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Thermal diffusivity measurements in sea water using transient thermal lens calorimetry

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Pulsed dual beam thermal lens method is utilized to determine the thermal diffusivity of sea water. A frequency doubled Q-switched Nd:YAG laser is used as the heating source and an intensity stabilized He-Ne laser to probe the transient thermal lens signal decay. The thermal diffusivity values of the sea water are found to vary with the salinity of seawater.

THERE has been renewed interest in recent years for developing new laser-based methods of determining the thermal conductivity and thermal diffusivity (D) of materials of different kind¹⁻⁵. This is mainly as a result of the rapid advances in materials science and the highly sensitive techniques using lasers for measurement of material properties. Despite its being a derived quantity, D is of considerable interest in heat flow studies, as it determines the rate of periodic heating or transient heat propagation through the medium. Besides its intrinsic

physical interest, the importance of D is due to the fact that like the optical absorption coefficient, it is unique for each material. This can be appreciated from the calculated values of D presented by Touloukian *et al.*⁶ for a wide range of materials. A knowledge of D of a material can be used to calculate thermal conductivity data. There are a number of presently existing steady-state and nonsteady-state methods of measuring thermal parameters⁶⁻⁹. However, there is some dissatisfaction with the length of time required to make reliable measurements, and in some cases, the large sample sizes required by these techniques impose intolerable limitations.

Methods based on photothermal effects are eminently suited for the measurement of thermal properties of materials. Most noncontact measurements are based on photothermal techniques utilizing modulated or pulsed laser beams for the determination of thermal diffusivities^{10,11}. Methods based on photothermal phenomena like photoacoustic effect, photothermal refraction and thermal lens (TL) techniques can be effectively utilized for

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material characterization and nondestructive evaluation. Among the various photothermal spectroscopic methods based on the thermal relaxation of excited species, TL spectroscopy has appeared to be very sensitive and powerful¹²⁻¹⁴. The TL technique can also be effectively utilized for multiphoton absorption studies, determination of absolute fluorescence quantum yield, and for monitoring certain slow chemical reactions¹⁵⁻¹⁸. The sensitivity of this technique is higher than that of the conventional transmission and reflection techniques because in the former the absorbed energy is measured directly. In fact, this effect can be observed using moderate laser intensities in media with absorption coefficient as low as 10^{-7} cm^{-1} .

The thermal characteristics of the sample may be expected to affect the nature of the signal observed, and this is particularly so with the diffusivity of the sample. The refractive index gradient diminishes with time and so does the TL signal. By monitoring this transient TL signal, D can be determined. The work of Gordon *et al.*¹⁹ on the thermo-optical effect in a liquid provides a basis for linking the rate of dissipation of the TL signal to a quantitative measure of D .

The optical and thermal properties of sea water are the basic building blocks of the physical and chemical oceanography. Even though, a few reports are available on the optical properties of the sea water^{20,21}, there is little understanding of the thermal properties of sea water. In this paper we report the D measurements in sea water using TL method. The upper surface of the sea is being heated by Sun's rays. During night, the upper layers get cooled down mainly due to heat conduction to lower layers. The temperature at the sea surface is determined by the rate of heat diffused from the upper layers to the deeper region and vice versa. Thus, we have carried out these measurements in different samples of sea water taken from different depths of sea. These results are compared with those obtained from artificial sea water. Thus a knowledge of D of sea water is of great importance in the field of oceanography.

Experimental set up

The schematic diagram of the experimental set up is shown in Figure 1. The 532 nm radiation from a frequency-doubled Q-switched Nd:YAG laser (Quanta ray DCR 11, 9 ns pulse width, maximum energy 110 mJ, repetition rate 10 Hz) was used as the pump beam. The probe laser used was the beam from an intensity stabilized He-Ne laser that produces linearly polarized TEM_{00} beam. The pump and probe beams are combined by using a dichroic mirror and made collinear by carefully adjusting the optical components in the x, y, z planes. In our set up the experiment is performed on a vibra-

tion-free table so that their is minimum error due to stray vibrations. Also the sample cuvette, the beam splitters as well as the detector are mounted on XYZ translators which can be aligned with very high precision. The collinearity of the pump and probe beams is ensured by z-scan method. The sample cuvette is aligned along the beam path and a position is selected where the TL signal is maximum. The pump beam was focused by a convex lens of focal length = 25 cm into a 0.5 cm quartz cuvette containing the sample. The probe laser was focussed by a convex lens of focal length $f=20$ cm.

