

The Equations for Thermophysical Properties of Aqueous Solutions of Sodium Hydroxide

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The survey of experimental data on isobaric heat capacity, viscosity and thermal conductivity of aqueous solutions of sodium hydroxide is presented. The equations for these properties are obtained on base of experimental data. The equation for isobaric heat capacity is obtained for the region of pressures up to 7 MPa and temperatures up to 523 K. It is valid for solutions at concentrations up to 4 mol/kg water. The equation for viscosity is valid for boiling solutions at temperatures up to 550 K at concentrations up to 3 mol/kg water. The equation for thermal conductivity is obtained for region of temperatures up to 400 K at pressures up to 15 MPa for solutions at concentrations up to 5 mol/kg water.

1. Introduction

The aqueous solutions of sodium hydroxide are applied in various branches of industry such as power engineering, chemical technology and so on. In spite of this there is a little equations for thermophysical properties of these solutions which would be suitable for using in industrial calculations. The aim of this report is to present equations for some of these properties based on experimental data valid in region of parameters and concentrations most important for power engineering and ones convenient for users.

2. Isobaric heat capacity

First experimental measurements of isobaric heat capacity were carried out at atmospheric pressures and in narrow temperature interval. Thomsen [1] fulfilled measurement of heat capacity of solutions at concentrations 1.1-23% (wt) at temperature 291 K. For more concentrated solutions at 16.5-47.4% values of heat capacity were obtained by Takker [2] in interval 292-297 K. In more wide temperature diapason 273-307 K investigation was carried out by Pratt [3] for solutions with content 0.6-16% of sodium hydroxide. Richards and Hall [4] measured heat capacity of solutions at concentrations 0.14-27.8% at temperatures from 288 to 293 K. Gucker and Schminke [5] obtained heat capacity values for solutions at concentrations 0.16-8.2% at one temperature 288 K. Investigation in temperature

diapason from 276 to 362 K was fulfilled by Beretetti and McCabe [6] for solutions at concentrations 4-51%. In region of high concentrations from 50 to 76% measurement of heat capacity was fulfilled by Wilson and McCabe [7] in range of temperatures 301-396 K. At saturation pressures for temperatures from 273 to 403 K Ackermann [8] carried out an investigation for solutions at molality 0.5-2 mol/kg. Puchkov, Barinova and Matveeva [9] carried out the measurement of average heat capacity in interval temperatures 25 K for solutions at concentrations from 5 to 50% in region of temperatures 293-673 K at pressures near to saturation one. These experimental values were described by equations which transformed form gives the possibility to calculate a true heat capacity. Allred and Woolley [10] published a results of investigation of diluted solutions at concentrations 0.04-0.4% in temperature interval from 288 to 313 K as values of apparent molar heat capacity using data for heat capacity of pure water from [11]. Roux, Perron and Desnoyers [12] presented the results of measurement also as apparent molar heat capacity values for solutions at molality 0.02-10.9 and at temperatures 277-328 K. They accepted values from [13] for heat capacity of water. The only measurements of heat capacity of sodium hydroxide aqueous solutions in region of elevated pressures up to 7 MPa was carried out by Simonson and Mesmer [14] in diapason temperatures from 323 to 523 K. These authors investigated solutions

at molality 0.1-4 mol/kg and represented the results as values of ratio of heat capacities of solution and that of water. Latter were determined with the help of equation of state from [15]. The uncertainty in heat capacity ratio is estimated as $(2-3)\times 10^{-4}$

Besides data of experimental works there are values of heat capacity calculated by Akerlof and Kegeles [16] on base of measurements of electromotive force for solutions at molality 0.1-12 mol/kg in temperature interval 273-343 K.

After preliminary comparison of experimental data of different works as input values for equation were accepted the data of works [10, 12, 14] and part of calculated values from [9] for parameters where another data are absent. The experimental values of apparent and relative heat capacities of solutions were recalculated into values of specific heat capacity using water heat capacity values used in each work.

