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Absolute Measurements of the Thermal Diffusivity of Aqueous Solutions of Sodium Chloride

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The laser-induced thermal grating technique was used to determine the thermal diffusivity of aqueous solutions of sodium chloride. In comparison with conventional measurement methods, this noninvasive optical technique has the advantage that no sensors need to be inserted in the sample. Therefore, this technique is especially suitable for the measurement of electrically conducting and corrosive liquids. The aqueous solutions studied have weight fractions of 5, 10, 15, and 20% sodium chloride. Measurement results for the thermal diffusivity are presented for aqueous solutions of sodium chloride in the temperature range 293 to 373 K at atmospheric pressure.

KEY WORDS: aqueous solution; diffraction; laser-induced thermal grating; sodium chloride; thermal conductivity; thermal diffusivity.

1. INTRODUCTION

Aqueous solutions of sodium chloride are commonly used as heat-transfer fluids for refrigeration service. This salt offers the lowest cost per liter of solution of any brine available. Aqueous solutions of sodium chloride can also be used in applications involving contact with foods and in open systems because of their low toxicity.

The thermal conductivity of aqueous solutions of sodium chloride has been investigated by a number of researchers [1–12]. Most of these measurements were carried out with a hot-wire technique. Because the aqueous solutions of inorganic salts are electrically conductive and highly

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corrosive, a special design of the hot-wire sensor was required. For the desired electrical insulation and corrosion protection, a thin platinum film (or wire) coated with a metal-oxide or ceramic layer was used. As a result, one needed to account for the thermal effects of the insulating layer [13]. The highly corrosive aqueous solutions could penetrate the insulation on the hot-wire probe, which led to experimental errors [4].

In this paper, we present the results of the absolute measurements of the thermal diffusivity of aqueous solutions of sodium chloride with a laser-induced thermal grating technique. No sensors are inserted in the sample for measurements using this noninvasive optical method. Therefore, this technique is especially applicable for the measurement of electrically conducting and corrosive liquids. The present paper presents the experimental data for the thermal diffusivity of aqueous solutions of sodium chloride in the temperature range 293 to 373 K at atmospheric pressure. Four compositions of the aqueous solutions were studied: 5, 10, 15, and 20% (by weight) sodium chloride.

2. MEASURING TECHNIQUE

The thermal diffusivity of aqueous solutions of sodium chloride was determined using the laser-induced thermal grating technique. The experimental apparatus is shown schematically in Fig. 1. The light pulses (pulse width $t_\mathrm{h} \approx 1000\,\mu\mathrm{s}$), which are used to induce the transient thermal grating, are produced by an Ar^+ laser ($\lambda_\mathrm{h} = 488$ nm, $P_1 = 1000$ mW) and a chopper. The laser beam from the Ar^+ laser is then split into two beams of equal intensity. These beams are focused and intersect each other at a small angle θ ($\theta \approx 0.5°$) in a sample of thickness d; see Fig. 1. The interference of the two laser beams leads to a sinusoidal distribution of light intensity in the sample, and a corresponding, spatially periodic temperature distribution (thermal grating) is produced by absorption of the laser light.

Due to the volume thermal expansion of the sample, the grating-like temperature distribution $\Delta T(t)$ leads to a spatial modulation of the refractive index n,

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

which acts as a diffraction grating and can be detected by a third laser beam. The probing beam from a He–Ne laser ($\lambda_\mathrm{p} = 632.8$ nm, $P_2 = 5$ mW) is focused into the intersection region of the two heating beams in the sample and diffracted by the grating. The first-order diffraction is spatially

