6106 *Macromolecules* **1993,** *26,* 6106-6110

Establishment of Phase Equilibria: Temperature Jump Experiments in a Spinning-Drop Apparatus

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Received April 20, 1993; Revised Manuscript Received July 26, 1993[⊛]

ABSTRACT: In a spinning-drop apparatus, used for the determination of interfacial tensions, it was investigated how phase-separated polymer solutions react on a rapid rise in temperature. These measurements, yielding an apparent interfacial tension as a function of time, demonstrate that new equilibria are achieved in four clearly separable steps. The first, very rapid one consists in the establishment of a *local* equilibrium *within* the interfacial area dividing the two coexisting liquids. During the second stage of much longer duration, solvent *and* solute are exchanged between the bulk material as a result of the gradients in the chemical potential that exist for both components in both phases; due to the higher mobility of the solvent, its flux dominates. This stage comes to an end as one of the coexisting phases assumes its equilibrium composition, i.e., falls on one end of the corresponding tie line. Despite this situation the entire system has not yet reached equilibrium since the composition of the other coexisting phase is not identical with that of the other end of the tie line. The third step, which is again long-lasting, is therefore characterized by the transport of only one component over the phase boundary, namely for one for which still exists a driving force. If the droplet consists of the dilute polymer solution and the matrix of the concentrated polymer solution, it is the solvent which migrates exclusively during that stage; in the opposite case it is the polymer. If the overall composition of the system corresponds to a point within the homogeneous region of the phase diagram, this third step is followed by a fourth. Ultimately, the new equilibrium is achieved by mere diffusion in the absence of a discontinuity in concentration. Since the spinning-drop experiments also allow the determination of the volume of the phases and the interfacial area between them, it is possible to determine the net fluxes for the first three stages; some preliminary data are given. Furthermore, it is possible to visualize the volume elements within which the composition has changed during equilibrium by jumping back to the lower starting temperature by means of the phase separation that takes place in these zones.

Introduction

One of the central questions in the understanding of extraction processes is the rate of the exchange of matter over the phase boundary existing between two liquids and of the role the interfacial tension σ plays in this context. In the field of polymers, where such extraction processes have only recently been developed,[1] some qualitative information on the importance of σ is already available. For the continuous polymer fractionation (CPF), where the lower molecular weight parts of a polymolecular material are extracted, it has turned out that this method works most effectively at moderate polymer concentrations and not (as expected from thermodynamic considerations) at very high dilution. This observation was interpreted in terms of an increase in the extraction rate as one raises the polymer concentration and moves toward the critical point of the system, where the interfacial tension approaches zero.

The present work with phase-separated polymer solutions was undertaken to prepare the ground for a study of the transfer of matter over the phase boundary; the spinning-drop method[2,3] was used for that purpose. It allows the determination of the interfacial tension and, at the same time, of the volume of the phases very precisely. For the present problem it appeared interesting to check how the system responds to temperature jumps. In particular, it should be investigated how the system changes from one equilibrium state into another and whether there exists a correlation between the changes in the volume of the droplet and the apparent interfacial tension σ^* calculated from its shape as a function of time; the term apparent is used as a remainder of the fact that one does not normally obtain equilibrium values in this manner.

The experimental procedure is demonstrated by means of Figure 1, which shows a schematic phase diagram for solutions of a molecularly uniform polymer (index 2) in a single solvent (index 1); it is drawn for normal systems where the density of the polymer is larger than that of the solvent.

The starting point of the measurements is the coexistence of two phases inside the tube of the spinning-drop apparatus at the temperature T_1. In the present case the droplet that is deformed by the rotation consists of the less concentrated coexisting polymer solution, i.e., of the sol phase, and the matrix of the more concentrated gel phase. Since the volume of the sol is typically on the order of 10^{-4} cm^3 and that of the matrix ca. 1 cm^3, the overall composition of the system corresponds to a point in the phase diagram that is very close to the gel branch of the coexistence curve. Naturally, the scheme has to be changed accordingly for systems where the polymer is less dense than the solvent; an example for that case has also been investigated.

