# DENSITY OF AQUEOUS SOLUTIONS OF $Na_2CO_3$–$NaHCO_3$

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The paper deals with a correlation of the ternary systems $H_2O$–$Na_2CO_3$–$NaHCO_3$. The corresponding data have been correlated with an equation presuming the additivity of partial molar volumes, the components being water and the so-called basic solutions of $Na_2CO_3$ and $NaHCO_3$. From the comparison of experimental and calculated density values of the solutions of $Na_2CO_3$–$NaHCO_3$, $Na_2CO_3$, and $NaHCO_3$ at 20 °C it follows that the given procedure provides very precise results.

The aqueous solution of $Na_2CO_3$–$NaHCO_3$ can be classified as a ternary mixture formed by mixing water (component 1), basic solution of $Na_2CO_3$ (component 2), and basic solution of $NaHCO_3$ (component 3). The mixing can well be expressed by a ternary diagram (Fig. 1) involving the whole solubility range using the solubility data for $Na_2CO_3$–$NaHCO_3$ in water[1]. The peaks 1, 2, 3 represent water and the two basic solutions (in Fig. 1, the basic solutions are presumed in saturated state), the sides correspond to the binary mixtures, and the individual points inside the triangle correspond to the ternary mixtures. The solutions of $Na_2CO_3$–$NaHCO_3$ represented by points in the side line $\overline{23}$ are classified as binary mixtures from the standpoint of the components defined, although they contain three kinds of molecules.

Even with the saturated basic solutions of $Na_2CO_3$ and $NaHCO_3$ it is impossible – by only mixing them or mixing the basic solutions and water – to prepare the $Na_2CO_3$–$NaHCO_3$ solutions covering the whole solubility region. A part of such solutions are represented by points outside the triangle 123, lying in the region limited by the $\overline{23}$ side and solubility line. They can, however, be prepared by mixing the basic solutions of $Na_2CO_3$ and $NaHCO_3$ and subsequent evaporation of a part of water or evaporation of a part of water from a ternary mixture. These ways of preparation of solutions are graphically represented in Fig. 1 by a line crossing the points 1, P, Q and R. The solution whose composition is given by the point R can be prepared in the following way: First the solution represented by the point Q is prepared by mixing the basic solutions 2 and 3 and then water is evaporated as indicated by the line QR. The evaporation of water from the ternary mixture (point P) is represented by the line PR. The proportions of components in the resulting solution ($x_{1R}$, $x_{2R}$, $x_{3R}$) can be found in the known way, i.e. from the intercepts formed on the sides $\overline{12}$ and $\overline{23}$ by the parallel drawn to the sides of triangle and crossing the point R. Then the amount of evaporated water can be determined by application of the lever rule.

The idea of basic solutions inclusive of mixing with evaporation of water was used earlier in the context of the correlation of viscosity data of aqueous solutions of mixed electrolytes[2–6]. The aim of the present work is to make use of the concept of basic solutions and of the presumption of additivity of the partial molar volumes of components for refining the correlation data concerning the density of aqueous solutions of $Na_2CO_3$–$NaHCO_3$ which were published earlier[4] without taking into account the notion of partial molar volumes.

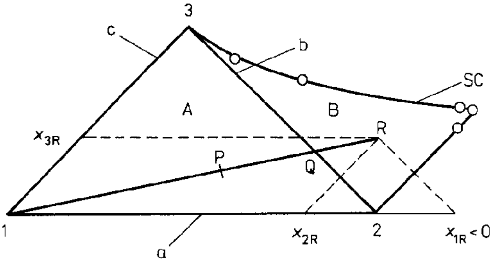

FIG. 1
Ternary diagram of system water (1)–solution of $Na_2CO_3$ (2)– solution of $NaHCO_3$ (3): Binary systems: a 1+2, b 2+3, c 1+3; ternary systems: A by mixing of 1+2+3, B obtained from 2+3 by evaporation of a part of water. SC solubility curve

