Transport Phenomena in Ternary Polymer Solutions*

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In this paper certain results from investigations on multicomponent transport involving macromolecules are summarized. The transport phenomena treated are sedimentation, diffusion and thermal diffusion. In ternary systems containing two polymers in a single solvent or one polymer in a mixed solvent various interesting interaction effects can be observed. These interactions are especially pronounced close to phase separation points and can also be correlated with the size of the molecules.

A good understanding of transport phenomena in multicomponent systems is of great importance for a number of reasons. In living organisms, for example, materia is transported inside the cells, across membranes and in various fluids. Invariably those systems consist of more or less concentrated multicomponent phases. Sometimes (as in cells) the concentrations and the composition are such that phase separation might occur, which at least in part could explain the nonisotropic structure of cells [7]. In modern polymer chemistry there also seems to be a tendency to concentrate interest on more sophisticated systems like copolymers, swollen systems giving a "texture", *etc.* Such systems must often be regarded as multicomponent. In chemical technology a number of processes — probably the majority — include transport in a multicomponent system of one sort or another. When investigating the mass, size and shape of macromolecules by the hydrodynamic methods, for example, one is often forced to use a multicomponent solution. Cellulose, for example, is not soluble in a simple solvent, hence composite ones like CED, Cadoxen, EWNN, *etc.* must be used (for a review see [16]). Proteins are generally studied in buffer solutions. Many other examples could be given.

During the last ten to twenty years there has undoubtedly been a great interest in transport phenomena in multicomponent systems and although some progress has been made a number of problems remain to be solved.

In this survey I will not try to review the whole field but rather bring up a few points, which perhaps could be of a more general interest.

Sedimentation

Let us begin with sedimentation and consider a sedimenting particle. The velocity of the particle depends (for unit accelerating field) on the particle mass and volume and on the solvent viscosity. The velocity will also depend on the concentration. The detailed

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analysis of the sedimentation process is very difficult and no definite explanation of the concentration dependence has so far been given. Apart from the trivial reasons that a concentration dependence of the partial specific volume, $\bar{v}$, and of the solution density, ϱ, should reflect, through the factor $(1 - \bar{v}\varrho)$, in a concentration dependence of the sedimentation coefficient, s, only qualitative or semiquantitative explanations can be given. It is immediately clear that s must depend on the viscosity of the medium, but probably some "microscopic" viscosity is operative, rather than the "macroscopic" one as measured in a capillary viscometer. Fig. 1 shows the situation for some macromolecules.

Most probably the hydrodynamic interaction is strong in sedimentation. For example, there must always be a "backward flow" of solvent, compensating for the flow of sedimenting material. This "backward flow" will increase with concentration [8].

If a second solute is present the situation will be further complicated. Let 1 designate the component of immediate interest and let 2 be the added component. The presence of 2 will of course effect $\bar{v}$, ϱ, the viscosity, and the backward flow, and hence the sedimentation coefficient of component 1, s_1, will be a function of both concentrations c_1 and c_2 (expressed as mass per unit volume). Of course s_2, the sedimentation coefficient

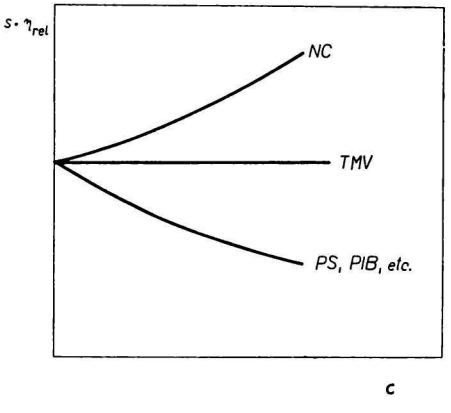

Fig. 1. Qualitative plot of the sedimentation coefficient multiplied by the relative viscosity *vs.* concentration for some macromolecules.
NC = nitrocellulose, TMV = tobacco mosaic virus, PS = polystyrene, and PIB = polyisobutylene.
This viscosity correction introduces an overcompensation for NC and an undercompensation for PS and PIB.