Equation for isobaric heat capacity of aqueous hydroxide solutions has a form

$$c_p = c_{p,w} - \sum_{j=1}^{j=5} \sum_{i=0}^{i=5} a_{ij} \tau^i m^j \quad (1)$$

where c_p -isobaric heat capacity of solution, kJ/(kg·K); $c_{p,w}$ - isobaric heat capacity of water, kJ/(kg·K); $\tau = T/T_0$; $T_0 = 273.15$ K; m –molality of solution, mol/kg. The values of coefficients a_{ij} are presented in Table 1. The data for heat capacity of water are calculated from the equation of state for water liquid phase from IAPWS Formulation IF – 97 [17].

Equation (1) is valid for solutions in the region of concentrations up to 4 mol/kg at pressures up to 7 MPa in range of temperatures from 273 to 523 K. In this region it describes the experimental values

Table 1. Values of coefficients a_{ij} of equation (1)

$a_{01}=9.8555259\times 10$	$a_{03}=1.9791083$
$a_{11}=-3.4501318\times 10^2$	$a_{13}=-5.3828966$
$a_{21}=4.8180532\times 10^2$	$a_{23}=5.5124212$
$a_{31}=-3.3440616\times 10^2$	$a_{33}=-2.5430046$
$a_{41}=1.1516735\times 10^2$	$a_{43}=4.5943595\times 10^{-1}$
$a_{51}=-1.5708814\times 10$	$a_{04}=-5.6191575\times 10^{-2}$
$a_{02}=-3.4357815\times 10$	$a_{14}=8.5936388\times 10^{-2}$
$a_{12}=1.1674552\times 10^2$	$a_{24}=-1.6966718\times 10^{-2}$
$a_{22}=-1.5776854\times 10^2$	$a_{34}=-1.4864492\times 10^{-2}$
$a_{32}=1.0577045\times 10^2$	$a_{05}=7.9944152\times 10^{-3}$
$a_{42}=-3.5099188\times 10$	$a_{15}=-1.5444457\times 10^{-2}$
$a_{52}=4.5935013$	$a_{25}=7.5030322\times 10^{-3}$

with standard deviations equal $\sigma = 0.032\%$ for data [13], $\sigma = 0.015\%$ for [10] and $\sigma = 0.074\%$ for [12]. Values from [8] not used as input ones have the scatter from -0.87 to $+1.4\%$

It is known that the temperature dependence of water isobaric heat capacity at low temperatures has an anomalous character. At atmospheric pressure it has a minimum at temperature equals 307.34 K [18]. The aqueous solutions of sodium hydroxide have analogues type of dependence for heat capacity at low concentrations (Fig.1) with minimum temperature decreasing when concentration is increasing. Minimum of dependence reaches temperature equals 0°C at molality of solution $m=0.455$ mol/kg. For more concentrated solutions minimum of heat capacity is absent.

2. Dynamic viscosity

The experimental investigations of dynamic viscosity of aqueous sodium hydroxide solutions are carried out mainly at atmospheric pressure also. Hitchcock and McIlhenny [19] measured viscosity of solutions at molality 1.1-8.3 mol/kg in temperature diapason 293-313 K. Krings [20] investigated solutions at concentrations 12.6-70% in range of temperatures from 295 to 343 K. For solutions at molality from 1.005 to 28.7 mol/kg measurement of viscosity was fulfilled by Kobus [21] in temperature diapason 298-353 K. Klochko and Godneva [22] carried out measurements for solutions at concentrations from 6.21 to 71.5% in range of temperatures 273-398 K. Baron and Matveeva [23] measured viscosity of solutions at concentrations from 3 to 47.6% in temperature range 298-363 K and then Baron and Tscherba [24] extended the measurements in region of more low temperatures from 246 to 288 K for the solutions at

