CORRELATION OF DENSITY OF AQUEOUS SOLUTIONS OF NaOH, KOH, Na_2CO_3, AND K_2CO_3

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The paper deals with the correlation of density of aqueous solutions of NaOH, KOH, Na_2CO_3, and K_2CO_3 using an equation based on the additivity of molar volumes of components, the components being water and the so-called basic electrolyte solution with precisely defined and measurable properties. The procedure mentioned has been tested at 20 °C using literature data. The procedure has been shown to give very precise results.

A number of physico-chemical, balance, simulation and other calculations in chemical engineering require the knowledge of densities of solutions. For aqueous solutions of electrolytes containing a single substance there are sufficient data in available literature[1,2] though not always complete with respect to the concentration and/or temperature ranges. This gap is filled by the monograph[3]. The present paper does not want to add data about other systems, its aim is to show – using known systems – a way of correlating the data with the help of an equation based on the additivity of partial molar volumes using the concept of basic electrolyte solutions.

THEORETICAL

On the basis of the definition of solutions in the correlation of viscosity data of mixtures of electrolytes[4 – 7] an aqueous solution of an electrolyte (with a single substance) can be classified as a binary solution. This solution is formed by mixing the solvent, i.e. water (index 1) and the basic solution (index 2), i.e. a solution with defined and precisely measurable properties. The molar volume of a binary solution is given by Eq. (*1*)

$$v_{\text{mix}} = \bar{v}_1 x_1 + \bar{v}_2 x_2 \,. \qquad (1)$$

If the concentration of substance j in solution is $c_{\mathrm{mix,j}}$, the molar volume of this solution can be determined from Eq. (*2*)

$$v_{\mathrm{mix}} = \frac{1}{\dfrac{\rho_{\mathrm{mix}} - c_{\mathrm{mix,j}} M_{\mathrm{j}}}{M_1} + c_{\mathrm{mix,j}}} \,. \tag{2}$$

From the mass balance of the mixing of water and basic solution it follows

$$c_{\mathrm{mix,j}} = \frac{p\, c_2\, \rho_{\mathrm{mix}}}{\rho_1 + p\, \rho_2} \,, \tag{3}$$

where

$$p = V_2/V_1 \,. \tag{4}$$

The volume ratio p can be expressed from Eq. (*3*)

$$p = \frac{c_{\mathrm{mix,j}}\, \rho_1}{c_2\, \rho_{\mathrm{mix}} - c_{\mathrm{mix,j}}\, \rho_2} \tag{5}$$

and, using this quantity and further quantities, it is possible to determine the mole fractions of water and basic solution in the mixture:

$$x_1 = \frac{c_1}{c_1 + p\left(\dfrac{\rho_2 - c_2 M_{\mathrm{j}}}{M_1} + c_2\right)} \tag{6}$$

$$x_2 = \frac{p\left(\dfrac{\rho_2 - c_2 M_{\mathrm{j}}}{M_1} + c_2\right)}{c_1 + p\left(\dfrac{\rho_2 - c_2 M_{\mathrm{j}}}{M_1} + c_2\right)} \,. \tag{7}$$

The connection of Eqs (*1*) and (*2*) and combination with Eqs (*5*) – (*7*) leads to Eq. (*8*) where γ_2 is given by Eq. (*9*).

$$\frac{1}{\frac{\rho_{mix} - c_{mix,j} M_j}{M_1} + c_{mix,j}} = \bar{v}_1 \frac{c_1}{c_1 + \frac{c_{mix,j}\,\rho_1}{c_2\,\rho_{mix} - c_{mix,j}\,\rho_2}\gamma_2} + \bar{v}_2 \frac{\frac{c_{mix,j}\,\rho_1}{c_2\,\rho_{mix} - c_{mix,j}\,\rho_2}\gamma_2}{c_1 + \frac{c_{mix,j}\,\rho_1}{c_2\,\rho_{mix} - c_{mix,j}\,\rho_2}\gamma_2} \qquad (8)$$

$$\gamma_2 = \left(\frac{\rho_2 - c_2 M_j}{M_1} + c_2\right). \qquad (9)$$

If the basic solution of the concentration c_2 and density ρ_2 is defined, the nonlinear Eq. (*8*) can be solved numerically to give the density ρ_{mix} of the solution with a given volume ratio p.