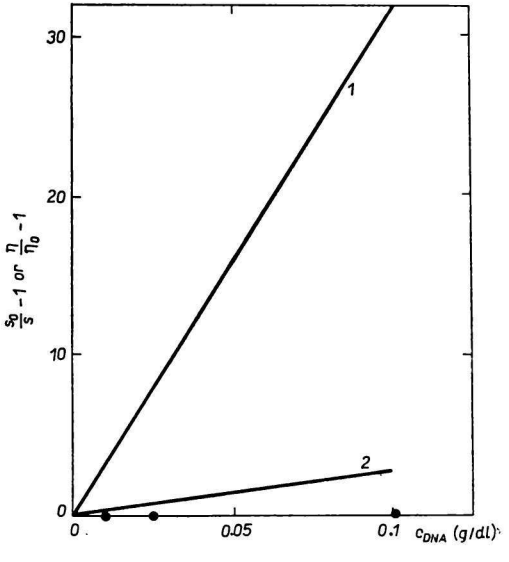

Fig. 2. Diagram showing the effect of various concentrations of deoxyribose nucleic acid (DNA) on the sedimentation of polystyrene latex particles with a diameter 2600 Å (curve *1*) and bushy stunt virus (filled circles). Curve *2* gives $\eta_{rel} - 1$ *vs.* c_{DNA} for comparison.
Data according to [41].

of component 2, will also depend on c_1 and c_2. The importance of this cross dependence has been known for a long time [21] and various methods have been devised to account for this often unwanted complication [49, 30, 44]. This so called Johnston—Ogston effect is usually ascribed to the hydrodynamic interactions during sedimentation. However, in a ternary solution subjected to sedimentation there may also be effects that are more properly described as "geometric" and "thermodynamic", and we will now consider those more in detail.

If the added component — 2 in our notation — consists of threadlike molecules like DNA or hyaluronic acid (HA), it will even at low concentrations form a three-dimensional network which also in general will move in the accelerating field. If the particles of component 1 are large enough, their sedimentation will be impeded or enhanced depending upon their tendency to move faster or slower, respectively, than the network. This effect has been investigated experimentally [40, 41, 26—29] and it has been found to be very pronounced in some cases. Fig. 2 shows the effect of various concentrations of the slow component DNA on the sedimentation of the fast components polystyrene latex particles (2600 Å) and bush stunt virus (300 Å). The sedimentation of the smaller virus particles is not at all affected whereas the velocity of the latex particles is greatly reduced. It is also seen that the change in relative viscosity due to the presence of DNA does not correlate with the sedimentation behaviour for these systems. Sometimes, however, the correlation between sedimentation and the viscosity due to the added component is very good. This is the case for the sedimentation of *T-3* bacteriophage, bushy stunt virus, and tobacco mosaic virus in fibrinogen solutions of various concentrations [40, 41]; *cf.* Fig. 1.

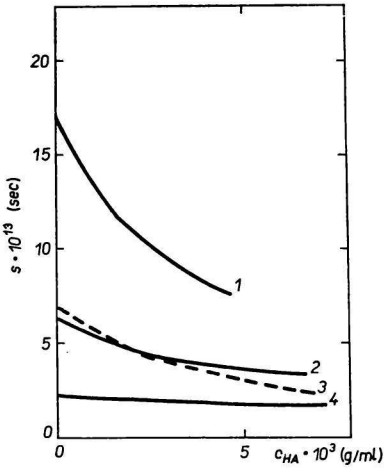

Fig. 3. Sedimentation coefficients of four proteins in the presence of hyaluronic acid: *1.* α-crystallin; *2.* γ-globulin; *3.* human fibrinogen; *4.* γ-crystallin. The concentrations of the four proteins were kept low and constant. From [27].

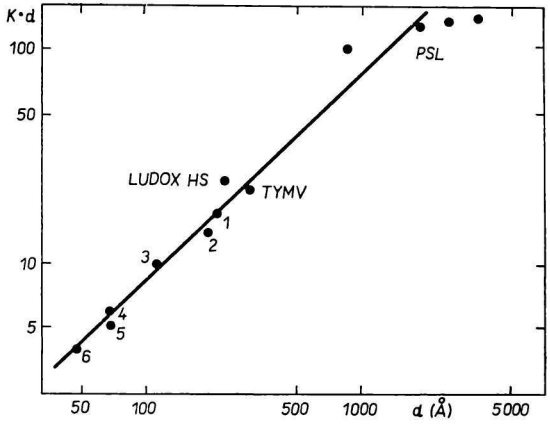

Fig. 4. Plot of the experimentally determined parameter $(K \cdot d)$ *vs.* the particle diameter, d.
PSL = various polystyrene latex samples, LUDOX HS = a colloidal silica fraction, TYMV = turnip yellow mosaic virus. *1.* fibrinogen: *2.* α-crystallin; *3.* γ-globulin; *4.* and *5.* albumins; *6.* γ-crystallin. From [27].

