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SYNTHESIS AND EVALUATION OF CATIONIC AND CATIONOGENIC POLYMERIC SORBENTS FOR REMOVING SURFACTANTS FROM AQUEOUS SOLUTIONS

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SUMMARY: Polymers based on 2-dimethylaminoethyl methacrylate (DMAEMA) crossslinked with ethylene glycol dimethacrylate (EGDMA) or N,N'-methylenebisacrylamide (MBAA) have been prepared by solution-suspension polymerization. Polymers containing ammonium groups were synthesized by quaternization of aminofunctional polymers obtained with ethyl or dodecyl bromide or by the polymerization of respective quaternized monomers. Influence of the content of DMAEMA in the polymers, nominal degree of crosslinking, length of alkyl substituent in quaternary ammonium groups as well as particle size on the sorption of anionic and nonionic surfactants from aqueous solutions has been studied.

Introduction

Sorption of surfactants from some kinds of industrial waste water may reduce effectively their concentration and undesired influence on the environment. Commercial surfactants are mainly of anionic character, though also nonionic ones are produced in large amounts. For this reason our study concerned the sorbents having basic properties, providing them the ability to absorb anionic surfactants on the basis of electrostatic interactions [1,2]. Some of the sorbents have been „equipped" with hydrophobic pendant chains because according to the literature, hydrophobic polymer-surfactant interactions play an important role in the sorption [3,4].

The aim of this work was the synthesis of hydrogel sorbents containing tertiary amino or quaternary ammonium groups and evaluation of the influence of the structure of the polymers on their sorption capabilities towards selected industrial surfactants.

Experimental

Materials

2-hydroxyethyl methacrylate and 2-dimethylaminoethyl methacrylate (MERCK) were distilled before the use and fractions boiling at 73-75^{0}C/5mmHg and at 48-52^{0}C/6mmHg,

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respectively, were collected. Initiator α,α'-azoisobutyronitrile (MERCK), was purified by dissolution in $CHCl_3$ and precipitation in methanol. Other reagents, solvents etc. and polyvinylpyrrolidone 25000-30000 (MERCK) were used as received. Technical grade surfactants: sodium dodecylbenzene sulfonate (paste) and Rokafenol N-8 were delivered by Z.Ch. Blachownia company. The former one was dried before the use to get anhydrous powder.

Synthesis of the sorbents

Polymerization. Procedure A [5,6].

Polymers based on 2-dimethylaminoethyl methacrylate (DMAEMA) and (2-methacryloyloxyethyl)dodecyldimethyl-ammonium bromide (DDBQMA) were prepared in a granular form by the copolymerization with 1.3-5.0 % (mol/mol) of ethylene glycol dimethacrylate or N,N'-methylenebisacrylamide (EGDM or MBAA, crosslinking agents) and various amounts of 2-hydroxyethyl methacrylate (HEMA). The polymerization was carried out in suspension of the solution of the monomers and α,α'-azoisobutyronitrile (AIBN) in cyclohexanol/dodecanol mixture (1:1, v/v) dispersed in aqueous solution of polyvinylpyrrolidone (PVP), following the procedure described by Horák and Švec [5]. Details were described earlier [6]. The beads obtained were fractionated on sieves and the fraction of $\phi = 0.30\text{-}0.49$ mm was used for evaluation of swelling and sorption properties.

Polymerization. Procedure B

Copolymerization of (2-methacryloyloxyethyl)ethyldimethylammonium bromide (EBQMA) was carried out at 70^0C for 4h in 24% (w/w) aqueous solution of the monomers in the presence of 0.3% (w/w, in relation to the monomers) of α,α'-azodiisobutyramidine dihydrochloride (AIBA). Resulted hydrogel block was disintegrated, washed with water and dried.

Quaternization of DMAEMA. Procedure C

Quaternization with ethyl (EB) or dodecyl bromide (DDB), in some cases also with ethyl iodide (EI), was carried out at room temperature in 2-fold excess of the monomer according to Uchida et al. [7]. After 2 days solid precipitate formed was filtered off, washed with acetone or diethyl ether and dried. The yield of EBQMA and DDBQMA was 74.0 and 38.5%, respectively. The structure of the products was confirmed by ^{1}H NMR.

