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Measurements of the Thermal Conductivity of Aqueous LiBr Solutions at Pressures up to 40 MPa

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This paper describes absolute measurements of the thermal conductivity of aqueous LiBr solutions in the concentration range 5 to 15*m* (molality), the temperature range 30 to 100°C, and the pressure range 0.1 to 40 MPa. The measurements have been performed with the aid of a transient hot-wire apparatus employing a thin tantalum wire coated with an anodic tantalum pentoxide insulation layer. In using the tantalum wire, a modification of the bridge circuit has been made to keep the electric potential of the wire always higher than the ground level in order to protect the insulation layer from breakdown. The experimental data, which have an estimated accuracy of ±0.5%, have been correlated in terms of the polynomials of concentration, temperature, and pressure for practical use. Also, it has been found that the pressure coefficient of the thermal conductivity decreases with increasing concentrations.

KEY WORDS: aqueous solutions; high pressure; lithium bromide; thermal conductivity; transient hot-wire method.

1. INTRODUCTION

Aqueous lithium bromide (LiBr) solutions have become widely used in absorption refrigerators and heat pumps. However, there are very restricted numbers of measurements of the thermal conductivity of these fluids, despite the fact that such data are indispensable to the design of these systems. In order to perform accurate measurements of the thermal conductivity of electrolyte solutions under high pressures, the authors have reported the working equations appropriate to the transient hot-wire measurement with coated wires [1], measurements of aqueous NaCl solutions under pressure [2], and the development of a high-temperature, high-pressure transient hot-wire apparatus [3]. As part of a series of

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papers, we present the experimental results for the thermal conductivity of aqueous LiBr solutions in the concentration range from 5 to 15*m* (molality), the temperature range from 30 to 100°C, and the pressure range from 0.1 to 40 MPa with an estimated accuracy of ±0.5%.

2. EXPERIMENTAL APPARATUS

The principle of the thermal conductivity measurements is based on the transient hot-wire method operated in an absolute way. Particularly, the present instrument employs a metallic wire coated with a thin electrical insulation layer in order to overcome the problems caused by direct contact between metallic wire and conducting liquid. Since the principle and the working equations appropriate to the transient hot-wire measurement with coated wire are available elsewhere [1], we confine ourselves here to describing the details of the experimental apparatus.

A cross-sectional view of the hot-wire cell together with the pressure vessel is shown in Fig. 1. The present transient hot-wire apparatus was designed specifically to measure the thermal conductivity of concentrated aqueous solutions of electrolytes at temperatures up to 200°C and pressures up to 50 MPa. The main frame of the hot-wire cell consists of a titanium plate 5 mm in thickness (3) on which semicircular sintered alumina disks (10) (Al_2O_3, 99.5%) are fastened on both sides. The hot-wire (9) is made up of a 25-μm-diameter tantalum wire (99.95% purity) and a tantalum pentoxide (Ta_2O_5) insulation layer about 0.18 μm thick, which is formed *in situ* by the process of anodization [4]. Two hot wires, differing only in their lengths (about 180 and 80 mm), are employed in order to compensate the end effects. Each end of the tantalum wire is electroplated by nickel and copper, then soft soldered to the platinum hook (8). The electroplating is done in the platinum hook by putting a droplet of electroplating solution with an inserting electrode in it. After mounting the wires, the platinum hooks and the other parts of the electrical conductors except for tantalum wires are painted with silicone rubber for insulation and the silicone rubber is hardened at 150°C for 12 h to ensure enough endurance. The anodization is performed in water with a current density of about 1 $mA \cdot cm^{-2}$ (maximum applied voltage, 110 V). According to our previous feasibility study of tantalum as a hot wire for the transient hot-wire method [5], tantalum can be used up to about 100°C as long as the electric potential of the wire is higher than the ground level. Therefore, we have concluded that tantalum is suitable as a hot wire applied to conducting liquids as long as the range of application is adequately assessed. The pressure vessel (7) is machined from Hastelloy C276 (this alloy has strong corrosion resistance against many electrolyte solutions even at high

