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Thermal Conductivity of Aqueous Na_2CO_3 at High Temperatures and High Pressures

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The thermal conductivity of three aqueous Na_2CO_3 solutions of molality (0.4966, 1.0483, and 1.6650) $mol \cdot kg^{-1}$ has been measured with a concentric-cylinder (steady-state) technique. Measurements were made at three isobars, (0.1, 10, and 30) MPa. The range of temperatures was (293.15 to 627.06) K. The total uncertainty of thermal conductivity, pressure, temperature, and molality measurements was estimated to be less than 2 %, 0.05 %, 30 mK, and 0.02 %, respectively. The experimental and calculated values of thermal conductivity for pure water from IAPWS formulation show excellent agreement within their experimental uncertainties (AAD within 0.44 %) in the temperature range from (308.4 to 704.2) K and at pressures up to 60 MPa. Correlation equations for thermal conductivity of the solutions studied were obtained as a function of temperature, pressure, and composition by a least-squares method from the experimental data. The AAD between measured and calculated values from this correlation equation for the thermal conductivity was (0.5 to 0.7) %.

Introduction

Aqueous solutions of electrolytes are widely used as heat bearers in the different branches of industrial thermal engineering, setups of heat and nuclear power stations, and geothermal energetics. Aqueous solutions of salts are used practically in production of all inorganic substances and reagents in which the chemical process are preceded. Aqueous systems play a significant role not only in chemical industry but also in technological processes in nature, e.g., geothermal systems, and in biological processes of living organisms. Oceans and underground waters are the largest reservoirs of aqueous electrolyte solutions. The aqueous Na_2CO_3 solutions are important components of natural fluids, and knowledge of their aqueous solution properties is important in understanding various geochemical processes, such as those related to subsurface brines, seafloor vents, geothermal energy production, and mineral scaling harms.

One of the main problems of studying electrolyte solutions is the investigations of their thermal properties and setting of the regularities between thermophysical characteristics of aqueous solutions and electrolyte concentrations. The thermal conductivity of solutions plays an important part in the calculations of thermal setups and heat exchangers.

Table 1. Experimental Thermal Conductivities, Pressures, Temperatures, and Molality of H_2O + Na_2CO_3 Solutions

	P/MPa = 0.1		P/MPa = 10		P/MPa = 30	
m	T	λ	T	λ	T	λ
$mol \cdot kg^{-1}$	K	$W \cdot m^{-1} \cdot K^{-1}$	K	$W \cdot m^{-1} \cdot K^{-1}$	K	$W \cdot m^{-1} \cdot K^{-1}$
0.4966	308.4	0.617	307.3	0.625	309.4	0.635
0.4966	329.2	0.643	328.7	0.650	328.5	0.655
0.4966	366.5	0.666	366.1	0.676	367.5	0.681
0.4966			384.2	0.680	383.8	0.690
0.4966			409.1	0.684	408.9	0.697
0.4966			439.2	0.681	439.7	0.690
0.4966			464.8	0.673	464.2	0.689
0.4966			507.3	0.640	507.7	0.667
0.4966			528.1	0.621	529.3	0.637
0.4966			553.7	0.583	554.3	0.616
0.4966					602.8	0.538
0.4966					627.6	0.486
1.0483	308.1	0.612	308.9	0.619	307.2	0.631
1.0483	327.3	0.639	330.1	0.646	328.7	0.651
1.0483	366.3	0.661	365.3	0.672	365.9	0.676
1.0483			379.1	0.677	382.5	0.685
1.0483			407.8	0.680	409.3	0.692
1.0483			438.1	0.675	438.4	0.685
1.0483			463.5	0.665	464.9	0.684
1.0483			507.2	0.636	508.3	0.662
1.0483			528.1	0.612	528.7	0.633
1.0483			553.2	0.577	553.5	0.611
1.0483					603.4	0.534
1.0483					628.6	0.483
1.665	307.5	0.607	308.5	0.614	309.7	0.623
1.665	328.1	0.634	329.2	0.641	328.5	0.645
1.665	366.8	0.656	365.7	0.667	365.1	0.671
1.665			382.7	0.672	382.8	0.680
1.665			407.5	0.675	408.7	0.687
1.665			439.2	0.670	439.0	0.680
1.665			464.9	0.667	463.7	0.679
1.665			506.7	0.631	507.7	0.657
1.665			529.3	0.607	529.4	0.628
1.665			555.8	0572	553.9	0.606
1.665					602.8	0.530
1.665					627.5	0.479