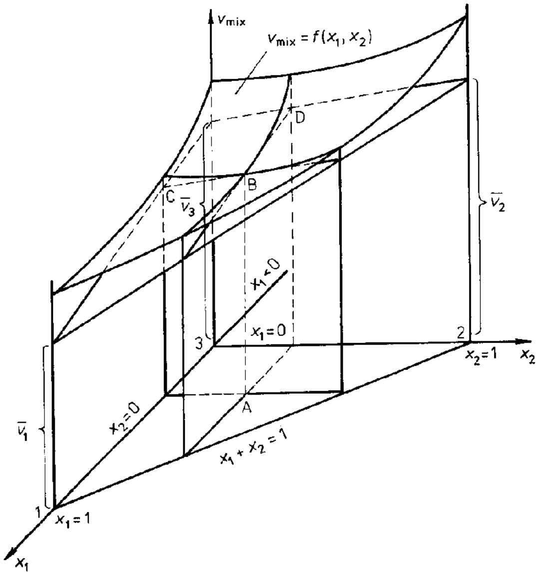

FIG. 2
A diagram for determination of partial molar volumes of ternary mixtures

## THEORETICAL

The molar volume of a ternary mixture can be obtained from the equation

$$v_{\mathrm{mix}} = \overline{v}_1 x_1 + \overline{v}_2 x_2 + \overline{v}_3 x_3 \; . \tag{1}$$

If the concentrations of the substances j and k (i.e. $Na_2CO_3$ and $NaHCO_3$) in this mixture are $c_{\mathrm{mix,j}}$ and $c_{\mathrm{mix,k}}$, then the molar volume of mixture is

$$v_{\mathrm{mix}} = [((\rho_{\mathrm{mix}} - c_{\mathrm{mix,j}} M_{\mathrm{j}} - c_{\mathrm{mix,k}} M_{\mathrm{k}})/M_1) + c_{\mathrm{mix,j}} + c_{\mathrm{mix,k}}]^{-1} \; . \tag{2}$$

In Eq. (*2*) $M_1$ stands for the molecular weight of water. By combining Eqs (*1*) and (*2*) it follows

$$[((\rho_{\mathrm{mix}} - c_{\mathrm{mix,j}} M_{\mathrm{j}} - c_{\mathrm{mix,k}} M_{\mathrm{k}})/M_1) + c_{\mathrm{mix,j}} + c_{\mathrm{mix,k}}]^{-1} = \\ = \overline{v_1} x_1 + \overline{v_2} x_2 + \overline{v_3} x_3 \; . \tag{3}$$

From the mass balance of mixing of water and the basic solutions of the concentrations $c_2$ and $c_3$ it follows

$$c_{\mathrm{mix,j}} = p c_2 \rho_{\mathrm{mix}}/(\rho_1 + p\rho_2 + q\rho_3) \tag{4}$$

$$c_{\mathrm{mix,k}} = q c_3 \rho_{\mathrm{mix}}/(\rho_1 + p\rho_2 + q\rho_3) \; . \tag{5}$$

The equations (*4*) and (*5*) make it possible to determine the volume ratios $p$, $q$ ($p = V_2/V_1$, $q = V_3/V_1$) necessary for obtaining the concentrations of substances j and k in the given solution after mixing.

$$p = c_{\mathrm{mix,j}} c_3 \rho_1/(c_2 c_3 \rho_{\mathrm{mix}} - c_2 c_{\mathrm{mix,k}} \rho_3 - c_{\mathrm{mix,j}} c_3 \rho_2) \tag{6}$$

$$q = c_{\mathrm{mix,k}} c_2 \rho_1/(c_2 c_3 \rho_{\mathrm{mix}} - c_2 c_{\mathrm{mix,k}} \rho_3 - c_{\mathrm{mix,j}} c_3 \rho_2) \; . \tag{7}$$

Then using the ratios $p$, $q$ and other quantities, one can express the fractions of components in the mixture

$$x_1 = c_1/z \tag{8}$$

$$x_2 = (p/z)[(\rho_2 - c_2M_\mathrm{j})/M_1 + c_2] \tag{9}$$

$$x_3 = (q/z)[(\rho_3 - c_3M_\mathrm{k})/M_1 + c_3] \, , \tag{10}$$

where

$$z = c_1 + p[(\rho_2 - c_2M_\mathrm{j})/M_1 + c_2] + q[(\rho_3 - c_3M_\mathrm{k})/M_1 + c_3] \, . \tag{11}$$

In Eq. (*8*), $c_1$ means water concentration 55.5 kmol $m^{-3}$.

For the points which at the same time lie outside the triangle 123 and in the solubility region it is $x_1 < 0$ (at the side of $\overline{23}$ it is $x_1 = 0$). This situation can physically be interpreted in such a way that the solutions represented by these points can be prepared by mixing the basic solutions and subsequent evaporation of a part of water or by evaporation of water from the ternary mixtures. With respect to the fact that water is removed from the systems in these cases, it is also $V_1 < 0$ and the volume ratios $p$ and $q$ assume negative values, too. The mole fractions of basic solutions $x_2$ and $x_3$ are increased in such a way that it is $x_1 + x_2 + x_3 = 1$.

