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Pseudo-zwitterionic microvesicles for sustained urea release

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Abstract: Zwitterionic microvesicles formed by catanionic system, based on sodium dodecyl sulfate and hexadecyltrimethyl ammonium bromide, have been investigated for sustained urea release using UV–visible absorption spectroscopy. The change in variables such as temperature, sonication time and initial urea concentration was related to urea entrapment efficiency and release from microvesicles. Korsmeyer–Peppas model was applied to highlight release mechanism and kinetics. Both diffusion and erosion were responsible for urea release and rate constant varied with change in conditions. The quantification of association between urea and catanionic vesicles in terms of binding constant (K_{bin}) and binding free energy showed that urea binding was thermodynamically favored. Our results indicate that biocompatible pseudo-zwitterionic vesicles have enormous potential to act as sustained release system for nitrogenous fertilizers such as urea.

Keywords: controlled-release; surfactant vesicles; fertilizer.

INTRODUCTION

Urea is one of most important nitrogenous fertilizers that provides 46 % nitrogen.[1] However, it has low fertilizer use efficiency and significant amount of urea applied to plants is degraded through volatilization and leaching.[2,3] Urea is hydrolyzed to CO_2 and NH_3 by the action of urease in wet conditions, leading to the loss of approximately half of the total amount applied.[4] Besides, it gives rise to the production of green house gases such as N_2O that can cause greater global warming than methane.[5] In order to ensure proper plant nutrition, avoid urea loss and prevent fertilizer's detrimental impact on environment, a controlled urea-release is imperative.[6]

There are several modes in which urea can be applied to plants. It can be directly injected into soil in the form of solution, spread on plants in coated form or as co-crystals[7] and loaded into lipid vesicles (as liposomes) for controlled rel-

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ease.[8,9] However, none of these modes is devoid of limitations. For instance, injected urea gives rise to fertilizer overdose that can damage seeds,[10] coated fertilizers may have improper absorption and they are prone to abrasion.[11] Liposomes may lack long-term stability and deliver cargo in short span of time.[12,13] The hydrolysis of phospholipids affects vesicle integrity and induces poration, resulting in enhanced release of entrapped molecules.[14]

Cationic or anionic amphiphiles form micelles in aqueous solution above critical micelle concentration (*CMC*), however, their equimolar catanionic mixture predominently exists in vesicles.[15] These (pseudo-zwitterionic) vesicles are composed of bilayers formed by ion-pairs of oppositely charged surfactants. They are more stable than micelles or lipid aggregates due to the absence of head-group repulsions.[16] It was found out during ecotoxicological assays that pseudo zwitterionic vesicles consisting of sodium dodecyl sulfate (SDS) and dodecyl trimethyl ammonium bromide (DTAB) were more biocompatible, compared to corresponding component surfactants.[16,17]

The size of catanionic aggregates varies, depending upon the ratio between individual surfactants and the vesicles formed in an equimolar mixtures have a hydrodynamic diameter of greater than 0.6 μm.[18,19] Recently, the potential of catanionic system has been evaluated for drug-delivery and related applications.[8,15,20] However, their candidature for sustained release of fertilizers has never been explored. Keeping in view the benefits associated with the use of catanionic mixture as a delivery system, the present work intends to investigate the potential of pseudo-zwitterionic system based on equimolar sodium dodecyl sulfate and hexadecyltrimethylammonium bromide (HTAB) for sustained-urea release. For this purpose, the urea entrapment and the release efficiency of pseudo-zwitterionic microvesicles will be evaluated. Besides, urea-vesicle binding proficiency, the effect of change in temperature, sonication time and initial urea concentration on encapsulation and release of nitrogeneous fertilizer will be emphasized. In addition, the release mechanism and kinetics will be explored.

