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Development of hydrogelator-based gel-entrapped base catalysts (GEBCs) as heterogeneous basic catalysts for the synthesis of 3-acetylcoumarins†

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New gel entrapped base catalysts (GEBCs) have been prepared by entrapping some organic and inorganic bases into a solid aqueous gel matrix. Sodium alginate, gelrite and carboxymethyl chitosan were studied for the preparation of GEBCs. The phase behaviour of binary systems (gelator + water) is well studied, but ternary systems (gelator + water + base) are not much studied. Addition of a base to a (gelator + water) system drastically affected the behaviour of the gel. The phase behaviour of ternary systems (gelator + water + base) was studied by developing the corresponding ternary phase diagrams. From this study, the promising homogeneous viscous phases were converted into hard, irreversible gel beads by cross-linking the gelator with divalent cations Ca^{2+}, Ba^{2+} and Sr^{2+}. These gel beads were studied for base entrapment efficiency and leaching of the base. The GEBCs were used for the condensation of salicylaldehydes and methyl/ethyl acetoacetate to obtain 3-acetylcoumarins.

1. Introduction

The emphasis on sustainable and environmentally benign processes has led to several changes in the chemical world. The development and use of heterogeneous, reusable catalysts in various chemical processes is also a part of these changes.[1] Heterogeneous catalysts have specific advantages over their homogeneous counterparts, such as easy separation of the catalyst and products, reusability, *etc.* Many solid bases have been reported in the literature, like metal oxides, supported alkalis or alkaline metals, anion exchange resins, hydrotalcites and immobilised organic bases on polymeric backbones.[2] However, these heterogeneous bases have many limitations. The basic strength of these bases is comparatively less, and hence the reactions need vigorous conditions, leading to an increase in the energy consumption. Still there are no efficient heterogeneous and reusable alternatives for classical bases like NaOH, KOH, piperidine and pyridine. Deactivation of solid bases under atmospheric conditions is also a major problem and the catalysts require calcination at high temperature for reactivation. The lower basic strength of solid bases also makes them ineffective for flow processes. In some processes inorganic bases like K_2CO_3 have been used in organic solvents to perform reactions in continuous flow in a fixed bed reactor.[3] But the interaction between the undissociated K_2CO_3 and the substrate present in the solution is not satisfactory in all cases. For many reactions we need a base catalyst which can give a combined effect of both homogeneous and heterogeneous catalysts. Entrapment of bases in porous polymeric matrix materials can accomplish this requirement.[4]

The concept of entrapment of enzymes into polymeric gel matrices is well documented.[5–7] But there are few reports on gel-entrapped acid–base catalysis. In 1975, Hines entrapped palladium complexes in poly(hydroxyethylmethacrylate) hydrogel and used the catalysts for hydrogenation.[8] David reported sol–gel entrapped catalysts and reagents using silica and alumina gels.[9–14]

We initiated work on gel entrapped base catalysts (GEBCs) using a hydrogelator agar agar, and entrapping alkalis and organic bases in the corresponding hydrogels.[15,16] Such GEBCs are easy to prepare and handle, can be prepared from biodegradable matrix materials and are efficient, economical and completely environmentally benign. Agar agar is a complex polysaccharide and forms a gel in water. At certain compositions of (agar agar–water–alkali) the gel formed is a solid which can be cut into pieces. We used NaOH- and KOH-entrapped GEBCs for base-catalyzed organic reactions. There are few other references on agar agar based GEBCs.[17–19] Agar agar based GEBCs have some limitations like poor gelation and poor stability.

In the present work we used hydrogelators, sodium alginate (Na Alg), gelrite (gellan gum), chitosan and carboxymethyl chitosan, to overcome the limitations of agar agar. These gelators have been used in several other areas as matrix materials.[20] Sodium alginate

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(Na Alg) and chitosan have been used to prepare some grafted co-polymers which can be used as base catalysts.[21–23] Chitosan is used as a catalyst in some reports.[24]

In this work, our aim was to entrap organic and inorganic bases in aqueous gel matrices of sodium alginate, gelrite and chitosan to prepare GEBCs, and to investigate the effect of bases on the gelation of these gelators, their base entrapment efficiency and the ability of GEBCs prepared from these gelators to catalyze organic reactions. To evaluate the utility of the GEBCs, a model base catalysed reaction of salicylaldehydes and methyl acetoacetate to 3-acetylcoumarins was carried out. 3-Acetylcoumarins are required in the synthesis of dyes[25] and chemosensors.[26]