The main objective of this paper is to provide new accurate experimental thermal conductivity data for aqueous Na_2CO_3 solutions at high temperatures up to 627.3 K and high pressures up to 30 MPa. The major chemical precipitates in lake systems are calcium, sodium, and magnesium carbonates and dolomite, gypsum, halite, and sulfate salts. Calcium carbonate is deposited as either calcite or arogonite when a lake becomes saturated with calcium and bicarbonate ions. Photosynthesis can also generate precipitation of calcium carbonate, sodium carbonate, or soda ash, Na_2CO_3, which are widely distributed in nature, occurring as constituents of mineral waters and as the solid minerals natron, trona (*q.v.*), and thermonatrite. Large quantities of this alkaline salt are used in making glass, detergents, and

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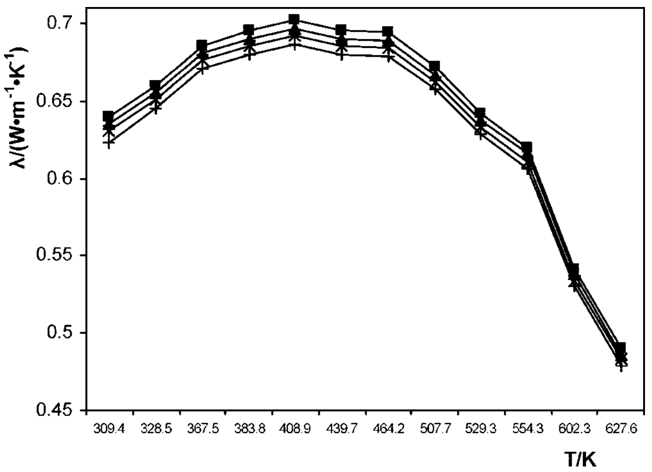

Figure 1. Measured values of thermal conductivity of $H_2O + Na_2CO_3$ solutions as a function of temperature for $P = 30$ MPa and various compositions: ■, pure water; ▲, 0.4966 $mol \cdot kg^{-1}$; *, 1.0483 $mol \cdot kg^{-1}$; +, 1.6650 $mol \cdot kg^{-1}$.

cleansers. Sodium carbonate is treated with carbon dioxide to produce sodium bicarbonate. The monohydrate form of sodium carbonate, $Na_2CO_3 + H_2O$, is employed extensively in photography as a constituent in developers. Washing soda (sal soda) consists of sodium carbonate decahydrate, $Na_2CO_3 + H_2O$, and it serves as a bleach for cotton and linen and as a household cleansing agent.

This work is a part of a continuing program on the transport properties of electrolytes in aqueous solutions. In previous studies,[1–7] we measured the thermal conductivity of 25 aqueous salt solutions at high temperatures up to 630 K and high pressures up to 100 MPa. Some of the reported thermal conductivities are inaccurate and inconsistent.

Experimental Procedures

The thermal conductivity of aqueous Na_2CO_3 solutions was measured by a concentric-cylinders (steady) technique. The experimental apparatus and procedures that were described previously[4–6] were used without modification. In this paper, only a brief discussion will be given.

The main part of the apparatus consisted of a high-pressure autoclave, thermostat, and thermal conductivity cell. The thermal conductivity cell consisted of two coaxial cylinders: an inner (emitting) cylinder and an outer (receiving) cylinder. The cylinders were located in a high-pressure autoclave. The deviation from concentricity was 0.002 cm or 2 % of the sample layer.

The autoclave was located in the thermostat. The thermostat was a solid (massive) copper block. The temperature in the thermostat was controlled by the heater.

The thermostat was supplied with a three-section heating element, PRT-10, and three chromel−alumel thermocouples were located on three different levels of the copper block. The temperature differences between various sections (levels) of the copper block were within 0.02 K of each other. The temperature was measured with a PRT and with three chromel−alumel thermocouples. Thermocouples were located on different levels of the thermostat to minimize the inhomogeneities of the temperature. One of the junctions of the differential chromel−copel thermocouple was located in the inner cylinder and tightly applied to the cylinder's wall. The second junction of the thermocouple was located in the shell capillary. Thermocouples were twice calibrated with a standard resistance thermometer. The difference between calibrations was 10 mK. The temperature-sensitive element of the thermocouple was located on the same level as the measured cell. The reading of the single thermocouples differs by ± 10 mK. The measurements were started when differences of readings of all the thermocouples were minimal (0.02 K). This thermal conductivity apparatus had been successfully employed in three previous studies of thermal conductivity of aqueous solutions $H_2O + Li_2SO_4$, $H_2O + Sr(NO_3)_2$, and $H_2O + Li(NO_3)_2$ at high temperatures and high pressures.

