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Interpretation of Nonmonotonic Rheokinetic Dependences of Fluidity Change

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Abstract

The results of rheokinetic measurements of changes in the fluidity of gel-forming compositions of various natures obtained by the methods of rotational and selection viscometry are presented. A technique for processing measurement results obtained by means of vibrational viscometry in measuring vessels of different sizes has been developed. Two directions of the interpretation of nonmonotonic rheokinetic dependences are considered.

Keywords: solid body, vibrational viscometry, rotational viscometry, rheokinetics, gelation point, gelling composition

INTRODUCTION

The concept of sustainable development implies efficient and rational use of natural resources. Under the conditions of steady increase in the fraction of hard-to-recover resources in the total balance of produced hydrocarbon feedstock, the urgent works are those dealing with the scientific foundations of production efficiency, in particular physicochemical methods of oil recovery enhancement, based on the application of specially developed compositions with the necessary rheological and colloid chemical properties. Gel-forming compositions that are used for redistribution of filtration fluxes are low-viscous Newton liquids under the surface conditions and lose their fluidity when pumped into a reservoir [1–5].

As a rule, the transformation of a liquid into a non-flowing solid body is traced by means of rheological measurements [6, 7]. Thus obtained rheokinetic dependence often exhibit complicated behaviour, which hinders the interpretation of the results of studies.

The extreme viscosity dependence recorded after the addition of a linking agent to polymer solutions may be explained by the competitive processes of compression and cluster growth [8, 9]. The first insignificant change in flowability is determined by cross-linking separate macromolecules, which leads to the formation of primary aggregates, with a small increase in viscosity. The clusters grow independently of each other for some time, which is similar to an increase in the volume concentration of solution in terms of rheological consequences. A parallel process of intracluster cross-linking causes their contraction, a decrease in volume concentration and the corresponding decrease in viscosity. Finally, the links formed between then cause the formation of a large percolation cluster – a gel.

The formation of colloid gels of non-polymeric nature also leads to non-monotonic rheokinetic dependence [10].

The work aimed to propose and substantiate the versions to interpret nonmonotonic fragments of the rheokinetic dependence recorded

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while the flowability of gel-forming compositions is changing.

EXPERIMENTAL

The objects of investigation were gel-forming compositions based on the system aluminium salt – carbamide – hexamethylenetetramine (GALKA) with different carbamide contents (30, 15, 7.5, 3.75 and 1.87 wt. %), aqua-aurate-30 (7.3–9.0 wt. %) and hexamethylenetetramine (9–12 wt. %). The compositions were prepared using distilled water, carbamide (GOST 2081-2010), hexamethylenetetramine (TU 6-09-09-353-74), aqua-aurate-30.

