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Thermodynamic Theory of Flowing Polymer Solutions and Its Application to Phase Separation[†]

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ABSTRACT: The stationary flow of polymer solutions is treated as a near-equilibrium process, to which the normal tools of thermodynamics can be applied if the energy stored in the sheared state is added to the Gibbs energy of the system at rest. The first part of the paper deals with the mathematical description of the experimental information concerning the two contributions to the Gibbs energy of sheared solutions, in particular with the calculation of the stored energy from measured flow curves. In the second part, these general considerations are applied to the phase separation of the flowing system *trans*-decalin/polystyrene. The results of the latter calculations confirm the experimental finding that the region of homogeneity is extended by shear and that the demixing curves of the flowing solutions normally exhibit two maxima instead of one. Furthermore, a new phenomenon is predicted, namely a shear-induced coexistence of three liquid phases at the temperature at which the two neighboring branches that evolve out of these maxima of the demixing curve cross. In addition, this intersection represents the largest extension of the dissolved state of the polymer that can be achieved by a given shear rate. It is called the eulytic point by analogy with the eutectic point. According to the present calculations, the eulytic point is shifted toward lower polymer concentrations as the shear rate is increased.

Introduction

Experimental observations concerning the influence of shear fields on the demixing of polymer-containing fluids already date back more than 30 years:[1] With two (incompatible) macromolecular solutes in a common solvent it was found that the homogeneous region of the system may extend on the order of 10 K as the solutions flow. The effects are much less pronounced with solvent/polymer binary systems: Here[2,3] the cloud points are normally changed by less than 2 K and the chemical potential of the solvent in the homogeneous solution is also only moderately influenced.[4,5] Theoretical calculations have been performed for special systems such as solutions of isotropic spheroids[6] or for special conditions such as the immediate surroundings of the thermodynamic critical conditions of system at rest.[7]

In the present paper a more general, phenomenological attempt is presented. It is based on two premises: (i) that it is possible to define a generalized Gibbs energy of the sheared system as the sum of its value at rest plus the energy stored during flow and (ii) that equilibrium thermodynamics can be applied to this function despite the fact that streaming systems present stationary states only. Premise i is likely to be permissible as long as the rheological properties of the system constitute functions of state. With premise ii it is necessary to check whether near-equilibrium conditions prevail for the systems and shear rates of interest. According to the subsequent model calculations, the stored energy is normally less than 10^{-3} of the Gibbs energy of mixing. Both premises can therefore be considered to be correct.

The phenomenological thermodynamic equations of the flowing polymer solutions and the general procedure are presented in the next section. A practical example, namely the calculation of the demixing of the flowing system *trans*-decalin/polystyrene (which is also being studied experimentally[8]), is given in the section on application to phase separation.

General Considerations

The thermodynamic description of polymer solutions at rest is normally performed by means of the well-known Flory–Huggins equation, which reads for the simplest case of a binary system in its reduced form

$$\tilde{G}_z = \bar{G}_z/RT = x_1 \ln \varphi_1 + x_2 \ln \varphi_2 + g x_1 \varphi_2 \qquad (1)$$

$\bar{G}$ is the molar Gibbs energy of mixing, R is the gas constant, and T is the absolute temperature. The index z indicates zero-shear conditions, x and φ are mole fractions and volume fractions, respectively, 1 stands for the solvent and 2 for the polymer, and g constitutes an interaction function into which all deviations from purely combinatorial behavior are incorporated.

The reduced molar energy, $\tilde{E}_s$, a polymer solution is able to store during stationary flow can be expressed as [9–11]

$$\tilde{E}_s = \frac{\bar{E}_s}{RT} = \frac{\bar{V}_1(1 + (N-1)x_2)}{RT} J_e^0 \eta^2 \dot{\gamma}^2 \qquad (2)$$

where $\bar{V}_1$ and $N\bar{V}_1$ are the molar volumes of the solvent and of the polymer, respectively, J_e^0 is the steady-state shear compliance, and η is the viscosity of the solution at the shear rate $\dot{\gamma}$.

