Starch Urea–Formaldehyde Matrix Encapsulation. IV. Influence of Solubility and Physical State of Encapsulant on Rate and Mechanism of Release*

P. G. SHUKLA, N. RAJAGOPALAN,† and S. SIVARAM

Polymer Chemistry Division, National Chemical Laboratory, Pune 411 008, India

SYNOPSIS

The influence of the physical state and solubility of the encapsulant on the rate and mechanism of release and swelling of the cross-linked starch–urea formaldehyde (St–UF) matrix has been studied by encapsulating model organic compounds. The release and swelling data have been analyzed in terms of the generalized equation $M_t/M_\infty = kt^n$ applicable for swellable controlled-release systems. This matrix system shows an inverse relationship of release rate with the cross-link ratio for all the encapsulants studied. The solid encapsulants have n values in the range of 0.22–0.41, indicating a Fickian or anomalous mechanism. Further, the release rate increases with solubility of the encapsulant. The liquid encapsulants have n values in the range of 0.5–1.5, indicating Case II or Super Case II transport mechanism. The release rates for liquid encapsulants are lower by one to three orders of magnitude than those for solid encapsulants and are not influenced by encapsulant solubility. This indicates a polymer chain relaxation-controlled mechanism of release for liquid encapsulants.

INTRODUCTION

Use of starch cross-linked with urea–formaldehyde (UF) as a matrix system for encapsulation of pesticides and the study of their release characteristics has been the subject matter of our previous publications.[1-4] To gain further insight into the release mechanism, we have encapsulated selected model organic compounds and studied the effect of their physical state and solubility in water on the swelling and release kinetics. This paper reports the results of this study.

EXPERIMENTAL

A. Materials

Maize starch powder from Anil Starch Product Ltd., India, was used as received. Urea (extra pure), formalin solution (37–40%) (S. D. Fine Chemicals Pvt. Ltd., India), and formic acid (Loba Chemie Industrial Co., India) were used as received. Sodium hydroxide was used as 0.6% solution in water. Spectral-grade methanol was used for all UV measurements. Model compounds used were 4-nitrophenol and acetanilide (Loba Chemie Ind. Ltd., India), dimethyl phthalate (Aldrich), 3-nitrotoluene (SISCO Research Laboratories Pvt. Ltd., India), and nitrobenzene (Indian Drugs and Pharmaceutical Ltd., India).

B. Encapsulation Procedure

Encapsulation of all compounds was carried out as described previously.[1] However, in the case of liquid encapsulants, the cross-linked product was wet-sieved through 5 mesh and dried in an air-draft oven at 35°C. The dried −5 + 10 mesh fraction was used for our studies. In one of the experiments (sample L3AM, Table II), the liquid compound was first mixed with UF prepolymer and subsequently with gelatinized starch.

* NCL Communication No. 5010.
† To whom correspondence should be addressed.

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C. Analysis

The quantity of the model compound incorporated into the matrix was estimated by a UV method using a UV-VIS spectrophotometer (Hitachi Model 220). Swelling and release-rate studies were conducted using procedures standardized earlier.[1]

RESULTS AND DISCUSSION

The six compounds used in the present study and their physical properties are given in Table I. All compounds were encapsulated using different urea to starch w/w ratios (X = 0.2, 0.4, 0.6, and 0.8). Samples with solid compounds were prepared with 3% and 20% w/w loadings. With liquid compounds, the matrix could not be loaded beyond 10% w/w. The samples prepared during the present study are listed in Table II. Additional studies on release of carbofuran from samples C3 and C6 were carried out in a 70% methanol–water mixture.

A good agreement between calculated and obtained values of % loading was noticed for both the solid compounds and dimethyl phthalate (liquid). But the other two liquid compounds gave % loading values that were less than calculated (Table II), presumably due to the evaporation during the encapsulation process because of their much higher vapor pressure (Table I). By modifying the encapsulation procedure (sample L3AM), % loading could be increased from 6.5 to 7.7%. To confirm that all the encapsulated material was being extracted by methanol–water mixture, the % loading of sample L3AM (with nitrobenzene) was determined by repeated extraction and also by degrading the starch–urea formaldehyde (St–UF) matrix by heating the sample in 2N HCl. The results were comparable.

A. Release of an Encapsulant from a Swellable Polymeric System

In the case of a nonporous swellable system when a glassy polymer is placed in contact with the penetrant, it undergoes macromolecular chain relaxation and volume expansion due to absorption of penetrant.[8,9] As a result, two distinct regions, namely, glassy and rubbery (gel), are established, separated by a sharp boundary that moves inward into the glassy polymer as additional penetrant is absorbed. The penetrant uptake can be analyzed by a generalized eq. (1):

$$(M_t/M_\infty)_s = k_s t^n \qquad (1)$$

where $(M_t/M_\infty)_s$ is the fractional uptake of penetrant at time t; k_s, a constant characteristic of the polymer–penetrant system; and n, an exponent characteristic of the mechanism of the penetrant transport. When the diffusion of the penetrant through the gel region is very slow as compared with the rate at which the gel–glassy polymer interface moves inward into the glassy core, the Fickian mechanism is observed with n = 0.5 (for a planar system). But when the relaxation process at the gel–glassy polymer interface is slower than the penetrant diffusion in the gel region, this interface advances at a constant velocity, resulting in a Case II or zero-order mechanism giving n = 1. The third type of mechanism, called non-Fickian or anomalous transport, with $0.5 < n < 1$, results when the dif-

Table I Physical Properties of Model Compounds

Model Compound	Nature	mp/bp[a] (1 atm) (°C)	Vapor Pressure[b] (mm) of Mercury at 35°C	Solubility in Water[a] at 25°C (ppm)	λ_{max} (nm)[d] (Water)
4-Nitrophenol	Solid	114.0	—	16,000	317
Acetanilide	Solid	113.5	—	5,400	238
Carbofuran	Solid	153.0	—	1,000[d]	278
3-Nitrotoluene	Liquid	230.0	0.4285×10^{-1} [c]	500	272
Nitrobenzene	Liquid	211.0	0.5486	1,900	267
Dimethyl phthalate	Liquid	282.0	0.2625×10^{-3}	4,300	276

[a] These properties are from Ref. 5.

[b] Vapor pressure at 35°C was calculated by the Antoine equation from the A, B, and C constants given in Ref. 6.

[c] As A, B, and C constants for 3-nitrotoluene were not available, and as vapor pressures of 2-nitrotoluene and 3-nitrotoluene at 50°C are similar (as shown in Ref. 5), the vapor pressure of 3-nitrotoluene at 35°C was calculated using the A, B, and C constants of 2-nitrotoluene.

[d] These values were determined in the present study.

