

Synthesis and Characterization of Novel Hydrophobically Modified Polybetaines as Pour Point Depressants

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ABSTRACT: A novel hydrophobic monomer was synthesized from the acetoacetic ester and dodecylamine by condensation reaction in mild conditions. The modification by the dodecyl groups monomer was involved in the Michael addition reaction with acrylic (or methacrylic) acid followed by radical polymerization. Both linear and crosslinked novel betaine-type polyampholytes bearing hydrophobic "tail" and hydrophilic "head" were obtained. The linear polymer was characterized by viscometry, FTIR, and Raman spec-

troscopy. Swelling–shrinking behavior of linear and crosslinked samples was studied in water–DMF and water–DMSO mixtures. The applicability of hydrophobically modified polybetaines as pour point depressants (fluidity improvers) was also demonstrated. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1042–1048, 2004

Key words: polybetaine, viscosity, micelles, gels, swelling

INTRODUCTION

The amphiphilic polymers consisting of polar and nonpolar parts are able to self-organization due to a unique capability to form stable micelles or aggregates in water or organic solvents.^{1–4} Polymers containing amphiphilic groups are useful to model the function of active transport and ion permeable biomembranes,⁵ to design novel gene transfer and drug delivery systems,⁶ as well as LB multilayers.⁷ Recently,⁸ the long-chain acrylic polymers, containing hydrophobic pendant side groups, or so-called hydrophobically modified alkali-soluble emulsion (HASE), were characterized in aqueous solution by various physicochemical methods. It was found that the HASE polymer exhibits a conformational transition from a compact hard sphere to a random coil during the process of neutralization. Laschewsky et al.^{1,9–11} comprehensively described the synthesis and characterization of zwitterionic polysoaps, which combine advantages of the behavior of bipolar ions and micellar polymers. Hydrophobically associating polyelectrolytes may be effective viscosity enhancers in high salinity media that make them useful in sewage treatment, flocculation, and oil recovery processes.^{12,13} Wide application of hydrophobically modified polyelectrolytes as effec-

tive oil-soluble drug reducers¹⁴ and pour point depressants¹⁵ is also well known.

In the present article we report the synthetic pathway, structural, phase, and conformational properties of hydrophobically modified polybetaines. The ability of hydrophobically modified polybetaines as pour point depressant was shown.

EXPERIMENTAL

Materials

Acetoacetic ester (ethyl acetoacetate) (99%), dodecylamine (99%), acrylic acid (99.5%), methacrylic acid (99%), initiator azoisobutyronitrile (AIBN), and crosslinking agent *N,N'*-methylenebisacrylamide (MBAA) were purchased from Aldrich. Acrylic and methacrylic acids were purified by distillation under low pressure and kept in a refrigerator. Reagent-grade solvents acetone, DMF, and DMSO, purchased from Aldrich, were used. Waxy crude oil mixture containing 89 wt % from Kumkol and 11 wt % from Akshabulak (Western Kazakhstan) was selected for testing the efficiency of polymer additives as oil depressants. The content of low and high molecular-weight hydrocarbons for Kumkol and Akshabulak oils determined by chromatographic analysis is shown in Table I.

Monomer synthesis

Eighteen milliliters of dodecylamine (DDA) were dropwise added to 10 mL of acetoacetic ester (AAE) under stirring during 3 h at room temperature. Inter-

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TABLE I
Distribution of Hydrocarbons and Paraffins
in Kumkol and Akshabulak Oils

Oilfield	Hydrocarbons and paraffins with C ₄ -C ₁₄ , wt %		Paraffins, with C ₁₅ -C ₄₄ , wt %		
	C ₄ -C ₈	C ₉ -C ₁₄	C ₁₅ -C ₁₉	C ₂₀ -C ₂₉	C ₃₀ -C ₄₄
Kumkol	16,32	20,49	22,06	32,36	9,75
Akshabulak	1,12	24,55	29,61	37,2	6,4

action of AAE with DDA proceeds by Scheme 1 and produces dodecylamino-but-2-enoic acid ethyl ester or ethyl 3-dodecylaminocrotonate (CRODDA). Dodecylamino-but-2-enoic acid ethyl ester is more energetically stable than the alternative tautomeric form 3-dodecylamino-butyric acid ethyl ester due to conjugation of C=C and C=O bonds and formation of intramolecular hydrogen bonds.¹⁶

After completing of reaction the mixture was additionally stirred 30 min and left overnight. The organic phase containing the key product CRODDA was separated from the aqueous phase. The yield of monomer is 98%. The purity of monomers was checked by FTIR.

