

THE DENSITY AND THE MOLAR VOLUMES OF THE SYSTEM $\text{Ca}(\text{NO}_3)_2\text{-KNO}_3\text{-H}_2\text{O}$

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Received February 4th, 1980

The temperature and concentration dependence of the density of the system $\text{Ca}(\text{NO}_3)_2\text{-KNO}_3\text{-H}_2\text{O}$ was studied over a temperature range from -20 to $+75^\circ\text{C}$ and for concentrations given by ionic fractions of the potassium salt of 0.1, 0.2, 0.3, 0.4, and 0.5. The mole fraction of salts ranged from 0.052 to 0.27. The temperature and concentration dependence of calculated molar volumes has been correlated with an empirical equation, assuming additivity of the molar volumes of the salts. Deviations from the additivity principle are discussed and their quantitative description is proposed.

In studying some physico-chemical properties, such as viscosity, conductivity, *etc.*, it is necessary to know the temperature and concentration dependences of density of the system. The currently used methods of correlating the density¹⁻⁴ with polynomials of various types become rather unwieldy in the case of ternary systems, since polynomials with a large number of constants are involved. The number of constants can be reduced by using the assumption that the molar volumes of the components are additive.

The classical procedure⁵ is based on the concept of the apparent molar volumes of salts. This approach, however, fails to give a good representation of the volume of concentrated aqueous solutions and non-aqueous melts. Therefore, we have started from the concept of molar volumes of salts which make up an environment (continuum) in which water occurs whose volume is altered by the salts.

As a model, we have chosen the ternary system $\text{Ca}(\text{NO}_3)_2\text{-KNO}_3\text{-H}_2\text{O}$ which permits one, owing to its ease of supercooling, to acquire information on the density over wide temperature and concentration ranges.

EXPERIMENTAL

Basic solutions for the measurements were prepared by mixing calcium nitrate solutions of known concentration with dried and purified potassium nitrate in pre-calculated amounts such that required values could be reached of the quantity Z , the cationic fraction of potassium nitrate, defined as

$$Z = n_{\text{K}^+} / (n_{\text{K}^+} + n_{\text{Ca}^{2+}}),$$

where n_{K^+} and $n_{Ca^{2+}}$ are the mole numbers of the potassium and calcium ions, respectively.

So prepared basic solutions of $Z = 0.1, 0.2, 0.3, 0.4,$ and 0.5 were either diluted with calculated volumes of water, or concentrated by evaporation, so that desired values could be reached of the molar ratio, R , defined as

$$R = n_{H_2O} / (n_{Ca(NO_3)_2} + n_{KNO_3}),$$

where n_{H_2O} , $n_{Ca(NO_3)_2}$, and n_{KNO_3} are the mole numbers of water, calcium nitrate, and potassium nitrate, respectively.

All chemicals (Lachema) were of analytical reagent grade, and were purified prior to use by double crystallization from aqueous solution.

Although the density is considered easily accessible to experimental determination, some difficulties are encountered when this quantity is measured on highly concentrated aqueous solutions. These difficulties involve crystallization of supersaturated solutions, hygroscopicity at low temperatures while evaporation of water at high temperatures.

Most of the problems were eliminated by employing a DMA 40 densimeter (Anton Paar). The sample with a volume of 0.7 ml was thermostatted for 5 min in the closed measuring cell of the densimeter. An analytical check confirmed that the sample composition remained constant over the time of density measurement.

The water content of each sample was checked indirectly, by chelatometric titration of calcium with the use of Kalkon indicator.

The density of the system $Ca(NO_3)_2$ - KNO_3 - H_2O was measured on series of samples with $Z = 0.1, 0.2, 0.3, 0.4,$ and 0.5 . The concentration range was approximately the same for all the series, ranging from $R = 4$ to $R = 18$. The temperature dependence of density was followed over the range from $-20^\circ C$, or, alternatively, from the lowest temperature at which the sample still did not show crystallization, to $+75^\circ C$. The choice of both the upper and lower limits of the temperature interval was dictated by the working range of the instrument.

Since some of the strongly supercooled solutions showed crystallization at as little as $-7^\circ C$, the measurements could not be performed over the same temperature interval with all the series.

