Measurements of the thermal conductivity of aqueous $SrCl_2$ and $Sr(NO_3)_2$ solutions in the temperature range 293 - 473 K at pressures up to 100 MPa[1]

I.M. Abdulagatov,[2,3] and U.B. Magomedov [2]

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[2]Institute for Geothermal Problems of the Dagestan Scientific Center of the Russian Academy of Sciences, 367030 Makhachkala, Kalinina 39-A, Dagestan, Russia.

[3]To whom correspondence should be addressed.

Abstract

Accurate high-pressure thermal conductivity measurements have been performed on H_2O +$SrCl_2$ and H_2O+$Sr(NO_3)_2$ mixtures at pressures up to 100 MPa in the temperature range 293-473 K by use of a parallel-plate apparatus. The concentrations studied were 0.025, 0.05, 0.10, 0.15, and 0.20 mass fraction of salts. The estimated accuracy of the method is about ±1.6%. The pressure, temperature, and concentration dependence of the thermal conductivity has been studied. Measurements were made on six isobars, namely: 0.1, 20, 40, 60, 80, 100 MPa. The thermal conductivity shows a linear dependence on pressure and concentration at all isotherms. Along each isobar a given concentration shows the thermal-conductivity maximum at temperatures about 413 K. The measured values of thermal conductivity at atmospheric pressure are compared with the results of other investigators. Literature data at atmospheric pressure reported by Ridel and Zaitzev et al. good fit our thermal conductivity within our estimated accuracy.

Keywords:: Aqueous solutions; Density; Parallel-plate method; Pressure; Salt; Temperature;Thermal conductivity; Water

1. Introduction

The variation of thermal conductivity as a function of the thermodynamic state (P,T,x) of aqueous solutions of salts is of engineering importance. Only limited experimental thermal-conductivity data over a wide range of temperatures, pressures, and concentrations are available in the literature.

The thermal conductivity of H_2O +$SrCl_2$ and H_2O+$Sr(NO_3)_2$ solutions has been investigated in the papers [1,2]. All measurements were performed at atmospheric pressure. In paper [1] the thermal conductivity of H_2O +$SrCl_2$ and H_2O+$Sr(NO_3)_2$ solutions were measured in the temperature range from 293 K to 373 K at pressure 0.10 MPa for concentrations from 0.025 to 0.2 mass fraction of salt using parallel-plate method. The thermal conductivity of liquid H_2O +$SrCl_2$ and H_2O+$Sr(NO_3)_2$ solutions at atmospheric pressure and temperature 293 K has been measured in paper [2] for concentrations from 0.05 to 0.25 mass fraction with coaxial-cylinder method.

In this investigation, a parallel-plate cell was constructed for measuring the thermal conductivity of aqueous solutions of salts in the liquid and vapor phases at high temperatures (up to 473 K) and high pressures (up to 100 MPa).

2. Experimental

The apparatus and experimental procedures have been described in detail in our previous publications [3-5], and only a brief description is given here. Essentially, it consist of a thermal-conductivity cell, a high-pressure vessel, a liquid thermostat, dead-weight pressure gauge, a water-to -oil separator, a containers for degased water and for solution, and backing pump. The thermal-conductivity cell consists of three plates: guard plate, upper plate, and lower plate. The guard plate is surrounded by a guard heater. The thermal-conductivity cell has a cylindrical form with a 21 mm height and 90 mm diameter. The cell is made from a stainless-steel, 12X18H10T. The fluid surrounds the cell and fills the gap between upper plate and lower plate. The all plates were polished with powder of successively smaller grain size (320 nm). In this way heat transport by radiation is small compared to the heat transport by conduction.

Thermal conductivity measurements a based on the measurement of the Q power transferred from the upper plate to the lower plate by conduction throuth the fluid layer, and ΔT the temperature difference across the fluid layer. The thermal conductivity λ of the fluid is deduced from the relation:

$$\lambda = \frac{Qd}{S\Delta T}, \qquad (1)$$

where Q is the power transferred from the upper plate to the lower plate, S=(36.38±0.01) cm^2 the effective area of the upper plate, d is the width of the measurement layer, and ΔT is the temperature difference across the measurement layer. The experimentally determined value of the power Q_{exp} is measured with an accuracy of ±0.12 %. The temperature difference $\Delta T_{exp.}$ can be determined to better than ±0.10 %.

The fluid sample is located in a small gap between a lower plate and an upper plate. Heat is generated in an upper plate and transferred through a horizantal fluid layer to a lower plate.

The thermal-conductivity cell is mounted inside a high-pressure vessel which placed in the liquid thermostat. A molten salt mixture (45 wt % KNO_3 +55 wt % $NaNO_3$) was used as the fluid in the thermostat. The fluid was circulated by a stirrer driven by a motor, and its temperature was maintained uniform within ±10 mK. The fluid temperature, which was detected by a platinum resistance thermometer, was automatically controlled. The measurements were performed with different values of ΔT in the range from 0.8 to 1.25 K. The pressures have been measured with an accuracy of ±0.05 % .