Polymer synthesis

Acrylic (or methacrylic) acid (0.8 mL, 0.5 mol) was added to CRODDA (2.2 mL, 0.5 mol), 2–3 mg of AIBN was added to monomer mixtures, and then the mixture was bubbled by nitrogen gas for 2 min and thermostated at 70°C for 1 h. Addition of AA (or MAA) to CRODDA leads to fast formation of a monomer product 3-[(2-carboxyethyl)dodecylamino]-but-2-enoic acid ethyl ester (or 3-[(2-carboxypropyl)dodecylamino]-but-2-enoic acid ethyl ester) via Michael addition reaction due to transfer of hydrogen atoms from the secondary amines of CRODDA to α -carbon atoms of unsaturated carboxylic acids (Scheme 2).

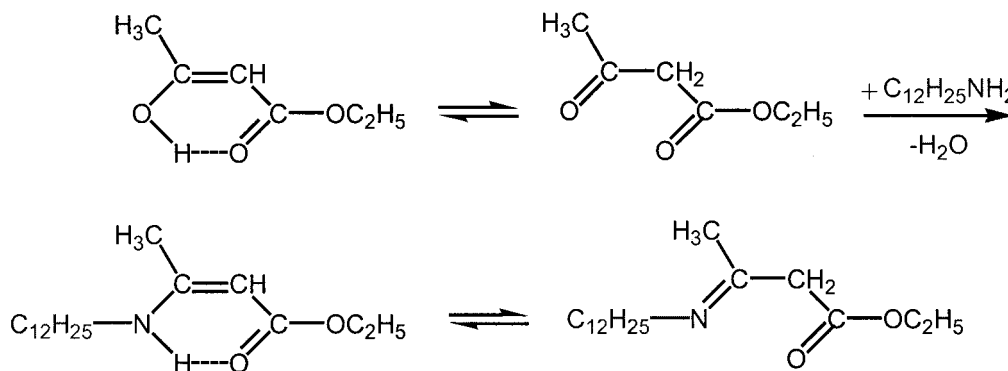
The radical polymerization of 3-[(2-carboxyethyl)dodecylamino]-but-2-enoic acid ethyl ester and 3-[(2-carboxypropyl)dodecylamino]-but-2-enoic acid ethyl ester leads to formation hydrophobically modified linear polybetaines abbreviated as CRODDA-AA and CRODDA-MAA, respectively. The linear polymers were thoroughly washed out by acetone. Crosslinked polybetaines were synthesized at the same conditions in the presence of MBAA (1–2 mg). The obtained gels were washed out by acetone to remove the sol fraction, dried in open air, and then in vacuum oven at room temperature.

Preparation of polymer depressants

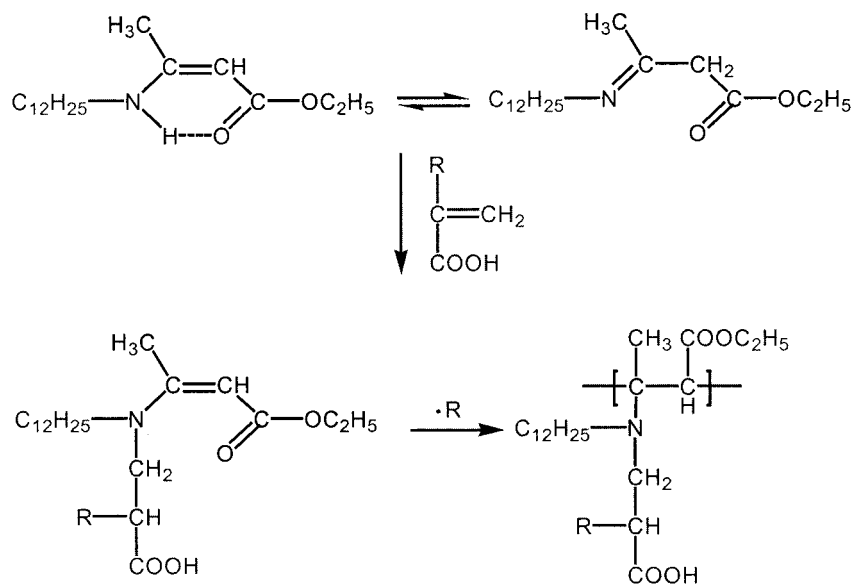
For preparation of polymer depressants three kinds of solvents were used; 100 ppm of linear CRODDA-MAA dissolved in DMF, *o*-xylene, and *n*-heptane was diluted by thermostated at 60°C oil and stirred vigorously during 1 min. One milliliter of CRODDA-MAA dissolved in appropriate solvents was added to 200 mL of crude oil.