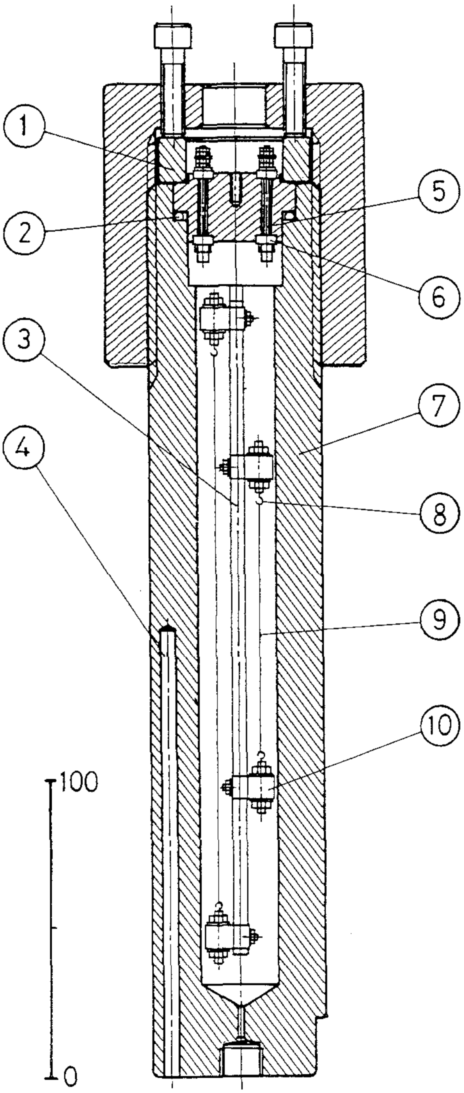

Fig. 1. Pressure vessel with hot-wire cell. (1) Thrust ring; (2) PTFE O-ring; (3) titanium plate; (4) thermometer well; (5) terminal; (6) PTFE seal; (7) pressure vessel (Hastelloy C276); (8) platinum hook; (9) titanium wire (ϕ, 25 μm); (10) alumina disk.

temperatures) which is sealed with a PTFE O-ring (2). Four electrical leads for each wire are brought out through the terminals (5). This construction can eliminate possible errors due to lead resistances, which may be more pronounced at high temperatures.

The block diagram in Fig. 2 shows the electrical system of the present apparatus, which includes the following modifications in comparison with that of Ref. 1. (i) The sampling rate of the transient voltages is increased up to about 40 times/s. (ii) The electric potential of the tantalum wire is kept higher relative to the pressure vessel (ground level) in order to prevent breakdown of the tantalum pentoxide insulation layer. (iii) R_2 is added so as to achieve a rigorously constant heat flux to the wires [6]. In Fig. 2, R_l and R_s denote the resistance of the long and short wires, respectively. The temperature rise of the metallic wire, whose end effects are compensated using long and short wires, is converted into voltage change with the bridge circuit. The voltage change is measured by a digital voltmeter (HP 3456A), which is triggered by a pulse generator with a repetition rate of about 40/s and a resolution of 0.1 μV. The resistances of the two wires are also measured at each measurement by the DVM with the aid of the four-terminal technique using a small current (1 mA). The current through the wires is measured by a DVM (HP 3478A) using a 1-Ω standard resistor, R_2. Almost all the data acquisition and instrument control except for the adjustment procedure of R_1 and R_2 can be performed using the microcomputer (HP 9000) communicating via the IEEE-488 interfaces.

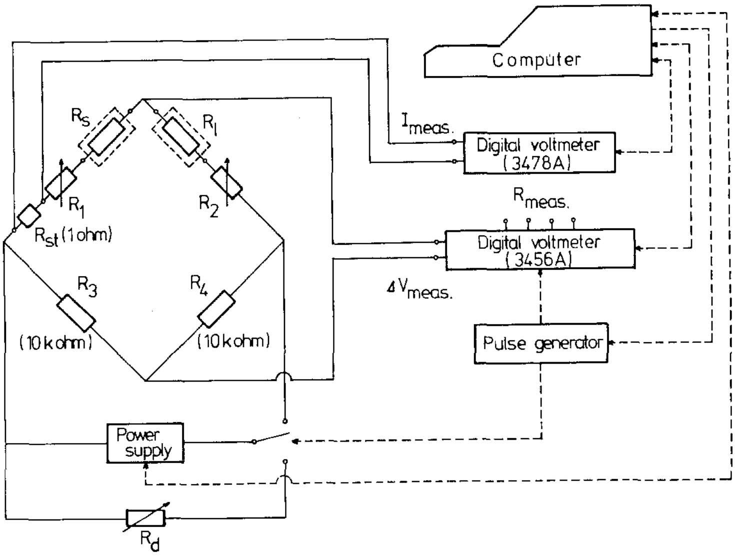

Fig. 2. Block diagram of electrical system.

