Diffusion and Equilibrium Studies for the System Acrylonitrile-Styrene-Polyethylene

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The solubilities of acrylonitrile and styrene in low-density polyethylene were measured at 0° and 27°C. over the entire range of compositions.

The ternary solubility data were analyzed in terms of the relationships developed by Krigbaum and Carpenter. It is shown that the behavior of the ternary system may be predicted from the Flory-Huggins interaction constants of the three pairs of binaries.

The rates of desorption of acrylonitrile and styrene from 48 mil thick sheets of polyethylene were measured at 27°C.

The solubility and rates of diffusion of various liquids in polyethylene are of interest from a number of points of view. Information on these subjects can lead to a better understanding of the structure of the polyethylene (*1*), and this information can be of use to the chemical industry for very practical reasons. Recent work (*2*) has demonstrated the utility of polymeric membranes as a means of separating otherwise difficultly separable materials. It has also recently become apparent that the solubility and rate of diffusion of liquids in polymeric films are of great import in graft polymerization.

Many investigators have studied the solubility of various liquids in different polymers (3), and recently scientists have made an intensive study of the solubility and rates of diffusion of organic liquids of widely differing structure in polyethylene. There have however been relatively few investigations of systems of the type liquid 1-liquid 2-polymer, particularly on systems in which polyethylene was the polymeric component.

Diffusion in polyethylene is assumed to occur by the solution of the diffusing liquid at the surface of the polyethylene and subsequent migration of the diffusing liquid from the region of high activity to low activity. The polyethylene is a semicrystalline material composed of interspersed crystalline and amorphous regions, the diffusing liquid being assumed to be soluble in the amorphous regions only (*1*). The process of diffusion therefore takes place as it does in a true liquid and not by passage of material through pores and cracks in the polyethylene.

EXPERIMENTAL

Samples of polyethylene used in this investigation were low-density polyethylene, containing no additives, and molded into 48 mil thick sheets (*8*). This material had a density of 0.91 to 0.92 and a molecular weight (weight average) of 21,000. The styrene and acrylonitrile were used without further purification.

Samples of the polyethylene were first washed with benzene to remove any soluble grease or other organic matter. They were then dried in an oven at 50°C. until they reached constant weight. The weighed samples were then placed in small glass bottles to which weighed amounts of liquid with which the sample was to be equilibrated were added. The bottles were then closed with screw-cap tops and allowed to stand for 24 hr. at 27°C. in a constant temperature bath. It had previously been determined that 24 hr. were more than ample time to allow the samples to come to equilibrium. Sufficient liquid was used so that the change in concentration in the liquid phase caused by the absorption of the liquid into the polyethylene caused a negligible change in the liquid-phase composition. After 24 hr. the bottles were removed from the bath and opened. At the instant that the samples were removed from the liquid a timing sequence was started with a stop watch. The samples were dried thoroughly between two pieces of absorbent paper, and any adhering lint from the paper was removed with a brush containing a small amount of polonium which acted to remove static charges from the polyethylene. Use of this procedure is most important since the presence of static charges on the polyethylene can cause errors in weighing.

The samples of polyethylene, which had had a small hole punched in them before the initial weighing, were then hung vertically from a hook on an analytical balance, and the loss in weight of the sample as a function of the time was noted over a period of several hours. The sample was allowed to remain on the balance until it had attained its final constant weight. Room temperature during the runs was 27°C. ± 1°C. No significant loss in weight of the polyethylene at the end of the run was found, indicating negligible solubility of the polyethylene in the liquid. With weight loss vs. time measurements the value of the diffusion coefficient was calculated by the method to be described. Both the experimental method and the method of calculation are due to McCall (*7*). Equilibrium solubility of the liquid in the polyethylene was found by extrapolating the results back to zero time.

