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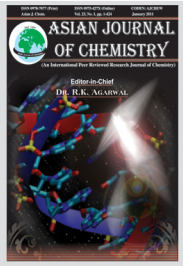

Preparation of Dialdehydecellulose-3,5-dinitrobenzoate and Adsorption of Urea Nitrogen and Creatinine onto It

LI JIAN* and LIANG ZU-PEI*

Department of Chemistry and Chemical Engineering, Weifang University, Weifang 261061, P.R. China

*Corresponding author: Fax: +86 536 8877561; Tel: +86 536 8877561; E-mail: lzpwfu@163.com; ljwfu@163.com

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Dialdehydecellulose-3,5-dinitrobenzoate (DAC-DNBZ) was prepared by esterification of 2,3-dialdehyde cellulose (DAC) and 3,5-dinitro benzoyl chloride (DNBC) in the lithium chloride/N,N-dimethylacetamide (LiCl/DMA) solvent system and pyridine as catalyst. The effects of molar ratio of the materials, the amount of catalyst, reaction temperature and reaction time on the degree of substitution (DS) of dialdehydecellulose-3,5-dinitrobenzoate were investigated. The results suggest that dialdehydecellulose-3,5-dinitrobenzoate product was used as adsorbent for urea nitrogen and creatinine.

Key Words: Dialdehydecellulose-3,5-dinitrobenzoate, Esterification, Adsorption, Urea nitrogen, Creatinine.

INTRODUCTION

Cellulose is the most abundant natural polymer on Earth and as the main constituent of plants, is readily renewable. A large number of hydroxyl groups exist in cellulose and cellulose chemical modifications occur easily. There are cellulose derivatives with various properties such as dialdehydecellulose (DAC)[1] and cellulose-3,5-dinitrobenzoate[2]. However, the cellulose derivatives with two types of functional groups are rare.

Urea and creatinine are two of the major metabolic end products and the removal of redundant urea and creatinine has been a major problem for patients suffering from chronic renal failure (CRF). Haemodialysis is the conventional treatment for CRF. However, It is bulky, cumbersome, expensive, time-consuming and difficult to handle[1]. Oral adsorbents, such as active charcoal[3] and oxystarch[4], could potentially delay the onset of haemodialysis therapy in patients who still have some renal function and reduce haemodialysis treatment times[3]. However, the adsorbent with selective adsorptions of both urea nitrogen and creatininte onto it has not been reported.

In the previous work[1,5-9], the adsorptions of urea nitrogen were prepared and used in the removal of urea nitrogen. In this work, DAC-DNBZ with aldehyde group and 3,5-dinitrobenzoyl one was prepared in the homogeneous LiCl/DMA solvent system. The adsorptions of both urea nitrogen and creatininte onto DAC-DNBZ were studied in batch system.

EXPERIMENTAL

α-Cellulose (degree of polymerization: 500, molecular weight: 243,000) was supplied by Huludao Chemical Co., Liaoning, China. Sodium periodate was obtained from Tianhe Chemical Reagent Co., Tianjin, China. Urease (EC 3.5.1.5, from jack bean) was obtained from BDH Chemicals Ltd., Poole, England. 3,5-Dinitrobenzoyl chloride was obtained from Dingxiang Chemical Co., Jiangsu, China. Creatinine, urea, *N*,*N*-dimethylacetamide and lithium chloride were obtained from Kewei Co., Tianjin, China.

Preparation of DAC: Preparation of DAC and determination of its percentage degree of oxidation (DO) followed the methods as reported[1]. The DAC with the DO 88 % was obtained. A modified method from the reports[5,6] was used in order to perform dissolution of DAC.

Acetylation of DAC: LiCl (8 g) was dissolved into 100 mL DMA at 45 ºC for 0.5 h. 2 g DAC (DO 88 %) was added to the LiCl/DMA solution. The mixture was stirred at 45 ºC for overnight. 20 g DNBC and 20 mL pyridine were added to the DAC solution prepared above. Reaction times ranged 12-62 h and temperatures from 30-70 ºC. The reaction was terminated when the mixture was poured into methanol (200 mL). The product was precipitated for 1.5 h and then filtered and washed thoroughly with methanol (3 × 100 mL). The resulting product was dried at 40 ºC under reduced pressure for 16 h.

