THE EFFECTS OF MOLECULAR ASSOCIATION ON MUTUAL DIFFUSION

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ABSTRACT

Limiting mutual diffusion coefficients (D_{12}) of a series of pseudoplannar polar compounds in various organic solvents at 298.2K and in ethanol at different temperatures ranging from 283.2K to 328.2K were measured by using the chromatographic peak-broadening method. The data were compared with those of the nonassociated pseudoplanar molecules of similar size and shape. Solutes capable of strong solute-solvent interactions in this work were found to diffuse slower than the nonassociated counterparts. The effects of molecular association on diffusion as well as the solvation numbers were determined for the polar solutes. It was found that the effects of hydrogen bonding and the solvation numbers are approximately equal for solutes containing the same polar group that forms hydrogen bonds with the solvent molecules. The effects as well as the solvation numbers are nonetheless different for different functional groups, with -OH > $-NH_2$ > -SH > -C(O)- in general. For both the associated and nonassociated solutes studied, there exists a linear relationship between the reciprocal of the diffusion coefficients and the molecular volume (V) of the solutes in a given solvent at constant temperature. It appears that the diffusivities are also insensitive to the mass of the nonassociated and associated solute molecules.

The temperature dependence of the diffusion coefficients was also studied, and a linear correlation between ln D_{12} and $1/T$ was found for all the aromatic solutes studied. From the plots of ln D_{12} against $1/T$, activation energies of different functional solutes were calculated. The activation energies for the solutes studied have the following order: phenols > aromatic amines > phenones > aromatic ethers > nonassociated solutes > 2-naphthalenethiol.

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I. INTRODUCTION

Diffusion can be referred to the net transport of material within a single phase in the absence of mixing by mechanical means or by convection. Diffusion phenomenon can result from concentration gradients, pressure gradients, temperature gradient and external force fields. Only the diffusion resulting from concentration gradients is considered here, *i.e.*, the discussion is limited to diffusion in isothermal and isobaric systems with no external force field. In this type of process, diffusion continues until concentrations in all regions of the phase become equal.

Diffusion plays a very important role in many areas such as biological systems, chemical reactions, environmental pollutions, industrial processes, etc. In biochemistry, for example, enzymes react with ligands at about diffusion controlled rate.[1] Protein growth may be determined by the diffusion of microdomains of protein till the preferred configuration is reached.[2] On a micrometer distance scale, the oxygenation or deoxygenation of red blood cell is determined both by the rate of molecular diffusion of oxygen from the serum (or aqueous solution) surrounding the erythrocyte into the cell and by the motion of the surrounding serum with respect to the cell.[3] In catalytic reactions, when the reactivity of catalyst is high enough, the efficiency of the catalytic process depends greatly on the diffusing speed of reactants toward or products away from the surface of the catalyst. In polymerization, polymer chain growth is also thought to be often controlled by diffusion. In pharmacology, the speed of the human intestine absorbs drugs is limited by diffusion. In food science, the rate of the release of flavor from food is controlled by diffusion. Diffusion has also a great

deal of applications in many separation techniques (*e.g.* distillation, mixing, extraction, condensation, etc.), pollution controls, dyeing of fabrics, drug designs, etc. In short, diffusion process is fundamental and ubiquitous in many fields. It is a fascinating subject, as central to our daily lives as to chemistry. Because of the importance of diffusion, there have been many experimental and theoretical studies in this area. The considerable experimental and theoretical interests are driven by the fact that a better understanding of the nature of molecular diffusion processes is needed in order to upgrade the theories and diffusion related technologies.

Diffusion is often studied in terms of diffusion coefficient. In 1835, Rudolf Fick stated his First Law of diffusion: the flux or flow through unit cross-section area of a component i by diffusion in the direction x is proportional to the gradient of concentration in that direction, *i.e.*,

$$J_{ix} = -D_i\left(\frac{\partial C_i}{\partial x}\right) \qquad (1)$$

where J is the flux and C refers to concentration. The proportionality constant D is the diffusion coefficient. The diffusion coefficient measures the transport of mass by molecules down a gradient in concentration (or more generally, in chemical potential). It can be measured by observing the rate at which boundary spreads, or the rate at which a more concentrated solution diffuse into a less concentrated one. The larger value of diffusion coefficient means the faster the diffusion.

When the above equation is applied to a two-component system, the diffusion coefficient is referred to as the mutual diffusion coefficient, D_{12}, where 1 denotes the solute and 2 is the solvent. If a solute in a very diluted concentration diffuses in a

mixture, the diffusion coefficient is normally definited as the limiting mutual diffusion coefficient. The diffusion coefficient or diffusivity is an important transport property that can be used for understanding and predicting the dynamic behavior of molecules as well as for designing various chemical and industrial processes. Nonetheless, it appears that our knowledge of diffusion or diffusion coefficients is still in its relative infancy. In particular, the diffusion behavior of associated molecules is not very well known.

In this project, the effects of molecular association on diffusion are investigated experimentally. The experiment involves measurements of limiting mutual diffusion coefficients of associated solutes and nonassociated solutes. The objective of this work is to study the diffusion behavior of different solutes having similar shape in terms of their functional groups at different temperatures in various organic solvents. It is hoped that this investigation can provide useful information for a better understanding of the diffusion of associated molecules and ultimately to the advancement of diffusion theories and to diffusion related technologies.

II. STATEMENT OF THE PROBLEM

Although theories of diffusion in gases and solids are well developed, diffusion in liquid is still not fully understood. Traditionally, diffusion in liquids has been described by the hydrodynamic theory represented by the Stokes-Einstein equation[4]:

$$D = \frac{kT}{f} = \frac{kT}{6\pi\eta r} \qquad (2)$$

where D is the diffusion coefficient, f is the frictional coefficient of the solute, k is Boltzmann's constant, T is the temperature, η is the solvent viscosity, and r is the solute radius. In this hydrodynamic theory, the diffusivity is related to the retarding force which acts on a sphere moving in a continuum. The frictional coefficient can be evaluated in terms of the sphere's radius and solvent's viscosity by Stokes' law, and the resulting expression is call the Stokes-Einstein equation. This equation accounts well for the diffusion of large spherical solutes, however, it fails completely for solute molecules smaller in size compared to the solvent molecules.[5-8] Although the Stokes-Einstein equation was basically derived for a very special situation, many investigators have used the form as a starting point in developing correlations. Several estimation methods for diffusion in liquids have been reviewed by Reid *et al.* [9]

Based on the van der Waals (VDW) picture, another theory called the rough-hard-sphere (RHS) theory was developed by Chandler.[10-11] This theory has been popularly used by many researchers in this field to interpret their experimental data.[12-43] For mutual diffusion, the RHS theory predicts diffusion coefficients as follows:[31,42,43]

$$D_{12} = \frac{3(kT)^{\frac{1}{2}}}{2n_2(\sigma_1+\sigma_2)^2}\left(\frac{1}{2\pi\mu}\right)^{\frac{1}{2}}\frac{A_{12}}{g_{12}}\left(\frac{D_{SHS}}{D_E}\right) \qquad (3)$$

where D_{12} is the limiting mutual diffusion coefficients, n_2 represents the number density of the solvent, μ is the reduced mass of solute and solvent, σ_1 and σ_2 refer to the molecular diameters of solute and solvent, respectively, A_{12} is the translation-rotation coupling constant, D_{SHS}/D_E represents the computed correction to the Enskog theory to take account of the correlated molecular motions, and g_{12} is the unlike radial-distribution function at contact. The RHS theory assumes that the structural arrangements and motions of molecules in liquid are determined primarily by the local packing and steric effects produced by the short-range repulsive intermolecular forces, and that weak dipole-dipole interactions and other attractive forces which vary slowly in space play only a minor role. Detail of the theory has been reviewed by Chandler *et al.* [44] In general, the RHS theory is successful in describing the diffusion behavior of mainly nonassociated molecules.

Neither the hydrodynamic theory nor the rough-hard-sphere theory can describe the diffusion behavior of associated molecules in liquids very well. This may be due to the lack of useful experimental data and systematic investigations that can clearly identify and evaluate the effects of molecular associations on diffusion. Molecular association involves mainly with hydrogen bonding, and hydrogen bonding exist commonly in many chemical and biological systems containing water, carboxylic acids, phenols, alcohols, amino acids, amines, etc. It is well recognized that hydrogen bonding can affect many physical properties such as boiling point and solubility.

Although it is expected that hydrogen bonding will also influence diffusion in liquids, the effect of it on diffusion is still not well known.

There appears to be only a few studies on the effect of molecular association on diffusion. Previously, Longsworth[45] and Tyrrell *et al.*[46], by using the Stokes-Einstein numbers in the hydrodynamic theory, have shown evidence of the effect of solute-solvent interaction on diffusion in water and in propane-1,2,-diol, respectively. However, the Stokes-Einstein equation is limited to cases in which the solute molecule is larger than the solvent molecule[5,6]. Recently, from their experimental data, Akgerman *et al.*[15] have extracted the combined effects of translational-rotational coupling and hydrogen bonding. Unfortunately, these two effects cannot be separated in their study. More recently, Tominaga *et al.*[47] have found that solute-solvent interactions decrease the diffusion coefficients of polar solutes in polar solvents. Nonetheless, it appears that more studies are needed for a better understanding of the effects of solute-solvent interactions on diffusion. The lack of information about the motion of associated molecules may hinder the development of the diffusion theories and related technologies.

III. AIMS AND METHODOLOGY

As mentioned above, systematically diffusion studies for associated solutes are relatively scarce. Previously, Chan *et al.* have found[25,26] that diffusivities are generally dependent on the shape and size of molecules but are insensitive to the mass and dipole moment of the nonassociated solute molecules. Recently, they have shown[13] that there is a linear relationship between the reciprocal of diffusion coefficient and the molecular volume of the nonassociated solutes having similar shape. More recently, they have also demonstrated[48] that the effect of hydrogen bonding on diffusion can be identified and quantified.

This present work, which is based on the above studies of Chan and coworkers,[13,25,26,48] aims to measure systematically the limiting mutual diffusion coefficients of nonionic solutes that are capable of forming strong intermolecular interactions with solvent molecules. The purpose is to find out the effects of molecular association on mutual diffusion. This will be accomplished by comparing the measured data of associated solutes with those of nonassociated ones. The objective is to study the diffusion behavior of different solutes having similar shape at different temperatures in various organic solvents. In particular, how functional groups would affect diffusion in various solvents and how temperature would affect diffusion in liquids are emphasized in this work.

There are many techniques for measuring mutual diffusion coefficients in liquids. These include the diaphragm cell method, interferometry, the capillary

method, the Taylor dispersion technique, etc.[49] In this work, the Taylor dispersion technique or the so-called chromatographic peak-broadening method[50,53-61] is used, as it is currently the fastest method for acquisition of diffusion data. Also, this method can provide data with relatively good precision.

To achieve the aim of this project, the limiting mutual diffusion coefficients of aromatic compounds containing one polar functional group which may form strong intermolecular interactions via hydrogen bonding will be measured. Since diffusivities depend on many factors, the effect of association must be separated from other factors. In this case, solutes which were chosen are all pseudoplanar in shape, so direct comparisons between the diffusion coefficients for nonassociated and associated solutes can yield meaningful results. For nonassociated solutes, aromatic compounds such as benzene, chlorobenzene, toluene, ethylbenzene, naphthalene, 1,2,4-trichlorobenzene, propylbenzene, mesitylene and biphenyl are used. In order to obtain mutual diffusion coefficients of associated molecules, aromatic compounds containing one polar functional such as phenols, aromatic amines, aromatic thiols, phenones, aromatic ethers are investigated. Solvents used in this experiment are ethanol, methanol, acetone and *n*-hexane. These solvents are selected to represent protic, aprotic, and hydrocarbon species. The solvents are also chosen because of their low molecular weight and viscosity. According to Chan's previous results,[13] the effects of solute shape on diffusion in such kind of solvent (except perhaps ethanol) are relatively insignificant. Thus any effect due to the slight change of solute shape after association will be minimized. The measurements for mutual diffusion coefficient are carried out mainly at 298.2K. For ethanol system, the experiments also involve measurements of

diffusion coefficients of nonassociated and associated solutes at 283.2K, 298.2K, 313.2K and 328.2K. To find out the effects of molecular association on diffusion, plots of $1/D_{12}$ *vs.* solute volume for the nonassociated solute are found first. The deviations of the $1/D_{12}$ values for the associated solutes from the nonassociated lines yield the effects. It is anticipated that this investigation will also lead to a better understanding of the nature of strong intermolecular interaction in solute-solvent systems.

IV. EXPERIMENTAL

As Cussler mentioned in his book,[49] measuring diffusion coefficients is reputed to be a very difficult task. Tyrrell[51] also stated that this is not an easy field in any sense. It is interesting to point out that it took eight years from the time when Thomas Graham worked on diffusion before precise data on diffusion coefficients began to be collected. Nowadays, however, many different techniques for measuring diffusion coefficients are available. Various methods such as the diaphragm cell method, the optical method, the Taylor dispersion technique, etc. have already been reviewed by Tyrrell and Harris.[52] In this work, the Taylor dispersion technique or the so-called chromatographic peak-broadening method is used. This method is chosen because it is a simple and fast technique for the determination of mutual diffusion coefficients in liquid systems, and the apparatus required is easy to construct with moderate cost. Moreover, it allows precise measurements at different temperatures. Currently, this method is widely used by many researchers.[5-10,13,15,27-31,47,48,50,53-61]

The basic principle of the Taylor dispersion technique is that when a pulse of solution is injected into a solvent undergoing laminar flow in a capillary tube as shown in Fig. 1(a), the pulse is immediately distorted into a parabolic shape by the streamline velocity [see Fig. 1(b)]. This distortion results in variation of concentration along the radial direction. Since solute molecules also diffuse from region of higher concentration to that of lower concentration, a combination of flow and diffusion would continuously change the concentration profile of the solute along

