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Thermal Conductivities of Aqueous $CdCl_2$ and $CdBr_2$ Solutions from 293 K to 473 K at Pressures up to 100 MPa

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Accurate high-pressure thermal conductivity measurements have been performed on $H_2O + CdCl_2$ and $H_2O + CdBr_2$ 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, 0.20, and 0.25 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, and 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 of 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 Eldarov and Zaitzev agree well with our thermal conductivity within our estimated accuracy.

1. Introduction

The variation of thermal conductivity as a function of the thermodynamic state (P,T,w) 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.

Eldarov (1980) reported the thermal conductivities of $H_2O + CdBr_2$ solutions measured in the temperature range from 293 K to 473 K at a pressure 0.10 of MPa for concentrations from 0 to 0.5 mass fraction of $CdBr_2$ using a parallel-plate method. The thermal conductivity of liquid $H_2O + CdCl_2$ and $H_2O + CdBr_2$ solutions at atmospheric pressure has been measured by Zaitzev and Aseev (1988) in the temperature range from 273 K to 373 K for concentrations from 0.02 to 0.20 mass fraction with a transient hot-wire apparatus.

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 250 MPa).

The thermal-conductivity measurements of aqueous $CdCl_2$ and $CdBr_2$ solutions at high pressures are part of a program on thermal conductivity measurements of aqueous salt solutions at high pressures (up to 200 MPa) and high temperatures (up to 673 K). The aim of the present study is to produce accurate data over wide pressure and wide temperature ranges and eventually establish new reference values.

2. Experimental Section

A schematic diagram of the experimental system is shown in Figure 1. Briefly, the system consists of a thermal-conductivity cell (8), a high-pressure vessel (7), a liquid thermostat (6), a dead-weight pressure gauge (5), a water-to-oil separator (4), a container for degassed water (9) and for solution (2), and a backing pump (3). A thorough description of the technique and the apparatus are given in previous publications (Abdulagatov and Magomedov, 1994, 1995, 1997). The thermal-conductivity cell consists of three plates: guard plate, upper plate, and lower plate. The guard plate is surrounded by a guard heater.

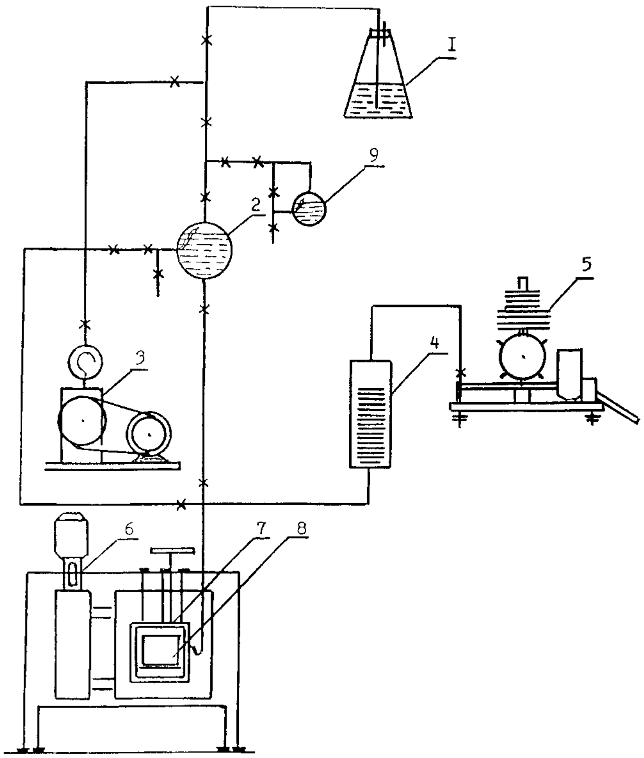

Figure 1. Schematic illustration of the experimental arrangement for high- pressure measurements of the thermal conductivity: 1, sample container; 2, container for degassed solution; 3, backing pump; 4, water-to-oil separator; 5, dead-weight pressure gauge; 6, liquid thermostat; 7, high-pressure vessel; 8, thermal conductivity cell; 9, container for degassed water.