Table II Description of Samples Used in the Study

Sample No.	Encapsulant	Urea/Starch Ratio w/w (X)	% Loading (w/w) Calculated	% Loading (w/w) Obtained
S1A	4-Nitrophenol	0.2	20.7	19.9
S1B		0.4	21.0	19.9
S1C		0.6	20.1	20.8
S1D		0.8	19.5	19.0
S1A3		0.2	3.2	3.1
S2A	Acetanilide	0.2	20.1	21.1
S2B		0.4	20.5	21.0
S2C		0.6	18.9	19.3
S2D		0.8	18.6	19.9
S2A3		0.2	3.2	3.2
L1A	3-Nitrotoluene	0.2	10.9	6.8
L1B		0.4	10.0	5.3
L1C		0.6	9.8	6.7
L1D		0.8	9.8	5.2
L2A	Dimethyl	0.2	9.9	11.3
L2B	phthalate	0.4	9.6	9.9
L2C		0.6	9.7	10.7
L2D		0.8	9.4	10.5
L3A	Nitrobenzene	0.2	10.8	6.5
L3AM		0.2	10.7	7.7
L3B		0.4	10.1	5.2
L3C		0.6	10.2	5.9
L3D		0.8	10.2	3.6
C1	Carbofuran[a]	0.2	3.06	3.07
C3		0.6	2.37	3.73
C6		0.6	19.46	19.66
B1	Without encapsulant	0.2	—	—
B2	(blank[a])	0.4	—	—
B3		0.6	—	—
B4		0.8	—	—

[a] For sample preparations see reference 1.

fusion and relaxation rates are comparable. In some of the systems, the value of n is found to be greater than one and the mechanism is called Super Case II transport. So far, very few examples are available that describe Super Case II transport.[10,11] Super Case II transport is observed at the end of the Case II transport in which the gel–glassy interface moves inward at a constant velocity and controls the size of the Fickian wave ahead of this interface. The change in the mechanism of transport from Case II to Super Case II occurs when the Fickian waves, advancing from both sides of the glassy core, meet at the center of the polymer. As a result, the expansion forces are exerted by the outer swollen gel region on the glassy core. This causes the rapid increase in the concentration of penetrant in the highly stressed glassy core. Thus, Super Case II transport is also called accelerated Case II transport. When the interface velocity is relatively low, the Fickian waves extend far ahead of the moving boundary and Super Case II begins early in the swelling experiment. But when the moving boundary advances rapidly as compared to Fickian diffusion into the glassy core, Super Case II transport is observed later during the experiment. If these Fickian waves do not overlap, then perfect Case II transport is observed until the end of the experiment.

When a swellable controlled-release system containing solute is brought into contact with the penetrant, in addition to swelling processes, the diffusion of solute through the swollen region (gel) to the external medium also takes place. The mecha-

nism of release can also be described by eq. (2) analogous to eq. (1):

$$M_t/M_\infty = kt^n \qquad (2)$$

where M_t/M_∞ is the fractional solute release at time t, k is a constant characteristic of the polymer–solute system, and the value of n gives the type of release mechanism.[12] The release of solute from the polymer system is determined by the relative position and velocity of the gel–glassy polymer interface.[8] When velocity of this interface is rapid as compared with the rate of solute transport through the gel region, the Fickian release mechanism is observed with $n = 0.5$, implying a decreasing release rate with time. If the diffusion of solute through the gel polymer is faster and the advancing of the gel–glassy interface becomes rate-determining, the release rate of the solute will be constant with time (zero order or Case II release with $n = 1$). The Super Case II release mechanism is observed when the release exponent n is greater than one, implying an increasing release rate with time. The Super Case II release of Sudan Red IV dye from the polystyrene film in the presence of n-hexane has been reported.[13] With Arrhenius plots it was shown that the mechanism of n-hexane sorption in polystyrene film controls the observed kinetics of dye release. These descriptions, however, are applicable only to a polymer system with a planar geometry.

Ritger and Peppas computed the n values for Fickian and Case II transport to be 0.45 and 0.89, respectively, for a cylindrical and 0.43 and 0.85 for a spherical polymer system.[14] For a certain specific distribution of spherical particles, Ritger and Peppas computed values of n as low as 0.3 and 0.45 for Fickian and Case II transport, respectively. Further reduction in their values could be expected when dealing with a polydisperse system of irregular shapes. Thus, in the case of the St–UF carbofuran system consisting of irregular granules, the bulk release showed that the n value is ~ 0.25, indicating Fickian or anomalous transport and single-particle release could confirm the mechanism to be anomalous, giving n values in the range of 0.55–0.65.[1] Case II release ($n = 1$) is not expected with particles of spherical geometry. It was also shown that the St–UF system

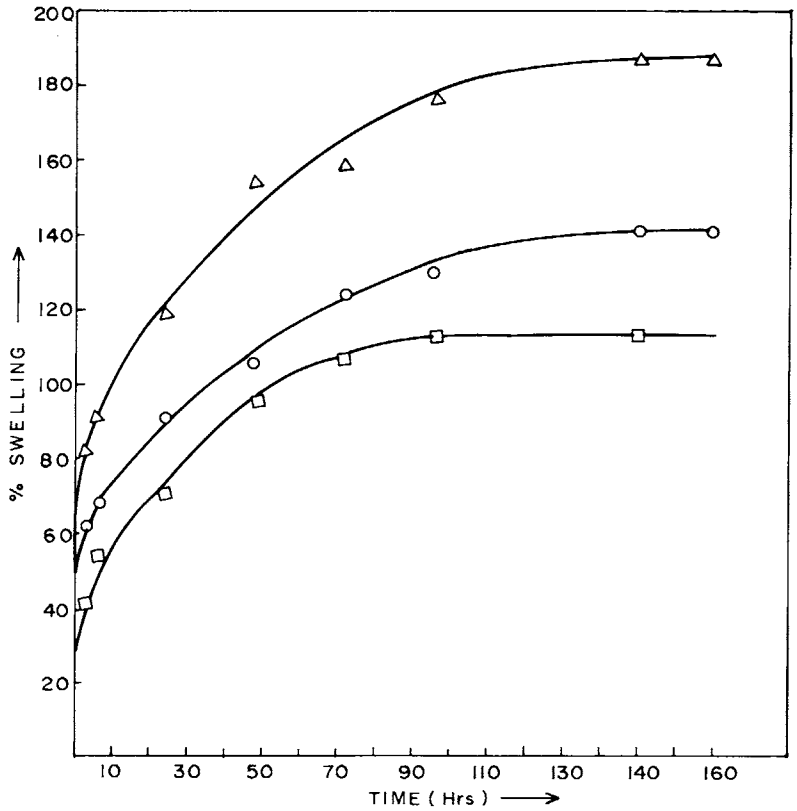

Figure 1 Plot of % swelling vs. time for St–UF samples containing (□) carbofuran, (○) acetanilide, and (△) 4-nitrophenol.