If a generalized reduced Gibbs energy is introduced according to

$$\tilde{G}_{\dot{\gamma}} = \tilde{G}_z + \tilde{E}_s \qquad (3)$$

it is possible to calculate by standard procedures the thermodynamic behavior of flowing solutions. For the activity $a_1^{\dot{\gamma}}$ of the solvent, as an example, one obtains

$$\ln a_1^{\dot{\gamma}} = \ln \varphi_1 + \frac{N-1}{N}\varphi_2 + \chi \varphi_2^2 + \frac{\bar{V}_1 \dot{\gamma}^2}{RT}\left[J_e^0 \eta^2 + x_2(1 + (N-1)x_2)\frac{\partial (J_e^0 \eta^2)}{\partial x_2} \right] \qquad (4)$$

where

$$\chi = g - (1 - \varphi_2)\frac{\partial g}{\partial \varphi_2} \qquad (5)$$

In order to perform quantitative calculations on the basis of the above equations, $g(x_2,T)$ and $J_e^0\eta^2(M,x_2,T,\dot{\gamma})$ have to be known (M is the molecular weight of the polymer).

For the description of the concentration and temperature dependence of the interaction parameter g, the following two expressions are useful: Equation 6a is based on theoretical considerations[12] and normally obtained from demixing data

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[†] Affectionately dedicated to Professor W. Stockmayer on the occasion of his 70th birthday.

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$$g = \alpha + \beta_0/(1 - \gamma\varphi_2) \qquad (6a)$$

α and γ are constants for a given system and β_0 is frequently observed to be a linear function of T^{-1}.

Equation 6b, on the other hand, constitutes an empirical series expansion

$$g = \frac{g_{00}}{T} + g_{01}T + \left(\frac{g_{10}}{T} + g_{11}T\right)\varphi_2 + \frac{g_{20}}{T}\varphi_2^2 \qquad (6b)$$

The individual coefficients g_{ij} are accessible from measurements of the chemical potential of the solvent as a function of composition and temperature.

The dependence of $J_e^0\eta^2$ on M, x_2, T, and $\dot{\gamma}$ may be obtained by combination of a number of known theoretical and empirical equations. According to ref 13 and 14, the following relation applies:

$$J_e^0\eta^2 = \frac{M}{c_2RT}\frac{S'}{S^2}(\eta - \eta_s)^2 \qquad (7)$$

with c_2 the polymer concentration (mass/volume), η_s the viscosity of the solvent, and S'/S^2 a constant. Several theories have been developed[15] in order to take account of the non-Newtonian flow behavior. In most cases they give quite complicated implicit functions. For this reason it seems preferable to use an empirical relation for the present purpose. The following equation has been found to describe the observed shear thinning with sufficient accuracy for the system discussed in the next section.

$$\eta - \eta_s = (\eta_0 - \eta_s)/(1 + k_v\tau_R\dot{\gamma}) \qquad (8)$$

η_0 is the zero-shear viscosity of the solution, k_v a constant, and τ_R the Rouse relaxation time,[16] which is given by

$$\tau_R = \frac{6}{\pi^2}\frac{\eta_0 - \eta_s}{RTc_2}M \qquad (9)$$

The concentration dependence of η_0, required for calculating the stored energy, is still one further functionality that must be known. Numerous relations have been proposed.[17,18] The Martin equation[19]

$$\eta_0 - \eta_s = \eta_s\tilde{c}e^{k_H\tilde{c}} \qquad (10)$$

can describe the actual behavior in solution up to comparatively high polymer contents, particularly with thermodynamically poor solvents. k_H is the Huggins constant and $\tilde{c}$ a reduced polymer concentration defined as $\tilde{c} = c_2[\eta]$, where $[\eta]$ is the intrinsic viscosity of the polymer in the particular solvent at a given temperature.

By means of eq 7–10, one obtains the following comparatively simple expression for the reduced stored energy of a flowing polymer solution according to eq 2:

$$\tilde{E}_s = \frac{S'}{S^2}x_2\left(\frac{\sigma\dot{\gamma}e^{k_H\tilde{c}}}{1 + 6k_v\pi^{-2}\sigma\dot{\gamma}e^{k_H\tilde{c}}}\right)^2 \qquad (11)$$

where σ/s, given by

$$\sigma = \eta_s[\eta]M/RT \qquad (12)$$

can be considered as a measure of the ability of a system to store energy.