How the temperature jump experiments were performed with normal systems is demonstrated by means of Figure 1: If T is altered very rapidly from T_1 to T_2, the composition of the phases coexisting at the lower temperature is practically unaltered (paths a in the phase diagram). Since the overall composition of the system corresponds at T_2 to a point within the homogeneous region of the phase diagram, the mixture has to become homogeneous after sufficiently long times (paths c of Figure 1 show the required overall effect only and do not correspond to actual changes of concentration with temperature). Prior to the present experiments the details of equilibration after T-jumps, i.e., of the total dissolution of the droplet and the homogenization of the entire mixture, were unknown.

[⊛] Abstract published in *Advance ACS Abstracts*, October 1, 1993.

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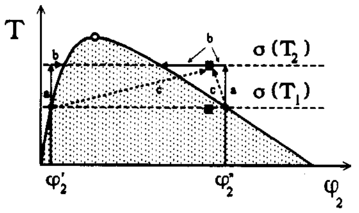

Figure 1. Schematic phase diagram demonstrating how the temperature jump experiments have been performed in a spinning-drop apparatus. The critical value of the volume fractions φ_2 of the polymer is indicated by the open circle; the full circles represent the composition of the phases coexisting at the starting temperature T_1. The overall composition of the two-phase system contained in the rotating tube (full square) is shown for a typical case in which the density of the less concentrated polymer solution is lower than that of the higher. At T_1 this point is situated inside the two-phase region, whereas it is located within the homogeneous regime at T_2. The significance of the different paths indicated in the figure by the arrows is discussed in the text.

Paths b of Figure 1 indicate how the composition of the coexisting phases would have to change at T_2 to establish $\sigma(T_2)$, the interfacial tension of the system at that temperature, at least temporarily.

Two kinds of temperature jump experiments were performed. In one series it was investigated how the shape and the volume of the droplet change with time (typically 8 h). In another series the equilibration of the system at T_2 was stopped after different times by jumping back to T_1. In this manner it is possible to visualize how far the transport of mass has proceeded at the higher temperature, since demixing takes place in those zones of the system which have changed in composition (i.e., are situated within the two-phase area of the phase diagram for T_1; cf. Figure 1).

Experimental Section

Substances. Polystyrenes PS-17.5 and PS-86.3 were purchased from Polymer Standards System (Mainz, Germany). The numbers of the abbreviation are identical with the (weight average) molar mass M in kg/mol). The molecular nonuniformity $U = (M_w/M_n) - 1$ of the PSs is 0.03. The polyisobutene sample PIB-8.9 (M_w = 8.9 kg/mol, U = 0.25) stems from a preparative fractionation[4] of a commercial sample (Oppanol B10 BASF, Ludwigshafen, Germany). Methylcyclohexane (MeCH) and anisole (ANL), both for synthesis, were purchased from Merck (Darmstadt, Germany). MeCH was redistilled and both solvents were dried by means of molecular sieves before use.

Methods. Spinning-drop experiments were performed on a commercially available apparatus (Krüss, Hamburg, Germany). This device has a thermal stability of ca. ±0.05 K according to test measurements with a thermocouple inserted into the cylinder. A detailed description of the experimental procedure has already been given.[5] One measures the diameter and length of the droplet as a function of the speed of rotation. Since it is essential to know how long it takes to establish temperature equilibrium after a *T*-jump, corresponding experiments were also performed. For the small differences between T_2 and T_1 of present interest, this time remains well below 5 min. With the small ΔT values required, no temperature overshoot is observed. The evaluation of the shape of the droplets with respect to the apparent interfacial tension σ^* and with respect to the volume and interfacial area of the suspended phase[3,6] was done by means of photographs. Differences in the densities of the coexisting phases are not required for the present investigation, where the kinetics of the establishment of the new equilibria after *T*-jumps is of prime interest and not σ itself. For the system MeCH/PS, for which the corresponding density has already been published,[6,7,8] it was, however, checked how $\sigma^*(t)$ relates to σ (*cf.* the discussion in the context of Figure 3).

