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Thermal Conductivity of Aqueous Potassium Chloride Solutions

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This paper presents new absolute measurements of the thermal conductivity of aqueous potassium chloride solutions using the transient coated-hot-wire technique. The data cover the range from 295 to 360 K at pressures slightly above the vapor pressures and over a concentration range of 0 to 3 $\mathrm{mol \cdot kg^{-1}}$. The instrument can be used to measure the thermal conductivity with a reproducibility of better than 0.2%, and a comparison of the present results with data available in the literature indicates that the uncertainty of the present data is better than 0.5%. An empirical correlation that reproduces the data within the claimed uncertainty is presented.

KEY WORDS: electrolyte solutions; potassium chloride aqueous solutions; thermal conductivity; transient coated-hot-wire technique.

1. INTRODUCTION

The important role played by aqueous solutions of electrolytes in a wide variety of areas from biology to geology is well recognized. The availability of reliable thermophysical property data on this kind of system is of great importance for applications and studies in these areas, from both industrial and scientific points of view. Properties of electrolyte solutions, such as the viscosity, diffusion coefficients, or electrical conductivity, have long been the subject of considerable attention and study [1–3]. However, for the thermal conductivity there is still a lack of sufficiently accurate data to support the development of reliable theoretical or semi-empirical equations in order to predict this property.

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The available data from 1951 to 1990 on the thermal conductivity of potassium chloride solutions are compiled by Abdulagatov and Magomedov [4]. Most of the data [4–10] were obtained by steady-state techniques, and consequently their nominal uncertainties are never better than 2%. Only recently [11–16] was the transient hot-wire technique successfully applied to electrolyte solutions producing data of the same level of uncertainty that has become normal for electrically nonconducting liquids (0.5%). In these recent developments, new instruments were developed from the classical transient hot-wire method in which the bare hot-wire is replaced by a coated hot-wire to avoid the problems derived from the electrical contact between the wire and the conducting liquid [13–17].

In the present paper, we present new absolute thermal conductivity measurements of three different compositions of potassium chloride solutions from 295 to 360 K, near the saturation vapor pressure, using the transient coated-hot-wire technique. The results are compared with the values of other authors, and the uncertainty of the data is estimated to be 0.5%. An empirical correlation with an estimated uncertainty of 0.5% is also proposed.

2. EXPERIMENTAL PROCEDURE

The thermal conductivity measurements were performed in an absolute manner with a transient coated-hot-wire technique described in detail elsewhere [16]. The Wheatstone bridge circuit used to record the resistance change and, therefore, the temperature rise of the wires is similar to the one described by Wakeham and Zalaf [17] where details of its construction are provided. Only a short description of the method and the appropriate working equations is provided here, since they have been described previously [18, 19].

The transient coated-hot-wire method is based on the use of a tantalum wire, anodized *in situ* with an insulating layer of tantalum pentoxide, simultaneously as a heat source and a temperature sensor, in contact with the test fluid. The temporal evolution of the wire temperature (ΔT_{id}), after a step voltage is applied, is recorded. According to the ideal mathematical model of an infinite line heat source, the thermal conductivity can be obtained from the slope of the line ΔT_{id} *versus* logarithm of time according to

$$\Delta T_{id} = \frac{q}{4\pi\lambda} \ln \frac{4kt}{r_i^2 C} \tag{1}$$

where q is the heat dissipation per unit length, λ is the thermal conductivity, t is the time, r_i is the radius of the wire, k is the thermal diffusivity, and C is equal to $\exp(\gamma)$ where γ is Euler's constant.

However, as a real instrument departs from its ideal model, a number of small corrections must be applied to the observed temperature rise of the wire. For the present measurements, an addition to the usual set of corrections of the transient hot-wire method [19] must be applied, due to the existence of the extra layer of the wire coating. Thus, from experimental measurements of the temperature of the wire, ΔT_w, the ideal temperature, ΔT_{id}, is obtained from

$$\Delta T_{id} = \Delta T_w + \sum_i \delta T_i \tag{2}$$

where the various corrections δT_i have been summarized elsewhere [16, 19] and the correction for the effect of the insulation that must be added in the present work is given in Refs. 14 and 20.

