

Synthesis and Evaluation of Acrylate Polymers for Improving Flow Properties of Waxy Crudes

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SYNOPSIS

N-Alkyl acrylates and *n*-alkyl methacrylates were prepared by esterification of acrylic and methacrylic acids with two long-chain alcohol blends NAFOL 2022 and NAFOL 1822. The prepared monomers were characterized and polymerized individually. In addition, copolymers of *n*-alkyl acrylate-*n*-alkyl methacrylate, and *n*-alkyl methacrylate-vinyl acetate and a terpolymer of *n*-alkyl acrylate-acrylic acid-vinyl acetate were also synthesized. These polymers were also characterized and then evaluated as flow improvers in Khalda mixture and Salam Egyptian waxy crudes. The majority of the prepared additives showed good performance in improving the flow properties of the tested crudes. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

It is known that crude oils may contain substantial quantities of waxy materials. When such oils are subjected to temperatures below their cloud points, the waxy constituents tend to deposit on cold surfaces or crystallize and agglomerate into a solid gel. The gelling or stiffening of the oil introduces rheological problems that interfere with normal oil production or pipeline transportation and cause handling problems.¹ The high wax crude oils are characterized by high pour point, high viscosity, high gel strength, and abundant wax deposits. A variety of mechanical, physical, and chemical treatments have been applied to alleviate these deposition and pumping difficulties.

The use of chemical additives (flow improvers/pour-point depressants) to help cure these difficulties in crude oils and residual fuel oils is a logical extension of the technology developed in lubricating oils and middle distillates.² A flow improver application is often the most economic and effective solution for the majority of such crudes flow troubles. The structure of these flow improvers is mostly

polymeric and their essential role is to slow down or to modify the crystallization of the paraffin constituent in the crudes.³⁻⁵

They improve the flow properties of oils and limit the surface deposition of crystals. However, it is not possible to select one chemical that can be used for all types of waxy crudes due to the complex variety in their composition (saturates, aromatics, polars, asphaltenes, resins, etc.). So far, these additives have been used individually through extensive laboratory and field experiments before commercial application.⁶

Recently, trials are being made to establish appropriate models for predicting the activity of flow improvers on the basis of the physicochemical properties of both the investigated crude oil and the used additive.⁷ Specific structures of acrylate/methacrylate polymers have been known for several decades as effective commercial flow improvers/pour-point depressants for some specific crude oil/residual fuel oil compositions.⁸⁻¹² Therefore, it was valuable to investigate the performance of acrylate/methacrylate polymers in some Egyptian waxy crudes. The present article deals with the synthesis of different acrylate/methacrylate polymeric structures and their evaluation as flow improvers in two local waxy crudes, namely, Khalda mixture (K.M.) and Salam (S.) crudes. The flow properties were assessed

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Table I Typical Analyses of Linear Long-chain Alcohol Blends (NAFOL)

	Long-chain Alcohol			
	NAFOL 1822		NAFOL 2022	
Alcohol composition (wt %)	C16—OH	1.0 max		
	C18—OH	15.0 ± 1.0	C18—OH	7.0 max
	C20—OH	15.0 ± 1.0	C20—OH	58.0 ± 6.0
	C22—OH	69.0 ± 2.0	C22—OH	30.0 ± 5.0
	C24—OH	1.0 max	C24—OH	6.0 max
Alcohol content (wt %)	Approx 98		Approx 95	
Density (g/mL)	Approx 0.811 (70/4)		Approx 0.817 (60/4)	
Solidification point (°C)	63–65		55–61	
Hydroxyl number (mg KOH/g)	175–180		160–175	
Saponification number (mg KOH/g)	0.3 max		4.0 max	
Neutralization number (mg KOH/g)	0.1 max		1.0 max	
Iodine number (mgI/100 mg)	1.0 max		3.5 max	
Water (wt %)	0.1 max		0.1 max	

through pour-point depression and rheology improvement. Correlating pour-point depression with a decrease in yield point and/or plastic viscosity was also tried.

EXPERIMENTAL

Materials Used

Two linear long-chain alcohol blends (NAFOL 2022 and NAFOL 1822) were supplied by the CONDEA Chemical Co. with the typical analysis listed in Table I. The other chemicals are of technical grade.

Two Egyptian waxy crudes, viz., Khalda mixture (K.M.) and Salam (S.), were used for evaluating the performance of the synthesized polymeric additives. Their physicochemical characteristics are given in Table II.

Synthesis of Acrylate/Methacrylate Monomers

The NAFOL 2022 acrylate monomer was prepared by reacting 21.6 g (0.3 mol) of acrylic acid with 61.4 g (0.2 mol) of a long-chain alcohol blend NAFOL 2022 (C₁₈—C₂₄), 0.4 g (0.22 mL) concentrated sulfuric acid as catalyst, 0.6 g hydroquinone as a polymerization inhibitor, and 150 mL toluene as a solvent. Reflux of the reaction mixture was continued until the theoretical amount of water of the reaction was collected azeotropically in a Dean and Stark trap. NAFOL 1822 acrylate was prepared in the same manner except that 60 g (0.2 mol) of an alcohol blend NAFOL 1822 (C₁₆—C₂₄) was used for esterification. NAFOL 2022 and NAFOL 1822 methacrylate monomers were synthesized similarly by esterification of 25.5 g (0.3 mol) of methacrylic acid with the corresponding molar ratios of alcohol blends, respectively.

