Multi-Component Diffusion in Polymer-Solvent Systems

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Annually, billions of dollars worth of products are produced by spreading a solution of a solvent and a polymer as a thin film on a substrate and then evaporating the solvent to form a polymer film or coating. These products range from commodities such as scotch tape and band aids to highly engineered membranes to purify water or separate gases or liquids. The formation of bubbles during the drying process cause defects and, the elimination of such defects is usually accomplished by slowing down the rate of the drying process which results in increased production cost.

One's first intuition would be to conclude that these bubbles are caused by the vapor pressure of the solvent being too high. Elementary experiments, however, quickly dispel such a conclusion. Simple bench-top types of experiments reveal the following observations:

(1) Bubble defects can appear at temperatures even below the boiling point of the pure solvent.

(2) Degassing the solutions reduces the tendency for bubbles to form.

(3) Bubbles can be eliminated by slowing down the rate of drying by controlling the velocity of the air passing over the evaporating solution.

(4) The phenomenon appears to be common for all solutions and is independent of specific solvent-polymer interactions.

(5) Bubbles form under both isothermal and non-isothermal conditions.

Observation (2) clearly indicates that bubble formation is associated with dissolved air. Consequently, in the following analysis we will consider for simplicity the ternary system of nitrogen-polymer-solvent. Preliminary examination of the thermodynamics of equilibrium of nitrogen in a solution of a polymer and a solvent indicates that the nitrogen solubility will qualitatively follow the functional relationship schematically presented in Figure 1. As this figure indicates, the solubility of nitrogen in the solution at a fixed temperature and pressure is expected to increase as the concentration of the solvent increases. This qualitative behavior is expected for all gas-polymer solutions based on the following fundamental thermodynamic considerations.

In order for nitrogen to dissolve in a polymer-solvent solution, the change in free energy for this mixing process must be negative. The change in free energy for all such mixing processes can be expressed in terms of two parameters as presented in equation 1 (*5*).

$$\Delta G_{\mathrm{mix}} = \Delta H_{\mathrm{mix}} - T\Delta S_{\mathrm{mix}} \qquad (1)$$

The free energy of mixing is related to the change in enthalpy during mixing of nitrogen in the polymer solution and the change in entropy during that mixing. The enthalpy change associated with an inert species such as nitrogen would be expected to be quite small and the overall process will be dominated by ΔS_{mix}. With any mixing process entropy will increase. It has been well established, however, that the entropy increase is less when a species such as nitrogen mixes with a macromolecule or a polymer as opposed to mixing with another small molecule (*5*). Consequently, for all nitrogen-polymer-solvent systems basic thermodynamics would indicate that, as shown in Figure 1, more nitrogen will be dissolved as the concentration of solvent in the polymer solution increases. One would have to find a polymer which has strong interactions with nitrogen (that is negative ΔH_{mix}) to reverse this behavior.

When a polymer solution is initially formed at a relatively high solvent concentration, it will very quickly go into equilibrium with nitrogen in the ambient air. For example, the initial state of the polymer solution before drying can be represented by point A on Figure 1. As solvent is evaporated from the solution, its concentration will decrease and consequently the dissolved nitrogen will enter a supersaturated state indicated by position B. At point B, it is possible that the supersaturated nitrogen could find a nucleation site and form a bubble. Because of the expected fast diffusion of nitrogen as opposed to the larger solvent molecules, one would anticipate that the thermodynamic driving force would quickly drive the nitrogen out of the solution into the ambient air and, thus, there would never be a state of significant nitrogen supersaturation during the drying process. Further analysis, however, reveals that other forces are acting which counter this effect.

To investigate the details of this process, we studied the system of nitrogen dissolved in a solution of polyvinyl acetate and toluene. In order to analyze this mass transfer process, we conducted extensive experiments to define the equilibrium relationship between a liquid phase consisting of the polyvinyl acetate, toluene, and nitrogen and a gas phase consisting of toluene and nitrogen. In addition, we measured and correlated the diffusion coefficients for all the binary pairs of this ternary liquid system. The thermodynamic equilibrium data were correlated with the Panayiotou-Vera equation of state (*6*) and the diffusivity data were correlated with commonly employed free-volume theories (*2, 7*). The extension of Fick's law of diffusion to a ternary system indicates that the diffusion fluxes of the solvent, J_S, and the nitrogen, J_N, are related to four independent diffusion coefficients (*4*).

$$-J_N = D_{NN} \frac{\partial C_N}{\partial Z} + D_{NS} \frac{\partial C_S}{\partial Z} \qquad (2)$$

$$-J_S = D_{SS} \frac{\partial C_S}{\partial Z} + D_{SN} \frac{\partial C_N}{\partial Z} \qquad (3)$$