In order to obtain the composition of the liquid absorbed by the polyethylene a further series of experiments was performed. The equilibration experiments were repeated. After equilibration the samples were removed from the liquid, dried rapidly between two sheets of absorbent paper, and immediately immersed in a flask containing dry ice. The sample, while still in the dry ice, was irradiated in a cobalt-60 source for sufficient time to allow all of the absorbed material to polymerize. In this way the absorbed material was fixed either in or on the polyethylene, and the sample could then be analyzed for nitrogen by a micro-Kjeldahl technique. From the nitrogen analysis and the total weight gain the composition of the liquid absorbed into the polyethylene could be calculated. Data for total weight gains but not composition of the absorbed liquid were also obtained at O°C.

RESULTS

Solubility

The results of the solubility measurements of pure and mixed monomers in polyethylene are shown in Figures 1 and 2. Figure 1 is a plot of the total weight gain in grams of liquid per 100 g. of polyethylene vs. the weight percent styrene in the liquid. Figure 2 is a plot of mole fraction of styrene in the polyethylene on a polyethylene-free basis vs. the mole fraction styrene in the liquid.

In general it will be noted from Figure 1 that the styrene is considerably more soluble in the polyethylene than is the acrylonitrile. This is not surprising in view of the highly polar nature of the acrylonitrile and the relatively lower polarity of the styrene. Qualitatively the results seem to follow the rule that has been found to be applicable in so many other cases that like dissolves like. Hildebrand (3) has put this in more quantitative terms by noting that materials having a similar solubility parameter will tend to have a greater mutual solubility. The validity of this statement can be seen from the values of the solubility parameter: polyethylene 7.9 (*4*), styrene 9.3 (*3*), acrylonitrile 10.5 (*3*). In addition it can be seen that the solubility of mixtures does not vary linearly with the composition of the mixture. Examination of Figure 2 reveals that the styrene is preferentially absorbed into the polyethylene.

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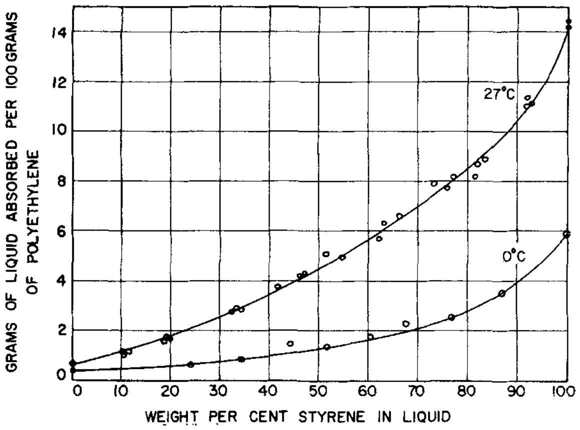

Fig. 1. Swelling of polyethylene by styrene acrylonitrile mixtures at 27° and 0°C.

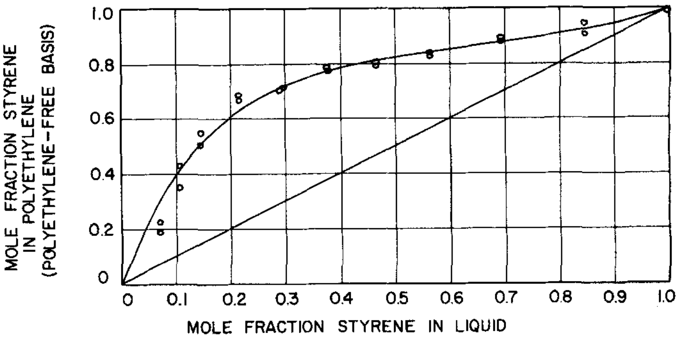

Fig. 2. Phase-equilibrium diagram for system styrene-acrylonitrile-polyethylene at 27°C.

