Synthesis and characterization of hydrophobically modified polymeric betaines

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Polymeric betaines containing long alkyl chains $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$ and $C_{18}H_{37}$ were synthesized by Michael addition reaction of alkylaminocrotonates and methacrylic acid (MAA). They were characterized by FTIR, ^{13}C NMR, DSC, DLS, GPC, cryo-TEM, viscometry and zeta-potential measurements. The polymers were fully soluble in DMF, THF and DMSO, partially dissolved in aromatic hydrocarbons (benzene, toluene, o-xylene) and formed colloid solutions in aqueous KOH. In aqueous KOH and DMSO solutions, hydrophobically modified polymeric betaines behaved as polyelectrolytes. The average hydrodynamic size and zeta potential of diluted aqueous solutions of hydrophobic polybetainess containing dodecyl-, tetradecyl-, hexadecyl-, and octadecyl groups were studied as a function of pH. Anomalous low values of the isoelectric point (IEP) of amphoteric macromolecules were found to be in the range of pH 2.7-3.4. According to DLS data, the average size of macromolecules tends to decrease with dilution. Zeta-potential of amphoteric macromolecules in aqueous solution is much higher than that in DMSO. The cryo-TEM results revealed that in both aqueous KOH and DMSO media, the micron- and nanosized vesicles existed. The structural organization of vesicles in water and DMSO is discussed. The wax inhibition effect of hydrophobic polybetaines at a decrease of the pour point temperatures of high paraffinic oils was better in comparison with commercial available ethylene-vinylacetate copolymers (EVA).

Keywords: polymeric betaines; vesicles; micelles; pour point depressants.

Гидрофобты-модифицирленген полимерлік бетаиндерді синтездеу және зерттеу

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Ұзын $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$ и $C_{18}H_{37}$ алкил тізбектерінен тұратын полимерлік бетаиндер алкиламинокротонаттардан және метакрил қышқылынан Михаэль реакциясы бойынша синтезделді. Олар ИҚ-Фурье, ЯМР ^{13}C спектроскопия, ДСК, ДЛЖ, ГПХ, крио-ПЭМ, вискозиметрия және дзета-потенциалды өлшеу әдістерімен сипатталды. Полимерлер толығымен ДМФА, ТГФ және ДМС, жартылай ароматты көмірсутектерде (бензол, толуол, о-ксилол) ериді және КОН сулы ерітіндісінде коллоидты ерітінді түзеді. Додецил-, тетрадецил-, гексадецил- және октадецильді топтары бар гидрофобты-модифицирленген полибетаиндер ДМСО және КОН сулы ерітінділерінде pH ортасына тәуелді зерттелді. pH 2.7-3.4 обылысында изоэлектрлік нүктенің (ИЭН) аномальді төменгі мәні табылды. ДЛЖ мәліметіне сәйкес макромолекулалардың мөлшері сұйылтқан сайын кішірейеді. Амфотерлі макромолекулалардың дзета-потенциалы ДМСО салыстырғанда сулы ерітіндіде жоғары болады. Крио-ПЭМ нәтижелері ДМСО және КОН ерітінділерінде де микронды және наномөлшерлі везикулдар бар екенін көрсетті. ДМСО және суда везикулдардың құрылымдық түзілуі талқыланады. Парафин жиналуын ингибирлеуші эффектісі және жоғары парафинді мұнайлардың аққыштығының азаюын төмендету коммерциялық қолжетімді сополимер этилен-винилацетатпен (ЭВА) салыстырғанда гидрофобты полибетаиндердің қатысында жақсы.

Түйін сөздер: полимерлік бетаиндер; везикулалар; мицеллалар; аққыштықты азайтатын депрессанттар.

Синтез и исследование гидрофобно-модифицированных полимерных бетаинов

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Полимерные бетаины, содержащие длинные алкильные цепи $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$ и $C_{18}H_{37}$, синтезированы из алкиламинокротонатов и метакриловой кислоты по реакции Михаэля. Они охарактеризованы методами ИК-Фурье, ЯМР ^{13}C спектроскопии, ДСК, ДЛС, ГПХ, крио-ПЭМ, вискозиметрии и измерением дзета-потенциала. Полимеры полностью растворимы в ДМФА, ТГФ и ДМСО, частично растворимы в ароматических углеводородах (бензол, толуол, о-ксилол) и образуют коллоидные растворы в водном растворе КОН. В растворах водного КОН и ДМСО гидрофобно-модифицированные полибетаины, содержащие додецил-, тетрадецил-, гексадецил- и октадецильные группы, изучены в зависимости от pH. Найдены аномально низкие значения изоэлектрической точки (ИЭТ) в области pH 2.7-3.4. Согласно данным ДЛС средние размеры макромолекул имеют тенденцию к снижению с разбавлением. Дзета-потенциал амфотерных макромолекул в водном растворе намного выше, чем в ДМСО. Результаты крио-ПЭМ показали на существование микронных и наноразмерных везикул как в растворе КОН, так и в ДМСО. Обсуждается структурная организация везикул в воде и ДМСО. Ингибирующий эффект парафиноотложения и снижение потери текучести высокопарафинистых нефтей в присутствии гидрофобных полибетаинов лучше, чем в случае коммерчески доступного сополимера этилен-винилацетат (ЭВА).

