

Equilibrium Interpretation of the Liquid Viscosity and Its Use for the Partial Expression of the Temperature Dependence of Melts Viscosity on State Diagrams

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Abstract: In the framework of the cluster associate model developed earlier by the authors, viscosity and fluidity are considered as the chaos sensitive properties of a liquid inherent in it not only in motion but also at rest, since they are based on the equilibrium Boltzmann distribution. In this model, the key characteristics are the thermal barriers of chaotization at the melting and boiling points, thereby the behavior of the liquid is determined by the action of three energy classes of particles—crystal-mobile, liquid-mobile and vapor-mobile. When turning to the consideration of viscosity and fluidity from simple substances to complex inorganic and alloys, more in-depth justification of the chaotization barriers responsible for the formation of clusters from the number of crystal-mobile particles is required, as well as methods for adapting the cluster associate model to experimental data.

Key words: Boltzmann distribution, viscosity, equilibrium, partial contribution, fluidity, temperature, alloy, the state diagram.

1. Introduction

Using thermal barriers at the melting point, it is shown that it directly reflects the chaotic process, since it is equal to the kinetic energy reserve of chaotic (thermal) particles motions. Therefore, to determine the share of crystal-mobile particles responsible for the viscosity of the melt, the chaotic barrier RT_m should be used. Therefore, in order to analyze the role of crystal-mobile particles, it is necessary to use formula.

$$P_{crm} = 1 - \exp\left(-\frac{T_m}{T}\right)$$

On the basis of the distribution of clusters previously found by the authors in terms of the number of crystal-mobile particles included in them, it was shown that all non-single crystal-mobile particles are responsible for the viscosity, and for fluidity all single particles, including crystal-mobile, liquid-mobile and vapor-mobile. This ensures the

superiority of the share of single particles over the share of crystal-mobile particles arranged in non-single clusters at the melting point, and thereby the fluidity of the melt. Based on the share distribution of clusters in terms of the number of particles entering into them, the share of non-single clusters responsible for the viscosity of the melt is expressed as

$$P_{cl} = P_{crm}^2 = [1 - \exp(-T_m/T)]^2$$

Possibility of application the equilibrium viscosity model developed by the authors based on the concept of randomized particles for its calculation from partial contributions and phase diagrams depending on the composition and temperature of the melt is shown. A model of the viscosity of a liquid alloy is proposed, in which the thermal barrier of chaotization at crystallization points (RT_{cr}) is used for the first time as a variable, calculated from the melting point for pure components and the liquidus line for the alloy, and as a whole reflects the essence of the virtual cluster theory of liquid and the adequacy of the concept randomized particles.

The framework of the concept of randomized

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particles, viscosity and fluidity are for the first time considered as properties inherent in liquids not only in motion but also at rest, since they are determined by the equilibrium distribution of crystal-mobile, liquid-mobile and vapor-mobile particles, virtual by their nature of continuous chaotic motion and interconversion. Viscosity is due to the presence of non-single crystal-mobile particles, arranged in clusters, associates and aggregations, and fluidity—the existence of free single crystal-mobile, liquid-mobile and vapor-mobile particles [1, 2].

The equilibrium nature of viscosity and fluidity makes it possible to draw an analogy with liquid properties determined by thermodynamics, for example, equilibrium vapor pressure or density. This analogy is all the more relevant when considering the properties of liquid metal alloys in a similar way to the properties of solutions. And here the most suitable for use is the law of Raoult [3].

2. Methods

By analogy with Raoult's law for ideal solutions and melts, the partial contribution of the viscosity of some component *A* to the total viscosity of the liquid will be expressed through its molar fraction X_A as

$$\eta_A = X_A \dot{\eta}_A \quad (1)$$

where $\dot{\eta}_A$ —viscosity of a pure substance *A*.

The total viscosity of the ideal melt must be equal to the sum of the partial viscosities for all of its components. Thus, for a two-component alloy

$$\eta = \eta_A + \eta_B = X_A \dot{\eta}_A + X_B \dot{\eta}_B \quad (2)$$

The rectilinear character of the dependence of the viscosity of an ideal melt on the mole fraction of any of the components is provided for a two-component liquid, since

$$X_B = 1 - X_A \quad (3)$$

$$\begin{aligned} \eta = \eta_A + \eta_B &= X_A \dot{\eta}_A + (1 - X_A) \dot{\eta}_B = \\ &\dot{\eta}_B + (\dot{\eta}_A - \dot{\eta}_B) X_A \end{aligned} \quad (4)$$

and the values $\dot{\eta}_A$ and $\dot{\eta}_B$ for a given temperature are constant.