When mixing only the basic solutions it is $V_1 = 0$, $p \to \infty$, $q \to \infty$, and the denominator of the fractions in Eqs (*6*) and (*7*) assumes the value of zero. In this case the mole fraction of water is $x_1 = 0$ and mole fractions of basic solutions are given by Eqs (*12*) and (*13*), in which $r$ means the ratio of volumes of basic solutions ($r = V_3/V_2$) obtainable from the mass balances of substances j or k (Eqs (*14*) and (*15*), respectively).

$$x_2 = [(\rho_2 - c_2M_\mathrm{j})/M_1 + c_2]/[(\rho_2 - c_2M_\mathrm{j})/M_1 + c_2 + r((\rho_3 - c_3M_\mathrm{k})/M_1 + c_3)] \tag{12}$$

$$x_3 = r[(\rho_3 - c_3M_\mathrm{k})/M_1 + c_3]/[(\rho_2 - c_2M_\mathrm{j})/M_1 + c_2 + r((\rho_3 - c_3M_\mathrm{k})/M_1 + c_3)] \tag{13}$$

$$r = (c_2\rho_\mathrm{mix} - c_\mathrm{mix,j}\rho_2)/c_\mathrm{mix,j}\rho_3 \tag{14}$$

$$r = c_\mathrm{mix,k}\rho_2/(c_3\rho_\mathrm{mix} - c_\mathrm{mix,k}\rho_3) \, . \tag{15}$$

Combining Eqs (*3*) and (*6*) – (*11*) we get Eq. (*16*)

$$\frac{1}{\dfrac{\rho_{\mathrm{mix}} - c_{\mathrm{mix,j}} M_{\mathrm{j}} - c_{\mathrm{mix,k}} M_{\mathrm{k}}}{M_1} + c_{\mathrm{mix,j}} + c_{\mathrm{mix,k}}} =$$

$$= \overline{v_1} \frac{c_1}{c_1 + \dfrac{c_{\mathrm{mix,j}} c_3 \rho_1}{c_2 c_3 \rho_{\mathrm{mix}} - c_2 c_{\mathrm{mix,k}} \rho_3 - c_{\mathrm{mix,j}} c_3 \rho_2} \gamma_2 + \dfrac{c_2 c_{\mathrm{mix,k}} \rho_1}{c_2 c_3 \rho_{\mathrm{mix}} - c_2 c_{\mathrm{mix,k}} \rho_3 - c_{\mathrm{mix,j}} c_3 \rho_2} \gamma_3} +$$

$$+ \overline{v_2} \frac{\dfrac{c_{\mathrm{mix,j}} c_3 \rho_1}{c_2 c_3 \rho_{\mathrm{mix}} - c_2 c_{\mathrm{mix,k}} \rho_3 - c_{\mathrm{mix,j}} c_3 \rho_2} \gamma_2}{c_1 + \dfrac{c_{\mathrm{mix,j}} c_3 \rho_1}{c_2 c_3 \rho_{\mathrm{mix}} - c_2 c_{\mathrm{mix,k}} \rho_3 - c_{\mathrm{mix,j}} c_3 \rho_2} \gamma_2 + \dfrac{c_2 c_{\mathrm{mix,k}} \rho_1}{c_2 c_3 \rho_{\mathrm{mix}} - c_2 c_{\mathrm{mix,k}} \rho_3 - c_{\mathrm{mix,j}} c_3 \rho_2} \gamma_3} +$$

$$+ \overline{v_3} \frac{\dfrac{c_2 c_{\mathrm{mix,k}} \rho_1}{c_2 c_3 \rho_{\mathrm{mix}} - c_2 c_{\mathrm{mix,k}} \rho_3 - c_{\mathrm{mix,j}} c_3 \rho_2} \gamma_3}{c_1 + \dfrac{c_{\mathrm{mix,j}} c_3 \rho_1}{c_2 c_3 \rho_{\mathrm{mix}} - c_2 c_{\mathrm{mix,k}} \rho_3 - c_{\mathrm{mix,j}} c_3 \rho_2} \gamma_2 + \dfrac{c_2 c_{\mathrm{mix,k}} \rho_1}{c_2 c_3 \rho_{\mathrm{mix}} - c_2 c_{\mathrm{mix,k}} \rho_3 - c_{\mathrm{mix,j}} c_3 \rho_2} \gamma_3} \,, \qquad (16)$$

where

$$\gamma_2 = (\rho_2 - c_2 M_{\mathrm{j}})/M_1 + c_2 \qquad (17)$$

$$\gamma_3 = (\rho_3 - c_3 M_{\mathrm{k}})/M_1 + c_3 \,. \qquad (18)$$

With the values of partial molar volumes of components at hand we can solve the nonlinear equation (*16*) (the concentrations of basic solutions being known) to obtain the density of aqueous solutions containing the substances j and k, i.e. $\rho_{\mathrm{mix}}$.