As pointed out by Alloush et al. [4], tantalum pentoxide becomes unstable when it is exposed to negative voltage and can act as an insulator only above ground potential. Therefore, an attempt has been made to keep the electric potential of the wire always higher than the ground level. We found that this scheme significantly improves the linearity of $\Delta V - \ln t$ signals even in the case when it seems to be impossible to perform a measurement without this applied voltage to the bridge. The voltage applied to the bridge was 1 to 5 V, which has to be low enough in comparison to the maximum voltage on the formation of tantalum pentoxide (110 V in this case) and high enough to prevent breakdown of the insulator. This modification may produce the error caused by the small leakage current through the insulation layer to the ground potential. However, since the leakage current is so small (less than 1 μA) and stable, the error can be neglected.

Table I. Thermal Conductivity of Aqueous LiBr Solutions; $c = 5.00\ m$ (30.3 wt%)

Temperature T (°C)	Pressure P (MPa)	Thermal conductivity λ ($W \cdot m^{-1} \cdot K^{-1}$)
31.03	0.10	0.5277
40.82	0.10	0.5360
60.72	0.10	0.5586
80.40	0.10	0.5751
100.32	0.10	0.5885
31.20	10.00	0.5323
40.78	10.00	0.5444
60.79	10.00	0.5626
80.27	10.00	0.5802
100.39	10.00	0.5942
31.25	20.00	0.5368
40.77	20.00	0.5463
60.67	20.00	0.5683
80.56	20.00	0.5826
100.37	20.00	0.5957
31.25	30.00	0.5400
40.74	30.00	0.5510
60.61	30.00	0.5688
80.47	30.00	0.5816
100.93	30.00	0.5907
31.30	40.00	0.5442
40.74	40.00	0.5531
60.75	40.00	0.5720
80.51	40.00	0.5900
100.12	40.00	0.6014

The entire pressure vessel is immersed in a well-stirred temperature-controlled silicone oil bath. The temperature of the sample is measured with a platinum resistance thermometer which was calibrated on the IPTS-68, and its accuracy is ±0.1 K. Pressure is generated by a hand-operated pressurizing pump and is measured with the aid of a Bourdon-type pressure gauge which is accurate to ±0.035 MPa.

3. RESULTS AND DISCUSSION

The thermal conductivity measurements have been performed in the concentration range of 5.00, 10.0, and 15.0 *m* (LiBr mol/kg H_2O), which corresponds to 30.3, 46.5, and 56.6 wt%, the temperature range of 30 to 100°C, and the pressure range of 0.1 to 40 MPa. The aqueous LiBr

Table II. Thermal Conductivity of Aqueous LiBr Solutions; $c = 10.0\ m$ (46.5 wt%)

Temperature T (°C)	Pressure P (MPa)	Thermal conductivity λ ($W \cdot m^{-1} \cdot K^{-1}$)
29.16	0.10	0.4682
40.67	0.10	0.4773
60.23	0.10	0.4908
80.27	0.10	0.5014
100.07	0.10	0.5109
29.36	10.00	0.4697
40.65	10.00	0.4802
60.15	10.00	0.4936
80.58	10.00	0.5022
100.10	10.00	0.5147
29.53	20.00	0.4722
40.68	20.00	0.4809
59.94	20.00	0.4949
80.45	20.00	0.5051
100.46	20.00	0.5130
29.70	30.00	0.4750
40.65	30.00	0.4850
60.05	30.00	0.4975
80.56	30.00	0.5080
100.48	30.00	0.5154
29.92	40.00	0.4785
40.63	40.00	0.4874
59.97	40.00	0.5007
80.49	40.00	0.5114
100.48	40.00	0.5190

solutions were prepared gravimetrically by means of a precision balance and the accuracy of the concentration is estimated as ±1%. $LiBr \cdot H_2O$ (stated purity of not less than 99% without further purification) was mixed with twice-distilled, ion-exchanged water. In order to confirm the concentration of samples thus prepared and also to check the degradation of the samples after measurement, the density of the samples was measured at room temperature with a precision pycnometer before and after measurement. We found that the change in density was less than 0.2% over the whole concentration range.

