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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Preparation and Hydrophobizing Properties of Carboxylic Acid *N*-[3-(Dimethylamino)propyl]amide Hydrochlorides

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Abstract—Carboxylic acid *N*-[3-(dimethylamino)propyl]amides were prepared in 90–95% yield by the reaction of carboxylic acid esters with *N,N*-dimethyl-1,3-diaminopropane in the presence of zeolites as catalysts. Hydrochlorides of these amides show promise as cationic surfactants for hydrophobization of the bottomhole formation zone of oil fields.

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In oil field mining by water flooding, the oil is recovered incompletely because of the negative effect exerted by ionic and molecular surface forces at interfaces in the oil–water–rock system in the capillary porous structure of the reservoir bed [1–3]. There are numerous methods for restricting the water inflow and intensifying the oil production. One of them is hydrophobization of the bottomhole formation zone by the action of surfactants on productive oil strata to eliminate the negative effect of capillary forces [1–6]. Hydrophobization, taking into account the properties of the reservoir bed and saturating fluids, allows the water saturation of the near-borehole zone to be reduced, the flow fronts to be changed, and the rock swelling to be prevented. Cationic surfactants are promising as hydrophobizing agents. They operate in both acidic and alkaline media and exhibit high antimicrobial activity [2, 4].

In this work, we suggested a procedure for preparing carboxylic acid *N*-[3-(dimethylamino)propyl]amide hydrochlorides and studied their hydrophobizing properties with the aim of developing new oil field reagents for restricting the water inflow and intensifying the oil production.

EXPERIMENTAL

In our study, we used *N,N*-dimethyl-1,3-diaminopropane (Acros Organics, 99%), butyric acid (Acros Organics, 99%), methyl oleate (Acros Organics, 70%), stearic acid (Khimreaktivsnab, pure grade), 3 and 4 Å molecular sieves (Acros Organics), and oil from the Petelinskoe field. Methyl butyrate and methyl stearate were prepared by standard procedures.

The NMR spectra were recorded with Bruker AM-300 (300.13 MHz for ^{1}H, 75.47 MHz for ^{13}C) and Bruker Avance-III 500 (500.13 MHz for ^{1}H, 125.47 MHz for ^{13}C) spectrometers at 298 K from $CDCl_3$ ad CD_3OD solutions with Me_4Si as internal reference. The IR spectra were recorded with a Shimadzu IR Prestige-21 device from thin films or mulls in mineral oil. The mass spectra were taken in the mode of chemical ionization at atmospheric pressure (CIAP) with an LCMS-2010 EV liquid chromatograph–quadrupole mass spectrometer (Shimadzu) under the following conditions: injection of acetonitrile solutions of samples with a syringe, eluent acetonitrile–water (95 : 5), flow rate 0.1 mL min^{-1}; recording of positive ions, capillary potential 4.5 kV; temperatures, °C: interface capillary 250, heater

200, and vaporizer 230; flow rate of the nebulizing (atomizing) gas (nitrogen) 2.5 L min^{-1}. The GLC analysis was performed with a Chrom-5 chromatograph equipped with a flame ionization detector and a 1200 × 5 mm stainless steel column, stationary phase 5% SE-30 on Inerton N-AW DMCS (0.125–0.160 mm), or with a GC-2014 Shimadzu chromatograph equipped with a flame ionization detector and a 30 m × 0.25 mm × 0.25 µm (HP–FAAP phase) capillary column under the following conditions: programmed heating from 80 to 220°C at a rate of 10 deg min^{-1}, carrier gas helium. The TLC analysis was performed on TLC Silica gel 60 F254 plates (Merck) using $CHCl_3$–MeOH (7 : 3) and hexane–Et_2O (9 : 1) eluents. The melting point was determined with a Boetius microstage.