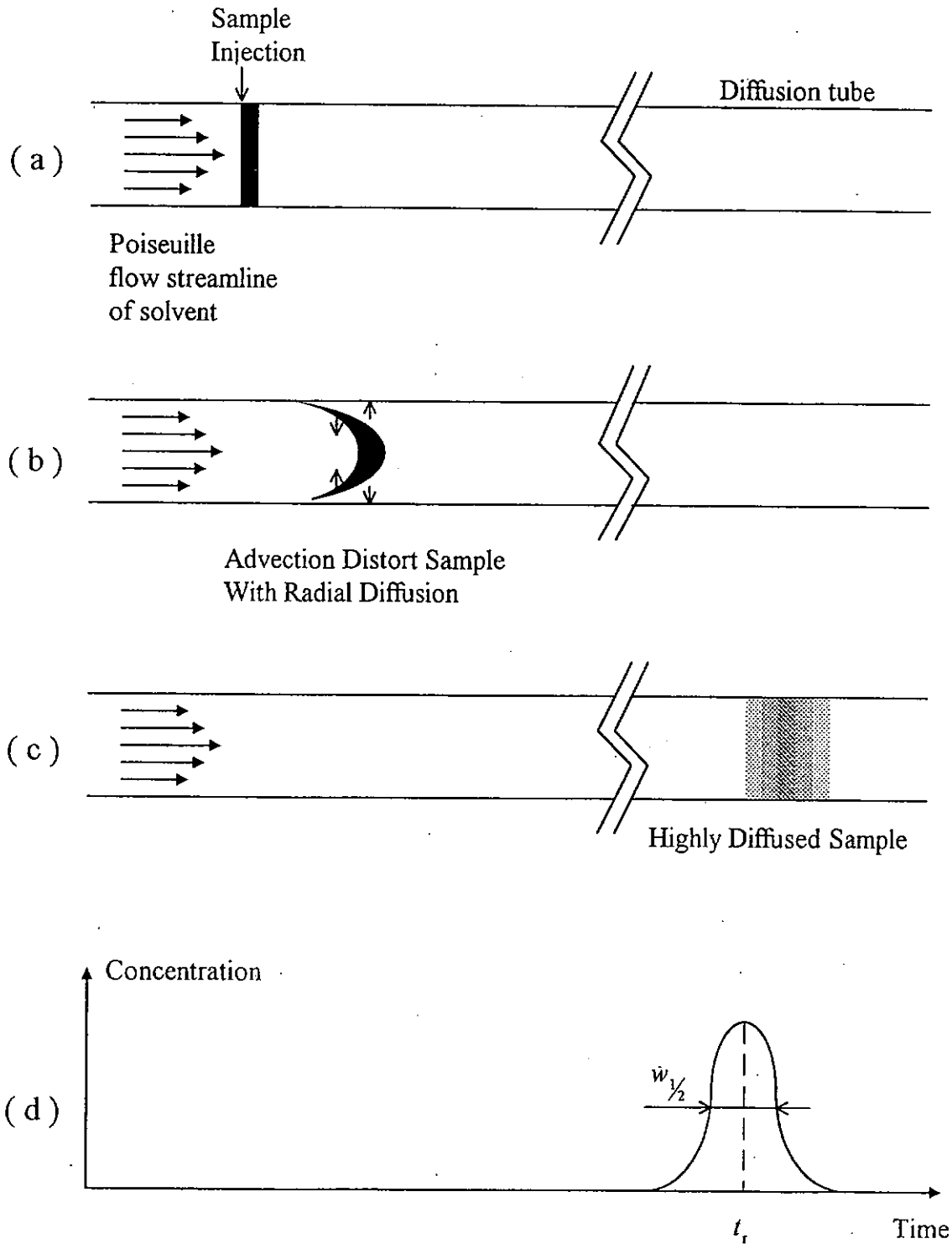

Fig. 1 Illustration of the dispersion of solutes in diffusion tube. (a) the sample of solute injected into the diffusion tube, (b) the advection distorted pulse, (c) the dispersion of the molecules due to poiseuille flow with molecular diffusion, (d) the gaussian peak obtained on the chart recorder.

the tube [(see Fig. 1(b)]. If the length of the capillary tube is long enough and the flow rate is low enough, Taylor[62] has shown that the distribution of the solute molecules is nearly Gaussian along the tube when the highly diffused pulse arrives at the end of the tube [Fig. 1(c) and 1(d)]. With a differential refractometer or other detector, the concentration distribution can be detected. The detected signal output can be connected to a chart recorder, and a Gaussian peak is normally obtained. A widely spread peak indicates that the diffusion coefficient is small, and a very sharp peak yields a large diffusion coefficient. By measuring the retention time (t_r) and the peak width at half peak height ($W_{1/2}$), Grushka *et al.*[50] has shown that the diffusion coefficient for the liquids can be determined from the following equation:

$$D_{12} = 0.2310 r^2 t_r / (W_{1/2})^2 \qquad (4)$$

where D_{12} is the mutual diffusion coefficient, r is the internal radius of the diffusion tube, t_r is the residence time of the solute in the tube, and $W_{1/2}$ is the width at half-height of the eluted peak. The precision of the chromatographic peak-broadening method can be obtained to as good as ±1%.

(A) Apparatus

The apparatus used in this method is consisted of different components, which are (1) a solvent delivery system, (2) a thermostat, (3) a sample injection device, (4) a diffusion tube, (5) a detector, and (6) a chart recorder. A schematic diagram of the apparatus is shown in Fig. 2. Fig. 3 shows the experimental set-up for the diffusion measurement in the laboratory of the Department of Applied Biology and Chemical Technology of the Hong Kong Polytechnic University. The apparatus is described in more details as follows:

1. The solvent delivery system

The solvent delivery system contains a solvent reservoir, two solvent delivery pumps, and a pulse damper. In this experiment, the solvent reservoir is a 2L round bottom flask equipped with a Teflon-coated magnetic stirrer. The two solvent delivery pumps are used separately for delivering (i) sample solution to the sample inlet of the detector, and (ii) pure solvent to the reference inlet of the detector (see Fig. 2). The sample pump is a Bio-Rad HPLC pump (model 1350), which can offer constant flow rate (±0.1%) with low pulsation. The flow rate is adjustable from 0.02 to 9.9 mL per minute in 0.01 mL per minute increments. To further minimize pulsation, a pulse damper (Scientific systems, Inc. model 20-0218) is added to the outlet of this pump, which is then connected to the injector as shown in Fig. 2. The reference pump is an Alcott HPLC pump (model 760A) which can offer constant (±0.5%) and low flow rate (< 1 mL per minute). The flow rate is selectable from 0.001 to 0.999 mL per minute in 0.001 mL per minute increments.

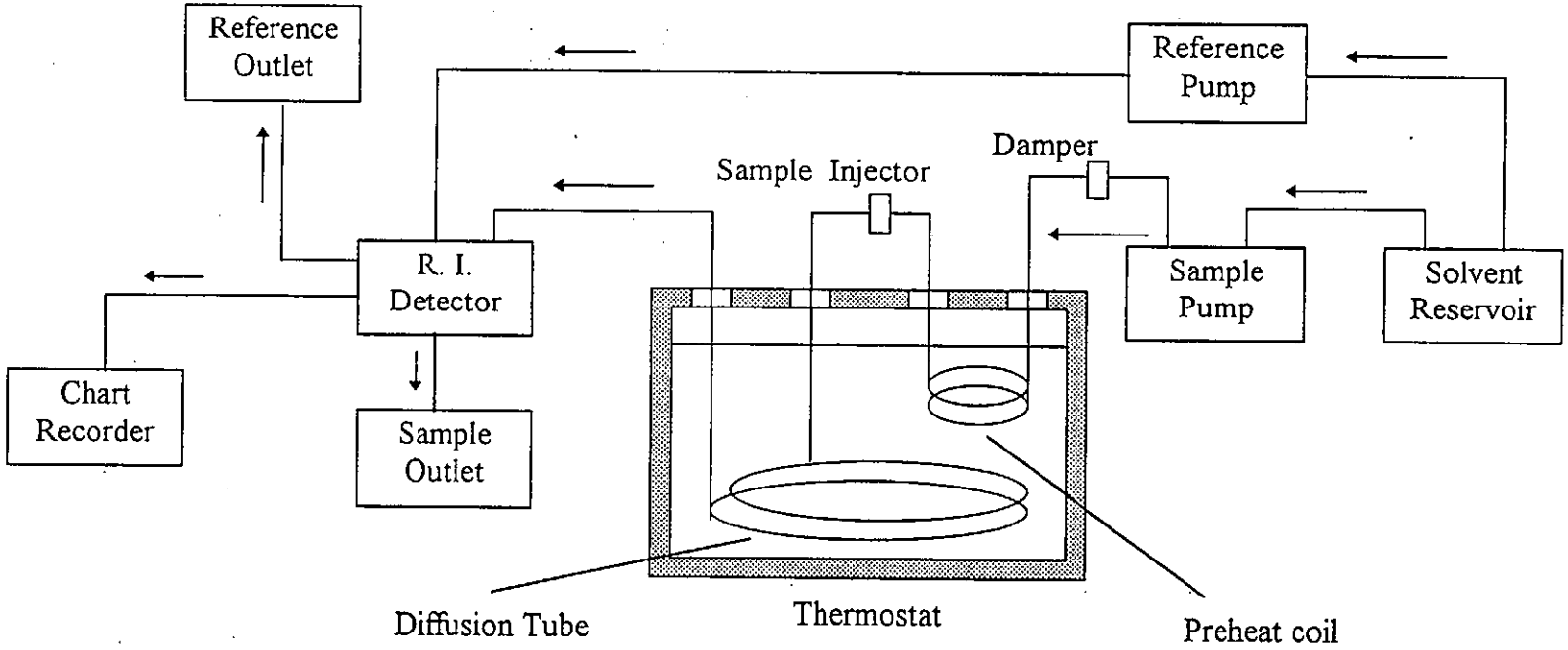

Fig. 2 Schematic Diagram of the Diffusion Apparatus

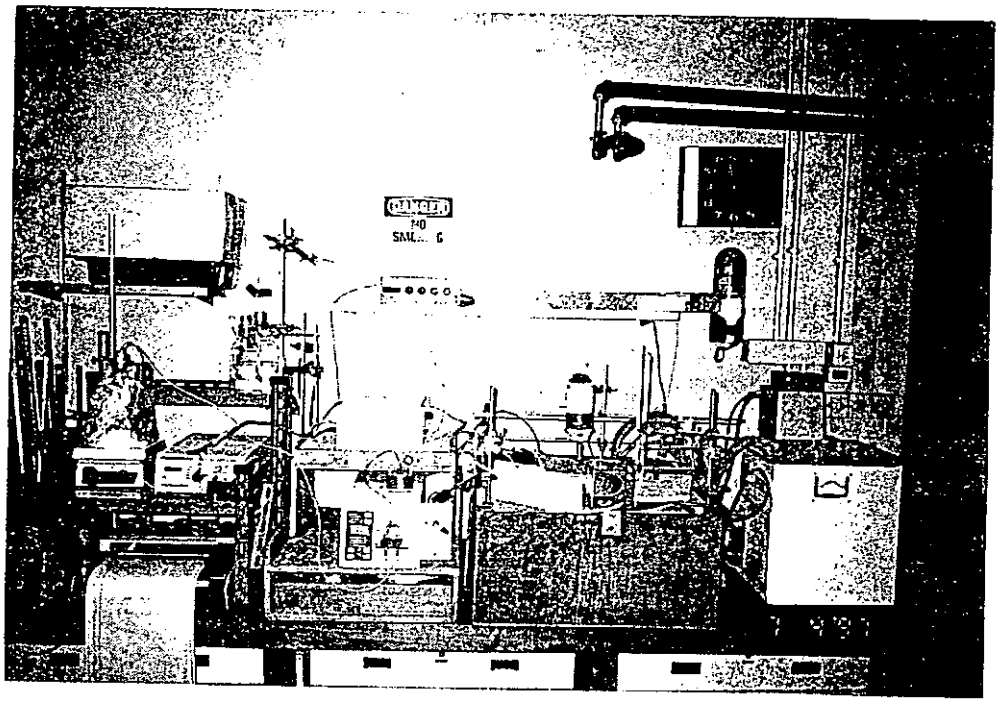

Fig. 3 The experimental set-up for the diffusion measurement

2. The thermostat

The thermostat used in this work consists of a water bath, a temperature controller, a cooling device, a heater, a mechanical stirrer, an immersion pump and Beckmann thermometers. The water bath is a ~ 70 L cylindrical container with 56 cm in diameter and 28 cm in height. The bath is placed in a wooden case and is well insulated with polystyrene foam to minimize heat transfer. The temperature of the bath is regulated by a Tronac temperature controller (model PTC-36) which is connected to a 1000 W heater and a temperature-controller probe immersed in the water bath. The cooling device is built by a coiled copper tubing connected to a refrigerated bath circulator (Neslab, model RTE-8). The temperature of the circulator, which can be controlled to within ±0.1K, is normally set at a few degrees below the temperature of the thermostat. To maintain uniform temperature within the thermostat, a propeller type of stirrer with speed up to 6000 rpm and an immersion pump were applied. The temperatures of the thermostat were measured by Beckmann thermometers which were calibrated against a certified thermometer (Kessler, No. 91888). The temperature of the thermostat can normally controlled to within ±0.02K in the temperature range of the experiment.

3. The sample injection device

The valve injector (Rheodyne model 7125) with a 50 μL sample loop was used throughout the experiment. The inlet of the injector was connected to the pre-heated solvent pumped down from the pulse damper and the outlet to the diffusion tube (see Fig. 2).

4. The diffusion tube

The diffusion tube was an 85.7m long stainless steel tube with 1.59 mm o.d. and 0.98 mm i.d. (Superior Tube Co.). The capillary tube was coiled in an about 40 cm diameter circle and immersed into the thermostat as described above. The inlet of the capillary tube was connected to the injector and the outlet to the differential refractometer.

5. The detector

A differential refractive index detector (Dynamax, model RI-1) was used in this experiment to detect the concentration profiles of the samples. The inlet of the sample cell is connected to the diffusion tube, and the inlet of the reference cell is connected to the reference pump which delivers pure solvent (see Fig. 2). As refractive index of a solution is proportional to its concentration, the signal output of the differential refractive index detector is therefore also proportional to concentration. The detector can thus detect the concentration profiles of the samples as they passed through the sample cell. Both outlet tubings were nonetheless raised about 40 cm high to provide a back pressure for avoiding degassing in the detector cells.

6. The chart recorder

The signal output of the differential refractometer was recorded by a chart recorder (Allen Datagraph, model 2125M). A chart speed of 40 cm per hour was selected throughout the experiment.

(B) Materials

1. Chemicals for calibration

Chemicals used for calibration were urea and water. The distilled water purchased from Watson's Hong Kong Ltd. was run through water purification system (Millipore, Milli-Q TM system) to get better purity. Urea (>99.5%, Fluka) was further purified by recrystallisation.

Other chemicals such as pyridine (99.9%, HPLC Grade, Aldrich), benzene (99.9+%, HPLC Grade, Aldrich), carbon tetrachloride (Analytical Reagent, Ajax), chlorobenzene (99.9+%, HPLC Grade, Aldrich), toluene (99.8%, HPLC Grade, Aldrich), and ethanol (>99.8%, Absolute Grade, E. Merck) were used as received for testing the accuracy and precision of the experimental method.

2. Solvents

Solvents used in this experiment were ethanol (99.8%+, E. Merck), methanol (99.9%+, Aldrich), acetone (99.9%+, Aldrich) and *n*-hexane (99%, Lab-scan). All solvents were degassed in ultrasonic bath for at least 30 minutes before use.

3. Solutes

All solutes used in this work are at least analytical grade with purity over 98%. They were obtained from several different suppliers. The solutes from Aldrich were benzene (99.9+%), chlorobenzene (99.9+%), toluene (99.8%), ethylbenzene (99+%), naphthalene (99+%), 1,2,4-trichlorobenzene(99+%, anhydrous), 1,2,4-trimethylbenzene (98%), mesitylene (98%), biphenyl (99%), 1-naphthol (99%+), 2-

naphthol (99%), aniline (99.5%), *p*-toluidine (99.9%), 4-chloro-2-methylaniline (99%), acetophenone (99%), *m*-methylacetophenone (98%), *p*-chloropropiophenone (98%), and 2-methoxynaphthalene (99%). Those purchased from E. Merck were biphenyl-2-ol (99%), 1-naphthylamine (99%), 2-biphenylamine (>98%), propiophenone (99%), 2-acetylnaphthalene (99%+), anisole (99%+), *p*-methylanisole (99%+), and 2-naphthalenethiol(99%). Solutes supplied by Fluka are p-cresol (99%), *p*-chloroaniline (99%+), and *p*-chloroanisole (98%). Those obtained from BDH were phenol (99.9%) and *p*-chlorophenol (99.5%). Mesitylene was purified by fractional distillation, all other solutes were used as received.

(C) Procedures

1. Sample preparation

Samples were prepared by dissolving 1-2% by weight of solute in solvent. All glassware (e. g. glass syringes, beakers, sample vials, flasks, stirring rods, pipettes, eye droppers, glass spatulas, etc.) for handling samples was cleaned by cleaning solution. The cleaning solution used was prepared by dissolving 92 g of potassium dichromate in 458 mL of water, in which 800 mL of conc. sulfuric acid was added. All required glassware was first soaked in the cleaning solution, then rinsed thoroughly with tap water and finally with distilled water before drying in an oven controlled at about 100°C overnight. The glassware was kept in a desiccator before use.