2. Experimental

Sodium alginate (food grade, sodium polymannuronate, minimum assay 91%) was purchased from Loba Chemie Pvt. Ltd, gelrite (deacetylated gellan gum) was purchased from Sisco Research Laboratories Pvt. Ltd, and chitosan (degree of deacetylation ≥75%) was purchased from HiMedia Laboratories Pvt. Ltd. The other reagents and substrates were purchased from Sigma Aldrich, Alfa acer and Loba Chemie Pvt. Ltd and were used as such. Melting points were recorded using an Analab melting point apparatus and are uncorrected. The IR spectra were recorded using a Perkin Elmer Spectrum-two spectrometer in ATR mode. Thermogravimetric analysis (TGA) was performed using a Perkin Elmer STA 6000 with a heating rate of 20 °C min^{-1}. The FESEM analysis was carried out using a Tescan MIRA 3 model. Beads were coated with Pt using a JFC 1600 Auto fine coater and then images were recorded. The ^{1}H NMR spectra were recorded using a Bruker 400 MHz NMR spectrometer.

2.1 Construction of ternary phase diagrams

Different compositions of gelator and base were taken, water was added and solution was stirred to equilibrate. The change in the phase was noted.

2.2 Preparation of gel entrapped base catalysts (GEBCs)

Viscous solutions of appropriate phases of (gelator + water + base) systems were injected into aqueous solutions of $CaCl_2$, $BaCl_2$ or $SrCl_2$ (0.5 M). The gel beads were separated by filtration and air dried in a desiccator over anhydrous $CaCl_2$ for 5 h.

2.3 Determination of the base entrapment efficiency of the GEBCs

The GEBC beads (3.0 g) were added to distilled water (DW, 30 mL) in a glass beaker. The beads were crushed completely and the mixture was stirred vigorously for 1 h. The solution was filtered. The filtrate was diluted to 100 mL in a volumetric flask and the amount of base present in the solution was determined conductometrically.

2.4 Leaching of the entrapped base

The GEBC beads (3.0 g) were taken in methanol (10 mL) and stirred in a glass tube (dia = 22 mm) using a magnetic bar with a stirring rate of 200 rpm at 27–30 °C. The beads were separated by filtration. The filtrate was diluted to 100 mL with DW. The amount of base present in the filtrate was determined conductometrically.

2.5 Reaction of salicylaldehyde and methyl acetoacetate in the presence of GEBC

2.5.1 Batch reaction. Salicylaldehyde (**1a**, 4.0 mmol), methyl acetoacetate (**2a**, 4.0 mmol) and methanol (20 mL) were taken in a round bottom flask (50 mL). The GEBC beads (1.0 g) were added and the reaction mixture was stirred at room temperature for 1 h. The solution was filtered and the filtrate was concentrated and chilled to obtain the solid product. The product was recrystallised from ethanol.

2.5.2 Flow reaction. A glass column (i.d. = 8 mm and l = 30 cm) was packed with GEBC beads (10.0 g). A solution of salicylaldehyde (0.2 M), methyl acetoacetate (0.2 M) in methanol (100.0 mL) was passed through the column at a flow rate of 1.0 mL min^{-1} using a peristaltic pump. Fractions of 20 mL each were collected and analysed for product formation.

3. Results and discussion

Among Na Alg, gelrite and chitosan, chitosan turned out to be ineffective as a gelator as it was insoluble in neutral and basic aqueous solutions. Hence, in order to make it soluble in aqueous solution, chitosan was converted to carboxymethyl chitosan by the reported procedure using monochloroacetic acid.[27,28] It formed a colloidal viscous solution in an aqueous basic medium, but could not form a hard gel. Na Alg and gelrite formed promising viscous homogeneous colloidal solutions. Divalent cations Ca^{2+}, Ba^{2+} and Sr^{2+} could cross-link the gelators in the solution to give hard gels. Hence, further study was carried out with these two gelators.

3.1 Ternary phase diagrams

The behaviour of a hydrogelator in water is affected significantly by the polarity of the medium, pH and the temperature of the system. The phase behaviour of the hydrogelators in aqueous systems is well studied. However, GEBC systems containing these gelators and bases have not been studied. Addition of a base to a (gelator + water) mixture affects noticeably the swelling and gelation properties of the resulting system. Hence, we studied the phase behaviour of (gelator + water + base) ternary systems by constructing the corresponding ternary phase diagrams (Fig. 1A–E and 2A–E). The different phases obtained in the phase diagrams are as follows.