The surface tension was determined with an ST-2 stalagmometer (Russia) at the interface of kerosene with an aqueous solution of the surfactant at 22°C. The surface tension of distilled water at the interface with air is 72.1 ± 0.2 mN m^{-1}.

The surface tension was calculated using the formula

$$\sigma = kn(\rho_1 - \rho_0),$$

where σ is the surface tension of the surfactant solution; *k*, stalagmometer constant equal to 9.4768; *n*, number of kerosene drops; ρ_0 and ρ_1, densities of kerosene and surfactant solution.

Experiments on studying the filtration properties were performed with a UIK-5(2) filtration installation (Glo-Bel Nefteservis, Russia) with the linear length of the core model from 25 to 500 mm. The core temperature could be controlled in the range from +30 to +150°C. The maximal values of the confining, stratum, and effective pressure were 80, 40, and 6 MPa, respectively.

The physicochemical constants of **IIIb** agreed with the published data [7].

Preparation of carboxylic acid amides IIIa–IIIc (general procedure). To 0.10 mmol of acid methyl ester **Ia–Ic**, 0.11 mmol of *N,N*-dimethyl-1,3-diaminopropane and 1.0 g of zeolites were added. The mixture was stirred for 12 h at 115–120°C. The released methanol was separated with a Dean–Stark trap. After the reaction completion, 30 mL of CH_2Cl_2 was added, the zeolites were filtered off, and the solvent was distilled off at reduced pressure.

***N*-[3-(Dimethylamino)propyl]butanamide IIIa** was prepared from 28.0 g (0.274 mol) of methyl butanoate and 30.8 g (0.301 mol) of *N,N*-dimethyl-1,3-diaminopropane in the presence of 2.8 g of zeolites. Yield 42.4 g (90%). Light yellow oily liquid. IR spectrum, ν, cm^{-1}: 1554 (CN), 1646 (C=O), 3289 (NH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.91 t (3H, ^2J 7.0 Hz, C^4H_3), 1.61 m (4H, C^3H_2, $NHCH_2CH_2CH_2$), 2.1 t (2H, ^2J 7.3 Hz, C^2H_2), 2.20 s [6H, $N(CH_3)_2$], 2.35 t [2H, ^2J 7.2 Hz, $CH_2N(CH_3)_2$], 3.29 m (2H, $NHCH_2$), 6.97 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 13.69 (C^4), 19.05 (C^3), 26.32 ($NHCH_2CH_2CH_2$), 38.63 (C^2), 38.87 ($NHCH_2$), 45.28 [$N(CH_3)_2$], 58.34 [$CH_2N(CH_3)_2$], 172.90 (C=O). Mass spectrum, *m*/*z*: 173 [M + H]. Found, %: C 62.80, H 11.71, N 16.28. $C_9H_{20}N_2O$. Calculated, %: C 62.75, H 11.70, N 16.26.

***N*-[3-(Dimethylamino)propyl]octadecanamide IIIb** was prepared from 30.0 g (0.10 mol) of methyl stearate and 11.24 g (0.11 mol) of *N,N*-dimethyl-1,3-diaminopropane in the presence of 3.0 g of zeolites. Yield 34.27 g (93%).

