VISCOSITY OF BINARY AND TERNARY LIQUID NONELECTROLYTE MIXTURES. DERIVATION OF CORRELATION EQUATIONS

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Equations for the correlation of viscosity of liquid binary and ternary mixtures were derived from the Eyring's theory of absolute reaction rates and from the three-molecule model of viscosity interactions. Another equation for the correlation of viscosity of binary mixtures was derived from the same theory and from the four-molecule model. Equations for the correlation of viscosity of binary and ternary mixtures were further derived from the quasi-crystalline model of liquids with the use of some relations of the kinetic theory of gases. The derived equations involve the same number of coefficients as the corresponding equations of McAllister or Chandramouli and Laddha and moreover are linear with respect to these coefficients.

Contemporary theories of the liquid state are in comparison with those of the gas and solid states inaccurate and incomplete. Relatively imperfect knowledge of the structure of liquids and hence imperfect general theory of the liquid state do not enable to derive an exact method for determining the viscosity of liquids including liquid mixtures. Therefore, various approximate methods were proposed, most of which correlate the viscosity of liquid mixtures with the properties of pure substances and with thermodynamic parameters that characterize the interactions among the individual components[1-8]. These methods are usually based on Eyring's theory[9-11], which is founded on chemical kinetics.

The following equation, which was derived by McAllister[12] from Eyring's theory and model concepts about the structure of a binary liquid mixture, seems to be most accurate:

$$\begin{aligned}\ln \nu_z = {} & x_1^3 \ln \nu_1 + 3x_1^2x_2 \ln \nu_{12} + 3x_1x_2^2 \ln \nu_{21} + x_2^3 \ln \nu_2 - \\ & - \ln (x_1 + x_2M_2/M_1) + 3x_1^2x_2 \ln [(2 + M_2/M_1)/3] + \\ & + 3x_1x_2^2 \ln [(1 + 2M_2/M_1)/3] + x_2^3 \ln (M_2/M_1) , \qquad (1)\end{aligned}$$

where x_1, x_2, ν_1, ν_2, M_1, M_2 denote molar fractions, kinematic viscosities, and molar masses of pure components 1 and 2, and ν_z is the kinematic viscosity of the mixture. Eq. (*1*) contains two coefficients, ν_{12} and ν_{21}, which are independent of the composition but depend on the temperature and must be determined from experimental data for viscosities of the liquid mixture.

According to certain authors[13-15], Eq. (*1*) is valid with an average error of less than 2%, standard deviation less than 2·5%, and this even for certain binary systems where the hydrogen bonds undergo a change during formation of a mixture from pure components.

Eq. (*1*) was generalized to ternary mixtures by Chandramouli and Laddha[16], who derived in a similar manner as McAllister[12] (from Eyring's theory and model concepts) the following equation:

$$\begin{aligned} \ln \nu_z &= x_1^3 \ln \nu_1 + x_2^3 \ln \nu_2 + x_3^3 \ln \nu_3 + 3x_1^2 x_2 \ln \nu_{12} + \\ &+ 3x_1 x_2^2 \ln \nu_{21} + 3x_1^2 x_3 \ln \nu_{13} + 3x_1 x_3^2 \ln \nu_{31} + 3x_2^2 x_3 \ln \nu_{23} + \\ &+ 3x_2 x_3^2 \ln \nu_{32} + 6x_1 x_2 x_3 \ln \nu_{123} - \ln (x_1 M_1 + x_2 M_2 + x_3 M_3) + \\ &+ x_1^3 \ln M_1 + x_2^3 \ln M_2 + x_3^3 \ln M_3 + 3x_1^2 x_2 \ln [(2M_1 + M_2)/3] + \\ &+ 3x_1^2 x_3 \ln [(2M_1 + M_3)/3] + 3x_2^2 x_1 \ln [(2M_2 + M_1)/3] + \\ &+ 3x_2^2 x_3 \ln [(2M_2 + M_3)/3] + 3x_3^2 x_1 \ln [(2M_3 + M_1)/3] + \\ &+ 3x_3^2 x_2 \ln [(2M_3 + M_2)/3] + 6x_1 x_2 x_3 \ln [(M_1 + M_2 + M_3)/3] . \end{aligned} \qquad (2)$$

Eq. (*2*) involves six binary coefficients ν_{ij} which can be calculated from experimental data for the corresponding binary subsystems, and one ternary coefficient ν_{123} which corresponds to the given system and depends on the temperature.