The effect of hyaluronic acid on the sedimentation rate of various proteins, polystyrene latex particles and colloidal silica has been extensively studied by *Laurent et al.* [26—28]. Some results are shown in Fig. 3. It has been found from these experiments that *for sufficiently high concentrations* c_{HA}, $\ln(s_0/s)$ is a linear function of $\sqrt{c_{HA}}$. Furthermore, the slope of such a linear plot correlates with the particle size and the following empirical relation has been suggested

$$\frac{s}{s_0} = A \exp(-Kd\sqrt{c_{HA}}), \qquad (1)$$

where s and s_0 refer to solutions with and without added hyaluronic acid, respectively. K and A are constants and d is the diameter of the sedimenting particle. In Fig. 4 ($K \cdot d$) has been plotted versus d in a double logarithmic diagram. In a later paper [29] the sedimentation of serum albumin and α-crystallin was studied in solutions of dextran, dextran sulfate, methyl cellulose, CM-cellulose, poly(vinyl alcohol) and chondroitin 4-sulfate of various molecular weights and concentrations. Essentially the same results were obtained as for hyaluronic acid. For the same degree of polymerization dextran sulfate was found to impede the sedimentation of the proteins to a much higher degree than dextran. This is probably due to a more pronounced network structure in the polyelectrolyte solution.

In an interesting application *Laurent* and *Persson* [27, 28] have used the difference in dependence on c_{HA} of the sedimentation of γ-globulin and fibrinogen (see Fig. 3) to accomplish a separation of these substances in the analytical ultracentrifuge. In buffer only one peak is observed for a mixture of these two proteins, but in 6.8×10^{-3} g/ml hyaluronic acid two peaks are clearly distinguished as shown in Fig. 5.

Partition measurements of serum albumin between buffer solutions and solutions containing hyaluronic acid have shown markedly different partitions in favour of the buffer solutions [32]. This thermodynamic interaction could imply a strong effect on the sedimentation rate, but this was not found [2].

It occurred to the present author that in a solution of two different synthetic polymers in a common solvent the interaction may be so strong (eventually it leads to incompatibility) that the sedimentation rate could be affected. From sedimentation investigations on mixtures of polystyrene (PS) and polyisobutylene (PIB) in toluene and 1-chloro-*n*-decane it appears as if such interaction actually occurs [47]. In general the interpretation of data from sedimentation in multicomponent systems is difficult owing to experimental complications (square dilution; accumulation of the second component at the boundary of the first — the accumulation can be so pronounced that inverse density gradients and hence convection occurs; strong mutual concentration dependence). The system PS—PIB—toluene, however, is convenient since only the refractive index increment of PS is different from zero. Hence only the flow of PS is measured refractometrically, and some of the difficulties with the interpretation of primary data are thus eliminated. Figs. 6 and 7 show the dependence of the sedimentation coefficient of polystyrene, s_{PS}, on the concentrations c_{PS} and c_{PIB}. A detailed analysis of these data seems to indicate that the following form for the concentration dependence is obeyed

$$\frac{1}{s_{PS}} = \frac{1}{s^0_{PS}}(1 + k_1 c_{PS} + k_2 c_{PIB} - k_{12} c_{PS} c_{PIB}). \qquad (2)$$

Here s^0_{PS} is the sedimentation coefficient of PS at infinite dilution (with respect to both PS and PIB); k_1, k_2 and k_{12} are positive constants. The presence of the last term in (2)

indicates that interaction occurs. The numerical values are such that for typical conditions this last term may contribute approximately 15% to the total value of the parentheses in (2). *Schachman* has earlier suggested an expression where only the linear terms in concentrations were used to express the concentration dependence. The presence of the "cross term", *i.e.* $k_{12}\, c_{PS}\, c_{PIB}$, indicates some sort of interaction, either hydrodynamic or thermodynamic in nature.

