DENSITIES AND MOLAR VOLUMES OF THE $Ca(NO_3)_2$–$CaBr_2$–H_2O SYSTEM

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Molar volumes and densities of mixtures consisting of water, calcium nitrate, and calcium bromide have been determined in the range of molar ratio of water within 3 to 18 and in the temperature range of 20 to 80°C. The obtained results have been described by an equation derived under the assumption that additivity of molar volumes of the components is valid.

The published results on molar volumes of ternary systems show that assumption of additivity of molar volumes can be applied in case of mixtures of anhydrous salts and molten hydrates[1–3] and for mixtures of molten hydrates[4], but that it is inapplicable for concentrated solutions[5]. Additivity of apparent molar volumes of electrolytes has been verified in the region of highly concentrated solutions[6] and used in the discussion of their structure[7]. Capability of highly concentrated calcium nitrate solutions[8] and derived ternary systems[9] to be supercooled allows to examine their densities in a wide temperature and concentration ranges and to verify validity of the assumption of additivity of molar volumes in the region of highly concentrated solutions. In the present paper, ternary system $Ca(NO_3)_2$–$CaBr_2$–H_2O is studied with the aim to rationalize processing and storing of extensive sets of experimental data on density in ternary systems.

EXPERIMENTAL

$Ca(NO_3)_2 . 4\,H_2O$ of A.R. grade purity (Lachema) and $CaBr_2 . x\,H_2O$ of R.G. purity (Merck) were employed for the preparation of samples. The mixtures to be followed were prepared by mixing weighed amounts of both salts in a calculated ratio and by addition or evaporation of water. The calcium content in the mixture was determined complexometrically, the water content was expressed as $R_H = n_{H_2O}/n_{Ca}$, where n_{H_2O} and n_{Ca} are amounts of water and calcium in the sample. Precision of the determination of the R_H value in the region of low concentrations amounted approximately to $\pm 0{\cdot}05$.

The densities were determined by a commercially available apparatus[10] with indicated precision of $\pm 0{\cdot}0005$ g cm^{-3} (Digital Densimeter DMA 40 manufactured by Anton Paar K.G.). Details concerning the calibration have been described elsewhere[11]. Analysis of the experimental arrangement, calibration and stability of temperature in the course of the measurements allows to consider precision of the obtained data to be better than $\pm 1 . 10^{-3}$ g cm^{-3}.

The density of mixtures with the water content within R_H values of 3 to 18 was determined for the anion fraction $y = n_{Br}/(n_{Br} + n_{NO_3})$ values of 0·1, 0·2, 0·3, 0·4, 0·5 and for binary system $CaBr_2$—H_2O. The measurement was carried out in the temperature range of 20 to 60°C provided that precipitation of the solid phase during lowering the temperature did not take place. Many solutions were present in a supercooled state during the measurements, but it is impossible to define them exactly because of the lack of a phase diagram of the system.

RESULTS AND DISCUSSION

The obtained density values for various mixtures of $Ca(NO_3)_2$–$CaBr_2$–H_2O were processed in a form of isothermal dependence of molar volume on the mole fraction of hydrated calcium bromide in mixture $Ca(NO_3)_2.aH_2O$–$CaBr.bH_2O$, in a way described in the literature[2]. It has been established by statistical evaluation of obtained parameters of straight-line regressive dependences for various combinations of the a and b coefficients in the range of 4 or 6 to 10 that validity of the assumption of additivity of molar volumes is limited not only to the mixture of molten $Ca(NO_3)_2$ . . 4 H_2O and $CaBr_2$.6 H_2O hydrates. A comparable fit to the linear dependence of molar volume upon composition was found also for further combinations of parameters a and b within the range examined.

For final treatment of the experimental data, limited additivity of molar volumes of the system components involving $Ca(NO_3)_2$, $CaBr_2$, and H_2O was assumed. The principle of the limited additivity starts from a conception of a ternary system of two salts and water whose molecules are deformed in the force field of ions.

The molar volumes of both salts were considered to be independent of concentration of the other components in the system, the molar volume of water being taken into account as a function of R_H, *i.e.* ratio of the number of water molecules to that of the salt molecules in the system. Effect of both salts on thus defined apparent molar volume of water was in the first approximation regarded as equivalent. The dependence of molar volumes on temperature t was approximated by a linear dependence in the form

$$V_i = A_i + B_i \, . \, t \qquad (1)$$

which is for the experimental temperature range fully in accordance with the published results[2,3].

