

EVALUATION OF SULFONATED ACRYLAMIDE-BASED TETRAPOLYMER AS A RHEOLOGY MODIFIER IN WATER-BASED DRILLING FLUID

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Abstract

The need for improved water-based drilling fluid systems for application in unfavourable wellbore conditions is a persistent challenge to oilwell drilling operation. This study evaluates the appropriateness of a synthetic tetrapolymer as a rheology modifier in water-based drilling fluid for application at elevated temperatures. The tetrapolymer, comprising acrylamide, sodium 2-acrylamido-2-methylpropanesulfonate, N-vinyl pyrrolidone and N-butyl propenoate (TPM4) was synthesized in aqueous medium by free-radical polymerization and characterized by Fourier transform infra-red (FTIR) spectroscopy. Experimental design using six factors involving monomer molar ratios, total monomer concentration, initiator dosage, reaction temperature, pH and reaction time, was used to establish the optimum conditions of synthesis of the tetrapolymer. Rheological and fluid loss properties of the tetrapolymer were assessed in water-based drilling fluids. The tetrapolymer effected about four-fold filtration loss control in 4% KCl bentonite-based mud compared to the blank at 140°C. It also exhibited good viscosification of the mud and favourably retained mud viscosity up to 150°C.

Key words: tetrapolymer; water-based mud; rheological property; filtration loss; temperature and salt resistance.

1. Introduction

Conventionally, muds have been classified into three categories namely, air, water and oil muds according to the base fluid used in their preparation [1]. Oil-based muds generally have superior temperature stability, lubricity and hole stabilizing attributes compared to water-based muds. Notwithstanding their unique properties that are difficult to match with those of water muds, their use is often associated with high costs, special handling, and environmental concerns, more especially with diesel-based fluids [2-3]. However, most of the world's drilling operations have used water-based muds which are formulated either using fresh water with or without added salts [1].

As the search for hydrocarbons advances deeper into the earth and the bottom of the ocean, however, high thermal and saline environments are encountered. Application of drilling fluids with suitable rheologies and filtration characteristics is necessary to achieve maximum efficiency of the drilling process [4-5]. Water based fluids, used in most U.S. offshore drilling operations consist of water, barite, clay, caustic soda, lignite, lignosulfonates and/or water-soluble polymers [6]. However, conventional fluid systems such as lignite, lignosulfonate, starch, or cellulose-based muds have been observed to fail in high temperature and saline environments [7].

Bentonite clay, characteristically possesses adequate rheological and adsorption properties for formulation of drilling fluids but tend to fail at high temperatures due to high flocculation [8]. Additionally, at low concentration, bentonite clay is unable to provide satisfactory rheological

properties required for optimum performance in oilwell drilling and requires the addition of polymers to enhance performance.

Different polymeric additives have been used in water based mud formulations in order to reduce filtration, limit cuttings dispersion, increase the carrying capacity of the fluid, and stabilize the suspension by dispersing the weighting agent. Different types of polymers of varied molecular weights, structures, functionalities and charge depending on their role within the formation have been applied. Notably, the thermal degradation of polymeric additives used for water-based formulations tend to badly affect fluid characteristics and induce at high temperature different phenomena such as loss of rheological properties, particle sedimentation, clay gelation, poor filtration characteristics with detrimental formation damage [9].

Owing to high flexibility of the partially hydrolyzed polyacrylamide chain in aqueous solution at high temperature and high salinity, it exhibits random or coil molecular conformation, which results in significant loss of viscosity. In recent years, much global research has been focused on the development of new polymers with high performance in high temperature and high salinity [10] and some progress has been made.

This investigation deals with the synthesis of a sulfonated acrylamide-based tetrapolymer tailored for dual functional property for viscosity enhancement and fluid loss reduction in water-based drilling fluids.

2. Experimental methods

2.1 Materials for synthesis of tetrapolymer

Acrylamide(AM), 2-acrylamido-2-methylpropanesulfonic acid (AMPS), N-Butyl propenoate (BP), N- Vinyl pyrrolidone (NVP), Dipotassium [(sulfonatoperoxy)sulfonyl]oxidanide ($K_2S_2O_8$), sodium pyrosulphite ($Na_2S_2O_5$), sodium chloride, and sodium hydroxide were of analytical grade except AMPS and used as received.