As in the case of deviations from Raoult's law, caused by the different interrelationships between

single-grade and different-grade molecules, deviations from the rectilinear dependence of viscosity (4) should be due to the same reasons. In the framework of the cluster associative theory of viscosity, it is determined by the share of non-single crystal-mobile particles. This share according to the probability of overcoming the melting barrier

$$P_{crm} = 1 - \exp\left(-\frac{\Delta H_m}{RT}\right) \quad (5)$$

or the chaotic barrier

$$P_{crm} = 1 - \exp\left(-\frac{RT_m}{RT}\right) = 1 - \exp\left(-\frac{T_m}{T}\right) \quad (6)$$

is higher than the heat or melting temperature of the pure substance. Therefore, for those close to these substances, maintaining the rectilinear nature of the relationship is more likely.

Since the direct comparison of the experimental and calculated data is not only due to the variations in the composition of the melt at a certain temperature but also the temperature dependences of the viscosity itself, it is necessary to give the calculated expression from them based on the cluster associate theory and understanding the viscosity as an equilibrium partial value.

For a two-component alloy such a dependence in the most general form, taking into account the mole fractions of the components *A* and *B*, is expressed as

$$\eta = X_A \dot{\eta}_{T,A} + X_B \dot{\eta}_{T,B} \quad (7)$$

where $\dot{\eta}_{T,A}$ and $\dot{\eta}_{T,B}$ —temperature dependences of the viscosity of components *A* and *B* in pure form.

Cluster associate models of these dependences will take the form

$$\dot{\eta}_{T,A} = \eta_{1A} (T_{1A}/T)^{a_{2A}(T_{2A}/T)^{b_A}} \quad (8)$$

$$\dot{\eta}_{T,B} = \eta_{1B} (T_{1B}/T)^{a_{2B}(T_{2B}/T)^{b_B}} \quad (9)$$

It should be noted that in all cases of analysis of temperature dependences from experimental data, a direct adaptation of these data to the cluster associate model of viscosity along the reference points from the experimental array for the alloy is required

$$\eta = \eta_{1al} (T_{1al}/T)^{a_{2al}(T_{2al}/T)^{b_{al}}} \quad (10)$$

With this dependence, one should also compare the partial (additive) type

$$\eta = \sum_{i=1}^n X_i \eta_{1i} (T_{1i}/T)^{a_{2i}(T_{2i}/T)^{b_i}} \quad (11)$$

to analyze the level of adequacy and nature of the alloy.

However, the linear additive partial represent of the viscosity is applicable only to ideal (perfect) solutions and for melts by an example for alloys with unrestricted mutual solubility is confirmed, which by phase diagrams of the first type is represented (Fig. 1) [4].

In the general case, for the state diagrams with eutectics and for the formation of chemical compounds, the liquidus line has a complex character, so that the fractional viscosity dependence cannot be expressed analytically expression in the framework of the modern cluster theory of the liquid structure, if one starts from the cluster structure only. This approach provides only a qualitative physical explanation for

the complex form of the viscosity curves. The possibility of an analytical expression for the dependence of viscosity on the share of variable components in accordance with the phase diagrams appears on the basis of the cluster associate theory within the framework of the concept chaotized particles, in which the share of crystal-mobile particles serves to form clusters and determines the viscosity of the liquid substance.

Before this concept, this question was considered in Refs. [5-10]. Thus, the authors of Refs. [9, 10] cite typical generalized phase diagrams of the state and viscosity with a variation in the composition of the two-component system and temperature (Fig. 2).

