solutions (less than 0.5 °C/h). Within the two-phase region the viscosity coefficient η can be determined reproducibly as long as the distance to the demixing temperature does not exceed a few degrees. In the case of cyclohexane, the normally open lower part of the apparatus containing the solution was sealed by means of steel cuffs in order to prevent losses of the solvent due to evaporation. The η values for the different velocity gradients were determined point by point; in addition some rheograms were also taken.

Results and Discussion

For a given solvent/polymer system and fixed molecular weight of the polymer, the viscosity coefficient depends on concentration, temperature (p = 1 bar), and shear rate D. In context with out present investigation, a potential non-Newtonian behavior of the polymer solution would only be a complicating side effect. For this reason we have looked for conditions under which η is independent of D.

Shear Rate Dependence. Figure 1 gives the results for the system cyclohexane/polystyrene (M = 390 000) and the indicated temperatures. For the lower molecular weight polystyrene in *trans*-decahydronaphthaline, no non-Newtonian behavior can be observed within the range of shear rates experimentally accessible with our apparatus. The "upturn effect" shown in Figure 1, which has already been reported in the literature,[10] will not be discussed here; the only conclusion we draw is that we are positively outside the non-Newtonian region at D = 1000 s^{-1} and that the non-Newtonian behavior observed at low D values vanishes as the demixing conditions are approached.

Temperature Dependence. An example for the variation of η with temperature can be seen in Figure 2 for cyclohex-

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† Dedicated to Professor M. L. Huggins in honor of his 80th birthday.

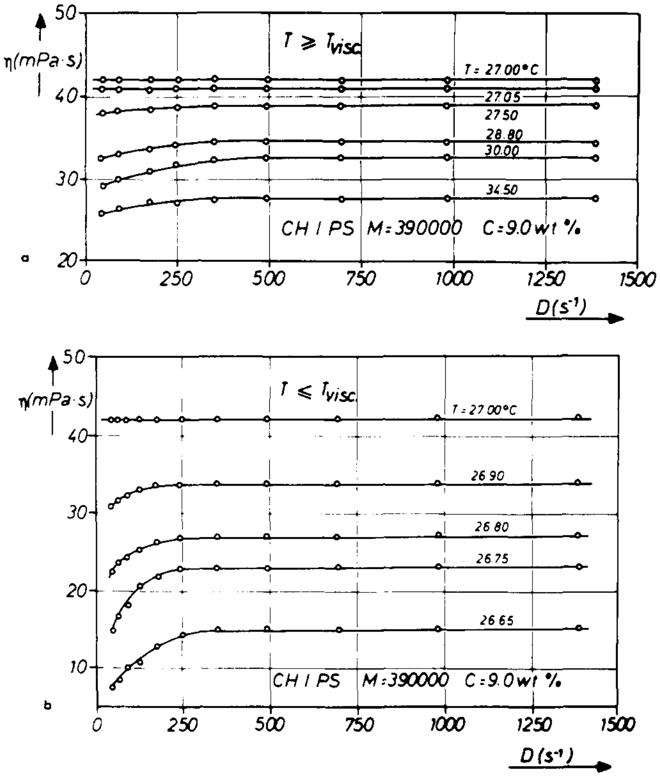

Figure 1. Shear rate dependence of the viscosity coefficient η for the system cyclohexane/polystyrene (M = 390 000), 9.0 wt % polymer content, and the indicated temperatures: (a) homogeneous region; (b) heterogeneous region, T_{visc} = viscometric demixing temperature.