## EXPERIMENTAL

The densities of aqueous solutions of $Na_2CO_3$, $NaHCO_3$, and $Na_2CO_3$–$NaHCO_3$ were determined along with the corresponding viscosities according to the procedure described in ref.[4] where a part of results is presented in tables. All the solutions were prepared from chemicals of p.a. purity grade (Lachema Brno). The densities were measured by means of a Gay–Lussac pycnometer of 25 ml volume, the total error of determination being assessed as ±0.1 kg $m^{-3}$. In accordance with the report[4] the following calculations concerning the temperature of 20 °C adopted the below-given concentrations and densities of basic solutions: for $Na_2CO_3$: $c_2$ = 1.947 kmol $m^{-3}$, $\rho_2$ = 1 186.7 kg $m^{-3}$; for $NaHCO_3$: $c_3$ = 1.063 kmol $m^{-3}$, $\rho_3$ = 1 057.9 kg $m^{-3}$. According to the solubility data of $Na_2CO_3$ and

$NaHCO_3$ in water[1,7] it is possible to denote the basic solutions of $Na_2CO_3$ and $NaHCO_3$ as ca 97% saturated at 20 °C.

## RESULTS AND DISCUSSION

### *Approximation of Dependence of Molar Volume upon Composition of Solution*

The calculation of density of solutions from the nonlinear equation (*16*) necessitates the knowledge of partial molar volumes of the individual components. For this purpose, Eq. (*2*) was used at first to calculate – from the density values – the molar volumes of solutions with various concentrations of $Na_2CO_3$ and $NaHCO_3$. As it is $x_1 + x_2 + x_3 = 1$, the dependence of molar volume on mole fraction can be expressed analytically by Eq. (*19*),

$$v_{\mathrm{mix}} = a_0 + a_1x_1 + a_2x_1^2 + a_3x_2 + a_4x_2^2\,, \quad t = \mathrm{const.} \tag{19}$$

in which only two constants have to be determined from experimental data, because

$$a_0 = v_3 \tag{20}$$

$$a_2 = v_1 - v_3 - a_1 \tag{21}$$

$$a_4 = v_2 - v_3 - a_3\,, \tag{22}$$

as it follows from the conditions $x_1 = 0$, $x_2 = 0$, $v_{\mathrm{mix}} = v_3$; $x_1 = 1$, $x_2 = 0$, $v_{\mathrm{mix}} = v_1$, and $x_1 = 0$, $x_2 = 1$, $v_{\mathrm{mix}} = v_2$. In the case given, the constants $a_1$, $a_3$ were determined by linear regression using Eq. (*19*). The data set involved the data concerning the solutions for which both $x_1 < 0$ and $x_1 > 0$. Table I presents the constants of Eq. (*19*) valid in the intervals of $x_1$ and $x_2$ from –0.334 to 1.000 and from 0.000 to 1.000, respectively. The suitability of the correlation equation obtained was judged by the mean quadratic relative error calculated from Eq. (*23*).

TABLE I
Constants of Eq. (*19*) at 20 °C ($m^3\ kmol^{-1}$)

| $a_0 . 10^3$ | $a_1 . 10^3$ | $a_2 . 10^5$ | $a_3 . 10^5$ | $a_4 . 10^5$ |
|---|---|---|---|---|
| 18.224 | –29.866 | 10.754 | –69.262 | 19.633 |

$$\delta = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(\frac{v_{\mathrm{mix},i}^{\mathrm{exp}} - v_{\mathrm{mix},i}^{\mathrm{calc}}}{v_{\mathrm{mix},i}^{\mathrm{exp}}}\right)^2} \; . \; 100 \qquad (23)$$

For a set of 58 data this error is 0.062%.

## *Determination of Partial Molar Volumes of Ternary Mixture*

A procedure has been suggested in the present paper for determining the partial molar volumes of components of ternary mixture, which procedure can be considered a three-dimensional modification of the method of intercepts for determination of molar quantities of components in a binary mixture[8].