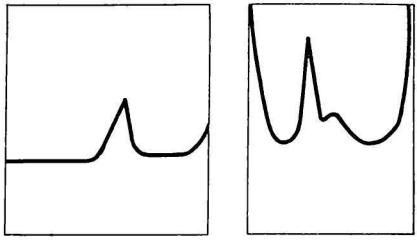

Fig. 5. Schlieren patterns from ultracentrifuge experiments with a mixture of γ-globulin and human fibrinogen (the same fractions as in Fig. 3) in *a*) buffer and *b*) 6.8×10^{-3} g/ml hyaluronic acid. From [29].

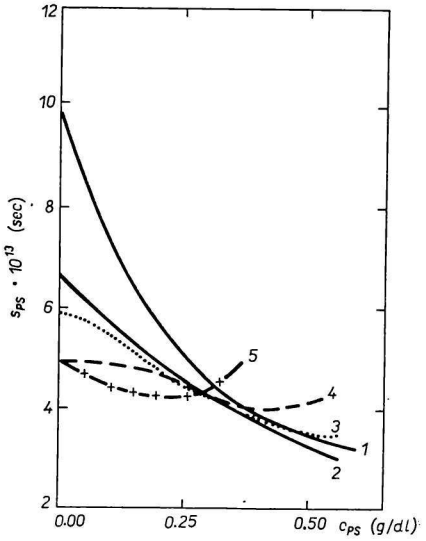

Fig. 6. s_{PS} plotted *vs.* c_{PS} for the following concentrations c_{PIB} (in g/dl): *1.* 0.0000; *2.* 0.2413; *3.* 0.3106; *4.* 0.4046; *5.* 0.6278.

Phillips and *Smith* [38] have recently published a discussion of the concentration dependence of sedimentation in a ternary system assuming a model for the hydrodynamic interaction. Although of value for less concentration dependent, non-interacting systems their treatment seems unable to provide an interpretation for the mixed polymer system discussed above. It is known that for the similar system polystyrene—poly(methyl methacrylate) (PMMA)—benzene the radius of gyration of PS decreases when PMMA is added [25]. This should be equivalent to an increase in the sedimentation rate as indicated by the minus sign in front of the cross term in (2). However, more experiments under more varied conditions seem to be necessary, before the question of the interactions can be definitely settled.

There exist modern theories for sedimentation in interacting multicomponent systems [17—19, 12—15, 37, 1]. In many cases it can be inferred from these theories that corrections due to coupling of flows are small. However, in some cases it is probable that the corrections become large. This is likely to be the case for two different polymers in the same solvent. We will indicate this by the following reasoning [48], which is based on the

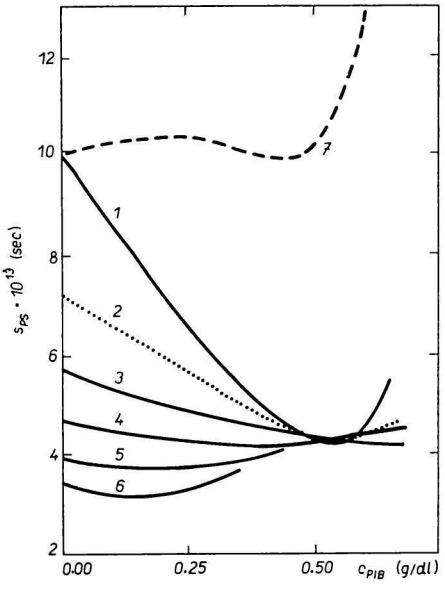

Fig. 7. The same data as in Fig. 6 but plotted *vs.* c_{PIB} for the following concentrations c_{PS} (in g/dl): *1.* 0.0; *2.* 0.1; *3.* 0.2; *4.* 0.3; *5.* 0.4; *6.* 0.5.
Curve *7* is curve *1* multiplied by the relative viscosity.