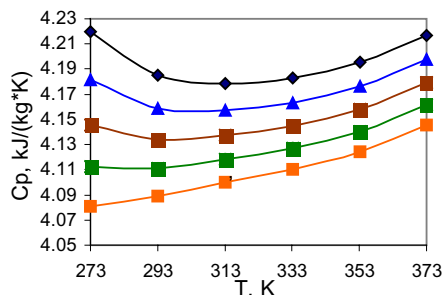


Fig. 1. Temperature dependence of heat capacity of solutions: \blacklozenge - water, \blacktriangle - $m=0.1$, \blacksquare - $m=0.2$, \blacksquare - $m=0.3$, \blacksquare - $m=0.4$

concentrations 5.2-24%.

Most extensive investigation of viscosity of aqueous sodium hydroxide solutions was carried out by Mashovets, Puchkov, Sergaev and Fedorov [25]. They measured the viscosity of solutions at molality 0.5-20 mol/kg in range of temperatures from 273 to 548 K and at pressures a little higher than saturation ones. This work is only one where measurements fulfilled at elevated pressures. The uncertainty in its results is estimated by authors as 1-1.5%.

The data of works [20 –24] were used as input values for elaboration of equation for viscosity of solutions with moderate concentrations. Values of saturation pressures for work [25] were calculated from equation [26]

The equation for viscosity of solutions was obtained in a form

$$\ln(\eta / \eta_w) = \sum_{j=1}^{i=3} \sum_{i=1}^{i=4} b_{ij} (T_0 / T)^j m^i \quad (2)$$

where η -viscosity of solution; η_w -viscosity of water at the same pressure and temperature; $T_0=293.15$ K; values of coefficients b_{ij} are presented in Table 2.

The viscosity of water can be calculated from equation given in [27]. But the viscosity in this document is presented in dependence on temperature and density. For industrial calculations it is more suitable often to have this property as function of temperature and pressure. Therefore an additional equation is prepared for viscosity of water

$$\eta_w = 1001.6(\tau + 1)^2 \exp \left[\sum_{i=1}^{i=10} c_i \tau^i \right] + \pi \sum_{i=0}^{i=9} d_i \tau^i \quad (3)$$

where η_w –viscosity, $\mu\text{Pa}\cdot\text{s}$, $\tau = (T_0/T - 1)$; $T_0 = 293.15$ K; $\pi = (p - p_{sw})$; p -pressure, MPa; p_{sw} – saturation pressure of water; the values of coefficients c_i and d_i are given in Table 3. The values calculated from equation given in [28] were

Table 2. Values of coefficients b_{ij} of equation (2)

$b_{11} = 5.7070102 \times 10^{-1}$	$b_{22} = 3.7957782 \times 10^{-1}$
$b_{21} = 4.9395013 \times 10^{-1}$	$b_{32} = -7.423751 \times 10^{-2}$
$b_{31} = -2.0417183$	$b_{13} = 4.9815412 \times 10^{-2}$
$b_{41} = 1.1654862$	$b_{23} = -4.8332728 \times 10^{-2}$
$b_{12} = -2.9922166 \times 10^{-1}$	-

Table 3. Values of coefficients c_i , d_i of equation (3)

I	c_i	d_i
0	-	$-3.18833435 \times 10^{-1}$
1	5.17341030	-1.07314454×10
2	9.81838817	-8.61347656×10
3	2.83021985×10	-6.50268842×10^2
4	7.02071954×10	-6.06767730×10^3
5	-9.92041252×10^2	-4.07022741×10^4
6	-1.13267055×10^4	-1.59650983×10^5
7	-5.10988292×10^4	-3.53438962×10^5
8	-1.18863488×10^5	-4.11357235×10^5
9	-1.41053273×10^5	-1.96118714×10^5
10	-6.78490604×10^4	-

used as input data during the preparation of equation (3). It describes viscosity of water on saturation line with standard deviation equals $\sigma = 0.052\%$ and describes viscosity of liquid under pressures higher than saturation ones with standard deviation equals $\sigma = 0.151\%$. The region of validity of equation (3) includes temperatures up to 623 K and pressures up to 30 MPa.