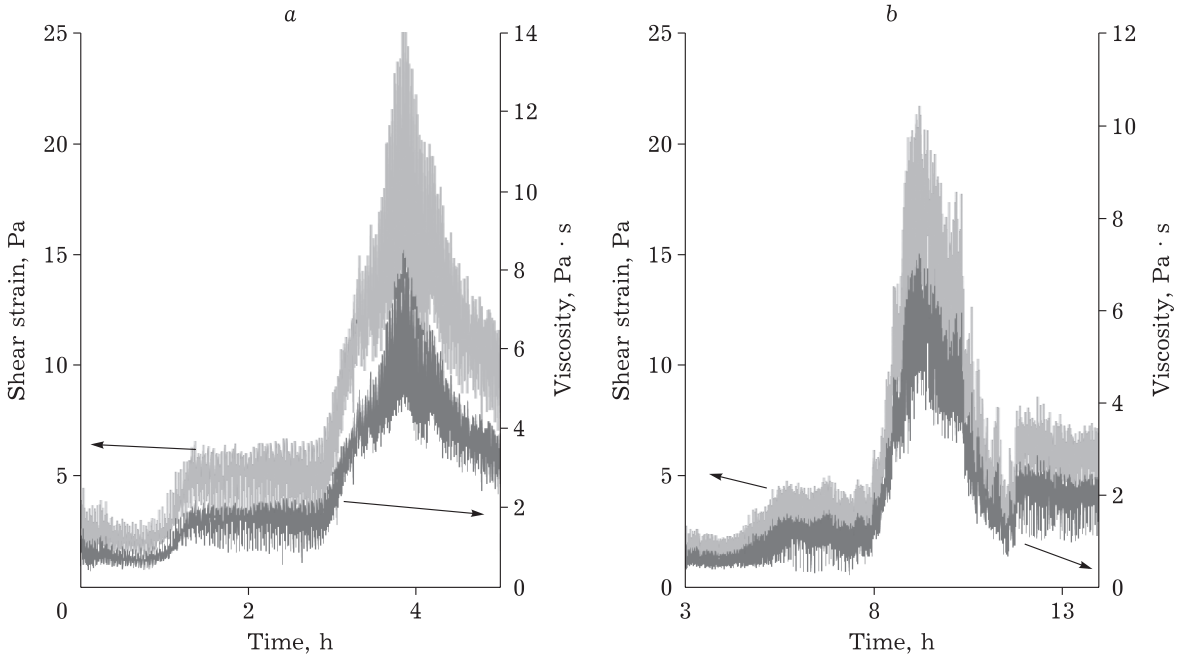

Fig. 1. Kinetics of gelation at 90 °C (rotational viscometry) for carbamide concentrations 30 (*a*) and 7.5 wt. % (*b*).

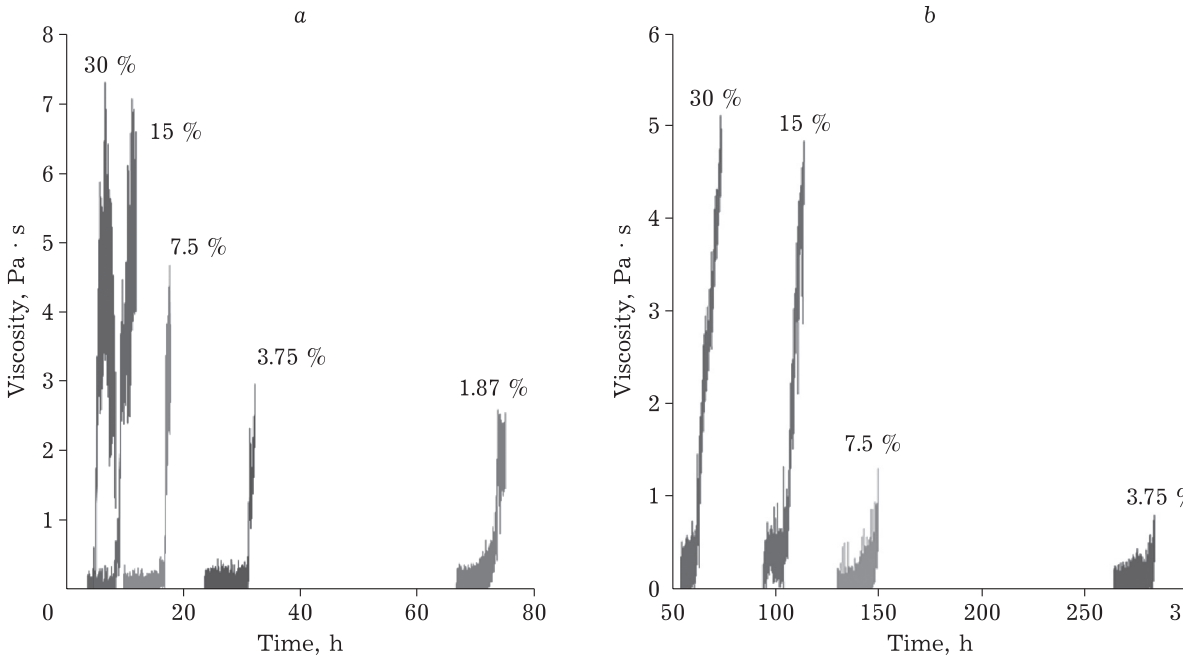

Fig. 2. Gelation kinetics for different initial concentrations of carbamide (rotational viscometry): thermostating at 80 (*a*) and 60 °C (*b*).