METHODS

Chromatographic analysis of paraffins from Kumkol and Akshabulak oilfields was carried out with the help of AutoSystem XL gas chromatograph (Perkin-Elmer, Norwalk, CT) according to ASTM D2887. FTIR and Raman spectra were recorded using a Perkin-Elmer Spectrum GX. The viscosity of polymer solutions was measured by Ubbelohde viscometer at $25 \pm 0.1^\circ\text{C}$. The swelling degree of gel sample was determined in DMF by the formulae: $\alpha = m - m_o/m_o$ (where m is the mass of gel swollen in DMF, m_o is the mass of dry gel). Preliminary dissolved in appropriate solvents CRODDA-MAA were added to preliminary heated up to 60°C oil mixture, thermostated during 1 h and followed by cooling at a rate of 35°C/h. A pour point of oil mixture with and without added



Scheme 1 Modification of acetoacetic ester by dodecylamine.



Scheme 2 Formation of monomer and polymer products.

depressants was measured by S.D.M.-530 apparatus (Germany) equipped by three chambers with constant temperatures 0, -17 , and -34°C according to ASTM D-5853. Kinematic viscosities were determined by Ubbelohde viscometer with appropriate capillary constants in thermostated bath Labovisco TV-2000 at temperature range from 10 to 60°C . Effective viscosity and

shear stress were measured with the help of rotational viscometer rheometer EuroPhysics Rheo 2000 (Brookfield, USA). The temperature and shear rates were controlled by the computer program RHEO 2000 (version 2.6). The regime of linear changing of shear rate ($0-80\text{ s}^{-1}$) at constant temperature was used for all experiments.