According to this figure, it is quite obvious that the forms of the viscosity curves repeat the form of the liquidus line, and as the melt temperature increases, the viscosity curves become smoother and more closely approximated. In Ref. [9], similar features of the viscosity curves for any melt temperature are explained

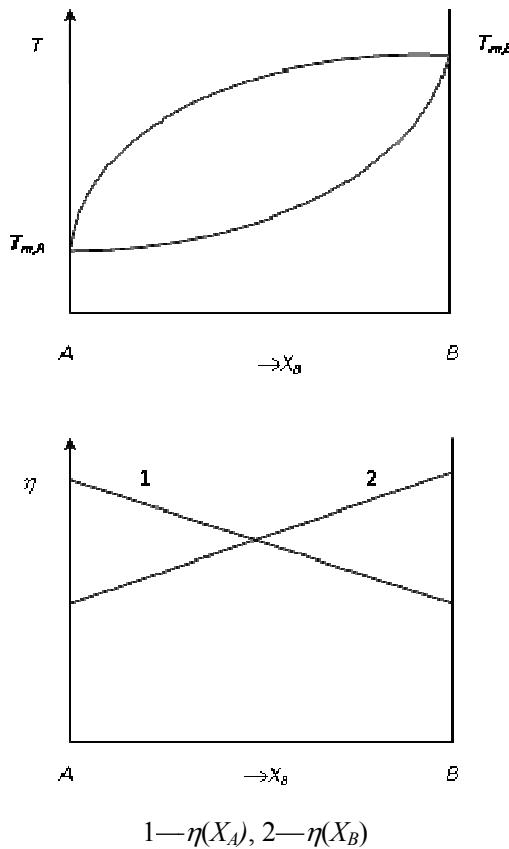


Fig. 1 Typical fusibility and viscosity diagrams for binary alloys with unrestricted solubility.

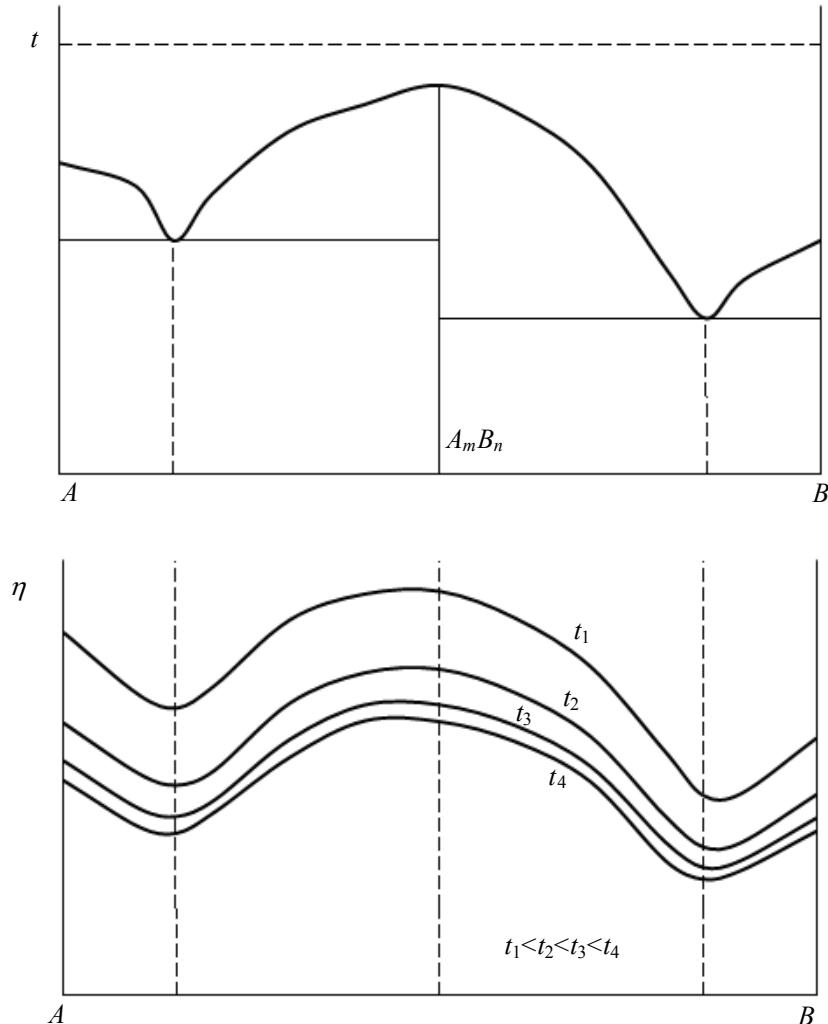


Fig. 2 Typical viscosity curves for a typical state diagram.

by the uneven overheating of the melt with different composition relative to the liquidus temperature. Where the superheating is more, there is less viscosity, and vice versa. With an increase in the melt temperature, the superheat value relative to the liquidus curve is leveled, and the viscosity curves are smoothed and brought together. In Ref. [10], as in Refs. [4-8], on the basis of the cluster theory of the structure of the liquid, the relationship between the specific and free volumes of various particles with the melt viscosity is analyzed: with an increase in these volumes, the mobility of the particles increases and the viscosity decreases.