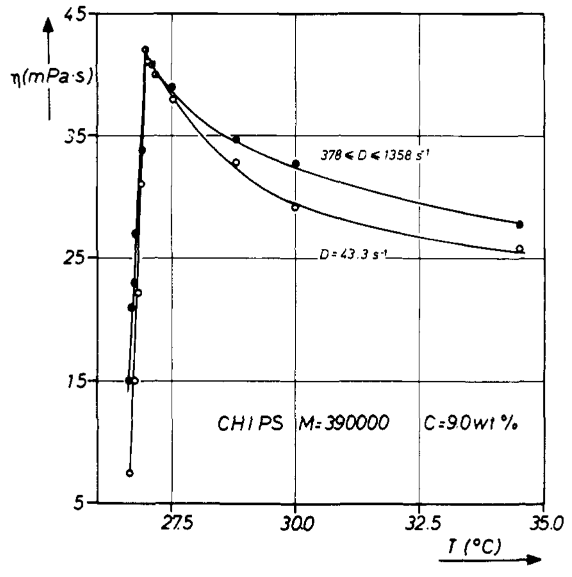

Figure 2. Temperature dependence of the viscosity coefficient η for the system cyclohexane/polystyrene (M = 390 000), 9.0 wt % polymer content, and the indicated shear rates.

ane/polystyrene (M = 390 000) and the shear rates are indicated. The fact that the curves obtained for Newtonian and non-Newtonian behavior are bound together at the viscosity summit demonstrates that the corresponding characteristic temperature does not depend on D for the systems under investigation. Preliminary experiments with still higher molecular weights of the polymer have however shown that it is shifted toward lower values when D is increased.

To enable a common representation for all concentrations of interest, a logarithmic scale was chosen for η in Figure 3. All

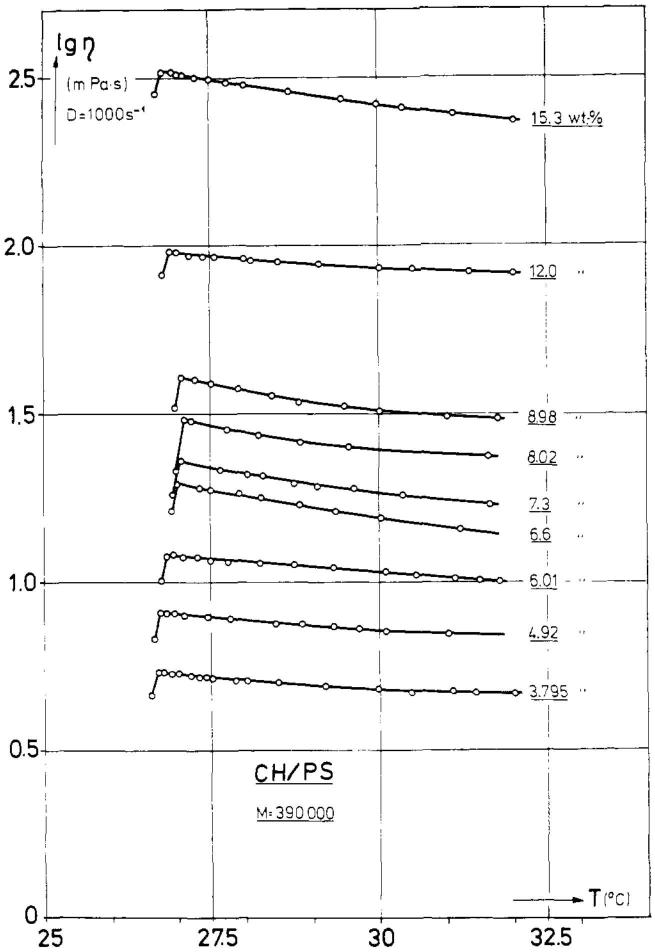

Figure 3. Temperature dependence of η for the system cyclohexane/polystyrene (M = 390 000) at D = 1000 s^{-1} for the polymer contents indicated.

isopleths fall into two parts, which are separated by a sharp bend: the homogeneous region at high temperatures and the two-phase region at low temperatures. Within the homogeneous region η increases when T is lowered according to a normal Arrhenius dependence plus an extra term due to the fluctuations resulting from the thermodynamic conditions prevailing as the demixing is approached. Within the two-phase region a rapid breakdown of η is observed when T is lowered still further. Both phenomena have already been discussed qualitatively by Ostwald[11] in connection with experiments reported for instance for solutions of albumin or starch but also for the system butyric acid/water and for melts of pure sulfur. Ostwald explained these findings on the basis of the "emulsoids" or colloids, which appear near phase separation, without giving a satisfying theoretical analysis. For the homogeneous part of the function $\eta(T)$, such a theory has meanwhile been elaborated by Fixman,[7] who calculated the extra viscosity resulting from fluctuations on the bases of the thermodynamics of irreversible processes. To the knowledge of the authors there exists however no equivalent treatment for the part of this function lying within the two-phase region.

