International Journal of Thermophysics, Vol. 21, No. 1, 2000

Thermal Diffusivity of Aqueous Solutions of Magnesium Chloride in the Temperature Range from 294 to 371 K

J. Wang[1] **and M. Fiebig**[2, 3]

Received March 3, 1999

The thermal diffusivity of aqueous solutions of magnesium chloride was determined in the temperature range 294 to 371 K and at atmospheric pressure. Using a noninvasive optical technique—laser-induced thermal grating (LTG)—the measurements were carried out in aqueous solutions of weight fractions of 5, 10, 15, and 20% magnesium chloride. The measurement results for the aqueous solutions are presented as a function of temperature and weight fraction.

KEY WORDS: Aqueous solution; diffraction; laser-induced thermal grating; magnesium chloride; thermal conductivity; thermal diffusivity.

1. INTRODUCTION

Thermophysical properties of aqueous salt solutions at elevated temperatures are important for understanding a variety of chemical processes, including desalination processes and corrosion in boilers.

While experimental data of the thermophysical properties such as the specific heat capacity c_p, the density ρ, the viscosity η, and the thermal conductivity λ and diffusivity a for aqueous salt solutions are available at temperatures below 293.15 K [1], very few values are available at higher temperatures. This is because the thermophysical properties, especially the transport properties of corrosive aqueous electrolytes, were difficult to measure at elevated temperatures.

---

[1] College of Power Engineering, University of Shanghai for Science and Technology, 516 Ju Gong Road, Shanghai 200093, People's Republic of China.

[2] Institut für Thermo- und Fluiddynamik, Ruhr-Universität Bochum, D-44780 Bochum, Germany.

[3] To whom correspondence should be addressed.

In this paper, we present experimental thermal diffusivity data for aqueous solutions of magnesium chloride in an extended temperature range. Measurements of the thermal diffusivity of aqueous solutions of 5, 10, 15, and 20 wt% $MgCl_2$ were performed with a laser-induced thermal grating technique (LTG). For temperatures from 294 to 371 K and atmospheric pressure, the experimental results for aqueous solutions of magnesium chloride are presented as a function of temperature and weight fraction of magnesium chloride. Such values are essential for testing models and theoretical equations used to describe the thermophysical properties of electrolyte solutions.

2. MEASUREMENT TECHNIQUE AND EXPERIMENTAL SETUP

The experimental setup of the laser-induced thermal grating technique (LTG) and the operating procedure used for the thermal diffusivity measurements were similar to those described in detail elsewhere [2–6]. The principle of the measurement is based on inducing a transient thermal grating in the liquid sample by two-beam interference and absorption of laser light and detecting the first-order diffraction intensity at the grating. Unlike the well-known hot-wire technique, no sensors have to be inserted in the liquid sample; therefore, this measurement technique is especially suitable for measurements of electrically conducting and corrosive liquids. In addition, this technique produces absolute thermal-diffusivity values without calibration procedures.

Two pulsed laser beams of identical wavelength λ_h and equal intensity ($I_A = I_B$) intersect at an angle θ ($\theta \approx 0.5$ deg) and create a periodic distribution of light intensity in the liquid sample by two-beam interference (Fig. 1). A spatially periodic distribution of temperature (thermal grating) corresponding to the interference fringes is then induced due to absorption

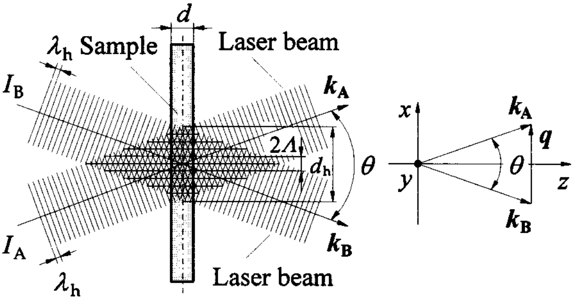

Fig. 1. Two-beam interference and laser-induced thermal grating (LTG).

of laser intensity. This temperature distribution results in a periodic distribution of the refractive index n (optical grating)

$$\Delta n(t) = \left(\frac{\partial n}{\partial T}\right) \Delta T(t) \tag{1}$$

where $\Delta T(t)$ is the amplitude of the periodic distribution of temperature.