The ternary solubility data for the system styrene-acrylonitrile-polyethylene can be analyzed quantitatively with the relationships developed by Krigbaum and Carpenter (5). In their development they assumed that the polymer was insoluble in the liquid phase and that the only reaction occurring was the swelling of the polymer by the liquid. This has been shown to be true in the case of polyethylene at the temperatures used in this investigation. If one therefore restricts the polymer to one phase and assumes that the swelling is occurring only in the amorphous regions of the polyethylene (*4*), then one can finally arrive at the following set of equations:

$$1/\phi_3 \ln \left[\frac{\phi_1 v_2}{v_1 \phi_2}\right] + (1-l) \ln \left(1-\phi_3-\frac{\epsilon}{v_2}\right) = (l\mu_{23}-\mu_{13}-\mu_{12}) + 2\mu_{12}\left(\frac{\epsilon}{\phi_3}+v_2\right) \quad (1)$$

$$(1-\phi_3+\epsilon/v_1)/(1-\phi_3-\epsilon/v_2) = \frac{\phi_1 v_2}{\phi_2 v_1} \quad (2)$$

Experimental data can be tested by plotting the left-hand side of Equation (1) vs. $(\epsilon/\phi_3 + v_2)$. The resultant plot should be a straight line with a slope of $2\mu_{12}$ and an intercept of $l\mu_{23} - \mu_{13} - \mu_{12}$. From the data shown in Figures 1 and 2 one can calculate the required quantities. Figure 3 is a plot of the left-hand side of the equations vs. $(\epsilon/\phi_3 + v_2)$.

The best straight line through the plotted points can be calculated by the method of least squares. Using this method one arrives at the following values for the slope and intercept of the line:

Slope	1.36
Intercept	4.11

One can immediately calculate the value of μ_{12} from the slope. Scott (6) has shown that the critical value of μ_{12} for two liquids is 2. Liquids with interaction constants greater than 2 are immiscible. Since styrene and acrylonitrile are completely miscible at the temperature in question, the value obtained for the interaction coefficient appears to be reasonable.

From the value of the intercept and the calculated value μ_{12} one can calculate the value of the term $l\mu_{23} - \mu_{13}$. If swelling data on the system styrene-polyethylene are available, the value of μ_{13} can be calculated and then, with this value, μ_{23} can be calculated. This value of the interaction coefficient for the acrylonitrile-polyethylene system can then be compared with the value calculated from the binary system, acrylonitrile-polyethylene data. The calculated values of the various constants are shown in Table 1.

Table 1. Flory-Huggins Interaction Constants in the System Styrene-Acrylonitrile-Polyethylene

	Ternary system	Binary system
μ(styrene-acrylonitrile)	0.68	0.68
μ(Styrene-polyethylene)	—	1.09
μ(acrylonitrile-polyethylene)	3.05	3.40

In view of the difficulty of measuring the extremely small solubility of acrylonitrile in polyethylene, the agreement between the values of μ(acrylonitrile-polyethylene) calculated by the two different methods can be considered good. It will be noted in Figure 3 that the one point which falls relatively far from the straight line through all the rest of the points is the one calculated from the data for a solution having a high acrylonitrile concentration and a low styrene concentration. It is in this region, where the total weight gain is smallest, that a small error in nitrogen analysis will cause a large error in the calculated value of the acrylonitrile concentration in the polyethylene.

As is noted from Equations (1) and (2) and borne out by the experimental data, the departure of the value of

$$R = \frac{\phi_1 v_2}{\phi_2 v_1}$$

from unity is greatest at high values of ϕ_3 and low values of v_1. In addition the agreement of the data with the theoretical prediction seems to justify the assumption that the phenomenon being observed is a case of absorption and not adsorption of the liquid on the surface.

The curve representing the solubility of the pure monomers and mixtures of the two monomers in the polyethylene at 0°C, is also shown on Figure 1. In general it is seen that the solubility in polyethylene is decreased at the lower temperature, as one might expect.