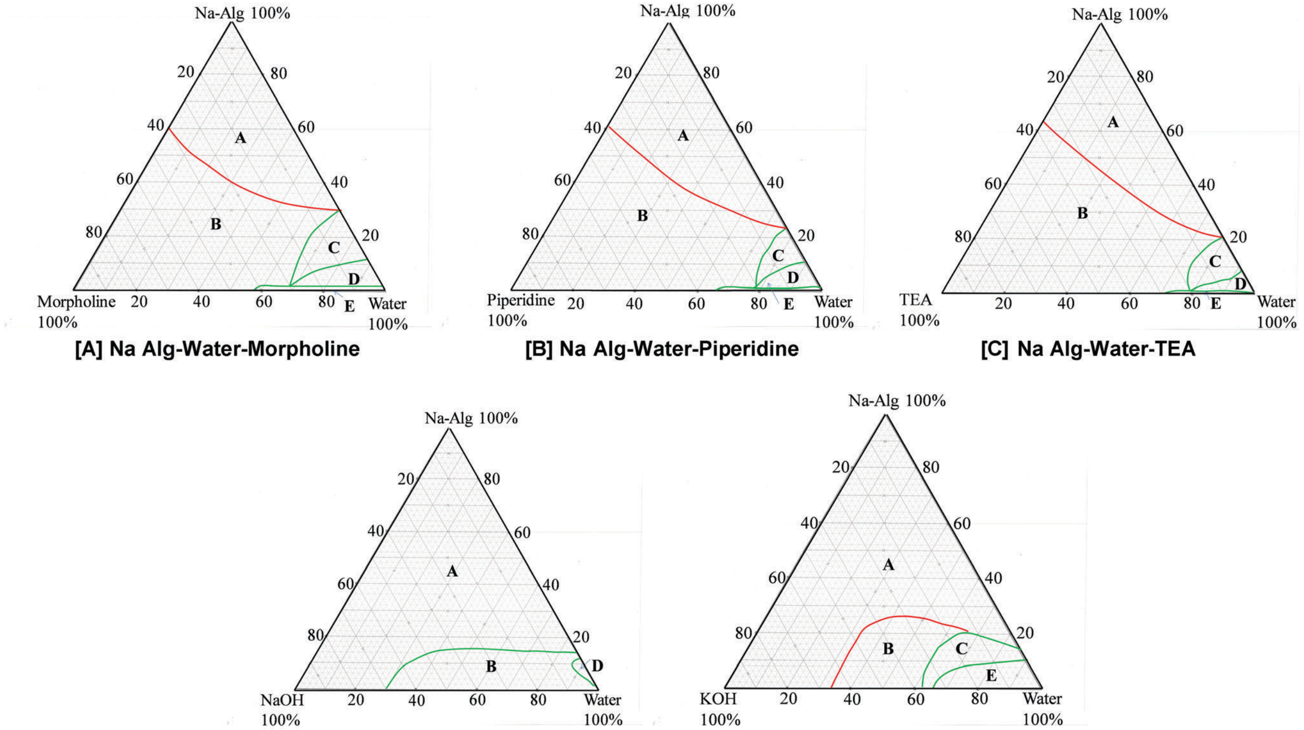
Phase A – Heterogeneous solid mass (heterogeneous solid rich phase)

Phase B – Biphasic mixture of solid and liquid (heterogeneous liquid rich phase)

Phase C – Viscous gel not free flowing (homogeneous solid rich phase)

Phase D – Viscous sol (homogeneous liquid rich phase)