Table II Physicochemical Properties of The Tested Western Desert Waxy Crudes

Test	Method	Crude	
		K.M.	S.
Specific gravity 60/60 (°F)	IP 160/87	0.8372	0.8298
A.P.I. gravity	Calculated	37.5	39
Pour point (°C)	IP 15/67 (86)	14	21
Kinematic viscosity	IP 71		
cst. (40°C)		4.24	4.58
cst. (60°C)		2.18	2.48
Wax content (wt %)	UOP 46/64	21.0	18.7
Asphaltene content (wt %)	IP 143/84	0.945	1.45

Table III Physicochemical Characteristics of the Prepared Acrylate Monomers

Monomer	mp (°C)	n_D^{50} (°C)	Elementary Analysis					
			C		H		O	
			Expt	Calcd	Expt	Calcd	Expt	Calcd
NAFOL 2022-acrylate	42	1.4463	77.92	78.41	12.15	12.50	9.93	9.09
NAFOL 1822-acrylate	44	1.4472	77.82	78.63	12.44	12.56	9.74	8.76
NAFOL 2022-methacrylate	38	1.4455	78.15	78.68	12.27	12.55	9.58	8.76
NAFOL 1822-methacrylate	41	1.4460	78.33	78.94	12.05	12.63	9.62	8.43

The prepared monomers were purified by distilling off the solvent at the end of the reaction at reduced pressure. The reaction mixture was then extracted with *n*-hexane, then washed with water to be free of catalyst and of any unreacted acid until the washings were neutral. The crude ester was then recrystallized twice from acetone (3.0 mL/g) at 0°C. The prepared monomers showed a white waxylike solid appearance.

These monomers were characterized through elemental analysis, melting points, and refractive indices n_D^{50} determination. Analysis data are given in Table III. The IR spectra of all the acrylate/methacrylate monomers are nearly identical. A representative infrared spectral pattern of the NAFOL 2022 acrylate monomer is shown in Figure 1 (a), which illustrates the C—H stretching vibration of methylenes —CH₂— absorbed strongly at 2950–2924 cm⁻¹. The ester carbonyl C=O appeared as a strong absorption at 1728 cm⁻¹ and the presence of the ester functionality was further supported by the appearance of a C—O stretching vibration at 1187 cm⁻¹. The characteristic C=C stretching appeared at 1633 cm⁻¹, whereas the C—H in plane deformation vibrations of these acrylic ester monomers appeared as doublets at 1322–1296 cm⁻¹. The C—H deformation vibration of methylenes appeared at 1466 cm⁻¹. A strong absorption of the bending vibration appeared at 720 cm⁻¹ for C—(CH₂)_{*n*}—C of the long alkyl moiety of the ester.

Polymerization of Acrylate/Methacrylate Monomers

Fifty grams of each of the four prepared monomers were subjected to a free-radical solution polymerization individually in the presence of 0.25 g (0.5 wt %) benzoyl peroxide as an initiator and 50 mL benzene as a solvent. The reaction mixture was heated to 70 ± 5°C for 20 min under nitrogen flushing; then,

the reaction mixture was stirred at this temperature utilizing a nitrogen blanket for 3 h. Thus, the four acrylate/methacrylate homopolymers numbered 1, 2, 3, and 4 were prepared.

A copolymer numbered 5 of NAFOL 2022 acrylate–NAFOL 2022 methacrylate was synthesized by using equal molar ratios of both comonomers and following the same aforementioned reaction conditions.

A copolymer numbered 6 of NAFOL 2022 methacrylate–vinyl acetate was prepared at the same preceding conditions except that the temperature of polymerization was 80 ± 5°C and the molar ratio of alkyl methacrylate to vinyl acetate was 4 : 1, respectively.

A terpolymer numbered 7 of NAFOL 2022 acrylate–acrylic acid–vinyl acetate comonomers was prepared at the same aforesaid conditions except that the temperature of polymerization was 85 ± 5°C and the molar ratio of comonomers was 4 : 2 : 1, respectively.

At the end of each reaction period, the polymer was precipitated with an excess volume of methanol, then filtered. Further purification was carried out by dissolution of the polymer in benzene and reprecipitation with methanol, filtration, and vacuum drying at 40°C for 3 h. The prepared polymers numbered from 1 to 7 showed a white solid powder appearance.