2. Experimental temperature control

Measurements for diffusion in ethanol were carried out at 283.2K, 298.2K, 313.2K, and 328.2K. All other systems were measured at 298.2K only. To obtain a constant temperature required for the thermostat, the circulator of the cooling device as described in IV (A) was first set at a few Kelvin's degrees below the required temperature. With the help of the temperature controller and heater, the bath was then brought up to the experimental temperature. The temperature of the thermostat was monitored by a Beckmann thermometer as described in IV (A). A combination of cooling and heating regulated by the temperature controller can normally maintain the thermostat temperature within ±0.02 K.

3. Solvent flow control and sample Injection

To ensure laminar flow, the constant flow rate in the diffusion tube was set at between 0.12 mL and 0.20 mL per minute. This will allow the sample to reach the detector from the injector within nine hours. The flow rate of solvent from the reference pump, however, is only set at somewhere between 0.008 mL and 0.040 mL per minute in order to reduce solvent wastage. It should be noted that when change of solvent in the diffusion tube was required, the tube was usually cleaned at least with twelve cycles of the new solvent. Before sample was transferred to the sample loop by a syringe, both the sample loop and the syringe were purged several times with the pure solvent used in the experiment. Sample injections were made at 1 to 1.5 hours intervals, and normally five to eight data were collected overnight.

4. Calibration

To ensure that the accuracy and precision of the system were acceptable, the apparatus was calibrated. Because the limiting diffusion coefficient of urea in water at 25°C is well recognized as a standard in the literature, it is selected for the calibration. The purification of urea and water have already been described in IV (B). About 30 measurements were carried out to include different flow rates, solute concentrations and detector attenuations. By averaging the data, Eq. (4) can be rewritten as follows:

$$D_{12} = 6.39104 \times 10^{-6} cm^3 s^{-1} \times t_r / (w_{1/2})^2 \qquad (5)$$

where t_r and $W_{1/2}$ are expressed in terms of cm in the chart. As mentioned before, the chart speed is fixed at 40 cm per hour. It should be noted that the average error of all urea data was about 0.9%, the maximum deviation being only 1.7%.

The apparatus was further tested by measuring the limiting diffusion coefficients of benzene, pyridine, chlorobenzene, carbon tetrachloride and toluene in ethanol at 298.2K. The results are shown in Table 1. Also shown in this table are values from the literature for comparison. All present data agree with those in the literature within 1.7 %, the average deviation being 1.05%.

5. Data acquisition

Approximately five to eight samples were injected each working day, and sufficient time was allowed between injections so that overlapping of peaks could be avoided. The data were all calculated by using Eq. (5). At least three measurements were made (normally in different days) to obtain an average diffusion coefficient. In case that a measurement is rejected because of its large deviation of value from others, the diffusion coefficient obtained is usually a result of four or more measurements.

Table 1 Comparisons between our experimental values and those in the literature

Solute	D_{12} / $10^{-9}m^2s^{-1}$		% Deviation
	This work	Lit. Value	
Benzene	1.82±0.02	1.79±0.01[13]	1.68
Pyridine	1.22±0.02	1.20±0.02[48]	1.67
Chlorobenzene	1.61±0.01	1.61±0.01[13]	0.00
Toluene	1.64±0.02	1.62±0.02[13]	1.23
Carbon tetrachloride	1.46±0.01	1.47±0.01[26]	0.68

Average=1.05

V. RESULTS

As mentioned above, the diffusion coefficients in liquids were determined by equation (5). Since the same diffusion tube was used throughout the experiment, therefore the value of 6.39104×10^{-6} was kept as a constant. By substituting the value of the residence time of the solute in the tube (t_r) and the width at half-height of the eluted peak ($W_{1/2}$), obtained from the experiment, the diffusion coefficients of different solutes were calculated.

(A) The limiting mutual diffusion coefficients of nonassociated solutes

For the nonassociated aromatic solutes, the limiting mutual diffusion coefficients in ethanol at 283.2K, 313.2K and 328.2K are listed in Table 2 to 4. Summarized in Table 5 are the limiting mutual diffusion coefficients of the nonassociated solutes *n*-hexane at 298.2K. For each diffusivity reported, at least three repeated measurements were performed and the results averaged. The uncertainty listed is the average absolute error. The precision of our data is about ±1%.

The limiting mutual-diffusion coefficient of benzene in ethanol has been reported by Babb and co-workers.[63] Our value of 1.82×10^{-9} m^2 s^{-1} at 298.2K as shown in Table 1 agrees very well with their value of 1.81×10^{-9} m^2 s^{-1}. The accuracy and reproducibility of data here are consistent with those reported in the literature[13,25,26,48] for measurements using the same technique.

Table 2 D_{12} and D_{12}^{-1} of nonassociated pseudoplanar solutes in ethanol at 283.2K

	$D_{12}/10^{-9}m^2s^{-1}$	$D_{12}^{-1}/10^9m^{-2}s$
Benzene	1.35±0.02	0.741
Chlorobenzene	1.21±0.01	0.826
Toluene	1.23±0.01	0.813
Ethylbenzene	1.11±0.01	0.901
Naphthalene	1.01±0.01	0.990
1,2,4-Trichlorobenzene	0.974±0.009	1.03
Propylbenzene	1.02±0.01	0.980
Mesitylene	0.975±0.009	1.03
Biphenyl	0.907±0.009	1.10

Table 3 D_{12} and D_{12}^{-1} of nonassociated pseudoplanar solutes in ethanol at 313.2K

	$D_{12}/10^{-9}m^2s^{-1}$	$D_{12}^{-1}/10^9m^{-2}s$
Benzene	2.32±0.02	0.431
Chlorobenzene	2.07±0.02	0.483
Toluene	2.10±0.02	0.476
Ethylbenzene	1.92±0.02	0.521
Naphthalene	1.76±0.02	0.568
1,2,4-Trichlorobenzene	1.69±0.02	0.592
Propylbenzene	1.76±0.01	0.568
Mesitylene	1.69±0.01	0.592
Biphenyl	1.58±0.01	0.633

Table 4 D_{12} and D_{12}^{-1} of nonassociated pseudoplanar solutes in ethanol at 328.2K

	$D_{12}/10^{-9}m^2s^{-1}$	$D_{12}^{-1}/10^9m^{-2}s$
Benzene	2.96±0.03	0.338
Chlorobenzene	2.65±0.03	0.377
Toluene	2.71±0.03	0.369
Ethylbenzene	2.46±0.03	0.407
Naphthalene	2.29±0.02	0.437
1,2,4-Trichlorobenzene	2.17±0.03	0.461
Propylbenzene	2.24±0.02	0.446
Mesitylene	2.17±0.02	0.461
Biphenyl	2.03±0.02	0.493

Table 5 D_{12} and D_{12}^{-1} of nonassociated pseudoplanar solutes in *n*-hexane at 298.2K

	$D_{12}/10^{-9}m^2s^{-1}$	$D_{12}^{-1}/10^9m^{-2}s$
Benzene	4.74±0.05	0.211
Chlorobenzene	4.24±0.04	0.236
Toluene	4.34±0.04	0.230
Ethylbenzene	3.96±0.04	0.253
Naphthalene	3.76±0.04	0.266
1,2,4-Trichlorobenzene	3.51±0.04	0.285
Propylbenzene	3.61±0.04	0.277
1,2,4-Trimethylbenzene	3.57±0.04	0.280
Mesitylene	3.54±0.03	0.282
Biphenyl	3.29±0.03	0.304

(B) The limiting mutual diffusion coefficients of associated solutes

For the associated aromatic compounds, the data include the following five classes: (1) phenols, (2) aromatic amines, (3) aromatic thiols, (4) phenones, and (5) aromatic ethers. The structure of these solutes containing one polar group investigated in this work are shown in Appendix 1. All solutes are pseudoplanar in shape. The mutual diffusion coefficients of the polar solutes in ethanol at 283.2K, 298.2K, 313.2K and 328.2K are reported in Table 6 to Table 9. The limiting mutual diffusion coefficients of the polar solutes in methanol, acetone and *n*-hexane at 298.2K are presented in Tables 10 to 12. These tables also include the reciprocal of diffusion coefficients. The reported values are the averages of three or more diffusion measurements. The average error being normally ±1%.

Table 6 D_{12} and D_{12}^{-1} of associated aromatic compounds in ethanol at 283.2K

	$D_{12}/10^{-9}m^2s^{-1}$	$D_{12}^{-1}/10^9m^{-2}s$
Phenols		
Phenol	0.610±0.007	1.64
p-Chlorophenol	0.577±0.006	1.73
p-Cresol	0.575±0.006	1.74
1-Naphthol	0.537±0.006	1.86
2-Naphthol	0.530±0.005	1.89
Biphenyl-2-ol	0.505±0.005	1.98
Aromatic Amines		
Aniline	0.874±0.009	1.14
p-Chloroaniline	0.774±0.008	1.29
p-Toluidine	0.785±0.008	1.27
4-Chloro-2-methylaniline	0.743±0.008	1.35
1-Naphthylamine	0.710±0.007	1.41
Aromatic Thiol		
2-Naphthalenethiol	0.863±0.009	1.16
Phenones		
Acetophenone	0.977±0.009	1.02
Propiophenone	0.920±0.009	1.09
m-Methylacetophenone	0.885±0.008	1.13
2-Acetylnaphthalene	0.784±0.008	1.28
Aromatic Ethers		
Anisole	1.15±0.01	0.870
p-Chloroanisole	1.08±0.01	0.926
p-Methylanisole	1.09±0.01	0.917
2-Methoxynaphthalene	0.892±0.009	1.12

Table 7 D_{12} and D_{12}^{-1} of associated aromatic compounds in ethanol at 298.2K

	$D_{12}/10^{-9}m^2s^{-1}$	$D_{12}^{-1}/10^9m^{-2}s$
Phenols		
Phenol	0.878±0.009	1.14
p-Chlorophenol	0.827±0.009	1.21
p-Cresol	0.845±0.007	1.18
1-Naphthol	0.765±0.008	1.31
2-Naphthol	0.752±0.008	1.33
Biphenyl-2-ol	0.716±0.007	1.40
Aromatic Amines		
Aniline	1.19±0.01[a]	0.840
p-Chloroaniline	1.10±0.01	0.909
p-Toluidine	1.11±0.01	0.901
4-Chloro-2-methylaniline	1.03±0.01	0.971
1-Naphthylamine	0.991±0.008	1.01
Aromatic Thiol		
2-Naphthalenethiol	1.11±0.01	0.901
Phenones		
Acetophenone	1.29±0.01	0.775
Propiophenone	1.22±0.01	0.820
m-Methylacetophenone	1.18±0.01	0.847
2-Acetylnaphthalene	1.04±0.01	0.962
Aromatic Ethers		
Anisole	1.54±0.01	0.649
p-Chloroanisole	1.43±0.02	0.699
p-Methylanisole	1.44±0.01	0.694
2-Methoxynaphthalene	1.20±0.01	0.833

[a] From Ref. 48

Table 8 D_{12} and D_{12}^{-1} of associated aromatic compounds in ethanol at 313.2K

	$D_{12}/10^{-9}m^2s^{-1}$	$D_{12}^{-1}/10^9m^{-2}s$
Phenols		
Phenol	1.17±0.01	0.855
p-Chlorophenol	1.09±0.01	0.917
p-Cresol	1.10±0.01	0.909
1-Naphthol	1.03±0.01	0.971
2-Naphthol	1.01±0.01	0.990
Biphenyl-2-ol	0.971±0.009	1.03
Aromatic Amines		
Aniline	1.63±0.02	0.613
p-Chloroaniline	1.46±0.02	0.685
p-Toluidine	1.49±0.02	0.671
4-Chloro-2-methylaniline	1.40±0.01	0.714
1-Naphthylamine	1.35±0.01	0.741
Aromatic Thiol		
2-Naphthalenethiol	1.41±0.02	0.709
Phenones		
Acetophenone	1.68±0.02	0.595
Propiophenone	1.59±0.02	0.629
m-Methylacetophenone	1.53±0.02	0.654
2-Acetylnaphthalene	1.37±0.01	0.730
Aromatic Ethers		
Anisole	1.99±0.02	0.503
p-Chloroanisole	1.86±0.02	0.538
p-Methylanisole	1.89±0.02	0.529
2-Methoxynaphthalene	1.58±0.02	0.633

Table 9 D_{12} and D_{12}^{-1} of associated aromatic compounds in ethanol at 328.2K

	$D_{12}/10^{-9}m^2s^{-1}$	$D_{12}^{-1}/10^9m^{-2}s$
Phenols		
Phenol	1.55±0.02	0.645
p-Chlorophenol	1.43±0.02	0.699
p-Cresol	1.46±0.02	0.685
1-Naphthol	1.37±0.01	0.730
2-Naphthol	1.35±0.01	0.741
Biphenyl-2-ol	1.29±0.01	0.775
Aromatic Amines		
Aniline	2.16±0.02	0.463
p-Chloroaniline	1.93±0.02	0.518
p-Toluidine	1.96±0.02	0.510
4-Chloro-2-methylaniline	1.83±0.02	0.546
1-Naphthylamine	1.77±0.02	0.565
Aromatic Thiol		
2-Naphthalenethiol	1.71±0.02	0.585
Phenones		
Acetophenone	2.18±0.02	0.459
Propiophenone	2.07±0.02	0.483
m-Methylacetophenone	2.00±0.02	0.500
2-Acetylnaphthalene	1.78±0.02	0.562
Aromatic Ethers		
Anisole	2.57±0.03	0.389
p-Chloroanisole	2.40±0.02	0.417
p-Methylanisole	2.43±0.02	0.412
2-Methoxynaphthalene	2.06±0.02	0.485

Table 10 D_{12} and D_{12}^{-1} of associated aromatic compounds in methanol at 298.2K

	$D_{12}/10^{-9}m^2s^{-1}$	$D_{12}^{-1}/10^9m^{-2}s$
Phenols		
Phenol	1.69±0.02[a]	0.592
p-Chlorophenol	1.58±0.02	0.632
p-Cresol	1.59±0.01[a]	0.629
1-Naphthol	1.46±0.02	0.685
2-Naphthol	1.45±0.01	0.690
Biphenyl-2-ol	1.34±0.01	0.746
Aromatic Amines		
Aniline	1.94±0.02[a]	0.515
p-Chloroaniline	1.78±0.02	0.562
p-Toluidine	1.79±0.02[a]	0.559
4-Chloro-2-methylaniline	1.69±0.01	0.592
1-Naphthylamine	1.63±0.02	0.613
Aromatic Thiol		
2-Naphthalenethiol	1.77±0.02	0.565
Phenones		
Acetophenone	2.07±0.02	0.483
Propiophenone	1.95±0.02	0.513
m-Methylacetophenone	1.92±0.02	0.521
2-Acetylnaphthalene	1.71±0.02	0.585
Aromatic Ethers		
Anisole	2.33±0.02	0.429
p-Chloroanisole	2.17±0.02	0.461
p-Methylanisole	2.19±0.02	0.457
2-Methoxynaphthalene	1.87±0.02	0.535

[a] From Ref. 48

Table 11 D_{12} and D_{12}^{-1} of associated aromatic compounds in acetone at 298.2K

	$D_{12}/10^{-9}m^2s^{-1}$	$D_{12}^{-1}/10^9m^{-2}s$
Phenols		
Phenol	2.93±0.03	0.341
p-Chlorophenol	2.66±0.03	0.376
p-Cresol	2.72±0.03	0.368
1-Naphthol	2.44±0.02	0.410
2-Naphthol	2.41±0.02	0.415
Biphenyl-2-ol	2.22±0.02	0.450
Aromatic Amines		
Aniline	3.17±0.04[a]	0.315
p-Chloroaniline	2.92±0.03[a]	0.342
p-Toluidine	2.94±0.03[a]	0.340
4-Chloro-2-methylaniline	2.68±0.03	0.373
1-Naphthylamine	2.60±0.02	0.385
2-Biphenylamine	2.22±0.02	0.450
Aromatic Thiol		
2-Naphthalenethiol	2.74±0.02	0.365
Phenones		
Acetophenone	3.23±0.03	0.310
Propiophenone	3.08±0.04	0.325
m-Methylacetophenone	2.99±0.03	0.334
2-Acetylnaphthalene	2.70±0.02	0.370
Aromatic Ethers		
Anisole	3.47±0.03	0.288
p-Chloroanisole	3.22±0.04	0.311
p-Methylanisole	3.27±0.03	0.306
2-Methoxynaphthalene	2.87±0.03	0.348

[a] From Ref. 48

Table 12 D_{12} and D_{12}^{-1} of polar aromatic compounds in *n*-hexane at 298.2K

	$D_{12}/10^{-9}m^2s^{-1}$	$D_{12}^{-1}/10^9m^{-2}s$
Phenol	4.24±0.04	0.236
p-Cresol	4.01±0.04	0.249
Biphenyl-2-ol	3.02±0.03	0.331
Aniline	4.27±0.04	0.234
1-Naphthylamine	3.46±0.04	0.289
2-Naphthalenethiol	3.37±0.03	0.297
Acetophenone	3.86±0.04	0.259
p-Methylanisole	3.87±0.04	0.258

VI. DISCUSSION

(A) The diffusion of nonassociated solutes

1. Correlation between mutual diffusion coefficient and van der Waals volume

For the nonassociated pseudoplanar solutes, the values of relative molecular mass[64] and the van der Waals volume (V) as calculated from group increments given in the literature, [65-68] are summarized in Table 13. The solutes in this table are listed in ascending order of their van der Waals volumes. When the reciprocal of the diffusion coefficients of the nonassociated pseudoplanar solutes is plotted against the van der Waals volume, a linear relationship is obtained for ethanol at 283.2K, 313.2K and 328.2K and for *n*-hexane at 298.2K. The plots of $1/D_{12}$ *vs.* V are shown in Figs. 4 to 7. It should be noted that similar straight-line results have been reported for ethanol,[13] acetone,[13] and methanol[48] at 298.2K.