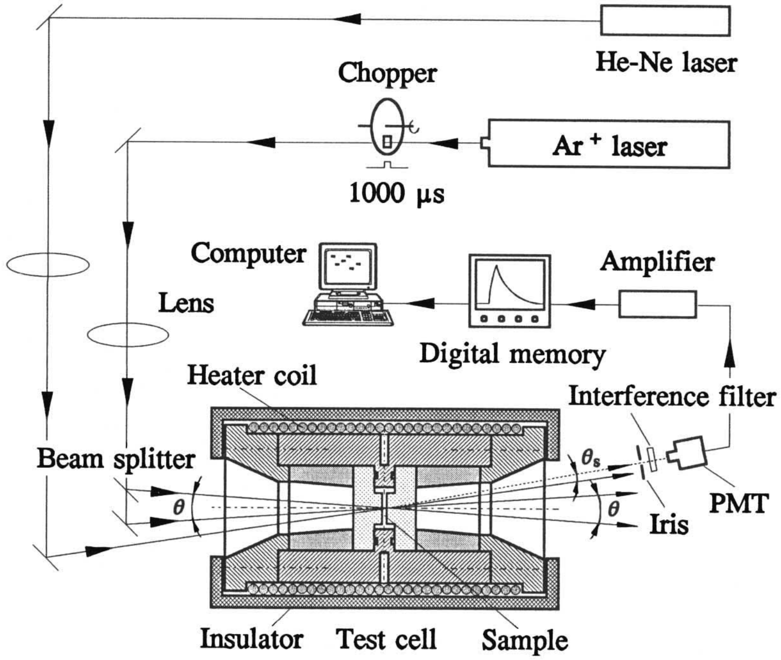

Fig. 1. Schematic diagram of the experimental apparatus.

and spectrally filtered by an iris ($d_I = 400\,\mu$m) and an interference filter to reduce stray scattered light and detected in the homodyne scheme by a photomultiplier tube (PMT). The output signal $v(t)$ from the PMT is amplified and then sent to digital memory, where $v(t)$, corresponding to the time dependence of the first-order diffraction $I_1(t)$, is displayed and recorded. The data for $v(t)$ are subsequently transferred to a personal computer for data analysis.

For homodyne detection, the data for the diffracted signal can be fitted to a single exponential by a least-squares algorithm to obtain the relaxation time $\tau/2$ of the first-order diffraction $I_1(t)$,

$$v(t) \propto I_1(t) \propto \phi_M^2(t) \propto e^{-2t/\tau} \tag{2}$$

where $\phi_M(t)$ is the maximum phase variation of the grating [14, 15],

$$\phi_M(t) = \frac{2\pi d\, \Delta n(t)}{\lambda_p} \tag{3}$$

The thermal diffusivity a of the sample is then determined by the following relation:

$$a = \frac{1}{\tau}\left(\frac{\Lambda}{2\pi}\right)^2 \tag{4}$$

where the grating period Λ can be obtained by measuring the intersection angle θ of both heating beams or the diffraction angle θ_s [16–18],

$$\Lambda \approx \frac{\lambda_h}{\theta} \approx \frac{\lambda_p}{\theta_s} \tag{5}$$

In our measurements, we determine the diffraction angle θ_s by measuring the intensity distributions of diffracted beams of +1 and −1 order with the PMT, whose position can be changed using a fine adjustment screw. The distance ΔX between both peaks of the intensity distributions is then calculated with the computer. As a result, the diffraction angle θ_s is determined to ±0.55% from ΔX and the known distance between the iris and the crossing point of both heating beams [18].

In this work, the thermal diffusivity of aqueous solutions of sodium chloride was measured in the temperature range 293 to 373 K at atmospheric pressure. Heat is supplied to the test cell by an electrical heater coil wound around the stainless-steel cell. The sample solutions are filled in the gap, 0.5 mm, between two glass windows. The temperature of the sample is adjusted and maintained using a temperature controller and a Pt-100 resistance thermometer [19].

3. ERROR ANALYSIS

From Eqs. (2)–(4), we obtain the equation

$$a = \frac{1}{\tau}\left(\frac{\lambda_p}{2\pi\theta_s}\right)^2 \tag{6}$$

The primary variables measured in the experiments by the laser-induced thermal grating technique are the probing laser wavelength λ_p, the diffraction angle θ_s, and the relaxation time $\tau/2$ of the first-order diffraction intensity $I_1(t)$.

To detect the thermal grating, we used a He–Ne laser ($\lambda_p = 632.8$ nm) as the probing laser, which has a high frequency stability. Hence, the contribution to the measuring uncertainty due to the departure from λ_p is very small and thereby negligible.

Due to optical imperfections, e.g., the Gaussian profile and focusing of the laser beams, the diffracted intensity $I_1(t)$ has a narrow spatial distribution centered at the diffraction angle θ_s [16]. As a result, we found that the first-order diffracted intensity $I_1(t)$ could be detected at different angles, even for a fixed intersection angle of the heating beams. As stated above, the diffraction angle θ_s can be determined by measuring the intensity distributions of diffracted beams of +1 and −1 order to an accuracy of ±0.55% [17].