(9*Z*)-*N*-[3-(Dimethylamino)propyl]octadec-9-enamide IIIc was prepared from a mixture of 30.0 g (0.101 mol) of methyl oleate and 11.4 g (0.111 mol) of *N,N*-dimethyl-1,3-diaminopropane in the presence of 3.0 g of zeolites. Yield 35.17 g (95%). Light yellow oil. IR spectrum, ν, cm^{-1}: 1549 (CN), 1645 ν(C=O), 3292 (NH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.85 t (3H, ^2J 7.0, $C^{18}H_3$), 1.20–1.30 m (20H, $C^{17}H_2$, $C^{16}H_2$, $C^{15}H_2$, $C^{14}H_2$, $C^{13}H_2$, $C^{12}H_2$, C^7H_2, C^6H_2, C^5H_2, C^4H_2), 1.60 m (4H, C^3H_2, $NHCH_2CH_2CH_2$), 1.97 m (4H, $C^{11}H_2$, C^8H_2), 2.11 m [2H, $CH_2N(CH_3)_2$], 2.21 s [6H, $N(CH_3)_2$], 2.34 m (2H, C^2H_2), 3.29 m (2H, $NHCH_2$), 5.30 s (2H, C^9H, $C^{10}H$), 6.97 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 14.05 (C^{18}), 22.61 (C^{17}), 25.70 (C^3), 26.05 ($NHCH_2CH_2CH_2$), 27.10 (C^8), 27.13 (C^{11}), 29.08 (C^4), 29.24 (C^{14}, C^6, C^5), 29.44 (C^{15}), 29.60 (C^{13}), 29.65 (C^7), 29.68 (C^{12}), 31.82 (C^{16}), 36.88 (C^2), 38.70 ($NHCH_2$), 45.29 [$N(CH_3)_2$], 58.49 [$CH_2N(CH_3)_2$], 129.66 (C^9), 129.90 (C^{10}), 173.02 (C=O). Mass spectrum, *m*/*z* : 367 [M + H]. Found, %: C 75.42, H 12.66, N 7.63. $C_{23}H_{46}N_2O$. Calculated, %: C 75.35, H 12.65, N 7.64.

Preparation of (9*Z*)-*N*-[3-(dimethylamino)propyl] octadec-9-enamide IIIc from olive oil. To 10.13 g (11.5 mmol) of olive oil, 3.86 g (37.8 mmol) of *N,N*-dimethyl-1,3-diaminopropane and 3.04 g of zeolites were added. The mixture was stirred for 12 h at 115–120°C. Then, 20 mL of CH_2Cl_2 was added, and the zeolites were filtered off and washed with water (5 ×

10 mL). The organic layer was dried over anhydrous Na_2SO_4, and the solvent was removed at atmospheric pressure. Yield 11.4 g (91%).

***N*-[3-(Dimethylamino)propyl]butanamide hydrochloride IVa.** Gaseous HCl was passed for 1.5 h through a solution of 20.7 g (0.120 mol) of *N*-[3-(dimethylamino)propyl]butanamide **IIIa** in 90 mL of CH_2Cl_2. The solvent was removed at atmospheric pressure. Yield 22.5 g (90%). ^{1}H NMR spectrum (CD_3OD), δ, ppm: 0.78 t (3H, ^2J 7.3 Hz, C^4H_3), 1.48 m (2H, $NHCH_2CH_2CH_2$), 1.78 m (2H, C^3H_2), 2.07 t (2H, ^2J 7.3 Hz, C^2H_2), 2.72 s [6H, $N(CH_3)_2$], 2.97 t [2H, ^2J 7.2 Hz, $CH_2N(CH_3)_2$], 3.14 m (2H, $NHCH_2$), 5.33 br.s (1H, NH). ^{13}C NMR spectrum (CD_3OD), δ, ppm: 12.57 (C^4), 19.00 (C^3), 24.17 ($NHCH_2CH_2CH_2$), 36.27 (C^2), 36.85 ($NHCH_2$), 42.10 [$N(CH_3)_2$], 55.05 [$CH_2N(CH_3)_2$], 176.21 (C=O). Found, %: C 51.76, H 10.15, Cl 17.00, N 13.45. $C_9H_{21}ClN_2O$. Calculated, %: C 51.79, H 10.14, Cl 16.99, N 13.42.