EXPERIMENTAL

Urea (≥ 99 %) and 4-dimethylaminobenzaldeyde (ACS reagent grade) were acquired from Sigma–Aldrich. Ionic surfactants, sodium dodecyl sulfate (~ 99%) and hexadecyltrimethylammonium bromide (98%) were the products of Alfa Aesar. All chemicals were used as received. All solutions were prepared in ultrapure water from Milli-Q Advantage A10 system of Millipore (France).

Surface tension measurements

The aggregation in pure and equimolar surfactant mixtures were determined using tensiometer (White Electrical Instrument Co. Ltd., UK), equipped with a platinum ring, at 293.15 K. Surface tension was plotted against *log* of surfactant concentration. The inflection points in graphs gave the critical micelle concentrations of SDS and HTAB as 8.2 and 0.91 mM, respectively. The vesiculation occurred in pseudo-zwitterionic surfactant at 0.06 mM. These values were in accordance with literature values.[21]

UV–visible spectroscopic measurements

Perkin Elmer Lambda 25 spectrophotometer was used for detection in the visible range. The urea encapsulation in pre-hydrated formulation was carried out by adding equimolar amounts of SDS and HTAB to particular amount of urea solution at fixed temperature, followed by sonication. The turbid solutions were filtered and the amount of free urea was detected by treating it with DMAB reagent and recording absorbance of chromogen at 425 nm.[22] For urea loading from anhydrous formulation, initially solid urea was added to equimolar quantities of surfactants and later hydrated and sonicated at fixed temperature. Again, free urea was detected as DMAB-urea adduct described above. The amount of catanionic mixture was 11.4 mM to ensure existence of all surfactant in the form of vesicles. The absorbance values were obtained as a differential of total and free urea.

Urea release from vesicles was studied by recording the time-dependent absorbance of urea solutions maintained at five different temperatures (293.15 to 325.15 K with a difference of 8.0 K between two values). The other variables were sonication time and initial urea concentration. The percent urea release was obtained from the amount of urea encapsulated initially and that released at particular time interval. The absorbance values were converted to corresponding release fractions using the molar extinction coefficient (ε) of DMAB–urea adduct, *i.e.*, 4.2×10^2 L mol^{-1} cm^{-1}.

The differential absorbance of DMAB-urea adduct was measured as a function of catanionic surfactant concentration to highlight urea-vesicle binding. Other variables such as urea concentration, temperature and sonication time were kept fixed during these experiments.

The temperature was controlled within ±0.1 K during the experiments using circulating water thermostat.

RESULTS AND DISCUSSION

Urea entrapment efficiency

The urea entrapment efficiency under different conditions was studied and the results are presented in Figs. 1–3.

Fig. 1 shows the percent urea encapsulation in pre-hydrated and post-hydrated formulations. When urea concentration is low, an encapsulation of above 90% occurs, and the difference is only slightly dependent on formulation type. The amount of free urea increases with increase in initial urea concentration. Still, between 65–70 % of urea is entrapped, when initial urea concentration is 5mM, showing that high amounts of urea can be loaded into cationic system. The pre-hydrated samples showed a random dependence of urea entrapment on initial urea concentration, which is probably due to the sequence in which components are added to formulation. When individual surfactants are added to urea solution, at first micelles formation takes place and urea is incorporated into cationic or anionic micelles. When second surfactant is added and system is subjected to sonication, micelle-to-vesicle transition occurs. During this transition, urea is partly released from aggregates. As free urea was measured immediately after sonication, without actually allowing the system to attain equilibrium, slight randomness is not beyond expectation.

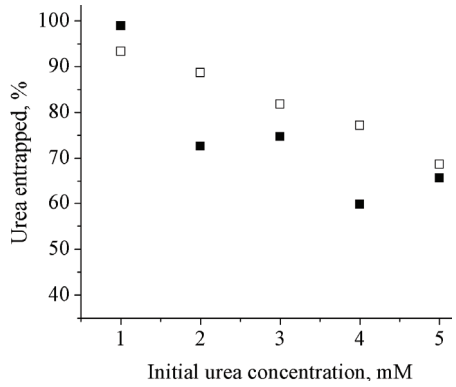

Fig. 1. Percent urea entrapment: pre-hydrated (closed symbol) *vs*. anhydrous (open symbol) formulation.