As the 532 nm radiation was passed through the sample, the molecules absorb some of the incident energy and get excited to higher energy levels. The subsequent deexcitation process can occur radiatively or nonradiatively. It is the nonradiative part that gives rise to TL formation. The resulting refractive index gradient follows the intensity distribution of the exciting pump beam. This causes the intensity in the centre of the probe He-Ne laser beam to fluctuate and this variation in the probe beam intensity is detected as the TL effect (see Figure 1). In the present work the intensity of the center portion of the transmitted probe beam was detected by using an optical fiber where the optical fiber also serves as the limiting aperture. The output of the optical fiber is detected by a photomultiplier tube that was coupled to a Mc-Person monochromator which further filtered out the scatterings of the excitation beam. The time-dependent lens signal is processed with a 200 MHz digital storage oscilloscope. All the measurements were made at 22°C.

Results and discussion

In the case of pulsed laser excitation, the pulse width of the heating laser is small (~ 10 ns) and the rate of the radiationless transition is fast compared to the decay rate of the TL effect. The signal strength reaches the maximum value instantly and decays with a characteristic

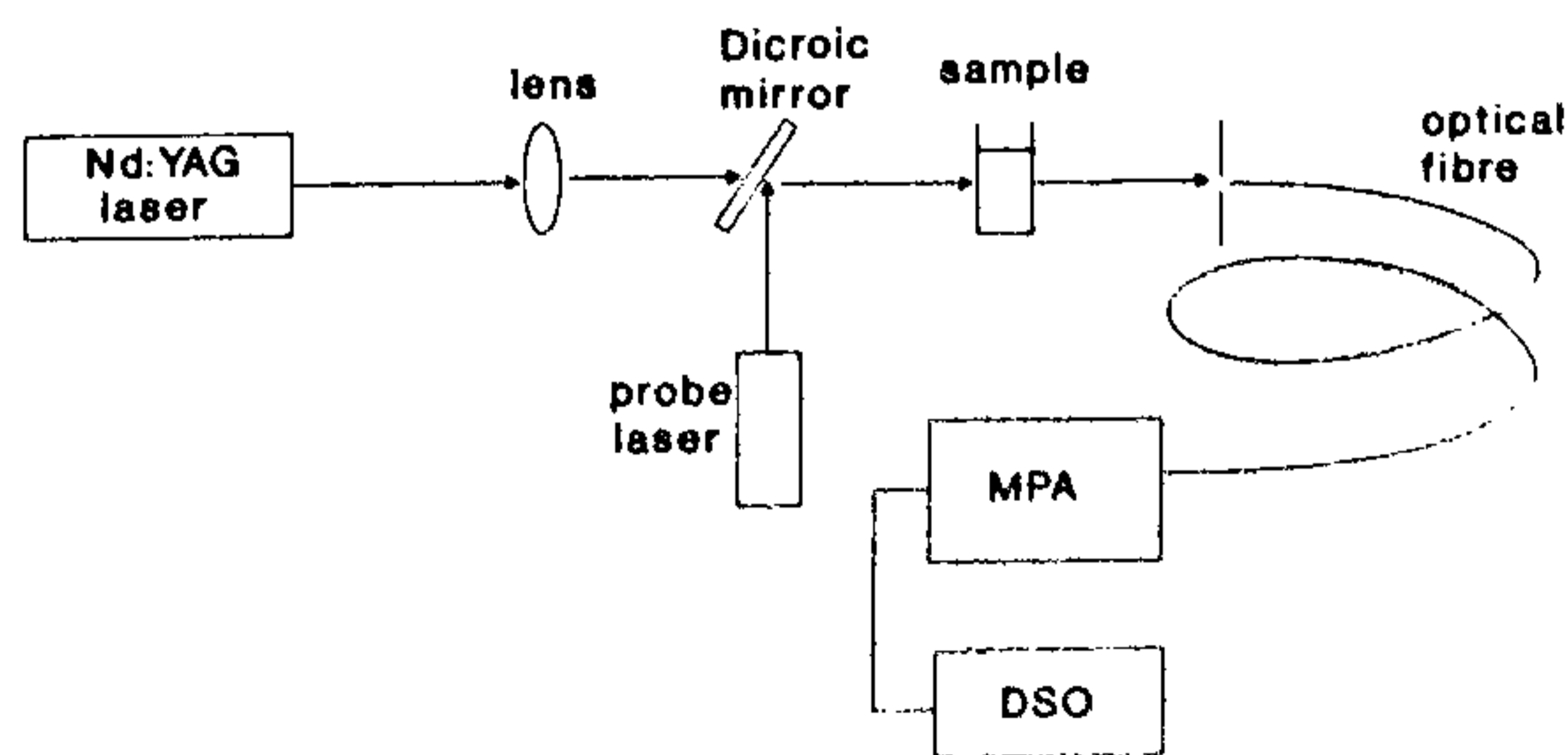


Figure 1. The pulsed thermal lens set up used in this experiment (MPA – monochromator-PMT assembly, DSO – digital storage oscilloscope).

time constant. The pulsed TL system has distinct advantages with respect to large enhancement factor and its background subtraction capability. Quantitative analysis of the TL formation are given by Twarowski and Kliger²² with experimental verifications.