In eleven ternary systems (the hydrogen bonds did not change), studied by Heric and Brewer[17], Eq. (*2*) is valid with a standard deviation less than 1·33% and maximum error less than 3·21%. Mussche and Verhoeye[15] found a standard deviation of about 1%.

Eqs (*1*) and (*2*) are rather complicated and therefore, in practice, simpler equations are preferred for the calculation of viscosity of liquid mixtures[3,18,19], which are, however, less accurate and in some cases even not applicable at all. Our aim was to derive for this purpose new equations which would fulfil the following conditions: They would be simpler than Eqs (*1*) and (*2*) and would not involve more coefficients than these, they would be linear with respect to these coefficients, and they would be practically as accurate as Eqs (*1*) and (*2*). Their derivation is given below.

Derivation of Equation Based on the Three-Molecule Model of Viscosity Interactions for Binary Mixtures

According to Eyring and Frenkel[11,20], the viscosities of pure components 1 and 2 are given as

$$\eta_1 = kT\tau_1/v_1\,, \quad \eta_2 = kT\tau_2/v_2\,, \tag{3a,b}$$

where k denotes Boltzmann's constant, T absolute temperature, v_1 and v_2 volumes occupied by a molecule of substance 1 or 2. The relaxation times of flow, τ_1 and τ_2, are given as

$$\tau_1 = (h/kT)\exp\left(\Delta g_1^{\ddagger}/kT\right), \quad \tau_2 = (h/kT)\exp\left(\Delta g_2^{\ddagger}/kT\right), \tag{4a,b}$$

where h denotes Planck's constant, $\Delta g_1^{\ddagger}$ and $\Delta g_2^{\ddagger}$ molecular activation free energies of viscous flow of the components 1 and 2. Analogously, the viscosity of the liquid mixture is given as

$$\eta_z = kT\tau_z/v_z\,, \tag{5}$$

where

$$\tau_z = (h/kT)\exp\left(\Delta g_z^{\ddagger}/kT\right). \tag{6}$$

The quantities η_z, τ_z, and $\Delta g_z^{\ddagger}$ represent the properties of the mixture.

The molecule 1 or 2 passes during its translation motion from one equilibrium position into another; at the same time it surmounts the energetic barrier. Simultaneously, a moving molecule interacts with molecules 1, 2, or with some combination of these, according to the local concentration. For the sake of simplicity, we shall restrict ourselves to a simultaneous interaction of three molecules, A, B, C. Let a molecule B to move between A and C (for a binary mixture, A, B, and C will be either 1 or 2). If all three molecules are number 1, then the interaction is of the type 111, *i.e.*, it represents a pure substance 1 and corresponds to the relaxation time of flow τ_1. Similarly, the interaction 222 represents the pure substance 2 and corresponds to the relaxation time of flow τ_2. Other interactions are of a mixed type and are given in Table I. If we assume that in a binary mixture with a molar fraction x_1 the molecules of substances 1 and 2 are distributed randomly and their number is statistically large, the probability of the interaction 111 will be equal to x_1^3. Similarly, we can express the probability of other interaction types, which are together with the relaxation times of flow given in Table I. The relaxation times of mixed types of interactions are defined as

$$\tau_{112} = (h/kT)\exp\left(\Delta g_{112}^{\ddagger}/kT\right), \tag{7a}$$

$$\tau_{121} = (h/kT)\exp\left(\Delta g_{121}^{\ddagger}/kT\right), \tag{7b}$$

$$\tau_{122} = (h/kT)\exp\left(\Delta g_{122}^{\ddagger}/kT\right), \tag{7c}$$

$$\tau_{212} = (h/kT)\exp\left(\Delta g_{212}^{\ddagger}/kT\right), \tag{7d}$$

where $\Delta g^{\ddagger}_{112}$ *etc.* are molecular activation free energies of viscous flow for the corresponding types of interactions. If we assume that the probability of the occurrence of a given interaction depends only on the concentration and that the relaxation time