Tables I to III contain the present experimental results for the thermal conductivity of three aqueous LiBr solutions. These values are the averages of two to four measurements, whose reproducibility was less than ±0.5%, at the same temperature and pressure. In all these measurements, the

Table III. Thermal Conductivity of Aqueous LiBr Solutions; $c = 15.0\,m$ (56.6 wt%)

Temperature T (°C)	Pressure P (MPa)	Thermal conductivity λ ($W \cdot m^{-1} \cdot K^{-1}$)
29.68	0.10	0.4286
40.47	0.10	0.4380
60.32	0.10	0.4524
80.53	0.10	0.4640
100.32	0.10	0.4737
29.84	10.00	0.4311
40.62	10.00	0.4395
60.40	10.00	0.4537
80.40	10.00	0.4676
100.26	10.00	0.4752
30.05	20.00	0.4328
40.54	20.00	0.4417
60.35	20.00	0.4556
80.48	20.00	0.4674
100.32	20.00	0.4768
30.15	30.00	0.4343
40.50	30.00	0.4435
60.40	30.00	0.4576
80.24	30.00	0.4713
100.35	30.00	0.4789
30.30	40.00	0.4371
40.54	40.00	0.4453
60.39	40.00	0.4602
80.26	40.00	0.4734
100.32	40.00	0.4818

current through the wires was adjusted to obtain a temperature rise of the wires of approximately 1 K at about 4 s after the initiation of heating. The accuracy of the present measurements was estimated to be $\pm 0.5\%$ according to the same assessment described in Ref. 1.

As an example of the present results, Fig. 3 shows the concentration dependence of the thermal conductivity at atmospheric pressure. In this figure the values for pure water are taken from our previous experimental data [2] and the concentration as the weight percentage is also given. The conversion equation for these two concentrations is $w = 100M_1c/(1000 + M_1c)$, where c is the molality (mol/kg H_2O), w is the weight percent, and M_1 is the molecular weight of LiBr. In addition, small

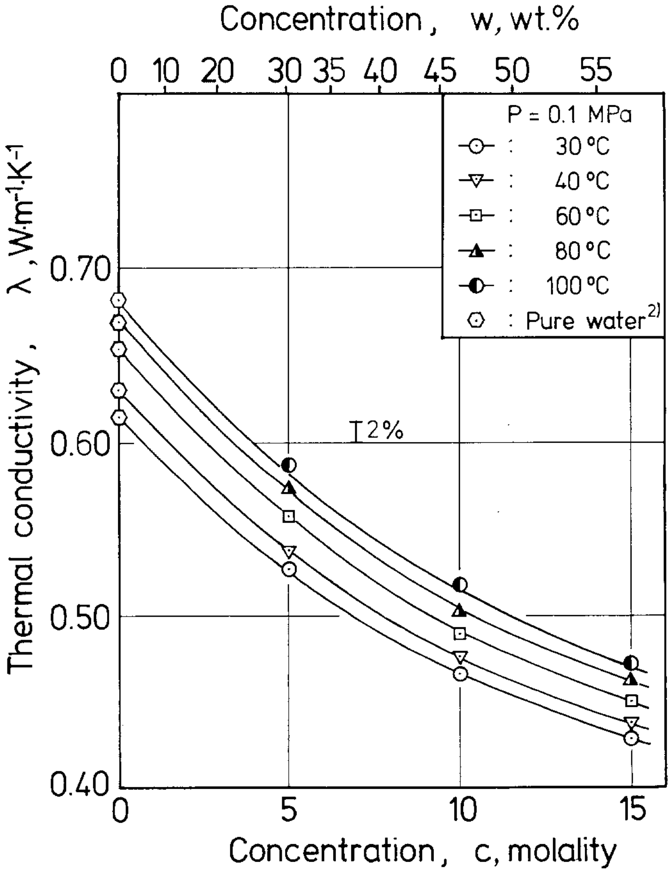

Fig. 3. Concentration dependence of the thermal conductivity of aqueous LiBr solutions at atmospheric pressure.