By means of the above equations it is now possible to calculate the entire thermodynamic behavior of flowing polymer solutions if their zero-shear behavior (i.e., the equilibrium thermodynamics) is known and if the corresponding rheological information is also available. The number of constants needed and their typical values can be seen from Table I of the next section, which presents some numerical calculations.

Table I

Data Used in the Calculation of the Thermodynamic Behavior of the Flowing System *trans*-Decalin/Polystyrene

Pure Components	
polystyrene	
no. of segments	$N = 5000$
density[a]	$\rho_2 = 1070\ \mathrm{kg{\cdot}m^{-3}}$
trans-decalin	
density[a]	$\rho_1 = 870\ \mathrm{kg{\cdot}m^{-3}}$
viscosity[a]	$\eta_s = 2.3 \times 10^{-3}\ \mathrm{Pa{\cdot}s}$
Solution	
thermodynamics (coefficients[b] of eq 6b)	$g_{00} = 179.6$ K, $g_{10} = 52.5$ K, $g_{20} = 16.2$ K; $g_{01} = 3.36 \times 10^{-4}\ \mathrm{K^{-1}}$, $g_{11} = 1.03 \times 10^{-4}\ \mathrm{K^{-1}}$
hydrodynamics	
intrinsic viscosity[a,c]	$[\eta] = 0.043\ \mathrm{m^3{\cdot}kg^{-1}}$
Huggins constant[a,d]	$k_H = 1.40$
constant[e] of eq 8	$k_v = 0.57$
constant of eq 7	$S'/S^2 = 0.20$

[a] Assumed to be constant within the present T interval of ca. 5 K. [b] Calculated from the data given by: Nakata, N.; Higashida, S.; Kuwahara, N.; Saeki, S.; Kaneko, M. *J. Chem. Phys.* **1976**, *64*, 1022. [c] Estimated from the calculated critical concentration c_{2c} (eq 1 and 6b) by means of the experimental observation (Brand, U. Examensarbeit, Mainz, 1980) that $[\eta]$ at the critical temperature is $2/c_{2c}$ irrespective of the molecular weight of the polymer. [d] Assumed to be identical with that measured for solutions of polystyrene in cyclohexane at the critical temperature of a sample comparable in molecular weight (Brand, U. Examensarbeit, Mainz, 1980). [e] Obtained from unpublished flow curves of the present system in the molecular weight, T, and concentration range of interest (Krämer, H. Ongoing Thesis, Mainz).

Application to Phase Separation

Dependence of demixing conditions of polymer solutions on flow constitutes the most obvious effect of the application of shear fields. We have studied this phenomenon for the system *trans*-decalin/polystyrene (TD/PS) by several experimental methods,[8] and it seemed interesting therefore to apply the concept outlined in the last section to this problem. The data necessary for computation of the corresponding phase diagrams are collected in Table I.

By means of eq 1 and 6b and eq 11 it is possible to obtain the reduced Gibbs energy $\tilde{G}_{\dot{\gamma}}$ of the flowing system according to eq 3 as a function of the mole fraction of the polymer. However, in the calculation of the composition of the coexisting phases by means of $\tilde{G}_{\dot{\gamma}}$, a problem turns up with the shear rates that are produced in the suspended phase by the flowing continuous phase. Two extremes are conceivable: (i) $\dot{\gamma}$ is the same in the two liquids; (ii) the $\dot{\gamma}$ value in the suspended droplets adjusts according to the shear stress applied to it via the continuous phase (i.e., $\dot{\gamma}\eta$ is the same in the two liquids). Theoretical considerations concerning macroscopic droplets exhibiting sharp phase boundaries favor assumption ii. The underlying premises are, however, not fulfilled in the present case, where at the cloud points of interest, the suspended phase consists of extremely small microscopic droplets and the insignificant interfacial tension leads to diffuse phase boundaries. In view of these facts and of the experimental procedure (determination of cloud point curves at a given shear rate), subsequent calculations were performed on the basis of assumption i. The composition of the coexisting phases can then be determined from $\tilde{G}_{\dot{\gamma}}(x_2)$ in the usual way by