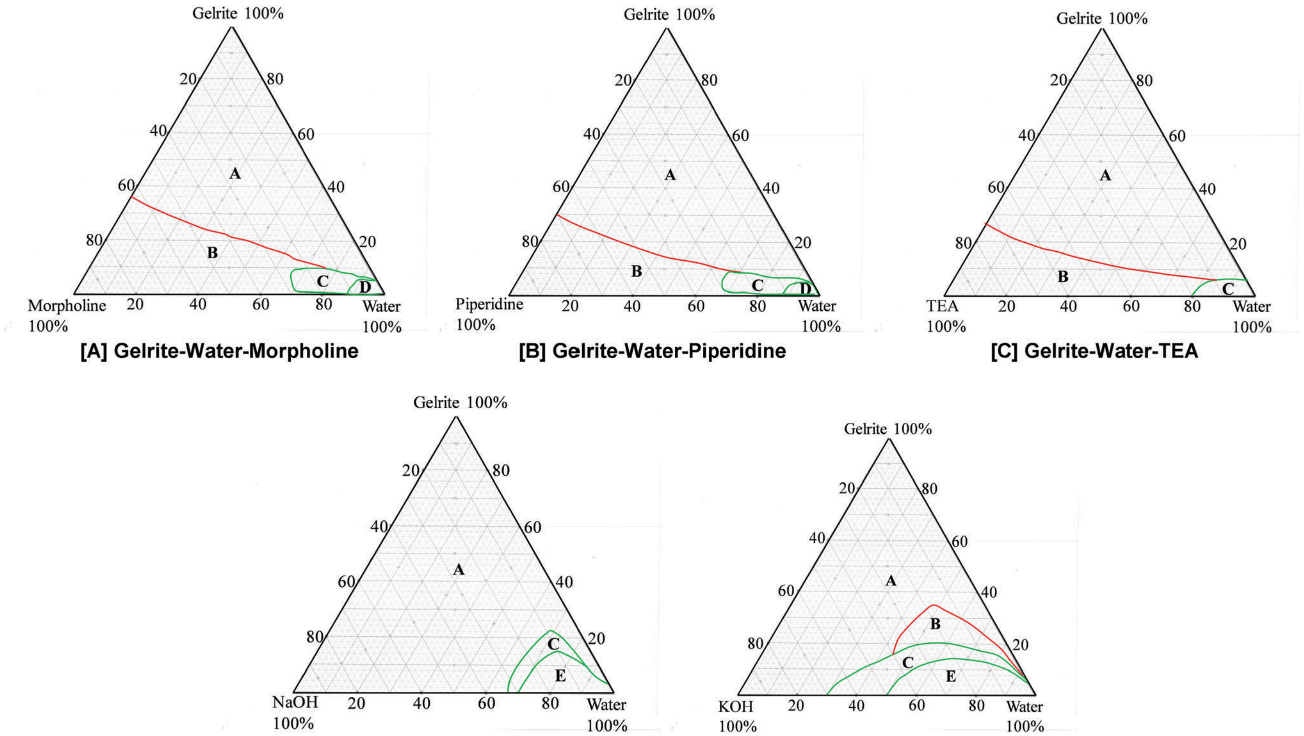
Phase E – Low viscosity sol



[A] Na Alg-Water-Morpholine [B] Na Alg-Water-Piperidine [C] Na Alg-Water-TEA

[D] Na Alg-Water-NaOH [E] Na Alg-Water-KOH

Fig. 1 Ternary phase diagrams of (Na Alg–water–base) systems.



[A] Gelrite-Water-Morpholine [B] Gelrite-Water-Piperidine [C] Gelrite-Water-TEA

[D] Gelrite-Water-NaOH [E] Gelrite-Water-KOH

Fig. 2 Ternary phase diagrams of (gelrite–water–base) systems.

3.1.1 Na Alg–water–base ternary systems. The phase behaviour of Na Alg–water with five bases, morpholine, piperidine, triethylamine, sodium hydroxide, and potassium hydroxide, was studied. In the phase diagram for the (Na Alg–water–morpholine) system (Fig. 1A), all the five phases were observed. A 40 : 60 mixture of Na Alg–morpholine formed heterogeneous solid phase A, but further addition of morpholine led to a heterogeneous biphasic mixture of solid and liquid (B). Addition of water to both these heterogeneous phases, A and B, converted them into homogeneous phases C–E. Phase C was homogeneous but, more viscous, and not free flowing. Addition of water to phase C converted it to phase D, which was a free flowing homogeneous sol. Further addition of water led to phase E which had very low viscosity. Similar phase diagrams were obtained for piperidine (Fig. 1B) and triethylamine (Fig. 1C).

The phase behaviour of Na Alg in aqueous solutions of sodium hydroxide and potassium hydroxide was completely different to that with organic bases [Fig. 1D and E]. Na Alg did not swell in NaOH solution and remained insoluble (Fig. 1D). Thus, most of the area was occupied by heterogeneous phases A and B, and only a small part showed homogeneous free flowing phase D. The observation was different for KOH (Fig. 1E); it showed four phases A, B, C, and E. The phase D was not observed.

3.1.2 Gelrite–water–base ternary systems. More swelling of gelrite in an aqueous medium resulted into much less area under the homogeneous phases compared to Na Alg (Fig. 2A–E). The maximum amount of gelrite that could be taken to form a homogeneous phase was 5–6%. Morpholine and piperidine containing systems showed four phases A, B, C and D (Fig. 2A and B). In the case of triethylamine, phase D was absent. It formed either a viscous mass or a heterogeneous mixture (Fig. 2C). With NaOH it formed a homogeneous phase, but it was less viscous (phase E), and similar behaviour was observed with KOH.

The basicity and solubility of the base had a profound effect on the phases. Thus there was a marked effect on phases A and B. There are reports on degradation of sodium alginate in alkaline solution. This might be the reason for the formation of poorly viscous homogeneous phase E in the case of Na Alg–KOH–water, gelrite–NaOH–water and gelrite–KOH–water. In the case of the Na Alg–NaOH–water system the homogeneous phase was negligible and it appeared only at NaOH amounts less than 0.5%; Na Alg did not swell or dissolve in NaOH solution.

3.2 Gelation study

The best gels obtained in the above study were still soft and when stirred in a non-aqueous solvent could not maintain their integrity. It is known that divalent and trivalent cations, particularly Ca^{2+} cations, cross-link the gelators through –COOH groups[29] (Fig. 3) and form a strong internal network which leads to a hard gel. Hence, promising gels from the above systems were treated with 5% aqueous $CaCl_2$ to make hard gels for catalysis. The gelation with Ba^{2+} and Sr^{2+} was also studied (see the ESI,† Table S1).