Table III Swelling Constant k_s and Diffusional Exponent n for St–UF Samples Containing Solid Encapsulant (~ 3% Loading)

Encapsulant (Sample No.)	Solubility in Water C_s (ppm)	$k_s \times 10^2$ $(\text{min})^{-n}$	Correlation Coefficient r	n	95% Confidence Level for n	
					Upper Limit	Lower Limit
Carbofuran (C1)	1,000	9.75	0.993	0.2834	0.3784	0.1884
Acetanilide (S2A3)	5,400	18.67	0.996	0.2248	0.2863	0.1633
4-Nitrophenol (S1A3)	16,000	25.10	0.994	0.2229	0.3036	0.1422

with solid encapsulant like carbofuran at higher loading has a porous structure.

B. Swelling Studies

Figure 1 shows the plots of percentage swelling as a function of time for samples C1, S1A3, and S2A3 containing carbofuran, 4-nitrophenol, and acetanilide, respectively. The swelling data was analyzed by eq. (1) and the values of the k_s and n are listed in Table III. The n values are similar (0.22–0.28) for all the three samples with 95% confidence limits of 0.14–0.38, implying that the swelling mechanism could be either Fickian or anomalous. However, the k_s value increases with increase in solubility of the encapsulant in water, indicating the osmotic effect (Fig. 2). This osmotic effect is a result of the presence of solute (encapsulant) in the polymer matrix.[1,15–17] Thus, as the water enters the matrix, solute in the matrix dissolves, creating a greater driving force for water to enter the matrix. In a previous paper,[1] we had shown that the osmotic effect is observed at lower levels of cross-linking. At higher levels of cross-linking, the increase in hydrophobicity seems to offset the osmotic effect.

Thus, 4-nitrophenol, having highest solubility in water (16,000 ppm), showed a faster rate of swelling ($k_s = 25.1 \times 10^{-2}$) and a higher equilibrium swelling, whereas carbofuran, with the lowest solubility (1000 ppm), showed a slower swelling rate ($k_s = 9.75 \times 10^{-2}$) and a lower equilibrium swelling. Acetani-

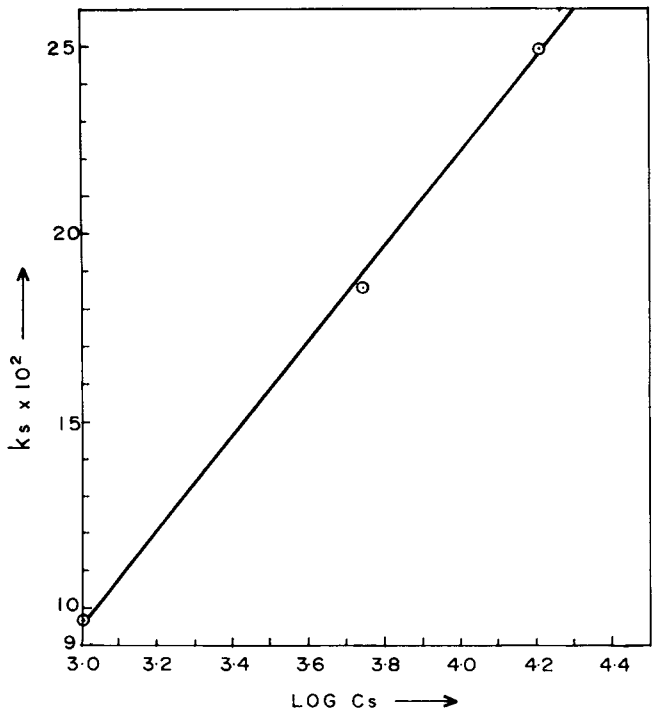

Figure 2 Correlation between swelling rate constant (k_s) and solubility of encapsulant (C_s).

lide, having a solubility of 5400 ppm, showed an intermediate k_s value (18.67×10^{-2}).

C. Release of Solid Encapsulants

Release-rate profiles of 4-nitrophenol and acetanilide samples having different degrees of cross-linking (X) are shown in Figures 3 and 4, respectively. k and n values calculated by eq. (2) are listed in Table IV. The release rate decreases with increase in degree of cross-linking from $X = 0.2$ to $X = 0.6$ for both encapsulants. By further increasing the X to 0.8, the release rate for 4-nitrophenol increased similarly to carbofuran,[1] but acetanilide showed further reduction in the release rate at $X = 0.8$.

The release rate constant k decreases with increase in the degree of cross-linking from $X = 0.2$ to $X = 0.6$ (sample nos. S1A, S1B, and S1C). This is expected because as the degree of cross-linking is increased, the hydrophilicity of the matrix is decreased,[1] the matrix structure becomes denser, and, thus, the rate of diffusion of the encapsulant through the swollen matrix decreases. The observed anomaly at $X = 0.8$ is attributed to two causes: (1) The optimum degree of cross-linking is obtained for a molar ratio of ~ 2.0 (urea: anhydroglucose repeating unit in the starch molecule) at $X = 0.6$; and (2) microvoids and cracks are produced by the internal stresses caused by the rigid nonhydrophilic UF condensates at $X = 0.8$. Similar to carbofuran, the n value remains almost constant, 0.40 ± 0.01, for samples S1A, S1B, and S1C, indicating that the release mechanism is not affected by a change in the degree of cross-linking.

In contrast, for acetanilide, the release rate further decreases from $X = 0.6$ to 0.8 and k remains constant but n decreases with increase in degree of cross-linking (sample nos. S2A, S2B, S2C, and S2D). The reason for the difference in behavior of 4-nitrophenol and acetanilide is not very clear at the present time.

D. Effect of Encapsulant Solubility

Results of effect of the encapsulant's solubility in the eluting medium with respect to different parameters like degree of cross-linking and % loading are shown in Figures 5 and 6 and Tables V and VI.