The focal length f of the induced TL by pulsed laser irradiation is given by²²

$$\frac{1}{f} = \frac{1}{f_0} \left(1 + \frac{2nt}{t_c} \right)^{-2}, \quad (1)$$

where f_0 is the steady-state focal length, n , number of photons absorbed in each transition and t_c is a characteristic time constant defined as:

$$t_c = \frac{\omega^2}{4D}, \quad (2)$$

where ω is the beam radius of the medium. Here

$$\frac{1}{f_0} = \frac{4lDN\sigma h\nu Hn^2}{kJ\omega^{2n+2}} \frac{d\eta}{dT} \left(\frac{2}{\pi} \right)^n, \quad (3)$$

where $D = k/\rho c$, $H = \int_0^t P(t) dt$; l , the thickness of the TL; N , molecules per cc; k , thermal conductivity; ρ , density; c , specific heat; η refractive index of the medium; ν , frequency of the pump beam; $P(t)$ pulsed laser power as a function of time; ω , beam radius; J , Joule's constant; σ , cross section for n photon absorption and n , number of photons absorbed. Since the temperature coefficient of the refractive index is negative for most liquids, the eqns. (1) and (2) predict that the TL will be divergent.

The transient TL signal can be expressed by

$$S = \frac{I_t - I_\infty}{I_t} = S_{t=0} \frac{1}{\left(1 + 2n \frac{t}{t_c} \right)^2}, \quad (4)$$

where

$$S_{(t=0)} = \frac{I_\infty - I_0}{I_0}, \quad (5)$$

where I_∞ , I_0 , I_t are the steady state TL signal, signal at time $t=0$ and signal at t respectively.

The characteristic time constant t_c is related to D and beam radius (ω) through the relation:

$$t_c = \frac{\omega^2}{4D}. \quad (6)$$

To eliminate the uncertainty in the determination of beam radius, a reference sample with known D is used to determine the D of the unknown sample. In our case

water was used as the reference sample. Thus,

$$D = D_{\text{water}} \frac{t_c^{\text{water}}}{t_c}. \quad (7)$$

The time dependence of the lensing phenomenon gives a detailed account of the thermal history of the sample medium. Clearly the magnitude of the TL effect depends on the competition between the rate of creation of the lens and the rate of decay of the lens, and these are related to the D of the medium.

Using the present set up, the thermal diffusivities of acetone and ethylene glycol were determined with water as the reference to confirm the validity of the present experimental scheme. The values obtained in the case of acetone ($1.07 \times 10^{-3} \text{ cm}^2/\text{s}$) and ethylene glycol ($9.65 \times 10^{-4} \text{ cm}^2/\text{s}$) agree well with corresponding reported^{23,24} values of these ($D_{\text{acetone}} = 1.08 \times 10^{-4} \text{ cm}^2/\text{s}$ and $D_{\text{ethyleneglycol}} = 9.71 \times 10^{-4} \text{ cm}^2/\text{s}$).

In steady-state experiment, care has to be taken to avoid the effect of convection. However in the present case the thermal gradient developed is axially symmetric about the pump beam. The laser pulse duration is ~ 10 ns and the thermal relaxation times are much smaller compared with time scales for microconvection. Hence in the development of TL theory it is assumed that thermal conduction is the most dominant mechanism of heat dissipation. Moreover, it has been observed that effect of convection in liquids begins to appear at higher pump power level²⁵. Therefore, the present measurements were performed at low power levels at which effect of convection is negligible.

The samples of sea water were collected from the Arabian sea at a distance of 100 km away from the shore of Cochin in the summer season. The sample collection was made upto a depth of 300 ft from the sea surface.

We performed D measurements in sea water samples using the pulsed double beam TL technique. The sample was taken in a quartz cuvette. Trace amounts of dye rhodamine 6G were added to increase the absorption of the pulsed laser beam, thereby increasing the TL signal intensity. This level of impurity does not affect the solvent thermal conductivity, since adding trace amounts of dye affect only the optical properties and not the thermal properties of the solvent. Thermal lens signals were obtained from water and different samples of sea water. Typical TL transient for water and sea water are given in Figures 2 a, b.

Eqn (4) leads us to the prediction that a plot of $S^{-1/2}$ will be a linear function of time. Verification of this prediction is shown in Figure 3. From the slope and intercept, the value of n/t_c can be determined. One can determine the value of n from measurements of the dependence of TL signal on laser energy E of the pump laser pulse, using the relationship¹⁹;

$$\frac{I_t - I_{t=\infty}}{I_t} \propto E^n \quad (8)$$

The variation of TL signal with laser energy for all the sea water samples studied showed a linear dependence, suggesting one photon absorption ($n=1$). From these measurements we calculated the values of characteristic time constant, corresponding to each sample. We have verified measured t_c with theoretical fit using eqn (4). The smooth curve obtained in Figure 2 gives such a theoretical fit, which has been obtained using eqn (4) taking t_c from the slope and intercept of the

linear plot (Figure 3). The agreement between the theoretical and experimental data is good. Using pure water as reference with $D = 1.43 \times 10^{-3} \text{ cm}^2/\text{s}$, we calculated D for the different sea water samples.