RESULTS AND DISCUSSION

The aim of the work was to verify the calculation of density of the aqueous solutions (according to Eq. (*8*)) encountered in the calculations of absorption. The starting data concerning solutions of NaOH, KOH, Na_2CO_3, and K_2CO_3 were taken from literature[2,8,9] and they correspond to the temperature of 20 °C. The basic solutions chosen

TABLE I
Properties of basic solutions, t = 20 °C

Component j	Ref.	M_j [a] kg kmol^{-1}	c_2 kmol m^{-3}	ρ_2 kg m^{-3}	$v_2 \cdot 10^3$ [b] m^3 kmol^{-1}
NaOH	8	40.00	19.419	1 531.2	16.31
KOH	9	56.11	13.076	1 499.4	17.98
Na_2CO_3	2	105.99	1.968	1 189.1	17.72
K_2CO_3	2	138.21	5.582	1 543.0	20.64

[a] Taken from ref.[3]; [b] calculated according to modified Eq. (*2*).

for our purposes (Table I) were always the solutions with the highest accessible concentration of electrolyte so that the procedure suggested might enable the density calculation in the largest possible concentration range.

The application of Eq. (*8*) to calculation of density of aqueous solution of electrolyte requires the knowledge of partial molar volumes of both water and the basic solution. These quantities represent a complex function of concentration of both the components and other physical properties of the system and can only be determined on the basis of experiment. One of the methods of determination of partial molar volumes of components in a binary mixture is based on a construction of tangent to the curve $v_{mix} = f(x_2)$ in the given point. From the intercepts formed by the tangent at the straight lines $x_2 = 0$ and $x_2 = 1$ it is then possible to determine the partial molar volumes[10]. The determination of the value of derivative from the direct measurements is useless due to the transformation of experimental error into the final result. A more advantageous procedure is based on the approximation of dependence of molar volume on mole fraction by a suitable, easily differentiated function.

Using available literature data, we calculated the values v_{mix} and x_2 of selected aqueous solutions with the help of Eqs (*2*), (*5*), and (*7*), the densities of aqueous solutions of NaOH and KOH being obtained by the recalculation of the apparent partial molar volumes of the substances published in refs[8,9]. The dependences of the molar volume of solution on the mole fraction of the basic solution are given in Fig. 1 for the individual solutions. It was shown that these dependences can be expressed very accurately by the 3rd order polynomials

$$v_{mix} = a_0 + a_1 x_2 + a_2 x_2^2 + a_3 x_2^3 . \qquad (10)$$

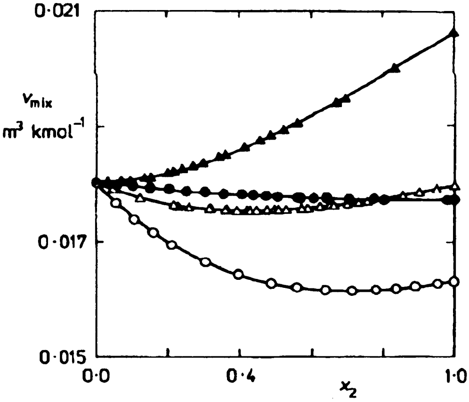

FIG. 1
Dependence of molar volume of aqeous solutions on mole fraction of basic solution of electrolyte: ○ NaOH, △ KOH, ● Na_2CO_3, ▲ K_2CO_3; —— the values calculated according to regression Eq. (*10*)

The constants of the regression relation (*10*) are given in Table II which also presents the mean quadratic relative errors and values of the maximum relative error for the individual electrolytes. When evaluating the coefficients of Eq. (*10*) we excluded those tabulated values for which the relative deviation between the values of molar volume calculated from the regression relation (*10*) and the v_{mix} values obtained by recalculation of starting data exceeded 0.1%.