Linear regression has been carried out for our nonassociated data, and the equations obtained are shown as follows:

Ethanol at 283.2K $\quad D_{12}^{-1} / 10^9 \mathrm{m}^{-2}\,\mathrm{s} = 5.38\times10^{-3}\ V/\text{Å}^3 + 0.302 \quad (6)$

Ethanol at 313.2K $\quad D_{12}^{-1} / 10^9 \mathrm{m}^{-2}\,\mathrm{s} = 2.97\times10^{-3}\ V/\text{Å}^3 + 0.191 \quad (7)$

Ethanol at 328.2K $\quad D_{12}^{-1} / 10^9 \mathrm{m}^{-2}\,\mathrm{s} = 2.29\times10^{-3}\ V/\text{Å}^3 + 0.151 \quad (8)$

n-Hexane at 298.2K $\quad D_{12}^{-1} / 10^9 \mathrm{m}^{-2}\,\mathrm{s} = 1.36\times10^{-3}\ V/\text{Å}^3 + 0.101 \quad (9)$

The correlation coefficients for equations (6), (7), (8) and (9) are 0.977, 0.979, 0.980 and 0.988, respectively. It can be seen that these four straight lines show good correlation.

Table 13 The relative molecular mass and van der Waals volume of nonassociated solutes

	Relative Molecular Mass [a]	van der Waals volume ($Å^3$)[b]
Benzene	78.1	81.1
Chlorobenzene	112.6	97.2
Toluene	92.1	97.6
Ethylbenzene	106.2	113.8
Naphthalene	128.2	125.4
1,2,4-Trichlorobenzene	181.5	129.3
Propylbenzene	120.2	130.0
1,2,4-Trimethylbenzene	120.2	130.7
Mesitylene	120.2	130.7
Biphenyl	154.2	152.4

[a] From Ref. 64

[b] The values are average from Refs. 65-68

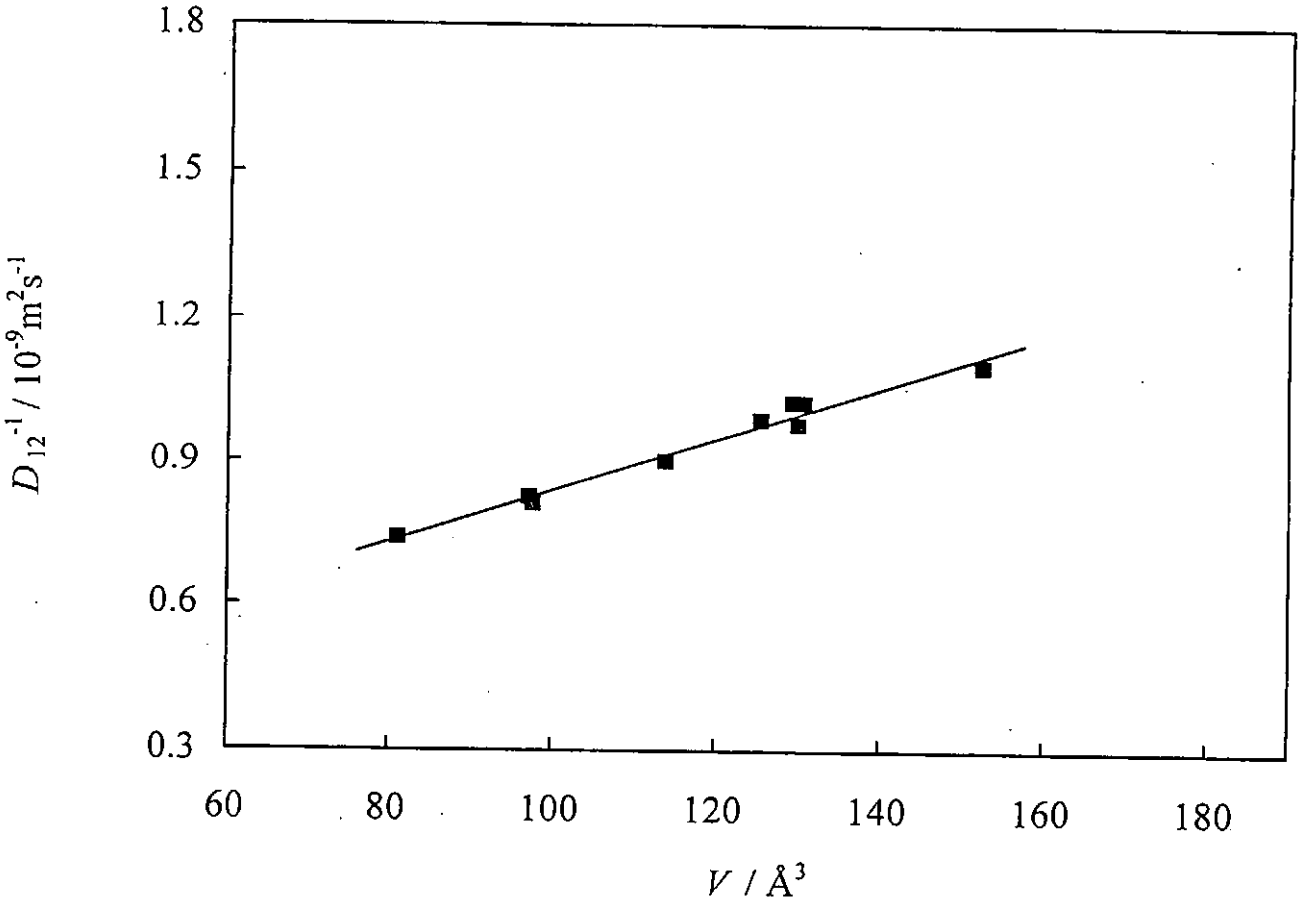

Fig. 4 Variation of $1/D_{12}$ with Molecular Volume of Nonassociated Solutes Diffusing in Ethanol at 283.2K

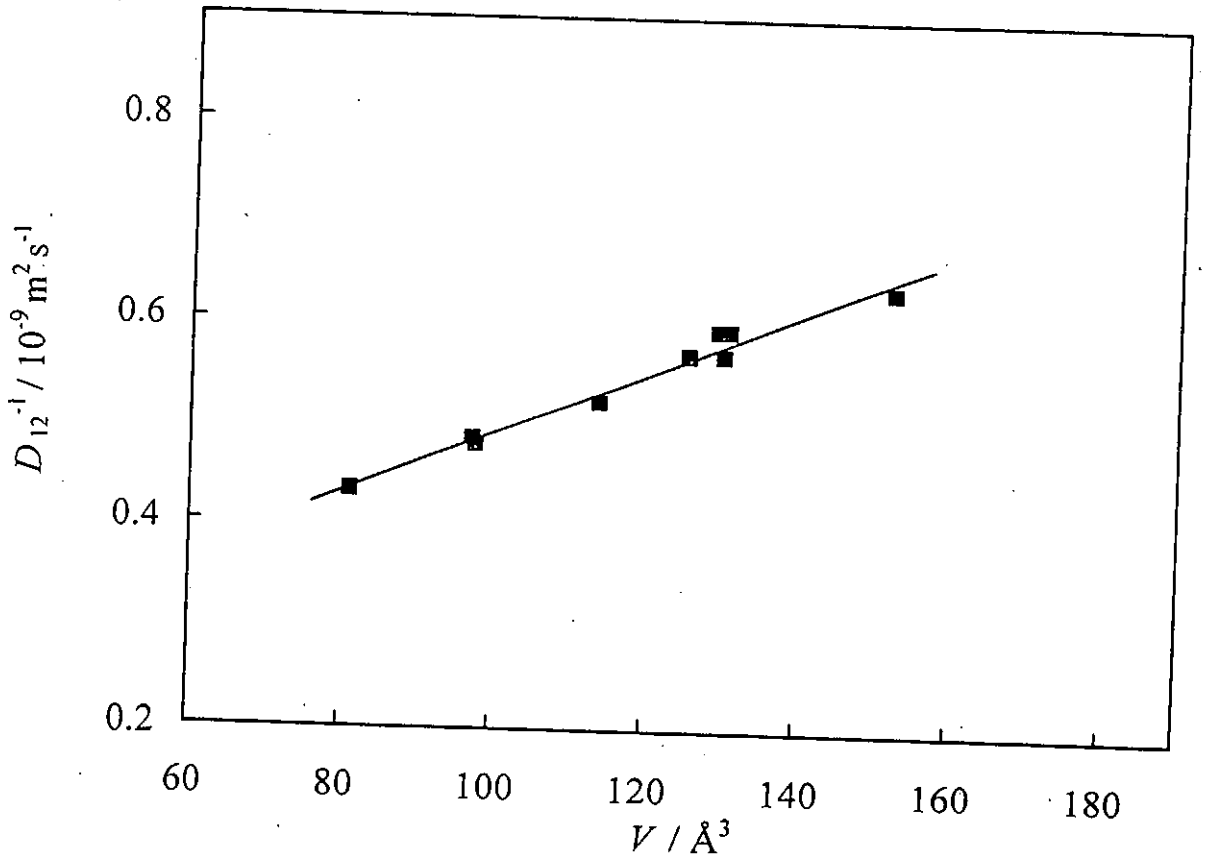

Fig. 5 Variation of $1/D_{12}$ with Molecular Volume of Nonassociated Solutes Diffusing in Ethanol at 313.2K

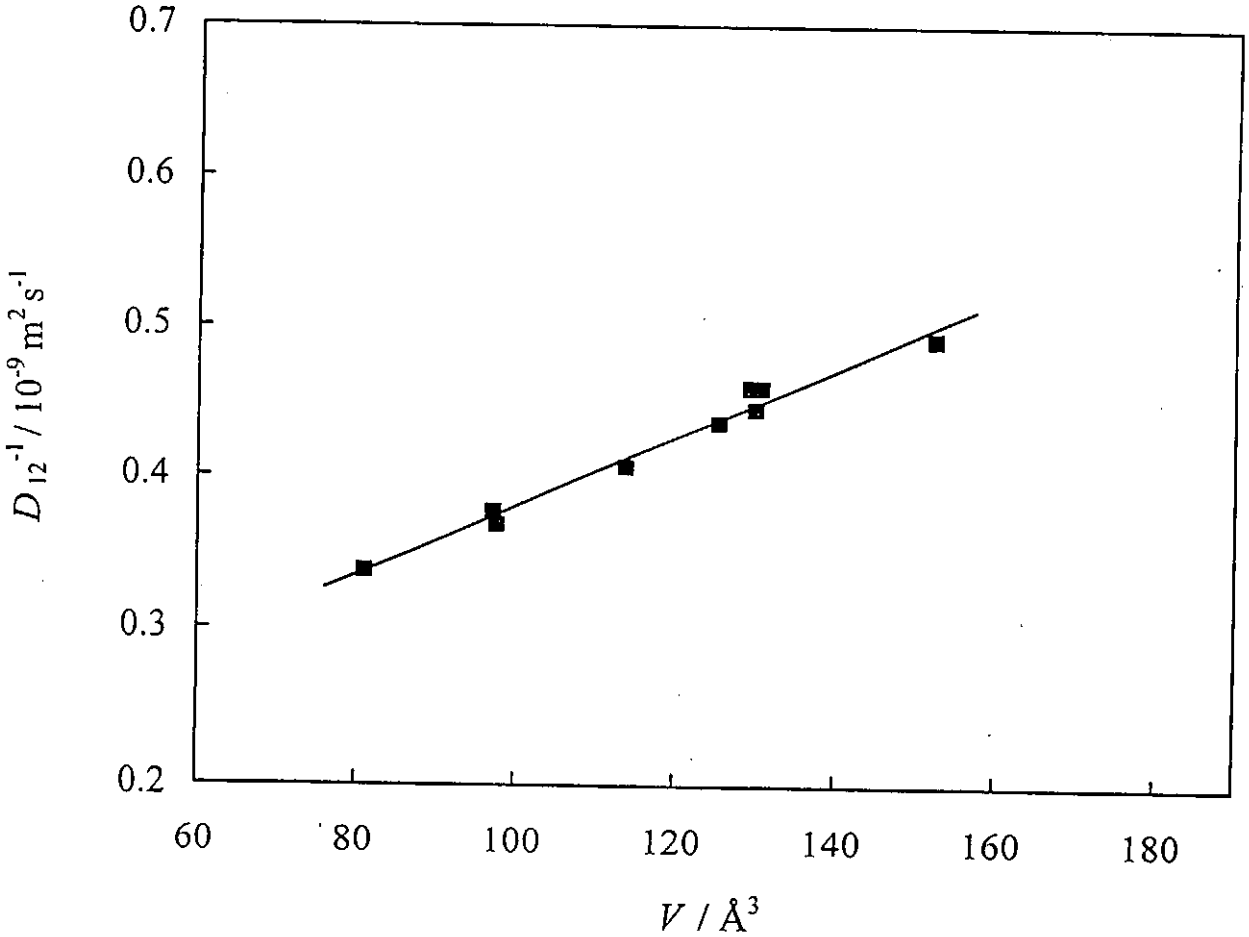

Fig. 6 Variation of $1/D_{12}$ with Molecular Volume of Nonassociated Solutes Diffusing in Ethanol at 328.2K