It is found that the D values of sea water vary with depth (Figure 4). The values of D decrease as the depth increases. The estimated D value for sea water at a depth of 30 ft is $3.65 \times 10^{-3} \text{ cm}^2/\text{s}$ and it is decreased to a lower value of $2.53 \times 10^{-3} \text{ cm}^2/\text{s}$ at a depth of 300 ft. We measured salinity and conductivity of the

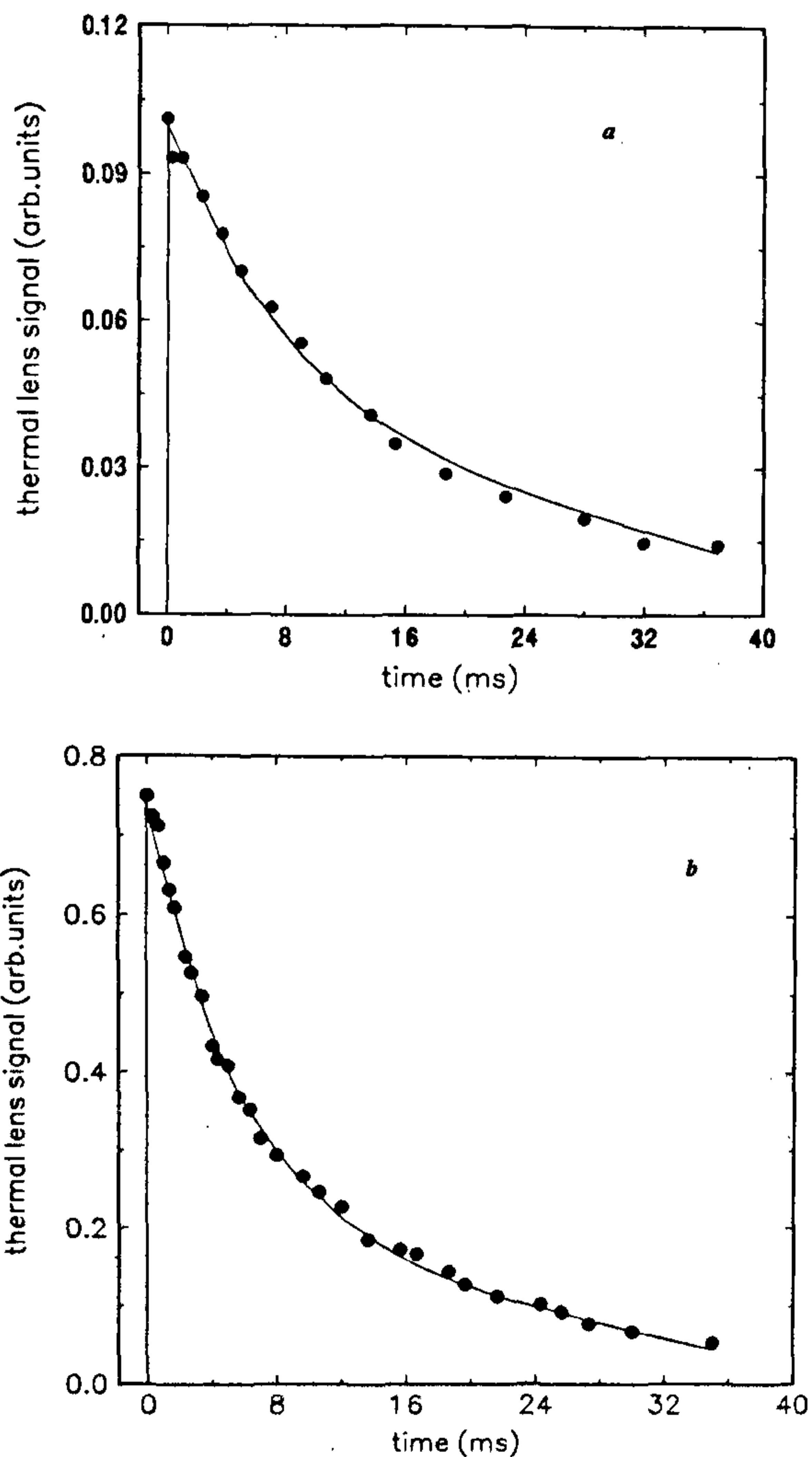


Figure 2. Transient decay curve measured by pulsed thermal lens technique for (a) water and (b) sea water sample (300 ft). The points in the figures represent the experimental data. The solid curves represent the theoretical fit obtained using eqn (4). The theoretical fits were made with measured values of t_c obtained from figure 3 ($t_c^{\text{water}} = 45 \text{ ms}$; $t_c^{\text{sea water}} = 26 \text{ ms}$).