The dimensions S and d of the thermal-conductivity cell entering in the working equation 1, need some corrections in order to account for the effect of changes due to the applied temperature and pressure. The cell constant has to be corrected for thermal expansion and compression. For the our apparatus this correction is given by

$$\frac{d}{S} = \left[1 - 0.152635 \cdot 10^{-4}(T - 293)\right]\left(\frac{d}{S}\right)_n , \qquad (2)$$

here $(d/S)_n$=0.0827684 m^{-1} the value of the cell constant at a temperature of 293 K and at pressure of 0.1 MPa. The effect of pressure is negligibly small in the pressure range of the experiments. The accuracy of the cell constant is ±0.3 %. Taking into account the errors of temperature, pressure and concentration measurements, the total experimental uncertainty of thermal conductivity, $\overline{\delta\lambda}$, not more ±1.6 %.The parallel-plate method is the configuration in which convection is least likly to occur. Convection heat transfer increases with increasing values of the Rayleigh number [6]. The Rayleigh number Ra is the governing dimensionless quantity:

$$Ra = \frac{g \cdot \alpha_p \cdot \Delta T \cdot d^3 \cdot C_p \cdot \rho^2}{\lambda \cdot \eta}, \qquad (3)$$

where g is the gravitational constant, α_p the thermal expansion coefficient of the fluid, ρ the density, C_P the specific heat at constant pressure , η the viscosity coefficient. To reduce the Ra a small gap distance d=301.0±0.1 μm was used, while the temperature difference ΔT employed in the measurements is 1 K. This is make it possible to minimize the risk of convection. Convection could develop when the Ra exceeds a certain critical value Ra_c, which is 2000 [7]. A possible cause of convection is any temperature gradient in the layer in the horizontal direction. The absence of convection can be varified experimentally by measuring the thermal conductivity with various temperature differences ΔT across the measurement gap. Example of such series of measurements are shown in Fig.1. The measured thermal conductivities were indeed independent of the applied temperature difference ΔT and power Q transferred from the upper plate to the lower plate.

The water was triply distilled, and degassed and had an electric conductivity of about 10^{-4} Ω^{-1} $\cdot m^{-1}$. The solutions were prepared gravimetrically from reagent-grade $SrCl_2$ and $Sr(NO_3)_2$ (purity of 99.7 %).

3. Experimental results and discussion

Experimental thermal-conductivity data were obtained as a function of temperature at six different isobars covering a range of pressures from 0.1 to 100 MPa. Some of the experimental results for H_2O+ $SrCl_2$ and H_2O+ $Sr(NO_3)_2$ solutions, including 300 thermal conductivity data for each systems, are presented in Tables I and II. The average temperature in the fluid layer equals T_L+0.5 ΔT, where T_L is the temperature of the lower plate.

The temperature dependence of the thermal conductivity of pure water and H_2O+ $SrCl_2$ solution along the various isobars at constant concentration are shown graphically in Fig.2. Along each isobar a given concentration shows the thermal-conductivity maximum at temperatures about 413 K. The maximum in thermal conductivity at ≈ 413 K indicates that the temperature coefficient $(\partial\lambda/\partial T)_{PX}$ has changed from positive to negative for all P and x. These observations are consistent with previous work on pure water and all aqueous salt solutions [3-5]. The dependence of the thermal conductivity on pressure P at various constant temperatures are illustrated graphically in Fig.3. The thermal conductivity increases monotonously with increasing pressure at each isotherm for all concentrations. The pressure coefficient of the thermal conductivity, $(\partial\lambda/\partial P)_{TX}$, is always positive and almost constantly for given T and x. Variations of the thermal conductivities of H_2O+ $SrCl_2$ solutions with the concentrations at selected isotherm-isobars are shown in Fig.4. From the data obtained it can concluded that the derivative $(\partial\lambda/\partial x)_{PT}$ is always negative and almost constantly for given P and T.

The measurements were compared with the values obtained by other authors [1,2]. The deviations are shown in Figs.5-7. The measurements of Zaitzev and Aseev [2] for H_2O +$SrCl_2$ and H_2O+$Sr(NO_3)_2$ which have been reported under the same conditions are in good agreement with present results in the overlaping range. The

average relative deviation was ±0.3% for H_2O+ $SrCl_2$, and -1.2 % for H_2O+$Sr(NO_3)_2$. The results given in paper [1] are deviate from ours by less than ±0.3%. The systematic errors were not found and the average deviation was ±0.25 %.