Figure 2 graphically represents, in a rectangular coordinate system ($x_1$, $x_2$, $v_{\mathrm{mix}}$), the surface $v_{\mathrm{mix}} = f(x_1, x_2)$ represented by Eq. (*19*). The definition region of the surface presented is given by the triangle 123 which forms a part of the plane $v_{\mathrm{mix}} = 0$ determined by the straight lines $x_1 = 0$, $x_2 = 0$, and $x_1 + x_2 = 1$. The point A in the plane $v_{\mathrm{mix}} = 0$ represents a state of a particular solution, the point B then is a point of the surface $v_{\mathrm{mix}} = f(x_1, x_2)$, and its height above the plane $v_{\mathrm{mix}} = 0$ represents the molar volume of a particular solution.

From analogy with the method of intercepts for determination of partial molar volumes of components in a binary mixture it is possible to find the partial molar volumes of components in a ternary mixture from the intercepts formed by the tangent plane to the surface $v_{\mathrm{mix}} = (x_1, x_2)$ in the point B at the straight lines $x_2 = 0$, $x_1 = 1$; $x_1 = 0$, $x_2 = 1$; and $x_1 = 0$, $x_2 = 0$. For mathematically expressing the tangent plane one must know two other points at it. These can be constructed, e.g., as the point of intersection of the tangent in point B in the direction of $x_2$ and the plane $x_2 = 0$ (point C) and as the point of intersection of tangent in point B in the direction of $x_1$ and the plane $x_1 = 0$ (point D). Hence the equation of the tangent plane to the surface $v_{\mathrm{mix}} = f(x_1, x_2)$, determined by the points B [$x_{1\mathrm{A}}$, $x_{2\mathrm{A}}$, $v_{\mathrm{B}}$], C [$x_{1\mathrm{A}}$, 0, $v_{\mathrm{C}}$], and D [0, $x_{2\mathrm{A}}$, $v_{\mathrm{D}}$], reads as follows:

$$\begin{vmatrix} x_1 & x_2 & v_{\mathrm{mix}} & 1 \\ x_{1\mathrm{A}} & x_{2\mathrm{A}} & v_{\mathrm{B}} & 1 \\ x_{1\mathrm{A}} & 0 & v_{\mathrm{C}} & 1 \\ 0 & x_{2\mathrm{A}} & v_{\mathrm{D}} & 1 \end{vmatrix} = 0 \; . \qquad (24)$$

The values of coordinates $v_{\mathrm{B}}$, $v_{\mathrm{C}}$, $v_{\mathrm{D}}$ of the points B, C, D can be determined from the equations:

$$v_{\mathrm{B}} = a_0 + a_1 x_{1\mathrm{A}} + a_2 x_{1\mathrm{A}}^2 + a_3 x_{2\mathrm{A}} + a_4 x_{2\mathrm{A}}^2 \qquad (25)$$

$$v_C = a_0 + a_1 x_{1A} + a_2 x_{1A}^2 \tag{26}$$

$$v_D = a_0 + a_3 x_{2A} + a_4 x_{2A}^2 \; . \tag{27}$$

The partial molar volumes of a particular solution, a point A, $\bar{v}_i$ ($i$ = 1, 2, 3) are obtained as a solution to Eq. (*24*) for $x_1 = 1$, $x_2 = 0$ ($\bar{v}_1 = v_{mix}$); $x_1 = 0$, $x_2 = 1$ ($\bar{v}_2 = v_{mix}$); and $x_1 = 0$, $x_2 = 0$ ($\bar{v}_3 = v_{mix}$).

In the case of binary mixtures the partial molar volumes are found by the known procedure[8] based on construction of tangent to the curve which is the line of intersection of the surface $v_{mix} = f(x_1, x_2)$ and the respective plane. Thus e.g. for a binary mixture 1+3 (water and basic solution of $NaHCO_3$), the curve expressed by Eq. (*19*) without the terms containing $x_2$ is the line of intersection of the surface $v_{mix} = f(x_1, x_2)$ and the plane $x_2 = 0$. The point A representing the considered binary mixture is at the $x_1$ axis, the point B is a point of the curve (the point C is identical with B), and the point D is at the $v_{mix}$ axis. The partial molar volumes of binary mixture, i.e. $\bar{v}_1$ and $\bar{v}_3$, are then determined from the intercepts formed by the tangent to the curve at the point B at the straight lines $v_1 = 1$, $x_2 = 0$ and at the $v_{mix}$ axis.

With respect to the fact that the partial molar volumes of components are functions of composition of solution, it was necessary to determine the partial molar volume by the procedure given for each of the 58 solutions measured.