In the formulation, where components were mixed in solid form and later hydrated and sonicated, only vesicles containing incorporated urea were formed, giving rise to more systematic behaviour. The overall decline in percent urea entrapment is reflective of the capacity of system to incorporate certain quantities of fertilizer. As indicated above, the system containing 11.4 mM pseudo-zwitterionic surfactant could incorporate between 65–70 % of 5 mM urea. Such behaviour is obviously due to antagonistic effect of urea on bilayer structure.[23] However, it has no serious implications.[24]

The percentage of urea entrapped into pseudo-zwitterionic vesicles shows an inverse dependence on sonication time (Fig. 2). The amount penetrated into vesicles is reduced in the beginning and later levelling is seen. Though sonication aids the formation of vesicles, excessive system-agitation gives rise to disruption of multi-lamellar vesicles into meta-stable small unilamellar vesicles, causing the release of cargo.[25]

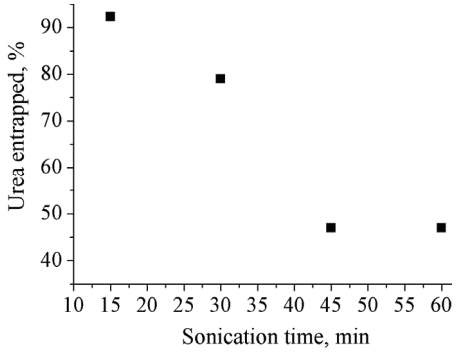

Fig. 2. Effect of sonication time on percent urea entrapment in zwitterionic vesicles.

Similar trends are observed with increase in temperature, and reduction in urea incoporation occurs with rise in system temperature, Fig. 3. Apparently, the compactness of zwitterionic vesicles is reduced when they are exposed to high temperatures and poration or channel formation with increase in vibrational

energy leads to greater urea release. In comparison to nearly 100 % entrapment at 293.15 K, mere 47 % of total fertilizer is enclosed in vesicles at 325.15 K. An overall impact is such that high system temperatures and high sonication durations disfavour urea entrapment.

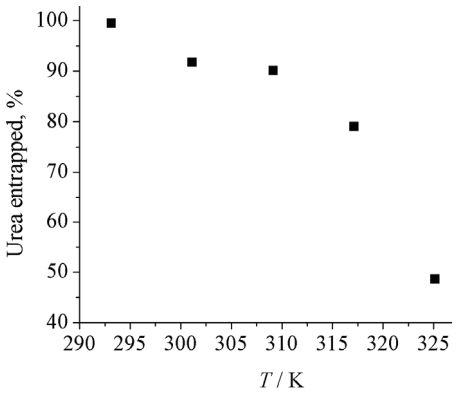

Fig. 3. Effect of temperature on percent urea entrapment in zwitterionic vesicles.

Urea release from microvesicles

The time-dependent release of urea from vesicles was monitored by measuring the amount of free urea at specific time intervals. The measurements were spread over the time span of 45 days. The temperature of the system was altered from 293.15 to 325.15 K with a difference of 8.0 K between two values and the percent urea release obtained at five different temperatures is shown in Fig. 4.

