CALCULATION OF MOLAR VOLUME OF TERNARY CRYOLITE-BASED MELTS

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Received September 22nd, 1972

The molar volume of binary melts containing Na_3AlF_6 as one component is expressed as a polynomial function of composition. It is assumed that the molar volume of ternary systems composed of known nonideal, resp. ideal binary systems can be calculated by an additive rule from the molar volumes of these binary systems. The proposed method of calculation has been verified on isothermal 1000°C sections of ternary systems Na_3AlF_6–Li_3AlF_6–LiF, Na_3AlF_6–Li_3AlF_6–AlF_3, and parts of ternary systems (cryolite corner) Na_3AlF_6–Li_3AlF_6–Al_2O_3, Na_3AlF_6–NaCl–Al_2O_3 and Na_3AlF_6–Al_2O_3–SiO_2.

If we want to assess the suitability of addition of a certain substance as an admixture into an electrolyte, it is necessary to examine the effect of this substance on physico-chemical properties of the given system. Density is one of the technically important parameters of molten salts. It depends on the difference between the densities of the melted electrolyte and the deposited metal whether the given system could be used for electrolytic deposition of this metal. Density is one of the parameters affecting the current efficiency of electrolysis. It is also possible to judge on the structure of the melt from its volumetric properties.

This work deals with a calculation of molar volumes of cryolite melts important from the point of view of aluminium production.

THEORETICAL

Calculations of the molar volumes of ternary systems containing molten salts were considered by Prisjazhnyj and Prichodko[1]. They report that the calculations of the density in ternary systems from those of pure salts, resp. of binary systems, is not supported sufficiently by theory, as the additivity rule holds only for the molar volume. They suppose in their calculations of the molar volume in ternary mixtures that this quantity may be calculated as an additive property from the corresponding binary systems, resp. that a knowledge of the deviation from ideality in the binary systems is sufficient for calculations of the molar volume of the ternary mixture.

In our calculations of the molar volumes of cryolite melts we started from the same assumptions as in the cited work[1]. However, the proposed method of the calculation of the molar volumes is different. Our method can be used even in the case when only two of the three constituent binary systems are known, which is in some cases very

important. Thus, for example, in a ternary Na_3AlF_6–NaCl–Al_2O_3 system it is not possible to determine experimentally the volumetric properties of the binary NaCl–Al_2O_3 system, as Al_2O_3 is not soluble in NaCl. Besides that, our method is very suitable for a computer processing of experimental data.

We propose the following method for the calculation of the molar volume for a ternary A–B–C melt. We express the molar volume of binaries A–B and A–C as a polynomial function

$$V_{AB} = b_0 + b_1 x_B + b_2 x_B^2 , \qquad (1)$$

$$V_{AC} = c_0 + c_1 x_C + c_2 x_C^2 , \qquad (2)$$

with V_{AB} and V_{AC} being the molar volumes of binary mixtures A–B and A–C, x_B and x_C mole fractions of components B and C, b_i and c_i coefficients of the polynomial function determined by the least squares method.

By supposing that the molar volume of the ternary system may be expressed as an additive function of two real binary systems, it follows for the molar volume of the ternary

$$V_{ABC} = \tfrac{1}{2}(b_0 + c_0) + b_1 x_B + b_2 x_B^2 + c_1 x_C + c_2 x_C^2 , \qquad (3)$$

where V_{ABC} is the molar volume of the ternary mixture, x_B and x_C are the mole fractions of components B and C in the ternary system.

If the binaries A–B and A–C exhibit an ideal behaviour with regard to volumetric properties, Eq. (3) assumes the form of

$$V_{ABC} = \tfrac{1}{2}(b_0 + c_0) + b_1 x_B + c_1 x_C , \qquad (4)$$

where

$$\tfrac{1}{2}(b_0 + c_0) = V_A ; \quad b_1 = V_B - V_A ; \quad c_1 = V_C - V_A$$

and V_A, V_B and V_C are the molar volumes of the pure components. It is obvious that coefficients b_0 and c_0 in Eq. (3) represent also the molar volume of the pure component A and that these coefficients are equal to one another within the experimental error.

RESULTS AND DISCUSSION

The proposed method of calculation of the molar volumes has been used for calculating the molar volumes of ternary cryolite systems. The volumetric properties of these systems are discussed in papers[2–7]. The calculations were performed on a CDC 3300 computer.

In Table I, the values are given of the polynomial coefficients from Eq. (1) for

calculating the molar volumes of binary cryolite systems at 1000°C. The accuracy of the experimental values in these systems is better than 0·2% except for the systems containing AlF_3 (ref.[7]). In the Na_3AlF_6–AlF_3 system, the accuracy of the experimental results is better than 0·5%.

Based on the data in Table I, the molar volume of the cryolite-based ternary melts was calculated according to Eq. (*3*).

