Effect of the Alkyl Chain Length on the Adsorption properties of Malonamide Chelating Resins

Ibrahim M. Ismail[1*], Masanobu Nogami[2], Kazunori Suzuki[2]

1) Cairo University, Chemical Engineering Department, Giza, Egypt

2) Institute of Research and Innovation, Kashiwa, Chiba, Japan

Abstract:

In order to investigate the effect of the alkyl chain length of malonamide chelating resins on the rate of uptake of U(VI) ions and Ce(III) ions, *N,N,N',N'*-tetraethylmalonamide (TEMA), *N,N,N',N'*-tetra-*n*-propylmalonamide (TPrMA), *N,N,N',N'*-tetra-*n*-butylmalonamide (TBMA) and *N,N,N',N'*-tetra-*n*-pentylmalonamide (TPeMA) chelating resins were synthesized by chemically bonding these function groups to CMS-DVB co-polymer beads. *N,N,N',N'*-tetraphenylmalonamide (TPhMA) chelating resin was also investigated and the results of these resins were compared with those of *N,N,N',N'*-tetramethylmalonamide (TMMA) previously reported. The batch technique was used to study the thermodynamic equilibrium, in terms of distribution coefficient, and the kinetics of the adsorption U(VI) and Ce(III) ions from 3 M HNO_3, Acid, and 3 M $NaNO_3$ + 0.05 M HNO_3, Salt, media. The introduction ratio of the function group into the polymer base and the uptake of U(VI) ions and Ce(III) ions were found to decrease with the increase in the alkyl chain length. The uptake was found to diminish in case of TPhMA resin due to the decrease of the function group ratio and the steric-hinder effect.

_____

* Corresponding Authors. Tel.: +202-7207852

Email: dr_ismail@instruchem.org & lojina_1999@yahoo.com

1. Introduction:

Malonamides have been adopted as suitable extractants for actinides and lanthanides in recent reprocessing technologies due to their high resistance to radiolysis, hydrolysis and low cost [1-7]. Other advantageous of these compounds are their ease of synthesis and incineration compared to organophosphorous extractants such as CMP (dihexyl-N,N-diethylcarbamoylmethylphosphonate) and CMPO (n-octyl (phenyl) - N,N-diiso-butylcarbamoylmethylphosphine oxide). The utilization of a number of malonamides of the formula $(RR`CON)_2CH_2$ where R and R` are alkyl radicals as an alternative extractants to TBP used in PUREX processing of spent nuclear fuels has been suggested by several researchers [3-5].

Mowafy and Aly found that the malonamides substituted with alkyl group (C_6H_{13}) or oxyalkyl group $(C_2H_4OC_6H_{13})$ at the central methylene carbon have the highest tendency to extract different metal ions than the other non-substituted malonamides at the central carbon atom [8]. Based on these findings we proposed the bonding of malonamides to chloromethylstyrene (CMS) and divinylbenzene (DVB) co-polymer through the central methylene carbon atom to synthesis chelating resins that can be used in fixed bed column [9-11]. In fact, the recent successful utilization of chelating resins in different difficult separation tasks supported their introduction as a promising technology for the treatment of contaminated aqueous solutions. Applying this technique, it is expected that the advantage of malonamides higher extractability will be gained

while the solubility problem encountered in solvent extraction systems is overcame. Moreover, the problem of the third phase formation, found by many researchers used amides compounds in solvent extraction system, will not be encountered. The structure of the amide function group was found to highly affect the separation behaviour of actinides and lanthanides in solvent extraction system [12]. The amidic alkyl chain length was found to highly affect the extractability of actinides and lanthanides by diglycolamides as was reported by Sasaki et al. They found that the shorter the chain length, the higher the extractability [13]. Other reports suggested that the use of butyl alkyl chain as a substitution for R and R` enhances the extractability of the malonamide functional group in solvent extraction system (from Nogami san). Therefore, the aim of this work is to investigate the effect of the alky chain length used to substitute R and R` on the adsorption properties of malonamide chelating resin. In a pervious work, we studied the effect of the pore diameter of the resin beads on the rate of adsorption of U(VI) ions and Ce(III) ions by TMMA resin [10]. Larger pore diameter of the resin beads was found to enhance the rate of uptake of U(VI) and Ce(III) ions from different solutions. Consequently, the largest possible pore diameter of polymer beads was utilized in this current contribution.

