Calculation of density and electrical conductivity of ternary melts Application to the cryolite-based melts

P. FELLNER and M. CHRENKOVÁ-PAUČÍROVÁ

Institute of Inorganic Chemistry, Slovak Academy of Sciences, 809 34 Bratislava

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A formal method for calculation of density and electrical conductivity of ternary melts was proposed. The calculation is based on the assumption that the deviation of corresponding molar quantities from additivity can be calculated knowing the contributions of boundary binary systems. The proposed method was tested for the case of cryolite-based melts, namely Na_3AlF_6—LiF—Al_2O_3 and Na_3AlF_6—Li_3AlF_6—Al_2O_3.

Был предложен формальный метод расчета плотности и электропроводности тройных расплавов. Расчет основан на предположении, что отклонения соответствующих молярных величин от аддитивности можно рассчитать на основании вклада граничных двойных систем. Предложенный метод был проверен на случае расплавов на базе криолита, а именно Na_3AlF_6—LiF—Al_2O_3 и Na_3AlF_6—Li_3AlF_6—Al_2O_3.

Determination of physicochemical properties of molten systems is in many cases experimentally difficult and for multicomponent mixtures also time-consuming. For these reasons complete physicochemical data on molten ternary systems are rather scarce. However, from the point of view of practical application the ternary mixtures are frequently used.

The aim of this work is to propose and to test the formal method which enables calculating the volume properties and electrical conductivity of ternary, respectively quaternary mixtures. The cryolite melts were chosen as a model system because the data on volume properties [1, 2] and on electrical conductivity [2, 3] were obtained in our laboratory and therefore they were available in numerical form, which is advantageous for further mathematical treatment.

Theoretical

The calculation of physicochemical quantities of ternary mixtures is based on knowledge of the concentration dependence of the corresponding parameter in boundary binary systems of the multicomponent system. The approach to the

calculation is similar as in the case of Gibbs excess energy which was used for calculation of phase diagrams of multicomponent systems [4]. A critical survey of correlation equations for the dependence of excess quantity on concentration can be found in [5].

The method of calculation will be demonstrated on the case of density. It is assumed that the molar property of multicomponent mixture can be in zero approximation estimated as the sum of contributions of pure components. In the first approximation it is then assumed that the deviation of multicomponent mixture from additivity can be expressed as the sum of contributions of single binary systems. In practical calculation, the parameter in question is transformed to the corresponding molar quantity. Density is to be transformed to molar volume and specific electrical conductivity to molar conductivity defined by the relation

$$\lambda = \varkappa M/\varrho = \varkappa V \tag{1}$$

where λ is the molar electrical conductivity, $\varkappa$ is the specific electrical conductivity, ϱ is the density, M is the mass of 1 mole of electrolyte, and V is the molar volume. The calculating procedure will be demonstrated on the case of volume.

The excess quantity V^E in the system having k components is defined by the relationship

$$V^E = V - \sum_{i=1}^{k} x_i V_i^0 \tag{2}$$

where V_i^0 is the molar volume of the i-th pure component. If we possess experimental data for boundary binary systems we can determine V^E in these systems as a function of composition. In this work it is assumed that this dependence can be expressed with good approximation by the empirical relationship

$$V^E = x_i x_j (A + B x_j) \tag{3}$$

where x_i and x_j are the corresponding mole fractions of the first and the second component and A, B are the empirical constants.

In the first approximation the excess quantity in ternary or quaternary system can be determined as the sum of contributions of single binary systems. Therefore, the volume of multicomponent mixture can be calculated according to the following relationship

$$V = \sum_{i=1}^{k} x_i V_i^0 + \sum_{i=1}^{k-1} \sum_{j>i}^{k} x_i x_j (A_{ij} + B_{ij} x_j) \tag{4}$$

The first term corresponds to the contribution of pure components to the total molar volume and the second term corresponds to the excess volume V^E for the k-component mixture. In the case when the value of molar volume of pure component is not experimentally accessible, *e.g.* of Al_2O_3 at the temperature

1000°C, this value is to be estimated by extrapolation based on known experimental data in binary system. If it is desired the molar volume or molar electrical conductivity can be transformed to density or specific electrical conductivity using definitions of these quantities.

As it follows from discussion this procedure yields very promissible results even for complicated and highly nonideal cryolite melts and the calculated values of density and electrical conductivity agree with experimental data within the error of measurement of the parameter in question.

Results and discussion

The proposed method of calculation has been tested for the case of density and electrical conductivity in the ternary systems Na_3AlF_6—LiF—Al_2O_3 and Na_3AlF_6—Li_3AlF_6—Al_2O_3 at 1000°C. In these systems where only the sodium cryolite regions are in both cases experimentally accessible it may be assumed that the excess value in ternary system would be estimated with sufficient accuracy on the basis of contributions of the two binary systems which can be measured.

The calculations were realized using programmable calculator HP 9821 A with plotter HP 9862 A.

