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Amangeldi A. Meldeshov[1], Aigul A. Abisheva[2], Baurzhan B. Kurmashev[3], Sholpan K. Kurmanova[4]

[1,2,3,4]Kazakh Academy of Transport and Communications named after M.Tynyshpayev, Almaty, Republic of Kazakhstan

MOLECULAR-KINETIC CHARACTERISTICS OF HIGH-VISCOSITY OIL FLOW THROUGH PIPELINES

Abstract. *Attempt of interpretation of high-viscous block, which is formed into the pipelines when surrounding temperature lowered, by the main equations of statistic theory of colloid-chemical balance.*

Keywords: *oil, viscosity, fluidity, pipelines.*

Introduction. While transportation of the highly paraffinic crude oil through the pipeline especially in winter due to low temperature of environment a side problem connected with formation of so called «paraffin plug» occurs and the pipeline rate of flow sharply reduces. At present this problem is mainly resolved by the way of construction of facilities heating the oil in certain intervals what is connected with additional costs. From the other side there are some cases when the temperature of highly paraffinic oil solidification can be considerably reduced by the way of implementation of surfactants of various concentrations depending on the type of oil and surfactants. Based on this we can assume that molecules of such kind of substances are adsorbed on the surface of colloid particles of oil and increase their aggregative stability and as a result prevent the formation of «paraffin plug».

Background. Course for successful resolution of this problem from the theoretical point of view first of all the problem of interpretation of viscosity nature μ should be solved which is included into the equation of Hagen-Poiseuille,

$$Q = \frac{\pi R^4 \Delta P}{8\,\mu l} \qquad (1)$$

which in due time had been created on the basis of experimental data analysis. Here Q is fluidity, ΔP – differential pressure, R and l are the radius and length of the pipe. It is known that first attempt to interpret the nature of μ for colloid-disperse system had been made by Einstein [1]. He developed the formula for the case when the suspension consists of solids which in suspension state are viscous fluid:

$$\mu = \mu_0\,(1 + 2.5\varphi) \qquad (2)$$

where μ is viscosity of the solution, μ_0 is the viscosity of pure solvent, $\varphi = \frac{Nv}{V}$, where N is the quantity of the particles in total volume, *v*- volume of one particle, V – total volume of the solution. But it is easy to notice that Einstein's formula includes N parameter which is somehow connected with the value of particles concentration, but there are no parameters with the help of which it would be possible to define the

value of temperature and nature of colloid particles. It comes out that on the basis of this proportion it is impossible to understand why heating of oil, i.e. increase of its temperature, results in decrease of the viscosity of the oil and therefore increase of its fluidity. It is also impossible to understand why the concentration and nature of surfactants which should be used depend on the concentration and nature of the oil itself. Please note, that these drawbacks also could not be eliminated by the authors of works [2-4] in which the following equations had been developed as the generalization of the equation (2):

$$\mu = \mu_0 \ (1 + 2.5\varphi + b \ \varphi^2) \tag{3}$$

$$\mu = \mu_0 \ (1 + \varphi \ \frac{1.15f}{\pi ln2f}) \tag{4}$$

$$\mu = \mu_0 \ (1 + 2.5\varphi + \frac{f2}{16}\varphi) \tag{5}$$

The equation #3 had been developed in order to take into account the role of high concentration, as for the equation #4, it takes into account the role of ellipsoidal shape of the particles, where f is the ratio of ellipsoid axes and derivation of the formula #5 shows the role of Brownian movement of the particles.