RESULTS AND DISCUSSION

The mean molar volumes of solutions were calculated from experimentally determined densities⁶ using the relation

$$V = (M_1x_1 + M_2x_2 + M_3x_3)/d, \quad (1)$$

where $M_1, M_2,$ and M_3 are the molar weights (g/mol) of the individual components, $x_1, x_2,$ and x_3 are the mole fractions of the individual components, d is the density in g/cm³, and V is the mean molar volume of a solution (cm³/mol) at a given composition and temperature.

A set of 192 molar volume data obtained in this way was combined with a set of 90 molar volumes calculated on the basis of density values measured by Ewing and Mikovsky¹ for the system calcium nitrate-water.

As a starting point for the data processing, we assumed the validity of the relation

$$V = (V_{01} + a_1t)x_1 + (V_{02} + a_2t)x_2 + (V_{03} + a_3t)x_3, \quad (2)$$

where the constants V_{01} , V_{02} , and V_{03} (cm^3/mol) have the meaning of the molar volumes of individual components at 0°C , the coefficients a_1 , a_2 , and a_3 ($\text{cm}^3/\text{mol K}$) characterize the thermal expansivity of the components, and t is the temperature in $^\circ\text{C}$.

Analysis of deviations of the calculated molar volumes from the experimental ones revealed that the molar volume of the system is given by the sum of molar volumes of components 1 and 2, and the formal molar volume of water. In the concentration range $2.71 < R < 12.4$, the latter varies linearly with R .

The same situation has been observed with the systems calcium nitrate–calcium bromide–water⁷ and calcium nitrate–calcium iodide–water⁸. The dependence of $V_{\text{H}_2\text{O}}$ on R has been allowed for by introducing the term bR into the expression for the formal molar volume of water, $V_{\text{H}_2\text{O}} = V_{03} + a_3t + bR$.

However, even this correction did not eliminate the deviations of the calculated molar volumes from the experimental ones, which still exhibited a linear dependence on Z . A further step was therefore to test whether there was a dependence of the formal molar volume of water on Z . The criterion for the fit of the correspondingly modified equation was the minimum of the sum of squares of deviations. The starting assumption may be considered as justified by the fact that the correction for Z applied to the molar volume of water results in a reduction of the sum of squares of deviations by 1.5 order of magnitude whereas similar corrections applied to the molar volumes of calcium nitrate and potassium nitrate do not reduce the sum of squares of deviations to any appreciable extent. Accordingly, the best agreement with experiment is attained with the use of the relation

$$V = (V_{01} + a_1t)x_1 + (V_{02} + a_2t)x_2 + (V_{03} + a_3t + bR + cZ)x_3, \quad (3)$$

where $x_1 = (1 - Z)/(1 + R)$, $x_2 = Z/(1 + R)$, $x_3 = R/(1 + R)$, and b and c are constants. The subscripts 1, 2, and 3 refer to calcium nitrate, potassium nitrate, and water, respectively.

Because of the appearance of R in the expression for the molar volume of water, Eq. (3) is unfit for extrapolations to the region of dilute solutions. The deviations in the molar volumes begin to increase for R higher than 12, which is, accordingly, the low-concentration limit of validity of the equation. Therefore, a set of 151 data for $R = 2.71\text{--}12.4$ and 55 data of Ewing and Mikovsky for $R = 2.75\text{--}8.98$ were used in the final data processing.

The least squares fitting yielded the following values for the constants of Eq. (3) and for the standard deviations:

TABLE I

Comparison of calculated molar volumes of $\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2$ and KNO_3 with the literature data