TABLE I

Relaxation Times of Flow τ and Interaction Probabilities P

Interaction type	τ	P
Three-molecular interactions, binary mixtures		
111	τ_1	x_1^3
112, 211	τ_{112}	$2x_1^2x_2$
121	τ_{121}	$x_1^2x_2$
221, 122	τ_{122}	$2x_1x_2^2$
212	τ_{212}	$x_1x_2^2$
222	τ_2	x_2^3
Three-molecular interactions, ternary mixtures		
111	τ_1	x_1^3
222	τ_2	x_2^3
333	τ_3	x_3^3
112, 211	τ_{112}	$2x_1^2x_2$
121	τ_{121}	$x_1^2x_2$
113, 311	τ_{113}	$2x_1^2x_3$
131	τ_{131}	$x_1^2x_3$
223, 322	τ_{223}	$2x_2^2x_3$
232	τ_{232}	$x_2^2x_3$
221, 122	τ_{122}	$2x_1x_2^2$
212	τ_{212}	$x_1x_2^2$
331, 133	τ_{133}	$2x_1x_3^2$
313	τ_{313}	$x_1x_3^2$
332, 233	τ_{233}	$2x_2x_3^2$
323	τ_{323}	$x_2x_3^2$
213, 312, 123, 321, 132, 231	τ_{123}	$6x_1x_2x_3$
Four-molecular interactions, binary mixtures		
1111	τ_1	x_1^4
2222	τ_2	x_2^4
1112, 1211, 2111, 1121	τ_{1112}	$4x_1^3x_2$
2211, 2112, 1212, 1221, 2121, 1122	τ_{1122}	$6x_1^2x_2^2$
2212, 2221, 2122, 1222	τ_{1222}	$4x_1x_2^3$

of flow of the mixture, τ_z, is an additive function of the relaxation times for the individual interaction types, we can write

$$\tau_z = x_1^3\tau_1 + 2x_1^2x_2\tau_{112} + x_1^2x_2\tau_{121} + 2x_1x_2^2\tau_{122} + \\ + x_1x_2^2\tau_{212} + x_2^3\tau_2 \,. \tag{8}$$

On rearranging and with the simplifying assumptions

$$\tau_{12} = (2\tau_{112} + \tau_{121})/3\,, \quad \tau_{21} = (2\tau_{122} + \tau_{212})/3 \tag{9a,b}$$

we obtain

$$\tau_z = x_1^3\tau_1 + 3x_1^2x_2\tau_{12} + 3x_1x_2^2\tau_{21} + x_2^3\tau_2 \,. \tag{10}$$

Here τ_{12} is the flow relaxation time for simultaneous interaction of two molecules "1" and one molecule "2"; and τ_{21} *vice versa*. The viscosity coefficients η_{12} and η_{21} are defined as

$$\eta_{12} = kT(v_1^2v_2)^{-1/3}\tau_{12}\,, \quad \eta_{21} = kT(v_1v_2^2)^{-1/3}\tau_{21} \,. \tag{11a,b}$$

On substituting Eqs (*3a,b*), (*10*), and (*11a,b*) in (5) and rearranging we obtain

$$\eta_z = x_1^3V_1\eta_1/V_z + 3\eta_{12}x_1^2x_2(V_1^2V_2/V_z^3)^{1/3} + \\ + 3\eta_{21}x_1x_2^2(V_1V_2^2/V_z^3)^{1/3} + x_2^3V_2\eta_2/V_z \,. \tag{12}$$