2. Experimental:

2.1. Synthesis of the chelating resins:

The synthetic procedure consists of two steps; the conventional suspension polymerization of chloromethylstyrene (CMS) and divinylbenzene (DVB) in the presence of 40 % methyl benzoate (MB) + 60% decane, pore producing solvent, which yields regular spherical beads, and the introduction of the functional group into these beads, in the

presences of DMF solvent, where the chlorine atom of CMS is substituted by the malonamide functional group. All chemicals used were of analytical grade and were used without any further purification. The scheme of the synthesis procedure is shown in Fig. 1.

2.2. Characterization of the chelating Resins:

The chelating resins synthesized were characterized by elemental analysis using CHNS-O Flash EA 1112 analyzer supplied by Thermo Finnigan Ltd, and IR spectrophotometry using FT/IR–410 spectrophotometer supplied by JASCO Ltd. To evaluate the swelling ratios of the resins in different solutions, a sample of each resin was stirred in an excess amount of a specific solution for 24 hours, vacuum filtrated, and then the volume of 1 g-wet of it was measured using density bottle. The volume of 1 g of the dried sample was also measured. The total acidity of the resins were measured by stirring a known weight of the vacuum filtrated resin in 100 ml of 0.1 M NaOH solution for 24 hours. A sample of the solution, after being filtrated, was titrated with 0.1 M HNO_3 standard solution using auto titrator model AUT-301 made by TOA, Japan. A weighted sample of the wet resin was dried in each run to calculate the moisture ratio.

2.3. Adsorption Properties:

The synthesized chelating resins were sieved and the fraction of the particle diameter range 0.3 - 0.5 mm was selected for further investigations. Two solution media of 0.05 M HNO_3 + 3 M $NaNO_3$, Salt, and 3 M HNO_3, Acid, were used for the batch tests. 1000 mg·dm^{-3} U(VI) or 200 mg·dm^{-3} Ce(III) ions were added to these solutions. These solutions were mixed with the resin beads in a batch vessel checked in a water bath at a constant

temperature. The solid/liquid ratios adapted was 1g-wet / 100cm^3 in case of U(VI) and 2g-wet / 100cm^3 in case of Ce(III). In case of kinetics studies, fraction samples were withdrawn from the batch vessel at appropriate intervals. While, in the case of thermodynamic studies, the vessel was checked tell equilibrium was attained. For each experimental run a weighted sample of the wet resin was dried to calculate the moisture ratio. The concentrations of all ions in the solution samples were measured by VISTA-PRO, CCD simultaneous ICP-OES supplied by Seiko Instruments & Varian Instruments.

3. Results and discussions:

3.1. Characterization of the prepared resins:

According to the synthesis scheme shown in Fig. 1, five chelating resins were prepared using a polymer base of 490 nm pore diameter, the pore diameter of the polymer base was measured using the mercury intrusion technique as was described in a previous work [10]. The synthesized resins were characterized in terms of elemental analysis and the results are shown in Table 1. Based on these results, the percentage of Cl atoms substitution as well as the percentage of the different functional groups introduction was calculated using the atom balance. The results of these calculations were also presented in Table 1. The difference between the values of the percentage of Cl atoms substitution and the percentage of the different functional groups introduction is believed to be due to the partial hydrolysis during the synthesis process. It is obvious that both of the percentage of Cl atoms substitution and the percentage of functional groups introduction decrease with the increase in the alkyl chain length. They both become of minimum values in the case of TPhMA. It seems that by increasing the size of the functional group, its introduction into the

polymer base is hindered. A similar conclusion was achieved when the introduction percentage of CMP, 61, was compared with these of TMMA [9]. The unexpected deviation of the Cl atoms substitution percentage in the case of TPeMA compared with other alkyl cases could be attributed to a higher degree of hydrolysis encountered in this particular case. This resin was synthesized in summer season, where the relative humidity is usually so high in Japan. In fact, hydrolysis has to be completely inhibited during the resin synthesis. Although, the synthesis reactions were carried out under inert gas blanket, Ar or N_2, hydrolysis reactions were not completely inhibited. The total acidity values were measured by titration method and are shown in Table 1. The acidity value depends on the synthesis condition, and in general is increased with the increase of humidity during the introduction of the functional group into the base polymer.