3.2.1 Na Alg–water–base ternary systems. To begin with the (Na Alg–water–morpholine) ternary system was studied. Phases A and B were heterogeneous and did not form a gel. Phase C was very viscous (paste) and did not pass through the syringe and when added in small portions to 5% aq. $CaCl_2$, only a soft gel was formed. Phase D was a homogeneous free flowing solution and when it was slowly injected into $CaCl_2$ solution, spherical hard gel beads were obtained. Phase E did not give a hard gel. Various compositions of phase D were used to prepare hard gels. The (Na Alg–water–piperidine) system showed the same behaviour and its phase D formed spherical hard gel beads. The phase D of (Na Alg–TEA–water) system formed soft gels; possibly due to less solubility of TEA in water. In the (Na Alg–NaOH–water) system phase D was almost negligible (Fig. 1D) and in the (Na Alg–KOH–water) system phase D was not observed (Fig. 1E). The homogeneous phase E was poorly viscous and did not form gel beads. Drops of phase E dissolved in Ca^{2+} solution.

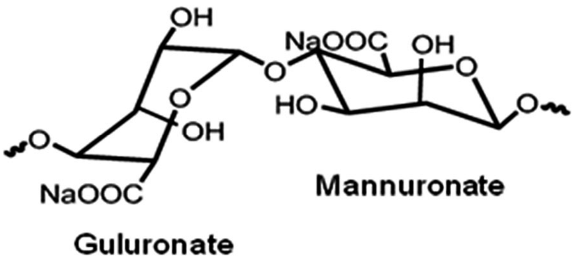


Fig. 3 Monomer units of Na Alg, 1,4-linked mannuronate and guluronate.

3.2.2 Gelrite–water–base ternary systems. In this system, phases A and B were dominant and, being heterogeneous, could not be used for making hard gels. The phase C was highly viscous and could not be converted into solid gels. With TEA, NaOH and KOH the favourable phase D could not be formed. NaOH and KOH gave poorly viscous phase E which also could not be converted into a hard gel. Only morpholine and piperidine gave the required phase D which could be converted into hard gels.

Swelling of gelrite in the aqueous solution was higher as compared to that of Na Alg. Hence the area of the homogeneous free flowing phase D was lower with morpholine and piperidine (Fig. 2A and B), and absent in TEA (Fig. 2C). It formed a heterogeneous mixture or a homogeneous thick paste in most cases. With NaOH and KOH, gelrite formed poorly viscous homogeneous phase E and sticky thick paste phase C (Fig. 2D and E). Degradation of gelrite might have taken place in alkaline solution.

As the phase D in the case of gelrite was very small the maximum amount of base which can be entrapped was around 4–6% and the same in the case of Na Alg was around 22–24%. The capacity of the gelrite system to entrap the base was much lower. Hence, for further work (Na Alg–water–morpholine) and (Na Alg–water–piperidine) systems were selected. They were cross-linked with Ca^{2+} ions to obtain hard gel beads, which were named as (Ca Alg–Mor) and (Ca Alg–Pip) gels.

3.3 Characterisation of GEBCs

The gel beads (Fig. S1, ESI†) were white. They had diameters in the range of 2.50–3.00 mm, and the mass per bead was in the range of 50.0–60.0 mg. The FT-IR spectra were recorded for Ca–Alg gel beads, (Ca Alg–Mor) and (Ca Alg–Pip) in ATR mode. The Ca–Alg gel bead showed bands at 3348 (broad, strong), 1604 (strong), 1418 (medium), 1031 (strong) and 791 (weak) cm^{-1}. In the case of (Ca Alg–Mor) and (Ca Alg–Pip) beads one extra

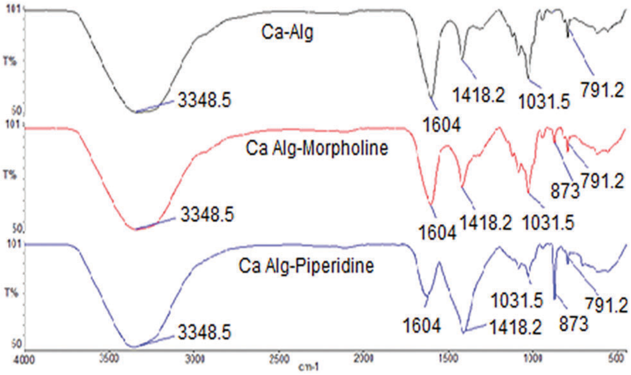


Fig. 4 FT-IR spectra of Ca–Alg and those of (Ca Alg–Mor) and (Ca Alg–Pip) gels in ATR mode.