If the instrument operates correctly, the corrected measured temperature rise, ΔT_{id}, should be a linear function of $\ln t$ provided that no forms of heat transfer other than conduction are developed in the measurement cells. Figure 1 shows an example of a plot of the deviations of corrected experimental data (ΔT, $\ln t$) from linearity, obtained for a typical run of a 2.94 mol · kg^{-1} KCl solution, at a reference temperature of 354.367 K and slightly above the saturation pressure. No point departs from the straight line by more than ±0.1 %, and no systematic curvature is observed. The

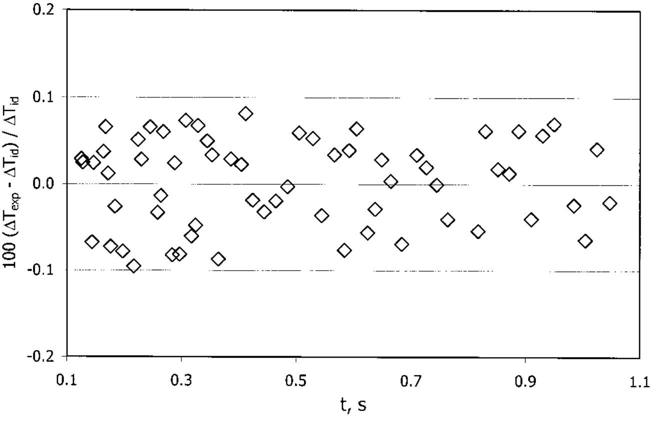

Fig. 1. Percentage deviations of the measured temperature rise as a function of the logarithm of time, from the linear fit for KCl solution 2.94 mol · kg^{-1}, at 354.367 K and near the saturation line.

same behavior was observed in all of the measurements reported. These results demonstrate that the instrument operates correctly and confirm the absence of significant heat transfer by radiation or convection.

3. RESULTS AND DISCUSSION

The thermal conductivity measurements have been carried out for the concentrations 0.25, 1.06, and 2.94 $\mathrm{mol \cdot kg^{-1}}$ ($\mathrm{KCl\ mol \cdot kg^{-1}\ H_2O}$) in the temperature range from 295 to 360 K at pressures slightly above the vapor pressures.

The potassium chloride solutions were prepared gravimetrically using a precision balance with a total capacity of 1000 g and a resolution of 0.1 g. Potassium chloride was supplied by Fluka Chemica puriss. p.a., and before weighing, it was dried at 150°C under vacuum for 24 hours. The water used in the preparation of the solutions was obtained from a Millipore device with an electrical conductivity of 18 $\mathrm{M\Omega^{-1} \cdot cm^{-1}}$. The estimated uncertainty in the final composition of the solutions is 0.04%.

The density data for the various compositions, necessary to apply the small corrections in the analysis of the data, were obtained from a correlation proposed by Grimes et al. [22], and those for the heat capacity were obtained from a correlation of Tanner and Lamb [23].

Table I contains the experimental results for the thermal conductivity of aqueous potassium chloride solutions at concentrations of 0.25, 1.06, and 2.94 $\mathrm{mol \cdot kg^{-1}}$ at a reference temperature T and near their vapor pressures, together with the experimental results for the thermal conductivity of water at the same conditions performed after the aqueous solution measurements. For the sake of clarity, only one set of the experimental values of the thermal conductivity of water is presented in Table I. Nevertheless, in Fig. 2 the good performance of our instrument can be confirmed by the plot of the deviations of both sets of data from the values calculated by the IUPAC recommended correlation [24]. It can be seen that almost all data depart no more than 0.5% from the proposed correlation which was assigned an uncertainty of 0.7%. From these considerations and according to the assessment procedure described elsewhere [16], the uncertainty assigned to these measurements is estimated to be 0.5%.

The simultaneous temperature and composition dependence of the thermal conductivity of KCl aqueous solutions has been represented by a polynomial in temperature and molality of the form:

$$\lambda(T, m)/(\mathrm{W \cdot m^{-1} \cdot K^{-1}}) = \sum_{i=0}^{2} \left[\sum_{j=0}^{2} a_{ij} (T/K - 273.15)^j \right] (m/\mathrm{mol \cdot kg^{-1}})^i \tag{3}$$

Table I. Thermal Conductivity, λ, of Aqueous KCl Solutions as a Function of Temperature T