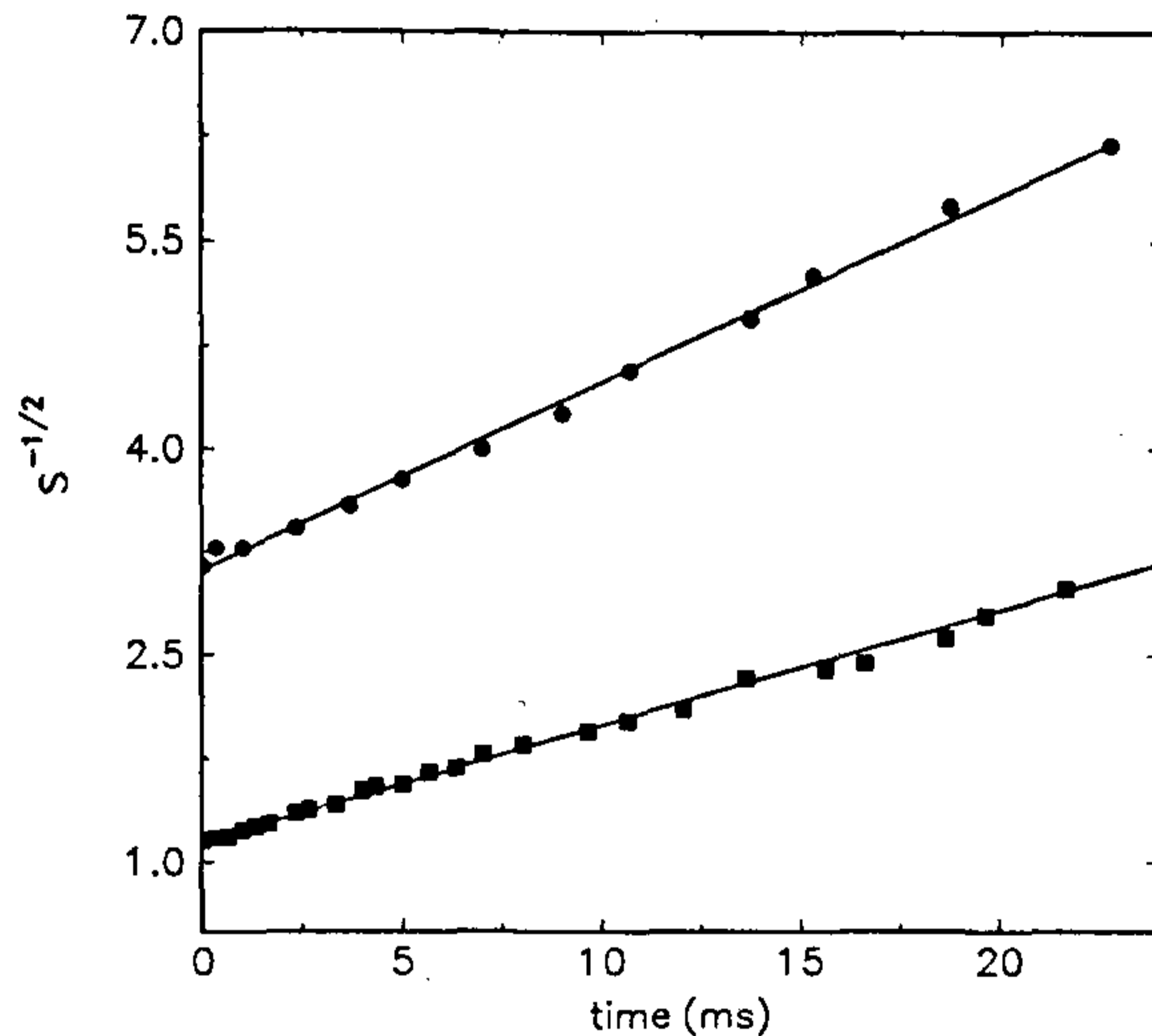


Figure 3. Typical linear plots of experimental data obtained using eqn (4). From the slope and intercept of these plots value of t_c is evaluated. [•] – water and [■] – sea water at a depth of 300 ft.