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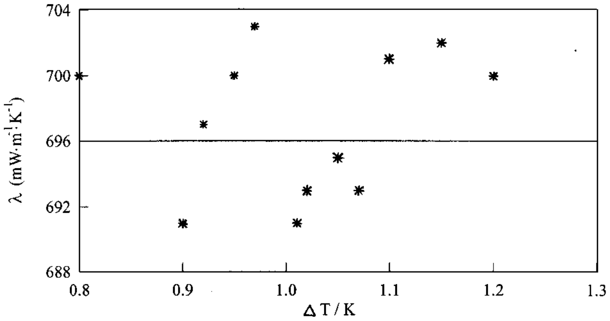

Figure 2. Measured thermal conductivity as a function of the applied temperature difference ΔT between upper and lower plates for the mixture H_2O + $CdCl_2$ (w = 0.2 mass fraction of $CdCl_2$, at pressure P = 100 MPa and temperature T = 473 K).

The thermal-conductivity cell has a cylindrical form with a 21 mm height and 90 mm diameter. The cell is made from stainless-steel, 12X18H10T. The fluid surrounds the cell and fills the gap between the upper plate and the lower plate. 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 are based on the measurement of the Q power transferred from the upper plate to the lower plate by conduction through the fluid layer and ΔT, the temperature difference across the fluid layer. The thermal conductivity λ of the fluid is deduced from the relation

$$\lambda = (Qd)/S\Delta T)$$

where Q is the power transferred from the upper plate to the lower plate (W), $S = (36.38 \pm 0.01)\ \text{cm}^2$ is 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 (K). The experimentally determined value of the power Q_{exp} is measured with an accuracy of ±0.12%. The temperature difference ΔT_{exp} can be determined to better than ±0.10%.

The thermal-conductivity cell is mounted inside a high-pressure vessel that is placed in the liquid thermostat. A molten salt mixture (45 mass % KNO_3 + 55 mass % $NaNO_3$) 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 determened 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 pressure of the fluid is transferred to oil via a mercury piston, and the oil pressure is measured with a dead-weight gauge. The pressures have been measured with an accuracy of ±0.05%.

The dimensions S and d of the thermal-conductivity cell need some correction 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

$$d/S = [1 - 0.152\,635 \times 10^{-4}(T/\text{K} - 293)](d/S)_n \quad (2)$$

where $(d/S)_n = 0.082\,768\,4\ \text{m}^{-1}$ is the value of the cell constant at a temperature of 293 K and a 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, $\overline{\delta\lambda}$, could be calculated as follows

$$\overline{\delta\lambda} = \delta\lambda + \frac{100}{\lambda}\left[\left(\frac{\partial\lambda}{\partial P}\right)_{T,w}\Delta P + \left(\frac{\partial\lambda}{\partial T}\right)_{P,w}\Delta T + \left(\frac{\partial\lambda}{\partial w}\right)_{P,T}\Delta w\right] \quad (3)$$

where $\delta\lambda = 100|\Delta\lambda/\lambda| = 1.0\%$; $\Delta P = \pm 0.025$ MPa; $\Delta T = \pm 0.015$ K, and $\Delta w = \pm 0.000\,05$ mass fraction are our estimates based on experiments. Values for the partial derivatives $(\partial\lambda/\partial P)_{T,w}$, $(\partial\lambda/\partial T)_{P,w}$, and $(\partial\lambda/\partial w)_{P,T}$ have been calculated using correlating equations for various experimental path (isotherm−isopleth, isobar−isopleth, and isotherm−isobar). In the present study, the total uncertainty of thermal conductivity was estimated to be less than ±1.5%.

Table 1. Experimental Thermal Conductivity λ ($mW\cdot m^{-1}\cdot K^{-1}$) of H_2O (A) + $CdCl_2$ (B) as a Function of Temperature

T/K	0.1−2	20	40	60	80	100
			$w_B = 0.025$			
293	597	605	613	624	632	642
313	627	636	645	655	662	668
333	649	660	669	678	686	695
353	666	676	685	696	705	716
375	676	687	698	709	719	730
393	683	697	711	721	730	741
413	684	702	714	725	735	745
433	679	698	712	723	734	746
453	672	693	707	720	730	742
473	659	681	695	712	723	736
			$w_B = 0.05$			
293	595	603	614	622	629	638
313	625	635	642	652	657	664
333	648	657	665	674	683	691
353	662	674	682	693	701	711
375	674	685	695	706	713	724
393	679	693	706	716	725	735
413	681	698	709	720	730	741
433	676	694	706	718	729	741
453	667	687	701	715	726	737
473	656	676	691	707	719	732
			$w_B = 0.10$			
293	591	598	607	614	620	628
313	620	626	636	644	648	655
333	642	652	658	666	674	680
353	656	667	674	685	693	701
375	667	676	686	697	706	716
393	674	685	699	708	716	723
413	675	690	702	712	720	730
433	670	686	701	710	719	729
453	662	680	694	707	716	725
473	650	670	685	698	709	720
			$w_B = 0.15$			
293	582	588	600	605	614	619
313	612	619	628	634	640	645
333	635	645	652	658	664	671
353	652	663	668	676	684	691
375	662	671	681	688	696	705
393	667	679	692	698	707	713
413	668	685	693	704	712	721
433	665	680	692	701	710	718
453	657	675	686	697	706	715
473	644	663	675	688	699	709
			$w_B = 0.20$			
293	575	585	593	598	605	610
313	607	615	622	627	631	635
333	629	636	639	650	655	661
353	643	654	659	667	674	680
375	655	663	672	679	685	695
393	660	672	682	689	696	702
413	662	676	685	692	701	707
433	657	674	683	691	699	706
453	651	666	679	686	695	701
473	639	654	667	679	688	696