The Homogeneous Part of $\eta(T)$. The evaluation of the temperature dependence of η for the homogeneous solutions with respect to the apparent activation energy for the viscous flow E_{A} according to

$$R\left(\frac{\partial \ln \eta}{\partial \left(\dfrac{1}{T}\right)}\right)_{c_2,D} = E_{\text{A}}$$

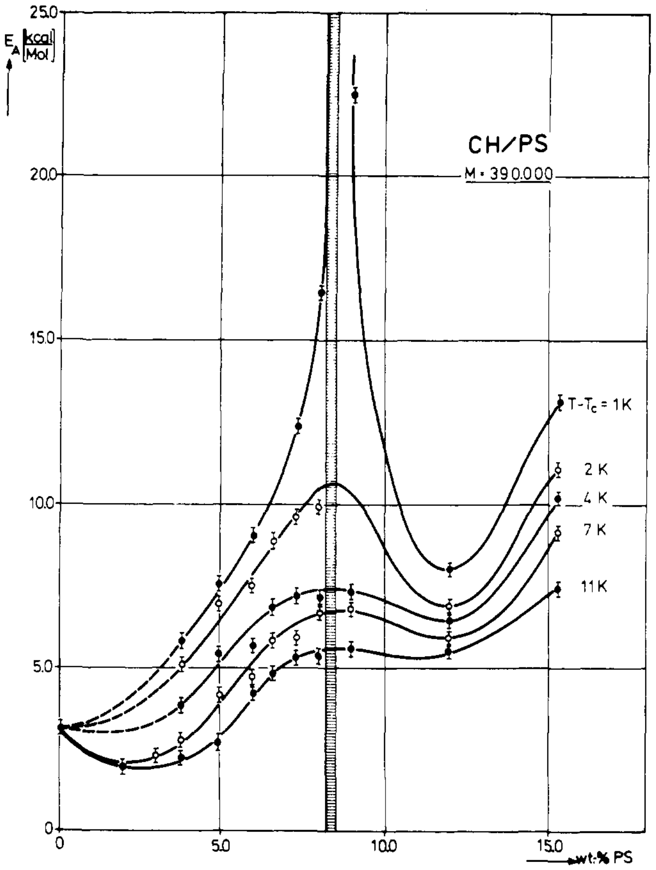

Figure 4. Apparent energy of activation E_A for the viscous flow of solutions of polystyrene (M = 390 000) in cyclohexane as a function of composition at the indicated distances from the critical temperature. The hatched stripe indicates the critical concentration obtained from the phase volume ratios (cf. Figure 5).

resulted in the correlations shown in Figure 4.

In most features the picture agrees well with that reported by Debye et al.[6] It differs however by the fact that the maxima in the isotherms of Figure 4 coincide with the thermodynamic critical concentration, as determined from the phase volume ratio[12] (Figure 5), whereas Debye had observed a pronounced discrepancy between the position of these maxima and the thermodynamic critical concentration obtained from the maximum dissymmetry of the light scattered from the solutions. The explanation for these findings may lie in the molecular nonuniformity of the polymer samples[6,8] which makes the critical concentration and the concentration of the maximum dissymmetry differ.

From the wider concentration range of the present measurements, additional information can be abstracted, namely the occurance of a minimum in the activation energy for the viscous flow at the larger $T - T_c$ values and ~2.5 wt % polystyrene. The theoretical reason for this probably lies in the fact that the polymer coils shrink as the temperature is lowered and therefore partially make up for the normal increase in the viscosity of the solutions, the effect being most operative in the region of moderate polymer concentrations.

The phenomenon under consideration is normally considered to be the explanation for the action of multigrade engine oils, the viscosity of which is more or less independent of temperature due to this compensating effect. The present interpretation is substantiated by earlier measurements on systems showing lower critical solution temperatures.[8] Here the solutions demix on heating, i.e., coil contraction and normal decrease in viscosity act parallel and a maximum in the energy of activation is found instead of a minimum.