Ключевые слова: полимерные бетаины; везикулы; мицеллы; депрессанты потери текучести.

CHEMICAL BULLETIN
of Kazakh National University
http://bulletin.chemistry.kz/

UDK 541.64+678.744
http://dx.doi.org/10.15328/cb645

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1. Introduction

Hydrophobic polyampholytes (HPA) are the unique class of macromolecules containing both ionizable and hydrophobic moieties in the main (or side) chain [1-3]. The structure, morphology, hydrodynamic and conformational properties of HPA depend on phase conditions (solid or liquid) and the influence of external factors such as pH, ionic strength, temperature, water-organic solvents etc. Two main concurring forces – electrostatic repulsion (or attraction) and hydrophobic interactions – are responsible for existence of macromolecules in amorphous, ordered, expanded, coiled and globular states. Specific properties of HPA are competition of "antipolyelelctrolyte" (expansion of macromolecular chain) and hydrophobic effects (aggregation) upon addition of salts.

One of the most interesting solution properties of HPA described by authors [4-5] is their ability to self-assemble into "schizophrenic" micelles, lamellar aggregate, vesicles and hydrogels.

The literature survey reveals that HPA are less studied than ordinary polyampholytes composed of only acidic and basic groups. In the pioneering works [6], a series of HPA were prepared by amidation of various alternating maleic anhydride copolymers of methyl, propyl and butyl alkyl vinyl ethers with N,N'-dimethyl-1,3-propanediamine. Acomb-like polyampholytes of α-olefins (C_6H_{12} – $C_{16}H_{28}$) and N,N-dimethylaminopropylmonoamide of maleic acid were synthesized by Tanchuk et al. [7-9]. Specific properties of HPA are solubilization of dye molecules in hydrophobic domain and gelation of aqueous solution upon increasing of temperature.

Laschewsky et al. [10-17] comprehensively described the synthesis and characterization of "head-type", "mid-tail type" and "tail-end type" zwitterionic polysoaps, which combine the advantages of the behavior of bipolar ions and micellar polymers.

Acrylamide-based hydrophobically modified polysulfo- and carbobetaines containing N-butylphenylacrylamide and varying amounts of the 3-(2-acrylamido-2-methylpropanedimethyl-ammonio)-1-propanesulfonate (AMPDAPS) or the 4-(2-acrylamido-2-methylpropyldimethyl-ammonio)butanoate (AMPDAB) were synthesized by micellar copolymerization [2].

Both "antipolyelectrolyte" effect and aggregation of hydrophobic groups leading to an increase of the hydrodynamic size upon an increase of salt concentration are observed. Both electrostatic attractions between ammonium and carboxylate groups and hydrophobic interactions between long flexible spacers are the driving forces of superstructure formation [18]

Hydrophobically associating polyampholytes may be effective viscosity enhancers in high salinity media, as they combine properties of hydrophobically modified neutral polymers and polyampholytes making them useful in sewage treatment, flocculation and oil recovery processes [19,20] as pour point depressants and inhibitors of wax deposition [21-22]. HPAs were synthesized through direct polymerization of sodium styrene sulfonate and vinylbenzyl dimethylhexadecylammonium chloride [23]. In order to develop protein nanocarriers, HPA were synthesized by the succinylation of ε-poly-l-lysine with dodecyl succinic anhydride and succinic anhydride [24]. Self-assembled HPA form nanoparticles through intermolecular hydrophobic and electrostatic interactions when dissolved in aqueous media.

A novel hydrophobically associating polyampholytes of poly(AM/AA/AMQC12) were synthesized by the free radical copolymerization of acrylamide (AM), acrylic acid (AA), and dimethyldodecyl(2-acrylamidoethyl)ammonium bromide (AMQC12) in water without any surfactants (named AAQ series) [25].

Polyampholytes containing betaine units and side cetyl radicals were obtained by modification of poly(4-vinylpyridine) with bromocarboxylic acids and alkyl bromides [26]. Their complex formation with liposomes was investigated. The insertion of side cetyl radicals into polybetaine molecules stabilizes their complexes with liposomes in the presence of salts. The cytotoxicity of the synthesized polyampholytes is one to two orders of magnitude lower than that of a cationic polymer with the same degree of polymerization.

Hydrophobically modified polysulfobetaines containing 3-[*N*-(2-methacroyloylethyl)-*N*,*N*-dimethylammonio]-propane sulfonate and varying amounts of the hydrophobic monomer stearyl methylacrylate were synthesized by micellar copolymerization [27]. The dynamic laser light scattering measurement revealed that both zwitterionic and hydrophobic associations were important in copolymer aggregation.