Fig. 2 shows the IR spectra of the chelating resins produced. In all cases, a strong band appeared at 1640 cm^{-1}, which is believed to be due to the C=O bond, which is a characteristic bond of the amide functional group. In case of TPeMA, there was a small carboxylic band around 1700 cm^{-1}, overlapped by the strong C=O band at 1637 cm^{-1}. Such band was not observed in other cases or in other diamide resins synthesized previously [9,10]. This finding supports the, previously discussed, explanation of the higher Cl substitution percentage in the case of TPeMA. Alkanes C-H stretching bond was observed around 2900 cm^{-1} in all cases. Its intensity increased with the increase of the alkyl chain length from TMMA to TPeMA.

Based on the elemental analysis data and the IR data, it can be suggested the synthesis was carried out according to the scheme given in Fig. 1, and the obtained resins can be used for the adsorption investigations.

3.2. Adsorption investigations:

3.2.1. Thermodynamic Equilibrium:

The thermodynamic equilibrium of U(VI) and Ce(III) ions adsorption from the two solution media of 0.05 M HNO_3 + 3 M $NaNO_3$ (Salt) and 3 M HNO_3 (Acid), in terms of distribution coefficient, were studied using the batch technique. The distribution coefficient, K_d, is defined here as

$$K_d = \frac{(C_o - C)}{C} \times \left(\frac{V}{M} \right) \tag{1}$$

where C_o is the initial concentration of adsorbed ions in solution, C is their concentration at equilibrium, V is the solution volume in cm^3 and M is the dry mass of the resin in gram. Table 2 shows the calculated K_d values of the U(VI) and Ce(III) ions adsorption from the Acid and Salt media. A general trend can be easily observed from these data. In all cases, the K_d values order is:

TMMA > TEMA > TPrMA > TBMA > TPeMA

This order agrees with the introduction ratio of the functional groups of the five resins and with the alkyl chain length. To elaborate whether this order is due to the introduction ratios of the functional groups or due to the alkyl chain length, a modified distribution coefficient, K_{dm}, was calculated according to

$$K_{dm} = \frac{K_d}{FIR} \tag{2}$$

where *FIR* is the functional groups introduction ratios given in Table 1.

The calculated values of the modified distribution coefficients are shown in Table 3. It is clear that the same general trend still exists, which suggests that the K_d values order shown above is due to the alkyl chain length. By increasing the alkyl length chain, the complexing of the adsorbed ions with the chelating function group is decreased, most probably due to steric hinder.

3.2.2. Rate of Uptake:

The rate of adsorption of U(VI) and Ce(III) from the two solution media of 0.05 M HNO_3 + 3 M $NaNO_3$ (Salt) and 3 M HNO_3 (Acid) were studied as a function of time using the batch technique. The obtained results are plotted as ion uptake by resin versus time. Figs. 3-6 show these plots for the rate of uptake of U(VI) ions from the Acid solution, the adsorption of U(VI) ions from the Salt solution, the adsorption of Ce(III) ions from the Acid solution and the adsorption of Ce(III) ions from the Salt solution by the five chelating resins, respectively. The order of the five resins rate of uptake is similar to the order of the distribution coefficient discussed before i.e. the rate is decreased with the increase of the alkyl chain length from C1 to C5.

Comparing the adsorption properties, equilibrium and rate of uptake, of U(VI) ions and Ce(III) ions by the five diamide resins, it is obvious that the diamide resins are all more selective towards U(VI) ions.

4. Conclusions:

Diamide chelating resins with different alkyl chain length and *N,N,N',N'*-tetraphenylmalonamide (TPhMA) chelating resin were synthesized and utilized for the separation of U(VI) ions and Ce(III) ions

from different media. The results of these resins were compared with those of *N,N,N',N'*-tetramethylmalonamide (TMMA) previously reported. The batch technique was used to study the distribution coefficient and the rate of uptake of U(VI) and Ce(III) ions from different media. The introduction ratio of the functional groups into the base polymer, the distribution coefficient, and the rate of uptake of U(VI) ion and Ce(III) ions were found to decrease with the increase in the alkyl chain length. In case of TPhMA chelating resin, no U(VI) or Ce(III) ions adsorption was observed. This is believed to be due to steric hinder.