Table 2. Experimental Thermal Conductivity λ ($mW\cdot m^{-1}\cdot K^{-1}$) of H_2O (A) + $CdBr_2$(B)

T/K	0.1−2	20	40	60	80	100
			$w_B = 0.025$			
293	596	606	615	623	632	639
313	625	636	645	652	658	665
333	647	659	667	676	684	691
353	663	675	684	695	703	713
375	674	687	695	707	717	727
393	680	695	707	718	729	738
413	681	700	710	723	732	742
433	677	698	708	722	733	743
453	669	692	702	718	729	738
473	657	679	692	708	724	734
			$w_B = 0.05$			
293	592	600	609	617	624	634
313	622	630	639	645	653	660
333	643	654	663	670	675	685
353	659	669	679	687	697	706
375	669	680	693	701	710	720
393	674	687	702	711	721	730
413	675	692	704	716	728	734
433	671	690	703	714	726	734
453	665	684	697	710	723	731
473	652	672	686	701	714	726
			$w_B = 0.10$			
293	583	591	599	606	613	623
313	612	622	628	636	642	648
333	634	643	653	659	665	674
353	649	659	668	675	684	692
375	660	669	679	688	697	709
393	664	679	690	697	708	716
413	666	683	693	703	713	724
433	661	679	691	703	712	720
453	655	674	685	698	708	717
473	642	663	675	689	700	714
			$w_B = 0.15$			
293	573	580	589	594	603	609
313	603	610	619	625	628	636
333	623	633	639	648	654	658
353	639	648	657	666	671	679
375	649	659	669	678	684	693
393	657	667	678	686	696	702
413	656	671	683	690	699	708
433	653	669	679	689	699	706
453	644	662	675	685	694	702
473	635	652	665	676	688	697
			$w_B = 0.20$			
293	565	572	579	584	590	596
313	592	599	607	612	617	621
333	614	621	628	635	639	645
353	630	637	643	653	658	664
375	643	647	655	663	669	676
393	646	656	666	672	679	685
413	647	659	668	676	684	690
433	643	657	666	675	682	689
453	635	651	661	670	679	686
473	625	640	651	663	672	680

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 (Michels and Sengers, 1962). The Rayleigh number Ra is the governing dimensionless quantity

$$Ra = \frac{g\cdot\alpha_P\cdot\Delta T\cdot d^3\cdot C_P\cdot\rho^2}{\lambda\cdot\eta} \tag{4}$$

where g is the gravitational constant ($m\cdot s^{-2}$), α_P the thermal expansion coefficient of the fluid (K^{-1}), ρ the density ($kg\cdot m^{-3}$), C_P the specific heat at constant pressure ($kJ\cdot kg^{-1}\cdot K^{-1}$), and η the viscosity coefficient (MPa·s). To reduce the Ra, a small gap distance $d = 301.0 \pm 0.1$ μm was used, while the temperature difference ΔT employed in the measurements is 1 K. This configuration minimizes the risk of convection. Convection could develop when the Ra exceeds a certain critical value Ra_c, which is 2000 (Shingarev, 1955). 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 different temperature differences ΔT across the measurement gap. Examples of such series of measurements are shown in Figure 2. 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.