Some experiments were also performed to determine the solubility of the pure monomers in samples of polyethylene to which had been grafted varying amounts of pure styrene and pure acrylonitrile. The results of some of these experiments are shown in Figure 4. As grafting occurs, the base material is no longer pure polyethylene but some new material which possesses the properties of the base polyethylene and the

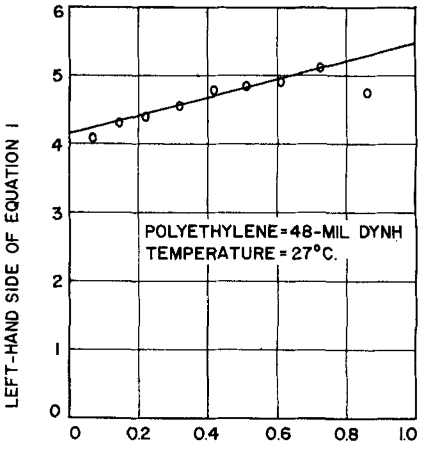

Fig. 3. Correlation of phase-equilibrium data by the method of Krigbaum and Carpenter.

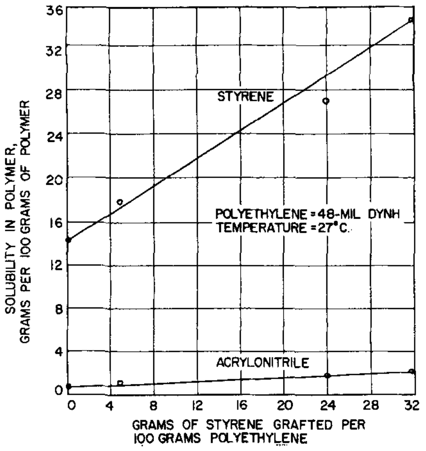

Fig. 4. Effect of grafting styrene to polyethylene on the swelling of the resultant polymer by styrene and acrylonitrile.

grafted monomers. On the basis of those considerations one might expect the solubility of the monomers in the grafted material to increase as the amount of grafting increases. One can again correlate this expectation with the Hildebrand solubility parameter. As either styrene or acrylonitrile is grafted to the polyethylene, the solubility parameter of the new polymer becomes closer to that of the monomers. Actually since the solubility parameter of the acrylonitrile is larger than that of the styrene, one would expect that the grafting of a small amount of acrylonitrile would have the same effect as the grafting of a larger amount of styrene. That this is not necessarily the case can be seen from the data in Table 2 which show the solubilities and percentage increase in solubilities of the monomers as a function of the amount and type of monomer grafted.

Acrylonitrile is not a more effective solubilizing agent for the styrene when the acrylonitrile is grafted because acrylonitrile is a highly polar material. In addition the significance of the solubility parameter for such a highly polar material is somewhat in doubt. Although no data are available, it is assumed that the liquid absorbed in a grafted polyethylene sample from a mixture of the two monomers will be richer in acrylonitrile than is the liquid absorbed in a nongrafted sample from a solution of the same composition. Thus as grafting proceeds, one might expect that the absorbed liquid will become progressively richer in acrylonitrile and the composition of the graft polymer will change correspondingly.

Diffusion

The diffusion process is assumed to follow Ficks law:

$$\frac{\partial C}{\partial t} = \nabla \cdot (D\nabla C)$$

If one considers a slab whose area is large and whose thickness is small, then one can assume that all of the diffusion occurs through the two faces of the slab. Based on this assumption and the fact that the diffusion coefficient is a function of the local concentration of the diffusing liquid (7), the following relationship can be obtained:

$$\frac{\partial C}{\partial t} = D_o \frac{\partial^2}{\partial x^2} [\int f(C)dC]$$

where $D = D_o f(C)$.