Characterization of the Prepared Polymers

The synthesized polymers were characterized in terms of melting point, weight-average molecular weight, polydispersity, and molecular weight distribution using a gel permeation chromatography technique against polystyrene molecular weight standards. The measurement was carried out by a high-performance liquid chromatography (HPLC) apparatus (Waters Model 510) at the following conditions:

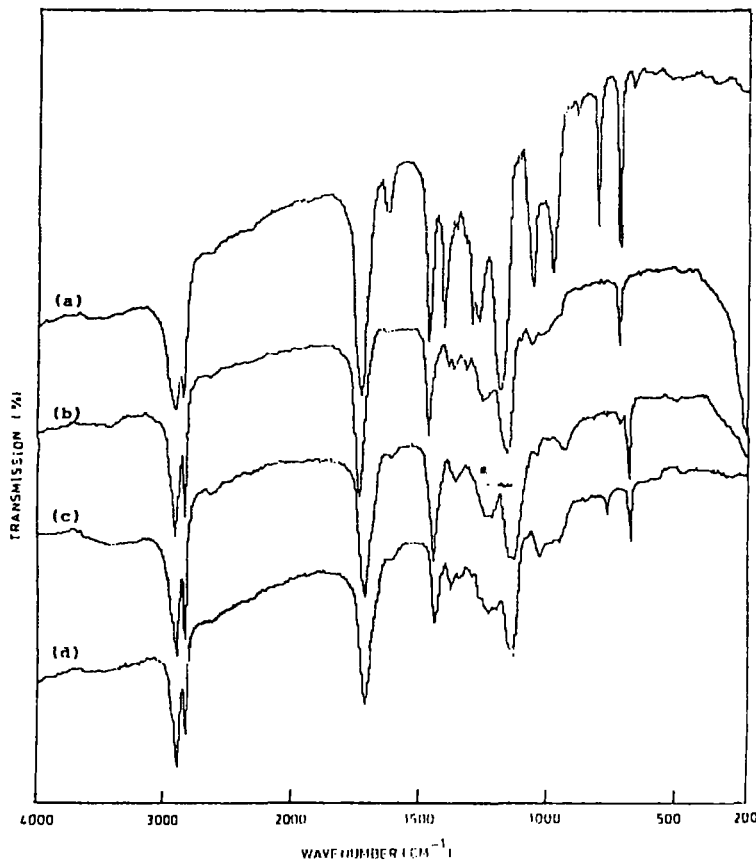


Figure 1 IR spectra of (a) NAFOL 2022 acrylate monomer, (b) NAFOL 2022 acrylate homopolymer, (c) NAFOL 2022 Acrylate-NAFOL 2022 methacrylate copolymer, and (d) NAFOL 2022 acrylate-acrylic acid-vinyl acetate terpolymer.

Solvent: Toluene HPLC grade
 Column: Ultrastyrigel 500; 1000; 10,000;
 100,000 Å
 Temperature: 25°C
 Flow Speed: 18 cm³ min⁻¹

Results are listed in Table IV and shown in Figure 2.

The IR spectra of the prepared polymers showed similar patterns as shown in Figure 1 curves (b), (c), and (d) for NAFOL 2022 acrylate homopolymer, NAFOL 2022 acrylate-NAFOL 2022 methacrylate copolymer, and NAFOL 2022 acrylate-acrylic acid-vinyl acetate terpolymer, respectively. The structure of these polymers was confirmed by the total absence of C=C stretching absorbed at 1633 cm⁻¹ in comparison with that of the monomer curve (a), i.e., there is no contamination of the polymers with the monomer.

Evaluation Tests

The seven prepared polymers were tested for their effectiveness as flow improvers for the two Egyptian

waxy crudes K.M. and S. through the pour-point test according to the ASTM D-97 procedure and rheological measurements (apparent viscosity, yield stress, and plastic viscosity) by the coaxial rotating viscometer (RHEOTEST 2.1).

RESULTS AND DISCUSSION

Influence of Average Molecular Weight of Acrylate/Methacrylate Polymers on Their Effectiveness as Flow Improvers

The seven synthesized polymers nos. 1-7 were assessed as flow improvers at 100 ppm concentration in both K.M. and S. crudes in terms of pour-point depression. Their weight-average molecular weight, polydispersity, and molecular weight distribution were determined by HPLC analysis. Results are listed in Table IV and illustrated in Figure 2. Data obtained showed that the prepared polymeric additives have different molecular weights varying from 14,220 to 90,270 and that the optimum effec-

Table IV Characterization of the Prepared Acrylate Polymers and Their Performance as Flow Improvers for Waxy Crudes at 100 ppm Concentration

Polymer No.	Composition	mp (°C)	M_w	Polydispersity Index	Pour Point Depression	
					K.M.	S.
1	NAFOL 2022 acrylate homopolymer	55-56	27,900	2.96	3	27
2	NAFOL 1822 acrylate homopolymer	61-62	36,980	4.85	6	30
3	NAFOL 2022 methacrylate homopolymer	45-46	55,160	1.79	3	15
4	NAFOL 1822 methacrylate homopolymer	47-48	14,650	1.40	0	15
5	NAFOL 2022 acrylate-NAFOL 2022 methacrylate copolymer	65	90,270	2.54	9	3
6	NAFOL 2022 methacrylate-vinyl acetate copolymer	45	23,460	1.24	15	6
7	NAFOL 2022 acrylate-acrylic acid-vinyl acetate terpolymer	45	14,220	1.28	9	9

tiveness is achieved at the range of 20,000 to 40,000 (polymers nos. 1, 2, and 6). It was also observed that the performance of homopolymers is improved with increasing the polydispersity index, i.e., with broadening of the molecular weight distribution. Polymer no. 2, with the highest polydispersity index

(4.85), accomplished the optimum pour-point depression with respect to other homopolymers, whereas polymer no. 4, with the lowest polydispersity (1.4), achieved the least depression. This result confirmed our preceding publication in this respect.¹³ It is obvious that K.M. crude showed a better re-