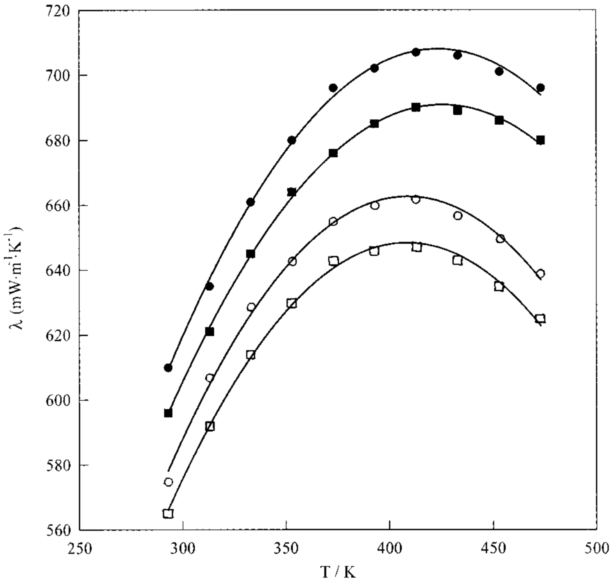

Figure 3. Variations of the thermal conductivities of $H_2O + CdCl_2$ and $H_2O + CdBr_2$ with temperature at selected pressures for concentration $w = 0.2$ mass fraction of salt. ○, $H_2O + CdCl_2$ at 0.1 MPa; ●, $H_2O + CdCl_2$ at 100 MPa; □, $H_2O + CdBr_2$ at 0.1 MPa; ■, $H_2O + CdBr_2$ at 100 MPa.

The water was triply distilled and degassed and had an electric conductivity of about 10^{-4} $\Omega^{-1}\cdot m^{-1}$. The solutions were prepared gravimetrically from reagent-grade $CdCl_2$ and $CdBr_2$ (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. The experimental results for $H_2O + CdCl_2$ and $H_2O + CdBr_2$ solutions, including 300 thermal-conductivity data for each system, are presented in Tables 1 and 2. The average temperature in the fluid layer equals $T_L + 0.5\Delta T$, where T_L is the temperature of the lower plate.

The temperature depedence of the thermal conductivity along the various isobars at constant concentrations is shown graphically in Figure 3. Along each isobar a given concentration shows the thermal-conductivity maximum at a temperature of about 413 K. The maximum in thermal conductivity at ≈413 K indicates that the temperature coefficient $(\partial\lambda/\partial T)_{Pw}$ has changed from positive to negative for all P and w. These observations are consistent with previous work on pure water and all aqueous salt solutions (Abdulagatov and Magomedov, 1994, 1995, 1997). The dependence of the thermal conductivity on pressure P at constant temperature is illustrated graphically in Figure 4. The thermal conductivity increases monotonously with increasing pressure at each isotherm for all concentrations. The pressure coefficient of the thermal conductivity, $(\partial\lambda/\partial P)_{Tw}$, is always positive and almost constant for given T

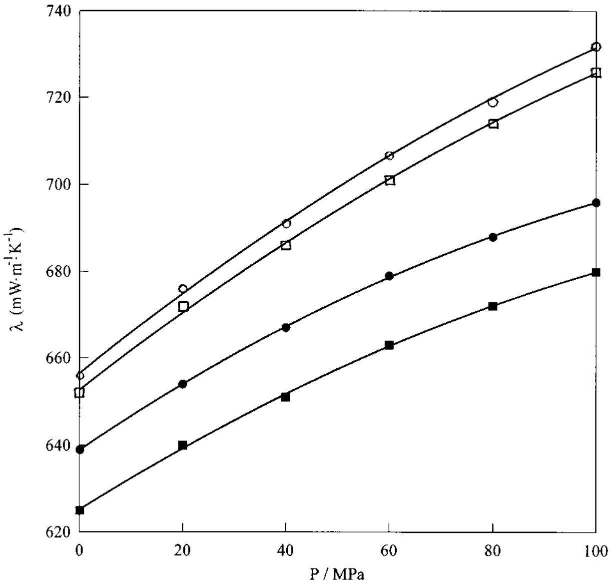

Figure 4. Variations of the thermal conductivities of $H_2O + CdCl_2$ and $H_2O + CdBr_2$ with the pressure at selected temperature T = 473 K for various concentrations. ○, $H_2O + CdCl_2$ at w = 0.05 mass fraction; ●, $H_2O + CdCl_2$ at w = 0.20 mass fraction; □, $H_2O + CdBr_2$ at w = 0.05 mass fraction; ■, $H_2O + CdBr_2$ at w = 0.20 mass fraction.