The calculation of density ρ_{mix} from the nonlinear Eq. (*8*) can be summarized in the following steps:

1. The choice of basic electrolyte solution (c_2, ρ_2) – the highest possible concentration of electrolytes was chosen.

2. The calculation of molar volume of water ($v_1 = 18.03 \cdot 10^{-3}$ m^3 kmol^{-1}) and of the basic solution, v_2 (see Table I) from Eq. (*2*).

3. Start of the iteration calculation under the presumption of $\bar{v}_i = v_i$ ($i = 1, 2$). This presumption is necessary because the $\bar{v}_i$ values ($i = 1, 2$) are a function of the mole fraction x_2 which depends on the density (see Eqs (*5*) and (*7*)).

4. The solution of the nonlinear Eq. (*8*) with respect to ρ_{mix}. The equation was solved by the secant method with the initial assessments $\rho_{mix}^{(0)} = \rho_1$ and $\rho_{mix}^{(1)} = \rho_2$. In this step the corrected values of ρ_{mix} are obtained.

5. Refining of $\bar{v}_i$ values ($i = 1, 2$) with the use of Eq. (*10*), the corrected ρ_{mix} values being used in calculating x_2.

6. The procedure in steps 4 and 5 is repeated until reaching a satisfactory agreement between two subsequent iterations. The criterion chosen for finishing the iteration procedure was the requirement of relative change in $\bar{v}_i$ ($i = 1, 2$) below 0.01% and, at the same time, that of the residuum of Eq. (*8*) below $5 \cdot 10^{-9}$ m^3 kmol^{-1}.

The results of the procedure mentioned are summarized in Tables III – VI comparing the tabulated and calculated density values of the aqueous solutions considered. The

TABLE II
Constants of polynomials (*10*) (in m^3 kmol^{-1}), t = 20 °C

Component	$a_0 \cdot 10^3$	$a_1 \cdot 10^3$	$a_2 \cdot 10^3$	$a_3 \cdot 10^3$	$\bar{\delta}$[a], %	δ_{max}[b], %
NaOH	18.01	-6.410	6.865	-2.163	0.046	0.089
KOH	18.02	-2.480	3.674	-1.238	0.039	0.085
Na_2CO_3	18.03	-0.761	0.613	-0.162	0.027	0.094
K_2CO_3	18.02	0.163	3.805	-1.352	0.040	0.096

[a] $\bar{\delta} = \left\{\frac{1}{n}\sum_{i=1}^{n}[(v_{i,tab} - v_{i,calc})/v_{i,tab}]^2\right\}^{1/2} \cdot 100$;

[b] $\delta_{max} = \max(|\delta_1|, |\delta_2|, \ldots |\delta_n|)$, where $\delta_i = [(v_{i,tab} - v_{i,calc})/v_{i,tab}] \cdot 100$ $i = 1, 2, \ldots n$.

precision of the correlation can also be evaluated from the values of the mean quadratic relative errors and from those of the maximum relative errors. From these values it follows that the calculation of density of aqueous solutions of NaOH, KOH, Na_2CO_3, and K_2CO_3 from Eq. (*8*) provided very precise results in all the cases.

The numerical solution of the nonlinear Eq. (*8*), which requires an iterative determination of ρ_{mix} and $\bar{v}_i$ (i = 1, 2), can be simplified by introducing the presumption $\bar{v}_i = v_i$ (i = 1, 2). However, this presumption causes an increase in relative errors between the tabulated and calculated density values. The simplified procedure was preliminarily verified for aqueous NaOH solutions, the relative errors found being ca 3%. In contrast to the earlier reports[4 – 7], which, like the present paper, are based on the concept of mixing water and basic solutions, the present paper adopts the partial molar volumes for the first time. The increase in reliability of the whole procedure is obvious.