4. Conclusions

By means of the guarded parallel-plate apparatus with the cylindrical thermal-conductivity cell, λ-P-T-x relationship for H_2O+ $SrCl_2$ and H_2O+ $Sr(NO_3)_2$ solutions has been measured in the range of temperatures from 293 K up to 473 K, and pressures up to 100 MPa and concentrations between 0.025 and 0.20 mass fractioin of salt ($SrCl_2$ and $Sr(NO_3)_2$) with an estimated uncertainty of ±1.6 %.

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References

[1] Ridel L., Chem. -Ing.-Techn., 3 (1951) 59.

[2] I.D. Zaitzev and G.G. Aseev, Physico - khimicheskie svoistva binarnykh i nogokomponentnykh rastvorov neorganicheskikh veshestv. Moscow. Khimiya. 1988.

[3] I.M. Abdulagatov and U.B. Magomedov, Int. J. Thermophysics, 15 (1994) 401.

[4] I.M.Abdulagatov and U.B.Magomedov,in H.J. White, J.V.Sengers, D.B.Neumann, and J.C.Bellows (Eds).Physical Chemictry of Aqueous Systems. Proc. of the 12th Int. Conference on the Proper. of Water and Steam. Begell House, New York; 1995, p.549.

[5] I.M. Abdulagatov and U.B. Magomedov, Ber. Bunsen-Ges. Phys. Chem., 101 (1997) 1.

[6] A. Michels and J.V. Sengers, Physica, 28 (1962) 1238.

[7] R.V.Shingarev, Convectivnyi teploobmen v uzkikh zilindricheskikh zazorakh. Ivanova. 1955.

Table I. Experimental Thermal Conductivity Data of $H_2O+SrCl_2$

	λ, mW· m^{-1} · K^{-1}					
T,K	0.1	20	40	60	80	100
x=0.025 mass fraction of $SrCl_2$						
293	597	605	615	624	630	640
313	628	636	645	655	660	667
333	650	660	670	678	687	695
353	666	676	685	698	707	716
375	677	687	697	710	720	730
393	681	695	710	721	730	740
413	682	700	712	724	737	746
433	679	698	710	725	735	745
453	670	691	705	720	730	740
473	660	680	695	712	725	736
x= 0.05 mass fraction of $SrCl_2$						
293	598	602	612	620	629	637
313	625	632	643	650	657	665
333	645	655	667	675	680	691
353	661	672	684	694	700	711
375	672	685	696	706	715	724
393	680	691	707	717	727	733
413	681	696	709	721	731	740
433	677	695	708	720	730	739
453	669	688	702	716	726	737
473	657	678	694	706	720	730

Table I. (Continued)

x= 0.10 mass fraction of $SrCl_2$

293	590	598	605	612	620	627
313	620	629	634	640	649	654
333	640	651	659	665	672	680
353	657	668	676	684	690	700
375	668	678	688	697	704	714
393	674	686	699	707	716	722
413	675	691	700	712	720	730
433	670	688	700	710	718	728
453	663	680	692	707	714	724
473	649	670	683	697	707	720

x= 0.15 mass fraction of $SrCl_2$

293	583	590	597	604	610	620
313	612	620	626	633	639	647
333	633	643	650	656	662	670
353	650	661	667	676	682	690
375	660	670	678	687	694	702
393	665	677	690	696	704	712
413	666	682	692	701	710	717
433	664	678	690	700	707	716
453	655	672	685	695	704	713
473	643	661	674	686	697	707

Table II. Experimental Thermal Conductivity Data of $H_2O+Sr(NO_3)_2$

	λ, mW· m^{-1} · K^{-1}					
T,K	0.1	20	40	60	80	100
x=0.025 mass fraction of $Sr(NO_3)_2$						
293	598	608	617	626	633	640
313	628	638	645	656	660	666
333	650	661	670	679	687	692
353	666	678	687	699	706	713
375	677	688	698	710	718	728
393	682	697	712	722	729	738
413	684	702	714	727	734	746
433	680	698	712	726	733	745
453	671	694	708	722	728	740
473	660	682	698	713	722	738
x=0.05 mass fraction of $Sr(NO_3)_2$						
293	596	604	612	619	626	635
313	624	635	640	650	655	663
333	648	655	665	672	680	688
353	660	673	680	691	700	709
375	672	682	693	703	712	724
393	680	690	705	714	724	733
413	680	696	707	719	729	738
433	675	692	705	718	728	739
453	667	689	701	713	723	735
473	658	679	690	704	716	730

Table II. (Continued)

x=0.10 mass fraction of $Sr(NO_3)_2$

293	588	596	605	612	619	627
313	619	627	635	642	648	655
333	640	650	660	664	672	680
353	656	667	675	683	690	700
375	666	680	686	694	703	715
393	672	685	697	705	715	725
413	673	690	701	710	718	730
433	670	685	700	710	720	729
453	662	680	695	706	714	724
473	650	670	682	696	707	720

x=0.15 mass fraction of $Sr(NO_3)_2$

293	583	591	600	605	612	619
313	612	621	629	635	640	645
333	636	642	652	660	665	670
353	650	660	670	678	685	690
375	660	670	680	688	695	705
393	666	677	690	698	705	712
413	667	682	694	704	710	720
433	663	680	692	702	710	717
453	655	674	688	699	705	713
473	643	662	677	688	700	708

FIGURE CAPTIONS

Fig.1 Measured thermal conductivity as a function of the applied temperature difference ΔT between upper and lower plates for mixture H_2O+ $SrCl_2$ (x=0.2 mass fraction of $SrCl_2$, at pressure P=100 MPa and temperature T=473 K).