After the laser pulse ($t > t_{\mathrm{h}}$, $t_{\mathrm{h}} \approx 1000\,\mu\mathrm{s}$), $\Delta T(t)$ characterizing the transient thermal grating decays with a relaxation time τ,

$$\tau = \frac{1}{aq^2} = \frac{1}{a}\left(\frac{\Lambda}{2\pi}\right)^2 \tag{2}$$

due to heat conduction in the heated region of the liquid sample. Here a is the thermal diffusivity of the liquid sample, q the modulus of the grating vector, and Λ the grating period,

$$\Lambda = \frac{\lambda_{\mathrm{h}}}{2\sin(\theta/2)} \approx \frac{\lambda_{\mathrm{h}}}{\theta} \tag{3}$$

In the present measurements, the modulus q of the grating vector is determined by measuring the diffraction angle θ_{s} instead of the intersection angle θ [4],

$$q = \frac{2\pi}{\lambda_{\mathrm{p}}} \sin\theta_{\mathrm{s}} \tag{4}$$

Therefore, we can evaluate the thermal diffusivity a of the sample by analyzing the decay of the thermal grating and determining the diffraction angle θ_{s}.

Obviously, the optical grating decays along with the periodic distribution of temperature at $t > t_{\mathrm{h}}$. When we focus a probing laser beam (wavelength λ_{p}) to the center of the grating, the intensity of the first-order diffracted beam, $I_1(t)$, is proportional to the square of the amplitude $\Delta T(t)$ of the periodic distribution of temperature [2, 7]

$$I_1(t) \propto \phi_{\mathrm{M}}(t)^2 = \left[\frac{2\pi d}{\lambda_{\mathrm{p}}}\left(\frac{\partial n}{\partial T}\right)\Delta T(t)\right]^2 \propto \exp(-2t/\tau) \tag{5}$$

where ϕ_{M} is the maximum phase variation of the grating. The time dependence of the first-order diffracted intensity $I_1(t)$ is detected in the homodyne scheme at the diffraction angle θ_s with a photomultiplier tube (PMT), whose output signal $v(t)$ is recorded by a digital memory unit. The relaxation time τ can thus be determined by fitting the acquired data for $v(t)$ to Eq. (5) with the least-squares method.

In the measurements of aqueous salt solutions, the time dependence $v(t)$ of the diffracted signal seems to decay exponentially as in the case of pure liquids; however, it cannot be analyzed with Eq. (5) to determine the relaxation time τ. Due to the Soret effect, the laser-induced periodic distribution of temperature leads to the phenomenon of phase separation, i.e., a concentration grating, which is superposed upon the thermal grating and decays far more slowly compared with the thermal grating. In this case, the maximum phase variation ϕ_M of the optical grating in Eq. (5) has to be modified as the sum of two terms [8],

$$\phi_M(t) = \phi_{\text{thermal}}(t) + \phi_{\text{concen.}}(t) \tag{6}$$

$\phi_{\text{thermal}}(t)$ is the phase variation of the thermal grating and decays exponentially with the relaxation time τ. $\phi_{\text{concen.}}(t)$ denotes the phase variation of the concentration grating and has a lifetime one to two orders of magnitude longer than the thermal grating. The diffracted signal can thus be modified and reduced to

$$v(t) \propto I_1(t) \propto \phi_M^2 = [\phi_{\text{thermal}}(t) + \phi_{\text{concen.}}(t)]^2 = (Ae^{-t/\tau} + Bt + C)^2 \tag{7}$$

to determine the relaxation time τ, we first take the square root of the measured data for $v(t)$ and fit the acquired data to

$$\sqrt{v(t)} \propto \sqrt{I_1(t)} \propto Ae^{-t/\tau} + Bt + C \tag{8}$$

with the standard nonlinear least-squares method of Marquardt and Levenberg [8, 9]. The accuracy of the relaxation-time evaluation is estimated to be 3%.