The Discontinuity in $\eta(T)$. When the temperature of a

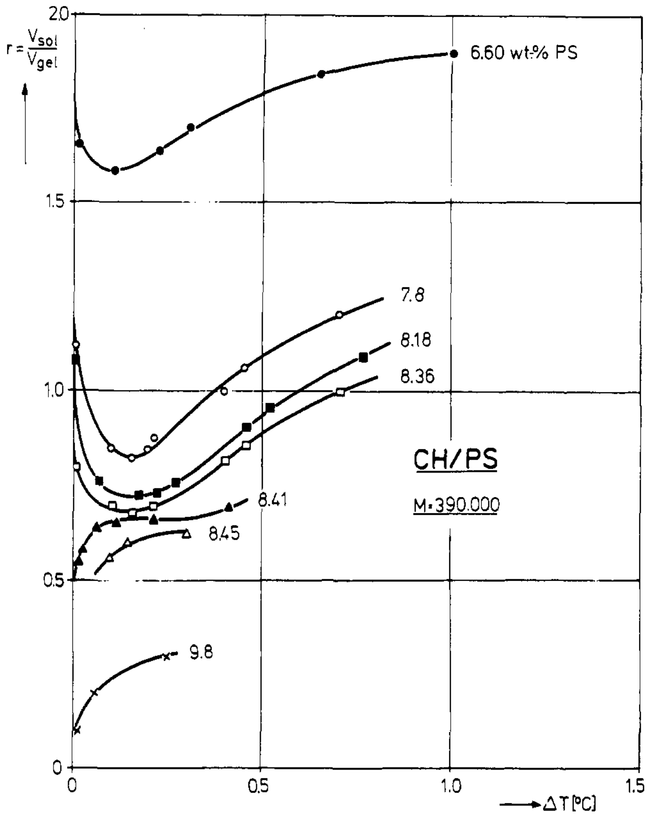

Figure 5. Phase volume ratios r as a function of the distance to the demixing temperature ΔT for the system cyclohexane/polystyrene (M = 390 000) and the polymer contents indicated.

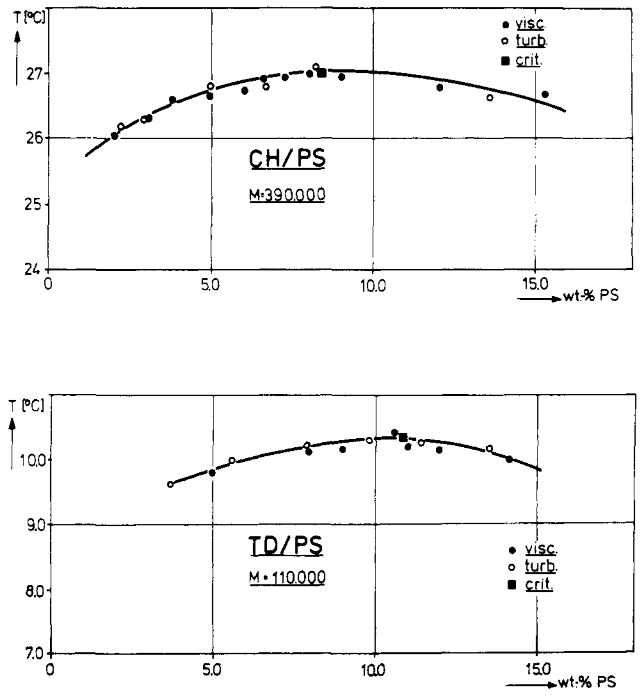

Figure 6. Demixing curves for the systems cyclohexane/polystyrene (M = 390 000) and *trans*-decahydronaphthaline (M = 110 000): (●) viscometric demixing points, (○) turbidimetric demixing points, (■) critical points.

given polymer solution is gradually reduced, a maximum in η occurs at T_{visc} (cf. Figures 2 and 3). From independent visual or turbidimetric[13] measurements of the cloud-point temperatures, T_{turb}, of these solutions it became obvious that these two temperatures practically coincide. In Figure 6 a compar-