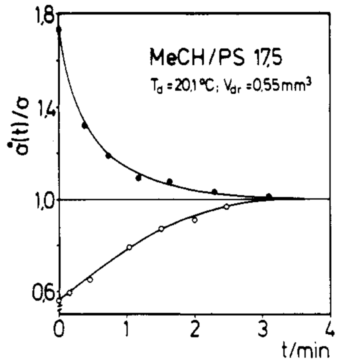

Figure 2. Kinetics of the establishment of the new equilibrium shape of the droplet after isothermal jumps in the speed of rotation of the spinning-drop apparatus. The apparent interfacial tension σ^* is obtained from the dimensions of the droplet at different times by means of the equations used to calculate the interfacial tension σ. For the open symbols the speed of rotation was changed at $t = 0$ from 2500 to 1890 rpm, and for the closed symbols, from 1890 to 2500 rpm. V_{dr} is the volume of the sol droplet.

Results and Discussion

Rotational Jumps. To be able to assess the kinetics of the establishment of a new equilibrium after *T*-jumps, it is first necessary to investigate the role the viscosity of the two coexisting liquids plays for that process. For this reason (i) the speed of rotation was changed for an equilibrium system at constant temperature, (ii) the shape of the droplet was measured as a function of time, and (iii) a value for the interfacial tension was calculated therefrom in the usual manner. The thus obtained apparent interfacial tensions σ^* do not (as already stated) necessarily represent an equilibrium property.[9] Here, however, it offers a simple and illustrative way to visualize the rate with which the new equilibrium is attained. Some representative results of rotational jump experiments are shown in Figure 2. They demonstrate that the adjustment of the system to a new speed of rotation requires only a few minutes.

Temperature Jumps: Mixing Experiments. By analogy to the procedure described for isothermal jumps in the speed of rotation, the change in the shape of the droplet is taken as a measure for the advancement in the establishment of the new equilibrium after the variation of *T*. For that purpose it is not necessary to determine the time dependence of the interfacial tension itself; it suffices to follow $\sigma^*(t)$ normalized to $\sigma(T_1)$ (its equilibrium value in the initial state). For the calculation of $\sigma^*(t)$ the variation of $\Delta\rho$, the changes in the density of the droplet and of the matrix phase, resulting from the exchange of matter over the phase boundary at T_2 was neglected. The changes in the volume of the droplet were, by analogy to σ^*, also normalized to the starting volume.

Figure 3 gives the result for the system MeCH/PS-17.5. As in all other cases the phase boundary remains sharp up to very long times; only just before it becomes invisible (after ca. 8 h when the droplet has shrunken to ca. 20% of the original size) it blurs out and the evaluation becomes difficult. The volume of the suspended phase diminishes exponentially with time, as expected. With $\sigma^*(t)$ the situation is different: After a quick reduction, this quantity passes a shallow minimum and remains constant after ca. 100 min at $\sigma(T_2)$ (the equilibrium value at T_2) until the end of the directly visible dissolution process. The equilibriuma data $\sigma(T_2)/\sigma(T_1)$ can be calculated from the constant region of $\sigma^*(t)/\sigma(T_1)$ by multiplication with the ratio of the differences in the densities of the phases coexisting at T_2 and T_1. For the examples given in Figure

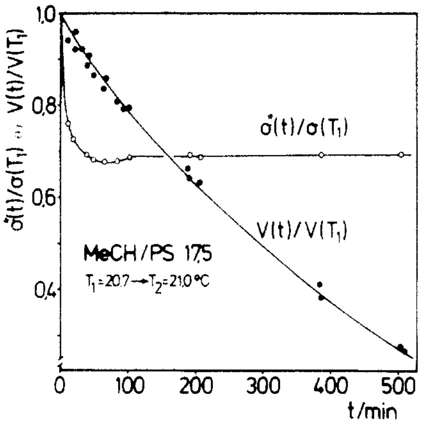

Figure 3. Time dependence of the apparent interfacial tension σ^* reduced to $\sigma(T_1)$ and of the volume V of the droplet reduced to its volume at T_1 after a temperature jump from 20.7 to 21.0 °C. For the present system MeCH/PS-17.5 the droplet consists of the sol phase.