This equation has been solved by McCall using a finite difference method similar to that used by Schmidt in heat conduction problems. McCall, using an IBM-650, computer has calculated the theoretical concentration profile for a selected form of

$$f(C) = e^{\delta C}$$

Using these profiles one can calculate the quantity of liquid remaining in the slab at any time during a desorption process by

$$Q = \int_0^L C dx$$

Theoretical curves of Q/C_oL vs. time for different values of the parameter δ can be calculated and the experimental data compared with the theoretical curves. The comparison is made in the following manner. The time for the value of Q/C_oL to fall to 0.5 is determined experimentally. From the theoretical curve for a given value of δ the number of steps required for the theoretical value of Q/C_oL to fall to 0.5 is calculated. From this value the time per step is calculated, from which a curve can be constructed of Q/C_oL for selected values of the time. This curve is then compared with the experimental curve and the closeness of fit determined. This process is repeated for various values of δ until the calculated and the theoretical curve agree. The value for which the calculated and experimental curves agree is taken as the proper value of δ. It can be shown that the shapes of the curves are not too sensitive to changes in δ so that the value of δ is probably accurate only to ±0.5.

Table 2. Solubility and Percentage Increase in Solubility of Styrene and Acrylonitrile in Samples of Polyethylene Grafted with Styrene and with Acrylonitrile

	No graft	Styrene graft*	Acrylonitrile graft†
Styrene solubility	14.4	34.2	15.8
% increase in solubility	—	124.0	11.0
Acrylonitrile solubility	0.67	2.0	1.8
% increase in solubility	—	200.0	170.0

* 32 g. of styrene/100 g. of polyethylene.
† 7.4 g. of acrylonitrile/100 g. of polyethylene.

There are two ways of calculating D_o. The most accurate method is to measure the slope of the curve of the ln Q vs. t at a time when $Q < C_oL/100$. Under such conditions C is very small, and D in the equation

$$D = D_o e^{\delta C}$$

will be very close to D_o.

Such a procedure can be used for materials which have an appreciable solubility in polyethylene and whose rate of desorption is accurately measurable at the low value of Q/C_oL required. It is seen from the experimental desorption-rate data that the rate of desorption of the acrylonitrile is much slower than that of the styrene. In addition the solubility of the acrylonitrile in polyethylene is much lower than that of the styrene. Under these conditions, it is impossible to measure the diffusion rate of acrylonitrile at very low values of Q/C_oL, and another less accurate method for the evaluation of D_o must be used.