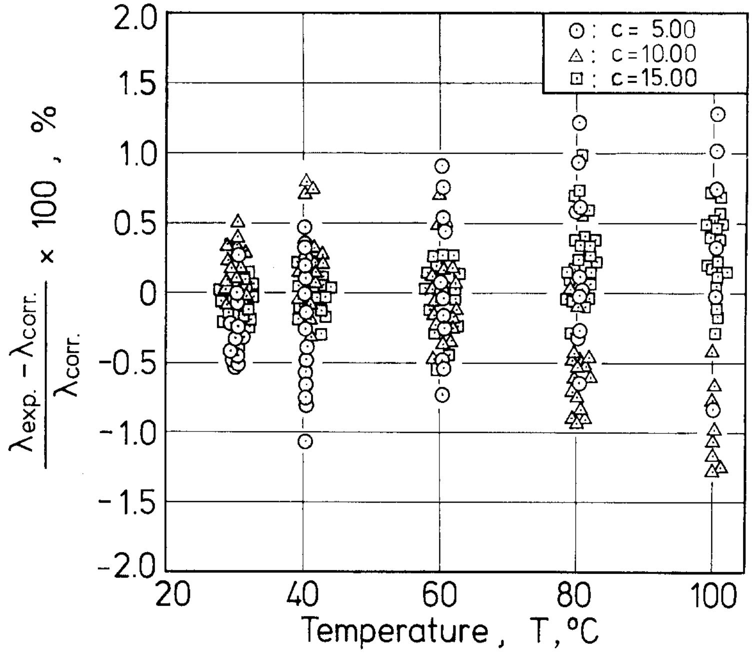

Fig. 4. Overall comparison between the present experimental results and the correlation Eqs. (2)–(4).

Table IV. Optimum Values of the Coefficients a_{ij} and b_{ij} in Eqs. (3) and (4)

i	$j=0$	$j=1$	$j=2$
		a_{ij}	
0	5.568456×10^{-1}	2.234787×10^{-3}	-9.931517×10^{-6}
1	-1.439285×10^{-2}	-2.183529×10^{-4}	1.411211×10^{-6}
2	2.630458×10^{-4}	9.420297×10^{-6}	-6.613053×10^{-8}
		b_{ij}	
0	9.212191×10^{-4}	-2.279278×10^{-5}	-7.560160×10^{-7}
1	-6.029333×10^{-6}	6.417047×10^{-7}	-1.092238×10^{-8}
2	5.585225×10^{-8}	-9.135250×10^{-9}	3.099199×10^{-10}

temperature differences of individual data are corrected to nominal temperatures using the following equation.

$$\lambda_{\text{nom}}(T_{\text{nom}}, P, c) = \lambda(T_{\text{r}}, P, c) + \left(\frac{\partial \lambda}{\partial T}\right)_{P,c} (T_{\text{nom}} - T_{\text{r}}) \tag{1}$$

Here T_{r} refers to the temperature at which the thermal conductivity is measured. This correction did not exceed 0.8 K.

The present experimental results were analyzed and correlated in terms of temperature, pressure, and concentration using polynomials. First, because the pressure dependence of the thermal conductivity is almost

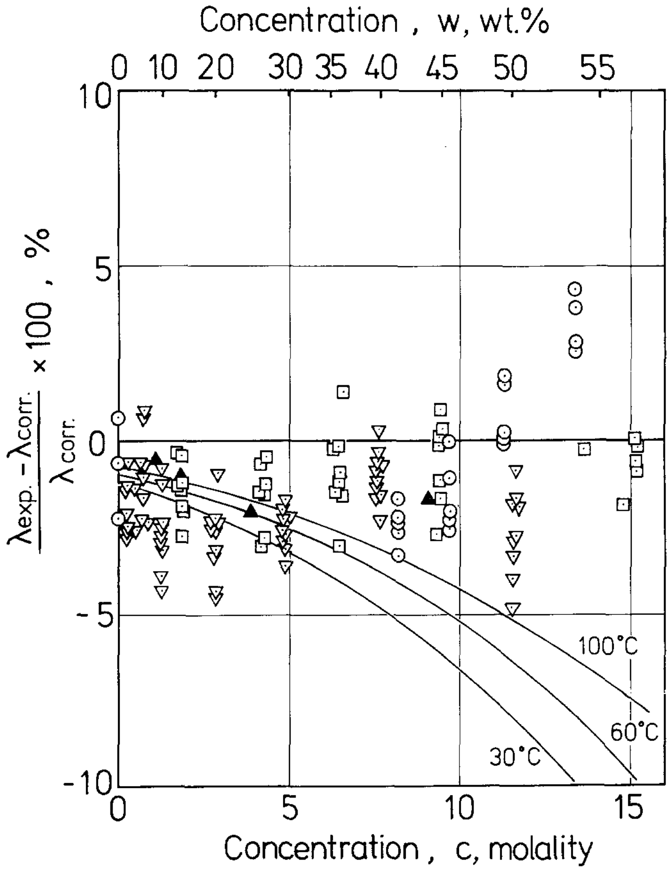

Fig. 5. Comparison of the present correlation with other previous data at atmospheric pressure. (▲) Ref. 12; (⊡) Ref. 7; (▽) Ref. 9; (⊙) Ref. 4; (——) Refs. 10 and 11.