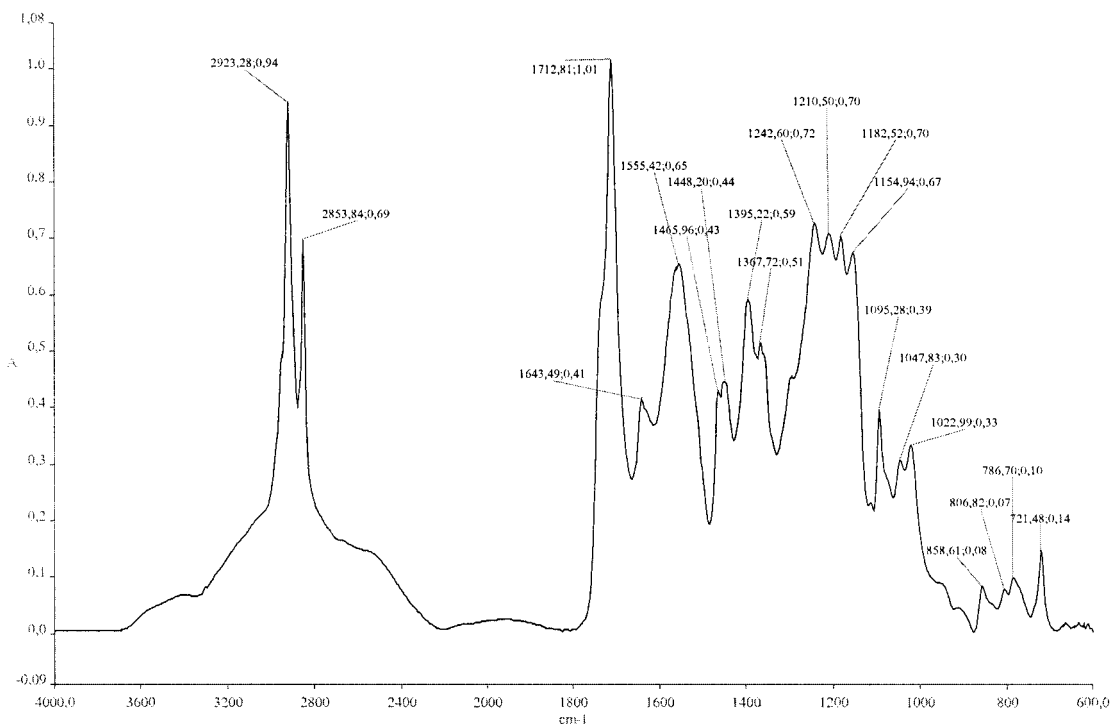


Figure 1 FTIR spectrum of CRODDA-AA.

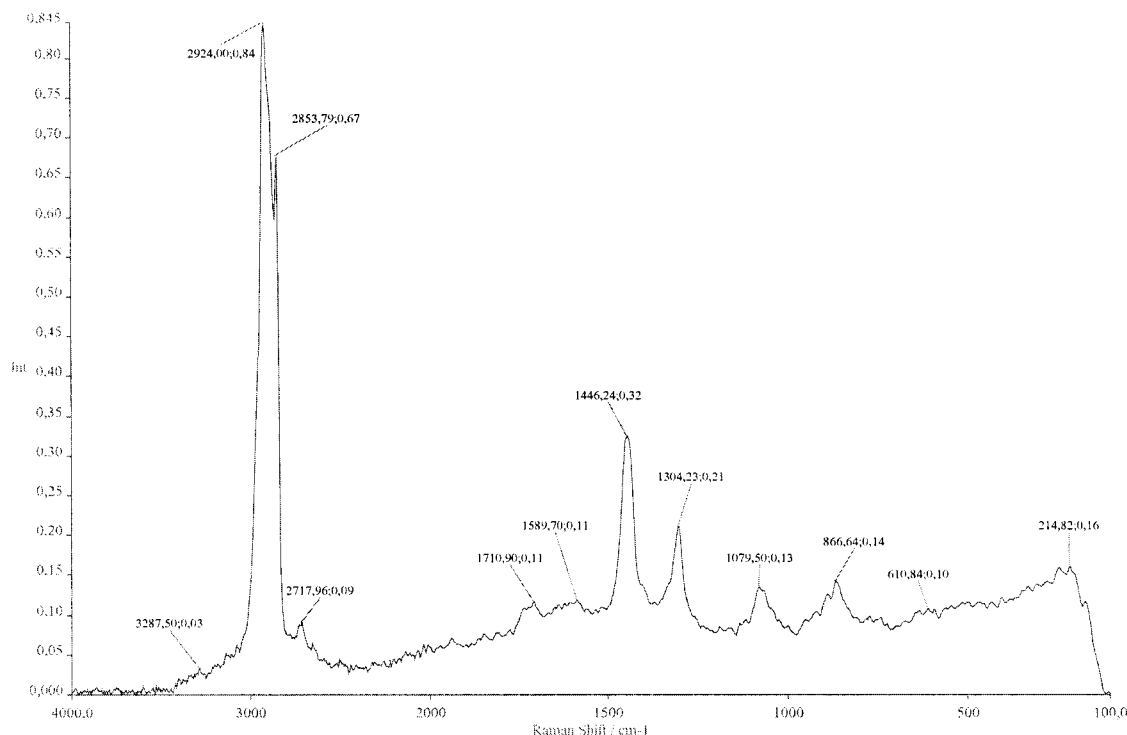


Figure 2 Raman spectrum of CRODDA-AA.

RESULTS AND DISCUSSION

CRODDA analogous to ethyl 3-aminocrotonate (CRO) itself¹⁶ does not polymerize due to π -conjugation of C=C and C=O bonds stabilized additionally by intramolecular hydrogen bonds (see Scheme 1). We have shown^{17,18} for the first time that the addition of electron acceptor monomers such as acrylic and methacrylic acids to CRO breaks the intramolecular hydrogen bonds, and via the Michael addition reaction produces so-called betaine-type monomers. It is also expected that involvement of CRODDA into Michael addition reaction takes place in the same way

TABLE II
Identification of FTIR and Raman Spectra
of CRODDA-AA (MAA)