***N*-[3-(Dimethylamino)propyl]octadecanamide hydrochloride IVb.** Gaseous HCl was passed for 1.5 h through a solution of 15.0 g (0.041 mol) of *N*-[3-(dimethylamino)propyl]octadecanamide **IIIb** in 90 mL of CH_2Cl_2. The solvent was removed at reduced pressure. Yield 16.0 g (97%). ^{1}H NMR spectrum (CD_3OD), δ, ppm: 0.90 t (3H, ^2J 7.0 Hz, $C^{18}H_3$), 1.28–1.32 m (24H, $C^{17}H_2$, $C^{16}H_2$, $C^{15}H_2$, $C^{14}H_2$, $C^{13}H_2$, $C^{12}H_2$, $C^{11}H_2$, $C^{10}H_2$, C^9H_2, C^8H_2, C^7H_2, C^6H_2), 1.60–1.63 m (4H, C^4H_2, C^5H_2), 1.92–1.97 m (4H, C^3H_2, $NHCH_2CH_2CH_2$), 2.25 t (2H, ^2J 7.1 Hz, C^2H_2,), 2.89 s [6H, $N(CH_3)_2$], 3.14 t [2H, ^2J 7.2 Hz, $CH_2N(CH_3)_2$], 3.28 m (2H, $NHCH_2$), 5.31 s (1H, NH). ^{13}C NMR spectrum (CD_3OD), δ, ppm: 13.03 (C^{18}), 22.31 (C^{17}), 24.48 ($NHCH_2CH_2CH_2$), 24.59 (C^3), 25.54 (C^4), 28.75(C^6) 28.94 (C^7), 29.01 (C^8), 29.04 (C^{15}), 29.15 (C^5), 29.20 (C^{14}), 29.26 (C^{12}), 29.35 (C^{13}, C^{11}, C^{10}, C^9), 31.64 (C^{16}), 35.38 (C^2), 35.71 ($NHCH_2$), 42.05 [$N(CH_3)_2$], 55.11 [$CH_2N(CH_3)_2$], 175.95 (C=O). Found, %: C 68.31, H 12.16, Cl 8.77, N 6.90. $C_{23}H_{49}ClN_2O$. Calculated, %: C 68.19, H 12.19, Cl 8.75, N 6.92.

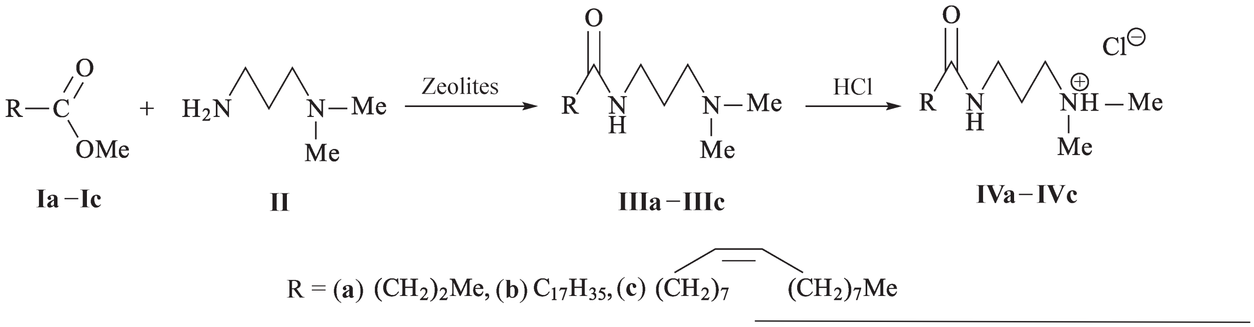
(9*Z*)-*N*-[3-(Dimethylamino)propyl]octadec-9-enamide hydrochloride IVc. Gaseous HCl was passed for 3 h through a solution of 15.0 g (41 mmol) of (9*Z*)-*N*-[3-(dimethylamino)propyl]octadec-9-enamide **IIIc** in 90 mL of benzene. The solvent was removed at reduced pressure. Yield 16.35 g (99%). ^{1}H NMR spectrum (CD_3OD), δ, ppm: 0.90 t (3H, ^2J 7.0 Hz, $C^{18}H_3$), 1.28–1.33 m (20H, $C^{17}H_2$, $C^{16}H_2$, $C^{15}H_2$, $C^{14}H_2$, $C^{13}H_2$, $C^{12}H_2$, C^7H_2, C^6H_2, C^5H_2, C^4H_2), 1.61 m (4H, C^3H_2, $NHCH_2CH_2CH_2$), 1.94 m (4H, $C^{11}H_2$, C^8H_2), 2.24 t [2H, ^2J 7.2 Hz, $CH_2N(CH_3)_2$], 2.89 s [6H, $N(CH_3)_2$], 3.14 t (2H, ^2J 7.1 Hz, C^2H_2), 3.29 m (2H, $NHCH_2$), 5.34 s (2H, C^9H, $C^{10}H$), 5.50 s (1H, NH). ^{13}C NMR spectrum (CD_3OD), δ, ppm: 13.06 (C^{18}), 22.31 (C^{17}), 24.54 (C^3), 25.53 ($NHCH_2CH_2CH_2$), 26.70 (C^8), 28.75 (C^{11}), 28.81 (C^4), 28.92 (C^{14}, C^6, C^5), 29.01 (C^{15}), 29.17 (C^{13}), 29.33 (C^7), 29.41 (C^{12}), 31.62 (C^{16}), 35.48 (C^2), 35.61 ($NHCH_2$), 42.07 [$N(CH_3)_2$], 55.14 [$CH_2N(CH_3)_2$], 129.34 (C^9), 129.45 (C^{10}), 175.77 (C=O). Found, %: C 68.49, H 11.74, Cl 8.77, N 6.97. $C_{23}H_{47}ClN_2O$. Calculated, %: C 68.53, H 11.75, Cl 8.80, N 6.95.