2.1.1 Synthesis of Acrylamide-sodium 2-acrylamido-2-methylpropanesulfonate-N-Vinyl pyrrolidone -N-Butyl propenoate Tetrapolymer

The AM-AMPS-VP-BP tetrapolymer, designated as TPM4, was synthesised by free radical tetrapolymerization in deionized water. The reaction was conducted in a three-neck flask equipped with a magnetic stirrer, nitrogen gas inlet tube and a thermostatic water bath under nitrogen sparging using $K_2S_2O_8/Na_2S_2O_5$ redox initiation. Total monomer concentration (1.4-2.4 molarity), monomers feed ratios of AM (38-58%)/AMPS(50-25%)/NVP(6-13)/BP(4-6%), pH (7-9.5), temperature (35-60°C) and initiator dosage(0.2-1.2wt%) were varied to optimize synthesis conditions. AMPS was first dissolved in deionized water and the pH adjusted to the desired value using 2MNaOH. Acrylamide was then dissolved in the mixture whilst N-Butyl propenoate was dissolved in N- Vinyl pyrrolidone before adding to the bulk. The pH of the mixed solutions was finally adjusted to the desired value whilst ensuring a constant reactant volume of 100cm³. The reactants system was purged of oxygen for at least 20minutes prior to initiation of the polymerization. Reaction was terminated after the desired time. The tetrapolymer was finally isolated and purified using excess acetone. Tetrapolymerisation reaction to produce TPM4 is shown in scheme 1.

2.2 Characterization of properties of tetrapolymer

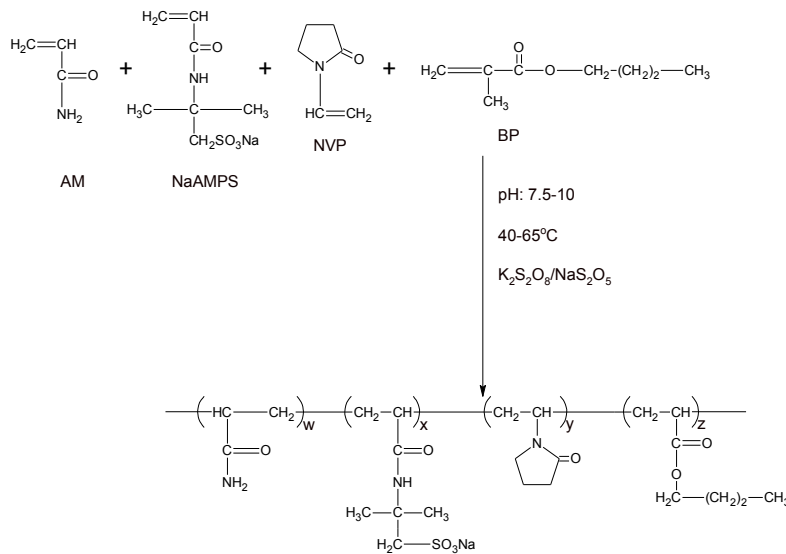
FTIR Spectrum of the tetrapolymer was recorded on a Nicolet 370 FTIR spectrometer (USA) from powder-pressed sample in the wave number range of 4000-400 cm⁻¹ [11-15].

The intrinsic viscosity, $[\eta]$ of the tetrapolymer was determined using Huggins' and Kraemer's equations according to API RP 63 1990 procedure [16]. Measurements were taken using Brookfield DV-III Ultra programmable Rheometer (Brookfield Engineering Lab, Middleboro, USA). The viscosity-average molecular weights of the tetrapolymer was estimated using the Mark-Houwink relationship stated below [12,17].

$$M_V = \left\{ 10000x \frac{[\eta]}{3.73} \right\}^{1/0.66}$$

2.3 Formulation and property evaluation of drilling fluid

Formulation muds A, B, and C were prepared using recipes as shown in Tables 1 & 2 and figure 6. Formulation muds were prepared by blending using a multi-speed mixer. Tests were conducted before and after hot-rolled aging for 16 hours by American Petroleum Institute (API) practice 131 [18]. Rheological properties were measured using ZNN-D6 six-speed rotary viscometer (Qingdao Haitonghai Specialized instrument Factory). API fluid loss was determined at applied nitrogen gas pressure of 100psi using ZNS-A filter press tester. Measurements after hot-aging involved cooling the drilling fluid to room temperature (25°C), stirring in a mixing cup using the multi-mixer for 5min and conducting the tests. Blank samples were prepared and tested under the same conditions in the absence of the tetrapolymer.