### *Solution to Nonlinear Equation (*16)

The calculation itself of the density of solution $\rho_{mix}$ from the nonlinear equation (*16*) for $t$ = const. can be summarized in the following steps:

*1.* The calculation of molar volumes of water and basic solutions from the densities of water and basic solutions of $Na_2CO_3$ and $NaHCO_3$ using Eq. (*2*), i.e. $v_i$ ($i$ = 1, 2, 3), $v_1 = 18.03 \cdot 10^{-3}$ m$^3$ kmol$^{-1}$, $v_2 = 17.74 \cdot 10^{-3}$ m$^3$ kmol$^{-1}$, $v_3 = 18.23 \cdot 10^{-3}$ m$^3$ kmol$^{-1}$.

*2.* Starting the iteration calculation of $\rho_{mix}$ for a given composition of particular solution expressed by the molar concentrations $c_{mix,j}$ and $c_{mix,k}$ under the presumption $\bar{v}_i = v_i$ (i = 1, 2, 3). This presumption is necessary because $\bar{v}_i$ ($i$ = 1, 2, 3) are functions of the mole fractions $x_i$ which in turn depend on density (see Eqs (*8*) – (*11*)).

*3.* Solving the nonlinear equation (*16*) with respect to $\rho_{mix}$. This equation was solved by the secant method with the initial estimates of $\rho_{mix}^{(0)} = \rho_1$ and $\rho_{mix}^{(1)} = \rho_2$ . In this step the values $\rho_{mix}$ are obtained for the given values of $\bar{v}_i$ ($i$ = 1, 2, 3).

*4.* Calculation of new $\bar{v}_i$ ($i$ = 1, 2, 3) values from Eq. (*24*) using the values of $x_1$ and $x_2$ calculated from Eqs (*8*) – (*11*) for the density $\rho_{mix}$ obtained in the previous step.

*5.* The procedure given in points *3*, *4*, and *5* was repeated until reaching the required tolerance for $\rho_{mix}$ and $\bar{v}_i$ ($i$ = 1, 2, 3) between two subsequent iterations. The criterion for stopping the iteration procedure was the requirement of relative change in $\bar{v}_i$ ($i$ = 1, 2, 3) smaller than 0.01% and the requirement of the residuum of Eq. (*16*) smaller than $5 \cdot 10^{-9}$ m$^3$ kmol$^{-1}$.

### *Density of Aqueous Solutions of $Na_2CO_3$ and $NaHCO_3$*

Using Eq. (*16*), one can determine not only the densities of solutions of $Na_2CO_3$–$NaHCO_3$ but also those of solutions of $Na_2CO_3$ and those of $NaHCO_3$. In this case the terms involving the ratio of volumes $q$ and/or $p$ will not make themselves felt in Eq. (*16*). For aqueous solutions of $Na_2CO_3$ it is $q = 0$ because $V_3 = 0$, and for those of $NaHCO_3$ it is $p = 0$ ($V_2 = 0$). Table II presents a comparison of experimental and calculated density values of the solutions of $Na_2CO_3$ or $NaHCO_3$ at 20 °C. From the tabular presentation of results it follows that the procedure suggested gives reliable results.

TABLE II
Comparison of experimental and calculated density values of aqueous solutions of $Na_2CO_3$ and $NaHCO_3$ at 20 °C

| $c_{\mathrm{mix,j}}$, kmol m$^{-3}$ | $c_{\mathrm{mix,k}}$, kmol m$^{-3}$ | $\rho_{\mathrm{mix,exp}}$, kg m$^{-3}$ | $\rho_{\mathrm{mix,calc}}$, kg m$^{-3}$ | $\delta \cdot 10^2$, % |
|---|---|---|---|---|
| | | Solutions of $Na_2CO_3$ | | |
| 0.196 | 0.000 | 1 019.4 | 1 018.7 | 6.9 |
| 0.397 | 0.000 | 1 040.1 | 1 039.4 | 6.7 |
| 0.595 | 0.000 | 1 060.8 | 1 059.4 | 13.2 |
| 0.785 | 0.000 | 1 078.6 | 1 078.3 | 2.8 |
| 0.978 | 0.000 | 1 097.2 | 1 097.1 | 0.9 |
| 1.025 | 0.000 | 1 101.6 | 1 101.7 | –0.9 |
| 1.332 | 0.000 | 1 129.1 | 1 130.8 | 15.0 |
| 1.804 | 0.000 | 1 173.8 | 1 174.0 | –1.7 |
| | | Solutions of $NaHCO_3$ | | |
| 0.000 | 0.209 | 1 010.8 | 1 010.8 | 0.0 |
| 0.000 | 0.311 | 1 016.7 | 1 016.8 | –1.0 |
| 0.000 | 0.415 | 1 022.6 | 1 022.7 | –1.0 |
| 0.000 | 0.620 | 1 034.4 | 1 033.9 | 4.8 |
| 0.000 | 0.823 | 1 045.9 | 1 044.2 | 16.2 |