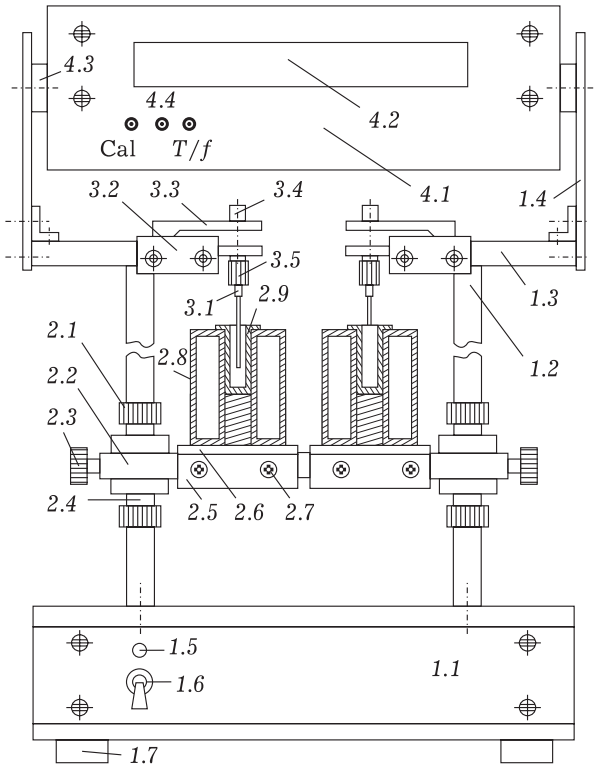

Fig. 3. Scheme of a two-probe version of vibrational viscometer Reokinetika: *1.1* – base of the stand rod; *1.2* – guide bars of the installation; *1.3* – immobile stand of the sensor; *1.4* – vertical plate; *1.5* – power supply indicator; *1.6* – power switch; *1.7* – base foots; *2.1* – fixing nut; *2.2* – mobile stand; *2.3* – fixing screw; *2.4* – sliding ram; *2.5* – basement of cell unit; *2.6* – basement of cell unit; *2.7* – screw; *2.8* – jacket-type thermostat; *2.9* – measuring vessel; *3.1* – probe of viscometer; *3.2* – case of vibrational sensor; *3.3* – vibrating tuning fork; *3.4* – counter-weight of probe; *3.5* – collet to fix the probe; *4.1* – face panel of thee control unit; *4.2* – display; *4.3* – muft; *4.4* – buttons of installation tuning for display image: Cal – calibration, *T/f* – switching period/frequency of vibrations.

The methods of investigation were rotational viscometry (rheometer Haake Viscotester iQ (Thermo Electron, Germany), measuring system of coaxial cylinders CC25 DIN/Ti) and vibrational viscometry (viscometer Reokinetika designed and developed at the IPC SB RAS, vibration frequency 400 Hz, a proofmass 2 mm in diameter, measuring cells 10, 12 and 15 mm in diameter). The results of measurements were rheokinetic dependence of shear stress, the viscosity of mechanical resistance on time. The value of mechanical resistance (Z) determined by vibrational viscometry, equal to the ratio of the force exerted on the proofmass to the velocity of its motion, is proportional to the outgoing signal of the vibrational viscometry sensor (U, mV) and a square root of the product of sample viscosity on its density. During measurements, reference and relative Z values are employed.

RESULTS AND DISCUSSION

The plots obtained with the help of Haake rheometers with the measuring cylinder rotating at a constant shear rate of 3 s^{-1} are shown in Fig. 1 and 2. The current shear strain and the corresponding viscosity in the solutions of the inorganic gel-forming system aluminium salt – carbamide – hexamethylenetetramine were recorded at 90, 80 and 60 °C [10].

Gel formation is accompanied by a sharp increase in mechanical resistance of the medium. The extreme fragments of the rheokinetic dependence recorded with the rotational rheometer are not connected directly with the viscosity value (formally, the disappearance of flowability corresponds to its infinitely high value) and may point to: 1) destruction of gel structure; 2) disturbance of the flow continuity in the inter-cylinder space; 3) slipping of the controlled object with respect to the solid moving wall.

On the other hand, plot fragments under consideration may depict real changes that occur in the object under control (the first version of interpretation), for example, similar to the above-considered competing processes of compression and cluster growth. In this case, additional information on the rheological behaviour of the object under investigation is necessary.

Tests were conducted out at different shear rates. Prior to gel formation, the indicated compositions demonstrated the properties of classical Newton liquids. After the process, they turned into viscoplastic objects. The spatial structure formed in them turned out to be able to sustain the increasing shear strain up to the critical value. After that, the gel was destroyed. This confirms the consumption concerning a connection of the plot fragments under consideration with the degradation of objects under control.