A series of amphoteric hydrophobic-associative flocculants were used to flocculate the montmorillonite suspensions [28]. The "antipolyelectrolyte effect" of polyampholyte and hydrophobic-associating interaction can endow excellent flocculation efficiency and salt tolerance.

The preparation and characterization of polymeric betaines based on aminocrotonates was reviewed in [29]. Stereochemistry and tautomeric transitions in aminocrotonates as well as kinetics and mechanism of formation of linear and crosslinked polybetaines proceeding via Michael addition reaction were outlined. As continuation of previous studies in the present paper we describe the synthetic protocol, physico-chemical properties and application aspect of hydrophobically modified polymeric betaines as pour point depressants.

2. Experimental

2.1 Materials

Acetoacetic ester (ethyl acetoacetate) (99%), dodecylamine (99%), tetradecylamine (99%), hexadecylamine (99%), octadecylamine (99%), MAA (99%), and azoisobutyronitrile (AIBN) were purchased from Aldrich. MAA was purified by distillation under the low pressure and kept in refrigerator. Reagent grade solvents acetone, DMF and DMSO purchased from Aldrich were used. Sodium dodecylsulfonate (SDS) is the product of Aldrich with purity of 99%. The mixture of waxy crude oil Buzachi-Mangyshlak (67:33 wt.%) and heavy oil of Mangyshlak (Western Kazakhstan) that are transported through main pipeline were selected for testing the efficiency of polymer additives as oil depressants. Highly viscous and highly paraffinic oil from Karazhanbas oilfield was used for oil displacement experiments.

2.2 Methods

^{13}C NMR spectra of polymer samples in DMSO were registered on impulse Fourier NMR spectrometer Bruker 400 MHz (Bruker, Germany). FTIR spectra were recorded with the help of Carry 660 (Agilent, USA) in KBr pellets. DSC measurements were performed on «LABSYS evo» (Setaram, France) at a heating rate 10°C/min. The M_n, M_w and M_z one of the sample dissolved in DMF was determined by using of gel-permeation chromatograph Malvern Viscotek 270 Dual Detector (UK) using the RI, LALS, and RALS detectors. The average hydrodynamic size and zeta-potential of colloid particles was determined with the help of Malvern Zetasizer Nano ZS90 (UK) at a room temperature. The viscosity of polymer solutions was measured by Ubbelohde viscometer at 25 ± 0.1°C. A pour point of oil with and without added depressants was measured by "S.D.M.-530" apparatus (Germany) equipped by 3 chambers with constant temperatures 0, -17 and -34°C according to ASTM D-5853.

3. Results and Discussion

3.1 Monomer synthesis

Preliminary melted alkylamines were dropwise added to acetoacetic ester (AAE) under the stirring during 3h at 60°C. The reaction mixture was left overnight at room temperature. Table 1 demonstrates the synthetic protocol of alkylaminocrotonates including the yield of abbreviated key products. Interaction of AAE with alkylamines proceeds according to Scheme 1. Alkylamino-but-2-enoic acid ethyl esters are more energetically stable than alternative tautomeric forms – 3-alkylamino-butyric acid ethyl esters due to conjugation of C=C and C=O bonds and formation of intramolecular hydrogen bonds [16].

3.2 Polymer synthesis

Polymerization of alkylaminocrotonates and MAA was carried out in benzene at 70°C in the presence of AIBN. Addition of methacrylic acid to alkylaminocrotonates leads to a formation of betaine monomers which undergo radical polymerization in the presence of AIBN (Scheme 2).

The monomer mixture was bubbled by nitrogen gas during 15 min, sealed into ampoule and thermostated at 70°C during 5 h. After completion of polymerization reaction, the precipitated product was washed out by acetone several times and dried at 70°C in vacuum oven up to constant mass. Table 2 represents the synthetic conditions of alkylaminocrotonates.

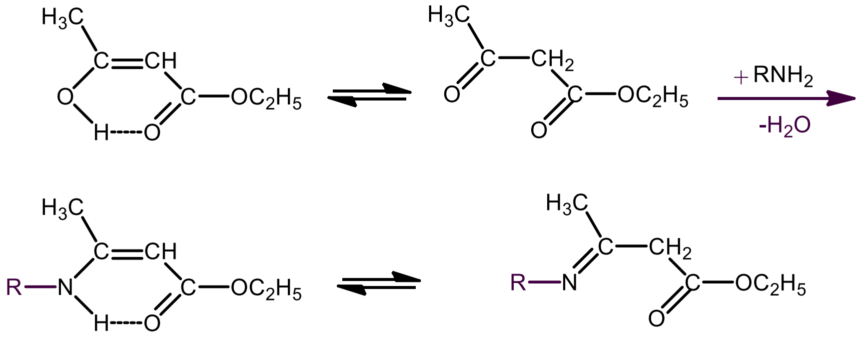
The radical polymerization of 3-[(2-carboxypropyl) alkylamino]-but-2-enoic acid ethyl esters leads to formation hydrophobically modified linear polybetaines abbreviated as CRODDA-MAA, CROTDA-MAA, CROHDA-MAA and CROODA-MAA respectively.