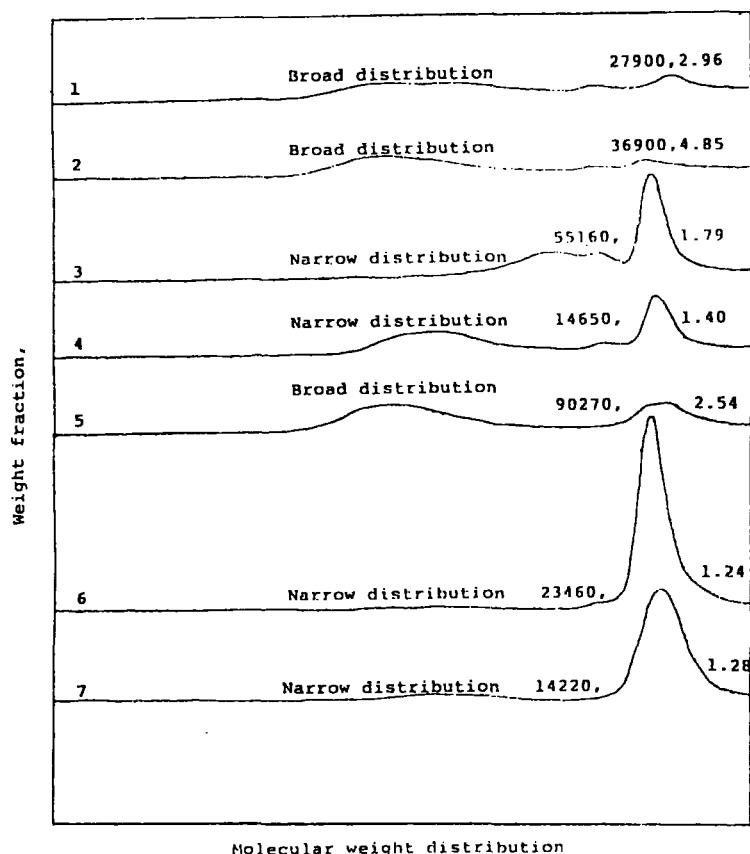
**Figure 2** Molecular weight distribution of the prepared acrylate polymers nos. 1-7.

Table V Effect of Concentration of Polymeric Flow Improvers on the Pour Point of Khalda Mixture (K.M.) Waxy Crude Oil

Concentration (ppm)	Pour Point (°C)						
	Polymer No.						
	1	2	3	4	5	6	7
Nil	14	14	14	14	14	14	14
100	11	8	11	14	5	-1	5
200	11	5	11	14	-1	5	8
300	11	2	14	14	11	5	14
400	11	5	14	14	14	5	14
500	11	5	14	14	14	8	14
1000	11	8	14	14	14	8	14

sponse to the copolymers/terpolymer than did S. crude, which was significantly affected by the homopolymers. Thus, it is concluded that average molecular weight and polydispersity index are substantial parameters controlling the effectiveness of the used polymeric additives. The influence of the structure of these polymers is difficult to be studied solely due to the previously mentioned factors that interfere with its effect on the flow characteristics of waxy crudes. However, the effect of the structure of polymers nos. 5-7 was studied generally. It was selected in such a way that the degree of overall polarity of the end groups in their lateral alkyl chains is decreased in the order $7 > 6 > 5$.

Comparing the effectiveness of these polymers with their polarity, it is observed that copolymer no. 6 of moderate polarity is of high efficiency. This result is correlated with that reported in the literature,¹⁴ which denotes that slight polar groups are needed in the flow improver structure—rather than nonpolar or highly polar—to improve interaction

with the precipitating paraffins associated with slight polar asphaltenes.

Influence of Concentration of Acrylate/ Methacrylate Polymers on Their Efficiency in Terms of Pour-point Depression

The two tested crudes K.M. and S. were also doped individually with concentrations 200, 300, 400, 500, and 1000 ppm of each of the seven prepared polymers successively. The doping temperature was adjusted to 55°C. The tested sample is heated at the doping temperature for 15 min, then injected with the additive at the prescribed concentration, stirred for 5 min, allowed to cool at room temperature until 35°C, and then subjected to pour-point determination. Results are presented in Tables V and VI. Data presented in Table V showed that K.M. crude responds substantially to the copolymers/terpolymer rather than to homopolymers and that polymers nos. 2, 5, 6, and 7 affect its flow property in such a way

Table VI Effect of Concentration of Polymeric Flow Improvers on the Pour Point of Salam (S.) Waxy Crude Oil

Concentration (ppm)	Pour Point (°C)						
	Polymer No.						
	1	2	3	4	5	6	7
Nil	21	21	21	21	21	21	21
100	-6	-9	9	6	18	15	12
200	-6	-15	6	3	18	3	3
300	-9	-18	3	3	9	0	0
400	-12	-18	3	3	3	0	0
500	-15	-18	0	0	3	0	-3
1000	-18	-18	0	0	0	0	-6

Table VII Influence of Polymeric Flow Improvers Nos. 2 and 6 on the Pour Point and Rheological Properties of Khalda Mixture (K.M.) and Salam (S.) Crudes at 14°C