As indicated by these equations, the diffusion flux of nitrogen is related not only to the concentration gradient of itself (the D_{NN} term) but is also coupled to the concentration gradient of toluene (the D_{NS} term). In the formulation presented here, diffusion fluxes are related to a volume average reference frame and the diffusion flux of the polymer can be determined from the two other diffusion fluxes. Of course, the diffusion fluxes can be related to many different reference frames without the loss of generality. In all formulations, however, four independent diffusion coefficients are required to completely define the diffusion process. Once the vapor-liquid equilibrium relationship for this ternary system as well as the diffusive process were completely defined, the coupled set of equations were solved to predict the concentrations of all the species as a function of position and time during this drying process. The details of this analysis follow the mathematical procedures which have been presented in the literature (*1, 2, 7*). A boundary condition for the governing equations is that the solutions sit on an inert substrate and there are no fluxes into the substrate. Also, at the liquid-gas interface, it is assumed that a mass transfer coefficient describes the transport of the volatile species in the vapor phase.

Extensive experimental work has shown that these cross terms or coupling terms (D_{NS} and D_{SN}) are usually a small fraction of the main diffusion coefficient terms and can be neglected (*4*). The predicted behavior when the cross terms are neglected in these cases is consistent with experimental observations.

There is a paucity of data for the values of the cross terms for polymer systems. Numerous theories have been developed which permit the prediction of these cross terms based on binary diffusion measurements and the thermodynamic behavior of the ternary system (*3*). Usually, the differences between these alternative theories are based on differences in assumptions concerning the relationships of the friction coefficients in the liquid system. In this modeling effort, all of the available theories were considered and the following discussion is qualitatively consistent with the predictions of all the alternative theories.

When considering the values of the main and cross terms in equations 2 and 3, one must remember that from a non-equilibrium thermodynamics point of view, the primary driving force for molecular diffusion are gradients in chemical potential. Consequently, when the driving forces are expressed in terms of gradients of concentration as is done in equations 2 and 3, all of the diffusion coefficients incorporate information concerning the thermodynamics of the system or more specifically gradients of the chemical potentials with concentration. The chemical potential is defined as (*5*):

$$\mu_N \equiv \left[\frac{\partial G}{\partial n_N}\right]_{P,T,n_i} \tag{4}$$

As discussed with reference to Figure 1, the free energy change with increased solvent concentration is negative and, thus, the corresponding chemical potential change is negative and the cross diffusion coefficient, D_{NS}, is negative. Consequently, in the case of the diffusion of nitrogen, as the solvent leaves the solution, the nitrogen will become supersaturated and there will be a driving force represented by the main term, D_{NN}, to force the nitrogen out of the solution. Simultaneously, the gradient in the toluene concentration will be forcing the nitrogen back into the solution. The net result is that to clearly model this overall diffusion process, the cross terms must be incorporated.

The following predictions are for a specific case of the isothermal drying at 40°C of a solution of polyvinyl acetate-toluene and nitrogen. The details of the parameters and physical properties used in these predictions are available (*1*). Figure 2 shows the results for the prediction of the nitrogen concentration near the bottom of the polymer solution with and without the cross coupling term. The concentration is given as the relative nitrogen saturation (RNS), i.e., the saturation concentration minus the actual concentration divided by the saturation concentration. Without the coupling diffusion term, one would predict that the nitrogen never attained super saturation and consequently there is never any potential to form bubbles. When the cross diffusion term is incorporated, however, super saturation is attained and bubble formation can result if an appropriate nucleation site is available. It should be emphasized that qualitatively this behavior is predicted by all the available models for describing diffusion in this ternary system. The key to this phenomenon is the unique thermodynamics for the solubility of an inert gas such as nitrogen in a polymer solution.

Figure 3 indicates that the nitrogen chemical potential in the same solution under identical conditions of temperature, pressure, and time has a much more complex behavior. After drying starts, the chemical potential of nitrogen near the bottom of the solution ($z = 0$) becomes higher than the chemical potential at the surface ($z = L$) which is in equilibrium with the air. In this particular illustration, we assumed that the mass transfer coefficient in the gas phase was essentially infinite so that the nitrogen in the solution at the surface of the solution is always in equilibrium with ambient gas. As Figure 3 shows, although the nitrogen becomes supersaturated at the bottom of the film, because of the gradient in toluene, there is a maximum in the chemical potential of the nitrogen and thus dissolved gas is trapped at the bottom of the solution where it can form a bubble.