3.3 Solubility

Hydrophobically modified polymeric betaines are soluble in DMF, DMSO, THF, aqueous KOH; they are partially soluble in benzene, toluene, o-xylene, and insoluble in methanol and saturated hydrocarbons.

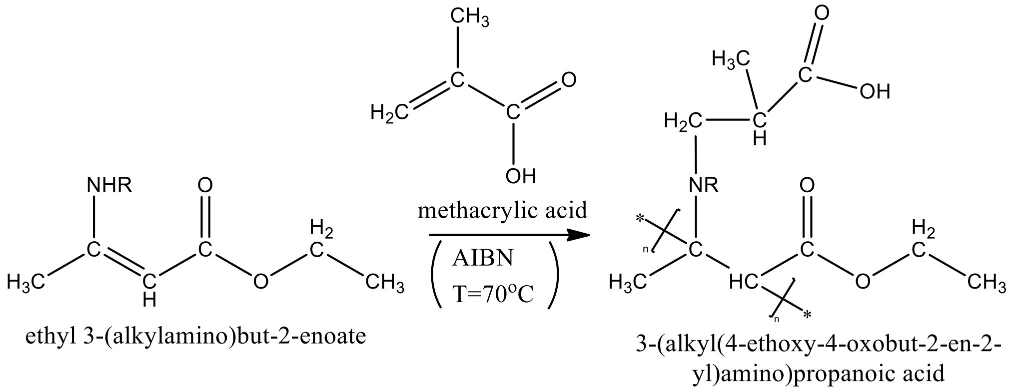
3.4 Preparation of polymer depressants

The CROODA-MAA (200, 500 and 1000 ppm) dissolved in benzene was added to oil mixture of Buzachi-Mangyshlak or Mangyshlak oil (200 mL) thermostated at 60°C and stirred vigorously during 30 min. The treated by polymeric depressant oil was cooled up of room temperature and the pour point temperature (PPT) of oil was measured.



where R is $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$ and $C_{18}H_{37}$

Scheme 1 – Formation of alkylaminocrotonates from AAE and alkylamines



where R is $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$, $C_{18}H_{37}$

Scheme 2 – Polymerization of alkylaminocrotonates in the presence of MAA

Table 1 – The synthetic protocol of alkylaminocrotonates from AAE and alkylamines

Alkylamines	Number of carbon atoms	The mass of alkylamine, g	The mass of AAE, g	Reaction temperature, °C	Yield of product, %	Abbreviation of monomers
Dodecylamine	12	10	7.02	60	>95	CRODDA
Tetradecylamine	14	10	6.10	60	>95	CROTDA
Hexadecylamine	16	10	5.39	60	>95	CROHDA
Octadecylamine	18	10	4.83	60	>95	CROODA

Table 2 – Synthetic protocol of hydrophobically modified polymeric betaines

Alkylaminocrotonate		Amount of MAA, g	AIBN, mg	T, °C	Yield of product, %
Abbreviation	Mass, g				
CRODDA	7	2.03	26.67	70	~50
CROTDA		1.85			~45
CROHDA		1.70			~43
CROODA		1.58			~39