$m = 0.00\ \mathrm{mol \cdot kg^{-1}}$		$m = 0.25\ \mathrm{mol \cdot kg^{-1}}$		$m = 1.06\ \mathrm{mol \cdot kg^{-1}}$		$m = 2.94\ \mathrm{mol \cdot kg^{-1}}$	
T (K)	λ ($\mathrm{W \cdot m^{-1} \cdot K^{-1}}$)	T (K)	λ ($\mathrm{W \cdot m^{-1} \cdot K^{-1}}$)	T (K)	λ ($\mathrm{W \cdot m^{-1} \cdot K^{-1}}$)	T (K)	λ ($\mathrm{W \cdot m^{-1} \cdot K^{-1}}$)
296.909	0.6031	298.689	0.5997	298.863	0.5797	297.327	0.5597
296.979	0.6066	299.059	0.6011	299.044	0.5819	297.388	0.5591
300.449	0.6120	300.392	0.6039	302.033	0.5861	302.072	0.5689
300.918	0.6118	300.548	0.6046	302.148	0.5856	307.002	0.5807
302.770	0.6115	308.352	0.6152	310.354	0.6041	307.449	0.5806
302.772	0.6147	308.394	0.6147	310.505	0.6013	307.600	0.5800
303.215	0.6160	308.454	0.6154	310.522	0.6005	312.494	0.5898
303.215	0.6160	316.510	0.6273	319.712	0.6148	312.574	0.5890
303.258	0.6162	316.696	0.6274	319.989	0.6148	313.222	0.5893
305.913	0.6189	325.243	0.6404	320.024	0.6170	321.218	0.6007
311.231	0.6268	325.368	0.6407	328.017	0.6260	321.355	0.6032
318.611	0.6383	325.503	0.6414	328.084	0.6298	325.641	0.6093
323.920	0.6436	335.473	0.6483	328.111	0.6256	325.958	0.6075
328.952	0.6464	335.679	0.6522	337.065	0.6403	325.974	0.6059
329.050	0.6465	345.730	0.6593	337.147	0.6401	333.405	0.6166
329.216	0.6482	345.888	0.6626	337.229	0.6377	333.819	0.6152
329.272	0.6504	353.852	0.6633	345.596	0.6472	333.968	0.6144
329.442	0.6513	353.872	0.6667	345.903	0.6476	340.362	0.6229
334.973	0.6523	358.446	0.6671	346.075	0.6490	340.585	0.6230
335.002	0.6555	358.455	0.6666	353.856	0.6512	340.846	0.6231
335.008	0.6564			353.894	0.6507	348.910	0.6302
340.701	0.6561					349.030	0.6283
340.928	0.6606					354.255	0.6325
344.101	0.6591					354.366	0.6331
344.504	0.6613					354.375	0.6313
345.829	0.6619					360.749	0.6378
347.523	0.6633					361.040	0.6360
349.924	0.6687					361.086	0.6344
350.189	0.6628						
350.268	0.6657						
355.106	0.6685						

where m is the molality of the solution and a_{21} and a_{22} were set equal to zero since they did not have statistical significance. The coefficients a_{ij}, together with their standard deviations, are given in Table II. The experimental results (Table I) are reproduced by Eq. (3) with a standard error of $0.0016\ \mathrm{W \cdot m^{-1} \cdot K^{-1}}$. Figure 3 shows the deviations of the present experimental data from Eq. (3). It can be seen that no systematic trend is observed, and most of the data depart no more than $\pm 0.5\%$ from the correlation. Included in the same figure are deviations from Eq. (3) of some experimental measurements of the thermal conductivity of water together

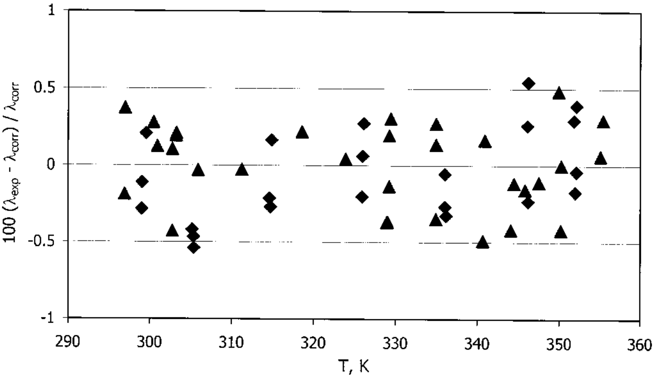

Fig. 2. Deviations of the experimental values of the thermal conductivity of water from the standard reference data given by the IUPAC recommended correlation [24]; ◆ performed before: ▲ performed after.

with values calculated with the correlation recommended by IUPAC. In no case do any of the data depart more than ±0.5% from Eq. (3).

Comparison of the present results with those of other authors is displayed in Fig. 4 as a function of temperature for the potassium chloride solutions. Most of the previous measurements [4–10] were performed with steady-state methods, and some of them are relative measurements [11]. From Fig. 4, it is observed that, except for the higher molality, there is good agreement between the values obtained by Eq. (3) and the data of Abdulagatov and Magomedov [4], well within the uncertainty of 2% claimed by the authors. The higher molality results fall in a range that was not covered by the fitting procedure, and so it is not unexpected that those values show larger deviations. There is also good agreement between our