The correlation of density of aqueous solutions of electrolytes is usually carried out with the use of Eq. (*11*) (ref.[3])

$$\rho_{mix} = \rho_1 + A\, c_{mix,j} + B\, c_{mix,j}^{3/2} \qquad t = \text{const.} \qquad (11)$$

TABLE III

Comparison of tabulated[8] and calculated density values of aqueous solutions of component j = NaOH according to Eqs (*8*) and (*11*), t = 20 °C

$c_{mix,j}$ kmol m^{-3}	$\rho_{mix,tab}$ kg m^{-3}	$\rho^{I}_{mix,calc}$ kg m^{-3}	$\delta^{I} \cdot 10^{2\,a}$, %	$\rho^{II}_{mix,calc}$ kg m^{-3}	$\delta^{II} \cdot 10^{2\,a}$, %
1.009	1 040.9	1 040.6	2.9	1 041.2	2.9
1.978	1 079.1	1 078.3	7.4	1 079.0	0.9
2.961	1 115.0	1 114.5	4.5	1 114.9	0.9
3.946	1 149.2	1 149.0	1.7	1 149.0	1.7
5.834	1 210.2	1 210.6	−3.3	1 210.0	1.7
7.641	1 263.9	1 264.5	−4.7	1 263.7	1.6
9.533	1 316.0	1 316.3	−2.3	1 315.6	3.0
10.940	1 351.7	1 352.0	−2.2	1 351.6	0.7
12.493	1 389.1	1 388.9	1.4	1 389.1	0.0
14.005	1 423.0	1 422.7	2.1	1 423.4	−2.8
15.297	1 450.4	1 450.1	2.1	1 451.0	−4.1
16.365	1 472.0	1 471.9	0.7	1 472.8	−5.4
17.407	1 492.6	1 492.5	0.7	1 493.1	−3.4
18.562	1 514.8	1 514.8	0.0	1 514.6	1.3
19.419	1 531.2	1 531.2	0.0	1 529.9	8.5

[a] Characteristics: $\bar{\delta}^{I}$ = 0.029 %, $\bar{\delta}^{II}$ = 0.034 %, n = 15; δ^{I}_{max} = 0.074 %, δ^{II}_{max} = 0.085 %.

For the individual solutions (NaOH, KOH, Na_2CO_3, K_2CO_3) the constants of Eq. (*11*) were determined by linear regression of the starting data sets like in the case of application of Eq. (*8*), and they are summarized in Table VII. The density values calculated from Eq. (*8*) are given in Tables III – VI. From the comparison of the mean quadratic relative errors it follows that the calculation procedure based on the nonlinear Eq. (*8*) provides more reliable results than that based on Eq. (*11*) in the cases of large concentration ranges, i.e. for the aqueous solutions of NaOH and KOH. In the cases of small concentration ranges (Na_2CO_3 solutions) both the methods exhibit comparable accuracy. For aqueous solutions of K_2CO_3, characterized by a larger relative change of molar volume in the given concentration interval (Fig. 1), it was found that the simple Eq. (*11*) gives more accurate results – judged by the value of mean quadratic relative error.

TABLE IV

Comparison of tabulated[9] and calculated density values of aqueous solutions of component j = KOH according to Eqs (*8*) and (*11*), t = 20 °C

$c_{\mathrm{mix},j}$ kmol m^{-3}	$\rho_{\mathrm{mix,tab}}$ kg m^{-3}	$\rho^{\mathrm{I}}_{\mathrm{mix,calc}}$ kg m^{-3}	$\delta^{\mathrm{I}} \cdot 10^2$ [a], %	$\rho^{\mathrm{II}}_{\mathrm{mix,calc}}$ kg m^{-3}	$\delta^{\mathrm{II}} \cdot 10^2$ [a], %
0.578	1 026.9	1 026.8	1.0	1 026.8	1.0
1.662	1 077.5	1 076.9	5.6	1 077.0	4.6
2.909	1 132.0	1 131.5	4.4	1 131.4	5.3
3.500	1 156.9	1 156.3	5.2	1 156.1	6.9
4.192	1 184.9	1 184.7	1.7	1 184.4	4.2
4.870	1 212.1	1 211.8	2.5	1 211.5	5.0
5.255	1 226.7	1 226.8	-0.8	1 226.6	0.8
5.636	1 241.3	1 241.6	2.4	1 241.3	0.0
6.037	1 256.6	1 256.8	1.6	1 256.7	-0.8
6.412	1 270.8	1 270.9	-0.8	1 270.8	0.0
7.101	1 296.3	1 296.3	0.0	1 296.4	-0.8
7.642	1 315.7	1 315.9	-1.5	1 316.1	-3.0
7.910	1 325.6	1 325.4	1.5	1 325.8	-1.5
8.646	1 350.6	1 351.4	-5.9	1 351.9	-9.6
9.324	1 375.0	1 374.8	1.5	1 375.5	-3.6
9.927	1 388.7	1 388.6	0.7	1 389.3	-4.3
10.024	1 398.7	1 398.7	0.0	1 399.4	-5.0
10.679	1 421.4	1 420.7	4.9	1 421.3	0.7
11.898	1 461.4	1 461.2	1.4	1 461.1	2.1
12.475	1 480.1	1 480.2	-0.7	1 479.5	4.1
13.076	1 499.4	1 499.4	0.0	1 498.4	6.7