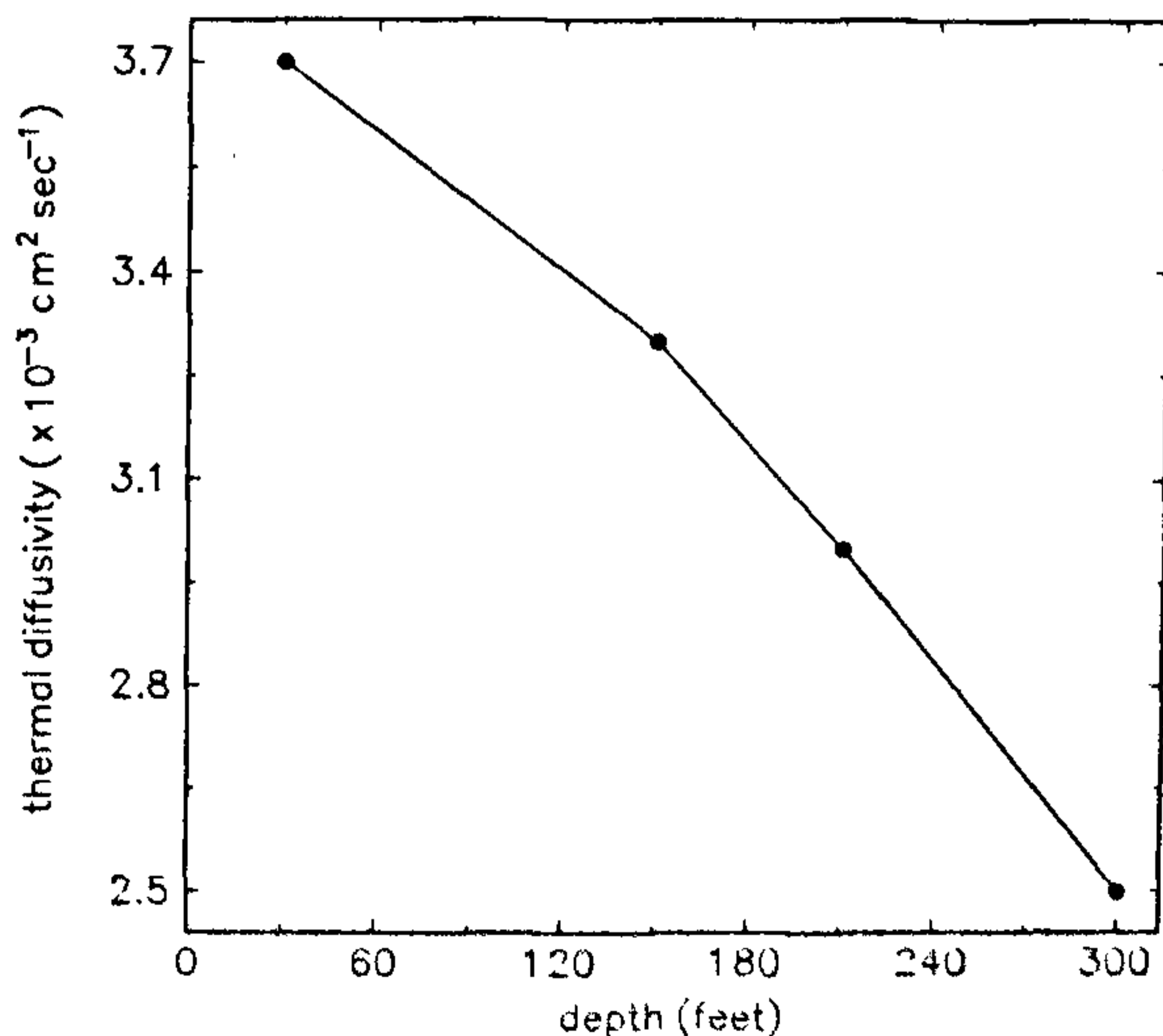


Figure 4. Variation of thermal diffusivity of sea water with depth.