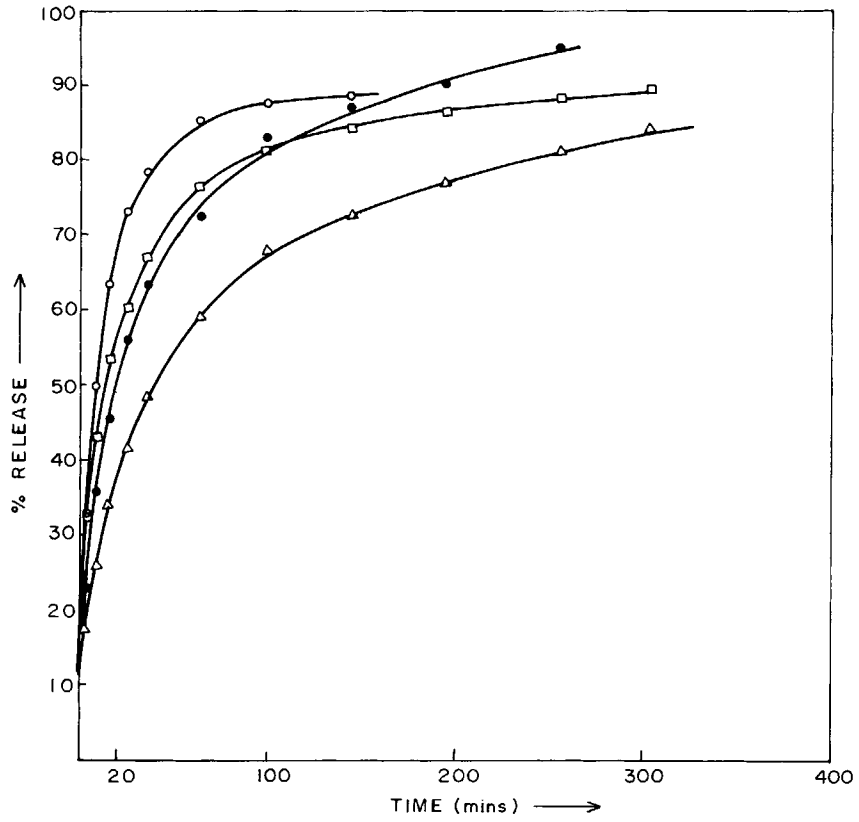

Figure 3 Release profiles of St–UF samples containing 4-nitrophenol having different levels of cross-linking X = (○) 0.2, (●) 0.4, (△) 0.6, and (□) 0.8.

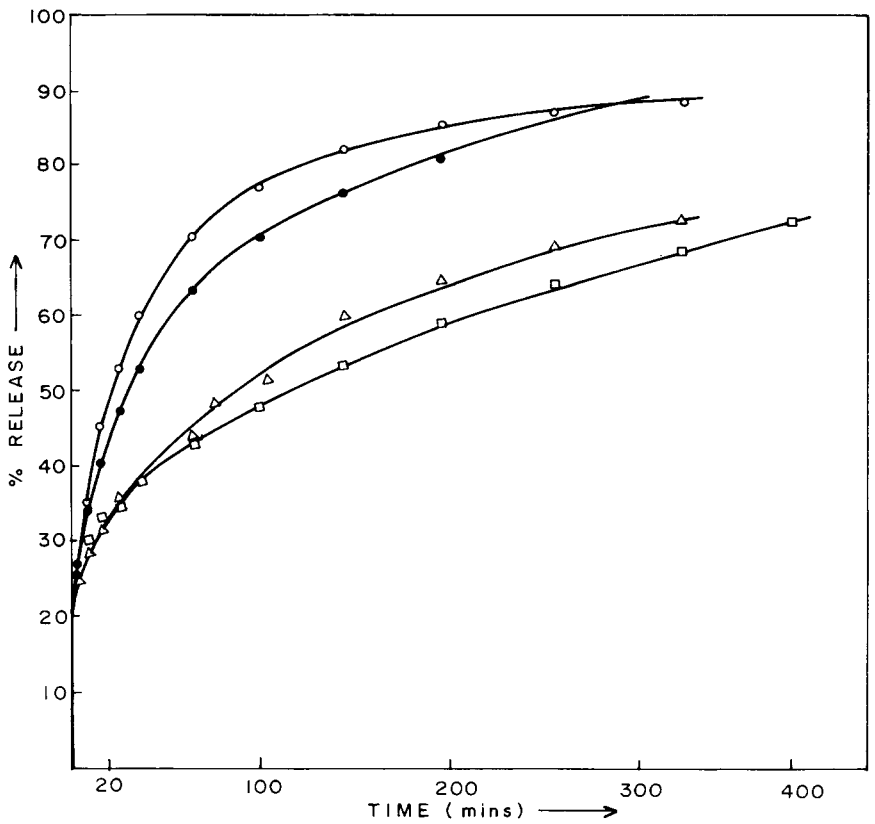

Figure 4 Release profiles of St–UF samples containing acetanilide having different levels of cross-linking X = (○) 0.2, (●) 0.4, (△) 0.6, and (□) 0.8.

Release of the encapsulant from a porous swellable system is a composite of two transport phenomena,[7,18] and the effective diffusion coefficient D_{eff} can be given by

$$D_{eff} = D_{iw}\epsilon^{5/3}/\tau + D_{ip}(1 - \epsilon^{2/3}) \qquad (3)$$

where D_{iw} and D_{ip} are the diffusion coefficients of the encapsulant in pure solvent and in swollen polymer, respectively, and ϵ is the porosity and τ is the tortuosity of the matrix. First, as the eluting solvent penetrates into the system, pores are filled with solvent through which the encapsulant diffuses to the surrounding medium. This diffusivity is governed by the encapsulant–solvent interaction that is related to the solubility of encapsulant in the eluting

Table IV Release Rate Constant k and Diffusional Exponent n of St–UF Samples Containing 4-Nitrophenol (S1) and Acetanilide (S2)

Sample No.	$k \times 10^2$ (min)$^{-n}$	Correlation Coefficient r	n	95% Confidence Level for n	
				Upper Limit	Lower Limit
S1A	20.19	0.9888	0.3952	—	—
S1B	14.01	0.9903	0.4159	0.6614	0.1704
S1C	10.86	0.9935	0.4012	0.5235	0.2789
S1D	20.31	0.9888	0.3314	0.6030	0.0598
S2A	15.60	0.9974	0.3733	0.4999	0.2467
S2B	17.56	0.9994	0.3085	0.3672	0.2498
S2C	14.04	0.9962	0.2859	0.3468	0.2250
S2D	14.04	0.9979	0.2727	0.3198	0.2256

solvent. Second, as the solvent penetrates into the system, progressive swelling of polymer occurs, leading to structural changes. The diffusion of the encapsulant also occurs through the swollen polymer and is not governed by the encapsulant solubility in the eluting solvent. In the case of a nonporous swellable system, when $\epsilon \rightarrow 0$, the latter transport mechanism assumes importance. Thus, release of the encapsulant is not dependent on its solubility in the eluting solvent.

When the release rate of carbofuran at the optimum degree of cross-linking ($X = 0.6$) and at lower loading (3%) (sample no. C3) was studied in the methanol–water mixture (70% methanol), the initial release was faster in the mixture than in water alone, but, subsequently, became very slow. The same matrix with 20% carbofuran (sample no. C6) showed a very fast release in the mixture over the entire release range (Fig. 5). Thus, for the St–UF matrix at lower loading (3%), the release rate is governed mostly by the second term of eq. (3), and at higher loading (20%), it is completely governed by the first term. These observations show that the St–UF matrix at lower loading (3%) results in a less porous nature, whereas higher loading (20%), it results in a more porous nature.