Degree of substitution (DS) determination: Determination of degree of substitution (DS) of DAC-DNBZ was done by reported method[11]. 0.3 g DAC-DNBZ was dissolved in 0.25 mol/L NaOH alcoholic solution (25 mL) and the solution was stirred at ambiance temperature for 24 h. The excess of base was then back titrated by 0.10 mol/L hydrochloric acid with phenolphthalein as an indicator. The procedure was repeated

at least tice and the degree of substitution (DS) of DAC-DNBZ was calculated according to the following formula.

$$DS = \frac{160 - V_0 - V_1 C_{HCl} 10^{-3}}{W - V_0 - V_1 C_{HCl} 10^{-3} M_{DNBC} - 35.5}$$

where V_0 and V_1 (mL) are the volumes of HCl solution for the blank and the sample, respectively; C_{HCl} (mol/mL) is the concentration of HCl solution; W (g) is the weight of DAC-DNBZ used; M_{DNBC} is the molecular weight of 3,5-dinitrobenzoyl chloride and 35.5 is the atom weight of chlorine.

Characterization of DAC-DNBZ: IR spectra of DAC-DNBZ were recorded on a RX FT-IR spectrophotometer. The surface morphology of DAC-DNBZ and DAC was characterized by scanning electronic microscope (SEM), at × 4000 magnification.

Adsorption of urea nitrogen onto DAC-DNBZ: Experiments of adsorption of urea nitrogen onto DAC-DNBZ followed the previous methods[1].

In experiments of adsorption of urea nitrogen onto DAC-DNBZ, 0.5 g DAC-DNBZ (DO 88 %), 50 mg immobilized urease in gelatin (IE, its enzymatic activity 528 IU/g) and 75 mL urea nitrogen solution (600 mg/L) were placed in a 150 mL Erlenmeyer flask and the flask was shaken on a shaker at 37 ºC. Every other period of time, the supernatant liquid 2 mL was taken out and placed in a 50 mL flask containing desired amount urease and residual urea were hydrolyzed to ammonia and carbon dioxide by urease catalyzing for 12 h. The concentration of urea nitrogen at t_i was determined by measuring the amount of ammonia liberated from the urease-catalyzed hydrolysis of urea. The amount of adsorption at equilibrium q_e (mg/g) was calculated as follows:

$$q = \frac{\sum (C_i - C_{i+1}) \times V_i}{W} (i = 0, 1, 2, 3\ldots)$$

where C_i and C_{i+1} (mg/L) are urea nitrogen concentrations at t_i and t_{i+1}, respectively, V_i (L) is the volume of the solution and W (g) is the weight of DAC-DNBZ used.

Adsorption of creatinine onto DAC-DNBZ: In experiments of adsorption of creatiine onto DAC-DNBZ, 0.5 g DAC-DNBZ (DS 0.54) and 75 mL creatinine solution (100 mg/L) were placed in a 150 mL Erlenmeyer flask and the flask was shaken on a shaker at 37 ºC. Every other period of time, the concentration of creatinine at t_i was determined followed the method of the Yan *et al.*[12]. The amount of adsorption q (mg/g) was calculated according to the formula,

$$q = \frac{\sum (C_i - C_{i+1}) \times V_i}{W} (i = 0, 1, 2, 3\ldots)$$

where C_i and C_{i+1} (mg/L) are creatinine concentrations at t_i and t_{i+1}, respectively, V_i (L) is the volume of the solution and W (g) is the weight of DAC-DNBZ used.

RESULTS AND DISCUSSION

Effect of DNBC/DAC molecular ratio on DS of DAC-DNBZ: The effect of DNBC/DAC molecular ratio on DS of DAC-DNBZ was investigated under these reaction conditions: 2 g of DAC solubilized in 100 mL LiCl/DMA 8 % (w/v), 20 mL pyridine, DNBC amounts between 10 and 25 g at 50 ºC for the reaction time 48 h. The results are shown in Table-1. It is seen from Table-1 that the DS increases significantly with increasing DNBC/DAC molecular ratio at the initial stage and the DS values reached a plateau value after DNBC/DAC molecular ratio 7:1. This might suggest that the number of activated hydroxy groups for the esterification is quantificational.

TABLE-1
EFFECT OF MOLAR RATIO ON THE DS OF DAC-DNBZ

DNBC/DAC	3:1	5:1	7:1	9:1	11:1
DS	0.21	0.38	0.54	0.57	0.59

Effect of pyridine amount on DS of DAC-DNBZ: Table-2 shows that the effect of pyridine amount on DS of DAC-DNBZ under these reaction conditions: 2 g of DAC solubilized in 100 mL LiCl/DMA 8 % (w/v), DNBC/DAC molecular ratio 7:1 at 50 ºC for the reaction time 48 h. As seen from Table-2, the DS increases significantly with increasing pyridine amount at the initial stage and the DS values reached a plateau value after addition of 20 mL of pyridine.