3 this factor is 0.947 [resulting from $\Delta\rho(T_2) = 0.072$ and $\Delta\rho(T_1) = 0.076$ g/cm^3]. At earlier times, where $\sigma^*(t)/\sigma(T_1)$ still changes, a similar conversion is impossible, since one does not know the average density within the droplet of nonuniform composition.

From $V(t)$ and the surface of the droplet at different times (calculated from its shape) it is possible to obtain some preliminary information concerning the net rate of exchange of the components of the mixture over the phase boundary. The example depicted in Figure 3 yields a net flux (volume per unit area and time) from the droplet into the matrix phase of ca. 6.5×10^{-9} m^3 m^{-2} s^{-1} immediately after the temperature jump. As the process proceeds, an asymptotic value, which is approximately half as large, is approached.

From the fact that the interface remains sharp after the T-jump during almost the entire time, one can conclude that *locally* the equilibrium is established practically instantaneously, notwithstanding the nonequilibrium prevailing outside this zone. To achieve overall equilibrium the transport has to take place over macroscopic distances. Due to the much higher mobility of the solvent as compared with that of the polymer, the exchange of matter over the phase boundary is dominated by the solvent (as can be directly seen from the mere fact that the droplet shrinks).

In the course of the establishment of the new equilibrium, the polymer concentration will rise on the sol side of the interface and fall on the gel side. The size of the element, within which the composition is different from that of the phases from which one started at T_1, grows steadily on both flanks of the phase boundary.

A prominent point is reached as soon as the droplet has achieved the composition given by the tie line in the phase diagram at T_2 (that process is symbolized in Figure 1 by the arrow b on the low-concentration side). The special situation just outlined can be directly registered by the fact that $\sigma^*(t)/\sigma(T_1)$ become independent of time. In contrast to that, it cannot be seen from the volume changes since the transport of matter goes on as before until the droplet is totally consumed. The minimum $\sigma^*(t)$ passes at shorter times results from the fact that the density of the droplet is not constant but has reached its equilibrium value only near the interface. It is reasonable to assume that the minimum would disappear upon the insertion of the (experimentally unknown) average density differences between the two coexisting phases.

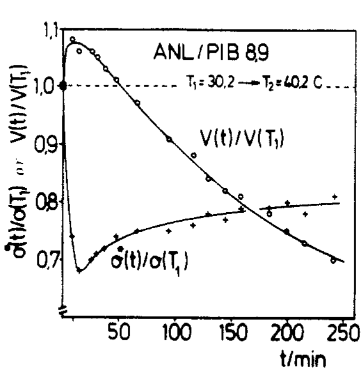

Figure 4. Time dependence of the apparent interfacial tension σ^* reduced to $\sigma(T_1)$ and of the volume V of the droplet reduced to its volume at T_1 after a temperature jump from 30.2 to 40.2 °C. For the present system ANL/PIB-8.9 the droplet consists of the gel phase.

To check whether the ideas just presented describe the actual situation correctly, T-jump experiments were also performed with a system where the sol phase is denser than the gel and therefore constitutes the matrix in spinning-drop experiments. In this case, realized with the system ANL/PIB-8.9, the solvent should no longer be transported out of the droplet but into it, since it now contains the more concentrated polymer solution. The results of these measurements are presented in Figure 4.

Indeed one observes an increase in the volume of the gel phase during the initial stages of the experiment as a result of the intrusion of solvent; thereafter the droplet is consumed in a manner similar to that described for the previous system. The—as compared with the previous system—much more pronounced minimum in $\sigma^*(t)$ results from the larger T-interval of the jump experiment. Unlike the volume, the interfacial tension shows no peculiarities. The local equilibrium is again rapidly established, and σ^* levels off as soon as the gel phase is diluted to the value of the equilibrium gel at T_2. The reason σ^* does not become constant after this prominent point is probably the following: Due to the molecular nonuniformity of the PIB, which—in contrast to that of PS—cannot be neglected, the fractionation associated with the establishment of phase equilibria will influence σ and consequently σ^* markedly, as has been demonstrated recently.[10]

Temperature Jumps: Mixing/Demixing Experiments. In the following it is investigated whether the processes of equalization of concentration described above can be visualized by means of a second jump, back from T_2 to the lower temperature T_1. By this procedure the ranges in which the composition has changed during the period the system was at higher temperature should become cloudly, since they correspond to points inside the miscibility gap. These experiments have been performed for the system MeCH/PS-86.3. The results of the jumps from T_1 to the higher temperature T_2 in terms of σ^* and of the volume of the sol droplet are shown in Figure 5 for the comparatively short times that are of interest in the context of the double-jump experiments.