The effect of solubility on release rate was studied by comparing the release data of samples having the same degree of cross-linking ($X = 0.6$) and loading (20%) but with different encapsulants (samples C6, S1C, and S2C; Table V). 4-Nitrophenol, having the highest water solubility, showed a faster release ($t_{50\%}$ = 40 min) compared to acetanilide ($t_{50\%}$ = 86 min), whereas carbofuran, having the lowest solubility, showed a slower release ($t_{50\%}$ = 412 min). Similar results have been reported for the release of drugs

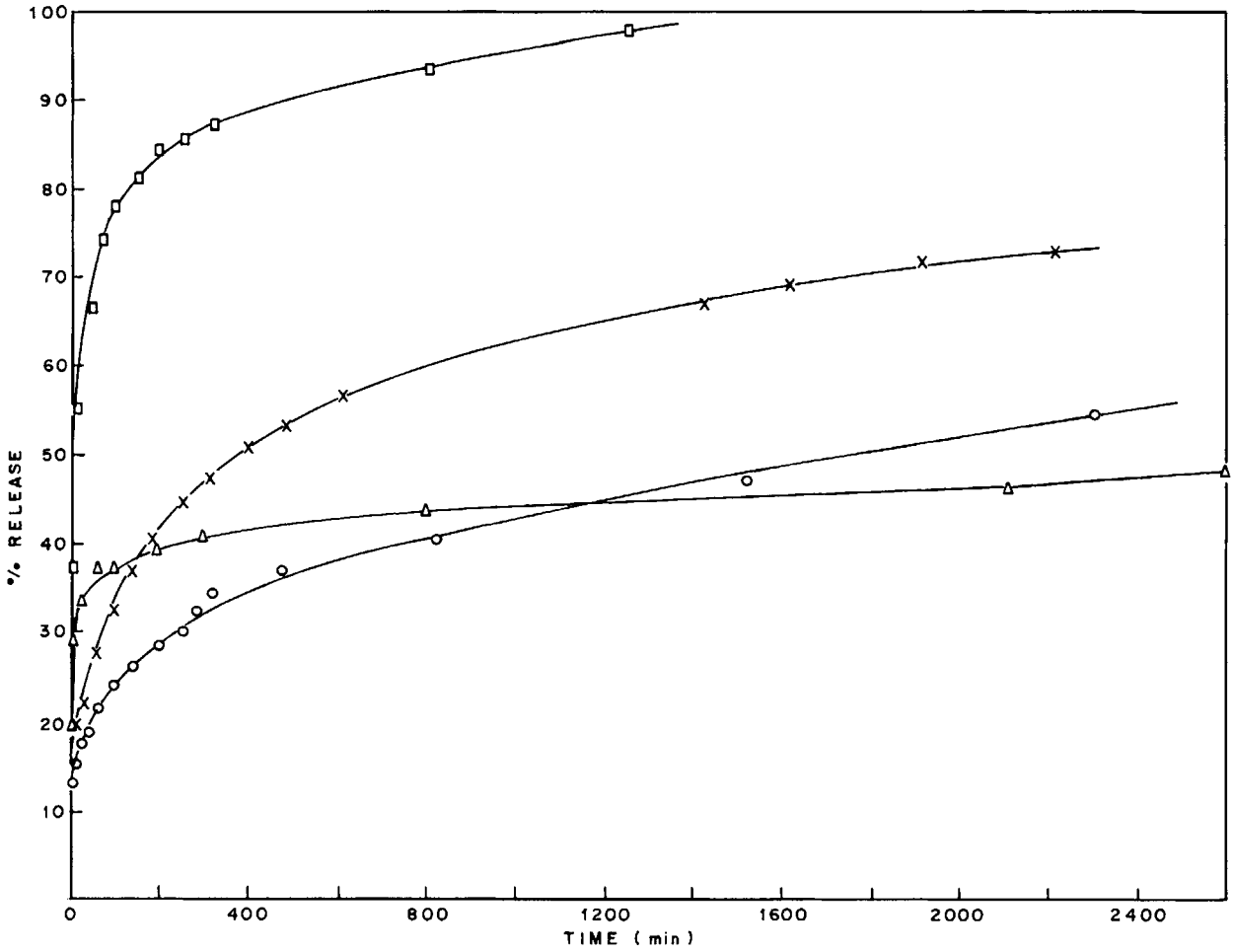

Figure 5 Release profiles of St–UF samples containing carbofuran having different loadings (○) 3% and (×) 20% in water and (△) 3% and (□) 20% in 70% methanol–water mixture.

Table V Release Rate Constant k, Diffusional Exponent n, and Half-life (Time for 50% Release) of St–UF Samples Containing Solid Encapsulant with $X = 0.6$ and ~ 20% Loading

Encapsulant (Sample No.)	Solubility in Water (ppm)	$k \times 10^2$ (min)$^{-n}$	n	Correlation Coefficient	Half-life (min)
Carbofuran (C6)	1,000	9.51	0.3149	0.995	412
Acetanilide (S2C)	5,400	14.04	0.2859	0.996	86
4-Nitrophenol (S1C)	16,000	10.86	0.4012	0.993	40

possessing different solubility from poly(2-hydroxyethyl methacrylate) microspheres.[19] This can be attributed either to the porous nature of the matrix or to the osmotic effect discussed earlier. But the samples taken for this study have a higher degree of cross-linking ($X = 0.6$) at which osmotic effect was not observed earlier.[1] Therefore, the increase in the release rate with increase in encapsulant solubility in water is most likely due to the porous nature of the matrix.

Values of n for carbofuran and acetanilide are similar (0.30 ± 0.015) and an increase in solubility from 1000 ppm (carbofuran) to 5400 ppm (acetanilide) results in an increase in k values from 9.51 $\times 10^{-2}$ to 14.04 $\times 10^{-2}$. Although the overall release increases with solubility due to the porous nature