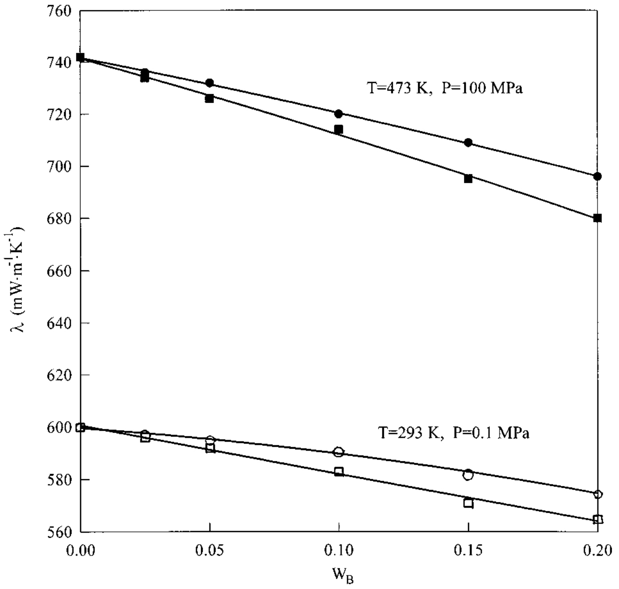

Figure 5. Variations of the thermal conductivities of $H_2O + CdCl_2$ and $H_2O + CdBr_2$ with the concentration at selected temperatures and pressures. ●, ○, $H_2O + CdCl_2$; ■, □, $H_2O + CdBr_2$.

and w. Variations of the thermal conductivities of $H_2O + CdCl_2$ and $H_2O + CdBr_2$ solutions with the concentrations at selected temperatures and pressures are shown in Figure 5. From the data obtained it can concluded that the derivative $(\partial\lambda/\partial w)_{PT}$ is always negative and almost constant for given P and T.

For the purpose of interpolation only, all measurements for $H_2O + CdCl_2$ and $H_2O + CdBr_2$ solutions have been correlated as a function of the T, P, and w, by an equation of the form

$$\lambda = \lambda_{H_2O}(P,T)[1 - A(w + 2 \times 10^{-4}w^3)] - 2 \times 10^{-8}PTw$$

$$\lambda_{H_2O}(P,T) = 7 \times 10^{-9}T^3 - 1.5113 \times 10^{-5}T^2 + 8.8016 \times 10^{-3}T - 0.862\,38 + 1.6 \times 10^{-6}PT \quad (5)$$

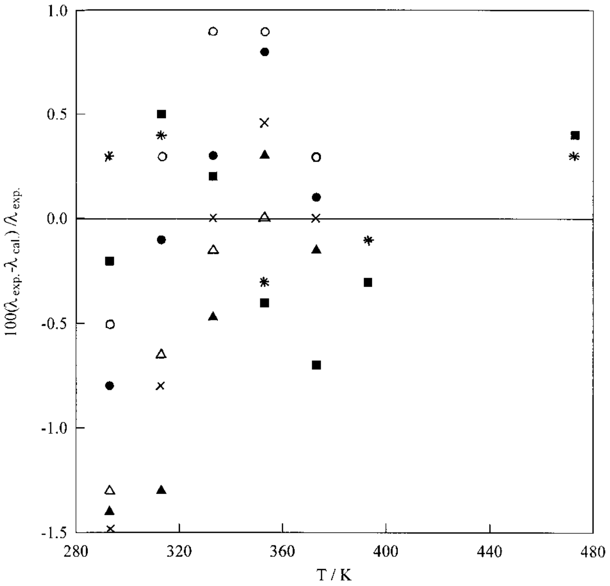

Figure 6. Percentage deviations in thermal conductivity of the literature values Eldarov (1980) and Zaitzev and Aseev (1988) from the present results at pressure P = 0.1 MPa for $H_2O + CdCl_2$. ○, w = 0.025 mass fraction; ●, w = 0.05 mass fraction; ×, w = 0.10 mass fraction; △, w = 0.15 mass fraction; ▲, w = 0.20 mass fraction (Zaitzev and Aseev, 1988); *, w = 0.10 mass fraction; ■, w = 0.20 mass fraction (Eldarov, 1980).