Fig.2 The thermal conductivity of H_2O and H_2O +$SrCl_2$ solution at various isobars as a function of the temperature for concentration x=0.2 wt. fraction of $SrCl_2$.

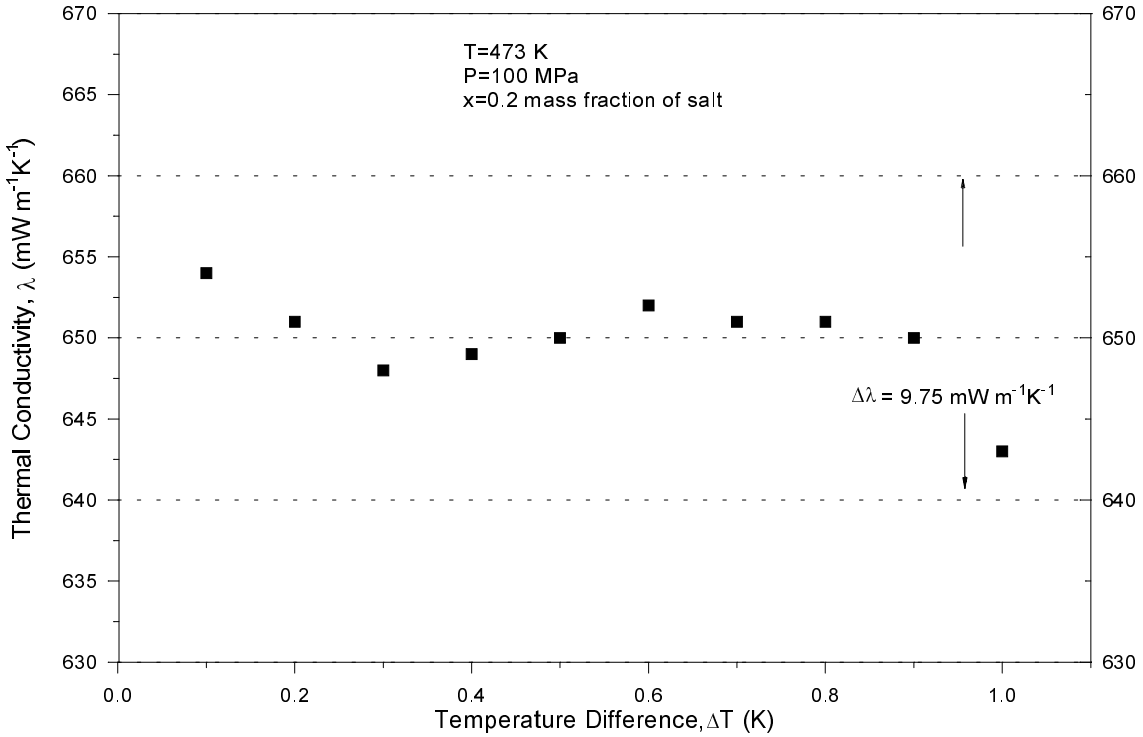
Fig.3 The thermal conductivity of H_2O and H_2O +$SrCl_2$ solution at various isotherms as a function of the pressure for concentration x=0.2 wt. fraction of $SrCl_2$.