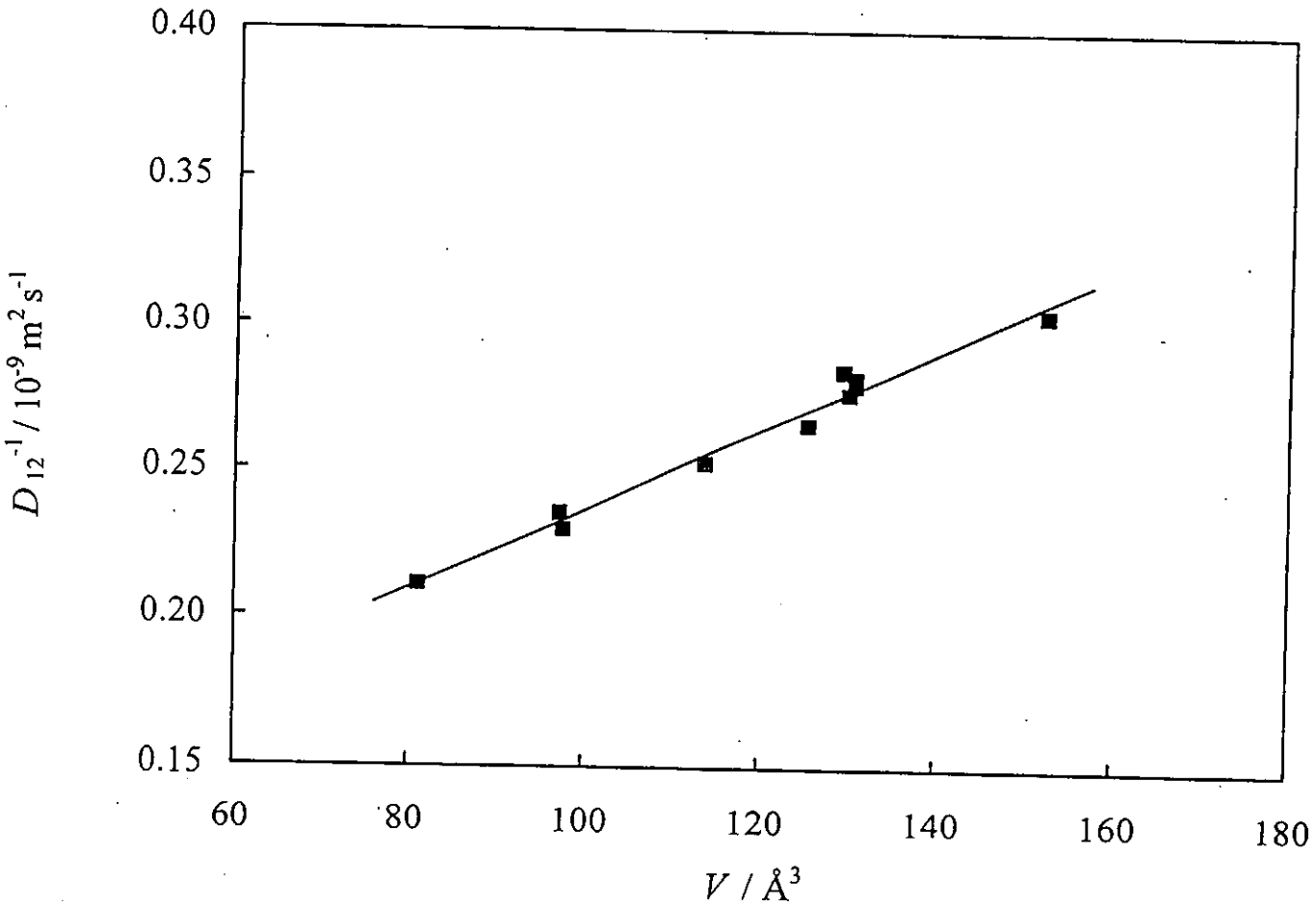

Fig. 7 Variation of $1/D_{12}$ with Molecular Volume of Nonassociated Solutes Diffusing in *n*-Hexane at 298.2K

For methanol, acetone and ethanol at 298.2K, the diffusivities reported in the literatures [13,48] can be fitted to the following equations:

Ethanol at 298.2K $D_{12}^{-1} / 10^9 m^{-2} s = 4.05\times10^{-3} V/Å^3 + 0.230$ (10)

Methanol at 298.2K $D_{12}^{-1} / 10^9 m^{-2} s = 2.30\times10^{-3} V/Å^3 + 0.192$ (11)

Acetone at 298.2K $D_{12}^{-1} / 10^9 m^{-2} s = 1.42\times10^{-3} V/Å^3 + 0.130$ (12)

The correlation coefficients for eqs. (10), (11) and (12) are 0.989, 0.996 and 0.995, respectively.

It is also of interest to point out that there exists a linear relationship between the slopes in Eqs. (9) to (12) and the solvent viscosities at 298.2K. The linear regression with a correlation coefficient of 0.999 is shown in Fig. 8. The viscosities (in cP) used for ethanol, methanol, acetone and *n*-hexane at 298.2K in Fig. 8 are 1.074, 0.544, 0.306 and 0.300, respectively.[64] Whether this conclusion is applicable for other solvent systems, however, awaits further diffusion data to verify.

2. The effect of molecular mass

It is of particular interest to compare the data between chlorobenzene and toluene. These two solute molecules are of about the same size and shape. The close resemblance in size between a chloride group and methyl group has already been discussed. [42] The two solutes are nevertheless different in molecular mass by 20%. The dipole moments for toluene and chlorobenzene are 0.36D and 1.69D, respectively. [68] Our data have shown that the diffusion coefficients of toluene and chlorobenzene are approximately equal in each solvent. This indicates that diffusivities are insensitive to the mass and dipole moment of the solutes molecules. Similar conclusions has also

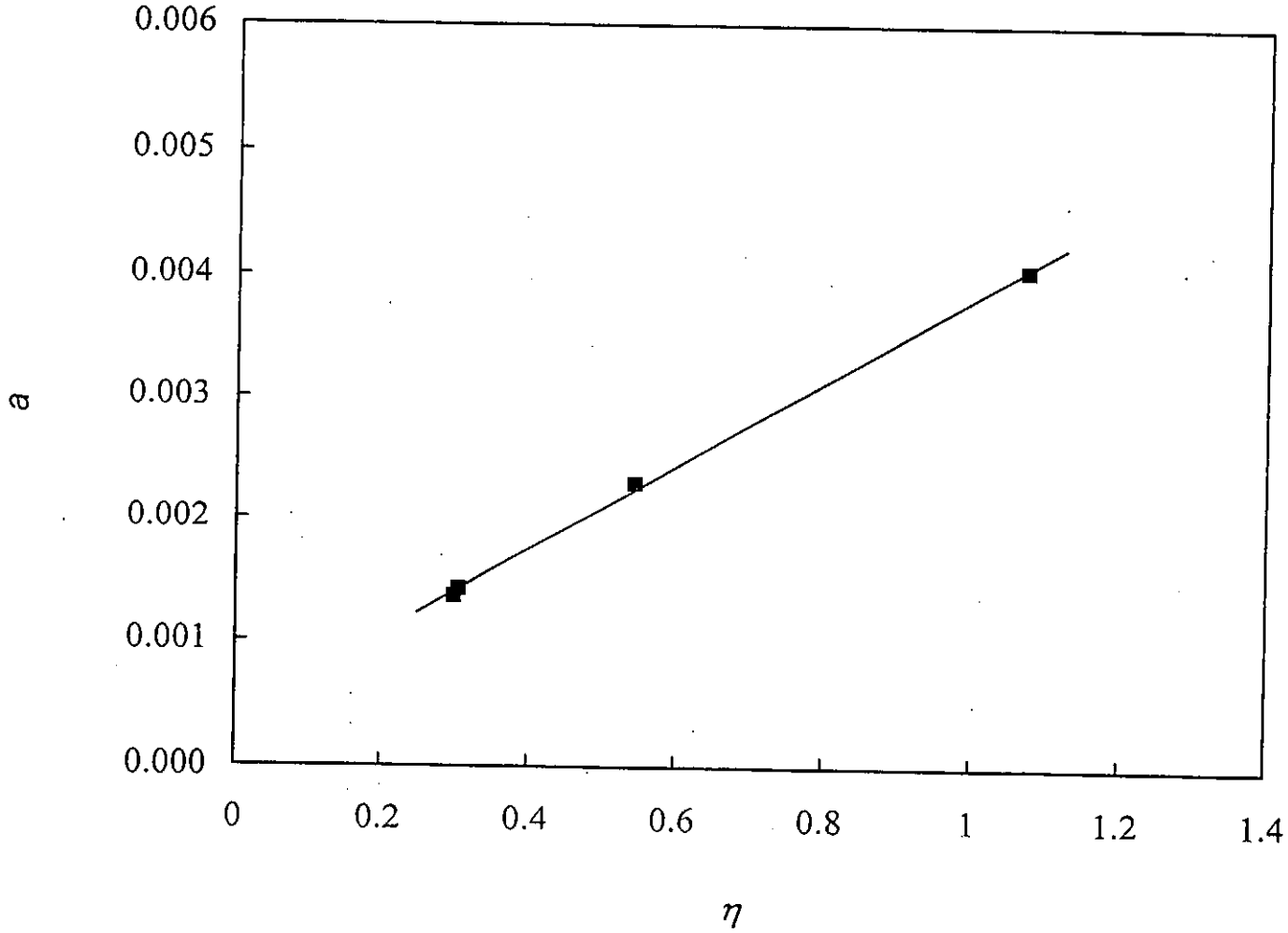

Fig. 8 Variation of slope (a) in linear regressions with Solvent Viscosity (η)

been reached in Chan's previous studies on the diffusion of di-substitued benzenes [25] and pseudospherical solutes. [26]

Another interesting comparison is available between 1,2,4-trichlorobenzene and 1,2,4-trimethylbenzene in *n*-hexane. These two aromatic solutes are also similar in size and shape. Table 13 shows a 50% increase in molecular mass from 1,2,4-trimethylbenzene to 1,2,4-trichlorobenzene. As indicated in Table 5, however, the significant mass increase yields only a small decrease in the diffusion coefficient. The above results of insensitivity of solute mass and dipole moment on diffusion further justifies the basic assumption made in the RHS theory, *i.e.* the molecular dynamics of dense fluids are determined primarily by the size and shape of the molecules.

(B) Diffusion of associated solutes at 298.2K

For the monosubstituted associated solutes, the values of relative molecular mass and van der Waals volume as calculated from group increments given in the literature, [64-68] are summarized in Table 14. The reciprocals of their diffusion coefficients in ethanol, methanol, acetone and *n*-hexane at 298.2K (shown in Tables 7, 10-12) have been plotted against the van der Waals volumes in Figs. 9 to 12. In each of the figures, the lowest straight line, which is for the nonassociated solutes, was redrawn here for comparison. It is interesting to compare the value of the 'associated' with those 'nonassociated' in Figs. 9 to 12. As all solutes are of similar shape, comparisons made at the same solutes volume actually yield the effects of association on diffusion. It should be noted that the effects of mass of solutes on diffusion can be considered as insignificant [13,25-26] within experimental error. From Figs. 9 to 12, it can be seen that aromatic ethers behave as nonassociated solutes in ethanol, methanol, acetone and *n*-hexane. To evaluate the effect of association on diffusion, we use percent deviation from the nonassociated straight line to express it. The percent deviation for monosubstituted aromatic solutes diffusing in ethanol, methanol and acetone at 298.2K are calculated and presented in Table 15.

Fig. 9 shows the variation of $1/D_{12}$ with molecular volume of the polar aromatic solutes diffusing in ethanol at 298.2K. Except for aromatic ethers, all $1/D_{12}$ data of the associated solutes deviate positively from the 'nonassociated' line. The deviations indicate that the diffusivities of the solutes are retarded by the volume increased due to hydrogen bonding with the solvent molecules. In this study, the increase in solute size cannot be attributed to solute-solute interaction because the

Table 14 The relative molecular mass and van der Waals volume of polar aromatic associated solutes

	Relative Molecular Mass [a]	van der Waals Volume ($Å^3$)[b]
Phenols		
Phenol	94.1	89.6
p-Chlorophenol	128.6	105.7
p-Cresol	108.1	106.2
1-Naphthol	144.2	133.9
2-Naphthol	144.2	133.9
Biphenyl-2-ol	170.2	160.9
Aromatic Amines		
Aniline	93.1	93.8
p-Chloroaniline	127.6	109.9
p-Toluidine	107.2	110.4
4-Chloro-2-methylaniline	141.6	136.2
1-Naphthylamine	143.2	138.1
2-Biphenylamine	169.2	165.1
Aromatic Thiol		
2-Naphthalenethiol	160.2	145.1
Phenones		
Acetophenone	120.2	117.0
Propiophenone	134.2	133.2
m-Methylacetophenone	134.2	133.5
2-Acetylnaphthalene	170.2	161.3
Aromatic Ethers		
Anisole	108.1	106.2
p-Chloroanisole	142.6	122.3
p-Methylanisole	122.2	122.7
2-Methoxynaphthalene	158.2	150.5

[a] From Ref. 64

[b] The values are averages from Refs. 65-68

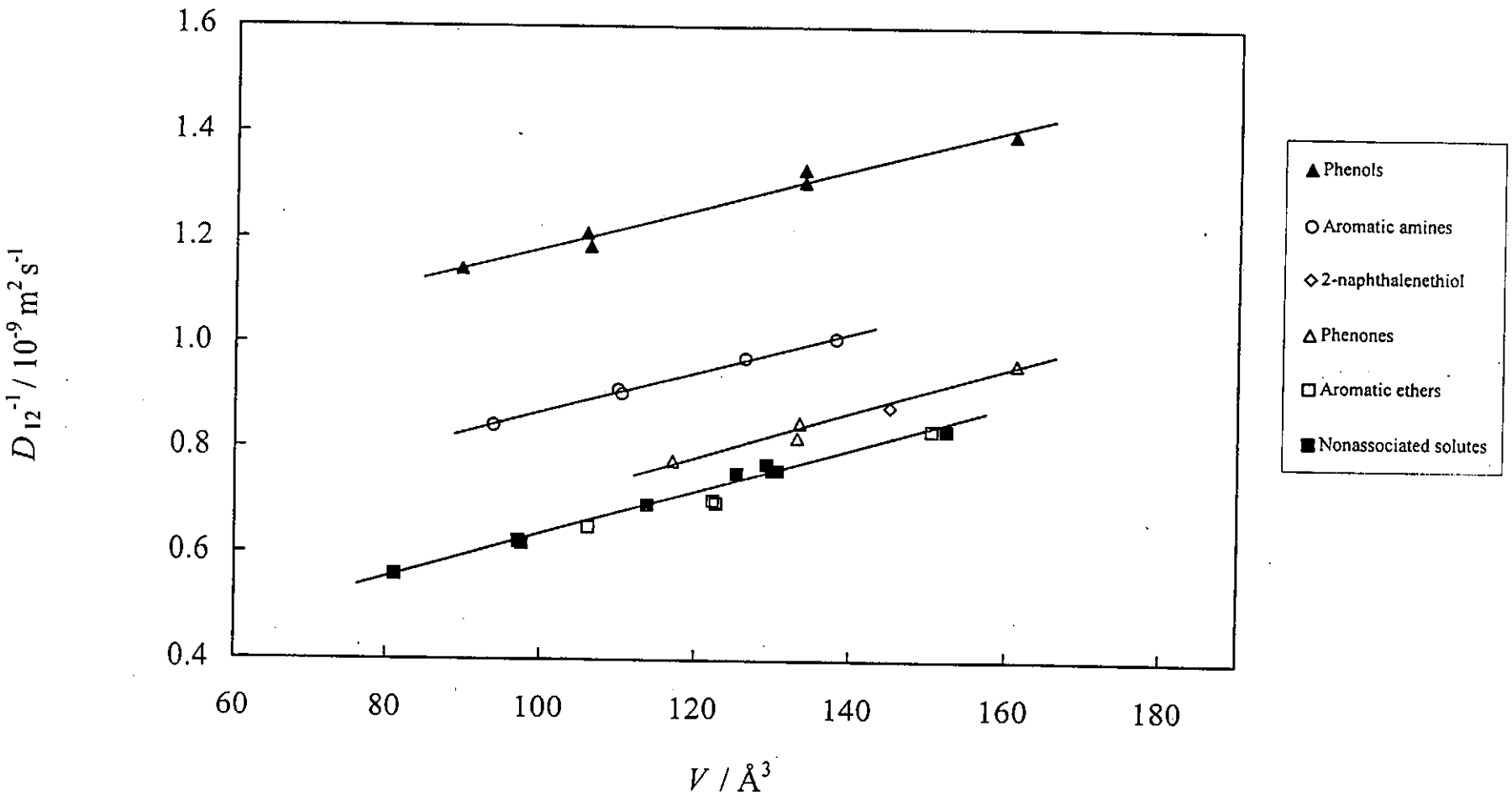

Fig. 9 Variation of $1/D_{12}$ with Molecular Volume of Polar Aromatic Solutes Diffusing in Ethanol at 298.2K