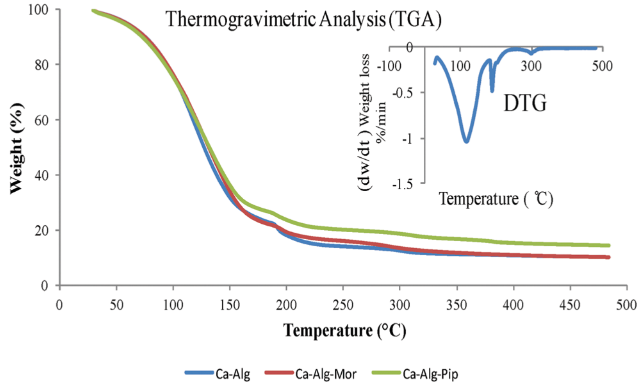


Fig. 5 TGA of Ca–Alg and those of (Ca Alg–Mor) and (Ca Alg–Pip) gels and DTG of Ca Alg.

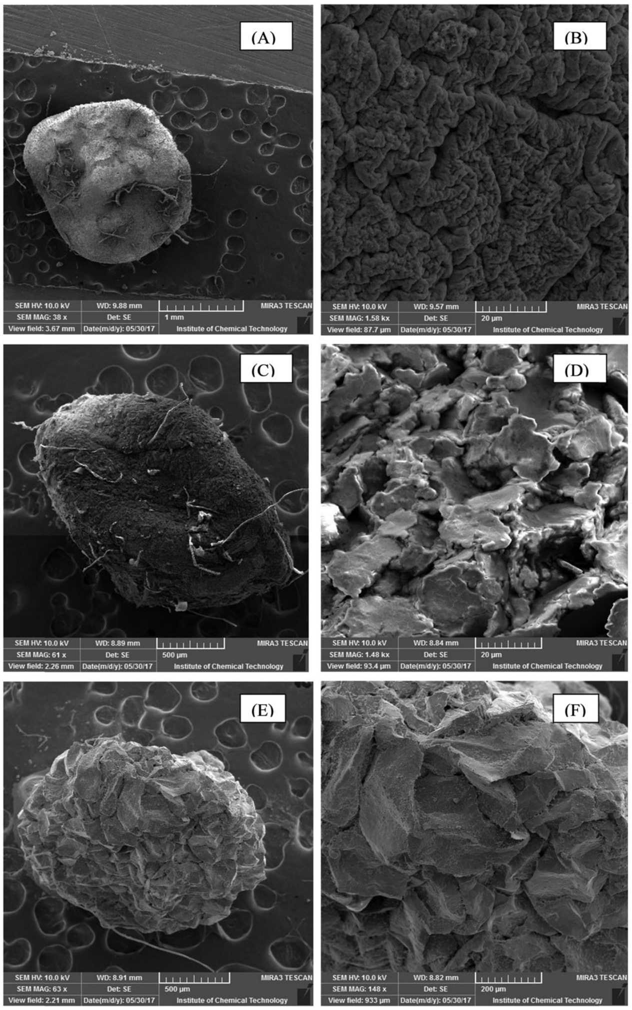


Fig. 6 FESEM images of [A] Ca–Alg gel beads, [B] the surface of the Ca–Alg gel beads, [C] Ca Alg–Mor gel beads, [D] the surface of the Ca Alg–Mor gel beads, [E] Ca Alg–Pip gel beads and [F] the surface of the Ca Alg–Pip gel beads.

band appeared at 873 cm^{-1} which was because of out-of-plane bending vibrations of N–H (Fig. 4). In thermogravimetric analysis (TGA), a significant weight loss for all gels was observed in the range of 90–150 °C (Fig. 5). The DTG graph showed two peaks one at around 100 °C which was for loss of water and bases, and a second at 200 °C which suggested decomposition of Ca–alginate (Fig. 5).

The FE-SEM images of Ca–Alg systems are shown in Fig. 6. The vacuum applied during Pt coating removed all the solvent from the gel beads, which caused a reduction in the diameter of the Ca–Alg gel beads of around 1 mm. The surface morphology of the Ca–Alg gel beads was different from that of the (Ca Alg–Mor) and (Ca Alg–Pip) beads.