The main systematic error sources, which must be considered in the evaluation of the relaxation time τ, are (a) sample thickness d, (b) intersection angle θ, (c) absorption coefficient α, (d) Gaussian beam intensity distribution w and focusing of laser beams f^*, and (e) heating pulse duration time t_h. Improper choice of these experimental parameters will cause imperfection of the one-dimensional heat conduction in the thermal grating region and thus distortions of the ideal experiment. As a result, the time dependence of the first-order diffraction $I_1(t)$ will lose its single-exponential behavior, and a systematic error will be created when using the fit evaluation procedure to determine the relaxation time τ. Wang et al. have studied the systematic error effects in detail using a numerical simulation [20]. They have also reported the experimental verification of the numerical predictions of the systematic errors [21]. In experiments, we can select the experimental parameters d, θ, α, w, f^*, and t_h to keep the systematic errors small, which result from the absorption, the Gaussian beam intensity distribution and focusing of laser beams, and the heating pulse duration. At a given sample thickness d and intersection angle θ, we can estimate the error due to the cell wall and correct the relaxation time τ determined by the fit evaluation procedure.

It should be noted that the intensity of the diffraction signal is inversely proportional to the square of the thermal diffusivity a or conductivity λ of the sample [15]. As a result, it is usually difficult to obtain an adequate signal-to-noise ratio for the determination of the relaxation time, when attempting to measure a liquid sample of relatively high thermal diffusivity or conductivity, e.g., water or aqueous solutions of salts. To solve this problem, it is necessary to increase the heating pulse duration time t_h properly, e.g., to 1000 μs in this work. Nevertheless, an excessive increase in the heating pulse duration time will lead to a high initial temperature amplitude ΔT_0 of the thermal grating, which will in turn cause a large value of the maximum phase variation of grating ϕ_M [15]. The basic theory is then no longer valid, and a distortion of the ideal experiment will arise and thereby lead to an error. Therefore, we must control the heating pulse duration time in experiments to get a small ϕ_M and a strong diffraction signal at the same time.

4. RESULTS AND COMPARISON WITH LITERATURE DATA

Thermal-diffusivity measurements of aqueous solutions of sodium chloride were performed by the laser-induced thermal grating technique in an extended temperature range, from 293 to 373 K. Four compositions of the aqueous solutions were studied: 5, 10, 15, and 20% (by weight) sodium chloride.

For the preparation of aqueous solutions, pure water was used for high-performance liquid chromatography (HPLC grade). The purity of the sodium chloride was in excess of 99%. Both chemicals were products of J. T. Baker B.V. Aqueous solutions were prepared using an electronic analytical balance, and the uncertainty in the weight fraction was estimated as about 0.06%.

Figure 2 shows a typical example of the time dependence of the diffracted signal for an aqueous solution of sodium chloride with a weight fraction of 10% NaCl in the relaxation period of the grating ($t > t_h$). For clarity, only 133 of the 4000 registered data points are plotted in Fig. 2. Note that the decay of the diffracted intensity looks qualitatively exponential, but it does not decay back to zero until time $t > 20$ ms. In fact the thermal grating in aqueous solutions of sodium chloride tends to create a certain amount of phase separation, i.e., a concentration grating due to the

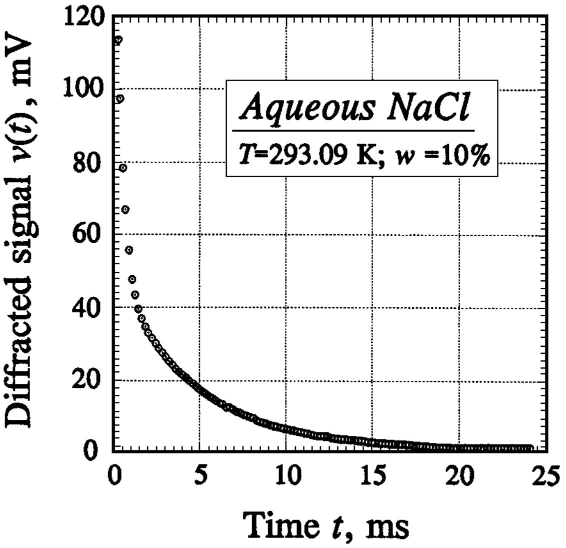

Fig. 2. Decay data for the diffracted signal for an aqueous solution of sodium chloride with a weight fraction of 10% NaCl at 293.09 K.