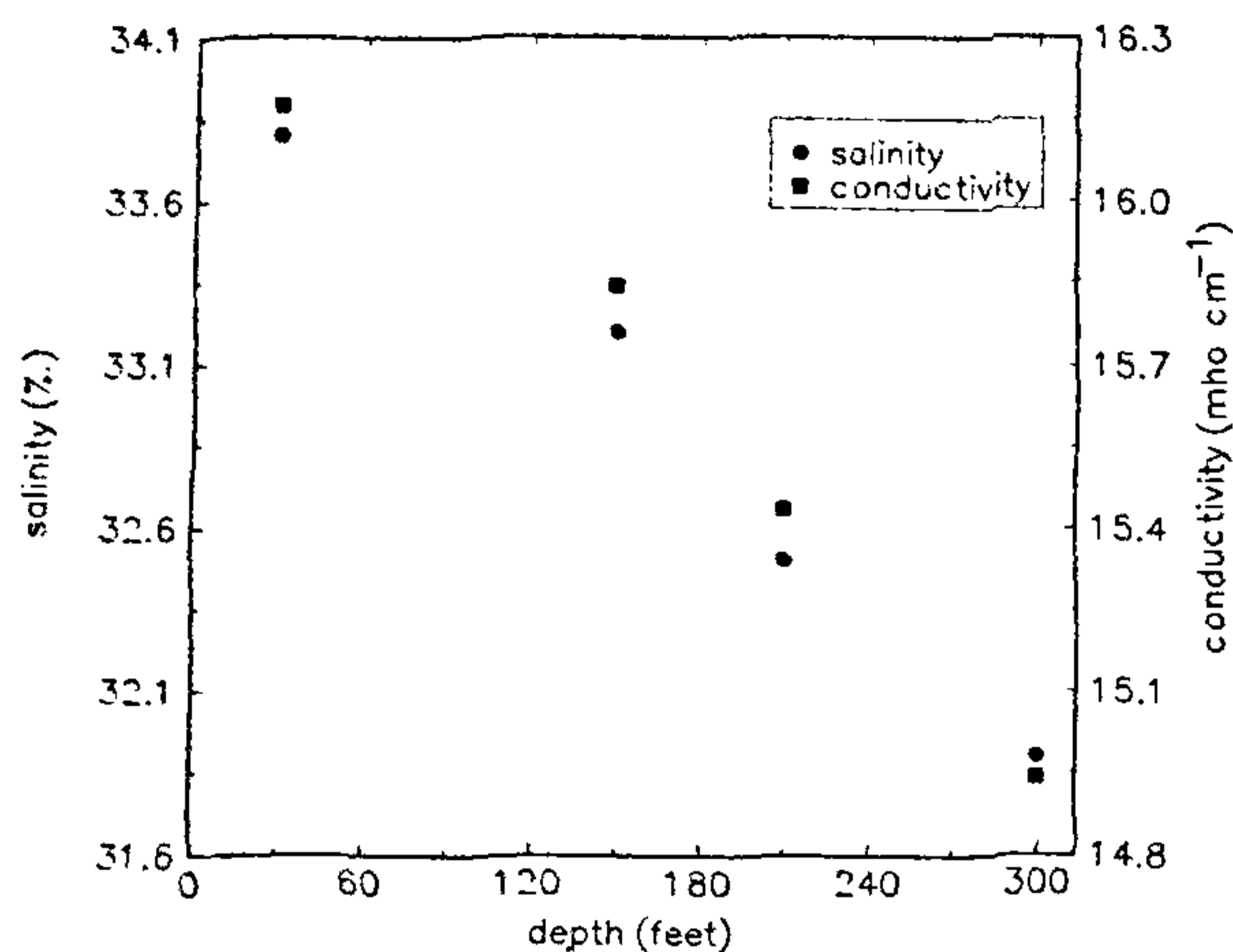


Figure 5. Variation of conductivity and salinity of sea water with depth.

sea water samples using salinity and conductivity meters respectively. The variation of these parameters with depth is shown in Figure 5. The salinity and conductivity values of these samples are found to decrease with increasing depth. Salinity does appear to be important in determining D .

The thermal characteristics of sea water are subjected to regional and seasonal variations. The seasonal change in wind direction and consequent reversal of ocean currents, together with the abrupt change in the pattern of precipitation may contribute towards large variations in the annual surface salinity. In order to verify the results obtained in sea water samples, we carried out similar measurements in artificially prepared sea water sample solutions. We have prepared artificial seawater in accordance with the reported method of Ott²⁶. The salinity of the artificial sea water was varied to study the effect of this parameter on D . The TL signal strength is maximum for the sample with highest salinity. A possible explanation for the TL signal enhancement upon increase in salinity is a change in the bulk refractive index which might alter the absorption coefficient of the solution. Figure 6 gives the variation of D with salinity of the artificial sea water. The D values obtained for artificial sea water also showed a similar trend with decreasing salinity.

From Figure 5 it is seen that salinity varies only from 34.1 to 31.6% and D varies from $3.7 \times 10^{-3} \text{ cm}^2/\text{s}$ to $2.5 \times 10^{-3} \text{ cm}^2/\text{s}$. On the other hand from Figure 6 for artificial sea water prepared in the laboratory, the variation in diffusivity for a variation in salinity from 25 to 20% is from $3.7 \times 10^{-3} \text{ cm}^2/\text{s}$ to $3.2 \times 10^{-3} \text{ cm}^2/\text{s}$. Thus the D values for sea water and artificial sea water follow different trajectories. Obviously the exact chemical composition in terms of both organic and inorganic