Finally, we consider the influence of drying rate on bubble formation. Figure 4 shows the results of the model when one increases the mass transfer coefficient in the gas phase by an order of magnitude. This of course can be physically attained by increasing the velocity of the gas flow over the evaporating solution. As Figure 4 shows, an increase in the speed of the drying results in a greater nitrogen supersaturation which occurs at an earlier time in the overall drying process. Consequently, high drying rates induce bubble formation.

In conclusion, this study is the first to indicate the mechanism which leads to bubble formation in the drying of polymer solutions. Basic polymer thermodynamics indicates that this tendency to form bubbles by the diffusive trapped nitrogen and possibly other components of air is probably true for all polymer-solvent systems. Furthermore, the analysis of the mechanism clearly shows that bubble defects are exasperated by increasing the speed of drying by enhancing gas flow over the solution to increase the evaporation rate.

Not only is this mechanism important in drying technology, but from a scientific point of view this is the first case in the literature where the cross terms in multicomponent diffusion have been shown to play a dominant role. In the absence of these cross terms, supersaturation and consequently bubble formation will not occur. Furthermore, these conclusions are independent of the specific model which is used to correlate and predict the diffusion coefficients in a ternary polymer system. The phenomena is driven by the unique characteristics of polymer solutions where the entropy of mixing is reduced when any species mixes with a system containing polymer chains as opposed to a system wholly comprised of relatively low molecule weight components. The implications of this study go far beyond the specifics of drying processes. These results indicated that polymer solutions may be unique in the importance of the coupling of diffusion between species and this mechanism may be important in other processes involving the diffusion of low molecular weight species in polymers such as polymer membrane separation processes and the devolatilization or purification of polymers.

References:

1. R. Pourdarvish, *Ph.D. Thesis*, The Pennsylvania State University, 2005.

2. S. Alsoy, J. L. Duda, *Journal of Polymer Science: Part B: Polymer Physics*, **37**, 1665 (1999).

3. P.E. Jr. Price, I. Hadj Romdhane, *AIChE Journal*, **49**, 2, 309 (2003).

4. E. L. Cussler, *Multicomponent Diffusion* (Elsevier, Amsterdam, 1976).

5. P. J. Flory, *Principle of Polymer Chemistry* (Cornell University Press: Ithaca and London, 1953).

6. C. Panayiotou, J. H. Vera, *Polymer Journal*, **14**, 681 (1982).

7. J. M. Zielinski, B. F. Hanley, *AIChE Journal*, **45**, 1, 1 (1999).

Acknowledgment:

We thank the 3M Corporation for funding of this project through the center for study of polymer-solvent systems, and Ilyess Hadj Romdhane, Peter Price and Craig Miller for assistance.

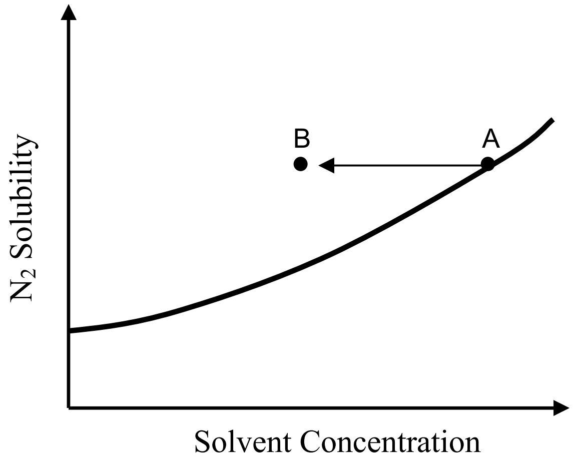

Figure 1: Typical behavior of nitrogen solubility in a polymer solution as a function of solvent concentration. A solution initially saturated with nitrogen at point A would become supersaturated as the solution dries and point B is approached.