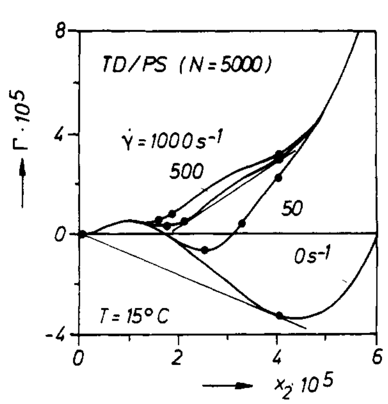

Figure 1. Example (T = 15 °C) for the determination of the composition of coexisting phases for the flowing system *trans*-decalin/polystyrene by means of the common tangent to the function $\Gamma(x_2)$ (cf. eq 13). x_2 is the mole fraction of the polymer. The shear rates $\dot\gamma$ are indicated on the curves. The full circles also give the composition of the coexisting solutions in those cases where no tangent is drawn.

means of the common tangent. For simplicity, the present evaluation was performed graphically, plotting the deviation of the above function from linearity according to

$$\Gamma = \tilde{G}_{\dot\gamma} - \frac{x_2}{x_2^*}\tilde{G}_z^* \qquad (13)$$

where x_2^* and $\tilde{G}_z^*$ are the coordinates of the point on the curve $\tilde{G}_z(x_2)$ (the reduced Gibbs energy of the unsheared system) to which the secant, used as the base line for further evaluation, is drawn from the origin. x_2^* is chosen such that the deviations of $\tilde{G}_{\dot\gamma}(x_2)$ from linearity are clearly visible and allow an easy construction of the common tangents. This modified procedure turned out to be necessary since the deviation of $\tilde{G}_{\dot\gamma}(x_2)$ from linearity is almost invisible if one plots the function itself.

Figure 1 provides an example for the determination of the composition of the coexisting phases as outlined above; x_2^* was chosen to be 6 × 10⁻⁵ for T = 15 °C. The maximum shear rate amounts to 1000 s⁻¹. The lowest curve represents equilibrium conditions (system at rest). The common tangent and the composition of the coexisting phases are indicated. Energy stored during stationary flow results in additional contributions to Γ via $\tilde{E}_s$ (cf. eq 2 and 3) which strongly depend on polymer concentration. At constant composition $\tilde{E}_s$ approaches a limiting value as the shear rate is increased (cf. eq 11). The application of a shear field can divide the miscibility gap observed at rest into two regions of phase separation, creating a zone of complete miscibility between them. This situation can be seen from the curve for 500 s⁻¹ in Figure 1, for which the common tangent is only drawn in the case of the solubility gap at the higher polymer contents. The region of additional homogeneity mentioned is situated between the two points at approximately x_2 = 2 × 10⁻⁵.

At temperatures only 1–2 K below the critical temperature of the system at rest and at shear rates of a few hundred to a few thousand s⁻¹, the miscibility gap observed for $\dot\gamma$ = 0 can be completely eliminated, in accord with experimental observations.[8] This result also agrees with previous theoretical calculations[7] on the basis of a forced subdivision of the droplets of the coexisting phases down to a molecular level. In terms of the evaluation presented in Figure 1, the phenomenon of shear dissolution is explained by storage of the energy $\tilde{E}_s$, which can completely undo the "upturn" in the function $\tilde{G}_z$ responsible for the phase separation in the absence of shear. A further particular situation arises as the two tangents to $\Gamma(x_2)$ degenerate into one, a situation not too far from that shown in Figure 1 for $\dot\gamma$ = 1000 s⁻¹. This behavior corresponds to a coexistence of three liquid phases in the flowing state.