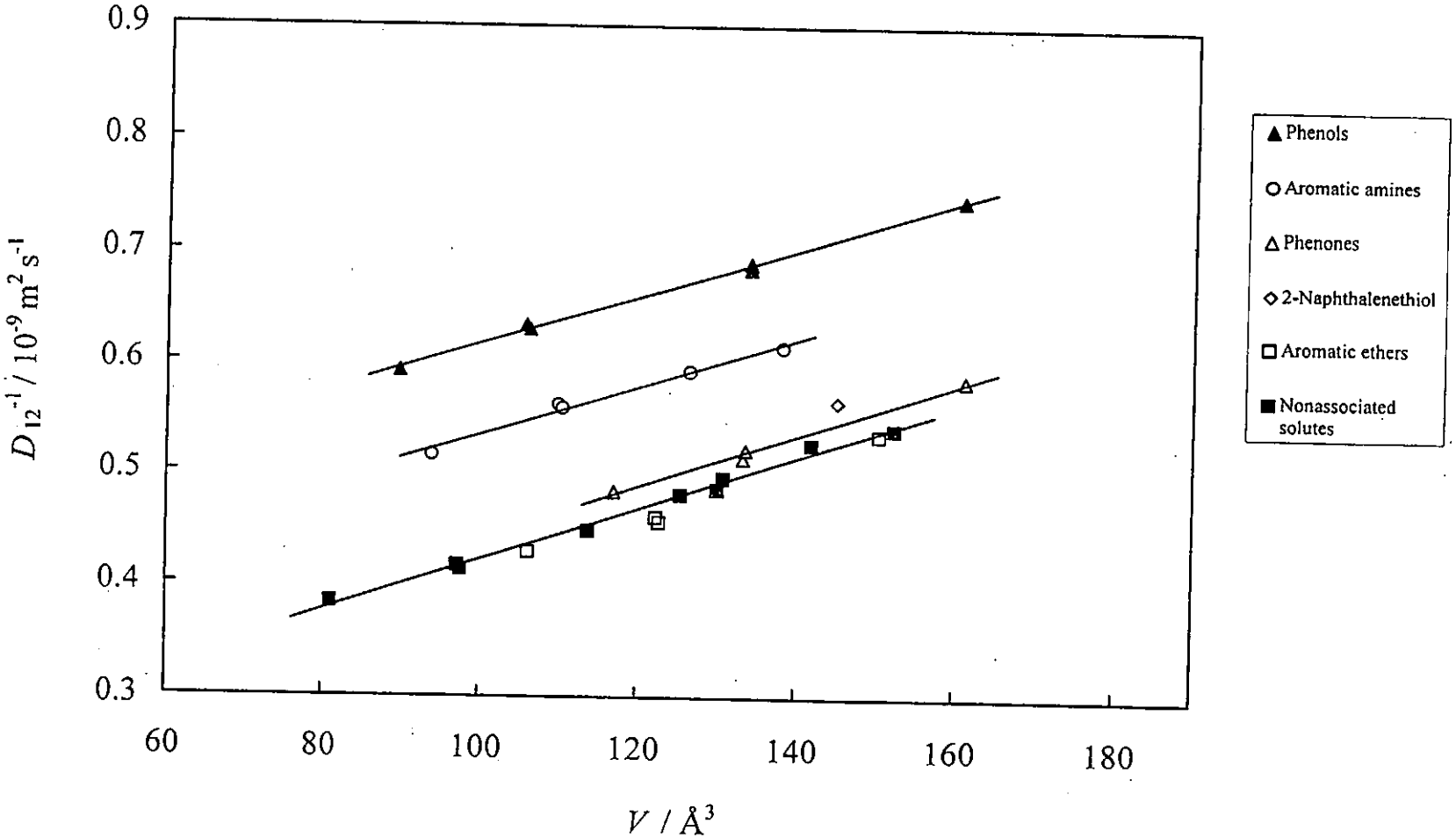

Fig. 10 Variation of $1/D_{12}$ with Molecular Volume of Polar Aromatic Solutes Diffusing in Methanol at 298.2K

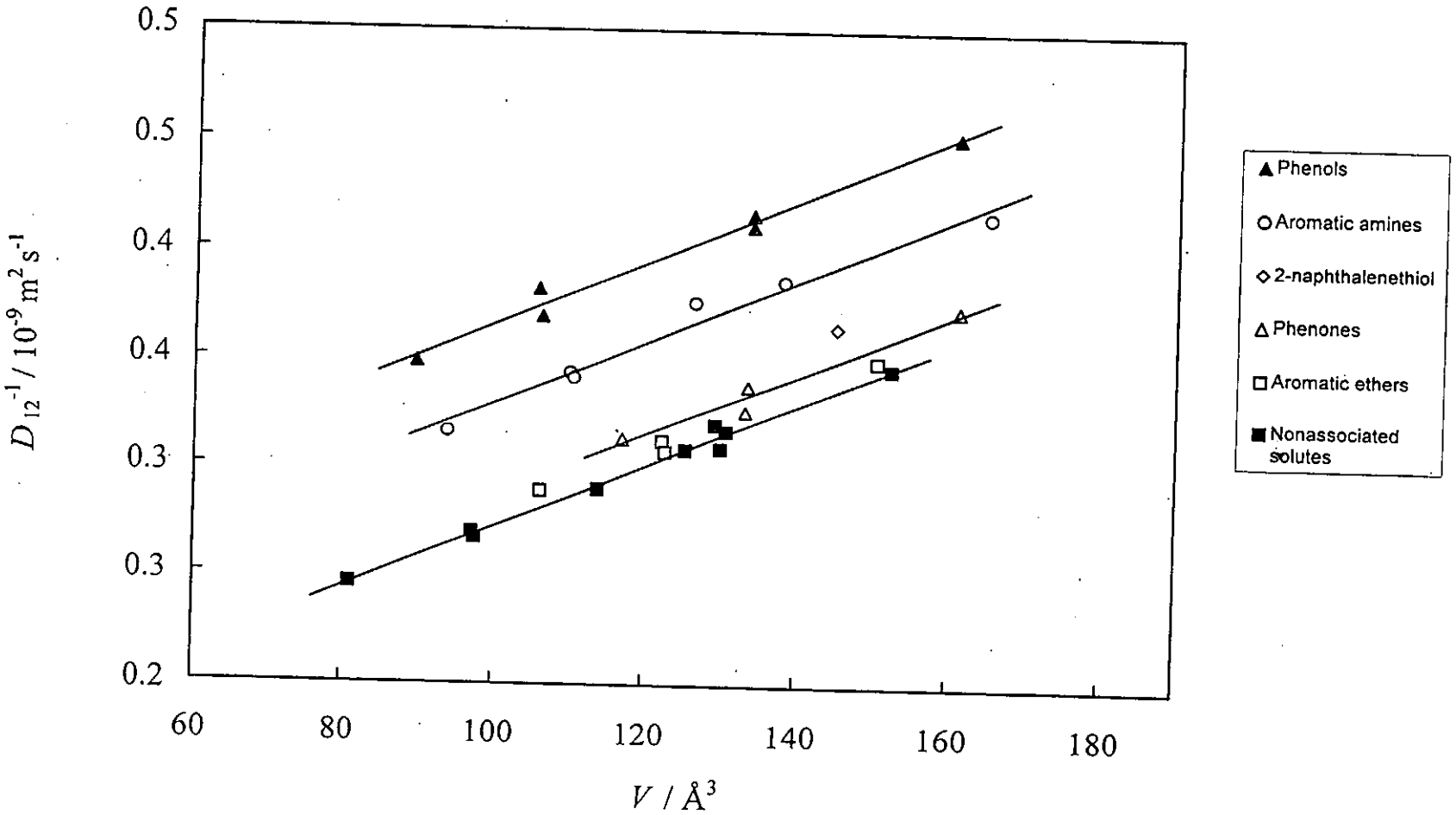

Fig. 11 Variation of $1/D_{12}$ with Molecular Volume of Polar Aromatic Solutes Diffusing in Acetone at 298.2K

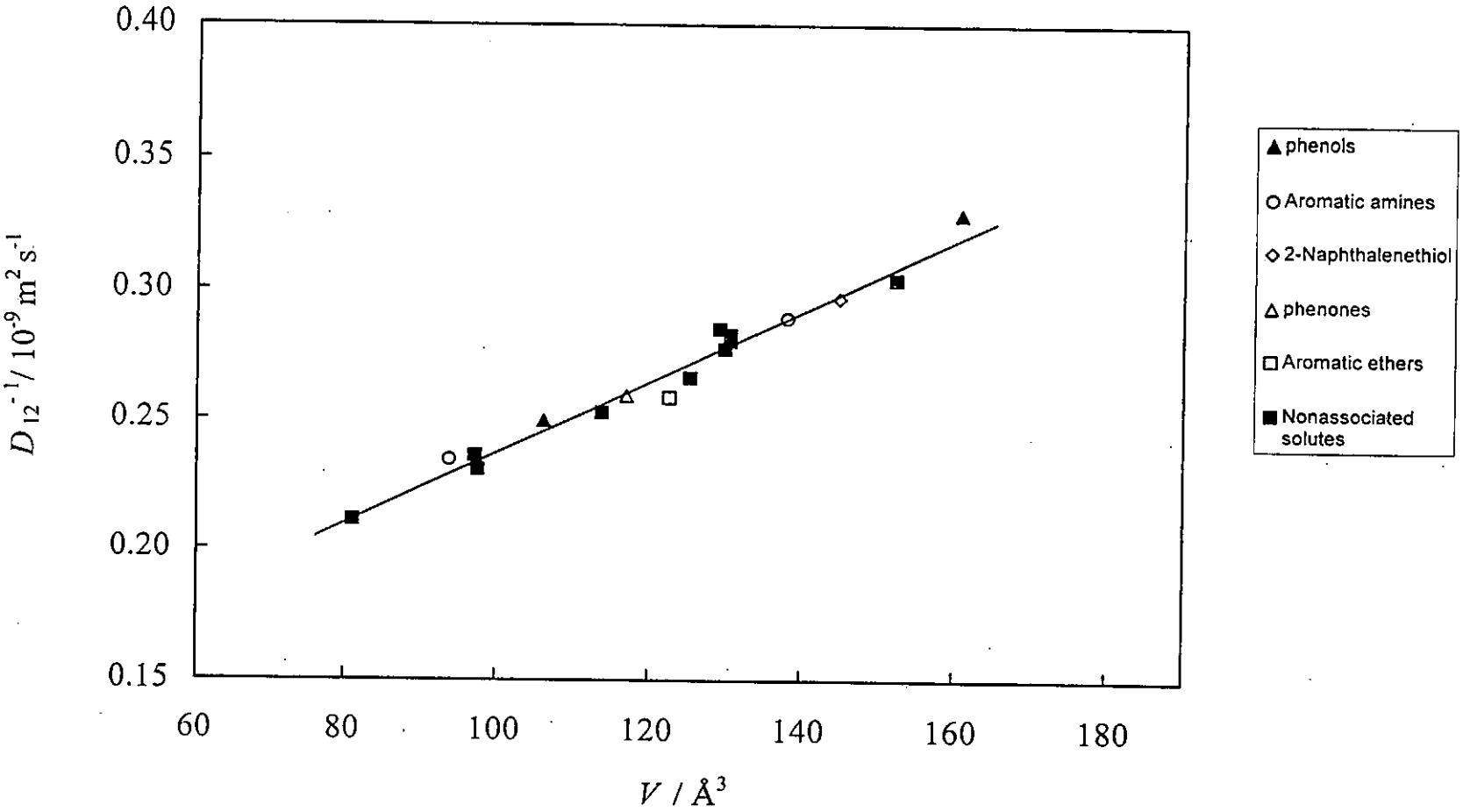

Fig. 12 Variation of $1/D_{12}$ with Molecular Volume of Polar Aromatic Solutes Diffusing in *n*-Hexane at 298.2K

Table 15 The percent deviation of polar aromatic solutes diffusing in ethanol, methanol, acetone and *n*-hexane at 298.2K from the 'nonassociated' line

	The percent deviation (%)			
	ethanol	methanol	acetone	*n*-hexane
Phenols				
Phenol	92.1	48.6	32.7	
p-Chlorophenol	83.4	45.4	34.3	
p-Cresol	78.9	44.1	31.0	1.6
1-Naphthol	68.4	37.0	28.1	
2-Naphthol	71.3	38.0	29.7	
Biphenyl-2-ol	57.3	32.8	25.8	2.7
Aromatic Amines				
Aniline	37.7	26.4	19.9	2.4
p-Chloroaniline	34.3	26.3	19.8	
p-Toluidine	32.7	25.3	18.7	
4-Chloro-2-methylaniline	30.3	22.6	20.6	
1-Naphthylamine	27.1	20.4	18.0	0.0
Aromatic Thiol				
2-Naphthalenethiol	6.6	7.5	8.7	0.6
Phenones				
Acetophenone	9.7	4.8	4.6	0.4
Propiophenone	6.0	2.9	1.8	
m-Methylacetophenone	9.4	4.4	4.7	
2-Acetylnaphthalene	8.1	3.9	3.3	

solutions are very dilute and the solvent ethanol is polar. In fact, experimental evidence has already shown that aniline molecules are not even self-associated in nonpolar *n*-tetradecane.[48] Similar results are observed in *n*-hexane in this work too. Fig. 12 shows the variation of $1/D_{12}$ with molecular volume of associated solutes diffusing in *n*-hexane at 298.2K. From Table 15, it can be seen that aniline deviates from the nonassociated line by only about 2.4%, which is close to the experimental error. In *n*-hexane, all other polar solutes studied do not indicate any solute-solute complex formation. Thus, the effect of solute-solute interactions on diffusion can be excluded in the more polar solvents in this study.

It is interesting that a linear relationship also exists between $1/D_{12}$ and V for all pseudoplanar solutes containing the same polar group. The regression lines for phenols, aromatic amines and phenones are also shown in Fig. 9. Remarkably, the slopes for all straight lines in the figure are nearly the same. From Fig. 9, it can be seen that aromatic ethers behave practically as nonassociated solute, and the strength of polar groups associated with the solvent through hydrogen bonding decreases in the sequence -OH > $-NH_2$ > -C(O)-.