In Fig. 2, the test cell used for determining the thermal diffusivity of aqueous solutions of magnesium chloride is shown with its typical dimensions (given in millimeters). In the cylindrical stainless-steel cell (1), two glass windows (2) are fixed with the mounting rings (3) and connecting pieces (4) to form a gap (5) of about 0.5 mm for the liquid sample. The sealing of the sample volume is effectively done using two pieces of O-ring (6) made of EPDM 211-70 (ethylpropylenediene), which is capable of fulfilling the necessary requirement for resistance to aqueous solutions of salts at elevated temperatures. The sample cell is electrically heated by a heating coil wound around the cylinder, and the temperature of the sample

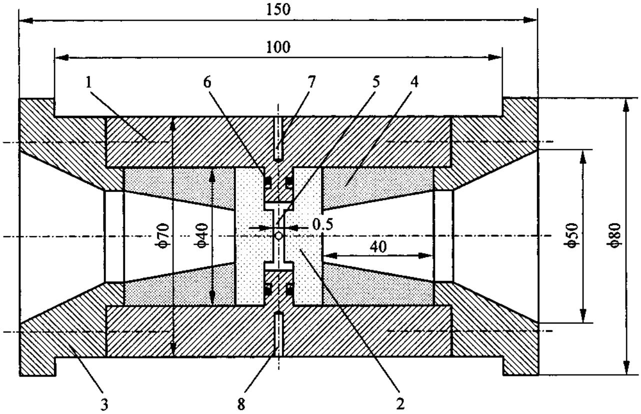

Fig. 2. Schematic of the test cell. (1) Cylinder of stainless steel; (2) glass window; (3) mounting ring; (4) connecting piece; (5) sample volume; (6) sealing O-ring; (7, 8) bores for Pt-100 resistance thermometers. Dimensions are in millimeters.

is regulated with a TCS temperature controller. Aside from the temperature regulation, measurements of the sample temperature are performed by a Pt-100 resistance thermometer and a resistance bridge (Model F16, AE$\mathit{\Lambda}$). In order to minimize the heat exchange to the surroundings and to achieve long-time temperature stability at elevated temperatures, the massive, electrically heated test cell is surrounded by foam material of low thermal conductivity in a protective plastic shell. The air near the glass windows is also heated to avoid large temperature gradients at the windows arising from convection.

3. RESULTS AND DISCUSSION

Aqueous solutions of 5, 10, 15, and 20 wt% $MgCl_2$ were prepared from Baker analyzed reagent-grade $MgCl_2 \cdot 6H_2O$ (purity not less than 98.5%) and distilled water. An electronic analytical balance with a sensitivity of ± 10 mg was employed to determine the weight fraction of $MgCl_2$ in the aqueous solutions to an accuracy of better than $\pm 0.06\%$ [3]. To provide suitable light absorption at the 488-nm argon-ion laser wavelength, a very small amount of water-soluble methyl red was added to each solution. We found that concentrations of about 0.025 wt% of methyl red were sufficient and gave an absorption coefficient $\alpha \sim 0.2\ \mathrm{mm}^{-1}$. The doped solutions were filtered several times to eliminate the scattered light arising from unsolvable tiny particles during the measurements.

Table I. Experimental Data for Thermal Diffusivity of Aqueous Solutions of Magnesium Chloride

5 wt%		10 wt%		15 wt%		20 wt%	
T (K)	a ($10^{-7}\,\mathrm{m^2 \cdot s^{-1}}$)	T (K)	a ($10^{-7}\,\mathrm{m^2 \cdot s^{-1}}$)	T (K)	a ($10^{-7}\,\mathrm{m^2 \cdot s^{-1}}$)	T (K)	a ($10^{-7}\,\mathrm{m^2 \cdot s^{-1}}$)
294.43	1.427	294.81	1.478	294.85	1.480	294.56	1.494
301.30	1.440	301.05	1.480	301.20	1.488	301.15	1.520
310.99	1.475	311.20	1.498	310.90	1.523	311.25	1.545
320.76	1.480	321.15	1.517	320.69	1.547	320.37	1.566
330.59	1.522	330.66	1.585	331.03	1.611	331.24	1.599
340.48	1.553	340.17	1.597	340.91	1.624	340.83	1.633
350.40	1.566	350.60	1.618	351.04	1.648	351.16	1.676
360.44	1.598	360.37	1.622	360.93	1.669	361.17	1.691
370.47	1.607	370.16	1.644	371.14	1.722	370.84	1.721

With the laser-induced thermal grating technique, the thermal diffusivity a was determined for the aqueous solutions of 5, 10, 15, and 20 wt% $\mathrm{MgCl_2}$ in the temperature range 294 to 371 K and at atmospheric pressure. The experimental data for the thermal diffusivity a obtained are listed in Table I, and the temperature dependence of the measured thermal diffusivity for aqueous solutions of the four concentrations is presented in Figs. 3–6, respectively. Each value for the thermal diffusivity in Table I is