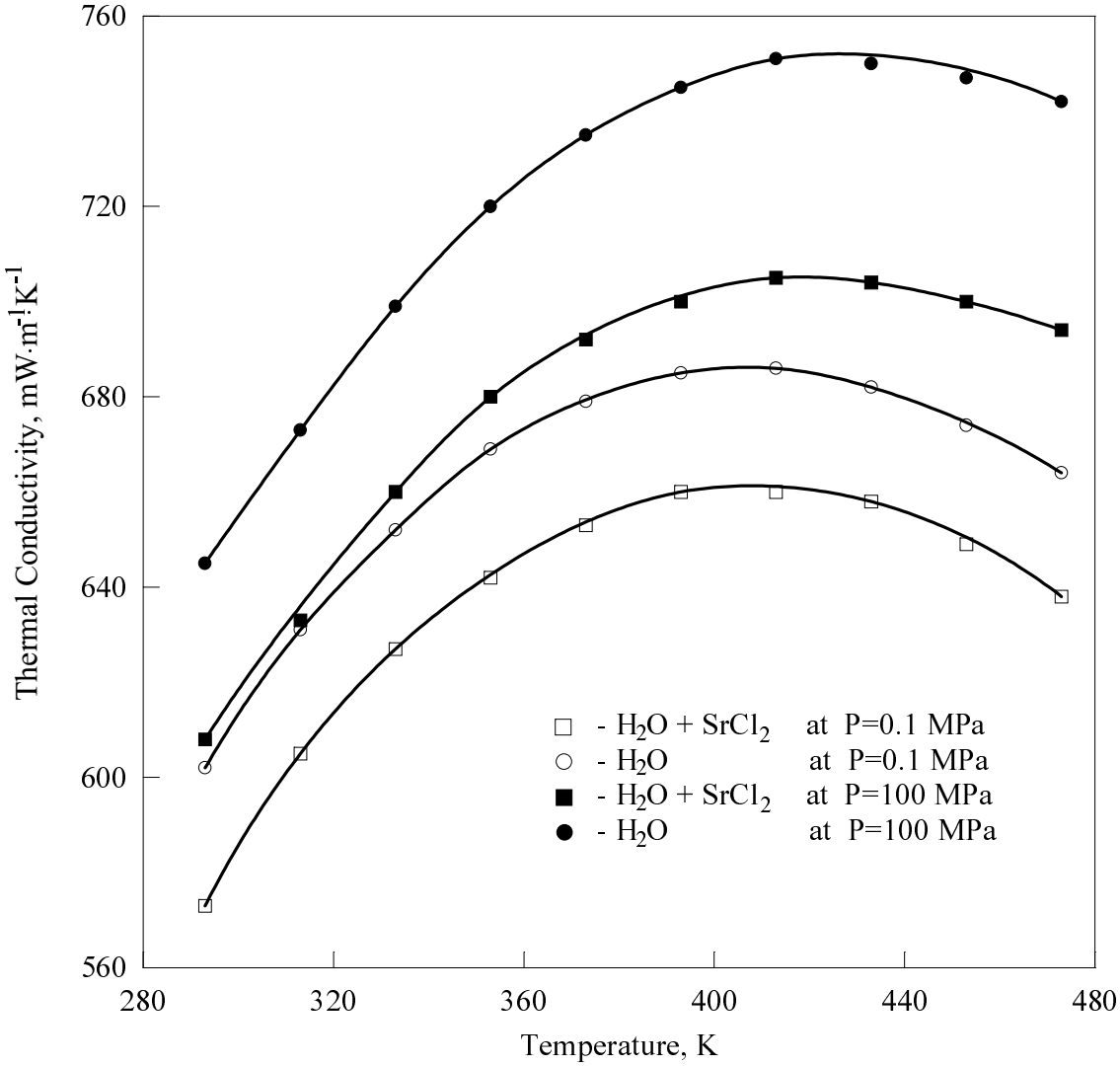
Fig.4 The thermal conductivity of H_2O +$SrCl_2$ solutions at various isotherm-isobars as a function of the concentration.