Equation (2) describes the viscosity of solutions at molality up to 3 mol/kg in temperature range from 273 to 548 K and under pressures up to 6 MPa. In this region the standard deviations of values of experimental works are as follows: for [25] $\sigma = 2.05\%$, for [23] $\sigma = 2.23\%$, for [24] $\sigma = 2.17\%$, for [21] $\sigma = 1.88\%$ and for [22] $\sigma = 3.37\%$. These deviations are rather big and engendered by great scatter of experimental values.

In Fig. 2 the temperature dependence of relative viscosity η/η_w is shown for solutions at different concentrations. It is known that different aqueous solutions of electrolytes have different types of this dependence. For some solutions relative viscosity increases when temperature increases, for others it decreases. It is clear from Fig. 2 that relative

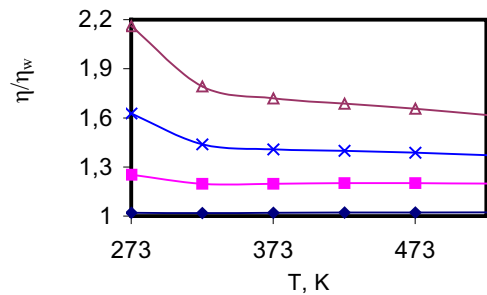


Fig. 2. Relative viscosity of solutions: \blacklozenge - $m = 0.1$, \blacksquare - $m = 1.0$, \times - $m = 2.0$, \triangle - $m = 3.0$.

viscosity of low concentrated aqueous solutions of sodium hydroxide increases and it decreases for more concentrated ones.

3. Thermal conductivity

The experimental investigations of thermal conductivity of aqueous solutions of sodium hydroxide are scant and carried out mainly at atmospheric pressure also. Ridel [29] measured the thermal conductivity of solutions at concentration 10.5-60% in temperature range from 274 to 353 K. Vargaftik and Osminin [30] measured the thermal conductivity at one temperature 293 K in range of concentrations from 0 to 40%. Also at one temperature 311 K the thermal conductivity of solutions with molality 1.36-16.4 mol/kg was measured by Losenicky [31]. The only investigation of thermal conductivity under elevated pressures up to 15 MPa was fulfilled by Guseinov [32] in temperature range from 298 to 401 K for solutions with concentrations up to 20%.

The experimental data of works [29-32] were used as input values for elaboration of equation. The equation obtained has a form

$$\lambda = \lambda_w + \sum_{j=1}^{i=3} \sum_{i=0}^{i=3} e_{ij} (T/T_0)^i m^j \quad (4)$$

where λ -thermal conductivity of solution, W/(m K); λ_w - thermal conductivity of water at the same pressure and temperature; $T_0=403.0$ K; m –molality of solution, mol/kg; values of coefficients e_{ij} are given in Table 4. The equations from [33] may be used for calculation of thermal conductivity of water where it is given as functions of temperature and density. Some times it is more suitable to calculate the thermal conductivity of water in dependence of temperature and pressure from additional equation

$$\lambda_w = \sum_{i=0}^{i=9} g_i \tau^i + \pi \sum_{i=0}^{i=9} q_i \tau^i \quad (5)$$

Table 4. Values of coefficients e_{ij} of equation (4)

$E_{01}=3.2900544 \times 10^{-1}$	$e_{12}=5.9100989 \times 10^{-2}$
$e_{11}=-1.1048583$	$e_{22}=-4.4407173 \times 10^{-2}$
$e_{21}=1.2503803$	$e_{03}=1.5069324 \times 10^{-3}$
$e_{31}=-4.4228179 \times 10^{-1}$	$e_{13}=-4.3273501 \times 10^{-3}$
$e_{02}=-2.1990820 \times 10^{-2}$	$e_{23}=3.3763248 \times 10^{-3}$