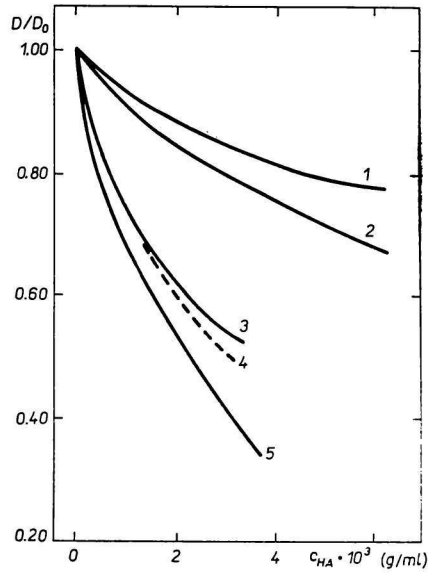

Fig. 8. The relative decrease in diffusion rate upon the addition of hyaluronic acid for *1.* and *2.* albumin; *3.* fibrinogen; *4.* α-crystallin; *5.* turnip yellow mosaic virus.
Curves *1* and *2* correspond to the same albumin fraction but the molecular weight of HA was 1.4×10^5 for curve *1* and 1.7×10^6 for curve *2*.
The higher molecular weight applies also to the other three curves. From [27].

equations given in [15] and the theory of polymer solutions developed in [9]. We will restrict the discussion to the special case when the solution is infinitely dilute with respect to 1. In order to make the relations more clear, we will, however, for a moment consider isothermal diffusion in a ternary system consisting of the solutes 1 and 2 and the solvent 0. For the flows J_1 and J_2 (defined with respect to the mean velocity of the volume element) we then have the relations [35, 36, 34]

$$J_1 = -D_{11} \operatorname{grad} c_1 - D_{12} \operatorname{grad} c_2,$$
$$J_2 = -D_{21} \operatorname{grad} c_1 - D_{22} \operatorname{grad} c_2, \qquad (3)$$

where the D_{ij}'s are the four diffusion coefficients of a ternary system as compared to one in a binary solution. The D_{ij}'s are expressible in terms of the so called phenomenological coefficients, L_{ij}, and of the derivatives of the chemical potentials with respect to concentrations, μ_{kj},

$$\mu_{kj} = (\partial \mu_k / \partial c_j)_{P,T,c_{i \neq j}}. \qquad (4)$$

The Onsager reciprocal relation reduces the number of independent diffusion coefficients from four to three. If $c_1 \to 0$ (*i.e.* the solution becomes infinitely dilute with respect to component 1) one can show that

$$\lim_{c_1 \to 0} D_{12} = 0 \tag{5}$$

whereas the rest of the D_{ij}'s tend to finite, in general non-zero, limits. In particular $D_{11} \to D_{11}^0$ when $c_1 \to 0$. The superscript ^{0} will here and in the following indicate infinite dilution with respect to 1.

Let us now return to the sedimentation of two different macromolecules in a common solvent and make the reasonable assumption

$$\lim_{c_1 \to 0} D_{12}\, \mu_{11} = 0. \tag{6}$$

We then arrive [15] at the following expression (valid for non-electrolytes)

$$\lim_{c_1 \to 0} s_1 = s_1^0 = D_{11}^0 \frac{\psi_1^0}{RT} \left(1 - \frac{\psi_2^0\, \mu_{12}^0}{\psi_1^0\, \mu_{22}^0}\right), \tag{7}$$

$$\psi_i = M_i(1 - \bar{v}_i \varrho). \tag{8}$$

The parenthesis in (7) obviously represents the correction due to coupling of flows. It thus remains to estimate μ_{12}^0 and μ_{22}^0 and this is done by forming the derivative of the expressions for μ_1 and μ_2 for a ternary system as given in [9]. After taking the expressions so obtained to the limit $c_1 \to 0$ and assuming for simplicity that $\chi_{01} = \chi_{02}$ and that the number of segments in two different macromolecules 1 and 2 is the same, *i.e.* $x_1 = x_2 = x$, we find

$$\frac{\mu_{12}^0}{\mu_{22}^0} = \frac{x - 1 + \chi_{12}^0 + 2\chi_{20}^0\, v_0^0}{\dfrac{1}{v_2} + x - 1 - 2\chi_{20}^0\, v_0^0}. \tag{9}$$