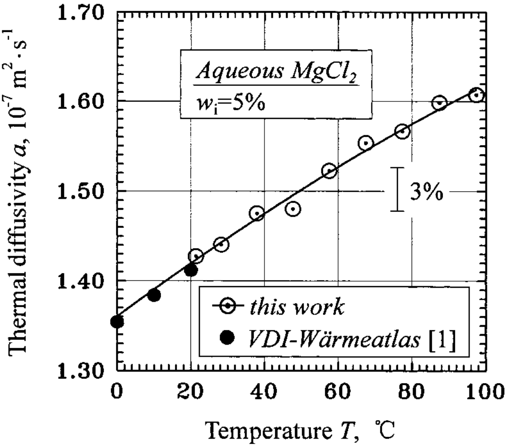

Fig. 3. Measured temperature dependence of the thermal diffusivity of the aqueous solution with 5 wt% $\mathrm{MgCl_2}$.

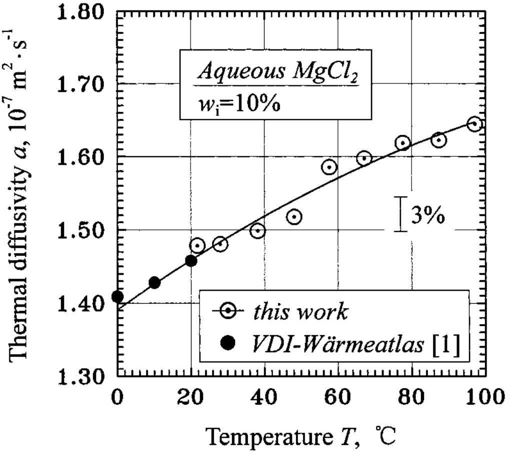

Fig. 4. Measured temperature dependence of the thermal diffusivity of the aqueous solution with 10 wt % $MgCl_2$.

the average acquired from ten independent measurements, the reproducibility σ/a of which is better than 3 %. As shown in Figs. 3–6, the thermal diffusivity of aqueous solutions of $MgCl_2$ increases, just as the thermal diffusivity of water, with increasing temperature in the temperature range 294 to 371 K. In addition, the thermal diffusivity of the aqueous solutions also increases with increasing weight percentage of $MgCl_2$.

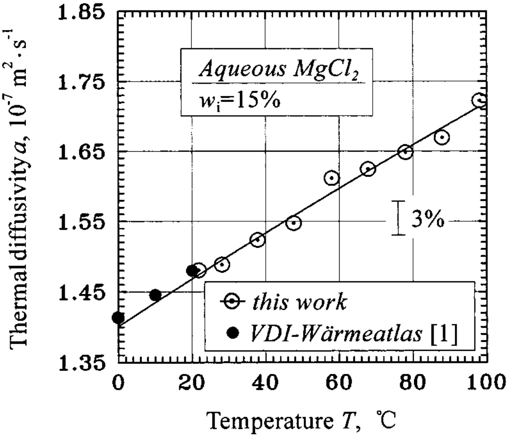

Fig. 5. Measured temperature dependence of the thermal diffusivity of the aqueous solution with 15 wt % $MgCl_2$.

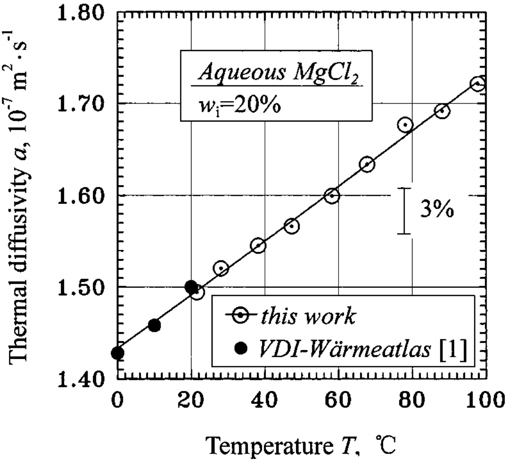

Fig. 6. Measured temperature dependence of the thermal diffusivity of the aqueous solution with 20 wt % $MgCl_2$.