Here we have introduced molar volumes V_1, V_2, V_z of components 1 and 2 and of their mixture. From the physical point of view, the mentioned substitution corresponds to the formation of a fictitious binary solution by mixing the components 1 and 2 with two hypothetical solutions in which only interactions of two molecules „1" with one molecule „2" and of two molecules „2" with one molecule „1" take place, respectively. Therefore, it appears more adequate to replace the molar volumes V_1 and V_2 by partial molar volumes $\overline{V}_1$ and $\overline{V}_2$; further we shall use the substitution

$$\varphi_1 = x_1\overline{V}_1/V_z\,, \quad \varphi_2 = x_2\overline{V}_2/V_z\,, \tag{13a,b}$$

where φ_1 and φ_2 are volume fractions of components 1 and 2:

$$\eta_z = x_1^2\varphi_1\eta_1 + 3\eta_{12}x_1(x_1x_2^2\varphi_1^2\varphi_2)^{1/3} + \\ + 3\eta_{21}x_2(x_1^2x_2\varphi_1\varphi_2^2)^{1/3} + x_2^2\varphi_2\eta_2 \,. \tag{14}$$

This is the final form of the correlation equation. The coefficients η_{12} and η_{21} are characteristic for the given binary system and depend on the temperature, but not on the composition. They have the dimension of dynamic viscosity and their calculation requires the knowledge of the viscosity of the binary mixture at least for two compositions.

Derivation of Equation for Viscosity of Ternary Mixtures from Trimolecular Model of Viscosity Interactions

To derive an equation for the correlation of viscosity of ternary mixtures, based again on Eyring's theory of absolute reaction rates, we supplement the starting equations (*3a*,*b*) by a new one for component 3:

$$\eta_3 = kT\tau_3/v\,. \tag{3c}$$

We assume again the validity of the two-dimensional trimolecular model; for the ternary mixture we have A, B, C equal to 1, 2, or 3. If the molecules of components 1, 2, and 3 are distributed randomly in the mixture and their number is statistically large, we can express the probabilities of the individual interactions similarly to the preceding case. All types of interactions with the corresponding relaxation times of flow and probabilities are given in Table I. If we assume that the probability of a given interaction depends only on the concentration and that the relaxation time of flow of the mixture is an additive function of the relaxation times for the individual types of interactions, we can write

$$\begin{aligned}\tau_z = {} & x_1^3\tau_1 + x_2^3\tau_2 + x_3^3\tau_3 + 2x_1^2x_2\tau_{112} + x_1^2x_2\tau_{121} + \\ & + 2x_1^2x_3\tau_{113} + x_1^2x_3\tau_{131} + 2x_2^2x_3\tau_{223} + x_2^2x_3\tau_{232} + \\ & + 2x_1x_2^2\tau_{122} + x_1x_2^2\tau_{212} + 2x_1x_3^2\tau_{133} + x_1x_3^2\tau_{313} + \\ & + 2x_2x_3^2\tau_{233} + x_2x_3^2\tau_{323} + 6x_1x_2x_3\tau_{123}\,.\end{aligned} \tag{15}$$

Further steps of the derivation are similar to the preceding case (compare ref.[21] for details). The final correlation equation is:

$$\begin{aligned}\eta_z = {} & x_1^2\varphi_1\eta_1 + x_2^2\varphi_2\eta_2 + x_3^2\varphi_3\eta_3 + 3\eta_{12}x_1(x_1x_2^2\varphi_1^2\varphi_2)^{1/3} + \\ & + 3\eta_{21}x_2(x_1^2x_2\varphi_1\varphi_2^2)^{1/3} + 3\eta_{13}x_1(x_1x_3^2\varphi_1^2\varphi_3)^{1/3} + \\ & + 3\eta_{31}x_3(x_1^2x_3\varphi_1\varphi_3^2)^{1/3} + 3\eta_{23}x_2(x_2x_3^2\varphi_2^2\varphi_3)^{1/3} + \\ & + 3\eta_{32}x_3(x_2^2x_3\varphi_2\varphi_3^2)^{1/3} + 6\eta_{123}(x_1^2x_2^2x_3^2\varphi_1\varphi_2\varphi_3)^{1/3}\,.\end{aligned} \tag{16}$$

The six binary coefficients η_{ij} can be calculated from measured viscosities of the corresponding binary mixtures. They are identical with those in Eq. (*14*) for the corresponding binary subsystem. Eq. (*16*) contains, in addition, a ternary coefficient, η_{123}, which depends on the temperature, but not on the composition of the system.