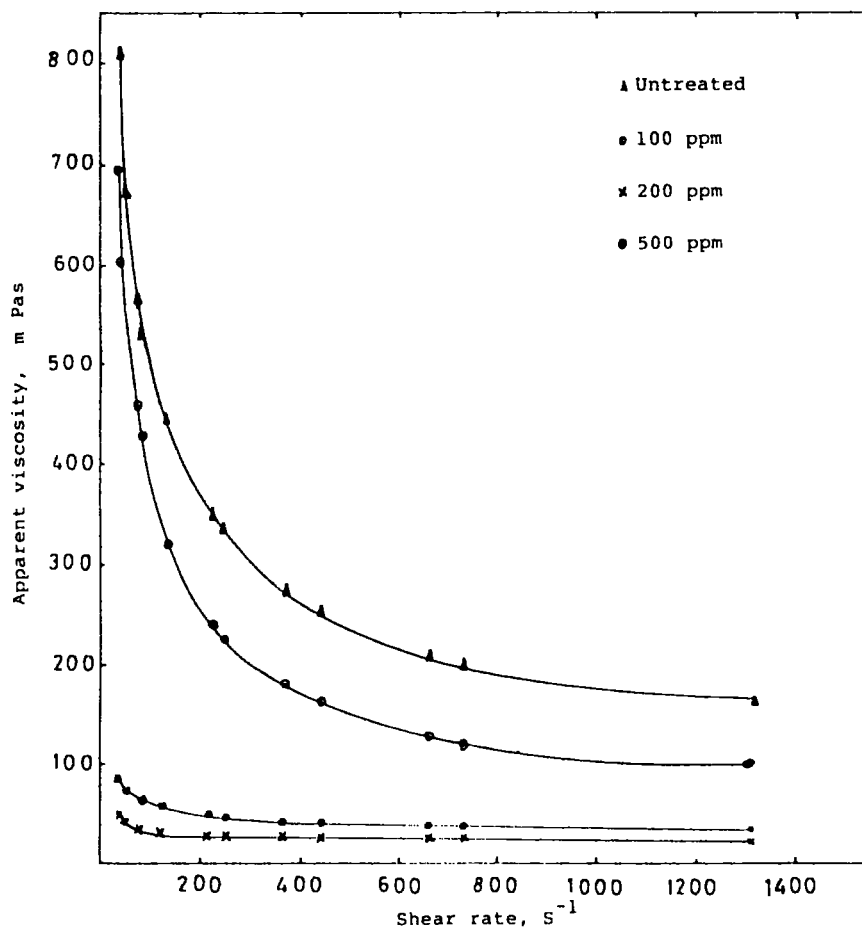
Additive Concentration (ppm)	Rheology							
	Pour Point (°C)		Yield Stress (Pa)		Plastic Viscosity (mPas)		Correlation Coefficient	
	K.M.	S.	K.M.	S.	K.M.	S.	K.M.	S.
Nil	14	21	37.705	5.892	142.07	17.31	0.9854	0.9961
100	-1	-9	30.482	0.608	79.78	7.54	0.9898	0.9959
200	5	-15	1.186	0.475	20.52	6.93	0.9997	0.9984
500	8	-18	3.052	0.701	31.87	7.09	0.9983	0.9991

that with increasing concentration the pour point decreases until a definite concentration is reached, above which the pour point starts to rise again and a worse flow properties are again obtained. This concentration differs from one additive to another.

The preferred polymeric additive in K.M. crude was polymer no. 6 ($\Delta P = 15^\circ\text{C}$ at 100 ppm concen-

tration). Data listed in Table VI reveal that S. crude responds to a greater extent to this family of polymers than does K.M. crude. With increasing concentration of the polymer, the pour point decreases. No reversion of pour point was observed.

A substantial pour-point depression was achieved at a concentration as little as 100 ppm. Polymer no.


Figure 3 Effect of polymer no. 6 on the apparent viscosity of K.M. crude at temperature 14°C.

2 achieved the optimum performance ($\Delta P = 30^\circ\text{C}$ at 100 ppm concentration). The observed difference in the flow behavior of the two crudes may be accounted for by their differences in compositions as shown in Table II, particularly their wax and asphaltene contents.

Influence of Acrylate/Methacrylate Pour-point Depressants on the Rheological Characteristics of Doped Crudes

To supplement a realistic low-temperature flow behavior of the tested crudes, rheological measurements have to be conducted. Data obtained from the pour-point test revealed that polymers nos. 2 and 6 are the preferred pour-point depressants for both S. and K.M. crudes, respectively. Hence, these additives were evaluated for their performance as flow improvers in the two tested waxy crudes through rheological measurements at concentrations of 100, 200, and 500 ppm. Measurement of the shear stress–shear rate relationship was conducted at constant temperature (14°C).

The experimental procedure starts with doping the crude with the additive at the prescribed concentration at 55°C ; meanwhile, the viscometer cup

is preheated to the same temperature, then loaded with 25 mL of the treated sample, and then the temperature is brought down to 14°C at a low shear rate of 7.29 S^{-1} (dynamic cooling). Shearing was continued for 15 min at the test temperature before evaluation. The shear stress–shear rate relationship was recorded for the tested samples. Experimental data were fitted to a Bingham plastic flow model using a linear regression computer program. The Bingham plastic flow model is represented by the equation

$$\tau = \tau_y + \eta_p \frac{du}{dr}$$

where τ is the shear stress (Pa); τ_y , the yield stress (Pa); η_p , the plastic viscosity (mPas); and du/dr = shear rate (S^{-1}).