The presented anticipations are in contrast to the employed conception of apparent molar volumes of salts. In this approach the molar volume of water is considered a constant parameter independent of concentrations of the components and all deviations from the additivity are included into the apparent molar volumes of the electrolytes, which may be expressed as a linear function of the second root of salt concentration[12]. This approach has been verified not only for dilute solutions, but it was also used for extrapolation towards the region of concentrated solutions by introducing apparent molar volume of anhydrous electrolyte and a series of simplifying anticipations.

The conception of the apparent molar volume of water, used by us, presents an alternate approach to the problem or molar volumes of highly concentrated solutions. On the basis of the given assumptions an equation was obtained describing dependence of the molar volume of the ternary system on temperature and composition in the form allowing extrapolation also beside the concentration region followed experimentally

$$V = (A_1 + B_1 t)\, x_1 + (A_2 + B_2 t)\, x_2 + [(A_3 + B_3 t + C_3 R_H)/(R_H + D_3)]\, x_3\,, \quad (2)$$

where $x_1 = (1 - y)/(R_H + 1)$, $x_2 = y/(R_H + 1)$, and $x_3 = R_H/(R_H + 1)$ are mole fractions of $Ca(NO_3)_2$, $CaBr_2$, and H_2O, respectively. A_1 to A_3 indicate molar volumes of the components at the temperature of 0°C, B_1 to B_3 denote coefficients of the temperature dependence of molar volumes of components; C_3, D_3 are coefficients of the concentration dependence of molar volume of water, and t denotes the temperature (°C).

The parameter values A_1 and B_1 were obtained by processing a set of eighty experimental data[13] of binary system $Ca(NO_3)_2$–H_2O in a concentration range, R_H, of 2·7 to 18. When using the given assumptions, values $A_1 = 68{\cdot}86$ and $B_1 = 0{\cdot}0264$. The calculated value of molar volume of $Ca(NO_3)_2.4\,H_2O$ amounts to 136·5 and 138·8 for temperatures of 60°C and 100°C, respectively, this being in good agreement with values 137·4 and 139·8 given in the literature[1,14].

With use of calculated values of parameters A_1 and B_1 a set of 134 experimental data on density for the y values within 0·1 – 0·5, and data achieved for binary system $CaBr_2$–H_2O were processed. The values of obtained parameters of equation (2) are summarized in Table I together with values of standard deviations.

It is true that statistical tests prove significance of the dependence of molar volume of calcium nitrate on temperature, but in the temperature range examined, the tempe-

TABLE I

Values and Standard Deviations of Parameters of Equation (2)

i	A_i cm^3 mol^{-1}	B_i cm^3 mol^{-1} K^{-1}	C_i cm^3 mol^{-1}	D_i —
1	68·86 ± 0·14	0·026 ± 0·001	—	—
2	56·69 ± 0·70	0·024 ± 0·017	—	—
3	15·19 ± 0·21	0·008 ± 0·001	2·53 ± 0·10	8·40 ± 2·43

rature dependence of molar volumes of salts may be for rougher approximations neglected. More significant is dependence of the molar volume of water on its concentration in the system, which may be accounted for mutual interaction of water molecules in the coordination sphere of ions. Extrapolated value of the molar volume of water amounts to 17·72 $cm^3 mol^{-1}$ at the temperature of 0°C, which is in good accordance with a value of 18·018 $cm^3 mol^{-1}$ established experimentally[15].

Even though anticipations used for the derivation of relation (*2*) are very simplifying, the agreement of the model with experimental data is fairly good. The suggested relationship allows to calculate and store data on density of a ternary system on the basis of small number of parameters obtained, for example, by processing of experimental data of binary systems. Precision of the density values thus obtained (mean relative deviation of 0·36%) is comparable with that of a series of further physico-chemical magnitudes to the calculation of which it is employed (viscosity, el. conductivity). Validity of the relationship is not limited by the liquidus temperature and the relationship can be therefore used for obtaining data in the metastable supercooled region, which are necessary for calculations in the field of crystallization. In comparison with the used relations[16], relationship (*2*) represents a very condensed form for expression of the temperature-concentration dependence of the density of ternary systems.

Precision of obtained experimental data and calculated parameters does not allow to draw any more detailed conclusion on structure of the studied system.

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