To check and confirm the accuracy of the method and procedure of the measurements, thermal conductivity data were taken for pure water in the temperature range from (300.6 to 704.2) K at pressures up to 60 MPa and for aqueous NaCl solutions along the isobar of 20 MPa and at a concentration of 4.278 $mol \cdot kg^{-1}$. This excellent agreement for test measurements confirms the reliability and accuracy of the measurements for $H_2O + Mg(NO_3)_2$, $H_2O + Ca(NO_3)_2$, and $H_2O + Ba(NO_3)_2$ solutions[7] and of the present measurements for $H_2O + Na_2CO_3$ and corrects operation of the instrument.

The solutions at the desired composition were prepared by mass. The composition was checked by comparison of the density of solution at 293.15 K and 0.1 MPa with reference data.

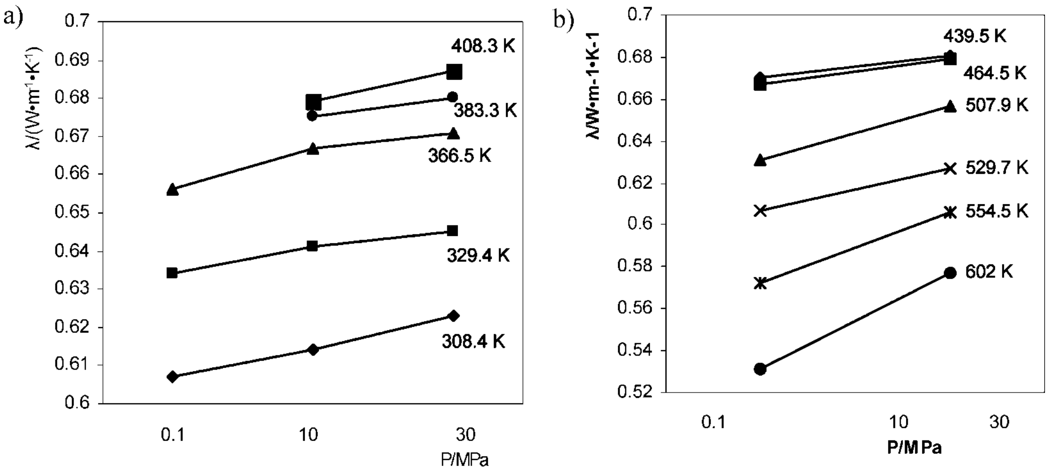

Figure 2. Measured values of thermal conductivity of $H_2O + Na_2CO_3$ solutions as a function of pressure for various temperatures and $m = 1.0483$ $mol \cdot kg^{-1}$.

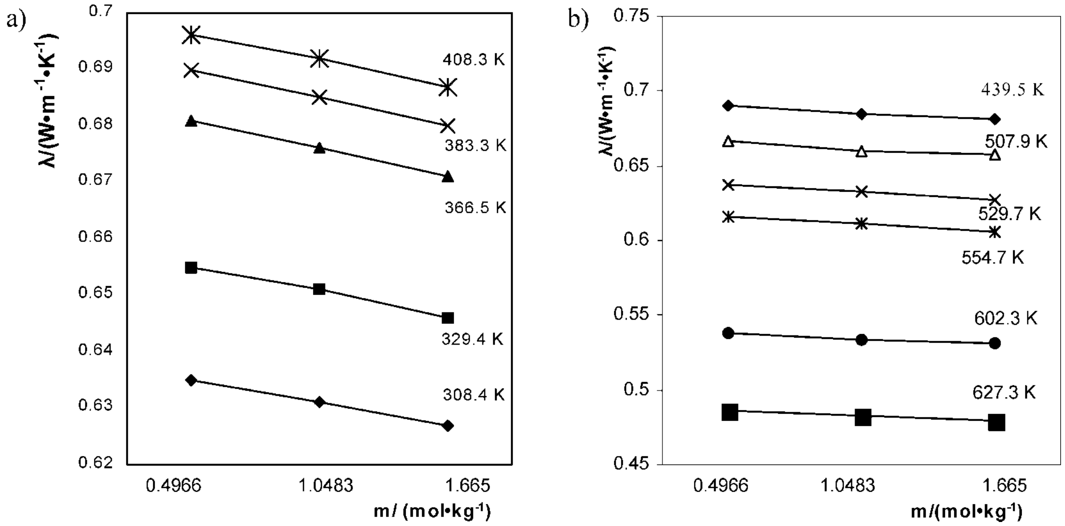

Figure 3. Measured values of thermal conductivity of $H_2O + Na_2CO_3$ solutions as a function of concentration along one pressure (30 MPa) and for various temperatures.