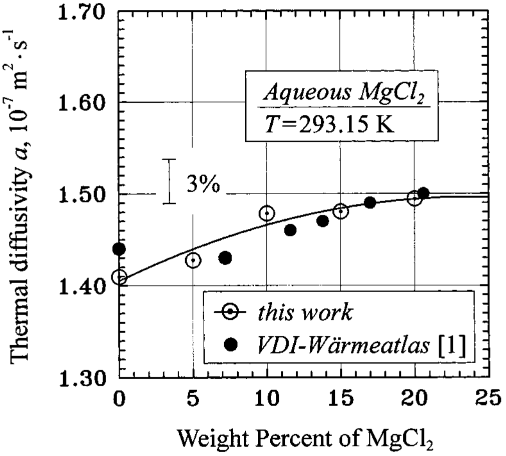

Fig. 7. Thermal diffusivity a of aqueous solutions of $MgCl_2$ at 293.15 K as a function of the weight percent of the solute.

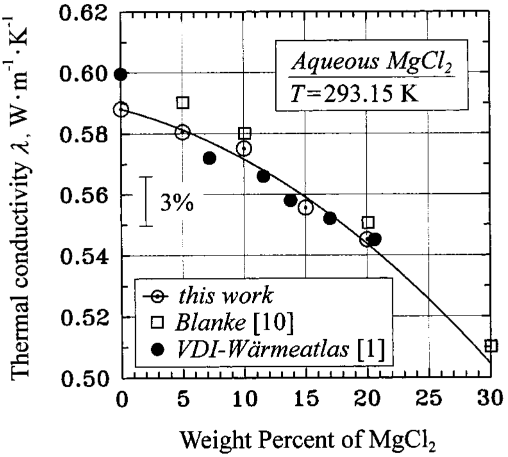

Fig. 8. Derived thermal conductivity λ of aqueous solutions of $MgCl_2$ at 293.15 K as a function of the weight percent of the solute.

Since no experimental data on the thermal diffusivity a and the thermal conductivity λ of aqueous solutions of magnesium chloride at temperatures above 293.15 = K have been reported in the literature, we extrapolated our measured results for the thermal diffusivity to the values at 293.15 K and calculated the thermal conductivity with the equation $\lambda = a\rho c_\mathrm{p}$ by using the density and the specific heat capacity data given in Refs. 1 and 9. From Figs. 7 and 8, the measured thermal diffusivity and the derived thermal conductivity at 293.15 K show very good agreement with the thermal diffusivity and the thermal conductivity values from Refs. 1 and 10. The deviations of the measured thermal diffusivity and the derived thermal conductivity values from the results for the thermal diffusivity and the thermal conductivity in Refs. 1 and 10 are within $\pm 3\%$.

ACKNOWLEDGMENT

The authors express their appreciation for the financial support of the work by the Deutsche Forschungsgemeinschaft under Grant Fi 139/41-4.

REFERENCES

1. *VDI-Wärmeatlas* (VDI-Verlag, Düsseldorf, 1991), Dd 8.
2. G. Wu, M. Fiebig, and J. Wang, *Fluid Phase Equil.* **88**:239 (1993).
3. J. Wang and M. Fiebig, *Int. J. Thermophys.* **16**:1353 (1995).

4. J. Wang, *Messung der Temperaturleitfähigkeit von Flüssigkeiten mittels laser-induzierter thermischer Gitter*, Fortschritt-berichte VDI (VDI-Verlag, Düsseldorf, 1995), p. 48.
5. J. Wang and M. Fiebig, *J. Heat Mass Transfer* **31**:83 (1995).
6. J. Wang and M. Fiebig, *Exp. Therm. Fluid Sci.* **13**:38 (1996).
7. Y. Nagasaka, T. Hatakeyama, M. Okuda, and A. Nagashima, *Rev. Sci. Instrum.* **59**:1156 (1988).
8. J. Wang and M. Fiebig, *Int. J. Thermophys.* **19**:15 (1998).
9. W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling, *Numerical Recipes in Fortran*, 2nd ed. (Cambridge University Press, Cambridge, 1992), pp. 678–683.
10. W. Blanke, *Thermophysikalische Stoffgrößen* (Springer-Verlag, Berlin, 1989), p. 112.