Scheme 1 Tetrapolymerisation reaction to produce TPM4

Table 1 Effect of tetrapolymer concentration on drilling fluid rheologies and fluid loss

Mud formulation A										
Water : 500ml; Bentonite clay: 25g; Na ₂ CO ₃ :1.25g; tetrapolymer : 0, 2.5g, 5.0g, 7.5g, 10.0g										
Property	Mud properties @ ambient temp at different tetrapolymer concentrations					Mud properties after aging @ 120°C for 16hrs at different tetrapolymer concentrations				
	Zero	0.5%	1.0%	1.5%	2.0%	Zero	0.5%	1.0%	1.5%	2.0%
	Blank	TPM4	TPM4	TPM4	TPM4	Blank	TPM4	TPM4	TPM4	TPM4
Apparent Viscosity, (AV)/cP	10.5	24	33	42	52	6	24	36	50	55
Plastic Viscosity, (PV)/cP	5	14	22	24	28	6	14	26	36	40
Yield point (YP)/ lb/100ft ²	11	20	22	36	48	0	20	20	28	30
10 Sec gel (G10'')/lb/100ft ²	5	7	7.0	9.0	9.0	0	1.0	2.0	2.0	3.0
10 min gel (G10')/ lb/100ft ²	8.5	10	11	13	14.0	0	1.0	2.0	3.0	4.0
API Filtrate loss, cm ³ /30min	28.5	20.5	17.0	14.0	14.0	43.0	31.5	26	25.0	19.5

Table 2 Effect of temperature on rheological and filtration properties of tetrapolymer incorporated mud

Mud Formulation B Water: 500ml; Bentonite clay:25g; Na ₂ CO ₃ :1.25g;Tetrapolymer:4.0g Blank mud contained no polymer						
Parameter	Mud properties before hot aging		Mud properties after hot rolled-aging at elevated temperatures			
	Ambient temperature (25°C)		120°C		140°C	150°C
	Blank	TPM4	Blank	TPM4	TPM4	TPM4
Apparent Viscosity (AV), cP	11.3	35	10	44	42.5	43
Plastic Viscosity (PV), cP	3.5	20	10	29.5	29.0	35
Yield point (YP), lb/100ft ²	15.6	30	0	29	27	16
10 Sec gel (G10''), lb/100ft ²	14	12	0	2.0	3.0	3.0
10 min gel (G10'), lb/100ft ²	19	13	0	3	3	3.0
API Filtrate loss, cm ³ /30min	24	16.5	107	21.5	25.5	28.0

3. Results and discussion

3.1 Optimized synthesis of tetrapolymer

Under the conditions investigated, the tetrapolymer could best be synthesized using monomer mole ratios of AM: AMPS:NVP:BP of 42:45:7:6, respectively, at total monomer concentration of 1.6 molarity (22.17wt/v%) and initiator dosage of 0.4wt% at temperature of 40°C using time of 3.5 hours and initial reactants system pH of 7.5. A yield of about 85% isolated dried tetrapolymer was obtained at the optimum condition.

3.2 Characterization

The FTIR spectrum of the TPM4 is presented in figure 1.