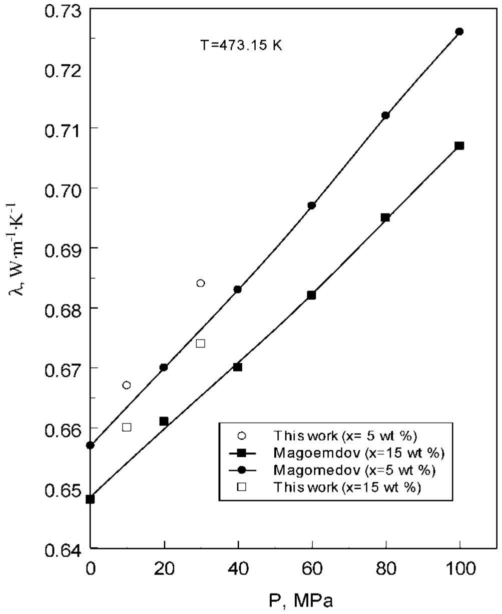

Figure 4. Comparisons of the thermal conductivity for $H_2O + Na_2CO_3$ solutions as a function of pressure.

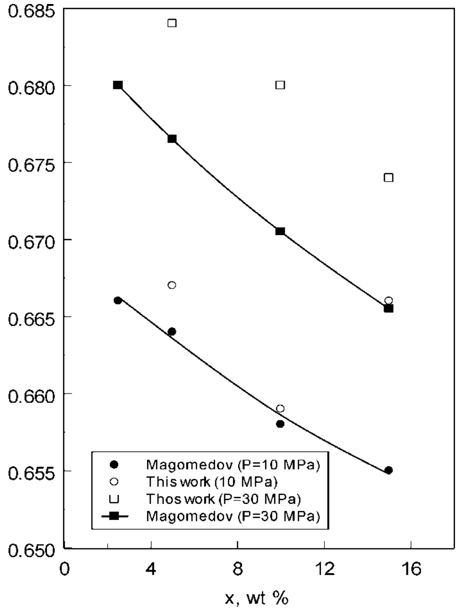

Figure 5. Comparisons of the composition dependence for $H_2O + Na_2CO_3$ solutions.

Results and Discussion

Measurements of the thermal conductivity for the aqueous Na_2CO_3 solutions were performed along three isobars (0.1, 10, and 30) MPa between (294.11 and 627.06) K of molality, namely, (0.4966, 1.0483, and 1.6650) $mol \cdot kg^{-1}$. The experimental temperature, pressure, composition, and thermal conductivity values are presented in Table 1. The thermal conductivity of $H_2O + Na_2CO_3$ solutions was measured as a function of temperature at constant pressure for various compositions. In Figure 1, the temperature dependence of the measured values of thermal conductivity for the $H_2O + Na_2CO_3$ solutions along various isobars and compositions is shown on each isopleth–isobaric curve. The thermal conductivity shows its maximum values at temperatures between (406 and 440) K depending on pressure and concentration. For pure water, this maximum occurs at temperatures between (409 and 421) K as pressure changes between (20 and 60) MPa. The thermal conductivity maximum is largely affected by composition and pressure. For example, for a concentration of 0.4966 $mol \cdot kg^{-1}$ at pressures of 30 MPa, the maximum, in the thermal conductivity, occurs at a temperature of about 410 K and shifts to the high temperature of about 425 K as composition changes. At the same isobar (10 MPa), the maximum of thermal conductivity for pure water occurs at a temperature of 405 K.

Figure 2 (parts a and b) shows the results of the thermal conductivity measurements for $H_2O + Na_2CO_3$ solutions as a function of pressure. The thermal conductivity increases almost linearly as the pressure increases in the temperature range up to 627.15 K and at pressures up to 30 MPa. The composition dependencies of the measured thermal conductivities for $H_2O + Na_2CO_3$ solutions for all isotherms and one isobar (30 MPa) are shown in Figure 3 (parts a and b). The thermal conductivity of the solution monotonically decreases with composition. As one can see from Figure 3 (parts a and b), the composition dependence of the thermal conductivity exhibits a small curvature at high compositions ($m > 1$ $mol \cdot kg^{-1}$).

Aseyev[8] reported thermal conductivity data for $H_2O + Na_2CO_3$ solutions at temperatures from (293.15 to 428.15) K and compositions between (2 and 22) wt %.