Soret effect. The decay data obtained in the measurements are thus a superposition of the diffracted signals from the thermal grating with a relaxation time τ and the concentration grating, the relaxation time τ_1 of which is one to two orders of magnitude longer than that of the thermal grating ($\tau_1 \gg \tau$). Therefore, we can no longer fit the decay data for the diffracted signal to the single exponential equation, Eq. (2), to obtain the relaxation time τ of the thermal grating.

Taking account of the contribution of the concentration grating to the diffracted signal, we obtain the maximum phase variation $\phi_M(t)$ of the grating as the sum of two terms,

$$\phi_M(t) = \phi_{\text{thermal}}(t) + \phi_{\text{concen.}}(t) \tag{7}$$

$\phi_{\text{thermal}}(t)$ and $\phi_{\text{concen.}}(t)$ are the phase variations of the thermal and concentration gratings, respectively. Since the concentration grating decays much more slowly than the thermal grating ($\tau_1 \gg \tau$), the time dependence of the diffracted intensity $I_1(t)$ can be modified as

$$I_1(t) \propto \phi_M^2(t) = [\phi_{\text{thermal}}(t) + \phi_{\text{concen.}}(t)]^2 = (Ae^{-t/\tau} + Bt + C)^2 \tag{8}$$

where A, B, and C are constants [22].

As the first step in data reduction, one should take the square root of the measured decay data $v(t)$. The data obtained are then fitted to

$$\sqrt{v(t)} \propto \sqrt{I_1(t)} \propto Ae^{-t/\tau} + Bt + C \tag{9}$$

with the standard nonlinear least-squares method of Marquardt and Levenberg [23] to evaluate the relaxation time τ of the thermal grating. The thermal diffusivity a of the sample is then determined by Eq. (4).

The experimental results for the thermal diffusivity of aqueous solutions of sodium chloride are presented in Table I. The values for the thermal diffusivity a at each temperature and composition listed in Table I are averages obtained from 10 independent measurements, the reproducibility σ/a of which is better than 3% (see Table I).

Few values for the thermal diffusivity a of aqueous solutions of sodium chloride have been reported up to now. A comparison between the thermal-diffusivity values found in the literature [24] and our experimental results is shown in Fig. 3. The thermal-diffusivity values at 293 K reported in the VDI-Wärmeatlas [24] agree with our experimental results within 3%.

To convert the measured thermal-diffusivity values a into values for the thermal conductivity λ, we used the relationship $\lambda = a\rho c_p$ and the

Table I. Thermal Diffusivity of Aqueous Solutions of Sodium Chloride

5%			10%			15%			20%		
T (K)	a ($10^{-7}\,\mathrm{m^2 \cdot s^{-1}}$)	σ/a (%)	T (K)	a ($10^{-7}\,\mathrm{m^2 \cdot s^{-1}}$)	σ/a (%)	T (K)	a ($10^{-7}\,\mathrm{m^2 \cdot s^{-1}}$)	σ/a (%)	T (K)	a ($10^{-7}\,\mathrm{m^2 \cdot s^{-1}}$)	σ/a (%)
293.45	1.441	2.14	293.09	1.476	2.30	293.36	1.479	2.24	293.42	1.475	2.79
303.96	1.466	1.75	303.17	1.487	1.63	303.30	1.532	1.53	303.45	1.510	2.26
314.08	1.519	2.82	313.11	1.528	2.04	313.26	1.550	2.28	313.42	1.540	1.99
323.55	1.535	2.73	323.12	1.578	1.95	323.33	1.579	2.79	323.41	1.570	1.89
333.02	1.601	2.20	333.17	1.600	2.30	333.12	1.603	2.22	333.34	1.593	2.38
343.16	1.632	1.99	343.34	1.642	2.33	343.47	1.655	2.25	343.05	1.642	2.26
352.74	1.688	2.22	353.04	1.689	1.97	352.28	1.699	2.91	353.16	1.686	2.87
363.14	1.698	2.01	363.20	1.713	2.87	363.32	1.725	2.45	363.26	1.733	2.12
373.25	1.729	2.90	373.05	1.767	2.78	373.14	1.771	2.24	373.37	1.760	2.21

