Entropy change at viscous flow of dispersive systems with a phase transition in their particles

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Based on the compensation effect, a method has been developed for the correct calculation of entropy changes at viscous flow of liquid dispersed systems using the Eyring equation. At temperature range of $313 \pm 10\,\mathrm{K}$ in dispersed systems with a liquid-like state of dispersed phase particles the presence of a specific phase transition is substantiated, at which changes in enthalpy and entropy undergo a jump in these systems.

Keywords: Eyring's equation, dispersed systems, phase transition.

There is no common view of the processes occurring within liquid dispersed systems (DSs) at viscous flow, not even in the case of DSs with solid dispersed phase particles [1]. Liquid DSs with a liquid-like state of particles, the size of which may be changed by temperature, shear strain, and phase transitions, are even less well understood. Oil dispersed systems (ODSs) with dispersed phase particles taking the form of nanoaggregates of asphaltene, resin, and paraffin molecules [2–8] are the examples of such systems. It has been demonstrated in [7,8] that liquid concentrated micellar dispersed systems (MDSs) with dispersed phase particles taking the form of micelles of surfactants and their aggregates are similar to ODSs in their viscous properties.

Let us examine which details of viscous flow of ODSs and MDSs may be revealed by the thermodynamic method of their study. This method relies on the Eyring equation for dynamic liquid viscosity $\mu = B \exp(\Delta G / RT)$, where ΔG is the Gibbs energy activation, R is the universal constant, B is the pre-exponential factor of the Eyring equation, and T is temperature. Since this equation is similar to Arrhenius and Frenkel equations $\mu = C \exp(E/RT)$, it is presumed in certain studies that energies $E = \Delta G$ of activation of viscous flow are determined based on the experimental dependences of $\ln \mu$ on $1/T$. However, the values of E for ODSs and MDSs determined this way typically increase with shear velocity due to the breakdown of their particles induced by shear strain. This does not agree with a reduction in their viscosity that is observed under these conditions [6–8]. This contradiction is resolved only if the influence of entropy on the DS viscosity is taken into account by introducing the following expression into the Eyring equation: $\Delta G = \Delta H - T\Delta S$, where ΔH and ΔS are the variations of enthalpy and entropy. Taking the logarithm of the Eyring equation, one then obtains

$$\ln \mu = \Delta H / RT - (\Delta S/R - \ln B) = \Delta H / RT - A. \quad (1)$$

It follows from (1) that, analyzing the experimental dependence of $\ln \mu$ on $1/T$, one finds the values of ΔH and A rather than of ΔG and B; ΔH is comparable to $E (\Delta G = \Delta H = E$ only at $\Delta S = 0)$, and the $\Delta S \neq 0$ values for ODSs and MDSs may be determined based on the value of A in (1):

$$A = \Delta S/R - \ln B. \quad (2)$$

The complexity of calculation of ΔS stems from the ambiguity of constant B in (2). The authors of [2,9,10] and a number of other studies determined the values of B using the Eyring relation

$$B = RT/(fV_M) = hN_a/V_M, \quad (3)$$

where $f \approx 6 \cdot 10^{12}\,\mathrm{Hz}$ is the frequency with which, according to the Eyring hypothesis, liquid molecules shift to new equilibrium positions; h is the Planck constant; N_a is the Avogadro number; and V_M is the molar liquid volume. However, it was demonstrated in [8], that the viscosity of ODSs and MDSs is governed by relaxation processes with their characteristic frequencies being 5–7 orders of magnitude lower than those assumed by Eyring. Therefore, one needs to find a way to calculate constant B in (1), (2) in order to correctly use the thermodynamic method for DS investigation.