The obtained data are listed in Table II and illustrated in Figures 3–8. From Figures 3 and 4, it is obvious that the apparent viscosity is decreased significantly with increasing concentration of each of the polymers nos. 6 and 2 in both K.M. and S. crudes, respectively, up to 200 ppm, particularly at low shear rates. A further increase of concentration leads to

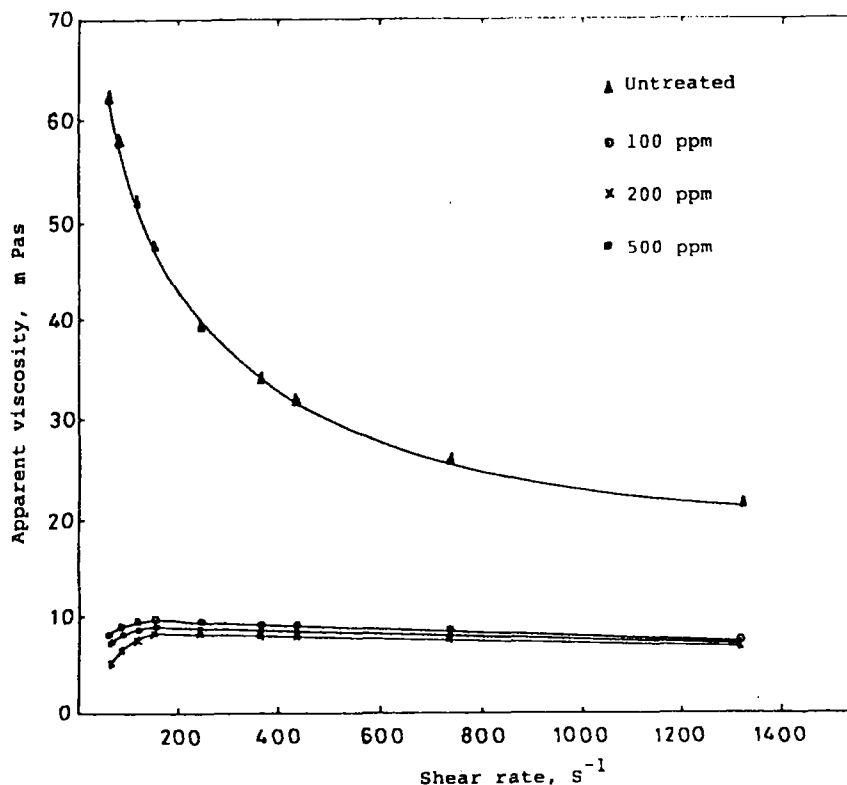


Figure 4 Effect of polymer no. 2 on the apparent viscosity of S. crude at temperature 14°C .

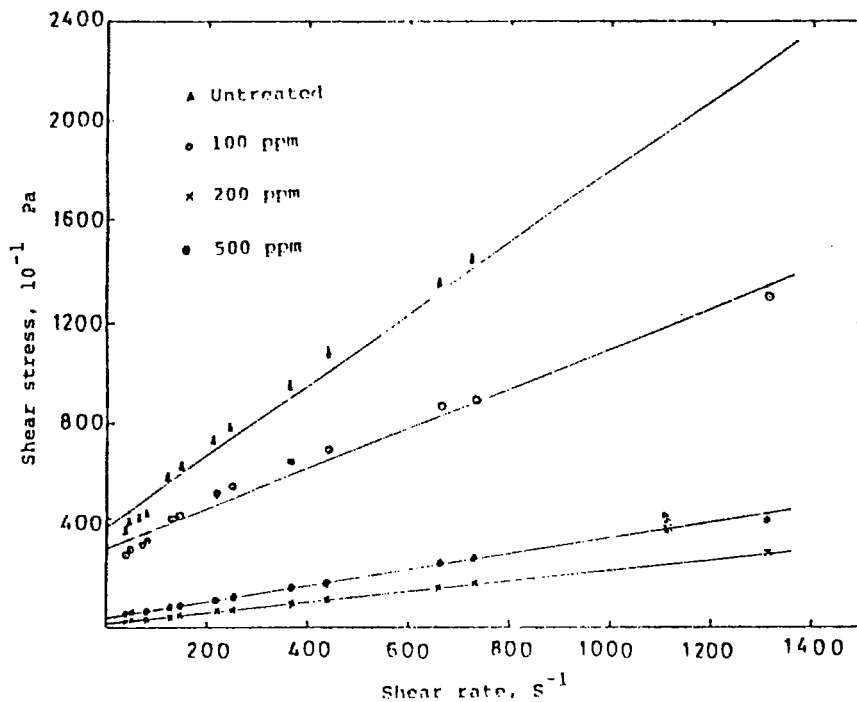


Figure 5 Effect of polymer no. 6 on the rheology of K.M. crude at temperature 14°C.