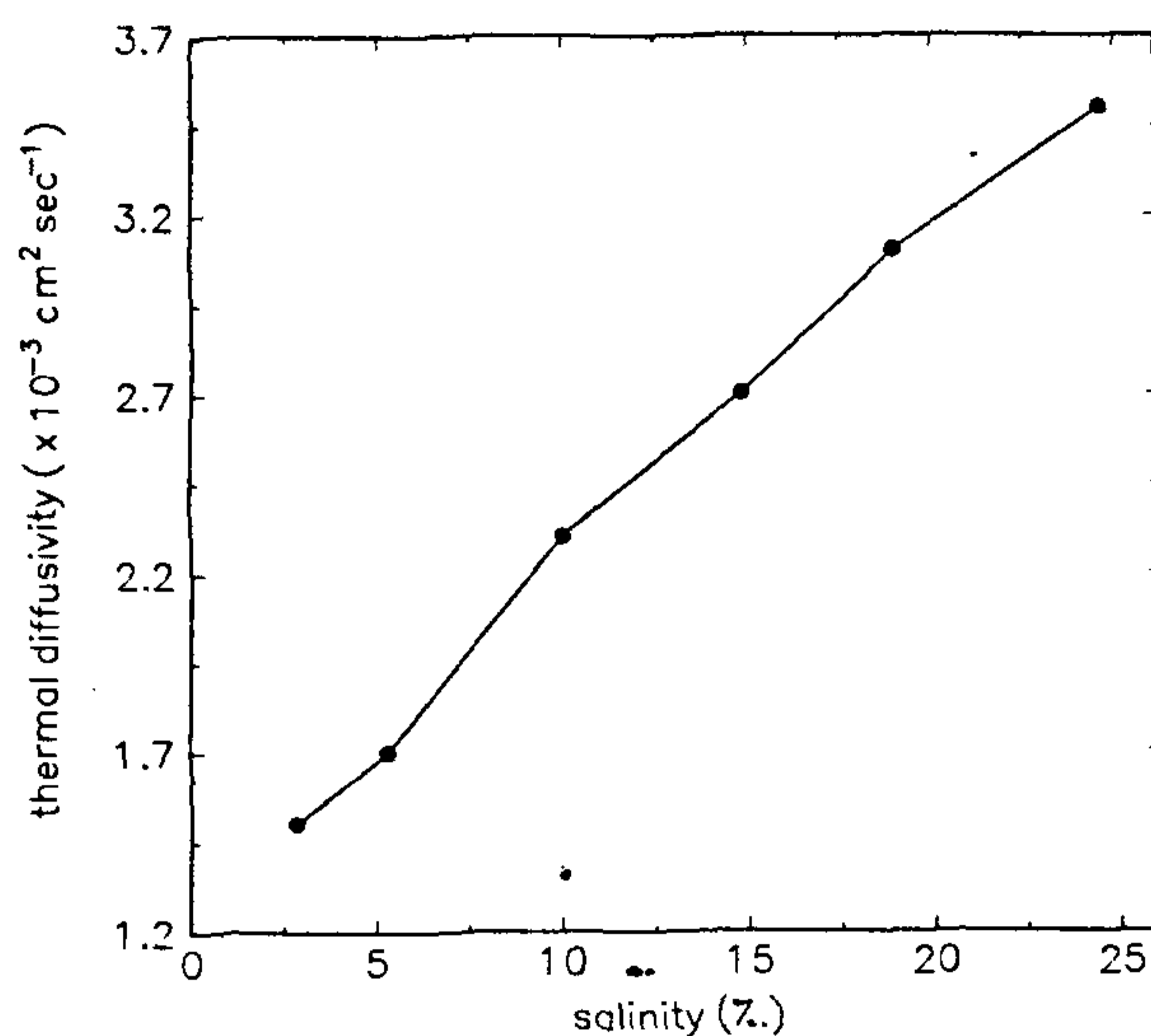


Figure 6. Variation of thermal diffusivity of artificial sea water with salinity.

materials cannot be same in both the cases. It is also likely that sea water will contain some amounts of suspended matter and microorganisms. This is borne out by the fact that the absorption coefficient of natural sea water (filtered) is $11 \times 10^{-4} \text{ cm}^{-1}$, while that of synthetic sea water is $8 \times 10^{-4} \text{ cm}^{-1}$ at 532 nm (ref. 27). Hence it is to be expected that the thermal diffusion coefficient of sea water and its synthetic analogue should follow different trajectories with respect to variation in salinity.

By comparing the above results with those obtained from the sea water samples, it is clear that the D values of the sea water decrease with decreasing salinity. It can be inferred that the upper parts of the sea contain more salt than the deeper regions. When the sea gains heat by the absorption of solar radiation, most of the heat is absorbed in the first few meters. Molecular conductivity could provide only a very slow transport of heat downwards and a steep temperature gradient would occur just below the surface. Evaporation of water from the sea surface by sun and wind leaves the water at the surface saltier. This result is in confirmation with the report that the salinity of sea water decreases with depth²⁸.

Conclusion

Thermal lens technique is successfully used for obtaining the thermal diffusivity values. Thermal diffusivity values of sea water are found to vary with depth of the sea at which the sample is collected. The thermal diffusivity measurements in artificial sea water showed a decrease in the value of thermal diffusivity with increasing dilution

of the sample. Thus salinity does appear to be important in determining the thermal diffusivity.

The thermal blooming technique offers a novel means of measuring thermal diffusivity. The method is simple and accurate. The obvious advantage of this method is that only small sample volumes are needed for making such measurements. Also, only a very short time is needed for the measurements and accurate results can be obtained with TL method.

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