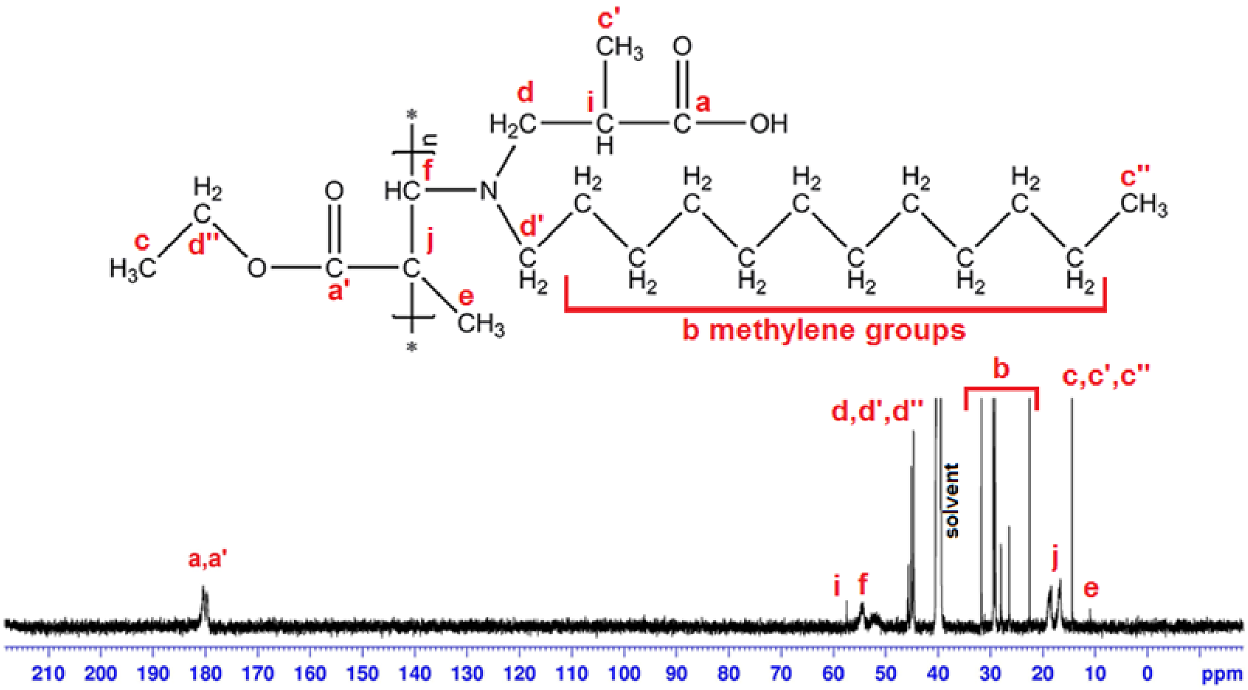


Figure 1 – ^{13}C NMR spectra of CRODDA-MAA in DMSO

Table 3 – Identification of FTIR spectra of alkylaminocrotonate monomers

Functional groups	Wavenumber, cm^{-1}			
	CRODDA	CROTDA	CROHDA	CROODA
$\nu(CH)_{as}$	2923 (vs)	2918 (vs)	2925 (vs)	2922 (vs)
$\nu(CH)_{s}$	2853 (s)	2849 (s)	2855 (s)	2850 (s)
$\nu(C=O)$	1652 (vs)	1649 (vs)	1651 (vs)	1650 (vs)
$\nu(C=C)$	1610 (vw)	1604 (vw)	1608 (vw)	1605 (vw)
$\nu(COC)$	1099 (w)	1096 (w)	1095 (w)	1099 (w)

Band intensities and vibration types: vs – very strong; s – strong; m – moderate; w – weak; vw – very weak; s – symmetric; as – asymmetric.

Table 4 – Identification of FTIR spectra of CRODDA-MAA, CROTDA-MAA, CROHDA-MAA and CROODA-MAA

Functional groups	Wavenumber, cm^{-1}			
	CRODDA-MAA	CROTDA-MAA	CROHDA-MAA	CROODA-MAA
$\nu(OH)$	3402	3422	3420	3419
$\nu(CH)_{as}$	2929 (vs)	2927(vs)	2928(vs)	2926(vs)
$\nu(CH)_{s}$	2856 (s)	2855(s)	2856(s)	2854(s)
$\nu(C=O)$	1701 (vs)	1703(vs)	1704(vs)	1703(vs)
$\nu(COO^{-})_{as}$	1541 (s)	1542(s)	1541(s)	1542(s)
$\nu(COC)_{as}$	1182 (w)	1183(w)	1181(w)	1182(w)

Band intensities and vibration types: vs – very strong; s – strong; m – moderate; w – weak; vw – very weak; s – symmetric; as – asymmetric.

3.5 ^{13}C NMR spectra of polymers

The structural unit and ^{13}C NMR spectra of CRODDA-MAA together with identification of functional groups are shown in Fig. 1. ^{13}C NMR spectra of CROTDA-MAA, CROHDA-MAA and CROODA-MAA are similar to CRODDA-MAA and differ from each other only by additional methylene groups.

3.6 FTIR spectra

Identification of FTIR spectra of monomers and polymers is given in Tables 3 and 4.

3.7 DSC measurements

DSC curves of CRODDA-MAA, CROTDA-MAA and CROODA-MAA are shown in Fig. 2. Broad peaks at 64, 73 and 101°C correspond to crystallization of long alkyl chains containing in the backbone of macromolecules. The endothermic transitions at 47, 58 and 89°C are also characteristic for dodecyl-, tetradecyl- and octadecylamines respectively (data are not shown). Crystallization temperature of hydrophobic groups in macromolecular chains is higher than alkylamines probably due to more ordered and densely structure. The broad peaks at the interval of temperature 207-224°C can belong to crystallization of whole macromolecules.

3.8 Viscosity

Hydrophobic polymers in aqueous KOH and in DMSO behave like polyelectrolytes, the reduced viscosity gradually increases with dilution (Fig. 3).

The lower viscosity of CROTDA and CROODA in DMSO may be connected with lower dielectric constant of organic solvent that retards the Coulomb repulsion of charged macromolecules.