v_i is the volume fraction of component i and χ_{ij} is the Flory interaction parameter; x is essentially the degree of polymerization. It is immediately clear that if the solution is extremely dilute with respect to component 2, $\mu_{12}^0/\mu_{22}^0 \approx 0$ and the interaction correction is vanishingly small. However, even in a relatively dilute solution (with respect to 2) the interaction, as estimated from (9), can be noticeable. Suppose that $v_2 = 0.001$ and $x = 1000$, $\chi_{12}^0 = 10$, $\chi_{01}^0 = \chi_{02}^0 = 0.25$, *i.e.* $\chi_{20}^0 = 250$, values which are highly realistic. Since $v_0^0 \approx 1$ it is then found that $\mu_{12}^0/\mu_{22}^0 \approx 0.3$. For $v_2 = 0.005$, and without changing the other parameters, we get $\mu_{12}^0/\mu_{22}^0 \approx 0.7$. If ψ_1^0 and ψ_2^0 are approximately equal it is thus obvious that very strong interaction will occur. Although the considerations above are admittedly approximate, they probably provide a correct order of magnitude.

Diffusion

The discussion has now reached a point where it is natural to consider diffusion in a ternary system. *Ogston* and *Sherman* [33] have investigated the diffusion of serum albumin, glucose and polyglucose in water solutions also containing various concentrations of hyaluronic acid. Increasing concentrations of hyaluronic acid were found to decrease the diffusion coefficient of the other components. In the presence of hyaluronic acid the

diffusion rate of serum albumin was higher for a higher albumin concentration. In a gelatin gel and in a collagen gel, however, the diffusion coefficients differed only slightly from those in water. The effect in hyaluronic acid is probably a composite one depending on viscosity, on the "micro-geometry" (three-dimensional network) and on thermodynamic interaction (*cf.* the partition experiment by *Ogston* and *Phelps* [32] mentioned earlier). From the experiments only qualitative conclusions can be drawn, however. The same is true for the diffusion experiments reported by *Laurent et al.* [27], the results of which are shown in Fig. 8. It is seen that hyaluronic acid drastically reduces the diffusion rate of albumin, fibrinogen, α-crystallin and turnip yellow mosaic virus. From the two curves for albumin it is seen that the diffusion rate is more reduced when the molecular weight of hyaluronic acid is higher. The diffusion results have been combined with the corresponding sedimentation data and it is found that s/D is an almost constant number independent of the hyaluronic acid concentration (see Fig. 9). This probably indicates that the effect is more hydrodynamic and "geometric" than "thermodynamic" in nature. It is very difficult, however, to draw any definite conclusions in this respect from the experiments since they have been evaluated as if the systems were binary (see the discussion below) and since opposing tendencies may compensate.

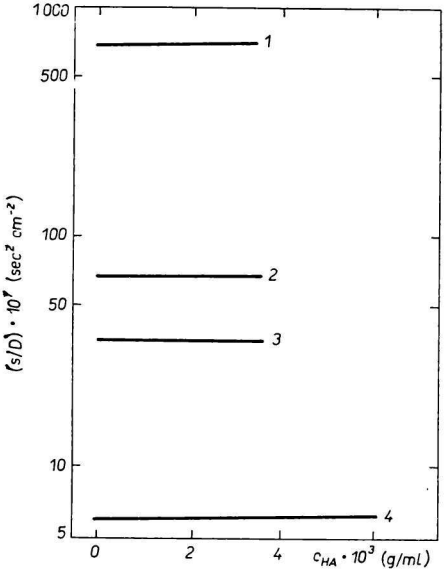

Fig. 9. s/D *vs.* c_{HA} for *1.* turnip yellow mosaic virus; *2.* α-crystallin; *3.* fibrinogen; *4.* albumin. From [27].

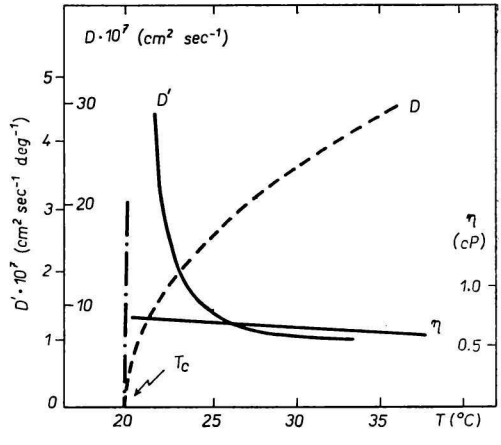

Fig. 10. Plot of the translational diffusion coefficient D, the thermal diffusion coefficient D', and the viscosity η, as functions of temperature for binary mixtures of nitrobenzene and *n*-hexane (average mole fraction = 0.5).
T_c indicates the critical solution temperature. From [5, 46].