RESULTS AND DISCUSSION

Numerous quaternary ammonium salts have been described in the literature. The majority of them have one cationic site and one hydrophobic substituent [7–9]. Data on preparation of cationic surfactants containing, along with a long-chain alkyl radical, an amide group and a cationic site in the form of a positively charged quaternary ammonium group are lacking.

In this study, we developed a two-step procedure for preparing *N*-[3-(dimethylamino)propyl]alkanamide hydrochlorides from carboxylic acid (butyric, stearic, oleic) esters and *N,N*-dimethyl-1,3-diaminopropane and evaluated the hydrophobizing properties of these compounds.

There are numerous procedures for preparing fatty acid amides [8, 9], which are intermediates in synthesis of surfactants. These amides are prepared, as a rule, by reaction of acids or their esters with amines on heating. We have found that the catalytic reaction of fatty acid methyl esters **Ia–Ic** with *N,N*-dimethyl-1,3-diaminopropane **II** in 1 : 1.1 molar ratio for 12 h at 115–120°C in the presence of aluminosilicate catalysts used previously for esterification of carboxylic acids [10] leads to the formation of *N*-[3-(dimethylamino)propyl]alkanamides **IIIa** and **IIIb** and of (9*Z*)-*N*-[3-(dimethylamino)propyl]octadec-9-enamide **IIIc** in 90, 95, and 93% yield, respectively. It should be noted that, when the reaction is performed under thermal conditions (115–120°C) and in the presence of catalytic amounts of sodium glycerate or methylate (10 wt %), the yield of the target products does not exceed 65%:



Under the chosen conditions, zeolites appeared to be effective catalysts of amidation of oleic acid triglyceride from olive oil with *N,N*-dimethyl-1,3-diaminopropane to obtain amino amide **IIIc** in 91% yield. The synthesized amino amides **IIIa** and **IIIb** were isolated by preparative column chromatography on SiO_2 and were characterized by ^1H and ^{13}C NMR spectra.