^{1}H NMR ($CDCl_3$)

EBQMA: δ [ppm] = 6.14 and 5.68 (2x1H, CH_2=), 4.68 (2H, -CH_2-N^+), 4.14 (-CH_2-O),

3.83 (2H, $CH_3\text{-}\mathbf{CH_2}\text{-}N^+$), 3.49 (6H, $(CH_3)_2\text{-}N^+$), 1.95 (3H, $CH_3\text{-}C{=}$),
1.47 (3H, $\mathbf{CH_3}\text{-}CH_2\text{-}N^+$)

DDBQMA: δ [ppm] = 6.15 and 5.68 (2x1H, $CH_2{=}$), 4.67 (2H, $\text{-}CH_2\text{-}N^+$), 4.17 ($\text{-}CH_2\text{-}O$),
3.65 (2H, $CH_3\text{-}\mathbf{CH_2}\text{-}N^+$), 3.52 (6H, $(CH_3)_2\text{-}N^+$), 1.95 (3H, $CH_3\text{-}C{=}$),
1.77(2H, $\text{-}\mathbf{CH_2}\text{-}CH_2\text{-}N^+$), 1.1-1.5 (18H, $\text{-}CH_2\text{-}\mathbf{(CH_2)_9}\text{-}CH_3$),
0.88 (3H,$\mathbf{CH_3}\text{-}(CH_2)_{11}\text{-}$)

Quaternization of the polymers. Procedure D

Samples of aminofunctional polymers obtained (ca. 1g) have been shaken vigorously with 50 cm^3 of ethanol and 10-fold molar excess of EB or EI, than left standing at room temperature. After 6 days the polymer was filtered off, extracted with acetone and dried at 50^0C.

Quaternization of the polymers. Procedure E

Samples of aminofunctional polymers obtained (ca. 1g) have been shaken with 80 cm^3 of DMF and 5-fold molar excess of DDB, than left standing for 24 h at 70^0C [*6*]. After cooling the polymer was separated by filtration, soaked in DMF, again filtered off and washed first with DMF and then with acetone, and dried at 50^0C.

Characteristics of the sorbents

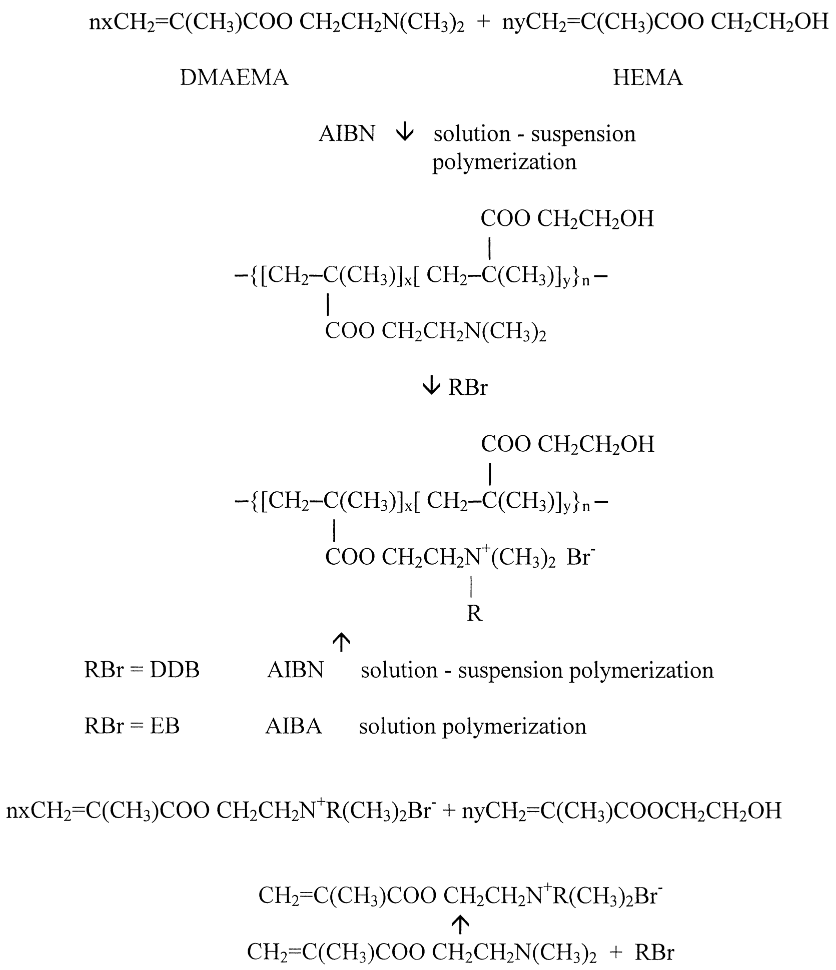
Swelling properties (water sorption, WS and equilibrium water content, EWC) were determined gravimetrically after 7-days soaking of a sample of a hydrogel in an excess of distilled water [*8*].