The increase in size of polar solute after association can be evaluated from the deviation of its $1/D_{12}$ value from the 'nonassociated' line at the same monosubstituted solute volume in ethanol at 298.2K in Fig. 9. This is equivalent to the increase in the van der Waals volume that produces such amount of $1/D_{12}$ deviation on the 'nonassociated' line. The linear regression lines of solutes containing -OH, $-NH_2$ and -C(O)- groups are nearly parallel to that of the nonassociated solutes indicate that the

increased sizes are approximately equal for all solutes containing the same polar group. The average number of ethanol molecules associated with a solute can be determined subsequently from the solute volume increased and the van der Waals volume of the ethanol monomer. The solvation numbers thus calculated for phenols, aromatic amines, phenones and thiols in ethanol at 298.2K are given in Table 16. Table 16 also shows the solvation numbers calculated for phenols, aromatic amines, phenones and thiols in methanol and acetone at 298.2K. The uncertainty listed is the estimated error. From this table, it is clear that all phenols on the average diffuse together with about 2.5 ethanol molecules and all aromatic amines with about one. Phenones are nonetheless only weakly associated with ethanol. The fact that there is little association between phenones and ethanol is not surprising as the solutes have to compete with other ethanol molecules for forming hydrogen bonds with the solvent. Due to steric hindrance and lack of a proton contribution to form hydrogen bonds, phenones and aromatic ethers are expected to be less competitive in this respect. It should be noted that ethanol is self-associated with an association number of 2.8 in the liquid state at 298.2K.[69,70] Although solvation numbers can also be calculated[71] from the well known Stoke-Einstein equation, however, the applicability of this equation is not valid for non-spherical solute molecules and for solute molecules which are small in size compared to the solvent molecules.[5-8] The effects of shape on mutual diffusion have been shown[13] as large as 26% in the case of *n*-tetradecane as solvent at 298.2K.

It is also interesting to note that the solvation numbers as shown in Table 16 are insensitive to the mass as well as the size of the monomeric solutes studied. For

Table 16 Solvation numbers (n) for polar aromatic solutes diffusing in ethanol, methanol and acetone at 298.2K

		n		
		In ethanol	In methanol	In acetone
Phenols				
Phenol		2.6±0.2	2.4±0.2	1.0±0.1
p-Chlorophenol		2.6±0.2	2.5±0.2	1.1±0.1
p-Cresol		2.5±0.2	2.4±0.2	1.0±0.1
1-Naphthol		2.5±0.2	2.3±0.2	1.0±0.1
2-Naphthol		2.6±0.2	2.4±0.2	1.1±0.1
Biphenyl-2-ol		2.4±0.2	2.3±0.2	1.1±0.1
	Avg. =	2.5±0.2	2.4±0.2	1.1±0.1
Aromatic Amines				
Aniline		1.1±0.1	1.4±0.1	0.6±0.1
p-Chloroaniline		1.1±0.1	1.5±0.1	0.6±0.1
p-Toluidine		1.1±0.1	1.4±0.1	0.6±0.1
4-Chloro-2-methylaniline		1.1±0.1	1.4±0.1	0.7±0.1
1-Naphthylamine		1.0±0.1	1.3±0.1	0.7±0.1
	Avg. =	1.1±0.1	1.4±0.1	0.6±0.1
Aromatic Thiol				
2-Naphthalenethiol		0.3±0.1	0.5±0.1	0.3±0.1
Phenones				
Acetophenone		0.3±0.1	0.3±0.1	0.2±0.1
Propiophenone		0.2±0.1	0.2±0.1	0.1±0.1
m-Methylacetophenone		0.3±0.1	0.3±0.1	0.2±0.1
2-Acetylnaphthalene		0.3±0.1	0.3±0.1	0.1±0.1
	Avg. =	0.3±0.1	0.3±0.1	0.2±0.1

aromatic solutes containing one polar group in this study, the solvation numbers are dependent only on the type of polar group attached.

(C) The temperature dependence of diffusivity of aromatic solutes in ethanol

The reciprocal of diffusion coefficients for the polar aromatic pseudoplanar solutes diffusing in ethanol at 283.2K, 313.2K and 328.2K as shown in Tables 6, 8 and 9 was plotted against the van der Waals volume in Figs. 13 to 15. Also displayed in these figures are the 'nonassociated' lines for comparison. As shown in the figures, the trends of the data are similar to those at 298.2K, which have been already discussed in the previous section (see also Fig. 9). For example, linear relationships also exist between $1/D_{12}$ and V for all nonassociated aromatic pseudoplanar solutes and all pseudoplanar solutes containing the same polar group. The regression lines for phenols, aromatic amines and phenones are also displayed in Figs. 13 to 15. From these figures, one can see that the slopes for all straight lines in each figure are about the same, and the strength of polar group associated with ethanol solvent through hydrogen bonding is greater in the order of -OH > $-NH_2$ > -C(O)-. In addition, these figures have also shown that aromatic ethers behave practically as nonassociated solutes. These findings have further indicated that the effects of hydrogen bonding on diffusion are due mainly to the type of polar group attached. For solutes containing the same polar group, however, the effects are approximately equal. The solvation numbers for phenols, aromatic amines, phenones and 2-naphthalenethiol diffusing in ethanol at 283.2K, 313.2K and 328.2K, as determined by the method described in the previous section, are presented in Table 17. The uncertainty listed is the estimated error. From this table, it can be seen that all phenols on average diffuse consistently together with more ethanol molecules than aromatic amines. Aromatic amines associate with more ethanol molecules than phenones. Except for 2-naphthalenethiol,

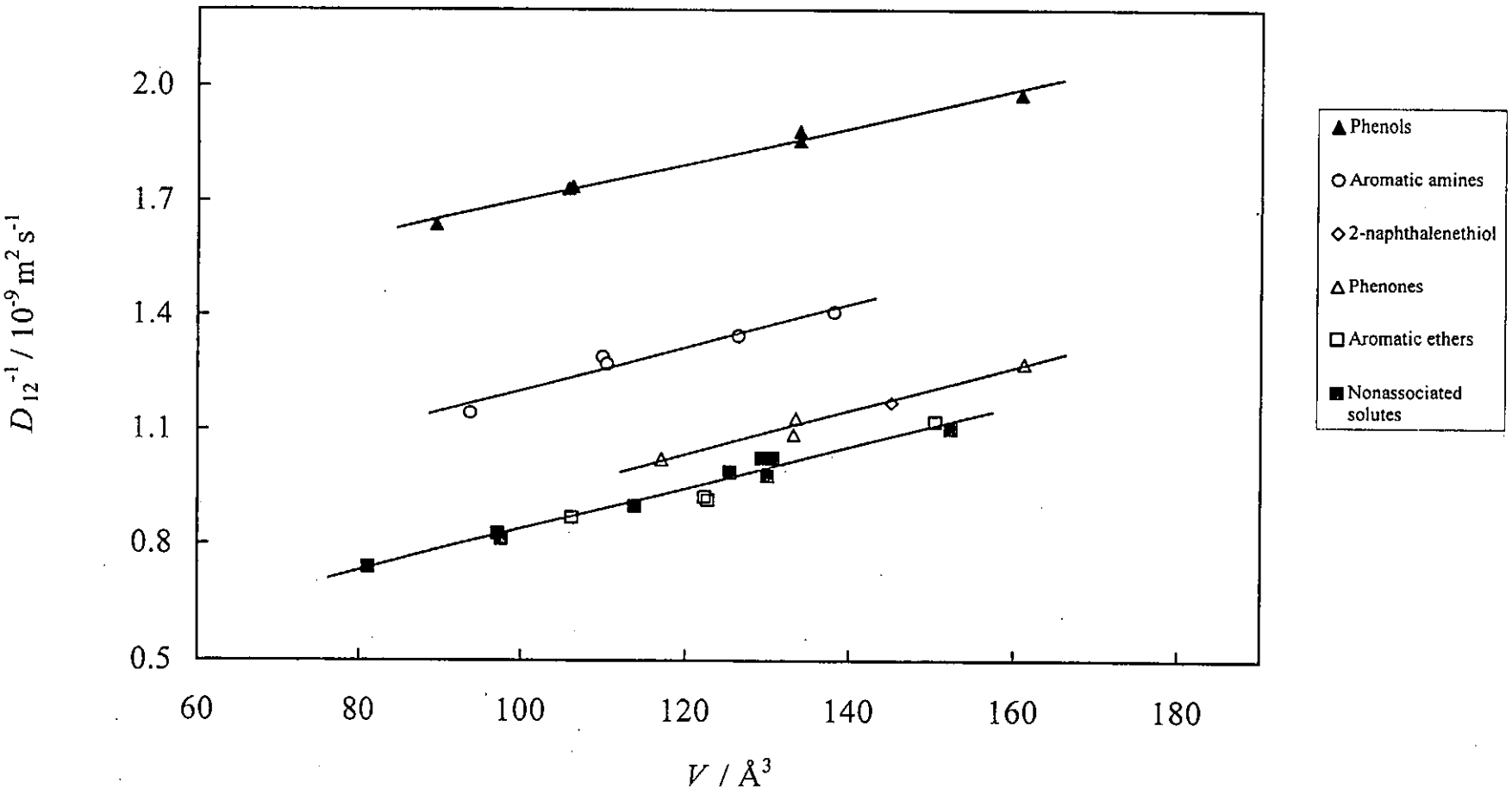

Fig. 13 Variation of $1/D_{12}$ with Molecular Volume of Polar Aromatic Solutes Diffusing in Ethanol at 283.2K

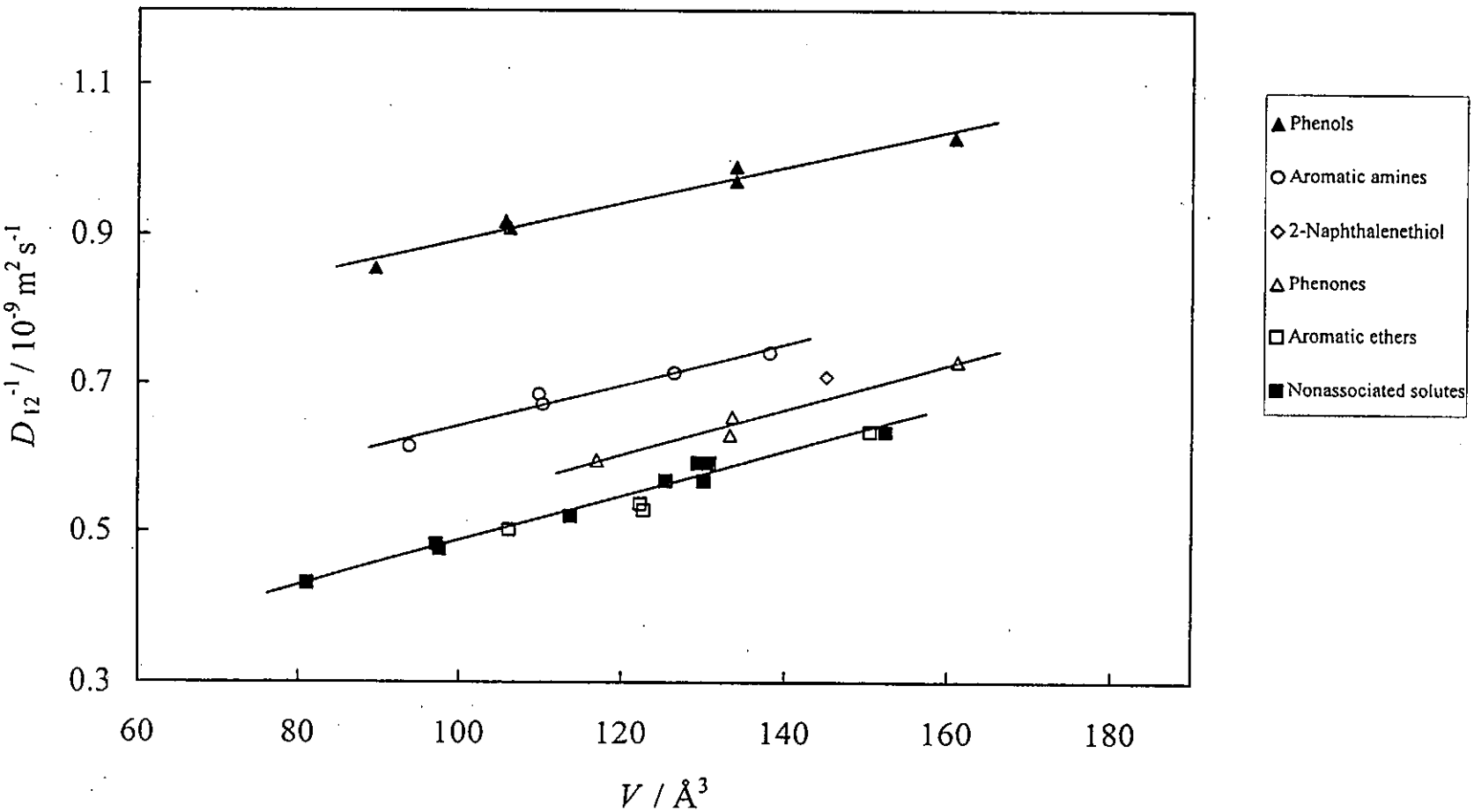

Fig. 14 Variation of $1/D_{12}$ with Molecular Volume of Polar Aromatic Solutes Diffusing in Ethanol at 313.2K

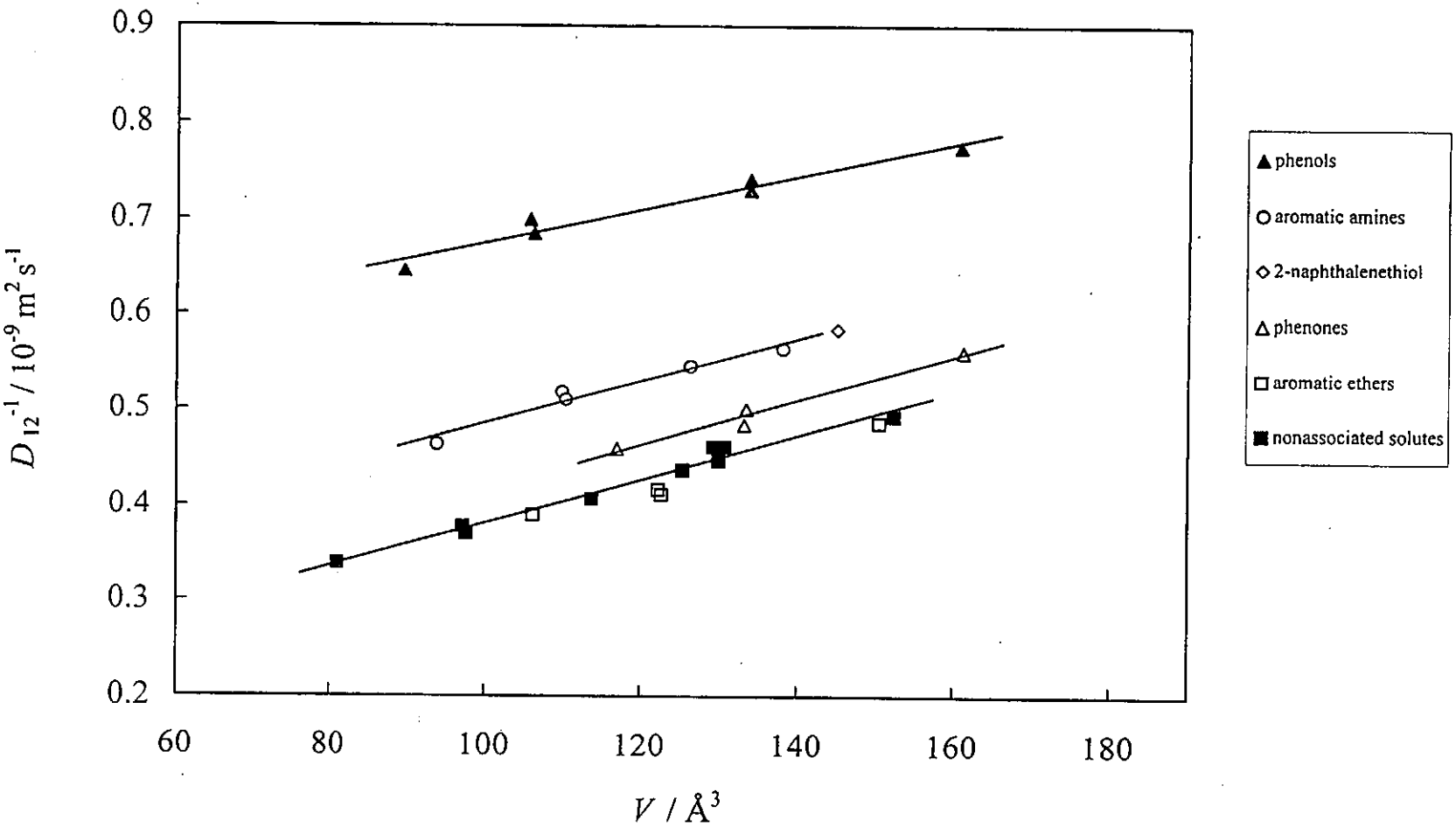

Fig. 15 Variation of $1/D_{12}$ with Molecular Volume of Polar Aromatic Solutes Diffusing in Ethanol at 328.2K