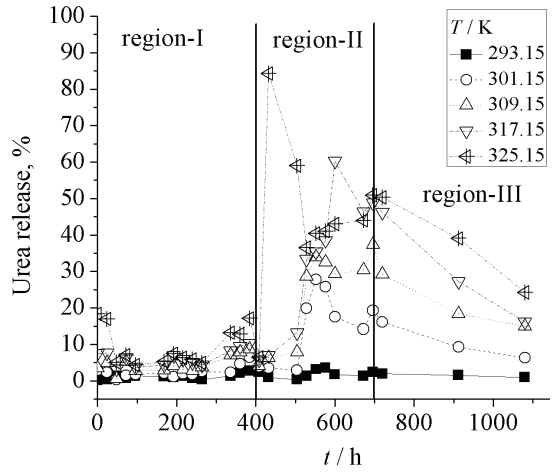

Fig. 4. Effect of temperature on urea release from zwitterionic vesicles as a function of time.

A sustained release of urea was observed for 45 days at 293.15 K, but only small proportion of urea (*i.e.*, between 0.4 to 3.5 %) was released from catanionic vesicles. On average, between 1–1.5 % of urea was released every day. At tem-

peratures higher than 293.15 K, the urea diffusion towards the bulk was facilitated and sustained release occurred for about 17 days (Fig. 4, region-I). The release was improved in region-I with the aid of temperature and at 325.15 K the amount of available (free) urea remained in the range 7–18 %. A deviation from this behaviour was observed in the following region-II, which could be related to temperature-dependent erosion. In this region percent urea release spiked to 84 % at 325.15 K on day 18. and decrease in temperature delayed the abrasion. In region-III (Fig. 4), a gradual recovery is observed, and system shifts back to the intial state. Such anomalous behaviour has been attributed to vesicle destabilization and subsequent healing of the system.[26]

In another experiment. the system was sonicated for different periods of times at 293.15 K and percent urea release obtained as a function of time is presented in Fig. 5. Again, the patterns similar to those observed during temperature change were seen and three regions could be identified. The maximum release was about 52 %, and the system partly deteriorated after 17 days of sustained release of 10–15 % for samples sonicated for 1 h. The system regained its stability in the latter stages marked as region-III in Fig. 5, revealing that the system has healed from the effects of agitation.[26]

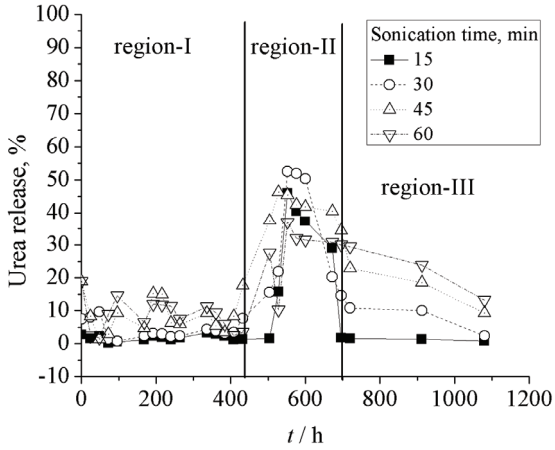

Fig. 5. Effect of sonication time on time-dependent urea release from vesicles.

Considering the system destabilization during the 3rd week, the effect of initial or total urea concentration on time-dependent urea release from microvesicles was investigated for two weeks only. The results of this investigation are shown in Fig. 6.

A continuous release of urea into the bulk took place, and the proportion of free urea showed a direct dependence on total urea content. Based on the trends, it is inferred that release of fertilizer could be raised 3 folds (*i.e.*, from less than 10 to nearly 30 %), merely by changing the initial urea concentration at 293.15 K.

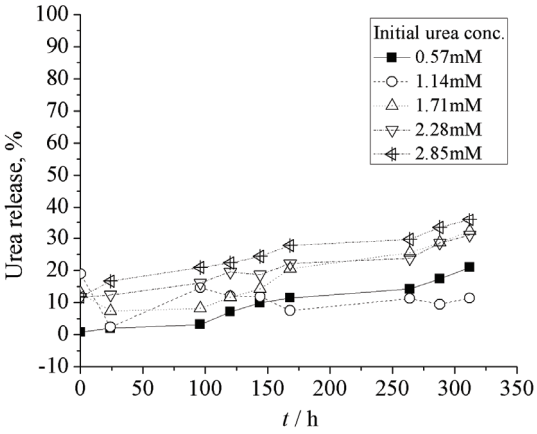

Fig. 6. Effect of initial urea concentration on sustained urea release as a function of time.