Table 2. Parameters α_{ijk} of Equation 1

$H_2O + Na_2CO_3$					
$i = 0$			$i = 1$		
K	$j = 0$	$j = 1$	K	$j = 0$	$j = 1$
0	0.7491905	$2.222695 \cdot 10^{-2}$	0	$-3.401097 \cdot 10^{-3}$	$6.96622 \cdot 10^{-5}$
1	$7.499794 \cdot 10^{-3}$	$-1.301403 \cdot 10^{-4}$	1	$1.49192 \cdot 10^{-5}$	$-4.854152 \cdot 10^{-7}$
2	$-9.4731427 \cdot 10^{-6}$	$1.6308652 \cdot 10^{-7}$	2	$-5.3058165 \cdot 10^{-8}$	$3.080093 \cdot 10^{-9}$

Magomedov[9] reported thermal conductivity data for $H_2O + Na_2CO_3$ solutions at pressures from (0.1 to 100) MPa at temperatures from (293.15 to 473.15) K and compositions between (2.5 and 20) wt %. Figure 3 shows comparisons of the thermal conductivity for $H_2O + Na_2CO_3$ solutions as a function of pressure for one selected isotherm (473.15 K) and isobars, (0.1 to 100) MPa, together with data reported by Magomedov. The thermal conductivity of the solution monotonically decreases with composition. Figure 4 shows comparisons of the composition dependence of the present thermal conductivity data for $H_2O + Na_2CO_3$ solutions with the data reported by Magomedov. The agreement between the this data and the data reported by Magomedov is (0.5 to 1.0) % at low temperatures (below 473 K) and low pressures (below 20 MPa) and (1.2 to 1.5) % at high temperatures (above 473 K) and high pressures (above 20 MPa). Figures 4 and 5 illustrate the good consistency of the dependence of thermal conductivity of $H_2O + Na_2CO_3$ measured in the present work and reported by Magomedov.

Correlation

Because of the lack of theoretical background on the temperature, pressure, and composition, the dependency of the thermal conductivity for empirical aqueous salt solutions is shown. The results of the (λ, P, T, m) measurements for $H_2O + Na_2CO_3$ solutions were represented by the equation

$$\lambda = \sum_{i=0}^{1}\sum_{j=0}^{1}\sum_{k=0}^{2} \alpha_{ijk} \cdot m^i \cdot P^j \cdot t^k \tag{1}$$

where λ is the thermal conductivity of the solution ($W \cdot m^{-1} \cdot K^{-1}$); t is the temperature in °C; P is the pressure in MPa; and m is the amount of substance per unit mass ($mol \cdot kg^{-1}$). At high concentrations ($m > 1\ mol \cdot kg^{-1}$), nonlinear terms for the composition dependence in eq 1 have to be included. Equation 1 describes the thermal conductivity of this aqueous salt solution with an accuracy that does not exceed the experimental uncertainty. The average absolute deviation between measured and calculated values with eq 1 is (0.5 to 0.7) %. The coefficients of eq 1 have been exclusively determined to minimize the mean quadratic deviation of the fitted experimental thermal conductivity values. The derived values of the coefficients α_{ijk} in eq 1 for this aqueous salt solution are given in Table 2. Equation 1 is valid in the temperature range from (290.15 to 627.15) K, at pressures up to 30 MPa and for composition up to 3 $mol \cdot kg^{-1}$.

Conclusion

The thermal conductivities of three aqueous Na_2CO_3 solutions have been measured with a coaxial−cylinder (steady) technique. Measurements were made at three isobars (0.1, 10, and 30) MPa for all solutions. The range of the temperatures was (293.13 to 627.06) K. The total uncertainty of thermal conductivity, pressure, temperature, and composition measurements was estimated to be less than 2 %, 0.05 %, 30 mK, and 0.02 %, respectively. The temperature, pressure, and concentration dependencies of thermal conductivity were compared with data and correlations reported in the literature. The reliability and accuracy of the experimental method was confirmed with measurements on pure water, toluene, and H_2O + NaCl. The experimental and calculated values of thermal conductivity for pure water from IAPWS formulation show excellent agreement within their experimental uncertainties (AAD within 0.44 %). Agreement between present measurements for aqueous NaCl solution and the data sets reported in the literature is within (0.64 to 1.72) %. The AAD between measured and calculated values of thermal conductivity for solutions from this correlation equation was (0.5 to 0.7) %. The measured thermal conductivity values of solutions were compared with the data reported in the literature by other authors. Good agreement {deviation within (0.72 to 1.25) %} is found between the present measurements and the data sets reported by other authors in the literature.

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