In the present study, the method for independent determination of two terms in expression (2) for A is based on examining the DS viscosity as a function of two factors: temperature and shear velocity. This method consists in calculating a set of ΔH and A values for a given DS based on linear approximations of the dependences of $\ln \mu$ on $1/T$ for several shear velocities. The obtained set is then used to determine the $A(\Delta H)$ dependence graphically. The examination of a large number of ODSs and MDSs (several tens of samples) revealed that their $A(\Delta H)$ dependences are linear (see Fig. 1).
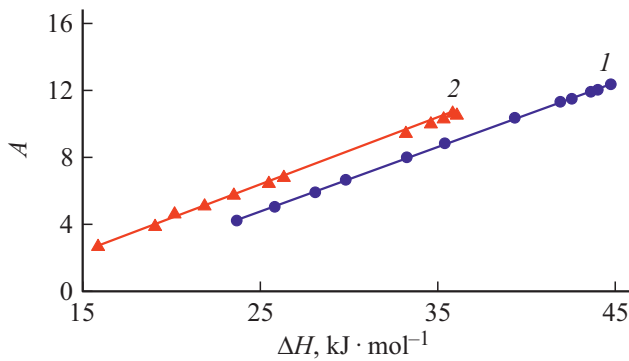
Figure 1. $A(\Delta H)$ dependences for MDS (98% neonol AF 9-12) (*1*) and ODS (from the West Salym oil field, Russia) (*2*) samples. The characteristics of these samples were detailed in [6].

Therefore, these dependences may be presented in the form of equations

$$A = \Delta S/R - \ln B = \beta \Delta H - A_o. \qquad (4)$$

Equating the constant and variable quantities in (4), we find that $\ln B = A_o$ and ΔS takes the form

$$\Delta S = \beta R \Delta H = R(A + A_o). \qquad (5)$$

Since β and ΔH assume positive values in the expression for $\Delta S = \beta R \Delta H$, the values of ΔS for the ODSs and MDSs studied here are strictly positive.

Taking (5) into account, one may present the Gibbs potential variation in the form

$$\Delta G = \Delta H - T\Delta S = \Delta H(1 - \beta RT) = \Delta H(1 - T/T^{**}), \qquad (6)$$

where $T^{**} = 1/\beta R$ is the temperature at which $\Delta G = 0$. Inserting (6) into (1), we come to the conclusion that the value of B is much higher than the values adopted in literature, since it is numerically equal to the DS viscosity at T^{**} rather than, as was assumed earlier, at $T \to \infty$.

According to Fig. 2, temperature T^{**} is equal to $T^* \sim 313\,\mathrm{K}$, which is the value corresponding to bends in the DS dependence of $\ln\mu$ on $1/T$ due to the jump-like variation of ΔH and ΔS. Similar bends in the dependences of $\ln\mu$ on $1/T$ were found in several other studies. It was assumed in [2–4] that they are induced in ODSs by a phase transition driven by the melting of paraffins contained in these ODSs. However, it was demonstrated in [5] that the phase transition corresponding to the melting of paraffins in ODSs induces bends in the dependences of $\ln\mu$ on $1/T$ at $T < 273\,\mathrm{K}$, while bends in the dependences of $\ln\mu$ on $1/T$ for ODSs and MDSs were observed in [6,7] at $T^* \sim 313 \pm 5\,\mathrm{K}$ regardless of the melting temperatures of their components (systems with $T^* \sim 313 \pm 10\,\mathrm{K}$ have been found by now).

The cause of this effect is found out by analyzing the equality of DS temperatures T^* and $T^{**} = 1/\beta R$ demonstrated in Fig. 2, which suggests that the range of

variation of these temperatures should be governed by the values of coefficient β in (4), (5). The results of calculations confirmed that the values of $\beta = (384 \pm 12) \cdot 10^{-6}\,\mathrm{mol/J}$ and the range of variation of $T^* = T^{**} = 313 \pm 10\,\mathrm{K}$ for the studied ODSs and MDSs agree well, thus effectively confirming the validity of relations (5), (6) for ΔS and ΔG determined in the present study.