Of course, such position of the question results in the problem of interpretation of the nature of viscosity μ in such a way that it can make it possible to disclose the nature of its temperature dependence and also the reason of why there is a necessity to use the so called notion of structural viscosity in highly-concentrated solutions. In order to solve this problem let's assume that the higher solution viscosity μ the higher the concentration of the colloid particles C_m. There is a ground to believe that solution viscosity can be strongly affected by the nature of colloid particles also, for example, the character of their collision. In cases when collision character of colloid particles is not elastic one, in order to make up the equations of colloid-chemical balance we can use the method of calculation which is mentioned earlier in the work [5]. According to main idea of this method by taking for basis the following symbolical equations:

$$C_M + C_M \leftrightarrow C_{MM} \tag{6}$$

$$C_M + C_{MM} \leftrightarrow C_{MMM} \tag{7}$$

$$C_M + C_{MMM} \leftrightarrow C_{MMMM} \tag{8}$$

$$C_{MM} + C_{MM} \leftrightarrow C_{MMMM} \tag{9}$$

$$\cdots\cdots\cdots\cdots$$

$$C_M + C_{MMMM\ldots} \leftrightarrow C_{MMMM\ldots M} \tag{10}$$

We have the possibility to develop the following balance equation:

$$K_{MM} = \frac{Cmm}{CmCm} \tag{11}$$

$$K_{MMM} = \frac{Cmmm}{CmCmm} \tag{12}$$

$$K_{MMMM} = \frac{Cmmmm}{CmCmmm} \tag{13}$$

$$K_{MMMM} = \frac{Cmmmm}{CmmCmm} \tag{14}$$

$$K_{MMMM\ldots M} = \frac{Cmmmm\ldots m}{CmCmmmm\ldots} \tag{15}$$

here, C_{MM}, C_{MMM}, $C_{MM\ MM}$,… $C_{MM\ MM\ldots M}$ mean the concentration of bimicellar, trimicellar, quatromicellar and polymicellar complex and K_{MM}, K_{MMM}, $K_{MMMM,}$ …$K_{MMMM\ldots M}$ are the constants of the balance of the correlation which can result in formation of such complexes. In order to use these equations of balance while solving of particular problems first of all the nature of these constants of balance should be defined. For solving this part of problem we take for basis the equations of type (11)-(15) and the equation of Langmuir adsorption isotherm as per the conclusions of the work [6]

$$C^0{}_A = \frac{C^0 bCA}{1+bCA} \tag{16}$$

And we can see a complete analogy. From the other side it is widely known the fact that within the limits of capabilities of molecular-kinetic theory the nature of adsorption coefficient b is interpreted [7] as the figure proportional to the adsorption heat,

$$b = exp\,\frac{\lambda}{RT} \tag{17}$$

here λ is the adsorption heat. As a result similarly we have the possibility to interpret the nature of the equations (11)-(15) and whereas we have:

$$C_{MM} = \exp^{\frac{\lambda_{MM}}{RT}} C_M C_M \tag{18}$$

$$C_{MMM} = \exp^{\frac{\lambda_{MMM}}{RT}} C_M C_{MM} \tag{19}$$

$$C_{MMMM} = \exp^{\frac{\lambda_{MMMM}}{RT}} C_M C_{MMM} \tag{20}$$

$$C_{MMMM} = \exp^{\frac{\lambda_{MMMM}}{RT}} C_{MM} C_{MM} \tag{21}$$

………………………………..

$$C_{MMMM\ldots M} = \exp^{\frac{\lambda_{MMMM\ldots M}}{RT}} C_M C_{MMMM\ldots} \tag{22}$$

Where $\lambda_{MM,}$, λ_{MMM}, $\lambda_{MMMM,\ \ldots,}$ $\lambda_{MMMM\ldots M}$ mean the energy of intermicellar interaction for various types of complexes.
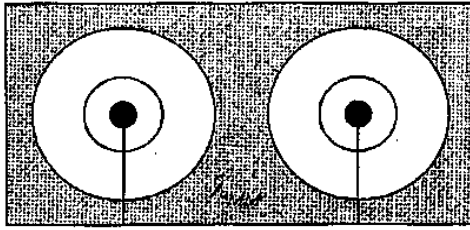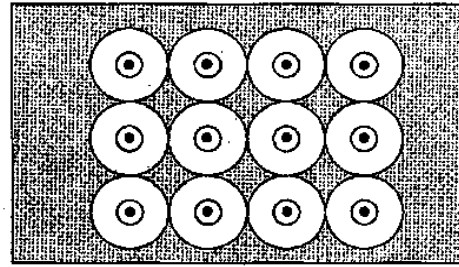
Fig. 1