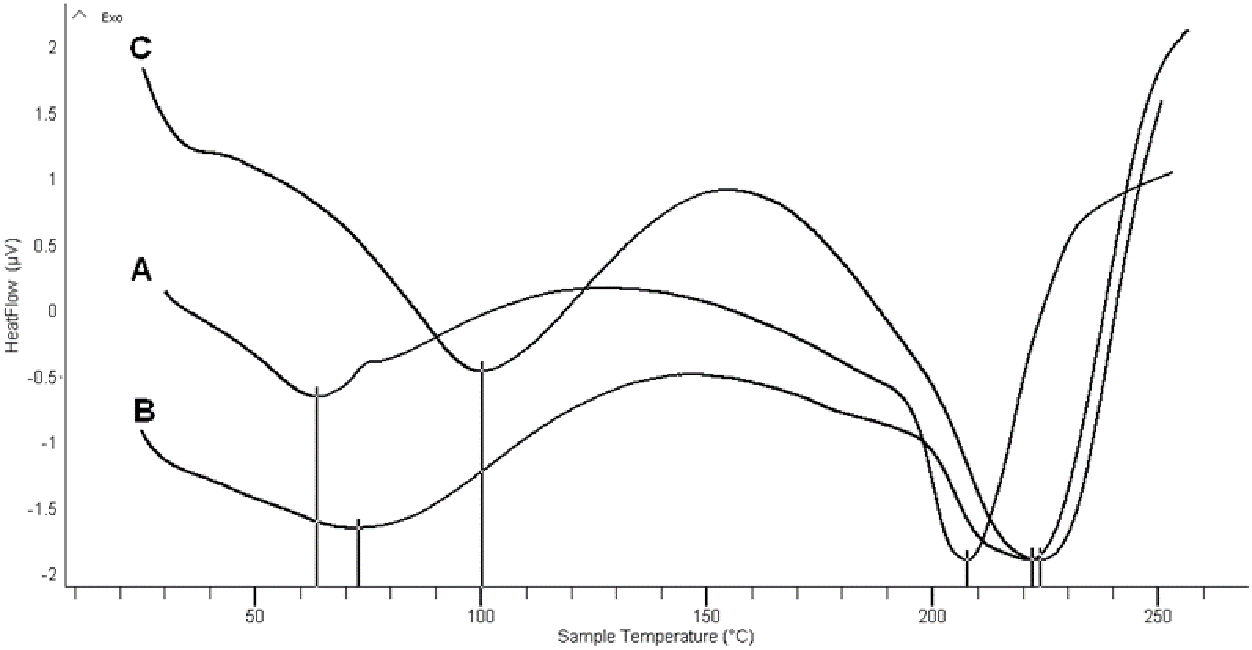


Figure 2 – DSC curves of CRODDA-MAA (a), CROTDA-MAA (b) and CROODA-MAA (c)

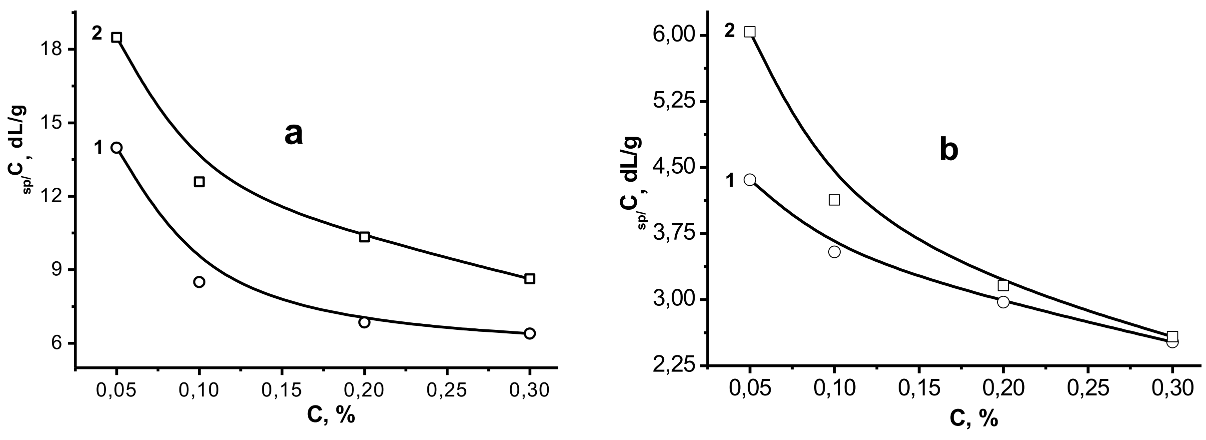


Figure 3 – Concentration dependences of the reduced viscosities of CROTDA (1) and CROODA (2) in aqueous KOH (a) and DMSO solutions (b)

3.9 The molecular masses and molecular mass distribution of CROHDA-MAA

The values of M_n, M_w, and M_z of CROHDA-MAA are high and the PDI is too wide (Table 5).

3.10 The average hydrodynamic size and zeta-potential of hydrophobic polymers.

It is expected that in aqueous KOH, hydrophobic polybetaines will form micellar structure stabilized by hydrophobic interactions of long alkyl groups, while in organic solvents, the formation of reversible micelles stabilized by intra- or interionic interactions of betaine groups is in favor as shown in Fig. 4.

The average hydrodynamic size and zeta-potential of CROTDA-MAA and CROODA-MAA measured in dilute aqueous KOH solutions are summarized in Table 6.