$\delta = [(\rho_{\mathrm{mix,exp}} - \rho_{\mathrm{mix,calc}})/\rho_{\mathrm{mix,exp}}] \cdot 100$

### *Density of Aqueous Solutions of $Na_2CO_3$–$NaHCO_3$*

The experimental and calculated (from Eq. (*16*)) values of density of aqueous solutions of $Na_2CO_3$–$NaHCO_3$ are compared in Table III. In the lower part of the table the aqueous solutions of $Na_2CO_3$–$NaHCO_3$ whose state is represented by the points lying

TABLE III
Comparison of experimental and calculated density values of aqueous solutions of $Na_2CO_3$–$NaHCO_3$ at 20 °C

| $c_{mix,j}$, kmol m$^{-3}$ | $c_{mix,k}$, kmol m$^{-3}$ | $\rho_{mix,exp}$, kg m$^{-3}$ | $\rho_{mix,calc}$, kg m$^{-3}$ | $\delta \cdot 10^2$, % |
|---|---|---|---|---|
| 0.256 | 0.780 | 1 068.9 | 1 068.8 | 0.9 |
| 0.981 | 0.422 | 1 119.9 | 1 120.1 | –1.8 |
| 0.895 | 0.384 | 1 110.1 | 1 110.0 | 0.9 |
| 0.984 | 0.226 | 1 110.4 | 1 110.1 | 2.7 |
| 0.582 | 0.626 | 1 092.9 | 1 092.6 | 2.7 |
| 0.389 | 0.731 | 1 079.7 | 1 079.3 | 3.7 |
| 0.389 | 0.850 | 1 085.6 | 1 085.4 | 1.8 |
| 1.298 | 0.354 | 1 146.4 | 1 146.2 | 1.7 |
| 1.558 | 0.213 | 1 163.1 | 1 162.7 | 3.4 |
| 0.103 | 0.105 | 1 015.5 | 1 015.4 | 1.0 |
| 0.111 | 0.505 | 1 039.3 | 1 039.4 | –1.0 |
| 0.302 | 0.275 | 1 045.5 | 1 045.8 | –2.9 |
| 0.607 | 0.128 | 1 067.2 | 1 068.0 | –7.5 |
| 1.211 | 0.113 | 1 125.2 | 1 125.5 | –2.7 |
| 1.204 | 0.308 | 1 134.5 | 1 135.1 | –5.3 |
| 1.416 | 0.218 | 1 149.0 | 1 150.1 | –9.6 |
| 1.700 | 0.040 | 1 168.2 | 1 166.7 | 12.8 |
| 0.186[a] | 0.997 | 1 073.9 | 1 072.9 | 9.3 |
| 1.453[a] | 0.853 | 1 092.3 | 1 091.7 | 5.5 |
| 0.680[a] | 0.731 | 1 107.8 | 1 107.3 | 4.5 |
| 0.927[a] | 0.598 | 1 123.7 | 1 124.0 | –2.7 |
| 1.508[a] | 0.407 | 1 166.6 | 1 167.8 | –10.3 |
| 1.700[a] | 0.490 | 1 188.1 | 1 188.8 | –5.9 |
| 1.102[a] | 0.679 | 1 145.3 | 1 144.2 | 9.6 |
| 0.696[a] | 0.788 | 1 112.5 | 1 111.7 | 4.5 |
| 0.554[a] | 0.880 | 1 101.1 | 1 102.7 | –14.5 |

[a] Solutions with $x_1 < 0$.

outside the triangle 123 and for which $x_1 < 0$ (see Fig. 1) are marked. The analysis of relative errors shows that also in this case, Eq. (*16*) provides highly accurate results for the solutions with both $x_1 > 0$ and $x_1 < 0$.

The whole set of 58 experimental data was evaluated on the basis of mean quadratic relative error – this error is 0.044%.