Derivation of Equation for Binary Mixtures from Four-Molecular Three-Dimensional Model of Viscosity Interactions

The three-molecular model of viscosity interactions does not always appear sufficiently adequate. Especially if different molecules differ considerably in their size, interactions of more than three molecules must be considered. According to McAllister[12], the four-molecule model is preferable when the ratio of diameters of two molecules is larger than 1·5; simultaneous interactions of seven or eight molecules are possible in mixtures with a low concentration of the component of a larger diameter.

Further we use the four-molecule model, since models involving interactions of more than four molecules lead to very complicated equations. Interactions of four molecules, A, B, C, and D, can be imagined in space so that one of them moves perpendicularly to the plane in which the remaining three molecules lie. For binary solutions, A, B, C, D will be numbered as 1 or 2. All types of interactions, the corresponding relaxation times of flow and the probabilities of individual interactions are given in Table I. The relaxation time of flow τ_{1112} means the mean value of relaxation times for interactions of three molecules "1" and one molecule "2"; analogously τ_{1122} is the mean value of relaxation times for interactions of two molecules "1" and two "2", and τ_{1222} is the mean value for interactions of one molecule "1" and three "2". As in the preceding cases, we assume that the relaxation time of flow of the mixture is an additive function of the relaxation times for the individual interaction types, hence

$$\tau_z = x_1^4\tau_1 + 4x_1^3x_2\tau_{1112} + 6x_1^2x_2^2\tau_{1122} + 4x_1x_2^3\tau_{1222} + x_2^4\tau_2 \,. \qquad (17)$$

We proceed similarly to the derivation of Eq. (*14*) to obtain

$$\eta_z = x_1^3\varphi_1\eta_1 + 4\eta_{1112}x_1^2(x_1x_2^3\varphi_1^3\varphi_2)^{1/4} + 6\eta_{1122}x_1x_2(x_1x_2\varphi_1\varphi_2)^{1/2} + + 4\eta_{1222}x_2^2(x_1^3x_2\varphi_1\varphi_2^3)^{1/4} + x_2^3\varphi_2\eta_2 \,. \qquad (18)$$

This correlation equation involves three binary coefficients defined as:

$$\eta_{1112} = \left[kT/(v_1^3v_2)^{1/4}\right]\tau_{1112}\,, \quad \eta_{1122} = \left[kT/(v_1^2v_2^2)^{1/4}\right]\tau_{1122}\,, \qquad (19a,b)$$

$$\eta_{1222} = \left[kT/(v_1v_2^3)^{1/4}\right]\tau_{1222}\,. \qquad (19c)$$

The coefficients η_{1112}, η_{1122}, and η_{1222} depend on the temperature but not on the composition of the given system. They have the dimension of dynamic viscosity and their determination requires the knowledge of the viscosity of a binary mixture at least at three compositions.

Derivation of Equation for Viscosity of Binary Mixtures from Quasicrystalline Model

Most theories of the liquid state assume that the liquid has a quasicrystalline structure. The arrangement of molecules around each molecule in the liquid is statistically equivalent, hence the probability of occurrence of a molecule in a given distance from another molecule is independent of their positions in the liquid. We shall assume that the molecules are arranged in a cubic lattice and the distance, Δ, between their centers can be expressed as

$$\Delta = (V/N_A)^{1/3} . \tag{20}$$

The molecules vibrate around their equilibrium positions and the transfer of momentum from one lattice plane to another is caused by collisions of those molecules which have a large amplitude, so that they reach the neighbouring plane.