V , cm^3/mol	Determined in the system	Ref.
$\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$, 100°C		
140.32	$\text{Ca}(\text{NO}_3)_2\text{-H}_2\text{O}$	1
139.73	experimental value	12
139.90	calculated value	12
140.23	extrapolation	^a
142.64	$\text{Ca}(\text{CO}_3)_2\text{-CaCl}_2\text{-H}_2\text{O}$ -extrapolation	13
139.76	$\text{Ca}(\text{NO}_3)_2\text{-CaBr}_2\text{-H}_2\text{O}$ -extrapolation	7
139.97	$\text{Ca}(\text{NO}_3)_2\text{-CaI}_2\text{-H}_2\text{O}$ -extrapolation	8
$\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$, 50°C		
137.52	$\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}\text{-NH}_4\text{NO}_3$	3
136.74	$\text{Ca}(\text{NO}_3)_2\text{-Li, K, Na, NO}_3$	14
136.18	$\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}\text{-KNO}_3$	9
137.00	$\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$	15
136.74	$\text{Ca}(\text{NO}_3)_2 \cdot 4 \cdot 09 \text{H}_2\text{O}\text{-Cd}(\text{NO}_3)_2 \cdot 4 \cdot 07 \text{H}_2\text{O}$	16
136.71		^a
137.73	$\text{Ca}(\text{NO}_3)_2\text{-CaCl}_2\text{-H}_2\text{O}$	13
136.49	$\text{Ca}(\text{NO}_3)_2\text{-CaBr}_2\text{-H}_2\text{O}$	7
136.58	$\text{Ca}(\text{NO}_3)_2\text{-CaI}_2\text{-H}_2\text{O}$	8
$\text{Ca}(\text{NO}_3)_2$, 25°C		
69.29	$\text{Ca}(\text{NO}_3)_2\text{-H}_2\text{O}$	1
69.19		^a
69.66	$\text{Ca}(\text{NO}_3)_2\text{-CaCl}_2\text{-H}_2\text{O}$	13
69.50	$\text{Ca}(\text{NO}_3)_2\text{-CaBr}_2\text{-H}_2\text{O}$	7
69.40	$\text{Ca}(\text{NO}_3)_2\text{-CaI}_2\text{-H}_2\text{O}$	8
KNO_3 , 100°C		
49.64	extrapolation from melts	9
50.00	$\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}\text{-KNO}_3$	12
50.23	extrapolation	^a
49.73	extrapolation from melts	17

^a This work.

$$\text{for } \text{Ca}(\text{NO}_3)_2: V_{01} = 68.45 \pm 0.15, a_1 = (2.609 \pm 0.217) \cdot 10^{-2};$$

$$\text{for } \text{KNO}_3: V_{02} = 47.55 \pm 0.28, a_2 = (2.667 \pm 0.340) \cdot 10^{-2};$$

$$\text{for } \text{H}_2\text{O}: V_{03} = 15.93 \pm 0.05, a_3 = (1.116 \pm 0.034) \cdot 10^{-2};$$

$b = (6.352 \pm 0.356) \cdot 10^{-2}$, $c = (87.15 \pm 5.58) \cdot 10^{-2}$. The V_{0i} values are given in cm^3/mol , a_i in $\text{cm}^3/\text{mol K}$, b in cm^3/mol , and c in cm^3/mol . The average relative deviation of the molar volumes is 0.13%, and the maximum relative deviation is 0.61%. These deviations are within the limits of accuracy of the experimental methods employed, namely $\pm 5 \cdot 10^{-4} \text{ g/cm}^3$ for the density measurement, $\pm 2 \cdot 10^{-3}$ for the determination of mole fractions of the individual components, and $\pm 0.05^\circ\text{C}$ for the temperature measurement.

The applicability of Eq. (3) was verified by comparing the calculated molar volumes of potassium nitrate, calcium nitrate tetrahydrate, and calcium nitrate with the literature data obtained with various binary and ternary systems. The results are summarized in Table I.

Although the assumptions involved in the derivation of Eq. (3) are largely simplifying, it is evident from Table I that our results agree even with those literature data which were obtained at temperatures outside the temperature range used in this work. In none of the cases do the deviations exceed 1.2%.

Another fact which is proved by extrapolation from non-aqueous salt melts is that with the use of Eq. (3) it is possible to extrapolate the molar volumes of ternary systems incorporating water to zero water concentration, thus arriving at molar volumes of non-aqueous supercooled binary systems.

Comparing the molar volumes of water resulting from Eq. (3) with those obtained in formally the same way by Kodejš⁷ and Novák⁸, we see that with our system the molar volume of water depends not only on R but also on Z . Kodejš and Novák studied systems with a common cation. Since in our case solutions with a common anion are involved, it may be concluded that within the given temperature and concentration ranges it is the cation that has the decisive influence on the magnitude of the molar volume of water. This statement further implies that the cation is probably hydrated preferentially. This finding is consistent with Angell's postulate⁹⁻¹¹ of the existence of hydrated bivalent cations in hydrated melts of calcium nitrate and magnesium nitrate.

The final conclusion which can be drawn from the dependence of the molar volume of water on Z is that in the system under study the potassium ion is much less hydrated than the calcium ion.

Reliable quantitative comparison with theory will only be possible when larger amount of experimental data covering various systems have been accumulated.

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Translated by M. Škubalová.