In both approaches to the interpretation of the form

of the viscosity curves, formulas for calculating the viscosity from the state diagrams depending on the composition and temperature of the melt are not found. This possibility appears on the basis of the concept randomized particles within the framework of the cluster associate theory of viscosity.

According to this theory, the viscosity by the share of non-single crystal-mobile particles grouped into n -dimensional clusters is determined [1, 2], and this share is based on the equations for the fraction of crystal-mobile particles (6) and for the share of single particles

$$P_{fr} = 1 - P_{crm}^2 = 1 - [1 - \exp(-T_m/T)]^2 \quad (12)$$

as

$$P_{cl} = P_{crm}^2 = [1 - \exp(-T_m/T)]^2. \quad (13)$$

This fraction refers to pure substances. The melting temperature T_m characterizes the point of crystallization T_{cr} identically equal to it. For alloys, it refers to the liquidus temperature, which indicates the temperature of the beginning of crystallization, which corresponds to overcoming the thermal barrier of melt chaotization equal to RT_{cr} . Therefore, in a more general expression, the share of cluster particles will be expressed as

$$P_{cl} = P_{crm}^2 = \left[1 - \exp\left(-\frac{RT_{cr}}{RT}\right)\right]^2 = \\ [1 - \exp(T_{cr}/T)]^2 \quad (14)$$

According to this formula, not only the temperature, but also the crystallization point in the range of the alloy composition studied can vary. If the phase diagram of the alloy is known, the share of clusters at a given melt temperature can be determined graphically for each composition in terms of coordinates X_B-T_{cr} .

3. Results and Discussion

For this purpose, the schematic diagram of the state depicted in Fig. 2 was presented in more detail, correlating it with a certain temperature, which allowed to determine T_{cr} on the liquidus line with variation of composition with inclusion of melting temperatures of components A and B , eutectic points and compound A_mB_n . The same data are given in Fig. 3 in comparison with typical viscosity curves in Fig. 2 according to the data [9, 10].

The figure shows a qualitative correspondence between the forms of the viscosity dependences and the share of clusters at different temperatures for all the features of the phase diagram, as well as the increase in the smoothness and the convergence of the curves with increasing temperature. This indicates the validity of the use of the dependence (14) for the share of clusters with the purpose of transition to the natural expression of the viscosity distribution over the composition of the alloy.

In view of the uniformity of the curves for the share

of clusters and the liquidus line, the transition from one melt temperature to the other is accompanied by a change in P_{cl} , which can be taken into account by the ratio of the share of clusters corresponding to the specific composition of the alloy. Since on the state diagram the liquidus line starts with the melting point of substance A and ends with the melting point of substance B , it is possible to estimate the deviations from the viscosity of pure substances A and B in the direction of the alloys viscosity at any temperature from the ratio of the share of clusters with melting barriers RT_m and crystallization by the liquidus RT_{cr} . Such a proportionality of the viscosity and share content of clusters is confirmed by linear correlation of the experimental data η_T and P_{crm}^2 [1, 2]. Then, taking into account the partial contributions of substances A and B to the alloy viscosity, we obtain expression

$$\eta_T = X_A \dot{\eta}_{T,A} \frac{P_{cl,cr}}{P_{cl,m,A}} + X_B \dot{\eta}_{T,B} \frac{P_{cl,cr}}{P_{cl,m,B}} \quad (15)$$

where

$$P_{cl,cr} = \left[1 - \exp\left(-\frac{T_{cr}}{T}\right)\right]^2 \quad (16)$$

$$P_{cl,m,A} = \left[1 - \exp\left(-\frac{T_{m,A}}{T}\right)\right]^2 \quad (17)$$

$$P_{cl,m,B} = \left[1 - \exp\left(-\frac{T_{m,B}}{T}\right)\right]^2 \quad (18)$$