Table II. Optimum Values of Coefficients a_{ij} in Eq. (3); Standard Deviations of the Coefficients in Brackets

i, *j*	*i* = 0	*i* = 1	*i* = 2
0	0.5524 [0.0016]	−0.0369 [0.002]	0.00738 [0.0006]
1	0.0024 [5.9×10^{-5}]	0.000259 [3.7×10^{-5}]	-7.5×10^{-5} [1.2×10^{-5}]
2	-1.2×10^{-5} [5.3×10^{-7}]	— —	— —

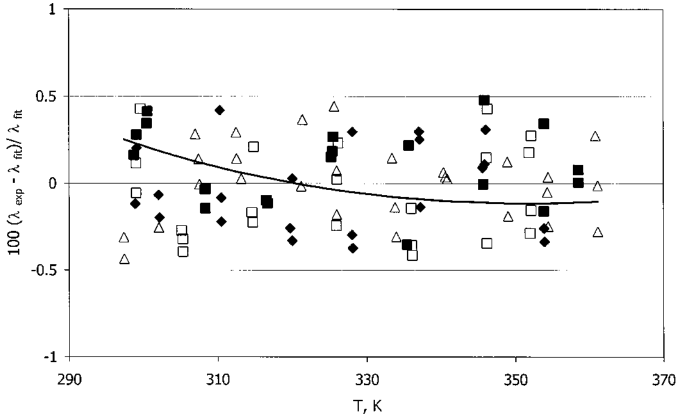

Fig. 3. Comparison of the experimental measurements of the thermal conductivity of KCl, as a function of temperature, with Eq. (3) (baseline); □, water; ■, $m = 0.25\ \mathrm{mol \cdot kg^{-1}}$; ◆, $m = 1.06\ \mathrm{mol \cdot kg^{-1}}$; △, $m = 2.94\ \mathrm{mol \cdot kg^{-1}}$; —, IUPAC recommendation [24].

values and those from Pepinov and Guseinov [10]. On the other hand, the data obtained by Davis et al. [21] performed with a nonsteady-state hot film sensor, show large deviations from the present data, up to 6%. This result may be due to the method used to perform the measurements. The authors used a platinum film deposited on a quartz rod, coating this film

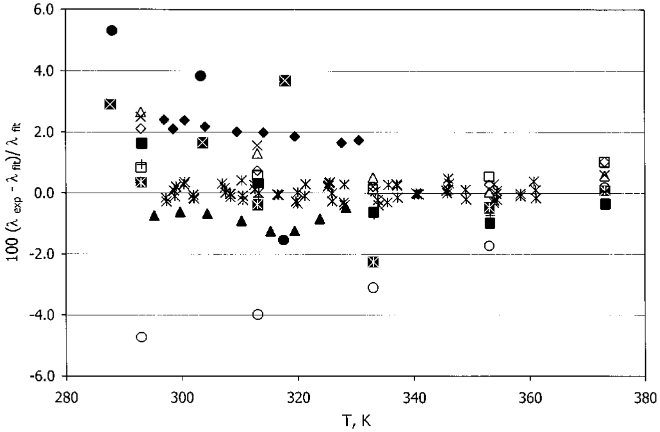

Fig. 4. Comparison of the experimental measurements of the thermal conductivity of KCl, as a function of composition, with Eq. (3) (baseline); ⚹, present work; [4] □, $m = 2.5\%$; ◇, $m = 5\%$; △, $m = 10\%$; ×, $m = 15\%$; ⧗, $m = 20\%$; ○, $m = 25\%$; [10] +, $m = 1\%$; ■, $m = 3\%$; [12] ◆, $m = 10\%$; ▲, $m = 20\ \%$; [21] ●, $c = 0.5\ \mathrm{mol \cdot L^{-1}}$; ⊠, $c = 3\ \mathrm{mol \cdot L^{-1}}$.

with quartz. However, the equation used for this sensor is not presented and it seems that the uncertainty claimed for the results of the salt-water solutions is too small.

The results obtained by Nagasaka and Nagashima [11] with a transient coated-hot-wire technique, using a coated tantalum wire, are only shown in a figure and cannot be compared with those of the present work. However, their conclusions are the same as those presented here, since the variation of the thermal conductivity with the composition is not linear.

Assael et al. [12] measured two potassium chloride solutions from 298 to 340 K using also a coated tantalum wire. Although there is good agreement with our results for the more concentrated solution, the deviations for the more dilute are slightly larger (±2%) than the estimated mutual uncertainty of the data (±1%).

4. CONCLUSIONS

Thermal conductivity results have been reported for different concentrations of aqueous potassium chloride solutions near the saturation line. The experimental results were obtained with the transient coated-hot-wire technique with an uncertainty of 0.5% and have been shown to be consistent with other measurements along the vapor pressure curves. A correlation as a function of temperature and molality is proposed which reproduces the present experimental data to within 0.5%.

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