linear in the present pressure region, the results along each isotherm were correlated as a function of pressure using

$$\lambda(T, P, c) = \lambda^0(T, c)[1 + \phi(T, c)P] \tag{2}$$

where $\phi(T, c)$ represents the pressure coefficient of the thermal conductivity, and $\lambda^0(T, c)$ is the thermal conductivity extrapolated to zero pressure. Then $\phi(T, c)$ and $\lambda^0(T, c)$ are correlated in terms of the equations

$$\lambda^0(T, c) = \sum_{i=0}^{2} \left(\sum_{j=0}^{2} a_{ij} T^j \right) c^i \tag{3}$$

$$\phi(T, c) = \sum_{i=0}^{2} \left(\sum_{j=0}^{2} b_{ij} c^j \right) T^i \tag{4}$$

where T is the temperature in °C, P the pressure in MPa, c the concentration in m, and λ the thermal conductivity in $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$. The optimum coefficients a_{ij} and b_{ij} in the above equations extracted by the least-square fittings are listed in Table IV. Equations (2) to (4) reproduce

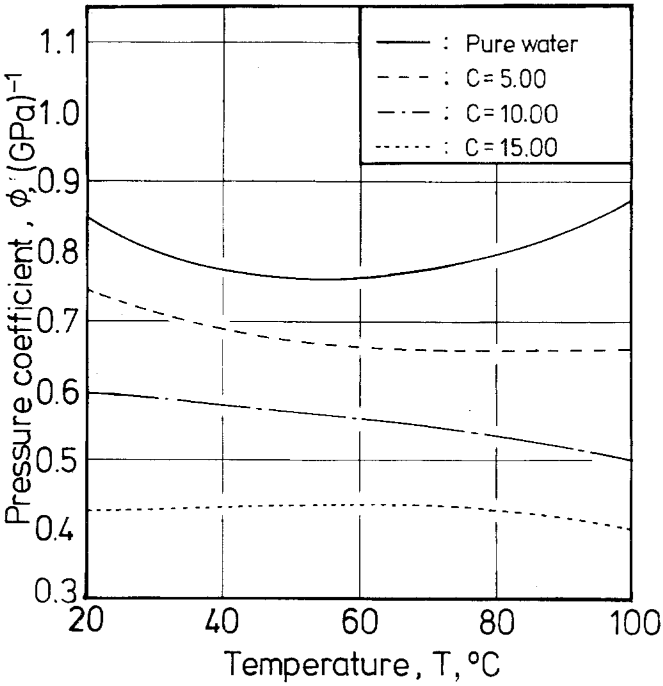

Fig. 6. The pressure coefficient of the thermal conductivity of aqueous LiBr solutions.

the entire body of experimental data within a mean deviation of 0.35% as depicted in Fig. 4.

For comparison, Fig. 5 shows the deviation plots of previous works from the present correlation at atmospheric pressure. The concentration dependence of the results of Uemura and Hasaba [7], measured with a steady-state concentric-cylinder method relative to pure water, generally agrees with the present correlation but their absolute values differ, with a maximum deviation of about −3%. Althoug the data of Alloush et al. [4], obtained by the same method as in the present study, show a different concentration dependence, they are still reasonably consistent with the present results within the mutual accuracies. It should be noted here that the expression of LiBr concentration in Ref. 4 has to be corrected [8]. Their lithium bromide mass fraction ξ is not LiBr in H_2O but $LiBr \cdot H_2O$ in H_2O. Therefore, their ξ values should be corrected as follows: $0.500 \rightarrow 0.414$, $0.550 \rightarrow 0.456$, $0.600 \rightarrow 0.497$, and $0.650 \rightarrow 0.538$. The results of Gruzdev et al. [9], measured with the aid of a steady-state concentric-cylinder method, are generally lower than the present correlation, with a mean deviation of about −2% and a maximum deviation of −5%. We also see that the assumption of linear concentration dependence proposed by Riedel [10] and extended with regard to the temperature dependence by McLaughin [11] is not valid for a high concentration range.

The present study is the first measurement of the thermal conductivity of aqueous LiBr solutions under high pressures. Figure 6 shows the temperature dependence of the pressure coefficient defined in Eq. (2) for three concentrations compared with that of pure water. Even though the uncertainty of the pressure coefficient may be about 20%, it can be observed from this figure that the pressure coefficient decreases with increasing concentrations. This tendency is similar to that of aqueous NaCl solutions which was previously studied [2].

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