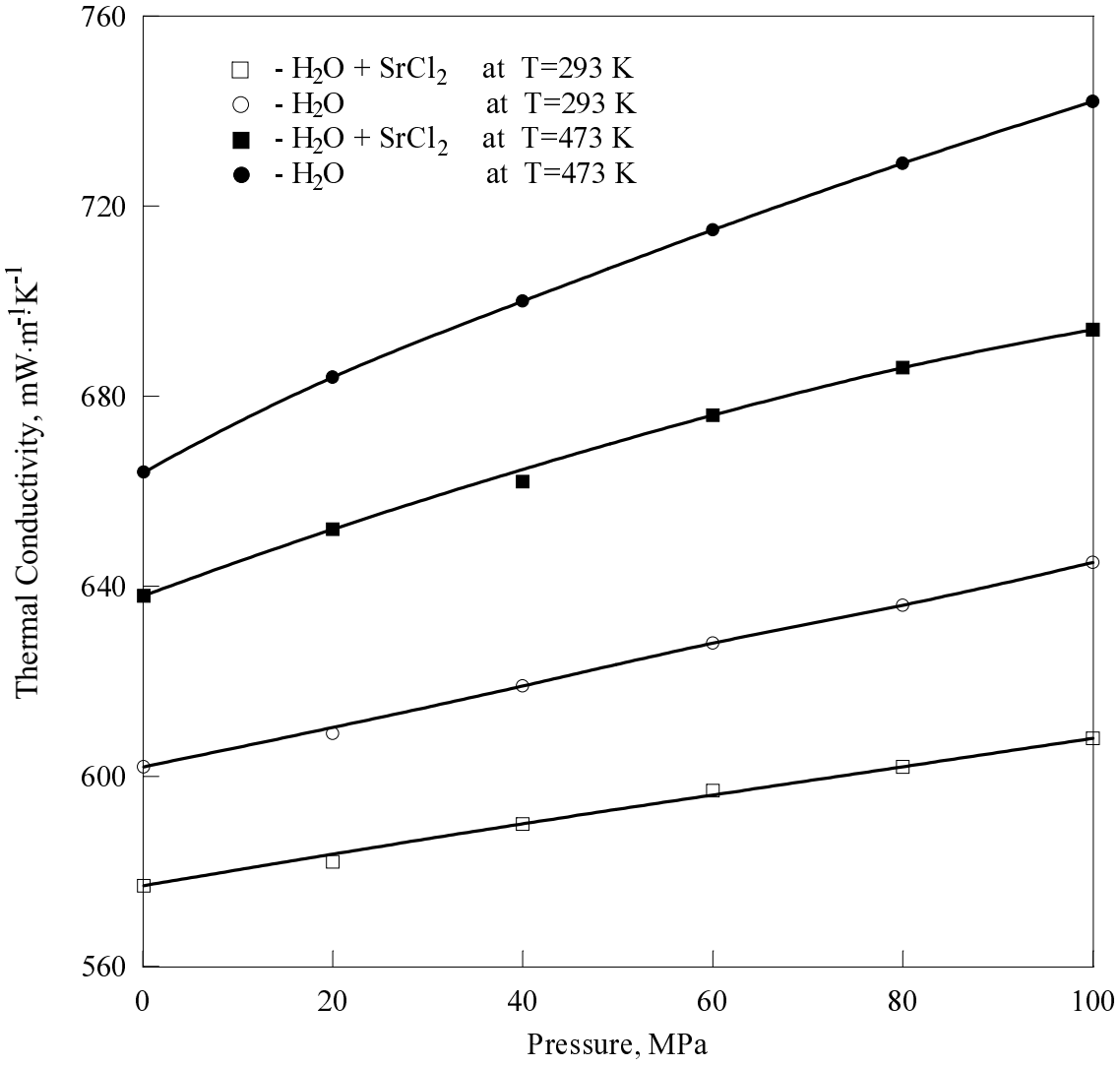
Fig.5 Percentage deviations, $\delta\lambda=100(\lambda_{exp}-\lambda_{this})/\ \lambda_{this}$, in thermal conductivity of the literature values [2] from the present results at pressure P=0.1 MPa for H_2O +$SrCl_2$.

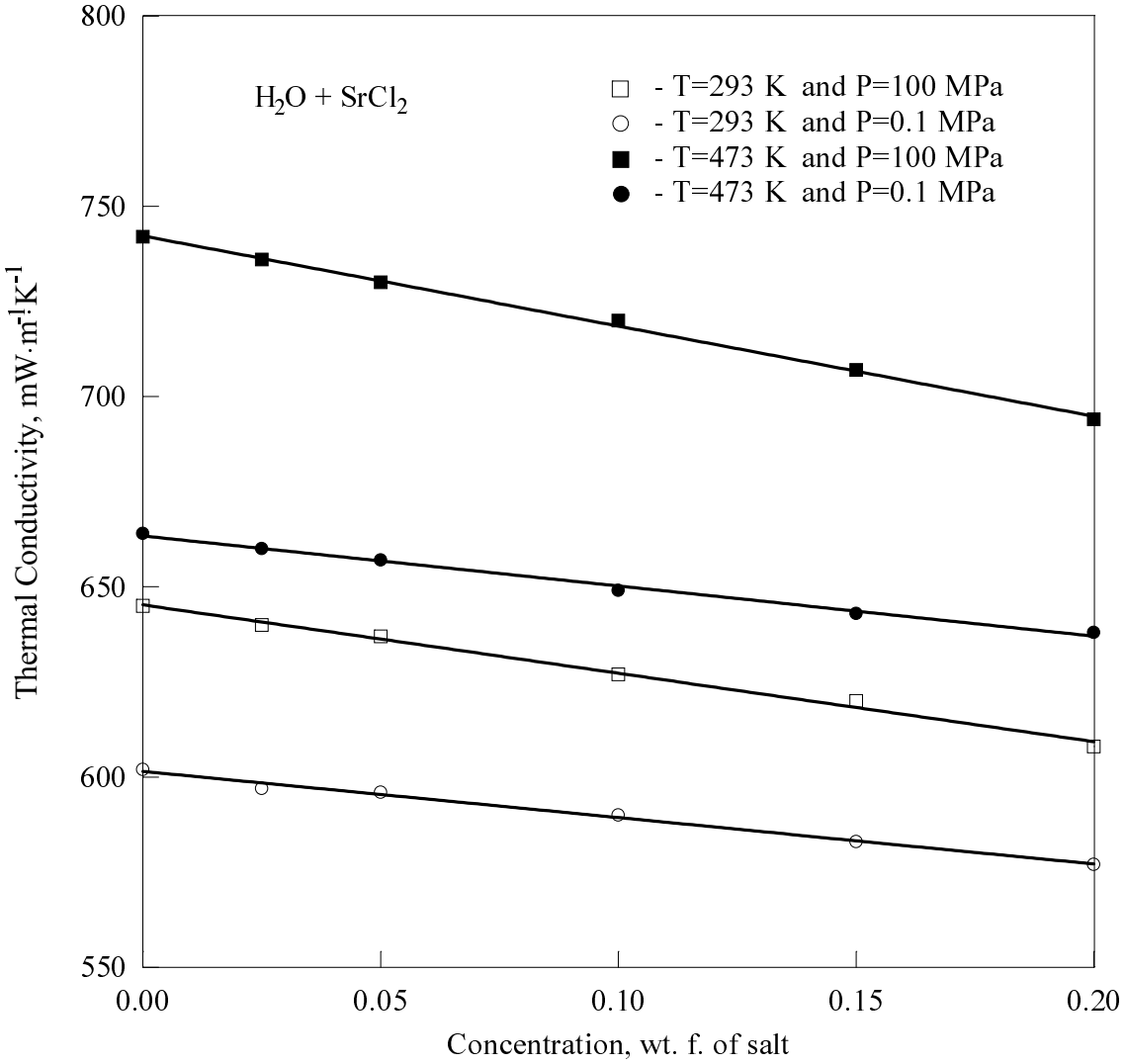
Fig.6 Percentage deviations, $\delta\lambda=100(\lambda_{exp}-\lambda_{this})/\ \lambda_{this}$, in thermal conductivity of the literature values [2] from the present results at pressure P=0.1 MPa for H_2O +$Sr(NO_3)_2$.