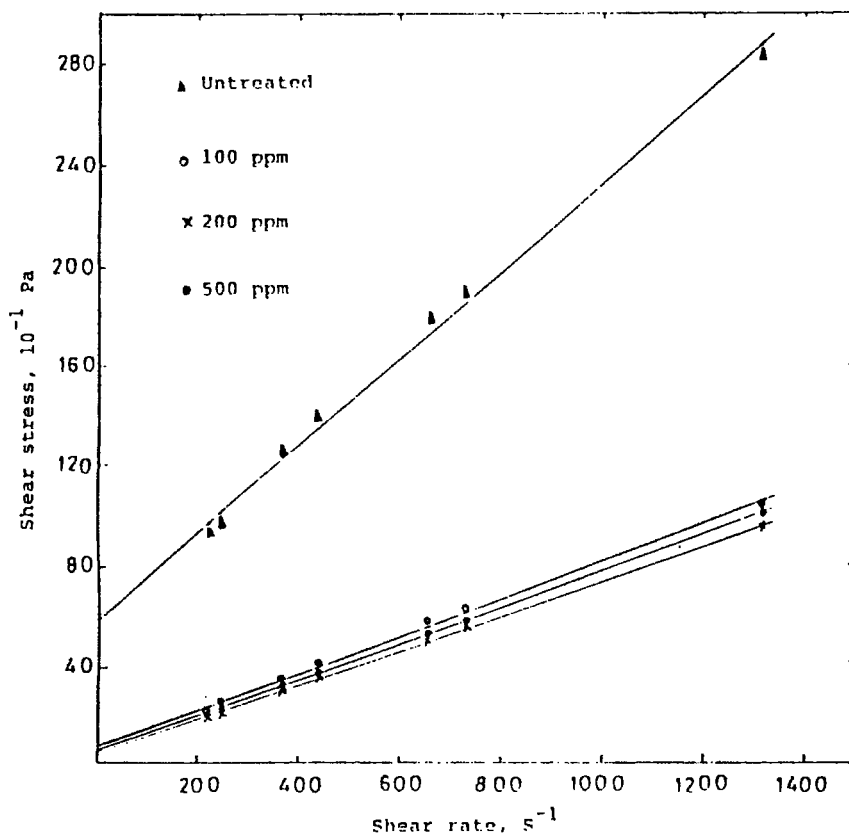


Figure 6 Effect of polymer no. 2 on the rheology of S. crude at temperature 14°C.

a reversion effect, and a slight increase in the apparent viscosity is observed.

Figures 5 and 6 illustrate the fitted experimental shear stress–shear rate measurements according to the Bingham plastic model. They showed that the minimum yield stress was attained at 200 ppm concentration for both the two additives nos. 6 and 2 in K.M. and S. crudes, respectively, at 14°C. It was found that in K.M. crude polymer no. 6 (200 ppm) reduced the yield point from 37.5 to 1.18 Pa at the pour-point temperature (14°C), whereas in S. crude, polymer no. 2 at the same concentration lowered the yield point from 5.89 to 0.47 Pa at 14°C, which is less than the pour point of S. crude by 7°C (Table VII). It was also observed that a 100 ppm concentration of additive no. 2 has a significant reduction effect on the yield point of S. crude, whereas additive no. 6 at the same concentration did not substantially affect the yield point of K.M. crude. Plastic viscosity was also decreased by treating the two crudes with both additives in a similar way. It was lowered from 142.07 to 20.52 mPas at a 200 ppm concentration of polymer no. 6 in K.M. crude, whereas it was reduced from 17.31 to 6.93 mPas at a 200 ppm concentration of polymer no. 2 in S. crude.

K.M. crude has worse flow properties initially in spite of its relatively low pour point (14°C). This was observed in its relatively high yield point (37.5 Pa) and high plastic viscosity (142.07 mPas), whereas S. crude showed good flow properties in

spite of its relatively high pour point (21°C); it was found to exhibit a lower yield point (5.89 Pa) and lower plastic viscosity (17.31 mPas) even at a temperature lower than its pour point by 7°C. This is attributed to the lower wax content and higher asphaltene content of the S. crude composition than those of K.M. crude (Table II).

Figure 7 demonstrates the activity of additive no. 6 in K.M. crude in terms of pour-point depression and reduction in yield point and plastic viscosity. It is apparent that both yield point and plastic viscosity vary similarly with increase in the additive concentration, whereas the pour point indicates approximately a similar variation pattern.

Figure 8 illustrates the relationship between pour-point depression and rheology improvement caused by additive no. 2 in S. crude. It is obvious that while both yield point and plastic viscosity vary similarly with increase of the additive concentration pour point varies in a different manner, i.e., there is no correlation between pour-point depression and rheology improvement in both crudes.