From the equation

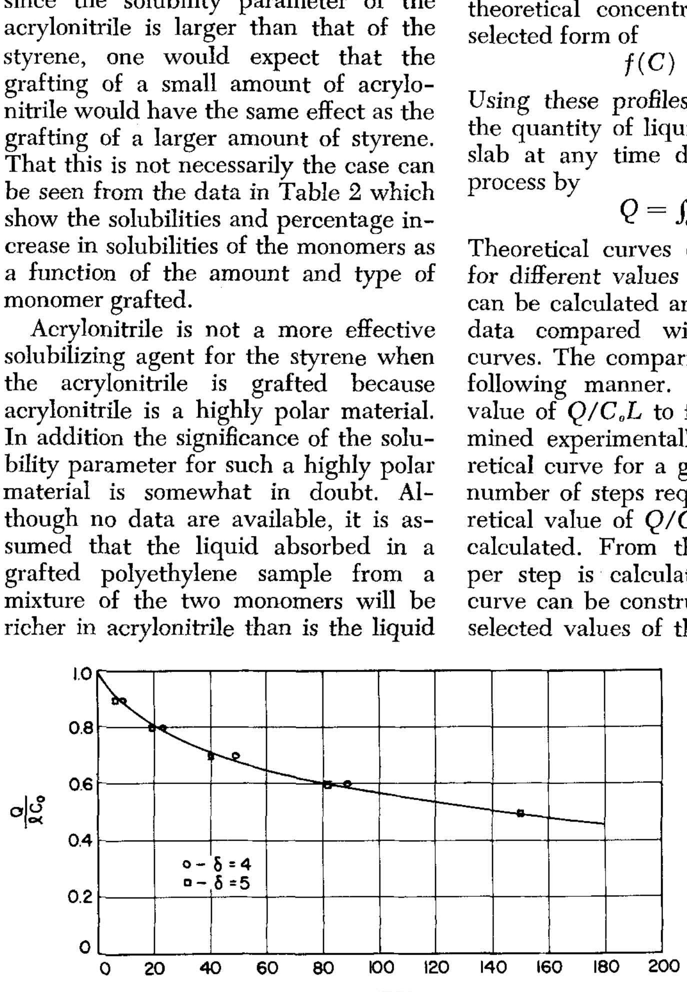

Fig. 5. Desorption of styrene from 48-mil dynh polyethylene at 27°C.

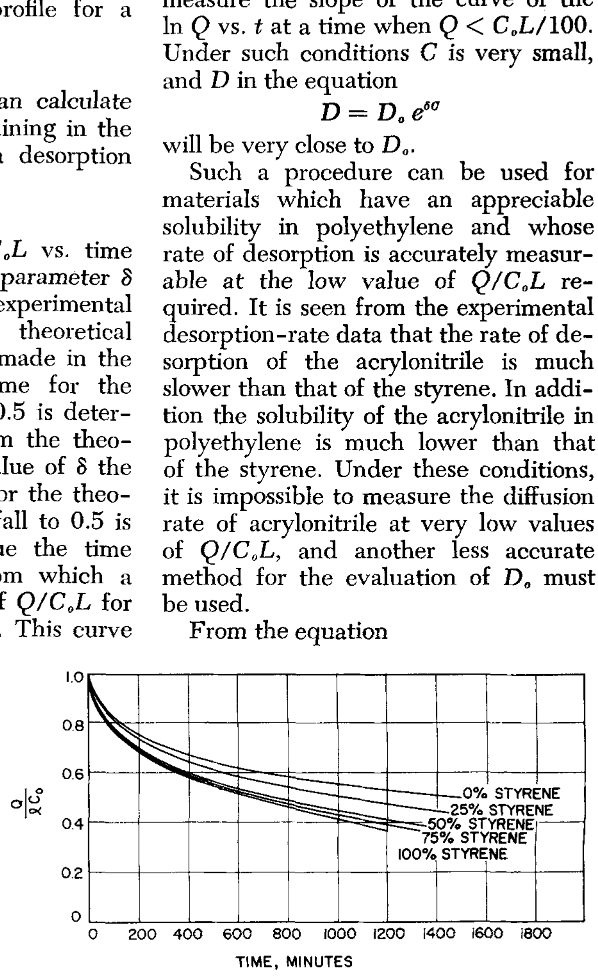

Fig. 6. Desorption of liquid from 125-mil dynk polyethylene at 27°C.

TABLE 3. COMPARISON OF MCCALL AND SLICHTER'S DATA WITH THOSE FROM THIS INVESTIGATION

Material	D_o	δ
Styrene	1.06	4
Benzene	1.18	4

$$K \equiv \frac{D_o \, \Delta t}{(\Delta x)^2}$$

where K, for convenience, is taken as 0.3, the value of D_o can be calculated if Δt and $(\Delta x)^2$ are known. Δx is easily obtained by dividing the measured thickness of the film by 20, since in the original theoretical calculations the slab was divided into 20 compartments. Δt the time interval for a step is calculated as described in McCall's original paper. The value of D_o calculated from the above equation will depend on the value of δ that is used. It has already been shown that the shape of the desorption curve is not very sensitive to changes in the value of δ, so that there may conceivably be a large error in the value of D_o calculated by this method.

In order to compensate for this error in the case of acrylonitrile the value of D_o for styrene was computed by both of the above methods and the ratio of the two values of D_o calculated. The value of D_o for acrylonitrile was then calculated by the second method, and it was arbitrarily assumed that the ratio would be the same for the acrylonitrile as it was for the styrene. With this assumption a more correct value of D_o is calculated for the acrylonitrile.