3.4 Base entrapment efficiency of the gel beads (EE)

As the viscous solution of (gelator–water–base) was added to aq. $CaCl_2$ one would expect the amount of base present in the hard gel to be nearly same as that in the respective phase D. However, in the preliminary study, we found that the total base present in the hard gel was less than the amount of base present in the solution of phase D. To find out the amount of base entrapped in the gel beads, the beads were crushed and stirred in water at room temperature (27–30 °C) to extract the base. The amount of base was determined by conductometric titration against HCl solution. The GEBCs were prepared from (6.0% Na Alg + 81% water + 13.0% morpholine) and using aqueous solutions of $BaCl_2$, $SrCl_2$ and $CaCl_2$ for cross-linking. There was no significant change in EE (Table S2, ESI†). Similar results were obtained for the GEBCs from (6.0% Na Alg + 85% water + 9.0% piperidine) and using the above three cross-linkers (Table S2 ESI,† entries 9–11). As there was no significant effect of cross-linking cations on EE, we selected $CaCl_2$ for further study. We tested the effect of Ca^{2+} concentration on the entrapment efficiency, using 5, 10, 15 and 20% $CaCl_2$ solutions. 10% $CaCl_2$ showed the highest EE.

Around 25–28% of the base was retained in the GEBCs in the process of formation of a hard gel. Some combinations of (Na Alg–water–morpholine) and (Na Alg–water–piperidine) systems (Fig. 1A, B and Fig. S2, ESI†) forming phase D were tested for entrapment efficiency and (6.0% Na Alg + 81% water + 13% morpholine) and (6% Na Alg + 85% water + 9.0% piperidine) were selected for further study, as they showed maximum entrapment efficiency (Table S3, ESI†).

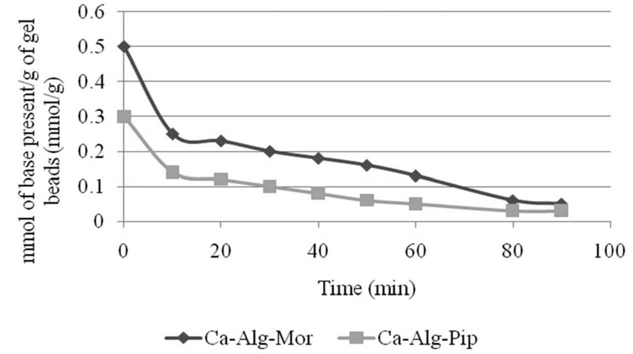


Fig. 7 Decrease in the amount of base present in the GEBCs w.r.t. time when stirred in methanol (GEBC beads 3.0 g, MeOH 10 mL, stirring with a magnetic bar at 200 rpm, temp 27–30 °C).

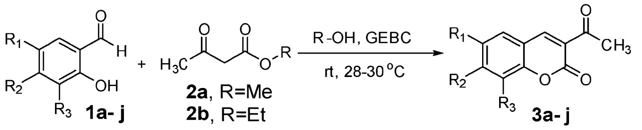
3.5 Leaching of base from GEBCs into methanol

For this study GEBCs (Ca10 Alg6–Mor13) and (Ca10 Alg6–Pip9) were used. As methanol is a common polar solvent for organic reactions and as we selected methanol for the reaction of salicylaldehyde and methyl acetoacetate, the tendency of the base to leach from the GEBCs into methanol was studied by stirring the GEBCs in methanol at room temperature.

The morpholine and piperidine slowly leached out in methanol (Fig. 7). The dark line shows the amount of morpholine and the faint line shows the amount of piperidine present in the GEBC beads.

3.6 Knoevenagel reaction of salicylaldehydes and methyl/ethyl acetoacetate in the presence of the GEBCs to obtain 3-acetylcoumarins

The reaction of salicylaldehyde (**1a**) and methyl acetoacetate (**2**) in the presence of a base gives 3-acetylcoumarin. This reaction has been carried out using different catalysts like piperidine, L-proline, pyridopyrimidine, L-lysine, and heterogeneous acids.[30–34] There is also a report with biocatalyst alkaline protease from *Bacillus licheniformis*.[35] Reaction of **1a** and **2** (Scheme 1) was carried using GEBCs (Ca10 Alg6–Mor-13) and (Ca10 Alg6–Pip-9) (Table 1). Both effectively catalysed the reaction in methanol and ethanol. The conversion was 100% in methanol and ethanol in 1 h and an excellent yield of **3a** was obtained. The results were equivalent to those obtained with these amines under homogeneous conditions (Table S4, ESI†). In other solvents (ethyl acetate, chloroform, THF, toluene) even after 3 h, the conversion of **1a** was not complete.



Scheme 1 Reaction of salicylaldehyde and acetoacetate ester.

Table 1 Reaction of **1a** ($R_1 = R_2 = R_3 = H$) and **2a/b** in the presence of GEBCs

Entry	**2**, Me/Et aceto-acetate	Solvent	Base	Reaction time (min)	Yield[a] of **3a** (%)
1	**2a**	Methanol	Ca10 Alg6–Mor13	50	82
2	**2b**	Ethanol	Ca10 Alg6–Mor13	60	85
3	**2a**	Methanol	Ca10 Alg6–Pip9	50	82
4	**2b**	Ethanol	Ca10 Alg6–Pip9	60	86

Reaction conditions: **1a** (4.0 mmol), **2a/b** (4.0 mmol), GEBC (1.0 g), methanol/ethanol (20 mL), rt (27–30 °C). [a] Isolated yield.