Binary Na_3AlF_6–Li_3AlF_6 and Na_3AlF_6–LiF systems behave almost ideally from the point of view of volumetric properties. Therefore it was possible to assume that molar volumes of the ternary Na_3AlF_6–Li_3AlF_6–LiF system[7,8] calculated according to Eq. (*3*) would be in good agreement with the experimental data. This assumption was confirmed in the whole concentration range. The deviation between the calculated and experimental values does not exceed 0·4% of the experimental quantity.

TABLE I

Constants of Eq. (*1*) for Calculating the Molar Volume ($cm^3\ mol^{-1}$) of Binary Systems at 1000°C

System	b_0	b_1	b_2	Validity range[a]
Na_3AlF_6–Li_3AlF_6	99·945	−15·154	− 3·061	0−1
Na_3AlF_6–LiF	100·050	−81·499	4·114	0−1
Na_3AlF_6–NaCl	99·801	−58·850	−24·267	0−1
Na_3AlF_6–AlF_3	100·020	−63·785	45·069	0−0·67
Na_3AlF_6–Al_2O_3	99·935	−31·959	−32·292	0−0·24
Na_3AlF_6–SiO_2	99·884	−69·841	− 3·116	0−0·18

[a] Mole fraction of the second component.

The Na_3AlF_6–Li_3AlF_6 system behaves almost ideally, the Na_3AlF_6–AlF_3 system nonideally. For a comparison between the molar volumes of the ternary Na_3AlF_6–Li_3AlF–AlF_3 system[4,10] calculated according to Eq. (*3*) and experimental ones, a section of this system was taken with a constant AlF_3 content of 16·65 mol%, which corresponds to the cryolite ratio of 2·5. It holds for the deviation between the calculated and experimental values that $V_{exp} - V_{calc} < 0{\cdot}4\ cm^3\ mol^{-1}$. Further we have at our disposal the values of molar volumes in the binary Li_3AlF_6–AlF_3 system. Experimental V_{exp} values in this system were precised by the least squares method[7] and compared with V_{calc} values obtained by Eq. (*3*) from molar volumes of Na_3AlF_6–Li_3AlF_6 and Na_3AlF_6–AlF_3 systems. For the systems containing 0, 10, 20, 30, 40, 50, 60, and 70 mol% AlF_3, the $V_{calc}(V_{exp})$ ($cm^3\ mol^{-1}$) values are as follows: 81·73 (81·79); 77·94 (78·13); 74·95 (74·12); 72·80 (71·73); 71·49 (69·34);

71·02 (67·70); 71·38 (66·99); 72·59 (67·38). Thus, the molar volume of one binary system was calculated in this case from known molar volumes of two binary systems. Satisfactory agreement between experimental and calculated values of the molar volumes is found only below 30 mol% AlF_3. It is necessary to note that during measuring densities in systems with a high AlF_3 content, especially in the Li_3AlF–AlF_3 system, considerable experimental difficulties are encountered and accuracy of the measurements decreases. Interestingly, the calculations have confirmed that the molar volume in the Li_3AlF_6–AlF_3 system decreases to the value of the AlF_3 concentration of ~50–60 mol%, but it increases again at higher AlF_3 contents. This fact might be explained by formation of complex AlF_4^- ion.

Volumetric properties in the ternary Na_3AlF_6–Li_3AlF_6–Al_2O_3 system were studied[9,10] up to the concentration 18 mol% Al_2O_3. Agrement between the experimental and calculated values of the molar volumes is excellent; it is better than the experimental error which is equal to 0·2%.

As the solubility of Al_2O_3 in a Na_3AlF_6–NaCl–Al_2O_3 system[2,6] at constant temperature decreases with increasing NaCl content, this system has been studied in the following concentration range: from zero to 16, 12, 10, and 7 mol% Al_2O_3 and, in the same order, from zero to 12, 20, 30, and 40 mol% NaCl. Deviations between the calculated and experimental molar volumes are comparable with the experimental error of 0·3%.

The Na_3AlF_6–Al_2O_3–SiO_2 system[5] was studied in the concentration ranges 0–12 mol% Al_2O_3 and 0–18 mol% SiO_2. Fair agreement between the calculated and experimental values has been found (0·4%). It is necessary to realize that especially the density measurements in the Na_3AlF_6–SiO_2 system can contain systematic errors due to a chemical reaction between the components in this system.

It has been shown on the given examples of the cryolite melts that the proposed method for calculating the molar volume of ternary melts according to Eq. (*3*) yields results which are in good agreement with experiment. A further advantage of this procedure is the possibility to decrease considerably the number of density measurements in ternary systems. It also enables to write down experimental results in a short and simultaneously accurate form. This last benefit is preserved even when the molar volumes calculated by Eq. (*3*) differ from experimental values. The deviation between experimental and calculated data may be expressed in this case in the form of an empiric function of concentration of both components.

The calculation of molar volumes in ternary systems according to Eq. (*3*) has been proved quite satisfactory in the case of the cryolite melts studied, as the difference between the calculated and experimental values is comparable with experimental error.

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Translated by K. Hlavatý.