We now shall apply some relations from the kinetic theory of gases to this model. In the case of transfer of moment of momentum in the mixture we can write the following equation for the distance Δ_z:

$$\Delta_z = 2\lambda_z/3 = (V_z/N_A)^{1/3} , \tag{21}$$

where λ_z is the mean free path of a molecule in the mixture. Its mean velocity $\bar{u}_z$ can be expressed as

$$\bar{u}_z = 3\eta_z/\varrho_z\lambda_z , \tag{22}$$

where ϱ_z is the density of the mixture. As will be obvious from further text, it is irrelevant whether we use Eq. (*22*) or the equation of Chapman[22], which differs from the former by the constant equal to 2·004 instead of 3.

On the assumption that only simultaneous collisions of three molecules participate in the transfer of momentum, we can apply the three-molecular model to the binary mixture (Table I); the individual types of interactions will be represented by simultaneous collisions of three molecules. If the molecules of the types 1 and 2 are randomly distributed in the mixture, their number is statistically large and the collision probability depends only on the concentration, and if we assume that the mean velocity of molecules in the mixture is an additive function of mean molecular velocities corresponding to the individual types of collisions, we can write

$$\bar{u}_z = x_1^3\bar{u}_1 + 3x_1^2x_2\bar{u}_{12} + 3x_1x_2^2\bar{u}_{21} + x_2^3\bar{u}_2\,, \tag{23}$$

where $\bar{u}_1$, $\bar{u}_{12}$, $\bar{u}_{21}$, $\bar{u}_2$ denote mean molecular velocities in such hypothetical liquids where only the following simultaneous collisions take place: three molecules "1"; two molecules "1" and one "2"; two molecules "2" and one "1"; and three molecules "2".

The mean molecular velocities in Eq. (*23*) are given as

$$\bar{u}_1 = 3\eta_1/\varrho_1\lambda_1\,,\quad \bar{u}_2 = 3\eta_2/\varrho_2\lambda_2\,, \tag{24a,b}$$

$$\bar{u}_{12} = 3\eta''_{12}/\varrho_{12}\lambda_{12}\,,\quad \bar{u}_{21} = 3\eta''_{21}/\varrho_{21}\lambda_{21}\,, \tag{24c,d}$$

where η''_{12} and η''_{21} are coefficients of viscosity. The mean free paths are given by the equations

$$\lambda_1 = 1{\cdot}5(V_1/N_A)^{1/3}\,,\quad \lambda_2 = 1{\cdot}5(V_2/N_A)^{1/3}\,, \tag{25a,b}$$

$$\lambda_{12} = 1{\cdot}5(V_{12}/N_A)^{1/3}\,,\quad \lambda_{21} = 1{\cdot}5(V_{21}/N_A)^{1/3}\,. \tag{25c,d}$$

By substituting Eqs (*21*), (*22*), (*24a – d*), and (*25a – d*) into (*23*) and using the equations

$$\varrho_{12} = M_{12}/V_{12}\,,\quad \varrho_{21} = M_{21}/V_{21}\,, \tag{26a,b}$$

with

$$V_{12} = (V_1^2V_2)^{1/3}\,,\quad V_{21} = (V_1V_2^2)^{1/3}\,, \tag{27a,b}$$

$$M_{12} = (2M_1 + M_2)/3\,,\quad M_{21} = (M_1 + 2M_2)/3\,, \tag{28a,b}$$

we obtain the equation

$$\begin{aligned}\eta_z = (M_1x_1 + M_2x_2)\,V_z^{-2/3}[x_1^3\eta_1V_1^{2/3}/M_1 + 3\eta'_{12}x_1^2x_2(V_1^2V_2)^{2/9} + {}\\ + 3\eta'_{21}x_1x_2^2(V_1V_2^2)^{2/9} + x_2^3\eta_2V_2^{2/3}/M_2]\,,\end{aligned} \tag{29}$$

where η'_{12} and η'_{21} are defined as

$$\eta'_{12} = \eta''_{12}/M_{12}\,,\quad \eta'_{21} = \eta''_{21}/M_{21}\,. \tag{30a,b}$$