The average hydrodynamic size of macromolecules tends to increase with the increasing polymer concentration due to formation of bigger aggregates stabilized by hydrophobic interactions. In DMSO, such tendency is also observed because of

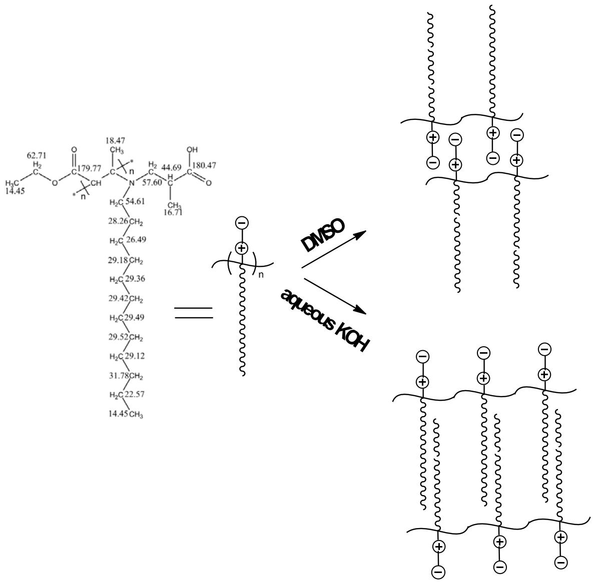


Figure 4 – Schematic representation of formation of micellar structures of hydrophobic polybetaines in aqueous KOH and DMSO solutions

Table 5 – The molecular mass of hydrophobically modified polymeric betaine based on CROODA-MAA

Polymer	Molecular mass, Dalton			P.D.I.
	M_n, x10^{-6}	M_w, x10^{-6}	M_z, x10^{-7}	
CROODA-MAA	1.56	8.85	4.68	5.68

Table 6 – The average hydrodynamic size and zeta-potential of CROTDA-MAA and CROODA-MAA in aqueous KOH and DMSO

Polymer	Concentration, g dL^{-1}	The average hydrodynamic size, nm		Zeta-potential, mV	
		Aqueous KOH	DMSO	Aqueous KOH	DMSO
CROTDA-MAA	0.05	258	-	-48.7	-4.3
	0.10	306	338	-60.0	-7.6
	0.20	316	411	-47.7	-8.2
	0.30	1576	429	-30.1	-5.4
CROODA-MAA	0.05	237	594	-47.8	-7.7
	0.10	253	2600	-45.5	-6.5
	0.20	487	5333	-42.3	-4.6
	0.30	1789	5560	-37.0	-3.5

formation of ionic associates. Extremely big aggregates in DMSO are characteristic for CROODA-MAA having long alkyl chains. Zeta-potential of macromolecules in both aqueous KOH and DMSO is negative due to ionization of carboxylic groups. Much lower zeta-potential of macromolecules in DMSO is probably connected with the low dielectric permittivity of organic solvent (ε = 39.5) leading to enhancement of charge compensation between positive and negative charges of betaine groups.

3.11 pH dependent average hydrodynamic size and zeta potential of diluted aqueous solutions of CROTDA-MAA and CROODA-MAA

According to zeta-potential measurement, the isoelectric point (IEP) of 0.01% aqueous solution of CROTDA-MAA corresponds to pH 3.4. At the same time, the minimal size of CROTDA-MAA obtained from DLS data is around of pH 2.5 (Fig. 5a). Such inconsistency may be attributed to fluctuation of the size of macromolecules near of the IEP and experimental errors in case of DLS measurements. The IEP of 0.01% aqueous solution of CROODA-MAA according to zeta potential measurement corresponds to pH 2.7. This value is in good agreement with DLS data ($\text{pH}_{IEP} \approx 2.9$) (Fig. 5b). Average hydrodynamic sizes of dilute aqueous solution of CROTDA-MAA and CROODA-MAA varied in the range of 40-150 nm and 70-150 nm respectively. Earlier [29], the IEP of poly(carboxyethyl 3-aminocrotonate) was observed near pH 2–2.1.

3.12 Evaluation of pour point depressant ability of hydrophobic polybetaines

Earlier, the PPT ability of CRODDA-AA (and MAA) was tested with respect to Kumkol-Akshabulak oil mixture (89:11 wt.%) [21]. Addition of 100 ppm CRODDA-MAA to crude oil decreased the pour point temperature (PPT) from +15 to -3°C. Depression of PPT was equal to 18°C. Later using our methodology [21], authors of the work [22] synthesized wax inhibitors CRODDA-MAA (or AA) and CROHDA-AA, and tested them as PPT and viscosity reduction for Malaysian waxy crude. It has been concluded that the effective wax inhibitor is CRODDA-AA, and at optimal concentration of 1000 ppm, it reduces the PPT by 12°C, from 57 to 45°C. The viscosity of crude oil is reduced from 5421 cP to 3220 cP upon addition of 1000 ppm CRODDA-AA. We have tested the hydrophobic polybetaine with the longest alkyl chain, namely CROODA-MAA, as wax inhibitor with respect to Mangyshlak and Buzachi-Mangyshlak (67:33 wt.%) crude oils transporting through main pipeline (Table 7). Best results show that CROODA-MAA with concentration of 500 ppm provides the depression of PPT at 18°C for crude from Mangyshlak and at 30°C for the oil mixture of Buzachi-Mangyshlak (67:33 wt.%). While the same concentration (500 ppm) of the commercial available polymeric depressant based on ethylene-vinylacetate (EVA) copolymer exhibits the depression of PPT 15°C with respect to Mangyshlak and 27°C with respect to Buzachi-