For low-molecular weight ternary systems *Gosting* and co-workers [11, 31, 10, 52] have developed very accurate methods to determine the four diffusion coefficients of the set (*3*) from free diffusion experiments using the Gouy method. Mostly water solutions have been studied. A few organic systems have been studied by means of a modified diaphragm cell technique [43, 6] and the diffusion of polystyrene in a mixed solvent consisting of toluene and cyclohexane has been investigated by *Cussler* and *Lightfoot* [53]. In this latter investigation the polystyrene concentration was essentially constant and quite high, approximately 5 g/dl. The data of Cussler and Lightfoot show that the cross coefficients are quite large, for a high cyclohexane content as large as *four times* the main diffusion coefficient. The frictional coefficients which are independent of the frame of reference chosen for the flows were also given. Their numerical values are less certain than those for the D_{ij}'s, but one could observe a clear tendency towards an increase in mutual friction between polystyrene and cyclohexane as the cyclohexane content was increased. The measurements were performed at 28°C, which is well below the Θ-temperature of $\sim$ 34°C in cyclohexane, but since the molecular weight of the sharp fraction of polystyrene ($M_w/M_n \approx 1.06$) was slightly lower than 200 000, no phase separation did occur even in pure cyclohexane. However, the very low diffusion coefficient of PS in pure cyclohexane ($\sim 1 \times 10^{-7}$ cm^2 sec^{-1} as compared to $\sim 9 \times 10^{-7}$ cm^2 sec^{-1} in pure toluene) seems to indicate that the conditions are close to those of phase separation. This may explain why the cross effects are so pronounced.

Transport phenomena in the vicinity of critical points and for compositions close to phase separation are very interesting indeed. It is known that when a binary, homogeneous solution is brought near to a critical point, the diffusion coefficient decreases rapidly and vanishes at the critical point [5, 42]. This is due to the derivative of chemical potential with respect to concentration becoming zero at the critical point. For the binary diffusion coefficient one has from the theory of irreversible thermodynamics

$$D = L \frac{\mu_{11}}{c_0 \bar{v}_0}, \qquad (10)$$

where L is the binary Onsager phenomenological coefficient. From the results of *Claesson* and *Sundelöf* [5] it is clear that for the system nitrobenzene—*n*-hexane D drops to zero at the critical point at the same time as $D/\mu_{11} \propto L \propto \eta$ stays almost constant and positive (see Fig. 10). For ternary systems the situation is more complex. *Kirkaldy* and *Purdy* [24] have recently treated this case theoretically and it is shown that at a phase separation point the determinant $|D_{ij}|$ vanishes. This ensues from the following reasoning. At a phase separation point the determinant $\mu_{11}\mu_{22} - \mu_{12}\mu_{21}$ equals zero. For a ternary system the D_{ij}'s are related to the μ_{ij}'s and the four Onsager phenomenological coefficients L_{ij}, through the matrix relation $\varrho[D_{ij}] = [L_{ij}] \cdot [\mu_{ij}]$. Since the determinant product follows the same relation and the determinant $|L_{ij}|$ stays finite one gets $|D_{ij}| = 0$. For a true ternary critical point, *i.e.* where the miscibility isotherm has been reduced to a point, all four diffusion coefficients D_{ij} vanish [24].

Let us now treat a problem of some practical interest. Imagine a free diffusion experiment in a ternary solution where the original concentration step of the added component is zero (*i.e.* $\Delta c_2 = 0$ for $t = 0$), whereas $\Delta c_1 \neq 0$. Can the diffusion of component 1 when the concentration c_1 is small be treated as a binary process? The general answer is no, although in many cases the binary treatment will be approximately correct. The reason is the following. If the step $\Delta\mu_2$ in chemical potential of component 2 across the boundary is not zero (which often will be the case even when $\Delta c_2 = 0$) there will be a tendency for component 2 to even out this difference by diffusion. There may also be