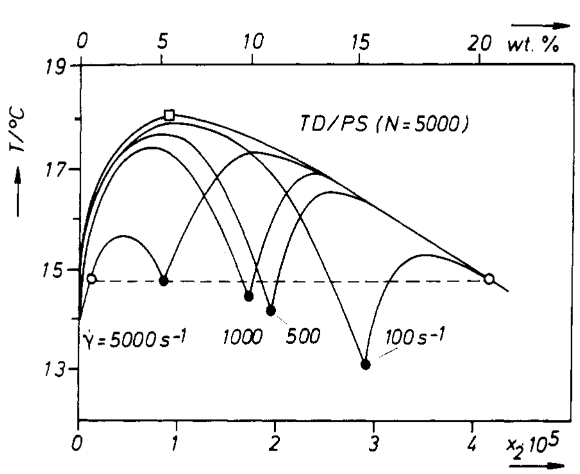

Figure 2. Demixing temperature of the system *trans*-decalin/polystyrene as a function of the mole fraction x_2 of the polymer at the indicated constant shear rates $\dot\gamma$ (at the upper abscissa the composition is also given in terms of weight percent polymer). The solid circles represent the eulytic points (cf. text); the dashed line shows, as an example, the coexistence of three phases at $\dot\gamma$ = 5000 s⁻¹.

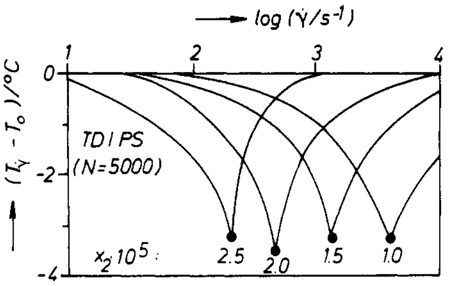

Figure 3. Difference between $T_{\dot\gamma}$, the demixing temperature of a given solution at the shear rate $\dot\gamma$, and T_0, that of the solution at rest, as a function of log $\dot\gamma$ for the system *trans*-decalin/polystyrene and the indicated mole fractions x_2 of polymer. The filled circles represent the eulytic points.

All the effects mentioned above can be seen more easily from Figure 2. In order to construct the phase diagrams shown for the indicated shear rates, the function $\Gamma(x_2)$ was evaluated, in the manner just discussed, at temperature intervals of 0.5 and 0.25 K, respectively. Due to the unavoidable inaccuracy of the graphical procedure and to the approximate nature of some of the equations, the precision of the results must not be overestimated. In particular, it cannot be decided yet whether the demixing curve of the flowing systems could slightly surpass that of the solution at rest at the highest concentrations and shear rates, since the accuracy of eq 8 deteriorates under these conditions. The theoretically derived bimodality of the demixing curves of the flowing polymer solutions is in accord with experimental findings.[7]

In spite of these limitations the following general behavior has been shown: Application of a shear field increases the homogeneous region in such a way that the phase diagram exhibits two maxima instead of one. The largest additional miscibility that can be achieved by a given shear rate is represented in the diagram by solid circles. For further discussion these points of maximum shear dissolution are called eulytic points by analogy with the term eutectic, which indicates the maximum extension of the liquid state with respect to the solid. At the eulytic temperature three phases coexist as shown in Figure 2 for $\dot\gamma$ = 5000 s⁻¹. Within the present range of variables, the

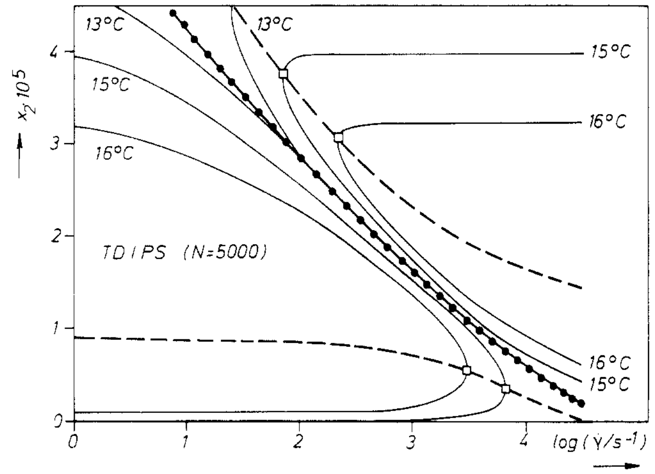

Figure 4. Dependence of the composition of the coexisting phases (x_2 is the mole fraction of polymer) on log $\dot{\gamma}$ ($\dot{\gamma}$ is the shear rate) for the system *trans*-decalin/polystyrene and the indicated temperatures: (●) eulytic line; (---) maxima of demixing curves.

eulytic point is shifted toward lower polymer concentrations and higher temperatures as the shear rate is increased.