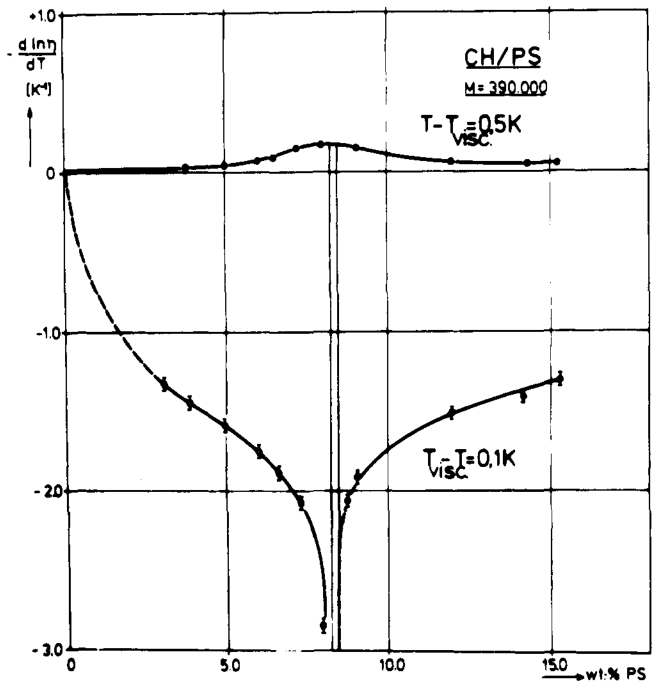

Figure 7. $-\mathrm{d}\ln\eta/\mathrm{d}T = E_A/RT^2$ as a function of the polymer content in the system cyclohexane/polystyrene (M = 390 000) at the constant indicated distances from the visometric demixing temperature. Upper curve: homogeneous region. Lower curve: heterogeneous region. The hatched stripe indicates the critical composition

ison of the demixing curves constructed from these data is given for the systems under consideration. The fact that the critical points (cyclohexane/polystyrene see Figure 5; *trans*-decahydronaphthalene/polystyrene[13]) are situated at the maxima of these curves indicates the high molecular uniformity of the polymer samples.

The Heterogeneous Part of $\eta(T)$. Contrary to the situation in systems at rest, the already demixed solutions remain highly dispersed over considerable times when sheared. It is thus possible to perform reproducible viscosity measurements within the two-phase region as long as the temperature difference from the demixing temperature does not exceed a few degrees. For all systems the viscosity stays unchanged at D = 1000 s^{-1} for several hours and the values for the homogeneous solutions can be re-established when the temperature is raised again.

As can be seen from Figure 3, the breakdown in viscosity upon the penetration into the two-phase region is much more pronounced for approximately critical concentrations than for the others. In Figures 7 and 8, it is therefore investigated whether this observation can be utilized for the determination of the critical composition. In the above-mentioned diagrams the negative relative change of η with temperature, $-\mathrm{d}\ln\eta/\mathrm{d}T$, is plotted as a function of polymer concentration for both the homogeneous and the heterogeneous region. In the former case this derivative is taken for the constant temperature difference of 0.5 K from T_{visc}, and in the latter this interval amounts to −0.1 K. Since T_{visc} unlike T_c varies with concentration, the upper curves in Figures 7 and 8 cannot be compared with the data of Figure 4 directly; $-\mathrm{d}\ln\eta/\mathrm{d}T$ was calculated from the viscosity η measured at T and from $\eta_{\max}$ measured at T_{visc}, using the approximation $[(\eta_{\max} - \eta)/\eta_{\max}]/(T - T_{\mathrm{visc}})$. The errors in the data referring to the two-phase region are probably considerably larger than indicated by the bars in the graphs (which only refer to the accuracy of the viscosity measurements) since $T - T_{\mathrm{visc}}$ contains the uncertainty in the determination of T_{visc}.