The series of photographs presented in Figure 6 give an example for the migration of the solvent from the sol droplet into the gel matrix. The series was taken after a residence time of 17 min at T_2 in a 1-min sequence starting with the time of the temperature jump from T_2 back to the lower temperature T_1.

These pictures are in accord with the expectation that the concentration of the gel has been changed most in the immediate vicinity of the phase boundary: The cloudiness starts to develop in this region, where the mechanism of phase separation is probably still of the nucleation and growth type; i.e., the kinetics should correlate with the

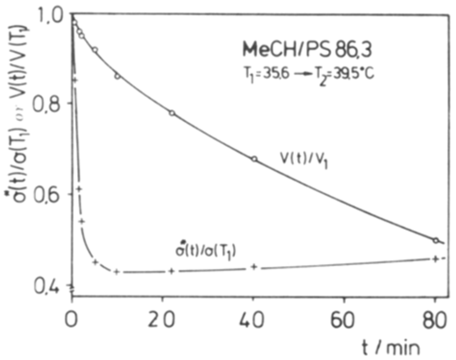

Figure 5. Time dependence of the apparent interfacial tension σ^* reduced to $\sigma(T_1)$ and of the volume V of the droplet reduced to its volume at T_1 after a temperature jump from 35.6 to 39.5 °C. The present system MeCH/PS-86.3 differs from that of Figure 3 only by the molar mass of the polymer.

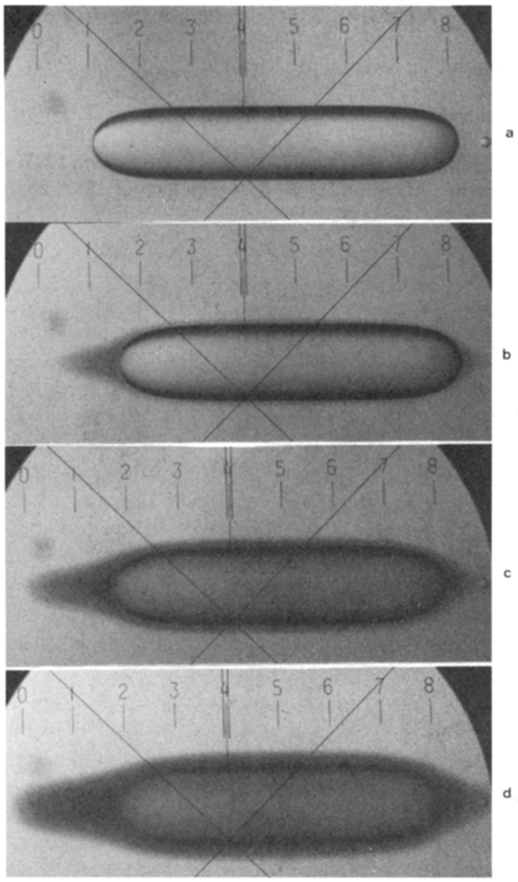

Figure 6. The series of photographs, showing a droplet of a dilute polymer solution in a matrix of a concentrated one, was obtained in the following way. First the experiment of Figure 5 was repeated up to a residence time of 17 min at 39.5 °C. Then the system was quenched back to the initial temperature of 35.6 °C (part a of the figure refers to the situation before the T-jump) and snapshots were taken at intervals of 1 min (parts b–d). The regions of the system that have changed in composition during the warmer period become cloudy, since they are now located in the interior of the miscibility gap.

degree of supersaturation. Later on, the turbidity also reaches more distant zones where the deviation from the new equilibrium concentration is much less.