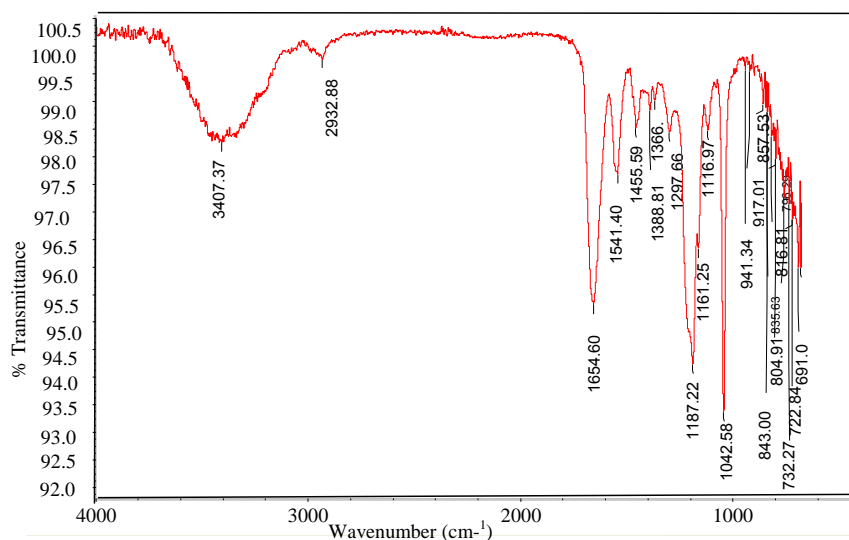


Figure 1 FTIR spectrum of TPM4

Comparative analysis of FTIR spectrum of tetrapolymer (TPM4) with some known spectra of homopolymers and copolymers [12-15] of similar monomers confirmed the presence of the four monomers. Broad peak at 3407.37 cm⁻¹ was attributed to the stretching vibration of -NH of amide of AM, NVP and AMPS. The absorption peaks observed at 2932.88 cm⁻¹ was due to

the stretching vibration of $-\text{CH}_2$. Peak at 1654.60 cm^{-1} was attributed to amide carbonyl stretching from AM and AMPS. Carboxylate stretching at 1388.81 cm^{-1} and 1541.40 cm^{-1} was attributed to BP. Band at 1455.59 cm^{-1} , revealed the characteristic signal of NVP. Spectral peaks at 1116.97 cm^{-1} , 1297.66 cm^{-1} and 1455.59 cm^{-1} were characteristic amide stretching of $-\text{CN}^-$ assigned to AM, NVP and AMPS. Bands recorded at 1161.25 cm^{-1} , 1187.22 cm^{-1} and 1042.58 cm^{-1} indicated asymmetric and symmetric stretching of sulfonate group of AMPS. The spectral analytical results were consistent with the chemical composition of TPM4 shown in scheme 1.

The intrinsic viscosity of the tetrapolymer was obtained as 2.65 dL/g while its viscosity-average molecular weight, estimated using Mark-Houwink as $6.85 \times 10^5\text{ Da}$.

3.3 Evaluation of drilling fluids

3.3.1 Effect of the polymer concentration on drilling fluid rheology and fluid loss

Results in Table 1 and figures 2, 3 followed some consistent trend with variation of TPM4 tetrapolymer concentrations in the drilling mud. Quantitative increase in the tetrapolymer concentration progressively increased the tetrapolymer incorporated mud (TPIM) rheological properties viz. apparent viscosity, plastic viscosity and yield point of the before and after hot-rolled aging at 120°C , as shown in fig. 2. However, filtration loss favourably and consistently reduced with increases in polymer concentrations as expected (fig. 3), hence, demonstrating the effectiveness of the tetrapolymer with dual functionality as a viscosity builder and a fluid loss reducer.