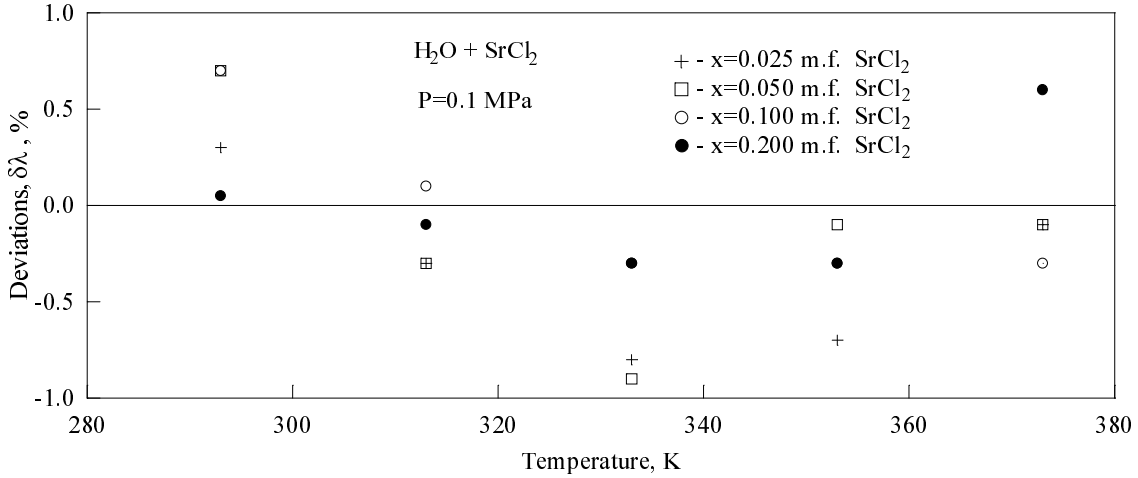
Fig.7 Percentage deviations, $\delta\lambda=100(\lambda_{exp}-\lambda_{this})/\ \lambda_{this}$, in thermal conductivity of the literature values [1] from the present results at pressure P=0.1 MPa and T=293 K for H_2O +$SrCl_2$ and H_2O +$Sr(NO_3)_2$ solutions.