Figure 3 demonstrates how many degrees the demixing temperature $T_{\dot{\gamma}}$ of the flowing solutions is lowered with respect to the equilibrium demixing temperature T_0 at various concentrations. The filled circles again represent the eulytic points. From this diagram it is obvious that for each solution there exists an optimum value of $\dot{\gamma}$ which most extends the homogeneous state. This finding is in accord with the results of the theory of shear dissolution.[7] Because of the possible inaccuracies already mentioned, it cannot be stated definitely that the difference between the eulytic temperature and T_0 is practically independent of polymer concentration as suggested by Figure 3.

Finally, Figure 4 shows the influence of shear rate on composition of the coexisting phases for the constant temperatures indicated. Note how the equilibrium solubility gap narrows as the system begins to flow and how the second solubility gap at the high-concentration end of the system shows up as $\dot{\gamma}$ is raised. The solid line indicated by the circles represents the eulytic curve, and the dashed lines represent maxima of the coexistence curves.

The extent to which the results of the above model calculations can be observed experimentally is being investigated[8] with the present system.

Added Note. Recent turbidimetric measurements with solutions of high molecular weight polystyrene (1 700 000) in *trans*-decalin have shown a diminution of the homogeneous region by shearing.[8] These findings can also be rationalized on the basis of the present approach, using direct experimental information concerning the stored energy.

Acknowledgment. The author thanks one of the referees for drawing his attention to the question whether the chemical potentials in the flowing two-phase system should be the same at constant shear rate or shear stress.

Registry No. Polystyrene (homopolymer), 9003-53-6; *trans*-decalin, 493-02-7.

References and Notes

(1) Silberberg, A.; Kuhn, W. *Nature (London)* **1952**, *170*, 450; *J. Polym. Sci.* **1954**, *13*, 21.
(2) Breitenbach, J. W.; Wolf, B. A. *Makromol. Chem.* **1968**, *117*, 163.
(3) ver Strate, G.; Philipoff, W. *J. Polym. Sci., Polym. Lett. Ed.* **1974**, *12*, 267.
(4) Champion, J. V.; Davis, I. D. *J. Chem. Phys.* **1970**, *52*, 381.
(5) Tjakraatmadja, H.; Hosemann, R.; Springer, *Colloid Polym. Sci.* **1980**, *258*, 1145.
(6) Heller, W.; Nakagaki, M. *J. Chem. Phys.* **1976**, *64*, 3797.
(7) Wolf, B. A. *Makromol. Chem., Rapid. Commun.* **1980**, *1*, 231. Schmidt, J. R.; Wolf, B. A. *Colloid Polym. Sci.* **1979**, *257*, 1188.
(8) Wolf, B. A.; Krämer, H. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 789. Krämer, H. Ongoing Thesis, Mainz.
(9) Janeschitz-Kriegl, H. *Adv. Polym. Sci.* **1969**, *6*, 170.
(10) Marucci, G. *Trans. Soc. Rheol.* **1972**, *16*, 321.
(11) Vanoene, H. J. *Colloid Interface Sci.* **1972**, *40*, 448.
(12) Koningsveld, R.; Kleintjens, L. A. *Macromolecules* **1971**, *4*, 637.
(13) Holmes, L. A.; Ninomiya, K.; Ferry, J. D. *J. Phys. Chem.* **1966**, *70*, 2714.
(14) Holmes, L. A.; Ferry, J. D. *J. Polym. Sci., Part C* **1968**, *23*, 291.
(15) Chee, K. K.; Rudin, A. *Trans. Soc. Rheol.* **1974**, *18*, 103.
(16) Rouse, P. E. *J. Chem. Phys.* **1953**, *21*, 1272.
(17) Nielsen, L. E. "Polymer Rheology"; Marcel Dekker: New York and Basel, 1977.
(18) Hoffmann, H.; Krömer, H.; Kuhn, R. "Polymeranalytik I"; Georg Thieme Verlag: Stuttgart, 1977.
(19) Martin, A. F. *Am. Chem. Soc. Meeting, Memphis* **1942**, *23*, 4.