Moreover, using experimental data on density of aqueous solutions of $Na_2CO_3$ and $NaHCO_3$ we determined the constants $A_i$ and $B_i$ of Eq. (*28*), which is used for correlating the density of electrolyte solutions with a single substance[7].

$$\rho_i = \rho_1 + A_i c_i - B_i c_i^{3/2} \quad , \quad t = \text{const.}, \quad i = \text{j}, \text{k} \quad . \tag{28}$$

Then the density of aqueous solutions of $Na_2CO_3$–$NaHCO_3$ was calculated from Eq. (*29*) according to ref.[7] using the constants $A_\text{j}$, $A_\text{k}$, $B_\text{j}$, $B_\text{k}$ (see Table IV).

$$\rho_\text{mix} = \rho_1 + (A_\text{j} c_\text{mix,j} + A_\text{k} c_\text{mix,k}) - (B_\text{j}^{2/3} c_\text{mix,j} + B_\text{k}^{2/3} c_\text{mix,k})^{3/2} \quad . \tag{29}$$

The suitability of Eq. (*29*) was verified by the calculation of mean quadratic relative error. For an identical set of 58 data this error is 0.077%. Tests of significance of the difference of residual scatter at the significance level of 5% showed that the calculation procedure according to Eq. (*16*) gives results which are statistically significantly better than those obtained from Eq. (*29*).

The report[4] dealing with correlation of viscosity data of aqueous solutions of $Na_2CO_3$–$NaHCO_3$ also gives the results concerning the correlation of density of solutions of $Na_2CO_3$–$NaHCO_3$ with the use of the simplified equation (*16*). There the simplification is given by the presumption that the partial molar volumes of components can be replaced by the molar volumes of components. From the tables presented in ref.[4] it follows that at 20 °C the deviations between the experimental and calculated density values of aqueous solutions with one substance are as high as 0.41%, being as high as 0.35% for solutions with two substances. Moreover, these deviations are unidirectional – always the calculated density values of solutions are smaller than those experimentally determined. The calculation procedure given in the present paper is more complex than that of ref.[4] (additional calculation of partial molar volumes) but it provides a

TABLE IV
Constants of Eq. (*28*) at 20 °C

| Substance | *A*, kg kmol$^{-1}$ | *B*, kg kmol$^{-1.5}$ m$^{1.5}$ | δ, % | *n* |
|---|---|---|---|---|
| $Na_2CO_3$ | 112.27 | 11.23 | 0.053 | 9 |
| $NaHCO_3$ | 63.67 | 6.90 | 0.025 | 7 |

substantially higher precision in correlations of density of aqueous solutions of $Na_2CO_3$–$NaHCO_3$.

## CONCLUSION

The densities of aqueous solutions of $Na_2CO_3$–$NaHCO_3$ have been correlated by means of an equation based on additivity of partial molar volumes. In applying this equation, we have used the earlier-introduced concept of basic solutions of $Na_2CO_3$ and $NaHCO_3$, i.e. solutions with precisely defined and measurable properties. Mutual mixing of these two solutions, or their mixing with water, or mutual mixing with subsequent evaporation of a part of water, or mixing of one individual solution with water can be used to prepare any solution of the given $Na_2CO_3$ and/or $NaHCO_3$ concentration. The comparison of experimental and calculated density data shows that the procedure suggested provides highly precise results and its application to other aqueous solutions containing two dissolved substances can be anticipated.

## SYMBOLS

| | |
|---|---|
| $A$ | constant in Eq. (*28*), kg kmol$^{-1}$ |
| $a_i$ | ($i$ = 0, 1 ... 4), constants in Eq. (*19*), m$^3$ kmol$^{-1}$ |
| $B$ | constant in Eq. (*28*), kg kmol$^{-1.5}$ m$^{1.5}$ |
| $c$ | molar concentration, kmol m$^{-3}$ |
| $M$ | molar mass, kg kmol$^{-1}$ |
| $n$ | number of experimental data |
| $p, q$ | ratios of volumes of basic solutions and water |
| $r$ | ratio of volumes of basic solutions, $r = V_3/V_2$ |
| $t$ | temperature, °C |
| $V$ | volume, m$^3$ |
| $v$ | molar volume, m$^3$ kmol$^{-1}$ |
| $\overline{v}$ | partial molar volume, m$^3$ kmol$^{-1}$ |
| $x$ | mole fraction |
| $z$ | group of physical quantities defined by Eq. (*11*), kmol m$^{-3}$ |
| $\gamma_i$ | ($i$ = 2, 3), group of physical quantities defined by Eqs (*17*) and (*18*), kmol m$^{-3}$ |
| $\delta$ | relative error, % |
| $\overline{\delta}$ | mean quadratic relative error, % |
| $\rho$ | density, kg m$^{-3}$ |
| Indexes | |
| calc | calculated value |
| exp | experimental value |
| $i$ | summation variable or related to substance (in Eq. (*28*)) |
| j | related to $Na_2CO_3$ |
| k | related to $NaHCO_3$ |
| mix | related to solution |
| 1 | related to component 1, i.e. water |
| 2 | related to component 2, i.e. basic solution of $Na_2CO_3$ |
| 3 | related to component 3, i.e. basic solution of $NaHCO_3$ |

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