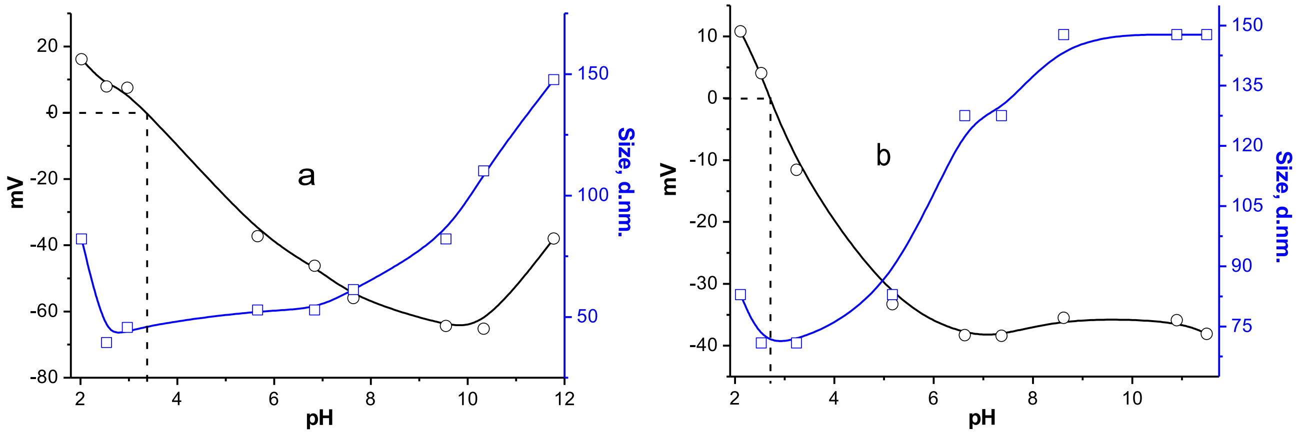


Figure 5 – Dependences of the average hydrodynamic size and zeta-potential of CROTDA-MAA and CROODA-MAA as a function of pH

Table 7 – Testing of CROODA-MAA as pour point depressant for Mangyshlak and Buzachi-Mangyshlak (67:33 wt.%) crude oils

Type of crude oil	CROODA-MAA, ppm	PPT, °C	PPT depression, °C
Mangyshlak	0	+27	0
	500	+9	18
Buzachi-Mangyshlak (67:33 wt.%)	0	+6	0
	200	-12	18
	500	-24	30
	1000	-24	30

Mangyshlak (67:33 wt.%) crude oils. Thus, the effectiveness of CROODA-MAA is higher than EVA that is widely applied as additive for oil transportation and paraffin inhibitors.

4. Conclusion

The hydrophobic polymeric betaines containing long alkyl chains C_{12}, C_{14}, C_{16} and C_{18} have been synthesized by Michael addition reaction of hydrophobically modified aminocrotonates and methacrylic acid. Polymeric betaines were characterized by FTIR, NMR, DSC, DLS, viscometry and zeta-potential measurements. The polymers were fully soluble in DMF and DMSO and formed colloid solutions in aqueous KOH. Low solubility of polymers was observed in aromatic hydrocarbons (benzene, toluene, o-xylene). In aqueous solution the hydrophobically modified polymeric betaines behave polyelectrolyte character. The average hydrodynamic size and zeta potential of diluted aqueous solutions of hydrophobic polybetainess containing dodecyl-, tetradecyl- and octadecyl groups were studied as a function of pH. Anomalous low values of the isoelectric point (IEP) of amphoteric macromolecules were found to be in the range of pH 2.7-3.4. According to DLS data the average size of macromolecules in dependence of pH changed from 230 to 5560 nm. Zeta-potential of amphoteric macromolecules in aqueous solution is much higher than that of DMSO. The formation of “schizophrenic” micelle structures is responsible for structural organization of hydrophobic polybetaines. In pure DMSO the low soluble in organic solvent betaine parts tend to aggregate and form intra- or interchain associates surrounded by hydrophobic corona. While in aqueous KOH the reversible micelle structure is stabilized by hydrophobic interactions of long alkyl chains. The synergistic effect of hydrophobic polybetaines in combination with commercial available ethylene-vinylacetate copolymers was observed in decreasing of the pour point temperatures of high paraffinic oils.

Acknowledgements

Authors thank the Ministry of Education and Science of the Republic of Kazakhstan for financial support (Grant No. 3397/ GF4 2015-2017).

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