The sorption of sodium dodecylbenzene sulfate (DBS) and ethoxylated phenol - Rokafenol N-8 (RF-8) from diluted aqueous solutions (1 or 2 g/dm^3) was characterized by determination of their concentration after predetermined period (1h, 2h and 7 days) of contacting the surfactant solution (50 cm^3) with a polymeric sorbent (0.1 g). Concentration of a surfactant in a solution was calculated from absorbance at λ_{max}. Both surfactants displayed strong UV absorption at 224 and 223 nm, respectively.

Results and Discussion

Synthesis

A number of functional, crosslinked hydrophilic polymers based on DMAEMA was prepared in granular form (max. size ca. 0.7-1.6 mm) according to the scheme 1. Beads form was convenient for further study of the sorption of surfactants. Hydrophilic, but neutral 2-hydroxyethyl methacrylate (HEMA) was used as the comonomer to reduce amino functionality.



$$nxCH_2{=}C(CH_3)COO\ CH_2CH_2N(CH_3)_2 + nyCH_2{=}C(CH_3)COO\ CH_2CH_2OH$$

DMAEMA HEMA

AIBN ↓ solution - suspension polymerization

$$-\{[CH_2{-}\underset{\displaystyle COO\ CH_2CH_2N(CH_3)_2}{C}(CH_3)]_x[CH_2{-}\overset{\displaystyle COO\ CH_2CH_2OH}{C}(CH_3)]_y\}_n-$$

↓ RBr

$$-\{[CH_2{-}\underset{\displaystyle COO\ CH_2CH_2\underset{\displaystyle R}{N^+}(CH_3)_2\ Br^-}{C}(CH_3)]_x[CH_2{-}\overset{\displaystyle COO\ CH_2CH_2OH}{C}(CH_3)]_y\}_n-$$

↑

RBr = DDB AIBN solution - suspension polymerization

RBr = EB AIBA solution polymerization

$$nxCH_2{=}C(CH_3)COO\ CH_2CH_2N^+R(CH_3)_2Br^- + nyCH_2{=}C(CH_3)COOCH_2CH_2OH$$

$$CH_2{=}C(CH_3)COO\ CH_2CH_2N^+R(CH_3)_2Br^-$$

↑

$$CH_2{=}C(CH_3)COO\ CH_2CH_2N(CH_3)_2 + RBr$$

Scheme 1. Synthesis of the sorbents based on DMAEMA

Aminofunctional polymers were obtained by copolymerization of DMAEMA, while those containing quaternary ammonium salts were obtained by quaternization of the former or by the polymerization of respective monomeric ammonium salts.

Suspension polymerization of hydrophilic monomers in o/w system was accomplished by use of amphiphilic organic solvents (cyclohexanol, dodecanol) which dissolved the monomers and prevented to some extent their dissolution in aqueous phase. Feed ratios, yields and swelling characteristics are shown in Tab.1.

Tab.1. Synthesis of N-containing hydrogels based on DMAEMA and respective quaternary salts

Polymer	Comonomers		X/Y feed ratio	Cross-linker	Synth. proc.	Yield	WS	EWC	Max. dry beads diameter
	X	Y	mol/mol	(mol %)		%	gH_2O/g	%	mm
K1	DMAEMA	HEMA	33/66	EGDMA (1.3)	A	85.0	2.16	68.3	0.71
K1SLC	EBQMA	HEMA	33/66	EGDMA (1.3)	B	73.0	12.12	92.4	0.57
K1SLC1	EBQMA	HEMA	33/66	MBAA (1.3)	B	79.0	11.90	92.2	1.07
K1SPB	DDBQMA	HEMA	33/66	EGDMA (1.3)	A	70.6	6.67	87.0	0.62
K2	DMAEMA	HEMA	33/66	EGDMA (5.0)	A	76.3	1.95	66.3	0.98
K3	DMAEMA	HEMA	50/50	EGDMA (1.3)	A	82.9	2.20	69.0	1.15
K4	DMAEMA	HEMA	66/33	EGDMA (1.3)	A	77.9	3.24	76.4	0.99
P5	DMAEMA	-	100/0	EGDMA (1.3)	A	59.8	4.37	81.4	1.62

Yield of the copolymerization was only ca. 60-85%, probably because of partial dissolution of the monomers, especially DMAEMA, in aqueous medium. The content of DMAEMA in the polymers, estimated by elemental analysis, amounted to 70-80% of that in the reaction mixture, probably because of its lower reactivity and/or better solubility in aqueous phase when compared with HEMA. The same approach, i.e. solution - suspension polymerization appeared to be convenient for the polymerization of relatively less hydrophilic ammonium salt - DDBQMA, while highly hydrophilic and water soluble monomer - EBMA cannot be polymerized in this way and solution polymerization in aqueous medium must be used.