Measurements with the help of vibrational viscometry also give ambiguous results. The same solutions were placed in an air thermostat at 90 °C in tightly closed steel cells. After the prescribed time interval, the cells were sequentially put out and cooled to room temperature. The proofmass of the Reokinetika viscometer [11] was put into them, and measurements were carried out. The version of the Reokinetika viscometer equipped with two identical probes and measure-

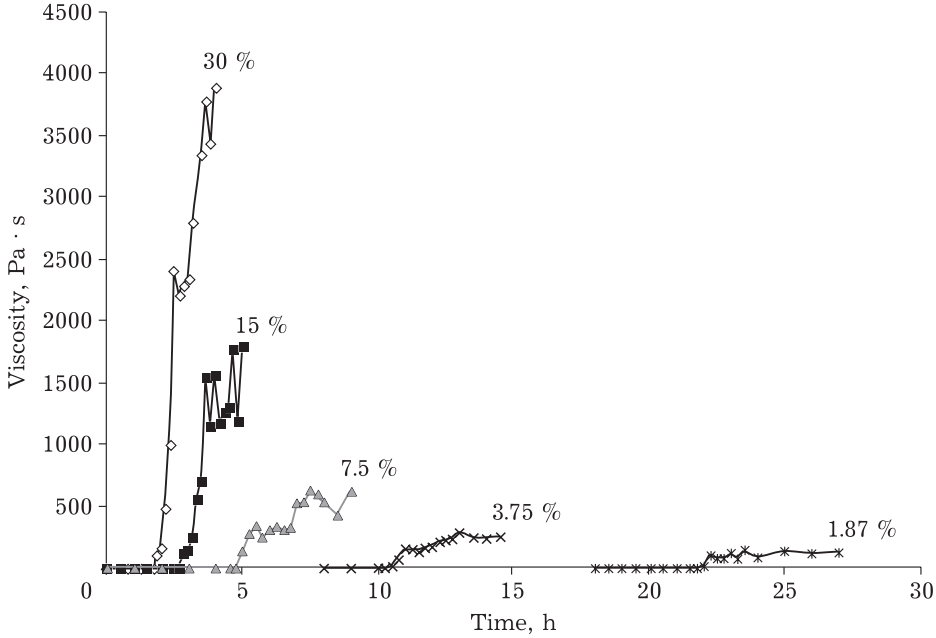

Fig. 4. Gelation kinetics for different carbamide concentrations (vibrational viscometry). Thermostating at 90 °C.

ment cells of different diameters is shown schematically in Fig. 3. Measurement results are shown in Fig. 4. The termination of gel formation is accompanied by a substantial increase in viscosity and the extreme fragments of recorded plots. A typical dependence of relative mechanical resistance Z on time is shown in Fig. 5 [12]. Three characteristic regions may be distinguished in this dependence: *1* – almost horizontal region corresponds to low-viscous solution; *2* – monotonic increase in mechanical resistance (viscosity) corresponds to process onset; *3* – a quasi-periodic fragment.

Vibrational measurements are carried out in a vessel of finite size, so experimentally observed maximal may be due to interference [13] of acoustic waves emitted by the sensor and reflected from the walls. In this case, the first version of the interpretation would be inadequate.

So, different physical reasons may have the same effect on rheokinetic dependences. Additional information on the object under study is also necessary in this case.

Information of this kind may be collected by performing parallel measurements in a vessel of another size. If the rheokinetic dependence obtained under different conditions are similar, the interpretation according to the first version is correct. If the dependences do not coincide, it is more reasonable to interpret them according to the second version considered below.

It was demonstrated in [12, 13] that rheokinetic dependence obtained for identical samples in vessels of different diameters diverge on the combined plot at the moment of gel formation, that is, when the sample loses its flowability. To simplify the situation, it is proposed to replace experimental nonmonotonic curves by the corresponding lines of the trend and by enveloping curves (the second version of interpretation).