As usual for partial values, taking into account $X_A + X_B = 1$, one can express the dependence of the alloy viscosity on the share content of one component:

$$\eta_T = P_{cl,cr} \left[\frac{\dot{\eta}_{T,A}}{P_{cl,m,A}} + X_B \left(\frac{\dot{\eta}_{T,B}}{P_{cl,m,B}} - \frac{\dot{\eta}_{T,A}}{P_{cl,m,A}} \right) \right] \quad (19)$$

Thus, remaining in the subordination of the partial dependence (15), the viscosity of the alloy turns out to be a complicated semiempirical function of the alloy composition, and in this dependence the liquidus temperature acquires a decisive informative meaning, along with temperature dependences of the viscosity for pure components.

For a specific expression of the alloy viscosity, using the partial contribution formula, we take the state diagram in Fig. 3, and the temperature dependences

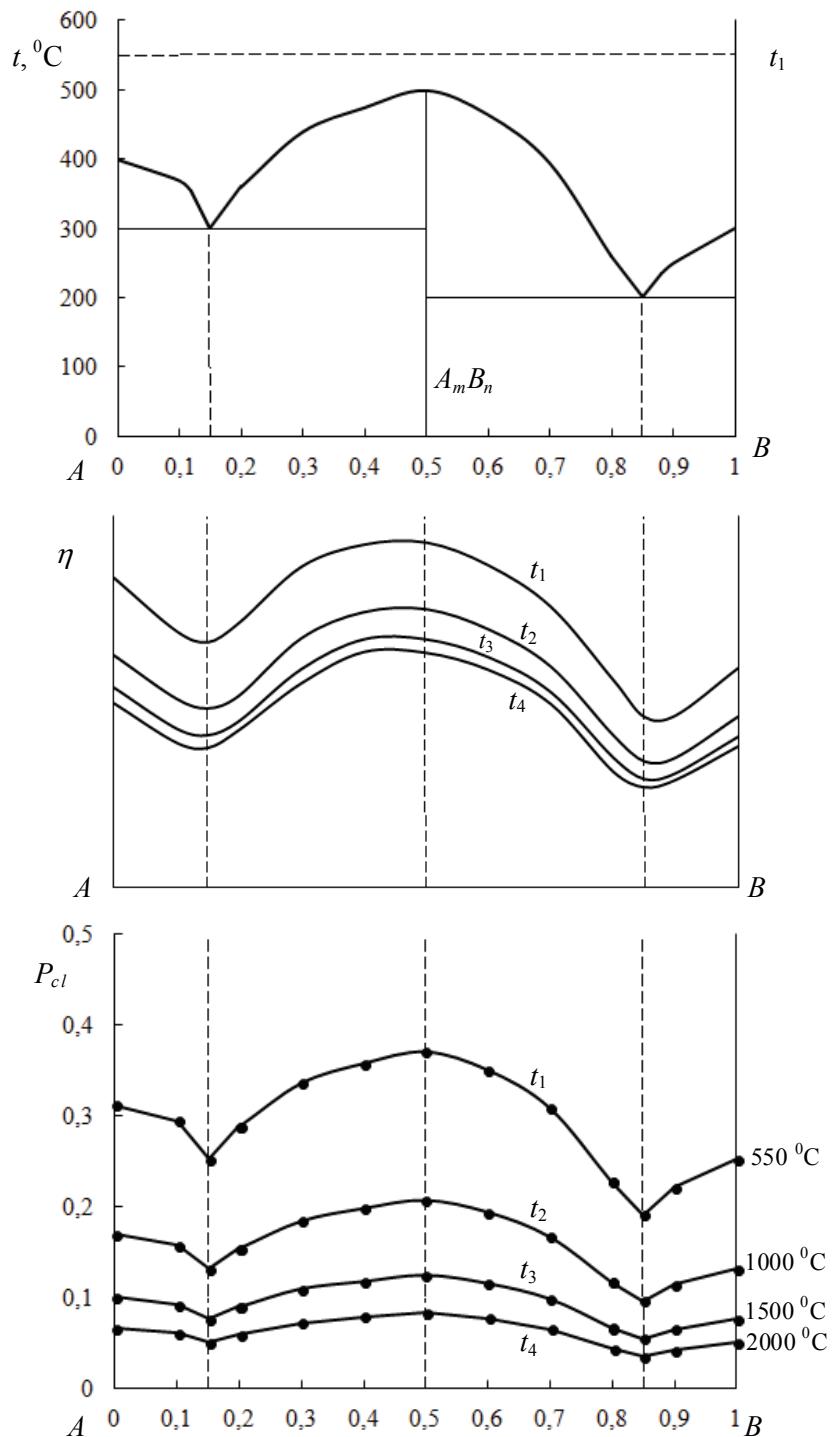


Fig. 3 Comparison of the viscosity of a typical alloy *AB* with the share of clusters at different temperatures.