References:

1. E. Mowafy, H. Aly, Solvent Extr. Ion Exch. 19 (4) (2001) 629.

2. C. Madic, J. M. Hudson, O. J. Liljenzin, P. G. Glatz, R. Nannicini, A. Facchini, Z. Kolarik, R. Odoj, *New Partitioning Techniques for Minor Actinides*, EUR 19149 EN; European Commission: Brussels, 2000; 7.

3. T. H. Siddall, J. Phys. Chem. 64 (1960) 1864.

4. G. Thiollet, C. Musikas, Solvent Extr. Ion Exch. 7 (5) (1989) 813.

5. L. Spjuth, J. O. Liljenzin, M. J. Hudson, M. G. Drew, P. B. Iveson, C. Madic, Solvent Extr. Ion Exch. 18 (1) (2000) 1.

6. S. El-Reefy, E. Mowafy, M. Abdel-Badei, H. Aly, Radiochemica Acta, 77 (1997) 195.

7. J. S. Preston, A. C, Dupreez, Solvent Extr. Ion Exch. 13 (1995) 391.

8. E. Mowafy, H. Aly, Solvent Extr. Ion Exch. 20 (2) (2002) 177.

9. M. Nogami, I. Ismail, M. Yamaguchi, K. Suzuki, J. Solid State Chem.

171, 353 (2003).

10. I. Ismail, M. Nogami, K. Suzuki, J. Sep. Purif. Technol. 31, 231 (2003).

11. Ismail, I. M.; Nogami, M.; Suzuki, K. Solvent Extr. Ion Exch. 21(3), 465 (2003).

12. Y. Sasaki, S. Tachimori, Solvent Extr. Ion Exch. 20 (1) (2002) 21.

13. Y. Sasaki, Y. Sugo, S. Suzuki, S. Tachimori, Solvent Extr. Ion Exch. 19 (1) (2001) 91.

Table 1 Properties of the chelating resins

	*TMMA	TEMA	TPrMA	TBMA	TPeMA	TPhMA
Total Acidity	0.2	1.2	0.8	0.5	0.2	-------
C %	70.90	77.59	79.21	81.37	80.61	81.22
H %	8.10	8.81	9.29	9.47	9.43	6.68
N %	7.50	6.13	4.99	3.67	3.26	3.00
O %	12.20	6.70	5.53	4.47	6.53	4.20
Cl %	0.70	0.77	0.98	1.02	0.17	4.90
Substituted Cl %	94.1	92.4	89.1	87.4	97.5	49.1
**Functional group introduction %	75.0	66.8	56.9	39.4	36.3	33.1

* Reference
** Based on N

Table 2

Distribution coefficient of U(VI) and Ce(III) ions adsorbed by different chelating resins

	TMMA	TEMA	TPrMA	TBMA	TPeMA
U(VI)/Acid	232.9	181.2	106.2	66.9	48.1
U(VI)/Salt	296.0	160.5	42.3	15.1	12.5
Ce(III)/Acid	70.6	48.2	20.5	14.9	3.2
Ce(III)/Salt	96.6	48.4	9.7	7.3	3.8

Table 3

Modified distribution coefficient of U(VI) and Ce(III) ions adsorbed by different chelating resins

	TMMA	TEMA	TPrMA	TBMA	TPeMA
U(VI)/Acid	310.6	271.3	186.7	169.9	132.5
U(VI)/Salt	394.7	240.2	74.3	38.4	34.4
Ce(III)/Acid	94.1	72.2	36.0	37.9	8.8
Ce(III)/Salt	128.8	72.4	17.0	18.5	10.5

List of Figures

CMS + DVB

40% MB + 60% Decane
18 hr

CH₂Cl

Screening

0.3 - 0.5 MM
Diameter

R = R` = C2, nC3, nC4, nC5 or phenyl

80°C, 24 hr*

Chelating resin

Functional Group

NaH, DMF*
60°C, 1hr

* Under inert gas

% T

TMMA*

100

50

10

4000   3500   3000   2500   2000   1500   1000   400

Wavenumber[cm –1]

% T

TEMA

100

80

60

40

4000   3500   3000   2500   2000   1500   1000   400

Wavenumber[cm -1]

% T

TPrMA

100

80

60

40

30

4000   3500   3000   2500   2000   1500   1000   400

Wavenumber[cm -1]

100
80
%T
60
40

TBMA

Wavenumber[cm-1]

100
80
%T
60
40

TPeMA

Wavenumber[cm-1]

100
80
60
%T
40
20

TPhMA

Wavenumber[cm-1]