As in the derivation of Eq. (*14*), also in this case it is more appropriate from the physical point of view to replace the molar volumes of components in Eq. (*29*) by partial molar volumes. Thus, we obtain the final equation

$$\eta_z = (M_1x_1 + M_2x_2)\,[x_1^{7/3}\varphi_1^{2/3}\eta_1/M_1 + 3\eta'_{12}x_1(x_1^{5/3}x_2^{7/3}\varphi_1^{4/3}\varphi_2^{2/3})^{1/3} + 3\eta'_{21}x_2(x_1^{7/3}x_2^{5/3}\varphi_1^{2/3}\varphi_2^{4/3})^{1/3} + x_2^{7/3}\varphi_2^{2/3}\eta_2/M_2]\,. \tag{31}$$

The coefficients η'_{12} and η'_{21} depend on the temperature but not on the composition.

Derivation of Equation for Viscosity of Ternary Mixtures from Quasicrystalline Model

The derivation of a correlation equation for ternary mixtures is based on the same model of quasicrystalline liquid structure as in the preceding case and also on the kinetic theory of gases. We assume that momentum is transferred only in simultaneous three-molecule collisions which can occur in different types given in Table I. The individual interaction types will be in this case represented by simulatenous collisions of three molecules. On similar assumptions as in the preceding section, we can write for the mean molecular velocity in a three-component mixture the equation

$$\bar{u}_z = x_1^3\bar{u}_1 + x_2^3\bar{u}_2 + x_3^3\bar{u}_3 + 3x_1^2x_2\bar{u}_{12} + 3x_1x_2^2\bar{u}_{21} + 3x_1^2x_3\bar{u}_{13} + 3x_1x_3^2\bar{u}_{31} + 3x_2^2x_3\bar{u}_{23} + 3x_2x_3^2\bar{u}_{32} + 6x_1x_2x_3\bar{u}_{123}\,. \tag{32}$$

Further we proceed as in the preceding case (for details see ref.[21]). The final correlation equation is

$$\eta_z = (M_1x_1 + M_2x_2 + M_3x_3)\,[x_1^{7/3}\varphi_1^{2/3}\eta_1/M_1 + x_2^{7/3}\varphi_2^{2/3}\eta_2/M_2 + x_3^{7/3}\varphi_3^{2/3}\eta_3/M_3 + 3\eta'_{12}x_1(x_1^5x_2^7\varphi_1^4\varphi_2^2)^{1/9} + 3\eta'_{21}x_2(x_1^7x_2^5\varphi_1^2\varphi_2^4)^{1/9} + 3\eta'_{13}x_1(x_1^5x_3^7\varphi_1^4\varphi_3^2)^{1/9} + 3\eta'_{31}x_3(x_1^7x_3^5\varphi_1^2\varphi_3^4)^{1/9} + 3\eta'_{23}x_2(x_2^5x_3^7\varphi_2^4\varphi_3^2)^{1/9} + 3\eta'_{32}x_3(x_2^7x_3^5\varphi_2^2\varphi_3^4)^{1/9} + 6\eta'_{123}(x_1x_2x_3)^{7/9}\,(\varphi_1\varphi_2\varphi_3)^{2/9}]\,. \tag{33}$$

This equation involves six coefficients η'_{ij}, which depend for the given system on temperature but not on composition. They are identical with the binary coefficients of Eq. (*31*) for the corresponding binary subsystems. The ternary coefficient η'_{123} in (*33*) also depends on temperature but not on composition.

It is interesting to compare Eq. (*12*) with (*29*): although they were derived on the basis of different theories, they are similar in form. Eq. (*29*) differs from (*12*) in that it involves molar masses of the components and that the volume quantities in it are raised to a power of 2/3, their influence being thus smaller.

Eqs (*14*), (*16*), (*18*), (*31*), and (*33*) are simpler than the corresponding equations of the cited authors[12,16], although they contain the same numbers of coefficients, which are moreover in a linear form.

A comparison of the derived equations with experimental data and with the equations of McAllister, Chandramouli and Laddha will form the subject of our next work[23].

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