Calculation of density

The volume properties of ternary melt Na_3AlF_6—Li_3AlF_6—Al_2O_3 and Na_3AlF_6—LiF—Al_2O_3 were experimentally studied up to the concentration of 30 mole % Al_2O_3 [1, 2]. In the case of the first system the calculated and experimental data are in a very good agreement and practically coincide (Fig. 1). In the case of the second system the deviation between experimental data and those calculated neglecting contribution of binary system LiF—Al_2O_3 to nonideality exceeds the error of measurements, *i.e.* 0.2%. However, after introducing suitable interaction parameter A_{ij} for the binary system LiF—Al_2O_3, which can be calculated from one experimental point in ternary system, the situation improves and the

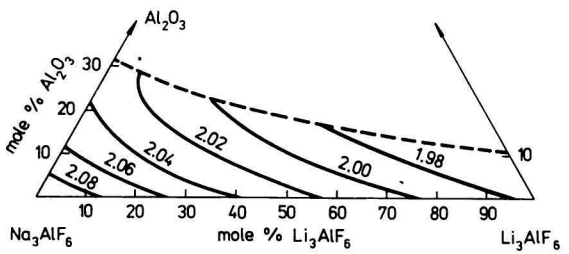

Fig. 1. Calculated density ϱ [g cm^{-3}] of the molten system Na_3AlF_6—Li_3AlF_6—Al_2O_3 at 1000°C.

agreement between two sets of data (calculated and experimental) is better than 0.2% (Fig. 2). The values of parameters V_i^0, A_{ij}, B_{ij} used in calculations are summarized in Tables 1 and 2.

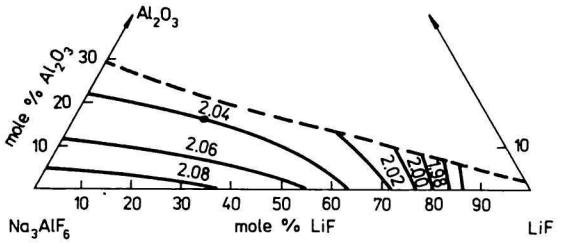

Fig. 2. Calculated density ϱ [g cm^{-3}] of the molten system Na_3AlF_6—LiF—Al_2O_3 at 1000°C.

Table 1

Values of molar volume V^0 and molar electrical conductivity λ^0 of pure components at 1000°C

Component	V^0, cm^3 mol^{-1}	λ^0, S cm^2 mol^{-1}
Na_3AlF_6	99.876	279.654
Li_3AlF_6	81.794	342.718
LiF	14.967	137.542
Al_2O_3	60.539*	121.093*

*The values are estimated by extrapolation.

Table 2

Values of the constants A and B in eqn (*3*) describing deviation from additivity in binary systems at 1000°C

System	Excess molar volume		Excess molar conductivity	
	A, cm^3 mol^{-1}	B, cm^3 mol^{-1}	A, S cm^2 mol^{-1}	B, S cm^2 mol^{-1}
Li_3AlF_6—Na_3AlF_6	2.1472	1.6911	−81.026	39.768
LiF—Na_3AlF_6	−1.8611	1.1656	−180.447	158.710
Na_3AlF_6—Al_2O_3	10.4749	−46.0635	−143.317	−443.189
LiF—Al_2O_3	−15.0000*	0	0	0
Li_3AlF_6—Al_2O_3	0	0	0	0

* Estimated on the basis of one experimental point in the ternary system Na_3AlF_6—LiF—Al_2O_3.

The authors were engaged also in calculating volume properties of further eight ternary mixtures: $BaCl_2$—$NaCl$—$MgCl_2$, $BaCl_2$—BaF_2—LiF, $BaCl_2$—BaF_2—KCl, CaF_2—LiF—NaF, BaF_2—LiF—NaF, $BaCl_2$—$NaCl$—KCl, $MgCl_2$—$NaCl$—KCl, $BaCl_2$—KCl—$MgCl_2$. Experimental data for the most of these ternary systems are unknown. The results of calculations of volume properties of these systems can be obtained from the authors.

Calculation of electrical conductivity

Procedure used for calculation of electrical conductivity is similar to that discussed in the former section. Also in this case the agreement between calculated and experimental data was very good, not exceeding experimental error which is 1%. The results of calculations are drawn in Figs. 3 and 4 and the constants used for calculation are summarized in Tables 1 and 2.

In all discussed cases it may be appreciated that the formal relationships are suitable to describe the experimental behaviour of binary systems and can be used for statistical treatment of experimental data. The significance of the proposed method of calculation of properties of ternary systems is mainly in saving a lot of experimental work. The method, however, can be used also for statistical treatment of experimental data and for presenting them in a condensed form.

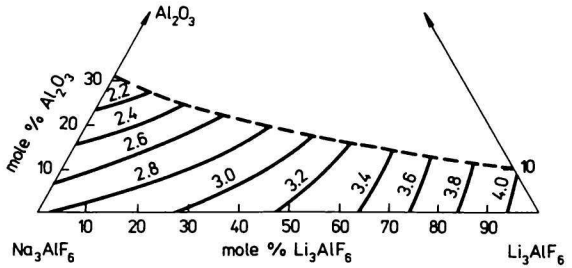

Fig. 3. Calculated specific electrical conductivity $\varkappa$ [S cm^{-1}] of the molten system Na_3AlF_6—Li_3AlF_6—Al_2O_3 at 1000°C.

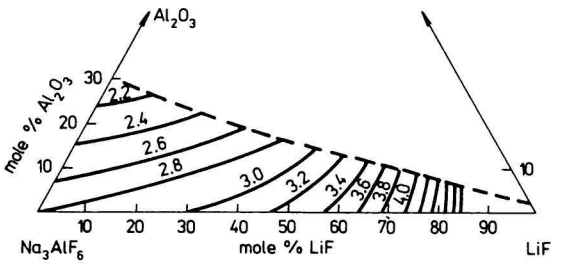

Fig. 4. Calculated specific electrical conductivity $\varkappa$ [S cm^{-1}] of the molten system Na_3AlF_6—LiF—Al_2O_3 at 1000°C.

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