CONCLUSION

The synthesized acrylate/methacrylate polymers with a long side chain (C_{18} – C_{24}) and average molecular weight of 20,000–40,000 proved to be effective flow improvers in both Salam (S.) and Khalda mix-

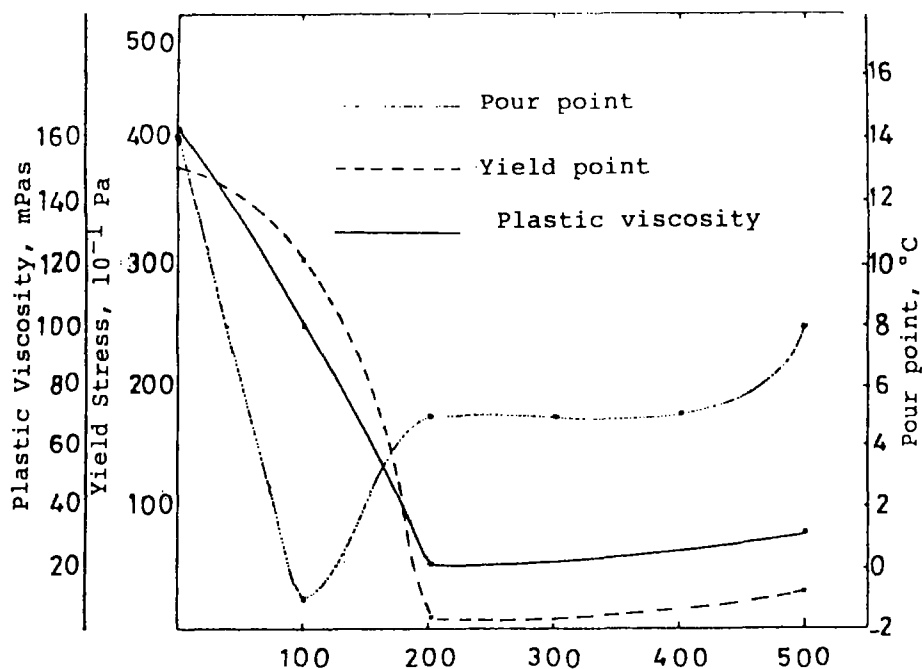


Figure 7 Variation of pour point, yield stress, and plastic viscosity with concentration of polymer no. 6 in K.M. crude.

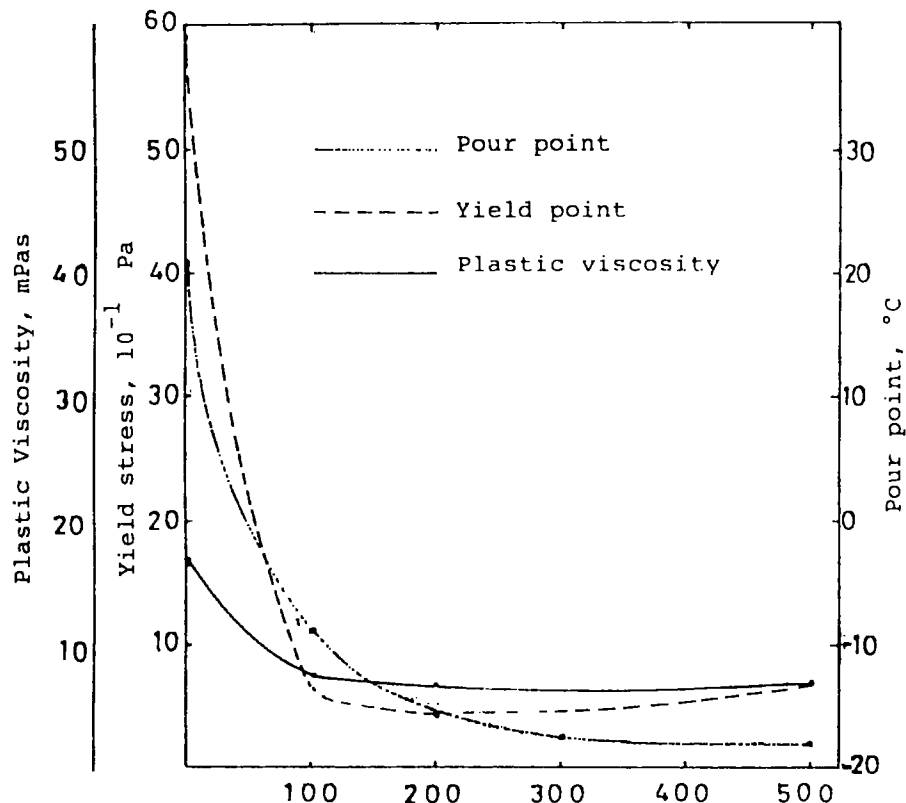


Figure 8 Variation of pour point, yield stress, and plastic viscosity with concentration of polymer no. 2 in S. crude.

ture (K.M.) waxy crudes. The C_{18} — C_{24} alkyl acrylate homopolymer achieved the optimum pour-point depression from 21 to -9°C , yield stress reduction from 5.89 to 0.47 Pa, and plastic viscosity decrease from 17.31 to 6.93 mPas at a concentration of 200 ppm in S. crude. The C_{18} — C_{24} alkyl acrylate-vinyl acetate copolymer attained the optimum flow improvement in K.M. crude at 200 ppm concentration. It could lower the pour point from 14 to -1°C , decrease the yield point from 37.5 to 1.18 Pa, and reduce the plastic viscosity from 142.07 to 20.52 mPas.

Our apprehension that there is a correlation between pour-point depression and rheology improvement caused by treating with flow improvers was not ascertained. The pour-point data are inadequate for realizing the actual low-temperature flow properties of untreated/treated waxy crudes. Rheological measurement is essential to indicate a precise low-temperature flow behavior.

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