Swelling

All the polymers obtained based on DMAEMA, appeared to be highly hydrophilic and swell up to equilibrium water content ranging from 42.2 to 93.0%. Quaternization of DMAEMA with short-chain EB or ethyl iodide (EI) generally increased, while that with long-chain DDB reduced hydrophilicity of both initial monomer and respective polymers, as it may be concluded from the comparison of swelling properties (Tab. 1 and 2).

Tab.2. Results of quaternization of DMAEMA and its copolymers

Initial monomer or polymer	Quaternization			Product	Products characteristics	
	reagent used	synthetic procedure	Yield %		WS gH_2O/g	EWC %
DMAEMA	C_2H_5Br	C	34.3	EBQMA	soluble	-
DMAEMA	$C_{12}H_{25}Br$	C	38.5	DDBQMA	insoluble	-
K1	C_2H_5Br	D	86.5	K1C	8.96	90.0
K1	C_2H_5I	D	89.2	K1A	8.72	89.7
K1	$C_{12}H_{25}Br$	E	76.3	K1B	1.80	64.2
K2	C_2H_5I	D	87.8	K2A	2.15	68.2
K2	C_2H_5Br	D	84.5	K2C	2.04	67.0
K2	$C_{12}H_{25}Br$	D	46.8	K2B	1.08	52.0
K3	C_2H_5I	D	97.8	K3A	12.3	92.5
K3	C_2H_5Br	D	82.0	K3C	12.0	92.3
K3	$C_{12}H_{25}Br$	E	66.0	K3B	4.05	80.0
K4	C_2H_5I	D	97.4	K4A	13.3	93.0
K4	C_2H_5Br	D	82.0	K4C	12.2	92.4
K4	$C_{12}H_{25}Br$	E	62.0	K4B	2.2	69.2
P5	$C_{12}H_{25}Br$	E	89.1	P5B	0.73	42.2

Unexpectedly, hydrogel obtained from quaternized monomer (K1SPB) displayed much higher water sorption than similar polymer obtained by quaternization of amino-functional polymer (K1B), probably because of different chemical and/or physical structure of both the polymers. It was observed that water sorption had depended to some extent also on the nominal crosslinking density and DMAEMA/HEMA feed ratio. Increasing the content of DMAEMA in the polymers and decreasing crosslinking density resulted in increasing swelling ability.

Sorption of surfactants

Results of evaluation of sorption properties of the hydrogels studied, excepting those containing iodide anion, are listed in Tab.3-5. The sorption properties of the latter could not be estimated correctly by UV method because of overlapping of the absorption bands of the surfactants and that of iodine (227 nm) formed in the solution as a result of oxidation of iodide ion.

It may be seen from the data collected in the Tab.3 that quaternization of the aminofunctional hydrogels with EB increase short term sorption effectiveness towards anionic surfactant.

Tab.3. Degree of surfactant removal from aqueous solution after 1 h contacting with a sorbent[a]

Sorbent	DMAEMA / DMAEMA+HEMA %mol	R	WS $cm^3/1g$	DBS sorption %	RF-8 sorption %
K1	33	-	2.16	7.1	46.2
K1C	33	$-C_2H_5$	9.96	33.0	4.0
K1SLC[b]	33	$-C_2H_5$	11.90	39.0	-
K1SLC1[b,c]	33	$-C_2H_5$	12.12	11.0	-
K1B	33	$-C_{12}H_{25}$	1.80	42.0	16.2
K1SPB[b]	33	$-C_{12}H_{25}$	6.67	17.3	41.2
K2C[d]	33	$-C_2H_5$	2.04	40.0	0.0
K2B[d]	33	$-C_{12}H_{25}$	1.08	15.0	2.0
K3C	50	$-C_2H_5$	12.00	64.0	0.0
K3B	50	$-C_{12}H_{25}$	4.05	38.0	-
K4	66	-	3.24	24.0	-
K4C	66	$-C_2H_5$	12.20	30.0	0.0
K4B	66	$-C_{12}H_{25}$	2.20	26.0	33.0
P5	100	-	4.37	40.0	36.0
P5B	100	$-C_{12}H_{25}$	0.73	23.0	50.1

[a] initial surfactant concentration equal to $1g/dm^3$, [b] obtained by the polymerization of respective monomeric quarternary ammonium salt, [c] MBAA used as a crossslinker , [d] feed mixture contained 5% of EDMA

After 7 days contacting the sorbents with more diluted DBS solution (initial concentration $1g/cm^3$) the surfactant was removed from the solution practically completely when polymeric ammonium salts were used. Long term sorption of the surfactants from more concentrated solution ($2g/cm^3$) revealed sorption capacity of the polymers. (Tab.4).