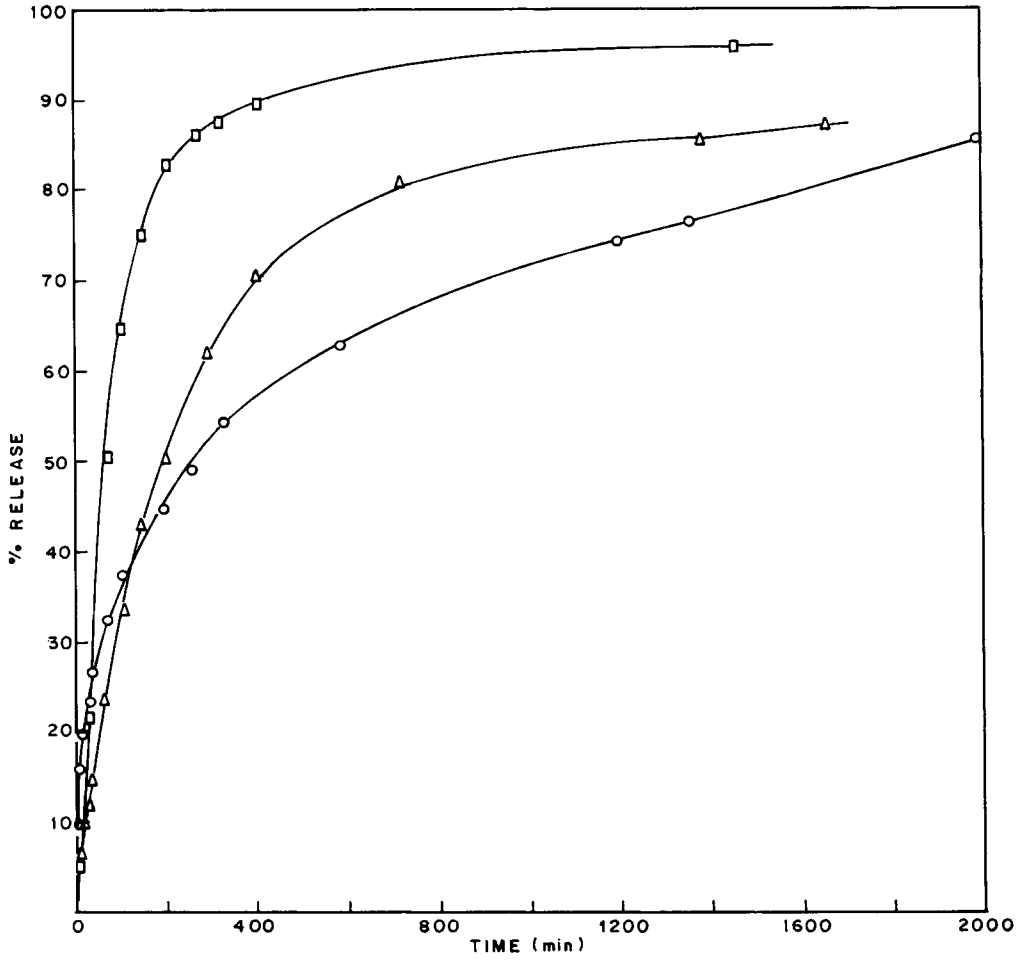

Figure 6 Release profiles of St–UF samples having the same degree of cross-linking ($X = 0.2$) and loading (3%): (○) carbofuran, (△) acetanilide, and (□) 4-nitrophenol.

Table VI Release Rate Constant k, Diffusional Exponent n, and Half-life (Time for 50% Release) of St–UF Samples Containing Solid Encapsulant with X = 0.2 and ~ 3% Loading

Encapsulant (Sample No.)	Solubility in Water (ppm)	$k \times 10^2$ $(\text{min})^{-n}$	n	Correlation Coefficient	Half-life (min)
Carbofuran (C1)	1,000	9.83	0.2877	0.998	280
Acetanilide (S2A3)	5,400	1.38	0.6795	0.999	197
4-Nitrophenol (S1A3)	16,000	0.457	1.085	0.986	75

of the matrix, the mechanism of release does not change significantly. However, a further increase in solubility (4-nitrophenol, 16,000 ppm) causes a change in the mechanism of release (n = 0.40). The latter encapsulant has the highest solubility among the solid encapsulants studied. Due to this, a large amount of the encapsulant is in a dissolved state in the swollen matrix at the time of preparation. As a result, both the matrix property (k) and the release mechanism (n) show a distinct difference.

The influence of osmotic effect, observed in swelling studies of samples S1A3, S2A3, and C1, which have lowest degree of cross-linking (X = 0.2), is compared with the encapsulant release behavior (Fig. 6 and Table VI). As the solubility of encapsulant increases, there is a significant increase in the n value, which is consistant with earlier findings[19] and reduction in k value. Although the overall release increases with solubility (compare $t_{50\%}$ values), reduction in k values is noticed. This is expected because as the osmotic effect becomes more prominent the diffusion of the penetrant into the glassy polymer is faster and these Fickian waves move rapidly to the center of the glassy core. This causes a shift of the release mechanism from anomalous (carbofuran) to Super Case II (4-nitrophenol).

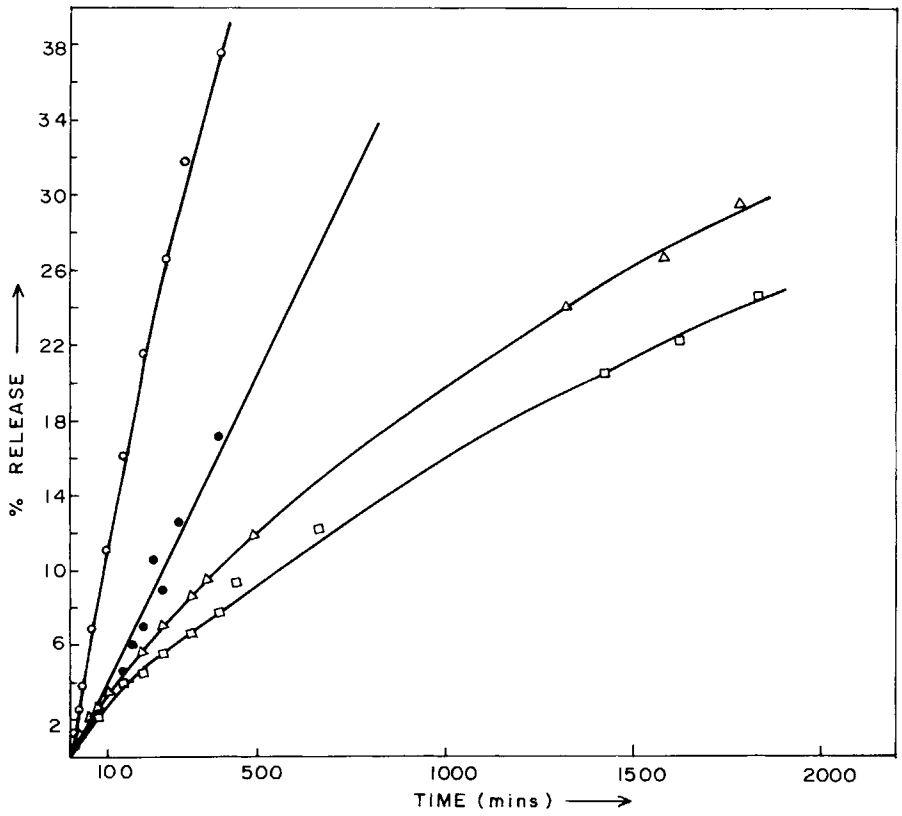

Figure 7 Release profiles of St–UF samples containing 3-nitrotoluene having different levels of cross-linking X = (○) 0.2, (●) 0.4, (△) 0.6, and (□) 0.8.

Also, as the Super Case II transport is believed to occur when the movement of the gel–glassy interface is slower than the penetrant diffusion in the glassy core, a significant reduction in the k value is noticed. It should be noted that since there is change in mechanism reduction in the k value does not imply a slower release rate.