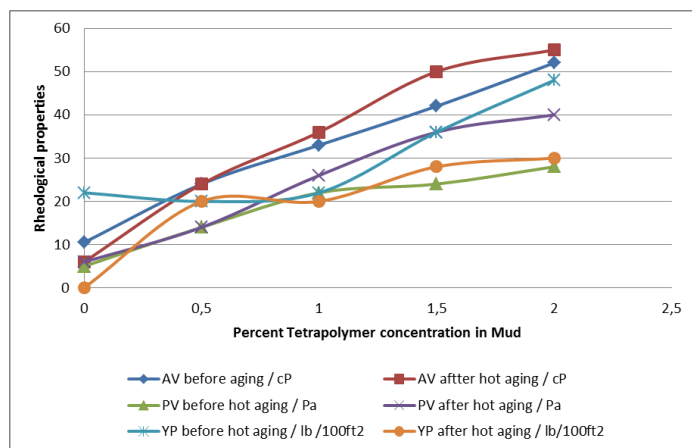


Fig. 2 Effect of TPM4 concentration on rheological properties of drilling mud

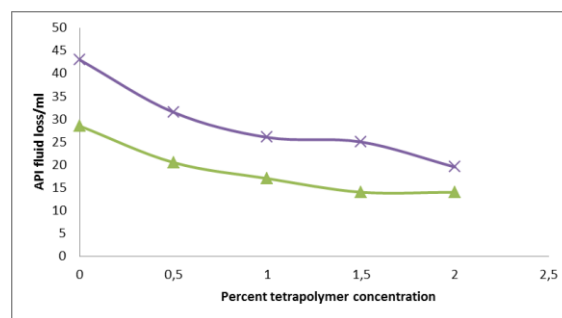


Fig. 3 Effect of TPM4 concentration on filtration loss of drilling mud

Comparatively, TPM4 exhibited superior fluid loss control with values ranging between $19.5\text{--}31.5\text{ cm}^3/30\text{ mins}$ compared to the blank with $43\text{ cm}^3/30\text{ mins}$ fluid loss after heat treatment. The tetrapolymer is a polyelectrolyte with anionic sulphonate ($-\text{SO}_3^-$) charges in the aqueous mud. Its efficacy in rheology modification is attributable to the electrical repulsion between polymer molecular chains due to the anionic charges, leading to molecular chain stretching. Additionally, the ionic interactions of the polyelectrolyte chains with the clay particles resulted in a large hydrodynamic volume with consequent enhancement of mud rheologies. The filtration reduction of the mud was attributed to the adsorption of the tetrapolymer molecules on clay edges, surfaces and subsequent interactions with the clay particles. The fluid loss reduction influence of the tetrapolymer suggests that excessive drag, high-pressure surges, differential-pressure sticking, reduction in production-zone permeability and increases in shale sloughing often associated with high filtration loss during wellbore would be minimized if the tetrapolymer is incorporated to a water-based mud.

3.3.2 Thermal stability of tetrapolymer incorporated mud (TPIM)

The tetrapolymer (TPM4) showed relative thermal stability through significant enhancement of rheological properties and fluid loss control of water-based drilling mud elevated temperatures, as displayed in Table 2 and figures 4 &5. It retained the apparent viscosity of the mud with a slight increase in plastic viscosity up to 150°C. The tetrapolymer incorporated mud (TPIM) yield point, however, reduced from 30 to 16.0 lb/100ft² while the blank completely lost its yielding point after heat treatment at 120°C. The filtration loss of TPIM increased gradually from 21.5 cm³/30min to 28.0cm³/30min respectively compared to excessive fluid loss of 107cm³/30min experienced by the blank after hot-rolled aging at 120°C. Hence, the tetrapolymer demonstrated relative effectiveness as a drilling mud additive for viscosity enhancement and fluid loss reduction at elevated temperatures. Structurally, the inclusion of the large side group AMPS and the rigid lactam group of vinyl pyrrolidone functionally protect and limit the equilibrium degree of hydro-lysis of the acrylamide within the TPM4 molecular structure and improve both thermal and hydrolytic resistance.