for typical simple substances *A* and *B* with melting points $T_{m,A} = 400$ °C and $T_{m,B} = 300$ °C (as indicated in the diagram) represent it in the form of the Frenkel equation with the activation barriers RT_m , accordingly $U_A = 5,600$ J/mol and $U_B = 4,764$ J/mol and

proportionality factors 0.184 and 0.147 mPa·s, providing a typical viscosity for metals near the crystallization point at about 0.5 mPa·s [1, 2]:

$$\eta_{T,A} = 0.184 e^{\frac{5600}{RT}} \quad (20)$$

$$\eta_{T,B} = 0.147 e^{\frac{4764}{RT}} \quad (21)$$

The results of calculations showing the partial contributions of components A and B , η'_A and η'_B , in the alloy viscosity are shown in Figs. 4 and 5.

From these data, an even more vivid picture of the distribution of the alloy viscosity in its composition and temperature is obtained, with an increase in the tendencies toward smoothing and convergence of the curves viscosity. This indicates the possibility of a direct comparison of the experimental and calculated data for the new viscosity model.

In this case, the temperature-viscosity dependences for pure components can be used in the form of cluster

associate models (8) and (9), thereby predetermining the transfer of these models to alloys of any composition in the framework of the partial dependence

$$\eta_T = X_A \dot{\eta}_{T,A} \left[\frac{1 - \exp(-T_{cr}/T)}{1 - \exp(-T_{m,A}/T)} \right]^2 + X_B \dot{\eta}_{T,B} \left[\frac{1 - \exp(-T_{cr}/T)}{1 - \exp(-T_{m,B}/T)} \right]^2 \quad (22)$$

As regards the partial contributions of components A and B to the alloys viscosity AB , judging from Fig. 5, these contributions are essentially nonlinear, which corresponds to the very complex character and nature of the dependence, which for the expression from different points of view continues research [11, 12].