[a] Characteristics: $\bar{\delta}^{\mathrm{I}} = 0.026$ %, $\bar{\delta}^{\mathrm{II}} = 0.038$ %, $n = 31$; $\delta^{\mathrm{I}}_{\mathrm{max}} = 0.059$ %, $\delta^{\mathrm{II}}_{\mathrm{max}} = 0.096$ %.

CONCLUSIONS

The applicability of an equation based on the presumption of additivity of partial molar volumes to calculation of density of aqueous solutions of NaOH, KOH, Na_2CO_3, and K_2CO_3 was tested. The calculation used the so-called basic solutions of electrolytes, established earlier, which have precisely defined and measurable properties. A solution of required concentration can then be obtained by mixing this basic solution with water. The analysis of experimental results shows that the procedure adopted provides reliable results and its application to correlations of density of other aqueous solutions can be anticipated.

TABLE V
Comparison of tabulated[2] and calculated density values of aqueous solutions of component j = Na_2CO_3 according to Eqs (*8*) and (*11*), t = 20 °C

$c_{\mathrm{mix},j}$ kmol m^{-3}	$\rho_{\mathrm{mix,tab}}$ kg m^{-3}	$\rho^{\mathrm{I}}_{\mathrm{mix,calc}}$ kg m^{-3}	$\delta^{\mathrm{I}}\,.\,10^{2\,a}$, %	$\rho^{\mathrm{II}}_{\mathrm{mix,calc}}$ kg m^{-3}	$\delta^{\mathrm{II}}\,.\,10^{2\,a}$, %
0.108	1 010.2	1 010.0	2.0	1 010.1	1.0
0.198	1 019.9	1 019.7	2.0	1 019.9	0.0
0.291	1 029.7	1 029.6	1.0	1 029.7	0.0
0.396	1 040.6	1 040.5	1.0	1 040.6	0.0
0.488	1 050.0	1 049.9	1.0	1 049.9	1.0
0.496	1 050.6	1 050.7	-1.0	1 050.8	-1.9
0.594	1 060.7	1 060.6	0.9	1 060.6	0.9
0.693	1 070.6	1 070.5	0.9	1 070.5	0.9
0.791	1 080.2	1 080.2	0.0	1 080.1	0.9
0.852	1 086.1	1 086.1	0.0	1 086.0	0.9
0.928	1 093.1	1 093.4	-2.7	1 093.4	-2.7
0.988	1 099.2	1 099.2	0.0	1 099.2	0.0
1.095	1 109.4	1 109.4	0.0	1 109.4	0.0
1.111	1 111.0	1 110.9	0.9	1 110.9	0.9
1.185	1 117.9	1 117.8	0.9	1 117.8	0.9
1.254	1 124.4	1 124.3	0.9	1 124.3	0.9
1.381	1 136.0	1 136.0	0.0	1 136.1	-0.9
1.482	1 145.2	1 145.3	-0.9	1 145.3	-0.9
1.577	1 153.8	1 153.9	-0.9	1 153.9	-0.9
1.923	1 184.8	1 185.0	-1.7	1 184.9	-0.8
1.968	1 189.1	1 189.1	0.0	1 188.9	1.7

[a] Characteristics: $\bar{\delta}^{\mathrm{I}}$ = 0.011 %, $\bar{\delta}^{\mathrm{II}}$ = 0.010 %, n = 21; $\delta^{\mathrm{I}}_{\mathrm{max}}$ = 0.027 %, $\delta^{\mathrm{II}}_{\mathrm{max}}$ = 0.027 %.