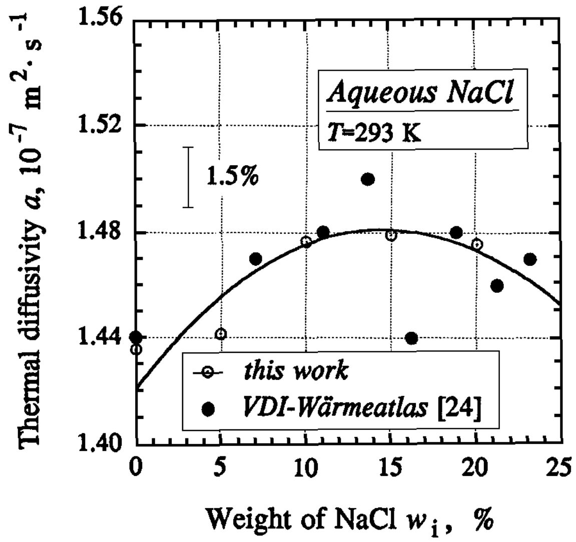

Fig. 3. Measured thermal diffusivity a of aqueous solutions of sodium chloride at 293 K in comparison to data in Ref. 24.

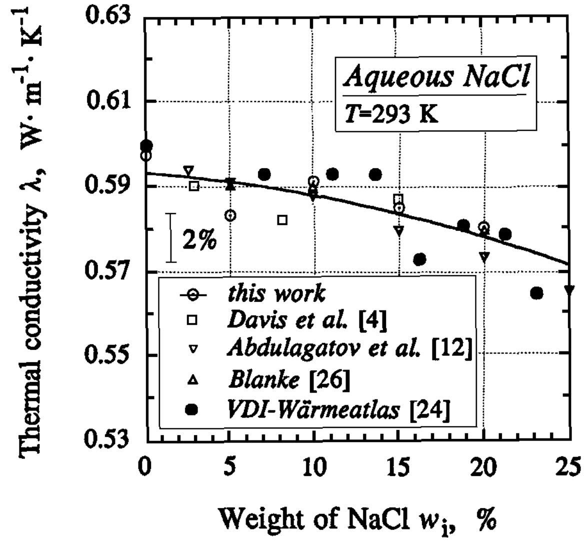

Fig. 4. Derived thermal-conductivity values λ from the measured thermal diffusivity a at 293 K in comparison to data in Refs. 4, 12, 24, and 26.

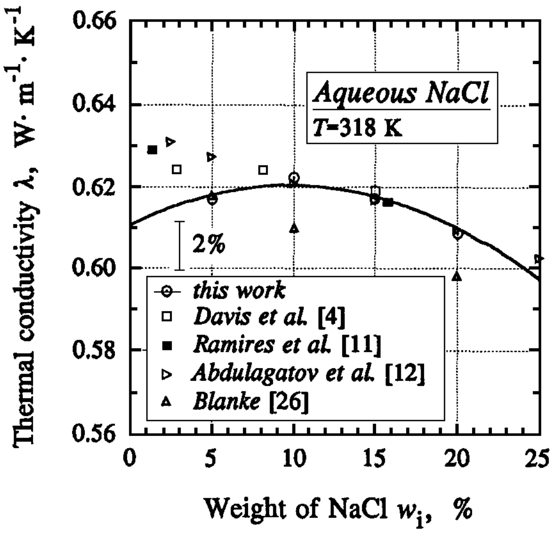

Fig. 5. Derived thermal-conductivity values λ from the measured thermal diffusivity a at 318 K in comparison to data in Refs. 4, 11, 12, and 26.

specific heat capacity and density data for aqueous solutions of sodium chloride available in Refs. 25 and 26. Figures 4 and 5 depict the thermal conductivity λ of other investigators [4, 11, 12, 24, 26] at 293 and 318 K for aqueous solutions of sodium chloride and the derived thermal-conductivity values from our measured thermal-diffusivity data. It can be seen in these figures that the thermal-conductivity data from Refs. 4, 11, 12, 24, and 26 agree with our derived values at 293 and 318 K within 2.5%.

The results presented indicate that the laser-induced thermal grating technique can be used for the absolute, accurate determination of the thermal diffusivity of aqueous solutions of inorganic salts. This technique has proven to be especially suitable for measurements of such electrically conducting and corrosive liquids.

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