Table 5. Values of coefficients of equation (5)

i	g_i	q_i
0	$5.99454842 \times 10^{-1}$	$5.31492446 \times 10^{-4}$
1	$-4.82554378 \times 10^{-1}$	$3.46658996 \times 10^{-4}$
2	$-4.31229616 \times 10^{-1}$	$1.23050434 \times 10^{-2}$
3	$-8.62555022 \times 10^{-1}$	$1.27873471 \times 10^{-1}$
4	$-3.80050418 \times 10^{-1}$	$-7.40820487 \times 10^{-1}$
5	4.85828450×10^0	-1.93072528×10^0
6	3.35400696×10^2	-1.22835056×10^2
7	1.08007806×10^3	-3.66150909×10^2
8	1.67727081×10^3	-5.31321978×10^2
9	1.04225629×10^3	-3.03153185×10^2

where λ_w –thermal conductivity, W/(m K); $\tau = (T_0/T - 1)$, $T_0=293.15$ K; $\pi = p - p_s$, p -pressure, MPa; p_s -saturation pressure, MPa; coefficients g_i and q_i are presented in Table 5. The equation (5) describes thermal conductivity of water in region of pressures up to 30 MPa and temperatures up to 623 K. Values of [33] were used as basis for this equation and it describes these data with average square deviations equal $\sigma = 0.007\%$ on saturation line and $\sigma = 0.198\%$ for liquid under other pressures.

Equation (4) is valid in region of pressures up to 15 MPa and temperatures from 273 to 405 K for solutions with concentration up to 5 mol/kg. In this region it describes the experimental data with average square deviations equal $\sigma = 0.45\%$ for [29], $\sigma = 0.43\%$ for [30], $\sigma = 1.0\%$ for [31] and $\sigma = 0.52\%$ for [32]

The character of change of thermal conductivity of solutions along saturation line is shown in Fig. 3. It is known that this dependence for water has anomalous behaviour. Aqueous solutions of sodium hydroxide remain that type of dependence. It can note also that heat conductivity of these solutions increases when concentration increases in contradiction to aqueous solutions of many others electrolytes.

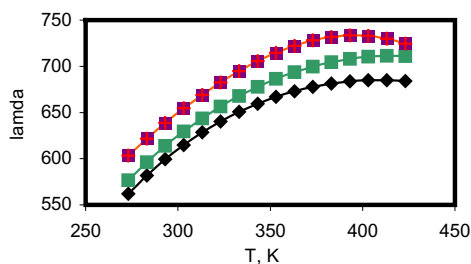


Fig. 3. Thermal conductivity of solutions on saturation line: \blacklozenge - water, \blacksquare - $m=1.0$, \blacksquare - $m=5.0$.

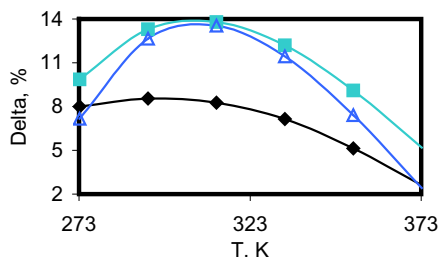


Fig. 4. Deviations of viscosity values from [34] and our once: ◆ - $m=1.0$, ■ - $m=2.0$, △ - $m=3.0$

4. Discussion

Extensive information about properties of aqueous solutions of electrolytes is given in reference book [34]. But it concerns mainly to solutions at atmospheric pressure and at temperatures up to 100°C. Values of heat capacity and heat conductivity from [34] agree with our ones within $\pm 1.5\%$. The divergences of viscosity values are bigger and are shown in Fig. 4. New equations presented in this work expand analytical representation of properties of sodium hydroxide solutions in region of higher temperatures and pressures.

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