Functional groups	Frequency, ^a cm ⁻¹			
	CRODDA-AA		CRODDA-MAA	
	FTIR	Raman	FTIR	Raman
$\nu(\text{CH})_{\text{as}}$	2923 (vs)	2926 (vs)	2919 (vs)	2928 (vs)
$\nu(\text{CH})_{\text{s}}$	2853 (s)	2853 (vs)	2848 (vs)	2853 (vs)
$\nu(\text{C}=\text{O})$	1712 (vs)	1711 (vw)	1698 (vs)	1709 (vw)
$\nu(\text{COO}^-)_{\text{as}}$	1555 (s)	—	1557 (m)	—
$\nu(\text{COC})_{\text{as}}$	1095 (w)	1080 (w)	1081 (w)	1082 (vw)

^a Band intensities and vibration types: vs—very strong; s—strong; m—moderate; w—weak; vw—very weak; v—stretching, s—symmetric, as—asymmetric.

(see Scheme 2). Transfer of hydrogen atoms from the secondary amine of CRODDA to α -carbon atoms of unsaturated carboxylic acids is responsible for the monomer formation. The proposed structure of CRODDA-AA (MAA) is confirmed by FTIR and Raman spectroscopy (Figs. 1 and 2). Disappearance of very intensive C=C bands at 1644 cm^{-1} confirms the involvement of double bonds into polymerization reaction. In addition, the bands of carbonyl group, sym-

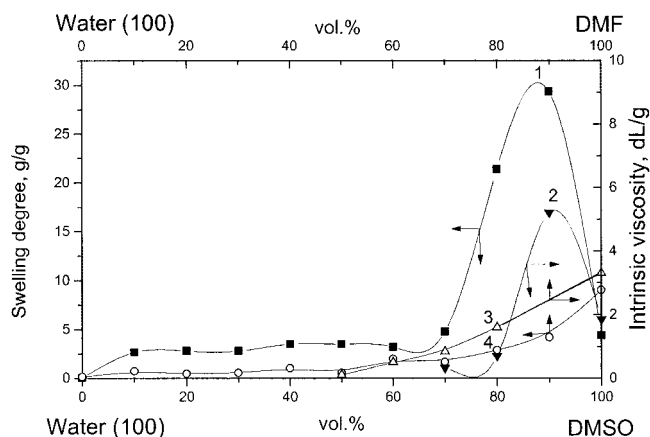


Figure 3 Dependence of the swelling degree (curves 1, 4) and intrinsic viscosity (curves 2, 3) of CRODDA-MAA on water-DMSO (curves 1, 2) and water-DMF (curves 3, 4) mixtures.

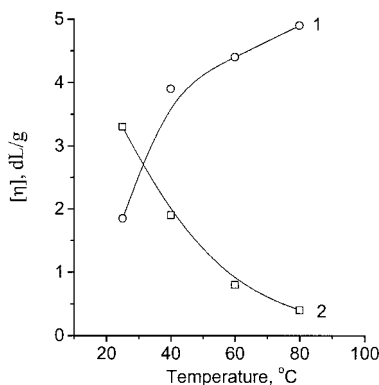
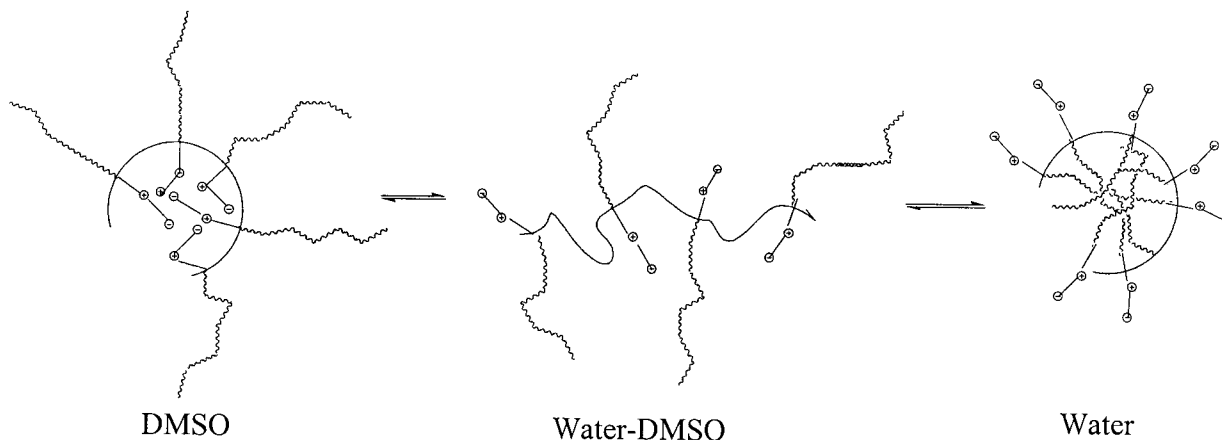