a hydrodynamic coupling of flows, since the phenomenological coefficients need not necessarily be zero. To clarify this it is instructive to consider the ratio of flows for $t = 0$ at the position of the boundary ($x = 0$) when $\Delta c_2 = 0$, $\Delta c_1 \neq 0$. One has from (*3*)

$$\left(\frac{J_2}{J_1}\right)_{t=x=0} = \left(\frac{-D_{21}\,\mathrm{grad}\,c_1 - D_{22}\,\mathrm{grad}\,c_2}{-D_{11}\,\mathrm{grad}\,c_1 - D_{12}\,\mathrm{grad}\,c_2}\right)_{t=x=0;\ \Delta c_2=0} =$$

$$= \left(\frac{D_{21}\,\mathrm{grad}\,c_1}{D_{11}\,\mathrm{grad}\,c_1}\right)_{t=x=0} \to \frac{D_{21}^0}{D_{11}^0} \text{ when } c_1 \to 0. \qquad (11)$$

It is thus seen that in the limit $c_1 \to 0$ the ratio of flows is finite and non zero if $D_{21}^0 \neq 0$ (which is physically possible). If the coupling is strong the ratio D_{21}^0/D_{11}^0 is likely to be comparable to 1 and hence the set (*3*) is necessary for a correct description. Strong coupling is likely to occur close to phase separation points. This has been shown both experimentally and theoretically for the system triethylamine—water—phenol [22]. That strong coupling occurs when a polymer is diffusing in a solvent—nonsolvent mixture is also indicated by recent experiments [20].

Accurate measurements of the four diffusion coefficients in a ternary system are experimentally very difficult. For certain initial conditions density inversions leading to convections develop during a run. Since these convections are generated by the diffusion process they are often highly reproducible. These effects were first treated by *Valtasaari* and *Hellman* [50] for the diffusion of cellulose in cupriethylene—diamine solutions (CED). In some cases convections may be caused also by coupling of flows [51, 39]. There exist also certain restrictions on the values of the D_{ij}'s which must be fulfilled if the solutions to the set of differential equations obtained from (*3*) by introducing the continuity equations shall have any physical meaning [23, 45, 4].

Thermal diffusion

A few years ago *Bonner* [3] published some interesting work on thermal diffusion of polymers. He used the moving boundary method from which the thermal diffusion coefficient D' is directly obtained. It was found that in good solvents D' is almost inde-

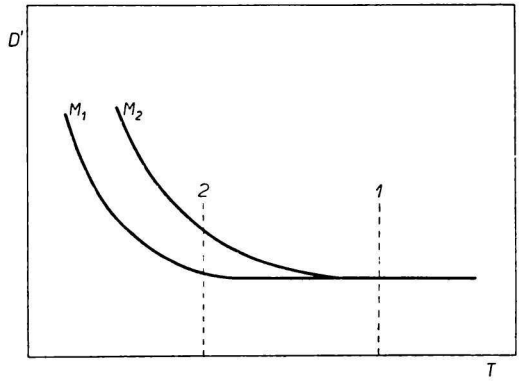

Fig. 11. Plot giving the possible variation of the thermal diffusion coefficient for polymers, D', with temperature, T, for two different molecular weights ($M_2 > M_1$) close to a phase separation point. The temperatures at the top (*1*) and bottom (*2*) of the thermal diffusion cell are indicated.

pendent of molecular weight. However, for polystyrene in cyclohexane well below the Θ-temperature (but above phase separation) strange stepfunctions in concentrations developed. This became very pronounced if the polymer consisted of a mixture of different molecular weight samples. The steps closer to the cold bottom plate of the cell migrated with a higher velocity than the main boundary. The detailed shape of these steps and plateaus could of course be due to convections, but it is almost certain that the convections must come from some feature of the thermal diffusion flow. One possible explanation is the following. From experiments on binary systems containing low-molecular-weight substances we know that the thermal diffusion coefficient increases strongly when the critical solution temperature is approached; see Fig. 10 [5]. For a homologous series of polymers the upper critical solution temperature is higher the higher the molecular weight. This could, if the situation is the same as for low-molecular-weight substances, give rise to a different temperature dependence of D' for different molecular weights and the heavier molecules should move faster than the less heavy ones if the temperature is such that the system is close to phase separation, see Fig. 11.

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