TABLE VI
Comparison of tabulated[2] and calculated density values of aqueous solutions of component $j = K_2CO_3$ according to Eqs (*8*) and (*11*), t = 20 °C

$c_{\text{mix, j}}$ kmol m^{-3}	$\rho_{\text{mix, tab}}$ kg m^{-3}	$\rho^{\text{I}}_{\text{mix, calc}}$ kg m^{-3}	$\delta^{\text{I}} \cdot 10^{2\,a}$, %	$\rho^{\text{II}}_{\text{mix, calc}}$ kg m^{-3}	$\delta^{\text{II}} \cdot 10^{2\,a}$, %
0.212	1 023.9	1 023.9	0.0	1 024.0	−1.0
0.430	1 049.6	1 049.2	3.8	1 049.6	0.0
0.605	1 069.7	1 069.1	5.6	1 069.6	0.9
0.859	1 098.0	1 097.4	5.5	1 097.8	1.8
0.982	1 111.5	1 111.0	4.5	1 111.3	1.8
1.286	1 144.2	1 143.8	3.5	1 144.0	1.8
1.358	1 150.9	1 151.5	−5.2	1 151.6	−6.1
1.521	1 168.9	1 168.7	1.7	1 168.7	1.7
1.711	1 188.6	1 188.5	0.8	1 188.3	2.5
1.877	1 205.4	1 205.4	0.0	1 205.2	1.7
2.134	1 231.2	1 231.4	−1.6	1 231.0	1.6
2.253	1 243.0	1 243.2	−1.6	1 242.9	0.8
2.553	1 272.5	1 272.7	−1.6	1 272.3	1.6
2.801	1 296.2	1 296.5	−2.3	1 296.2	0.0
2.970	1 312.2	1 312.5	−2.3	1 213.3	−0.8
3.177	1 331.6	1 331.8	−1.5	1 331.7	−0.8
3.384	1 350.7	1 351.0	−2.2	1 351.0	−2.2
3.962	1 402.6	1 403.1	−3.6	1 403.6	−7.1
4.098	1 416.0	1 415.2	5.7	1 415.7	2.1
4.812	1 478.0	1 477.4	4.1	1 478.0	0.0
5.582	1 543.0	1 543.0	0.0	1 542.6	2.6

[a] Characteristics: $\bar{\delta}^{\text{I}}$ = 0.032 %, $\bar{\delta}^{\text{II}}$ = 0.025 %, n = 21; $\delta^{\text{I}}_{\text{max}}$ = 0.056 %, $\delta^{\text{II}}_{\text{max}}$ = 0.071 %.

TABLE VII
Constants of correlation Eq. (*11*)

Component	A, kg kmol^{-1}	B, kg m$^{1.5}$ kmol$^{-1.5}$
NaOH	47.12	−4.48
KOH	52.48	−3.94
Na_2CO_3	115.06	−12.96
K_2CO_3	127.90	−12.86

SYMBOLS

A	constant of Eq. (*11*), kg $kmol^{-1}$
a_i	($i = 0, 1, 2, 3$) constants of polynomial (*10*), $m^3\,kmol^{-1}$
B	constant of Eq. (*11*), kg $m^{1.5}\,kmol^{-1.5}$
c	molar concentration, kmol m^{-3}
M	molecular weight, kg $kmol^{-1}$
n	number of tabulated data
p	ratio of volumes
V	volume, m^3
v	molar volume, $m^3\,kmol^{-1}$
$\bar{v}$	partial molar volume, $m^3\,kmol^{-1}$
x	mole fraction
γ_2	a combination of physical quantities, kmol m^{-3}
δ	relative error, %
$\bar{\delta}$	mean quadratic relative error, %
ρ	density, kg m^{-3}

Indexes

calc	calculated value
j	related to component, i.e. NaOH, KOH, Na_2CO_3, K_2CO_3
max	maximum value
mix	related to solution
tab	tabulated value
1	related to component 1
2	related to component 2
I	calculation according to Eq. (*8*)
II	calculation according to Eq. (*11*)

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