TABLE-2
EFFECT OF THE AMOUNT OF PYRIDINE ON DEGREE OF SUBSTITUTION (DS) OF DAC-DNBZ

Pyridine amount (mL)	10	15	20	25	30
DS	0.13	0.46	0.54	0.56	0.56

Effect of temperature on DS of DAC-DNBZ: Table-3 shows that the effect of temperature on DS of DAC-DNBZ under these reaction conditions: 2 g of DAC solubilized in 100 mL LiCl/DMA 8 % (w/v), DNBC/DAC molecular ratio 7:1 and 20 mL pyridine for the reaction time 48 h. As seen from Table-3, DS increases significantly with increasing temperature at the initial stage and the product was in yellow and gray at temperature 60 and 70 ºC, respectively. This might be due to the DAC with aldehyde groups was partially carbonized at the high temperature.

TABLE-3
EFFECT OF TEMPERATURE ON DEGREE OF SUBSTITUTION (DS) OF DAC-DNBZ

Temperature (ºC)	30	40	50	60	70
DS	0.08	0.25	0.54	Yellow	Gray

Effect of reaction time on DS of DAC-DNBZ: Table-4 shows that the effect of reaction time on DS of DAC-DNBZ under these reaction conditions: 2 g of DAC solubilized in 100 mL of LiCl/DMA 8 % (w/v), DNBC/DAC molecular ratio 7:1 and 20 mL pyridine at 50 ºC. As seen from Table-4, the DS increases significantly with reaction time increase and the DS 0.54 was obtained after the reaction time 48 h. When the reaction time last 60 h, DS was 0.57.

TABLE-4
EFFECT OF REACTION TIME ON DEGREE OF SUBSTITUTION (DS) OF DAC-DNBZ

Reaction time (h)	12	24	36	48	60
DS	0.28	0.35	0.46	0.54	0.57

Infrared spectroscopy: Fig. 1 shows the infrared spectrum of DAC and DAC-DNBZ. The adsorption peaks at 1637 cm^{-1} due to C=O (aldehyde) stretching from DAC and DAC-DNBZ. An adsorption peak at 1740 cm^{-1} due to C=O (ester) stretching from DAC-DNBZ. Two adsorption peaks at 1548 and 1347 cm^{-1} due to -NO_2 stretching from DAC-DNBZ. Two adsorption peaks at 1060 and 719 cm^{-1} are believed to correspond to -Ar group of DAC-DNBZ. These indicate that the esterification product obtained by the reaction of DAC and DNBC was DAC-DNBZ.

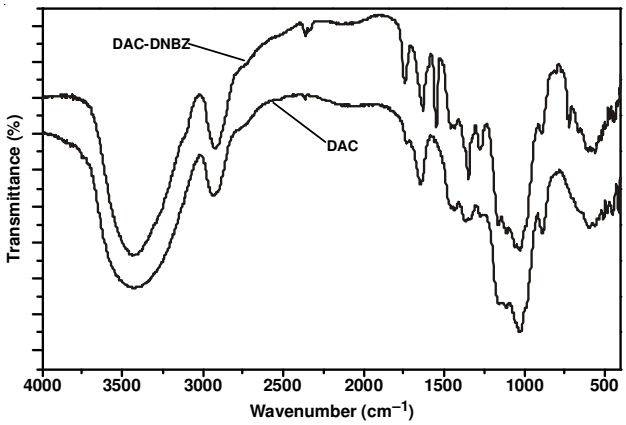
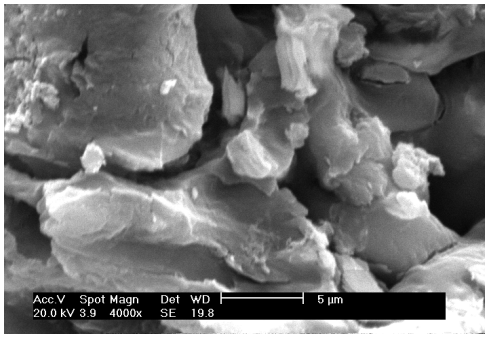
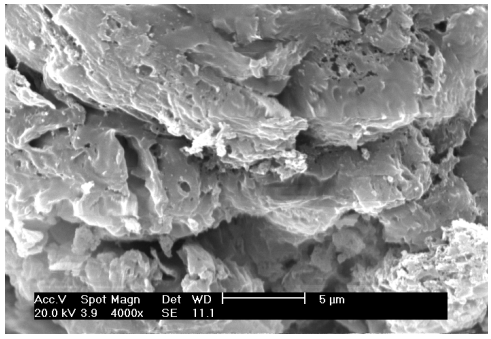