The obtained data highlight the importance of compensation effect for the viscosity of ODSs and MDSs. The compensation effect is the only one that provides an explanation for the reduction in viscosity at higher shear velocities, which is typical of ODSs and MDSs in spite of the accompanying increase in the values of ΔH due to the breakdown of dispersed phase particles into smaller agglomerates [6–8]. It turned out that two thermodynamic functions (enthalpy and entropy) governing the viscosity of ODSs and MDSs are affected by shear strain in such a way that the effect of an ΔH increase on viscosity is offset by a proportional ΔS increase. This conclusion was drawn in [6–8] for ΔS values determined using formula (2) up to an undefined constant. Expression (5) for $\Delta S = \beta R \Delta H$ obtained in the present study allows one to establish that ΔH at $T = T^* = T^{**}$ is compensated fully by ΔS; i.e., $\Delta G = 0$. At $T > T^*$, the values of $\Delta G < 0$. In classical thermodynamics, this is indicative of a spontaneous DS transition to a more stable equilibrium state with smaller particles. Let us also take into account the fact that either first-order derivatives (first-order phase transitions) or second-order derivatives of the Gibbs potential (second-order phase transitions) undergo jumps in phase transitions at the macrolevel. Both derivatives of the Gibbs potential with respect to temperature undergo jumps at temperature T^* of the phase transition identified in the present study (external pressure $p \approx 10^5\,\mathrm{Pa} = \mathrm{const}$ in all experiments). The first-order derivative $(\partial G/\partial T)_p = -S$ jump is revealed by the ΔS jump at T^*, while the jump in ΔH, which induces the jump in heat capacity C_p, provides evidence of the
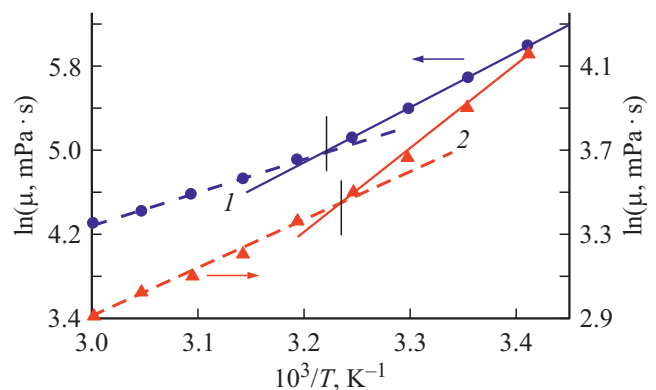

Figure 2. Typical temperature dependences of the viscosity of ODSs and MDSs obtained at a shear velocity of 6.6 (*1*) and 26.6 s^{-1} (*2*) for the samples from Fig. 1. *1* — MDS (98% neonol AF 9-12), *2* — ODS (oil from the West Salym oil field, Russia). Vertical lines denote temperatures $T^{**} = 1/\beta R$ for these samples.

second-order derivative jump:

$$(\partial^2 G/\partial T^2)_p = -(\partial S/\partial T)_p = -(\partial H/\partial T)_p/T = -C_p/T.$$

The ΔS and ΔH jumps (i.e., the presence of $\Delta(\Delta S)$ and $\Delta(\Delta H)$) at temperature T^* are evidenced by a change in the slopes of dependences of $\ln\mu$ on $1/T$ at $T < T^*$ and $T > T^*$ in Fig. 2.

The phase transition in ODSs and MDSs revealed by the bend in temperature dependences of their viscosity plotted in $\ln\mu$ and $1/T$ variables is then a new specific phase transition that has no counterpart at the macrolevel and corresponds to a jump-like change in ΔH and $\Delta S = \beta R\Delta H$. Its temperature T^* is defined by coefficient β in expressions (4) and (5) for the compensation effect. This phase transition in ODSs and MDSs should be identified by the bend in the dependence of $\ln\mu$ on $1/T$ only at shear stress $\tau < \tau^* \approx 10\,\text{Pa}$. These bends vanish at $\tau > \tau^*$, since strong shear strain has almost the same effect as heating to $T > T^*$ in terms of inducing the breakdown of labile dispersed phase particles in ODSs and MDSs [6,7].

Conflict of interest

The authors declare that they have no conflict of interest.

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