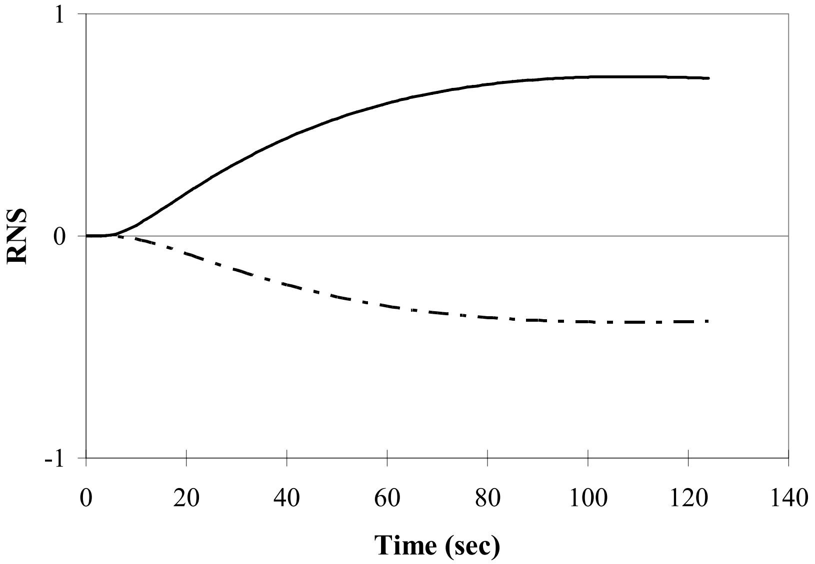

Figure 2: Model calculations for the relative solubility of nitrogen as a function of the drying time for a solution of polyvinyl acetate and toluene at 40°C. The lower dashed curve shows the relative nitrogen saturation at the bottom of the solution near the impermeable substrate based on the absence of coupling diffusion coefficients. The upper solid curve shows that supersaturation of nitrogen is predicted near the bottom of the solution when the coupling diffusivities are included in the model.

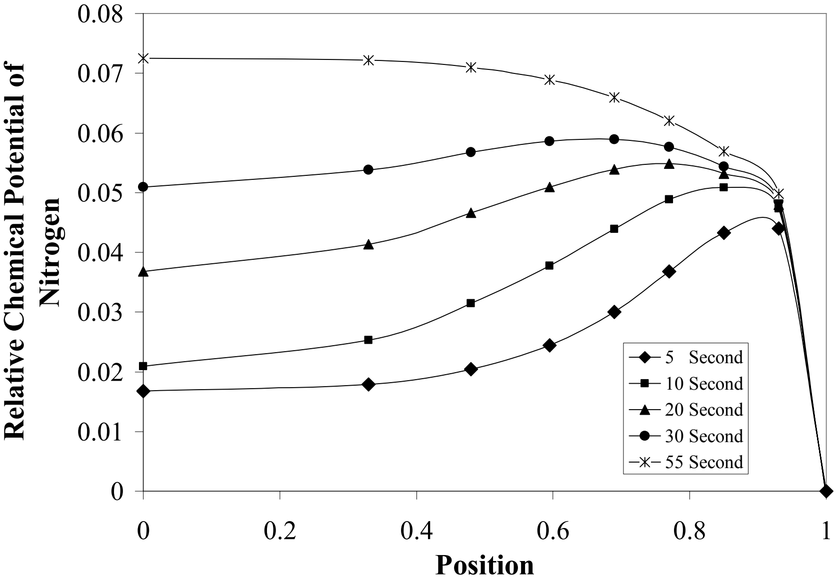

Figure 3: Model calculations for the relative chemical potential of nitrogen as a function of the drying time and the position for a solution of polyvinyl acetate and toluene at 40°C.

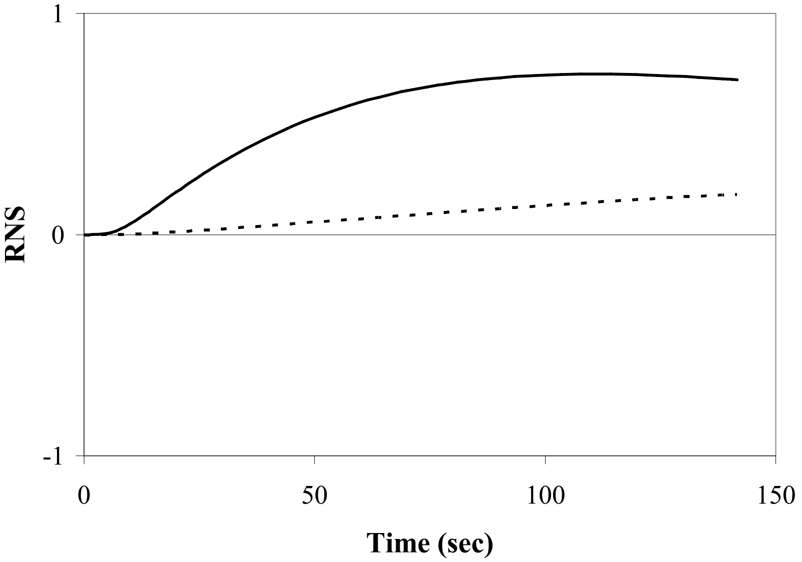

Figure 4: Influence of speed of drying on nitrogen supersaturation in a solution of polyvinyl acetate and toluene at 40° C. The mass transfer coefficient in a gas phase above the drying solution for the solid line is ten times the mass transfer coefficient used in the model to predict the lower dashed curve. The amount of nitrogen supersaturation is increased and the maximum occurs earlier in the drying process when the speed of drying is increased by increasing the velocity of the air over the polymer solutions.