Fig. 2

There is a ground to assume that in such systems the higher viscosity of the solution μ the higher the concentration of such complexes. Therefore we possess the possibility to interpret the nature of viscosity μ on the base of the following equation:

$$\mu_{MM} = \exp^{\frac{\lambda_{MM}}{RT}} C_M C_M \tag{23}$$

$$\mu_{MMM} = \exp^{\frac{\lambda_{MMM}}{RT}} C_M C_{MM} \tag{24}$$

$$\mu_{MMMM} = \exp^{\frac{\lambda_{MMMM}}{RT}} C_M C_{MMM} \tag{25}$$

$$\mu_{MMMM} = \exp^{\frac{\lambda_{MMMM...M}}{RT}} C_M C_{MMMM...} \tag{26}$$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

$$\mu_{MMMM...M} = \exp^{\frac{\lambda_{MMMM...M}}{RT}} C_M C_{MMMM......} \tag{27}$$

As we can see according to the equation (23) the viscosity of highly diluted solution depends on concentration of colloid particles C_M, on energy of interaction of two colliding colloid particles λ_{MM} (figure 1) and also it depends on the temperature T. Due to the reason that in this case the quantity of such bimicellar complexes will not be so much it can be assumed that the solution as a whole will stay low-viscous and the formation of these complexes as a whole does not affect their changes. But the situation sharply changes in that case when it concerns the highly-concentrated solution described in equation (27). In this case due to the affect of the energy of interaction of polymicellar complex $\mu_{MMMM...M}$ there is a possibility of formation of three-dimensional structure formation similar to two-dimensional model which is seen in the figure 2. In case of high temperature due to chaotic movement of colloid particles such system can still stay enough fluid but in case of fall of temperature due to occurrence of the moment when the influence of $\lambda_{MM...M}$ can be more considerable than the influence of RT it can result in hardening of the system as a whole.

As it was already mentioned when adding some types of surfactants the structural viscosity even of the highly paraffinic oil will reduce to such extent that the oil could stay fluid even if the surrounding temperature is quite low. That is why it is required to generalize the equation (27) exactly for this case. By generalization

of equation (27) assuming that the molecules of surfactants on the surface of colloid particles form monomolecular layer the following equation comes out:

$$\mu = \exp^{\frac{\lambda_{MMMM\dots M}}{RT}} C_M C_{MMMM\dots} \exp\frac{\lambda A}{RT} \dots \exp\frac{\lambda A}{RT} C_{A\dots} C_A C^0 \dots C^0 \qquad (28)$$

where C_A and C^0 mean the concentration of the surfactants molecules and active centers on the surface unit and λ_A means the adsorption energy of surfactants molecules. Please note that analysis of this equation provides us the possibility to realize that as a result of introduction of surfactants into the system the structural viscosity of the solution reduces in that case if the energy of $\lambda_{MM\dots M}$ reduce as a result of adsorption of molecules of surfactants on the surface of the colloid particles of oil. In case if as a result of adsorption of surfactants molecules $\lambda_{MM\dots M}$, the energy of intermicellar connection is increasing then it can lead to the increase the strength of plug, i.e. increase of structural viscosity.

Conclusion

Therefore on the basis of the equations (23)-(27) it is better to describe the experimental data than on the basis of equations (2)-(5), because the derivation of these equations besides the concentration of colloid particles of oil and surfactants take into account the energy of intermicellar interactions and the adsorption energy of molecules of surfactants to the surface of colloid particles. More or less correctly it is possible to take into account the roles of nature of colloid particles themselves and surfactants and also the role of temperature. Of course while description of experimental data these equations should be more specific, and in order to make it possible it is required to take into consideration the natures of colloid particles and used in this case additives.

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Мақалада тұтқырлығы жоғары мұнайдың аққыштығы жайлы есептеулер келтірілген.
Түйін сөздер: *мұнай, тұтқырлық, аққыштық, құбырлар.*

В статье рассматриваются расчетные данные по текучести высоковязкой нефти.
Ключевые слова: *нефть, вязкость, текучесть, трубопроводы.*