Mechanism of urea release

The mechanism of urea release was identified by using Korsmeyer–Peppas model.[27] This model relates the fraction released to rate constant k and release coefficient n as:

$$\frac{M_t}{M_\infty} = kt^n \tag{1}$$

Where M_t/M_∞ represents the fraction of urea released at time t.

According to this model, a quasi-Fickian or Fickian transport involving diffusion occurs when $n \geq 0.5$. When n ranges 0.5–1.0, a non-Fickian transport takes place across the barrier that involves both diffusion and erosion mechanisms. A time independent zero-order kinetics is involved when $n = 1$.[28] In order to highlight the effect of temperature, sonication time and initial urea concentration on release, the mechanism in Eq. (1) was employed under different conditions.

At 293.15 K, the quasi-Fickian transport was involved and urea release predominantly occurred through diffusion since $n < 0.5$ (Table I). At $T \geq 301.15$ K, $n > 0.5$, which indicated non-Fickian transport and involvement of both diffusion and erosion mechanisms. For all n values above 0.5, an increase in magnitude of k is observed with the increase in temperature, showing that the transport of urea from vesicles into the bulk is favoured by it. The ephemeral pore formation in the

TABLE I. Magnitudes of release coefficient (n) and rate constant (k) obtained at different temperatures

S. No.	T / K	n	k
1	293.15	0.28327	0.002856
2	301.15	0.87812	0.000304
3	309.15	0.84061	0.000681
4	317.15	0.68810	0.002380
5	325.15	0.65824	0.003993

bilayer structure, which is more likely to occur at high temperatures, is the most probable reason for the release of significant quanitites of entrapped urea into the bulk.

The magnitude of n did not vary much when sonication time was altered and values of $n > 0.5$ were recorded in all the cases. It gives the indication that system agitation promotes abrasion and anomalous non-Fickian transport of urea across the bilayers.[25] With the expection of low value recorded for the system sonicated for 15 min, the magnitude of k varied only slightly with the increase in duration of sonication. The slight randomness of k values also reflect an irregular transport of fertilizer. The results are summarized in Table II.

TABLE II. Magnitudes of release coefficient (n) and rate constant (k) obtained at different sonication times

S. No.	Sonication time, min	n	k
1	15	0.59161	0.000920
2	30	0.51744	0.003425
3	45	0.65565	0.002952
4	60	0.60391	0.003588

Random trends in n and k were recorded with the increase in the initial urea concentration (Table III), which could be related to the trend observed earlier for the impact of urea concentration on entrapment efficiency. Quasi-Fickian or Fickian transport occurred and diffusion mechanism was dominant when percent urea entrapment was small. When urea was entrapped in high percentages, non--Fickian and unusual transport took place, showing the invovlement of both erosion and diffusion mechanisms. The antagonistic effects of urea on bilayer structure may be responsible for such behaviour.[23]

TABLE III. Magnitudes of release coefficient (n) and rate constant (k) obtained at different initial urea concentrations

S. No.	Initial urea concentration, mM	n	k
1	0.57	0.94337	0.000791
2	1.14	0.50717	0.007353
3	1.71	0.34297	0.037923
4	2.28	0.61327	0.007802
5	2.85	0.29243	0.060344

Urea-vesicle binding

The association between urea and vesicle can be represented as an equilibrium:[29]

$$nU + V_m \leftrightarrows U_nV_m \quad (2)$$

where n urea molecules are bound to vesicle containing m monomers of catanionic surfactant. The ratio between bound and free urea will generate a partition coefficient, K_c:

$$K_c = \frac{U_V}{U_F} \tag{3}$$

where U_v and U_F are the concentrations of vesicle-bound and free urea, respectively.