In principle, it should be possible to obtain information on the rate with which matter is transported from one phase into the other from these pictures and from the changes in the volume of the droplets as a function of time. However, it must first be investigated to what extent the centrifugal field influences the data in the case of long-time experiments and whether an extrapolation to zero speed of rotation is required.

Conclusions

The results of the temperature jump experiments demonstrate that a new equilibrium is adjusted in four clearly distinguishable steps.

(i) In the first stage the transport of matter over the phase boundary is driven by the gradient of the chemical potential within the interfacial area of the system at the previous equilibrium conditions. It leads to the establishment of a *local* equilibrium and is so short that it is comparable to the time required for the achievement of temperature equilibrium.

(ii) In the second step the transport of matter is caused by the gradient of the chemical potential outside the interfacial area; i.e., it starts in the regions of the two bulk phases which are linked up with the phase boundary. This stage lasts many minutes (on the order of 1 h) and comes to an end as soon as the droplet phase (the volume of which is only ca. 0.01% of the matrix) has achieved the composition given the corresponding end of the tie line describing the equilibrium behavior at the measurement temperature T_2. During step ii both components are transported over the phase boundary, but the solvent is naturally—due to its higher mobility—dominating the resulting flux at least to the beginning of this stage. If the droplet contains the sol phase, this situation leads to its monotonous shrinkage. However, if it is made up by the gel phase, the intruding solvent results in an expansion only in the first instance. In the course of equilibration the concentration gradient will be reduced much more rapidly on the gel side than on the sol side due to the smallness of the droplet and the higher mobility of the solvent. For this reason the transport is increasingly taken over by the polymer as the process proceeds. The time at which the (opposite) fluxes of the components over the interface become equal can be seen from the maximum of $V(t)/V(T_1)$ in Figure 4.

(iii) The third step is characterized by the fact that driving forces only exist on one side of the interface, since *local* equilibrium has already been achieved in the interface and in the entire interior of the droplet. This stage lasts for even longer times than the last one and goes on until the droplet is totally consumed, i.e., when its opposite interfaces touch each other. If the droplet consists of the sol, the transport is exclusively taken over by the solvent (out of this phase), since driving forces no longer exist for the migration of the polymer into the sol, where the composition has locally reached the equilibrium value for T_2. The situation is just the opposite if the droplet consists of the gel; here the transport is entirely taken over by the polymer. In both cases the interface of the droplet retreats and the composition in its interior remains constant.

(iv) In the final step, phase boundaries—i.e., concentration jumps—are no longer involved. The equalization of concentration takes place exclusively via diffusion in a continuous environment. Normally, this period is probably the longest in the achievement of equilibrium, at least with the present systems of extreme phase volume ratios.

For a better understanding of the processes taking place in the CPF, it suffices to discuss stages ii and iii. The initial period i is short and negligible with respect to the residence time of the droplets in the apparatus, particularly if the compositions of feed and extracting agent are chosen properly. The last period iv can definitely be excluded since the system is not allowed to become homogeneous during the CPF.

In terms of the results obtained for the system ANL/PIB, where the droplet consists of the gel phase, it is possible to discuss the extraction in a realistic manner. Within stages ii and iii polymer is transported from the gel into the sol phase, and the driving forces are located outside the interfacial region. Knowing these details, one can now try to rationalize the experimental observation that the efficiency of fractionation can increase within a certain range of composition as its working point of the CPF is shifted toward the critical point of the system, despite the fact that the thermodynamic driving forces of the process are reduced.

Starting from the plausible assumption that the rate-determining step of the required extraction of polymers from the gel into the sol phase consists in their release from the interfacial zone, the following explanation can be given: At large σ (far from the critical conditions), the average polymer concentration is considerably higher in this transition region than at low σ (close to the critical conditions) due to the pronounced dissymmetry of the binodal line. This fact implies that the viscosity of the interphase is much less in the latter case than in the former, and consequently the rate of transport is much higher. In molecular terms this means a diminution of the average mesh size (i.e., of the distance between entanglement points of the polymer) as one approaches the critical conditions; the polymer molecules can therefore more easily free themselves from the interface and migrate from the gel into the sol phase.

Acknowledgment. The authors thank the "Max-Buchner-Forschungsstiftung" for the stipend granted to M.H.

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