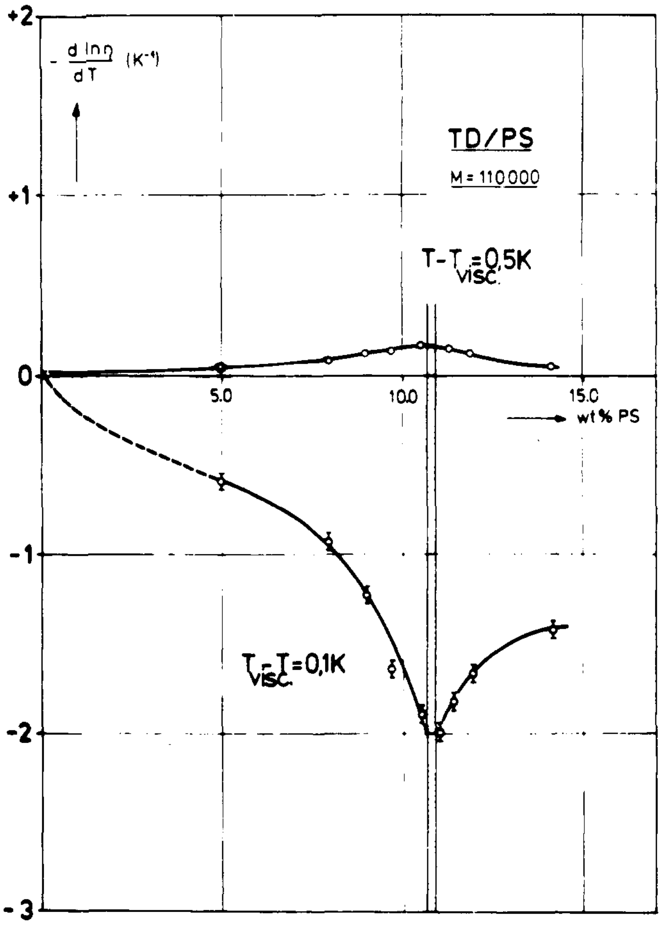

Figure 8. $-\mathrm{d}\ln\eta/\mathrm{d}T = E_A/RT^2$ as a function of the polymer content in the system *trans*-decahydronaphthaline/polystyrene (M = 110 000) at the constant indicated distances from the viscometric demixing temperature. Upper curve: homogeneous region. Lower curve: heterogeneous region. The hatched stripe indicates the critical composition.

From Figures 7 and 8 it becomes obvious that η breaks down most rapidly for the critical composition in both systems. The viscometric investigation of polymer solutions in their demixing region thus constitutes an additional possibility for the determination of consolute data. At present only some qualitative explanation can be offered for the observed behavior: In addition to the normal reduction in η due to the decreasing contribution of the critical excess viscosity (common to all demixing binary liquids), extra effects can be observed with polymer solutions. They result from the normally highly different polymer content of the coexisting phases which in turn makes their viscosity very dissimilar. For both sub- and supercritical overall polymer concentrations it is assumed that the less viscous phase (sol) forms the matrix in which volume elements of high polymer concentration (gel) are immersed, contrary to the situation at rest, where droplets of sol are segregated upon the demixing of supercritical solutions. In both cases the systems can be looked upon as sponge, built by the sol and bearing holes filled with the gel, when the solutions are sufficiently stirred.

When the polymer concentration of the original solution is far from critical, the concentration in one of the two coexisting phases does not differ widely from it, as long as the distance from the demixing temperature is kept small (in the present case 0.1 K). For subcritical concentrations the reduction in viscosity can be explained by the "deactivation" of some polymer molecules resulting from their transfer into droplets of gel. In the case of supercritical conditions on the other hand, the segregated sol forms three-dimensional