Figure 4 Influence of temperature on the intrinsic viscosity of CRODDA-MAA dissolved in DMSO (curve 1) and DMF (curve 2).

metric, asymmetric, and rocking vibrations of CH groups, symmetric and asymmetric modes of carboxylate ions are appeared (Table II).



The behavior of linear and crosslinked CRODDA-MAA with respect to the water-DMF mixture is different from the water-DMSO system. In the water-DMF mixture both the intrinsic viscosity and swelling degree of CRODDA-MAA gradually decreases with increasing of the water content (Fig. 3). It is interesting to note that the temperature dependence behavior of CRODDA-MAA in DMSO and DMF is opposite. Increasing the temperature increases the intrinsic viscosity of CRODDA-MAA in DMSO, while it decreases it in DMF (Fig. 4). It may be the result of different solvent quality with respect to functional groups of CRODDA-MAA.

One of the effective methods to minimize the problems caused by the wax deposition is addition of polymeric inhibitors called pour point depressants (PPDs) or fluidity improvers. Commonly used PPDs are poly- α -olefines,¹⁹ polyalkylmethacrylates, and ethylene-vinylacetate (EVA) copolymers.²⁰⁻²² The specific peculiarities of pour point depressants (PPD) are

Figure 3 shows the changing of the intrinsic viscosity and swelling degree of CRODDA-MAA in water-DMSO mixtures. In pure DMSO the insoluble betaine parts of CRODDA-MAA tend to aggregate and form intra- or interchain associates surrounded by hydrophobic corona. Addition of 10 vol % of water to DMSO considerably increases both the viscosity and swelling degree. Reasonable explanation of this phenomenon may be unfolding of macromolecules due to preferential solvation of betaine parts of CRODDA-MAA by water and dodecyl ones by organic solvent. However, the further enrichment of water-organic mixture by water causes shrinking of macromolecules due to reversible micelle formation stabilized by hydrophobic interactions of long alkyl chains. Insolubility of CRODDA-MAA at more than 30 vol % of water is probably connected with strong compactization of polymer particles. Speculative structure of CRODDA-MAA in DMSO, water-DMSO, and water environment may be represented as following.

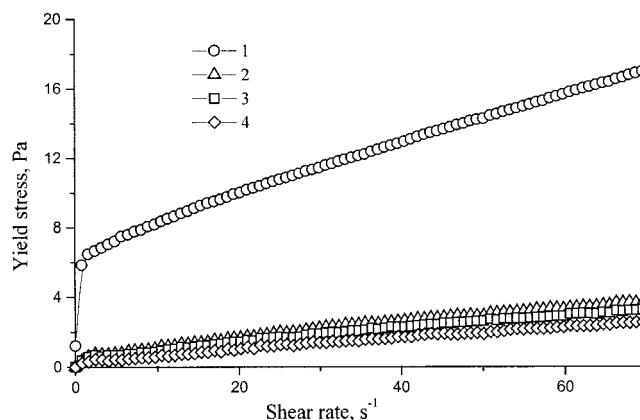


Figure 5 Dependence of the yield stress on shear rate for Kumkol-Akshabulak crude oil (curve 1) and in the presence of CRODDA-MAA dissolved in DMF (curve 2), heptane (curve 3), and *o*-xylene (curve 4).