The operations that can be made on the basis of the obtained data arrays include:

– calculated levelling of the sensitivity of parallel measurements;

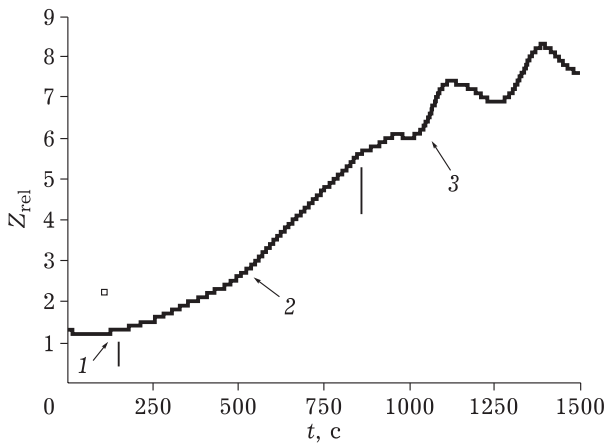

Fig. 5. Typical dependence of relative mechanical resistance (Z_{rel}) on time (t): *1* – almost horizontal region; *2* – monotonic increase in Z_{rel} (viscosity); *3* – quasi-periodic fragment.

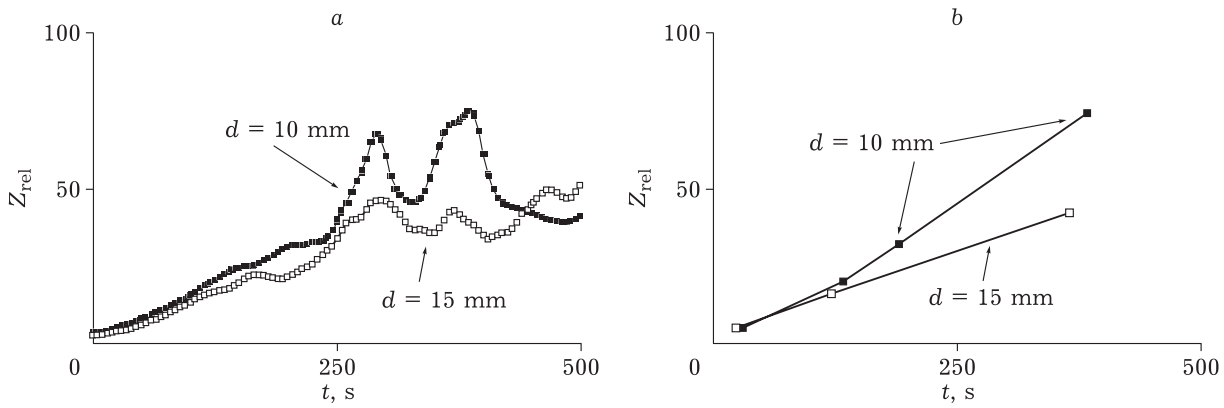

Fig. 6. Dependences of mechanical resistance (Z_{rel}) on time (t) for binary gel-forming composition GALKA, recorded at 20 °C (*a*), and their enveloping curves (*b*). d – diameter of measuring cell, mm.

– plotting the corresponding graphs;
– envelope plotting;
– their approximation;
– plotting of approximating graphs;
– plot alignment and visualization of the adjustment layer.

In the adjustment layer, the gel formation point is in the selected region.

The specific procedure for the treatment of experimental data with the help of Origin software is described step by step in [14].

The dependences of mechanical resistance Z on time for the binary composition GALKA (*a*), recorded at 20 °C, and their envelopes (*b*) are presented in Fig. 6. With an increase in wave course (experimentally this means an increase in cell diameter from 10 to 15 mm), the positions of maxima on the obtained curves shift to longer time (for the binary composition under consideration – to structure hardening). Thus, it may be concluded that the recorded polyextremal fragments are of interference nature, and enveloping curves diverge at the point of gel formation.

CONCLUSION

Thus, the rheokinetic dependence exhibits ambiguous behaviour in the region of flowability loss by the sample. Additional information is necessary for their adequate interpretation, which may be achieved by relying on vibrational viscometry through experiments involving measuring vessels of different sizes. A procedure has been proposed for the treatment of measurement results, and two versions of interpretation of the dependence recorded under the conditions of flowability loss: the first one suggests that the extreme fragments of plots depict real changes in the sample; the second one implies that experimentally observed maxima are not connected with the real properties of the sample but are due to interference.

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