Hydrochlorides of *N*-[3-(dimethylamino)propyl] butanamide (**IVa**), *N*-[3-(dimethylamino)propyl] octadecanamide (**IVb**), and (9*Z*)-*N*-[3-(dimethylamino) propyl]octadec-9-enamide (**IVc**) were prepared in 90, 97, and 99% yield, respectively, by passing gaseous HCl through solutions of amino amides **IIIa–IIIc** in methylene chloride or benzene.

To determine the possibility of using compounds **IVa–IVc** as hydrophobizing agents in oil production, we studied how these compounds influence the contact angle, surface tension, and filtration properties.

For all the surfactants **IVa–IVc**, the contact angle increased with increasing concentration of aqueous solutions, but for compound **IVc** containing the oleic acid moiety this effect is more pronounced (Table 1). Therefore, it can be expected that cationic surfactant **IVc** will hydrophobize the rock surface better.

The ways of neutralizing water retained in capillaries are primarily associated with the ability of surfactants to reduce the surface tension at interfaces in the oil–water–rock system.

Table 1. Contact angles of solutions of surfactants **IVa–IVc**[a]

Surfactant	Contact angle θ, deg, at indicated concentration of aqueous surfactant solutions, %			
	0.25	0.5	1.0	2.0
IVa	25.3	29.2	33.4	44.4
IVb	38.7	44.7	45.6	53.8
IVc	46.3	50.3	56.0	63.6

[a] The contact angle for distilled water is 38.1°.

Table 2. Surface tension at the interface of an aqueous solution of surfactants **IVa–IVc** and kerosene

Surfactant concentration, %	Surface tension, mN m^{-1}, for indicated surfactant		
	IVa	**IVb**[a]	**IVc**
2.0	21.78	–	4.12
1.0	14.88	–	4.13
0.5	33.96	7.33	5.62
0.25	33.81	7.55	6.57
0.125	28.42	7.42	7.68

[a] Dash: the solution is turbid and heterogeneous.

Table 3. Results of filtration experiments with a 0.5% solution of surfactant **IVc** in SSW

Run no.	Solution	Permeability, 10^{-3} μm^2			Restoration factor
		to gas	to oil before solution injection	to oil after solution injection	
1	Simulated stratal water	236	40.4	31.1	0.77
2	00.5% **IVc** in SSW	277	44.9	36.8	0.82

Our data on the dependence of the surface tension at the interface between an aqueous solution of hydrochlorides **IVa–IVc** and kerosene on the surfactant concentration show that cationic surfactant **IVc** efficiently decreases the surface tension and is promising as a hydrophobizing agent for restricting the water inflow and intensifying the oil production (Table 2).

The capability of surfactants to preserve without deterioration the filtration properties of a stratum, in particular, the phase permeability to oil, is of particular importance. The effect of (9*Z*)-*N*-[3-(dimethylamino) propyl]octadec-9-enamide hydrochloride **IVc** on restoration of the permeability to oil was checked in an experiment on filtration of a 0.5% surfactant solution in simulated stratal water (SSW, NaCl solution of 1.18 g cm^{-3} density) through an oil-saturated model core with the initial absolute permeability (to gas) of 277×10^{-3} μm^2. The phase permeability to oil in the presence of surfactant **IVc** in SSW was 36.8×10^{-3} μm^2; i.e., it decreased by 18% (Table 3). This result can be considered as good, because with the traditional salt solution, SSW, the permeability decreased by 23%.

Thus, the use of cationic surfactant **IVc** in formulations for oil production will favor the rock hydrophobization, restoration of the reservoir bed characteristics, and restoration of the permeability to oil after jamming.

CONCLUSIONS

A study of the physicochemical and filtration properties of (9*Z*)-*N*-[3-(dimethylamino)propyl]octadec-9-enamide hydrochloride prepared from oleic acid esters and *N,N*-dimethyl-1,3-diaminopropane in the presence of catalytic amounts of zeolites has shown that this compound is promising as a cationic surfactant for hydrophobization of the bottomhole formation zone of oil fields.

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