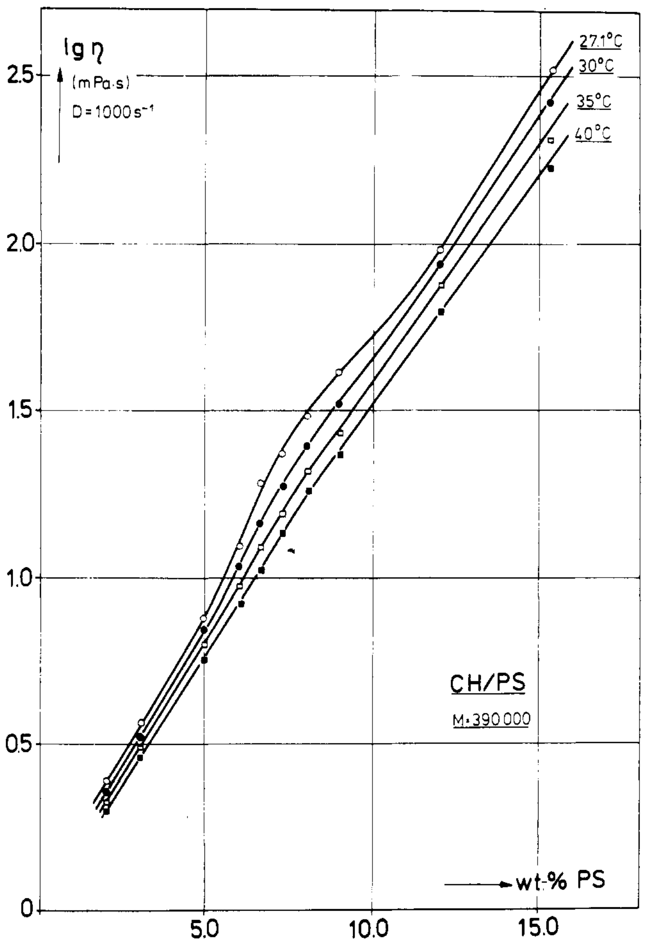

Figure 9. Concentration dependence of log η at D = 1000 s^{-1} for the system cyclohexane/polystyrene (M = 390 000) at the indicated temperatures.

channels in between domains of high polymer concentration and thus acts as a lubricant. The critical concentration itself is characterized by the fact that the phases which are created at the critical temperature possess the same composition and the same volume under this limiting condition; it also implies that the coexisting phases show the greatest possible difference from the original solution for a fixed distance to the demixing temperature. For the critical composition deactivation and lubrication thus play the most important role and the greatest breakdown in viscosity can be observed. Another influence not discussed so far could stem from the interfacial tension which should lead to the maximum degree of dispersity for critical concentration, since this quantity tends to zero at the consolute point.

Concentration Dependence. For the discussion of the increase in the viscosity of a polymer solution with concentration, the entanglement concept plays an important role.[9] This approach led to the introduction of critical molecular weights and critical concentrations. The latter are normally obtained from a double logarithmic plot of the viscosity coefficient vs. concentration, where it manifests itself as the intersection of two linear portions. When the present data are evaluated in this manner, it turns out, however, that no such transition points can be observed for the conditions under consideration since smooth upward curvature is obtained.

On the other hand it is known since 1887 from the work of Arrhenius[14] that linear relations between log η and the concentration are frequently observed for electrolytes and already in the early days of polymer science this behavior was found with some linear macromolecules.[15] Figure 9 demonstrates that this simple dependence is approached for the systems under investigation, when the temperature becomes sufficiently higher than critical, whereas a characteristic additional effect, stemming from fluctuations, is superimposed in the neighborhood of the critical composition at small temperature differences. In physical terms the linear dependence of log η on concentration means that the relative increase in viscosity upon the addition of a certain amount of polymer is constant; the value of this constant reflects the effectiveness of the added polymer and depends on temperature.

The increase in the slope of the baselines in Figure 9 with the reduction of T can thus be explained, in agreement with Klein and Woernle,[16] by the corresponding increase of the Flory–Huggins parameter χ, which measures the Gibbs free energy of formation of contacts between a solvent molecule and a polymer segment. Since χ increases as T is lowered, segement/segment contacts become favored over solvent/segment contacts and this leads to a stronger interconnection of the individual polymer coils by temporary links and to the observed increase in the effectiveness of added polymer. This reasoning is also supported by the results for relatively dilute solutions for which the initial dependence of viscosity number on concentration, as expressed by the Huggins constant k_H,[17] is also found to increase when the thermodynamic conditions become worse.[18]

Note Added in Proof. After completion of the manuscript it came to our knowledge that a viscometric titration, similar to the procedure just described, is used in industry to determine the demixing of highly viscous solutions (R. Kuhn, unveröffentl Berichte der Bayer AG (1970), cited in M. Hoffmann, H. Krömer, and R. Kuhn, "Polymeranalytik", Thieme Verlag, Stuttgart, 1977).

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