The propensity of urea for zwitterionic vesicles was quantified in terms of binding constant, K_{bin}, using the differential absorbance as:[30]

$$\frac{1}{\Delta A} = \frac{1}{K_c \Delta A_m (C_U + S_V)} + \frac{1}{\Delta A_m} \tag{4}$$

where ΔA is the differential absorbance. K_c is the partition coefficient ($K_{bin} = K_c \times$ moles of water per liter). ΔA_m is the maximum value of differential absorbance. C_u is the urea concentration and S_v is the vesiculated surfactant concentration.

The corresponding binding free energy change is given by:[31]

$$\Delta G^o_{bin} = -RT \ln K_{bin} \tag{5}$$

where R is universal gas constant and T is absolute temperature.

The value of binding constant obtained (using Eq. (4)) from linear plot between ΔA^{-1} and $(C_u + S_v)^{-1}$ (Fig. 7) was 2847.73. The corresponding binding free energy change calculated using Eq. (5) was –19.71 kJ mol^{-1}. These values show that urea binding with vesicles is an energy efficient process. The change in conditions forces the system to re-equilibrate and triggers urea-release.

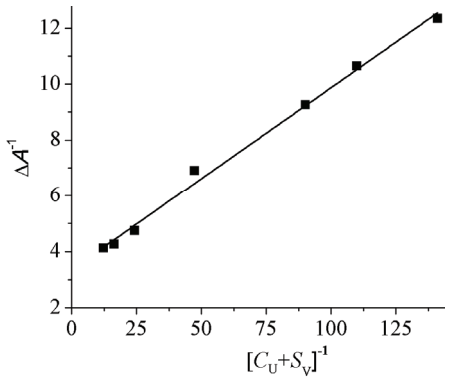

Fig. 7. Relationship between ΔA^{-1} and $[C_u + S_v]^{-1}$ for urea–catanionic surfactant system.

CONCLUSIONS

Pseudo-zwitterionic vesicles can entrap urea with high efficiency, when utilized in solution form or as anhydrous formulation. The entrapment is favoured by low temperature and lack of sonication. The initial urea concentration has limit-

ing effect on urea incorporation into the vesicles. On the other hand, the release is promoted by higher temperature, longer sonication time and higher initial urea concentrations. The release of urea from microvesicles followed diffusion and erosion mechanisms and the rates were high at high temperatures. The binding of urea to vesicle was spontaneous, as reflected by the negative value of binding free energy. The results unravel the potential of zwitterionic vesicles as vehicles of sustained release of fertilizers. Such systems can be optimized for the sustained release of fertilizers over a long period of time, which would definitely economize the agriculture through enhancement of fertilizer use efficiency.

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ИЗВОД

ПСЕУДО-ЦВИТЕРЈОНСКЕ МИКРОВЕЗИКУЛЕ ЗА ПОТПОМОГНУТО ОСЛОБАЂАЊЕ УРЕЕ

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Цвитерјонске микровезикуле које формира катјонско–анјонски систем базиран на натријум-додецилсулфату и хексадецилтриметиламонијум-бромиду су испитиване за потпомогнуто ослобађање урее применом UV–видљиве апсорпционе спектроскопије. Показана је веза између промена у температури, времену излагања ултразвуку и полазне концентрације урее са ефикасношћу хватања и ослобађања урее из микровезикула. Показано је да су процеси дифузије и ерозије одговорни за ослобађање урее као и да се брзина реакције мењала при промени услова. Квантификација повезивања урее и катјонско–анјонских везикула у смислу константе везивања (K_{bin}) и слободне енергије везивања показали су да је везивање урее термодинамички фаворизовано. Добијени резултати указују да биокомпатибилне цвитерјонске везикуле имају велики потенцијал као систем за потпомогнуто ослобађање азотних ђубрива као што је уреа.

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