E. Release of Liquid Encapsulants

Release-rate profiles of all the three liquid encapsulants, 3-nitrotoluene, dimethyl phthalate, and nitrobenzene, are shown in Figures 7, 8, and 9, respectively. The release data analyzed in terms of k and n values are given in Table VII. All the encapsulants showed a decrease in release rate with increase in degree of cross-linking up to $X = 0.6$. The n values are higher than those for solid encapsulants, whereas the k values are lower by one to three orders of magnitude. Also, $t_{50\%}$ values are much higher than those of solid encapsulants. In case of St–UF samples that are irregular particulate systems, these n values indicate Case II or Super Case II transport, wherein the release is governed by the relaxation of polymer chains. The change in release mechanism and reduction in release rates in these samples can be explained in terms of the nonporous nature of the systems where the first term in eq. (3) becomes zero ($\epsilon = 0$). In the St–UF systems containing liquid encapsulants, it can be seen that although nitrobenzene is 3.8 times as soluble as 3-nitrotoluene the $t_{50\%}$ values for the former are in the range of 1300–6500 min, whereas for the latter, these are in the range of 400–5400 min. Similarly, the difference between $t_{50\%}$ values of dimethyl phthalate and 3-nitrotoluene is not significant in spite of their differences in solubility.

These observations show that, unlike solid encapsulants, the release rates in the case of the liquid encapsulants examined are invariant with their solubility in the penetrant. Further confirmation of this was obtained by studying the release rate of nitrobenzene sample (L3B) in 50% aqueous methanol (Fig. 10). An increase in encapsulant solubility by a factor of 20 by varying the penetrant led to a drastic reduction in the release rate. The reduction in release rate in aqueous methanol is attributed to its poor penetrant property as compared to water. No definite explanation for this behavior can be offered at the present time. With liquid encapsulants factors, such as encapsulant–matrix interactions and hydrogen bonding could become important in ad-

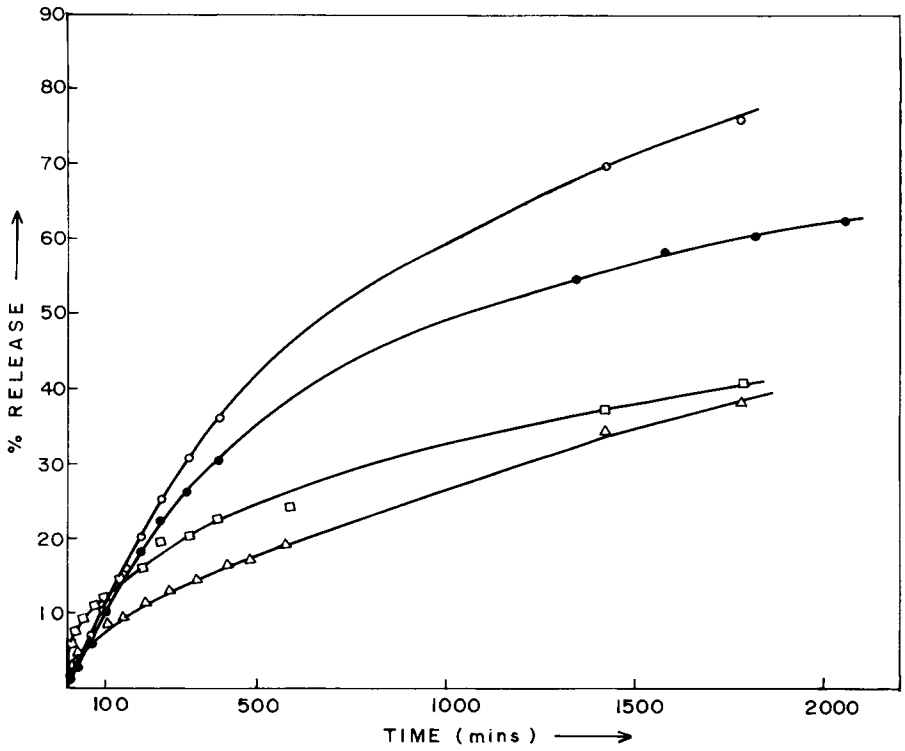

Figure 8 Release profiles of St–UF samples containing dimethyl phthalate having different levels of cross-linking X = (○) 0.2, (●) 0.4, (△) 0.6, and (□) 0.8.

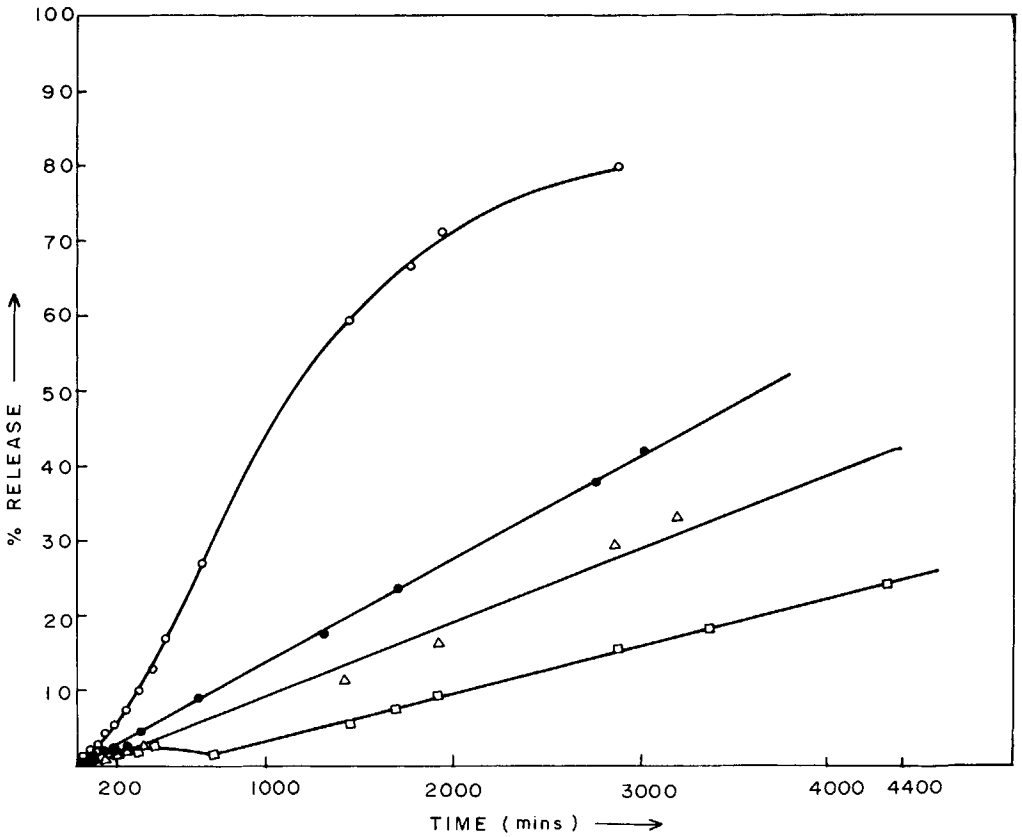

Figure 9 Release profiles of St–UF samples containing nitrobenzene having different levels of cross-linking X = (○) 0.2, (●) 0.4, (□) 0.6, and (△) 0.8.

dition to the solubility of the encapsulant in the penetrant. A more detailed study will be necessary to unequivocally establish the factors responsible for this behavior. Until such time, the present conclusions in case of liquid encapsulants must remain tentative.