Figure 5 shows sample experimental curves for the desorption of styrene and acrylonitrile from polyethylene at 27°C. The points on these curves are calculated from a theoretical curve by means of the best value of δ shown on the individual curves. Using the best values of D_o and δ for several runs with each liquid one obtains the following equations for the diffusion coefficients for styrene and acrylonitrile in DYNH polyethylene:

$$D_{st} = 1.06 \times 10^{-8} \, e^{4C}$$

$$D_{an} = 0.34 \times 10^{-8} \, e^{2.7C}$$

C varies from 0 to 1.

TABLE 4. COMPARISON OF D FOR ACRYLONITRILE AND STYRENE AT EQUIVALENT MOLAR CONCENTRATIONS IN POLYETHYLENE

	Styrene	Acrylonitrile
Saturation concentration, g./100 g. polyethylene	—	0.7
Equivalent molar conc.	0.0132	0.0132
C	0.0955	1
D	1.55×10^{-8}	5.1×10^{-8}

It is seen from these values that the diffusion coefficient for styrene is greater than that for acrylonitrile and also varies more with the concentration. At first thought this result might seem surprising. The styrene is a relatively large and bulky molecule, while the acrylonitrile is a more nearly linear molecule. On this basis one might expect that the acrylonitrile would diffuse more rapidly. However when one considers the highly polar nature of the acrylonitrile in comparison with the styrene, this result is not so surprising. This phenomenon has already been seen in the low solubility of the acrylonitrile in the polyethylene. McCall and Slichter (*1*) in their recent study of the diffusion rates of several hydrocarbons in polyethylene have computed the values of D_o and δ for benzene by the first method described. A comparison of their values for D_o and δ for benzene with those determined for styrene in this investigation is shown in Table 3. The value of D (acrylonitrile) is less than D (styrene) for any given value of C. However when the values are compared at equal molar concentration in the polyethylene, it is seen that the value of D (acrylonitrile) is greater than that of D (styrene). As an example the value of D is computed for acrylonitrile and for styrene at a molar concentration equivalent to the saturation concentration of acrylonitrile in polyethylene. These values are shown in Table 4. From this it can be seen that the acrylonitrile has a better plasticizing action than has the styrene, per molecule absorbed.

A series of auxiliary experiments was performed with samples of DYNK polyethylene with a molecular weight of 30,000. The desorption rates were measured on samples 125 mils thick in the same way as described previously. Over-all rates of desorption were measured for mixtures of styrene and acrylonitrile ranging in composition from pure styrene to pure acrylonitrile. The results of these experiments are shown in Figure 6. McCall (*7*) has demonstrated that the value of Q/C_oL is independent of the sample thickness. Since all of these samples were prepared in the same manner as the DYNH samples, the results should be comparable. It is seen that the desorption rate decreases as the percentage acrylonitrile in the absorbed liquid increases. These experiments do not however indicate how rapidly the individual monomers in the mixture diffuse. Such information could be obtained by continuously analyzing the samples for one of the components of the mixture as the desorption proceeds.

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NOTATION

C = fraction of saturation concentration
C_o = saturation concentration
D = diffusion coefficient, sq. cm/sec
D_o = diffusion coefficient at $C = 0$
K = scale factor
L = slab thickness
Q = quantity of liquid remaining in slab at any time, t
R = $\dfrac{\phi_1}{\phi_3} \Big/ \dfrac{v_1}{v_2}$
t = time
v_1 = volume fraction of liquid 1 in liquid phase
v_2 = volume fraction of liquid 2 in liquid phase
V_1 = molar volume of liquid 1
V_2 = molar volume of liquid 2
x = space coordinate
l = V_1/V_2

Greek Letters

δ = constant
ϵ = variable defined by Equation (2)
μ = Flory-Huggins interaction parameter
ϕ_1 = volume fraction of liquid 1 in ternary phase
ϕ_2 = volume fraction of liquid 2 in ternary phase
ϕ_3 = volume fraction of polymer in ternary phase

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