Tab.4. Degree of surfactant removal from aqueous solution after 168 h contacting with a sorbent[a]

Sorbent	DMAEMA ------------------------ DMAEMA+HEMA % mol	R	WS $cm^3/1g$	DBS sorption %	RF-8 sorption %
K1	33	-	2.16	60.2	75.3
K1C	33	$-C_2H_5$	9.96	78.0	-
K1SLC[b]	33	$-C_2H_5$	11.90	81.0	-
K1SLC[b,c]	33	$-C_2H_5$	12.12	80.0	-
K1B	33	$-C_{12}H_{25}$	1.80	64.3	55.4
K1SPB[b]	33	$-C_{12}H_{25}$	6.67	80.0	95.5
K2C [d]	33	$-C_2H_5$	2.04	70.0	0.0
K2B [d]	33	$-C_{12}H_{25}$	1.08	51.0	12.0
K3C	50	$-C_2H_5$	12.00	85.0	0.0
K3B	50	$-C_{12}H_{25}$	4.05	84.0	89.0
K4C	66	$-C_2H_5$	12.20	95.0	0.0
K4B	66	$-C_{12}H_{25}$	2.20	84.0	87.0
P5	100	-	4.37	-	30.0
P5B	100	$-C_{12}H_{25}$	0.73	97.3	60.7

[a] initial surfactant concentration equal to $2g/dm^3$, [b] obtained by the polymerization of respective monomeric quaternary ammonium salt, [c] MBAA used as a crossslinker , [d] feed mixture contained 5% of EDMA

Long term sorption of the surfactants from more concentrated solution ($2g/cm^3$ revealed sorption capacity (Tab.4). The degree of sorption of DBS was within the range of 50 to ca 95% and was higher for quaternized polymers than for initial amino-functional ones. The sorption of anionic DBS by more hydrophilic sorbents, i.e. those quaternized by EB, was generally more effective than that by more hydrophobic sorbents carrying dodecyl substituent.

Polymers containing quaternary ammonium salts, which were more hydrophobic due to dodecyl substituent (K1B, K1SPB,K2B,K3B,K4B) appeared to be more effective sorbents of nonionic surfactant RF-8 than those which were more hydrophilic because of the presence of shorter ethyl substituent, but the results obtained so far are generally non equivocal.

The size of the particles and thus their specific surface influenced the degree of surfactant sorption after short term (1 h) contacting a sorbent K1SLC with surfactant solution. Removal of DBS from aqueous solution was much faster when small particle sorbent was used, probably due to bigger particle surface and shorter diffusion distance. No distinct effect of particle size on degree of surfactant removal was observed after long exposition of the sorbent on surfactant solution (Tab.5). Similar results were obtained when the sorbent was crosslinked with MBAA (K1SLC1). Thus, the size of the sorbent particles influences the rate of the sorption, but has no effect on sorption capacity.

Tab.5. Influence of the size of particles on the course and effectiveness of sorption of DBS from aqueous solutions by granular, crosslinked copolymers of EBQMA (K1SLC).

Size of particles mm	Duration of sorption h	Degree of sorption from 1 g/dm^3 solution %	Degree of sorption from 2 g/dm^3 solution %
< 0.30	0	0	0
	1	57	44
	48	97	79
	168	100	81
0.30-0.49	0	0	0
	1	39	30
	48	91	81
	168	100	81
> 0.49	0	0	0
	1	20	22
	48	90	76
	168	100	81

Conclusions

Hydrogels based on 2-dimethylaminoethyl methacrylate are effective sorbents of anionic surfactant - sodium dodecylbenzene sulfate and can be used for its removal from diluted aqueous solutions. Quaternization with short chain alkyl bromide generally increases the swelling ability as well as the effectiveness of the sorption of anionic surfactant but decreases the sorption of nonionic one (ethoxylated phenol). Quaternization with long chain dodecyl bromide decreases swelling ability, but in the case of the hydrogels with high content of aminofunctional units increases sorption capacity of nonionic surfactant.

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