Fig. 1. FTIR spectra of DAC and its esterification products DAC-DNBZ

Surface morphology as presented by scanning electronic micrographs: Fig. 2(a) and (b) shows the surface characteristics of DAC and DAC-DNBZ, respectively. As seen from Fig. 2(a) and (b), there are a great deal of holes on the surface of DAC and some holes on the surface of DAC was covered with DNBZ-groups when DAC-DNBZ was prepared by the reaction of DAC and DNBC.



(a) DAC × 4000



(b) DAC-DNBZ × 4000

Fig. 2. SEM spectra of DAC and DAC-DNBZ

Esterification reaction scheme: The overall suggested esterification reaction mechanism of DAC and DNBC using pyridine as the catalyst in LiCl/DMA solvent system is given in **Scheme-I**.

Adsorption of both urea and creatine onto DAC-DNBZ: Fig. 3 shows adsorption quantity of urea nitrogen onto DAC-DNBZ with DO 88 % and DS 0.54 in phosphate buffer at pH 7.4, temperature 37 ºC and urea nitrogen concentration 600 mg/L and the adsorption quantity of urea nitrogen onto DAC-DNBZ was 31.4 mg/g for adsorption 8 h.

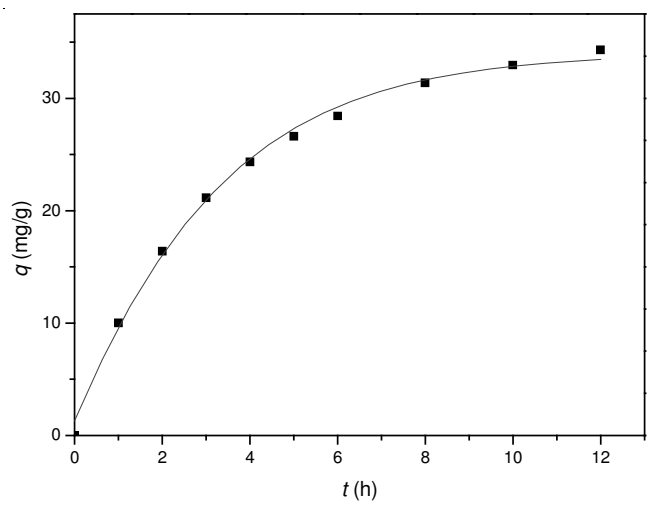


Fig. 3. Adsorption quantity of urea nitrogen onto DAC-DNBZ

Fig. 4 shows adsorption quantity of creatinine onto DAC-DNBZ with DO 88 % and DS 0.54 in phosphate buffer at pH 7.4, temperature 37 ºC and creatinine concentration 100 mg/L. After 8 h for adsorption, the adsorption quantity of creatinine onto DAC-DNBZ was 2.6 mg/g.