TABLE III
Pour Point and Kinematic Viscosities of Kumkol-Akshabulak Oil Mixture

CRODDA-MAA, 100 ppm	Kinematic viscosity, cSt					PPD, °C
	20°C	30°C	40°C	50°C	60°C	
Crude oil without depressant	9.87	5.43	4.07	3.22	2.76	15
Preheated oil without depressant	9.40	5.68	4.21	3.33	2.76	6
Depressant prepared in DMF	7.44	5.81	4.42	3.46	2.91	0
Depressant prepared in <i>o</i> -xylene	7.21	5.56	4.33	3.10	2.80	3
Depressant prepared in <i>n</i> -hexane	7.37	5.60	4.36	3.13	2.89	-3

(1) the crystallization of mixture of long alkyl chains (C_{14} – C_{25}) of depressants together with paraffin-forming components of oil; (2) the presence of polar components of depressants retarding the process of cocrystallization; (3) the formation of small paraffin crystals due to spatial retarding of big crystal growth.²³ The PPD effectiveness of CRODDA-MAA is shown on Table III for the Kumkol-Akshabulak oil mixture (89 : 11 wt %). The best depressive activity is observed for CRODDA-MAA dissolved in *n*-heptane. Figure 6 shows the plot of shear stress vs. shear rate for crude oil in the presence and absence of CRODDA-MAA. Without the added depressant the waxy oil behaves like viscoplastic fluid. Doped by CRODDA-MAA waxy oil approaches Newtonian liquid, the shear stress decreases considerably due to modification of paraffin crystals by hydrophobic macromolecules. Figure 6 demonstrates the changing of plastic viscosity and yield stress on temperature for crude oil in the presence of depressant dissolved in various solvents. The best results are obtained for CRODDA-MAA prepared in *o*-xylene. For instance, at -5 and 0°C the addition of CRODDA-MAA dissolved in *o*-xylene decreases the yield stress seven to eight times in com-

parison with crude oil itself. In oil environment CRODDA-MAA represents the micelles consisting of hydrophilic core (betaine groups) and hydrophobic edge (dodecyl groups). The PPD mechanism of CRODDA-MAA with respect to waxy crude oil suggests the adsorption of definite fractions of paraffin molecules on the surface of micelles and retarding further agglomeration. Thus, the micellar structure of CRODDA-MAA is probably responsible for improvement of waxy crude oil fluidity.

CONCLUSION

Condensation of acetoacetic ester and dodecylamine produces dodecyl derivative of ethyl 3-aminocrotonate, which exists in enamine and imine tautomeric forms. Modified by dodecyl radical ethyl 3-aminocrotonate is able to react with unsaturated carboxylic acids via Michael addition reaction. The structure of hydrophobically modified polybetaines was identified by combination of IR and Raman spectroscopy. The changing of the intrinsic viscosity and swelling degree of hydrophobically modified polybetaines in water–DMSO is similar. The compact state of linear and crosslinked polymers in water and DMSO is explained by hydrophobic interactions of long alkyl chains in water and formation of intra- or interchain associates in DMSO. Conformational transition of macromolecules in water–DMSO mixture is due to solvation of betaine parts by water and dodecyl ones by organic solvent. The depressive activity of hydrophobically modified polybetaines with respect to crude oils is probably connected with adsorption of paraffin molecules on the surface of polymer micelles that retards the growth of paraffin crystals.

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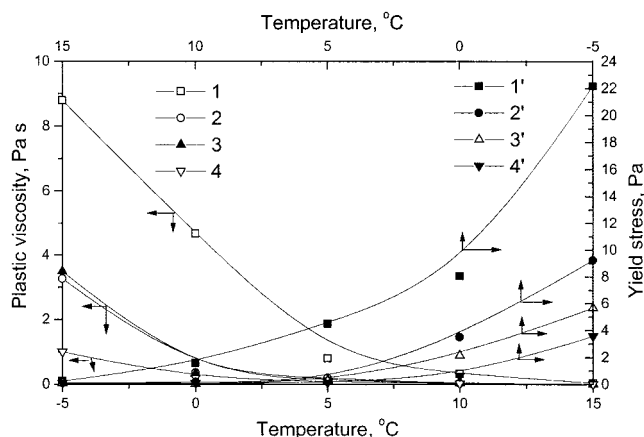


Figure 6 Dependence of the plastic viscosity (curves 1–4) and the yield stress (curves 1'–4') on temperature for Kumkol-Akshabulak crude oil (curves 1, 1') and in the presence of CRODDA-MAA dissolved in DMF (curves 2, 2'), heptane (curves 3, 3'), and *o*-xylene (curves 4, 4').

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