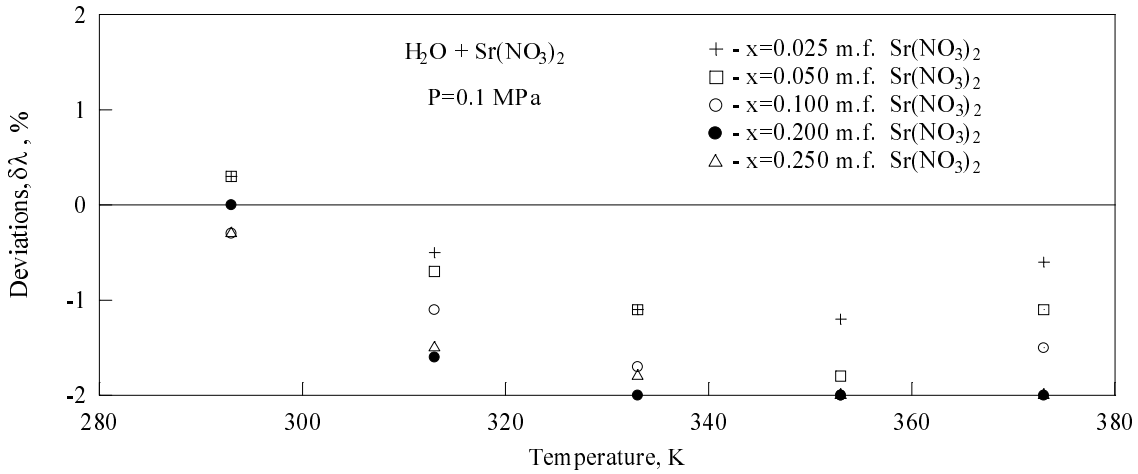

T=473 K
P=100 MPa
x=0.2 mass fraction of salt
Δλ = 9.75 mW m-1K-1
Thermal Conductivity, λ (mW m-1K-1)
Temperature Difference, ΔT (K)
670
665
660
655
650
645
640
635
630
0.0
0.2
0.4
0.6
0.8
1.0

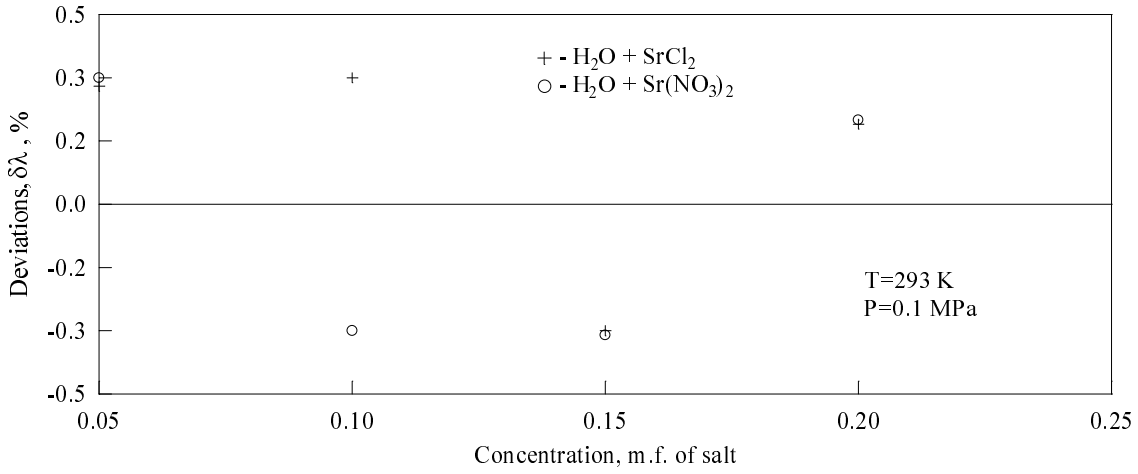

760
720
680
640
600
560
280
320
360
400
440
480
Thermal Conductivity, mW·m-1K-1
Temperature, K
- H2O + SrCl2 at P=0.1 MPa
- H2O at P=0.1 MPa
- H2O + SrCl2 at P=100 MPa
- H2O at P=100 MPa


760
720
680
640
600
560
0
20
40
60
80
100
Thermal Conductivity, mW·m-1·K-1
Pressure, MPa
- H2O + SrCl2 at T=293 K
- H2O at T=293 K
- H2O + SrCl2 at T=473 K
- H2O at T=473 K


800
750
700
650
600
550
0.00
0.05
0.10
0.15
0.20
Thermal Conductivity, mW·m-1K-1
Concentration, wt. f. of salt
H2O + SrCl2
- T=293 K and P=100 MPa
- T=293 K and P=0.1 MPa
- T=473 K and P=100 MPa
- T=473 K and P=0.1 MPa


1.0
0.5
0.0
-0.5
-1.0
Deviations, δλ , %
280
300
320
340
360
380
Temperature, K
H2O + SrCl2
P=0.1 MPa
+ - x=0.025 m.f. SrCl2
□ - x=0.050 m.f. SrCl2
○ - x=0.100 m.f. SrCl2
● - x=0.200 m.f. SrCl2


H2O + Sr(NO3)2
P=0.1 MPa
+ - x=0.025 m.f. Sr(NO3)2
□ - x=0.050 m.f. Sr(NO3)2
○ - x=0.100 m.f. Sr(NO3)2
● - x=0.200 m.f. Sr(NO3)2
△ - x=0.250 m.f. Sr(NO3)2
Deviations, δλ , %
Temperature, K
2
1
0
-1
-2
280
300
320
340
360
380


0.5
0.3
0.2
0.0
-0.2
-0.3
-0.5
0.05
0.10
0.15
0.20
0.25
Deviations, δλ , %
Concentration, m.f. of salt
+ - H2O + SrCl2
○ - H2O + Sr(NO3)2
T=293 K
P=0.1 MPa