Table VII Release Rate Constant k and Diffusional Exponent n of St–UF Samples Containing Liquid Encapsulant 3-Nitrotoluene (L1), Dimethyl Phthalate (L2), and Nitrobenzene (L3)

Sample No.	k (min)$^{-n}$	Correlation Coefficient r	n	$t_{50\%}$ (min)	95% Confidence Level for n	
					Upper Limit	Lower Limit
L1A	1.18×10^{-3}	0.9990	0.9770	490	0.9974	0.9567
L1B	2.90×10^{-4}	0.9867	1.0380	1312	1.0768	0.9992
L1C	1.37×10^{-3}	0.9990	0.7146	3830	0.7226	0.7066
L1D	1.28×10^{-3}	0.9980	0.6951	5357	0.7074	0.6828
L2A	4.27×10^{-3}	0.9946	0.7134	794	0.7543	0.6725
L2B	2.94×10^{-3}	0.9920	0.7515	929	0.7954	0.7076
L2C	6.42×10^{-3}	0.9973	0.5415	3111	0.5675	0.5155
L2D	21.4×10^{-3}	0.9974	0.3920	3098	0.4188	0.3652
L3A	1.80×10^{-4}	0.9980	1.1050	1306	1.1138	1.0962
L3B	1.13×10^{-4}	0.9970	1.0246	3641	1.0442	1.0050
L3C	1.17×10^{-6}	0.9940	1.4770	6491	1.5160	1.4380
L3D	2.14×10^{-5}	0.9960	1.1900	4689	1.2156	1.1643

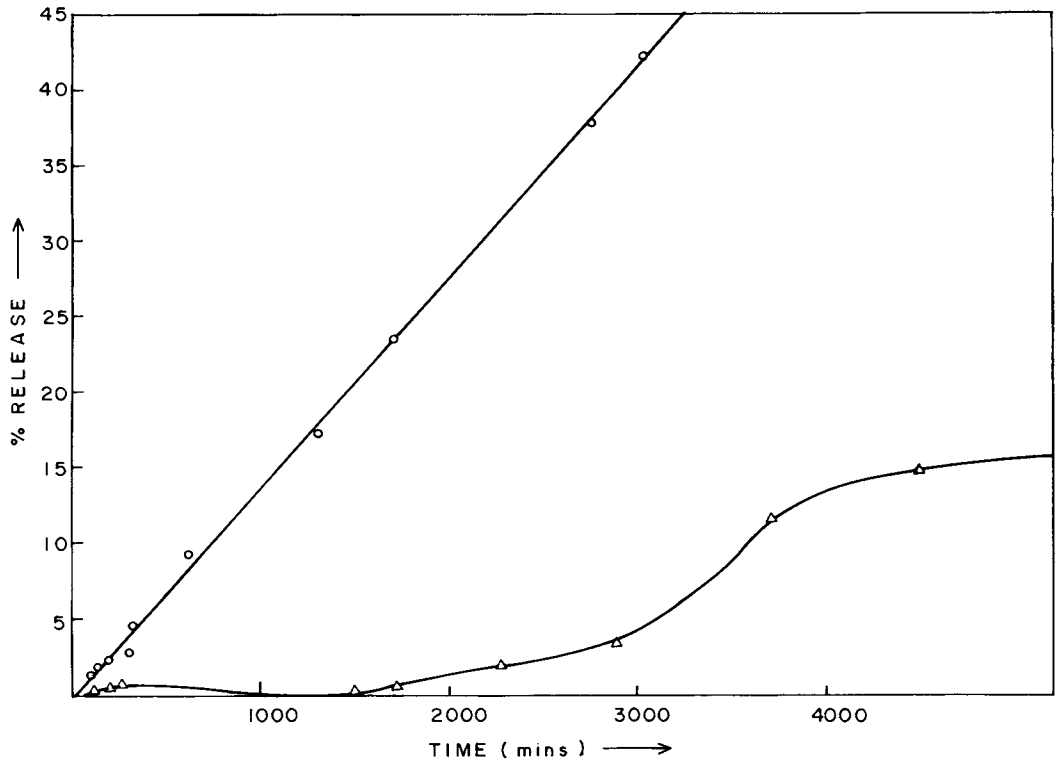

Figure 10 Release profiles of St–UF samples containing nitrobenzene (L3B) in (○) water and (△) 50% aqueous methanol.

Since Case II or Super Case II release is controlled by the velocity of gel–glassy interface, the release-rate values indicate the movement of this gel–glassy interface. When the velocity of this moving interface is very slow as compared to the diffusion of penetrant in glassy core, the Super Case II transport results in an early stage of experiment. It is expected that when the value of n increases, shifting the release mechanism from nonFickian to Case II or Super Case II, the value of k should decrease. It can be noticed from Table VII that sample L3C, having the highest n value (1.447), has also the lowest k value (1.17×10^{-6}), whereas sample L2D, having the lowest value of n (0.3920), has also the highest value of k (21.4×10^{-3}). Such a low value of n for sample L2D can be attributed to the fact that as this sample has the highest degree of cross-linking ($X = 0.8$) this particular sample may have some microvoids or cracks. Except for 3-nitrotoluene, the release rate for all the samples decreases with increase in the degree of cross-linking from $X = 0.2$ to $X = 0.6$ and again increases at $X = 0.8$. Thus, in almost all the St–UF samples containing liquid encapsulants, the release is governed mostly by the molecular relaxations occurring at the gel–glassy interface.

CONCLUSION

(1) Dispersion of the solid encapsulant in a cross-linked starch–urea formaldehyde matrix at lower loading results in a less porous system, but at higher loading, a porous matrix system is obtained. (2) A liquid encapsulant leads to a nonporous matrix system and the efficacy of encapsulation depends on the vapor pressure of the encapsulant. (3) The rate of swelling of the matrix having a low degree of cross-linking depends on the encapsulant solubility in the penetrant. (4) The rate and mechanism of release of an organic compound depends on the physical state of the encapsulant and also on the degree of cross-linking of the matrix. (5) The release of solid encapsulants from a porous matrix is governed by an Fickian or anomalous release mechanism characterized by high release rates that show dependence on the solubility of the encapsulants in the penetrant. (6) The release of liquid encapsulants from the St–UF matrix is governed by Case II or Super Case II transport. The release rates in these systems are much lower and are controlled by polymer chain relaxation. These rates are invariant with the solubility of the encapsulant in the penetrant.

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