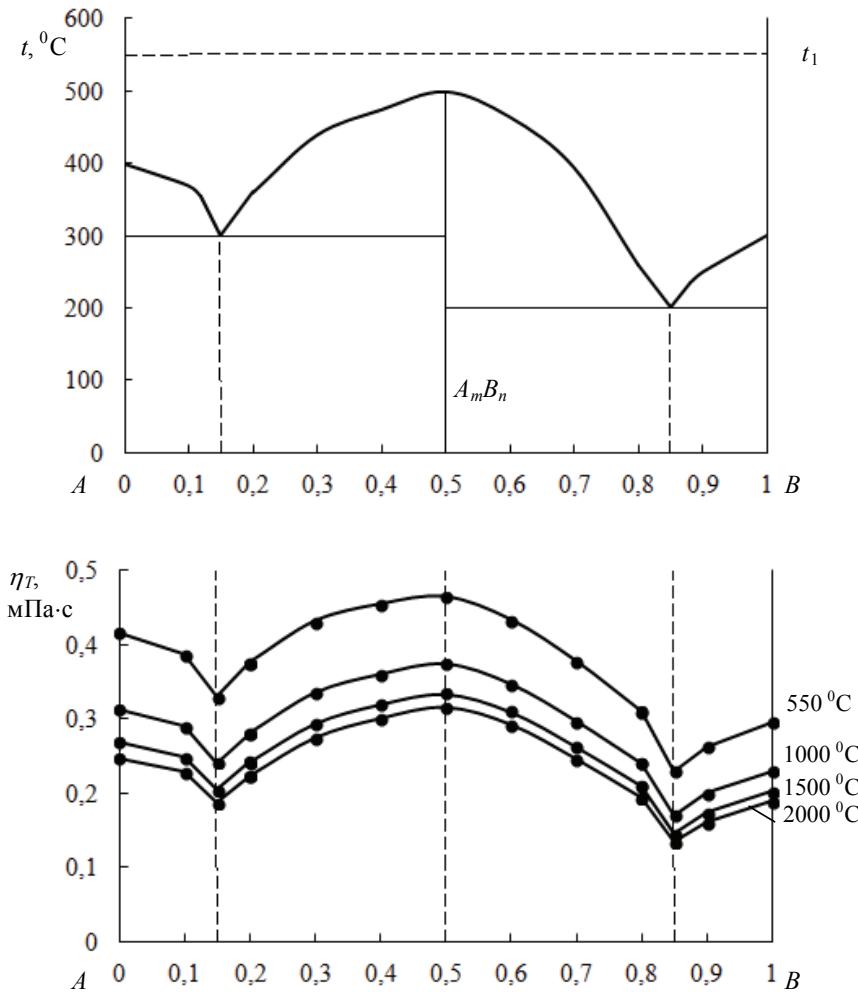


Fig. 4 The distribution of the alloy viscosity AB η_T by a typical state diagram.

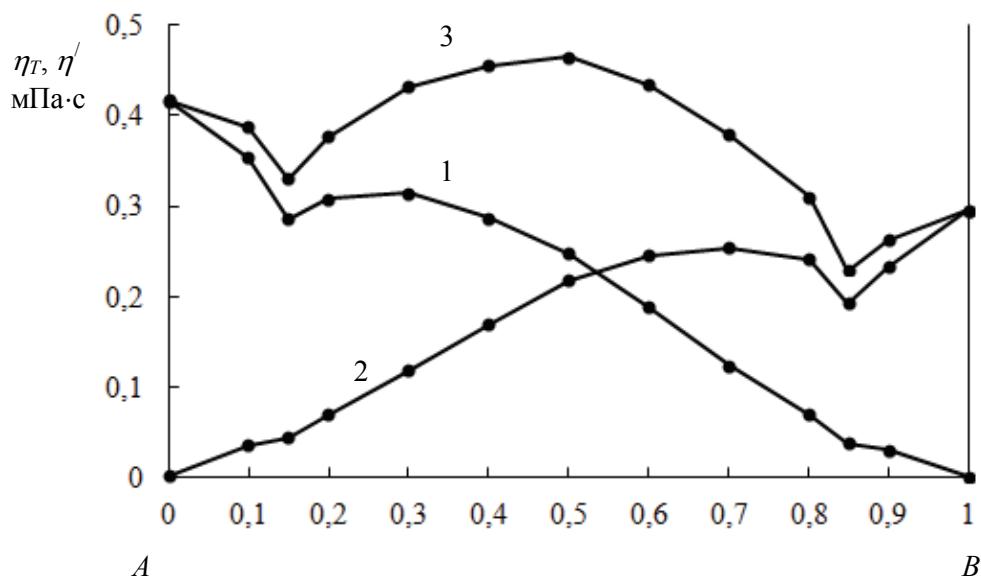


Fig. 5 Dependence of the partial contributions of the components *A* (1) and *B* (2) to the alloy viscosity *AB* (3) on its composition at the temperature 550 °C.

In any case, the probabilistic approach to the solution of such a problem has a certain perspective and a mathematical model for the direct connection of viscosity with the temperature, composition, and viscosity of pure components that it provides.

4. Conclusions

It is possible that the understanding of viscosity as a characteristic of only motion with the disappearance of it at rest is somehow connected with the historically long development of the notion of mass. The existence of mass bodies was detected only with the application of force to them, which causes acceleration. In the absence of force, the body maintains a state of rest or uniform rectilinear motion, and nothing indicates the presence of mass in it. Bearing in mind this analogy, it can be argued that the detection of viscosity under the influence of a force (gravitation or mechanical force) does not at all exclude the existence of viscosity in a calm liquid, especially since such a rest “only dreams”, being realized by a high-intensity motion of molecules in subordination to the Boltzmann distribution with the formation of virtually bound and free particles. The latter are responsible for the fluidity of the liquid, which manifests itself only under the action of the

same forces; therefore, all calculations performed to substantiate the partial viscosity of the computations are also valid for fluidity, taking into account the opposite or feedback of these two properties.

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