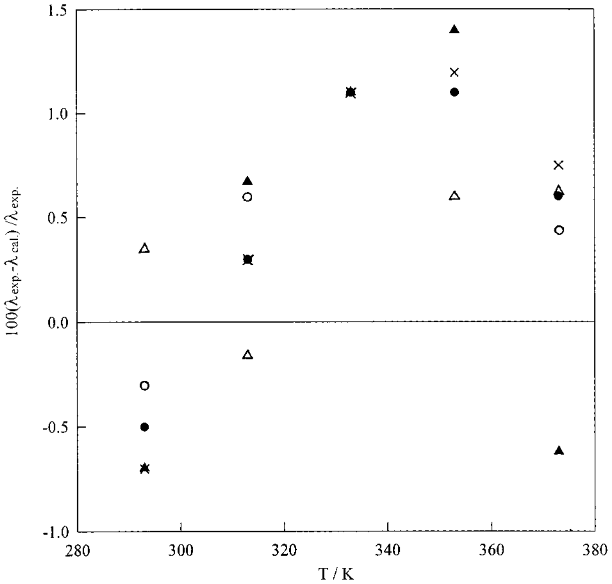

Figure 7. Percentage deviations in thermal conductivity of the literature values (Zaitzev and Aseev, 1988) from the present results at pressure P = 0.1 MPa for $H_2O + CdBr_2$. ○, w = 0.025 mass fraction; ● w = 0.05 mass fraction; ×, w = 0.10 mass fraction; △, w = 0.15 mass fraction; ▲, w = 0.20 mass fraction.

where T is the temperature in K, P is the pressure in MPa, w is the concentration in mass %, λ is the thermal conductivity in W $m^{-1}K^{-1}$, and $\lambda_{H_2O}(P,T)$ is the thermal conductivity for pure water. The values of adjusting parameter A for $H_2O + CdCl_2$ and $H_2O + CdBr_2$ solutions are 0.001 65 and 0.002 78, respectively. The maximum deviation of fits is ±1.0%.

The measurements were compared with the values obtained by other authors Eldarov (1980) and Zaitzev and Aseev (1988). The deviations are shown in Figures 6 and 7. The measurements of Zaitzev and Aseev (1988) for $H_2O + CdCl_2$ and $H_2O + CdBr_2$ that have been reported under the same conditions are in good agreement with present results in the overlaping range. The systematic errors were

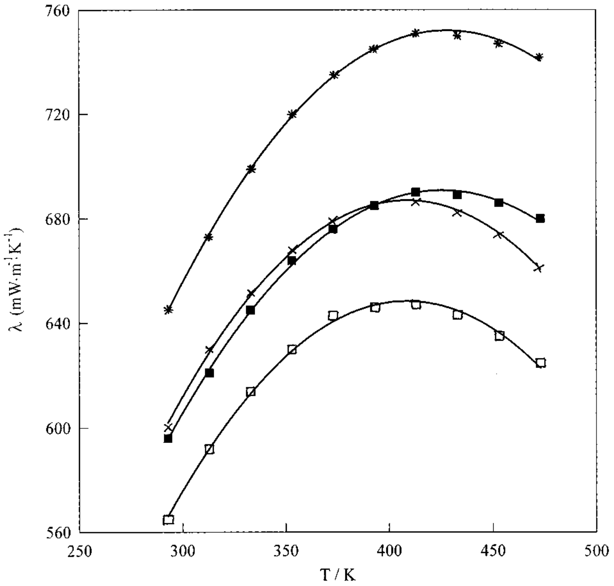

Figure 8. Thermal conductivity of H_2O + $CdBr_2$ solutions and pure water as a function of temperature along the different pressures. ×, pure water at 0.1 MPa (Magomedov, 1995); *, pure water at 100 MPa (Magomedov, 1995); □, H_2O + $CdBr_2$ solution at $w = 0.2$ mass fraction and $P = 0.1$ MPa (this work); ■, H_2O + $CdBr_2$ solution at $w = 0.2$ mass fraction and $P = 100$ MPa (this work).

not found, and the average deviation was ±0.5%. Only for a few experimental points did the deviation reach ±1/1.3%. The results given by Eldarov (1980) deviate from ours by less than ±0.5%. The systematic errors were not found, and the average deviation was ±0.22%.

In Figure 8 we give the results of thermal conductivity measurements for H_2O + $CdBr_2$ solutions together with our previously results for pure water Magomedov (1995).

4. Conclusions

By means of the guarded parallel-plate apparatus with the cylindrical thermal-conductivity cell, the $\lambda - P - T - w$ relationship for H_2O + $CdCl_2$ and H_2O + $CdBr_2$ solutions has been measured in the range of temperatures from 293 K up to 473 K, pressures up to 100 MPa, and concentrations between 0.025 and 0.20 mass fractioin of salt ($CdCl_2$ and $CdBr_2$) with an estimated uncertainty of ±1.5%.

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