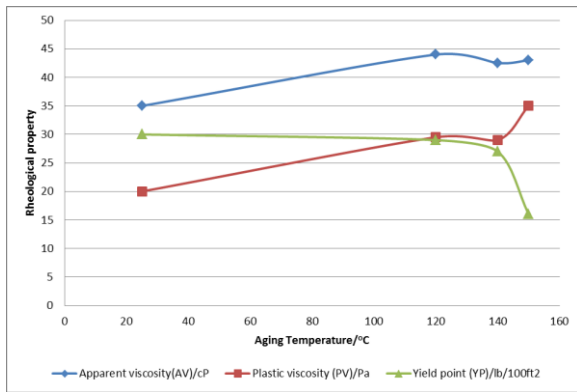


Figure 4 Effect of aging temperature on rheological properties of drilling mud

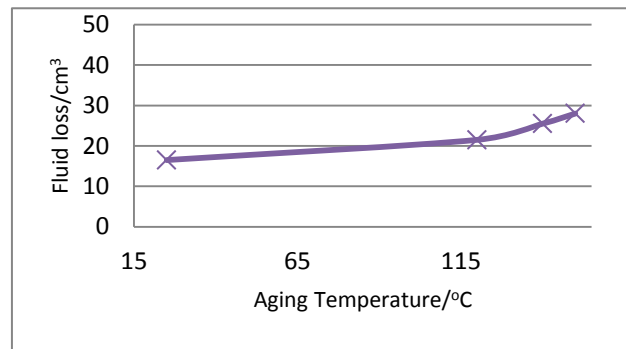


Figure 5 Effect of aging temperature on fluid loss of drilling mud

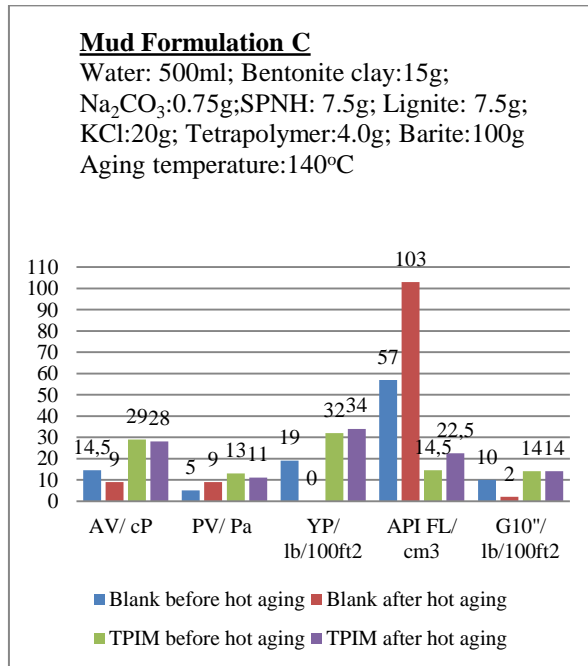


Figure 6 Effect of tetrapolymer additive on rheological and filtration loss properties of salt contaminated drilling mud

3.3.3 Effect of salinity and elevated temperature on the performance of tetrapolymer

Formulation mud C contained 4% KCl, including the other ingredients as listed on figure 6. The aim of this test was to examine the effectiveness of the TPM4 in salt contaminated environment at an elevated temperature. As shown in figure 6, the incorporation of TPM4 in the mud doubled its viscosity and effectively retained the mud viscosity before and after heat treatment at 140°C compared to the blank which lost almost 38% viscosity under similar conditions. Plastic viscosity and yield point of the TPIM were also apparently retained under the same conditions while the blank completely lost its yield point. The unaged TPIM exhibited about four-fold filtration loss control (14.5cm³/30min) compared to the blank (57.0 cm³/30min) while hot-aged TPIM retained nearly four-and-half-fold fluid loss control (22.5 cm³/30min) compared to the hot-aged blank (103cm³/30min). Again while the blank gel strength reduced by a factor of 5, the TPIM retained its gel strength of 14.0 lb/100ft² (figure 6) after hot aging. The result, exhibited conspicuous thermal resistance and salt tolerance of tetrapolymer in the salt contaminated muds, compared to the blank mud, which suffered severe loss of fluid retention capacity and experienced flocculation of the bentonite clay particles because of electrolytic interaction.

4. Conclusion

Water soluble tetrapolymer (Acrylamide-sodium salt of 2-acrylamido-2-methylpropanesulfonic acid-N-Vinyl pyrrolidone -N-Butyl propenoate) were successfully synthesized by free radical polymerization with high yields at optimum conditions. The tetrapolymer could best be synthesized using monomer mole ratios of AM/AMPS/NVP/BP of 42:45:7:6, respectively at total monomer concentration of 22.17wt/v% and initiator dose of 0.4wt% at temperature of 40°C, reaction time of 3.5 hours and initial reactants system pH of 7.5.

The tetrapolymer effected about four-fold filtration loss control in 4% KCl bentonite-based mud compared to the blank at 140°C. It exhibited good viscosification of the mud and favourably retained the viscosity of the mud up to 150°C

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Abbreviations and Formulae

AMPS	2-Acrylamido-2-methylpropane sulfonic acid	PV	plastic viscosity, Pa
BP	N-butyl propenoate	YP	yield point, lb/100ft ²
AM	Acrylamide	G _{10"}	gel strength at 10sec, lb/100ft ²
VP	N-vinyl pyrrolidone	G _{10'}	gel strength at 10min, lb/100ft ²
TPIM	tetrapolymer incorporated mud	API FL	API filtrate loss, cm ³ /30min
TPM4	tetrapolymer	API	American Petroleum Institute
SPNH	sulfomethyl humate and phenolic resin	AV	1/2Φ ₆₀₀
Φ ₆₀₀	Dial reading at 600rpm	PV	Φ ₆₀₀ - Φ ₃₀₀
Φ ₃₀₀	Dial reading at 300rpm	YP	Φ ₃₀₀ -PV
Φ ₃	Maximum dial reading at 3rpm	G ₁₀	Φ ₃
AV	apparent viscosity, cP	dL/g	decilitre per gramme

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