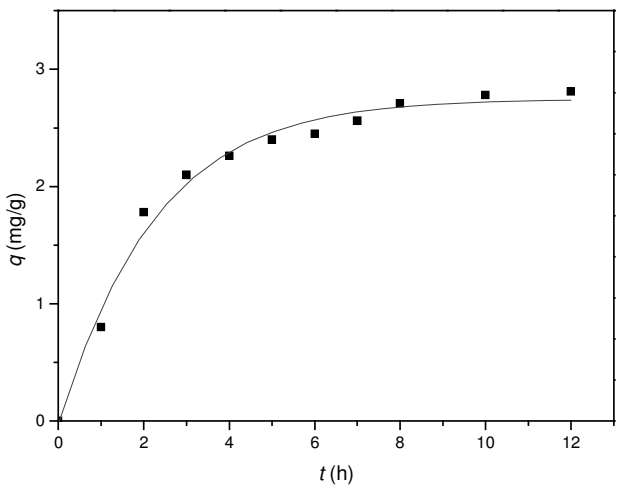
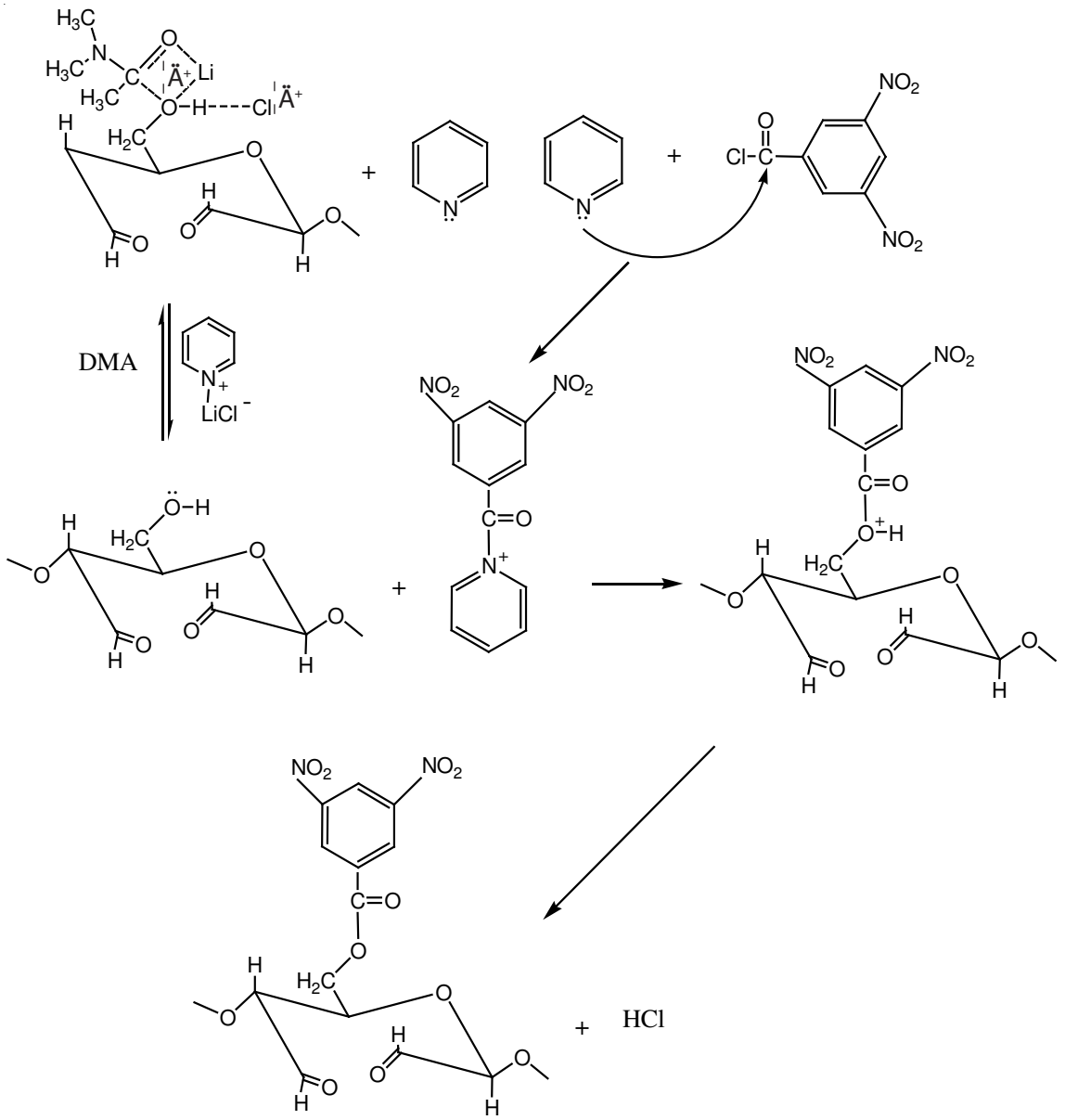


Fig. 4. Adsorption quantity of creatinine onto DAC-DNBZ

These data suggest that the dialdehydecellulose-3,5-dinitrobenzoate (DAC-DNBZ) ester could be used in further applications in removal of urea nitrogen and creatinine for chronic renal failure patients by oral administration.



Scheme-I: Suggested reaction mechanism for estrification of DAC and DNBC using pyridine as catalyst in the LiCl/DMAC solvent system

Conclusion

A novel adsorbent for urea nitrogen and creatinine was prepared. Dialdehydecellulose-3,5-dinitrobenzoate (DAC-DNBZ) was prepared by esterification of DAC and DNBC in the LiCl/DMA solvent system and the effects of molar ratio of the materials, the amount of catalyst, reaction temperature and reaction time on the DS of DAC-DNBZ were investigated. DAC-DNBZ could be used in further applications in removal of urea nitrogen and creatinine for chronic renal failure patients by oral administration.

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