Table 2 Reaction of **1a–j** and **2a** ($R–CH_3$) using GEBCs

Entry	R_1	R_2	R_3	Product (**3**)	Yield[a] of **3a–j** (%)	m. p. (°C)
1	H	H	H	**3a**	82	117–118
2	H	H	OMe	**3b**	92	165–166
3	Br	H	H	**3c**	90	217–218
4	NO_2	H	H	**3d**	55	195–196
5	Cl	H	H	**3e**	74	221–222
6	Br	H	OMe	**3f**	70	204–205
7	NO_2	H	OMe	**3g**	62	215–216
8	H	$N(CH_2CH_3)_2$	H	**3h**	50	148–149
9	H	OH	H	**3i**	52	240–241
10	2-Acetyl-3*H*-benzo[*f*]chromen-3-one			**3j**	60	181–182

Reaction conditions: **1a–j** (4.0 mmol), **2a** (4.0 mmol), methanol (20 mL), GEBC (Ca10 Alg6–Mor13) (1.0 g), rt (27–30 °C), time 1 h. [a] Isolated yield.

Table 3 Reaction of **1a–b** and **2a** ($R–CH_3$) using (Ca10 Alg6–Mor13) in continuous mode

	Yield[a] (%)	
Fraction	**3a** ($R_1 = R_2 = R_3 = H$)	**3b** ($R_1 = R_2 = H$, $R_3 = OMe$)
1	85	95
2	73	81
3	55	62
4	33	42

Reaction conditions: **1a–b** (0.2 M) and **2a** (0.2 M) in MeOH, reactor volume = 5.5–6.0 mL, flow rate-1.0 mL min^{-1}, rt (27–30 °C), Product isolated from fractions of 20.0 mL, GEBC beads (10 g), (Ca10 Alg6–Mor13) cross-linked with 10% aqueous $CaCl_2$. [a] Isolated yield.

Under optimum conditions, a series of salicylaldehydes were reacted with **2a** (Table 2). To see the recyclability of the catalyst, the GEBC was filtered from the reaction mass and used as such for the next cycle. The very poor yield obtained in the second cycle was possibly due to the leaching of the base from the GEBC.

The reaction was also attempted in continuous mode by passing a solution of **1a–b** (0.2 M) and **2a** (0.2 M) in methanol at a rate of 1.0 mL min^{-1} through a glass column (inner diameter 8 mm, length 30 cm, Fig. S3, ESI†) filled with GEBC (Ca10 Alg6–Mor13) at rt (27–30 °C) using a peristaltic pump. Under these conditions the yield of product was noted in each fraction of 20.0 mL; the results are given in Table 3.

In order to see the differential effect of the reaction catalysed by GEBC and that by the base leached out from the GEBC, 20 mL methanol was passed through the GEBC column and the eluent was collected. The reaction was attempted in the eluent collected. Poor yield of the product (30%) was obtained in 3 h. On the other hand, the continuous mode reaction gave excellent yield (85%) in 15 min. Therefore, the reaction was mainly assisted by the base present in the gel beads.

4. Conclusion

(Na Alg–water–base) and (gelrite–water–base) systems were studied for phase behaviour. Na Alg systems with morpholine and piperidine bases gave promising viscous homogeneous phase. When these phases were treated with Ca^{2+}, Ba^{2+} or Sr^{2+} ions, cross-linking took place among the gelator molecules and hard gels were formed in which the base was trapped. These solid GEBCs were useful heterogeneous base catalysts for reaction in a non-aqueous medium. The carboxymethyl chitosan and gelrite could not be used to prepare GEBCs. Triethylamine, sodium hydroxide and potassium hydroxide could not be entrapped in the Ca–Alg gel. From this study, GEBCs (Ca10 Alg6–Mor13) and (Ca10 Alg6–Pip9) were found to be very promising. They could be used for catalysing Knoevenagel reaction of salicylaldehydes and methyl acetoacetate to form 3-acetylcoumarins. These catalysts did not require any pretreatment and were convenient to use for flow reactions. This new strategy of preparing solid GEBCs can be extended to different gelators to prepare gels with entrapped organic and inorganic bases (GEBCs) which can be used for various base-catalysed reactions.

For this type of gel-entrapped catalyst, leaching of the entrapped base from the gel phase to the solution phase appears to be a concern. Detailed study w.r.t. partitioning of the entrapped base in the gel phase and solution phase at equilibrium needs to be studied. A combination of a suitable gelator and a suitable solvent for the reaction phase to retain the catalyst in the gel phase is required for such a reaction.

Conflicts of interest

There are no conflicts to declare.

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