Table 17 Solvation numbers (n) for polar aromatic solutes diffusing in ethanol at different temperatures

		n		
		283.2K	313.2K	328.2K
Phenols				
Phenol		3.1±0.3	2.6±0.2	2.5±0.2
p-Chlorophenol		3.2±0.3	2.7±0.2	2.6±0.2
p-Cresol		3.2±0.3	2.7±0.2	2.5±0.2
1-Naphthol		3.1±0.3	2.5±0.2	2.3±0.2
2-Naphthol		3.2±0.3	2.7±0.2	2.4±0.2
Biphenyl-2-ol		3.0±0.3	2.4±0.2	2.2±0.2
	Avg.=	3.1±0.3	2.6±0.2	2.4±0.2
Aromatic Amines				
Aniline		1.2±0.1	1.0±0.1	0.8±0.1
p-Chloroaniline		1.5±0.1	1.1±0.1	1.0±0.1
p-Toluidine		1.4±0.1	1.0±0.1	0.9±0.1
4-Chloro-2-methylaniline		1.3±0.1	1.0±0.1	0.9±0.1
1-Naphthylamine		1.3±0.1	0.9±0.1	0.8±0.1
	Avg.=	1.3±0.1	1.0±0.1	0.9±0.1
Aromatic Thiol				
2-Naphthalenethiol		0.3±0.1	0.6±0.1	0.9±0.1
Phenones				
Acetophenone		0.3±0.1	0.4±0.1	0.3±0.1
Propiophenone		0.3±0.1	0.3±0.1	0.2±0.1
m-Methylacetophenone		0.4±0.1	0.4±0.1	0.4±0.1
2-Acetylnaphthalene		0.4±0.1	0.4±0.1	0.4±0.1
	Avg.=	0.4±0.1	0.4±0.1	0.3±0.3

the solvation number generally decreases as temperature increases. This is not surprising since when temperature gets higher, the molecules possess more kinetic energy; the association of solutes and solvent molecules therefore become weaker. It is of interest to note that when the natural logarithm of the average solvation number of each type of solutes is plotted against $1/T$ (see Fig. 16), a fairly linear relationship was also obtained.

In this study, all diffusion data have indicated that temperature affects the diffusivity, *i.e.*, the higher the temperature, the greater the diffusivity. For the temperature dependence of diffusivity, Ertl and Dullien have indicated[72] that at temperature well above the freezing point, the Arrhenius equation is quite suitable. The equation is

$$D = Ae^{-E_D/RT} \qquad (13)$$

where D is the diffusion coefficient, A is a constant, E_D is the activation energy, R is the gas constant and T is the absolute temperature. For a short temperature range, it can be assumed that the activation energy is independent of temperature, and eq. (13) becomes

$$\ln D = C - E_D / RT \qquad (14)$$

where C is a constant. The plots of natural logarithm of mutual diffusion coefficient ($\ln D_{12}$) *vs.* the reciprocal of absolute temperature ($1/T$) for the aromatic solutes studied, which included nonassociated compounds, phenols, aromatic amines, phenones, aromatic ethers and 2-naphthalenethiol are shown in Figs. 17 to 22. From these figures, it is clear that there exists a straight-line relationship between $\ln D_{12}$ *vs.* $1/T$ for all associated and nonassociated solutes studied. The data here thus obey the

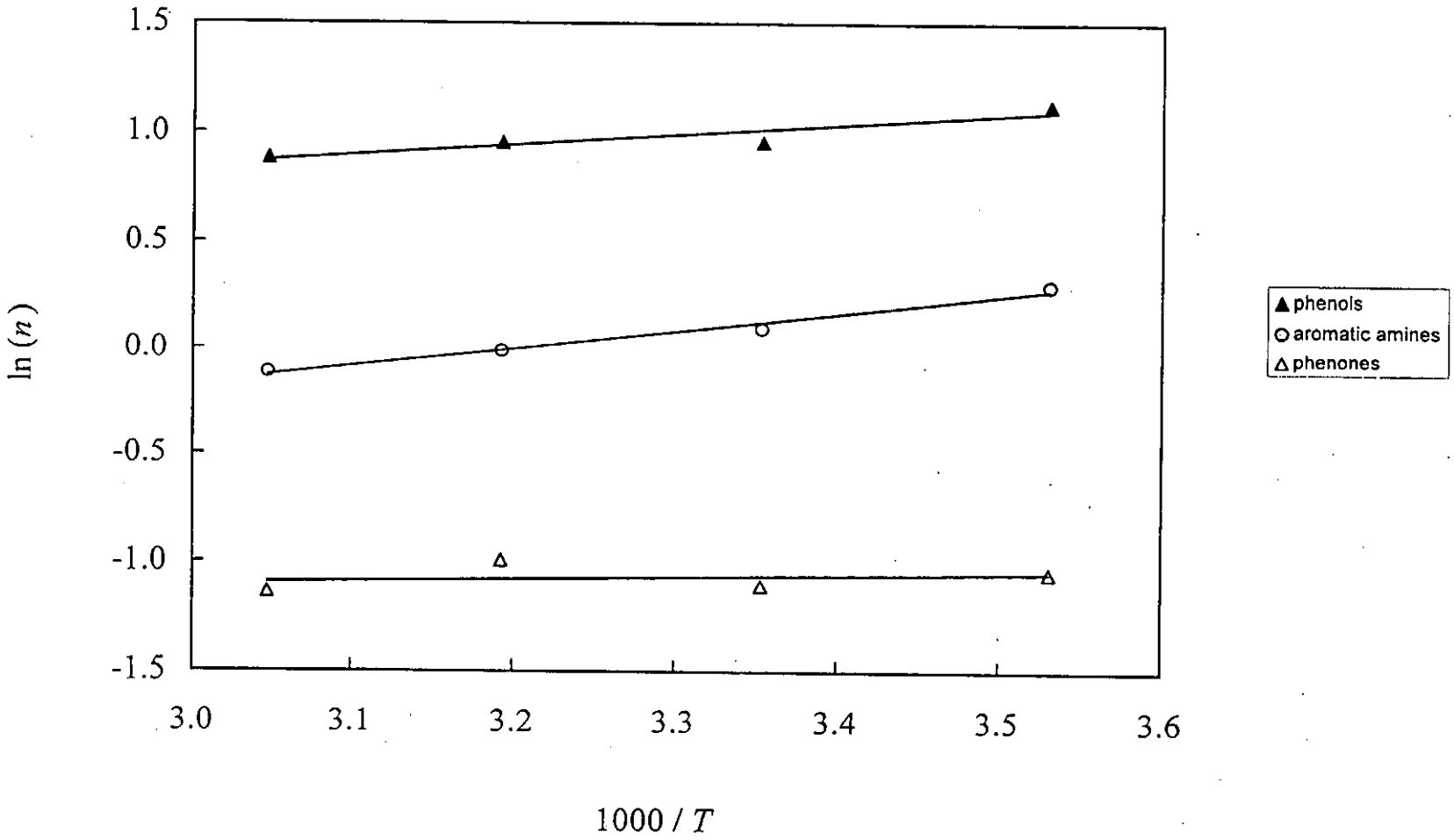

Fig. 16 . Plot of natural logarithm of the solvation number *vs* . 1/*T*

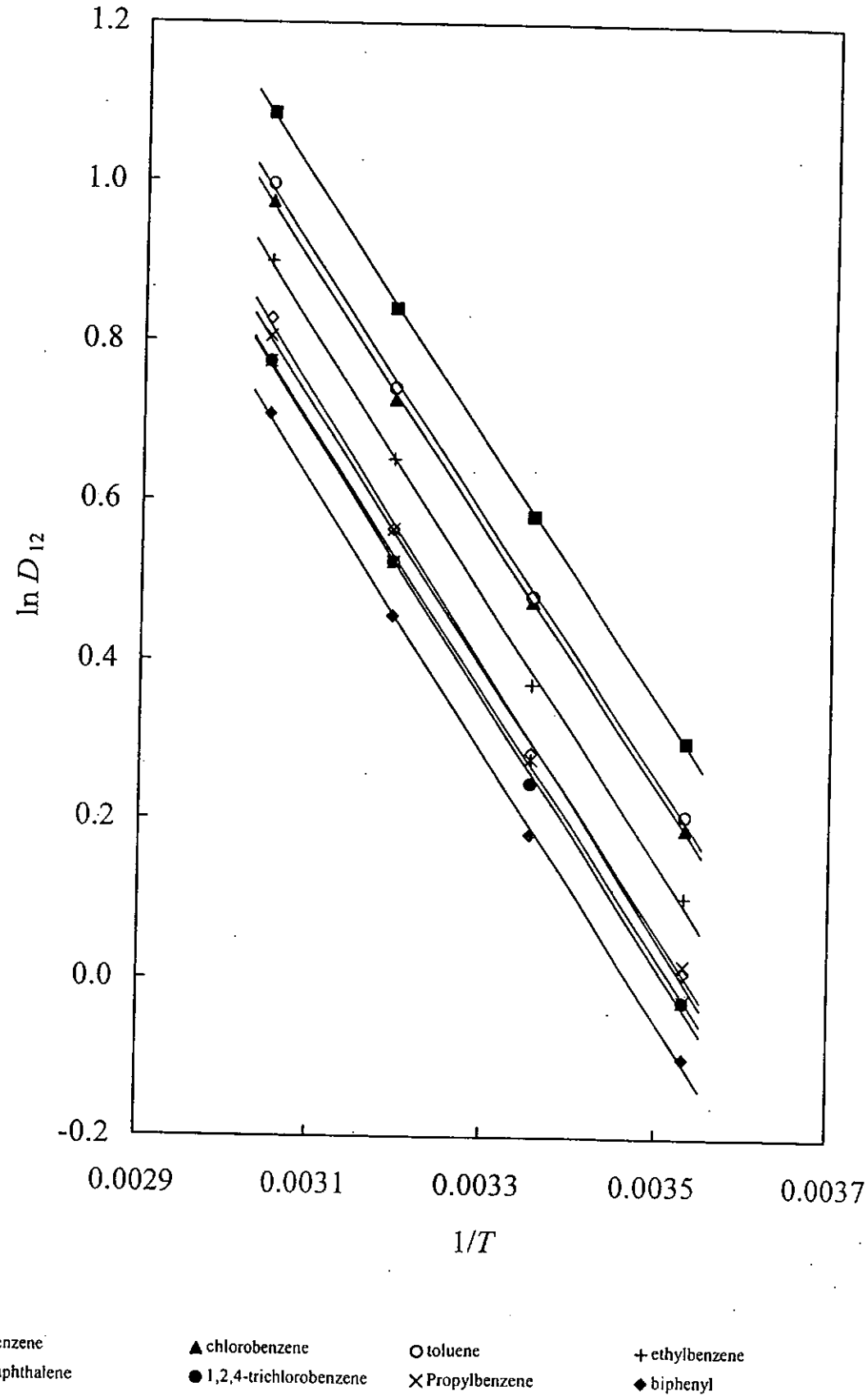

Fig. 17 Plot of ln D_{12} *vs.* $1/T$ for nonassociated solutes

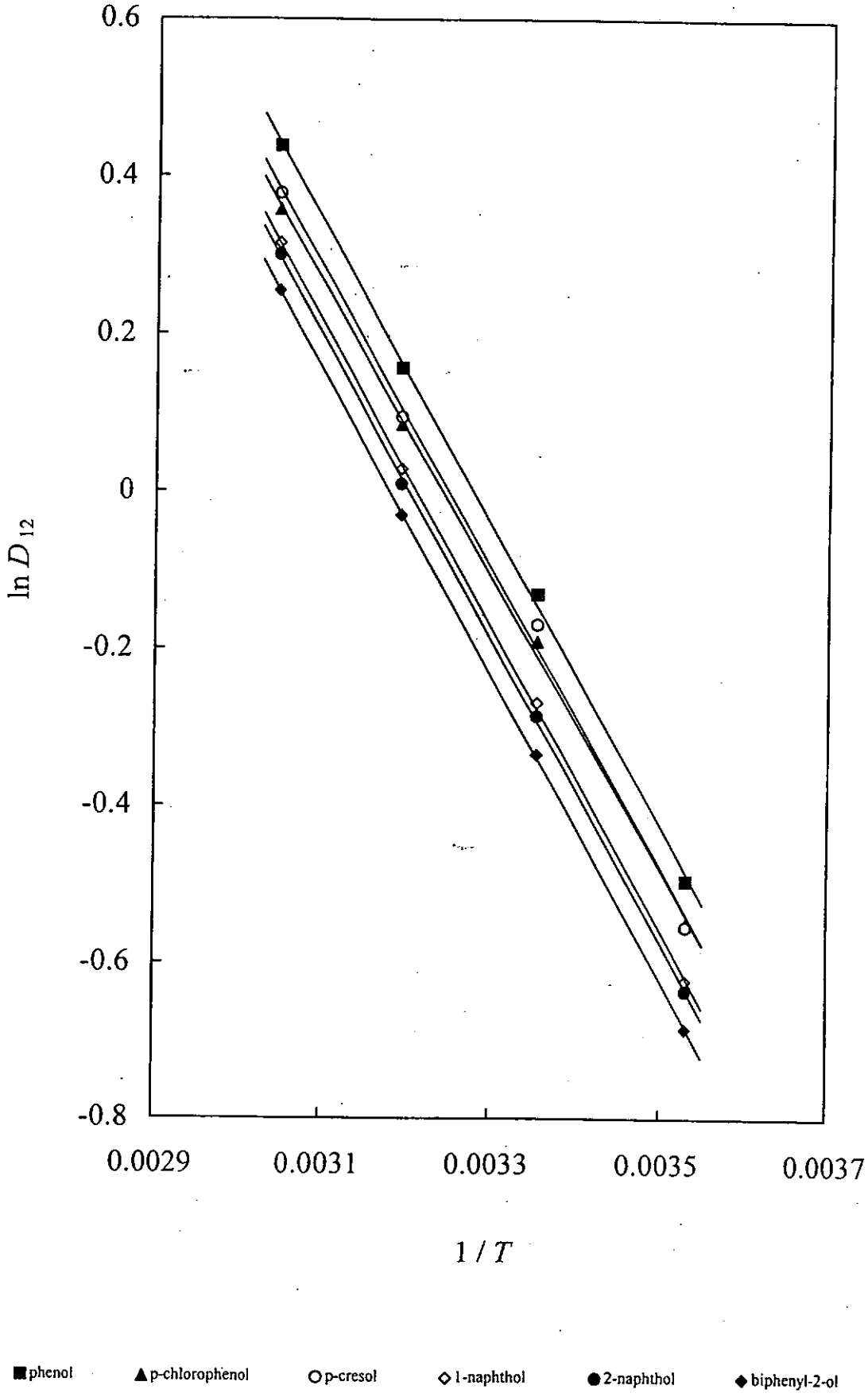

Fig. 18 Plot of ln D_{12} *vs*. $1/T$ for phenols

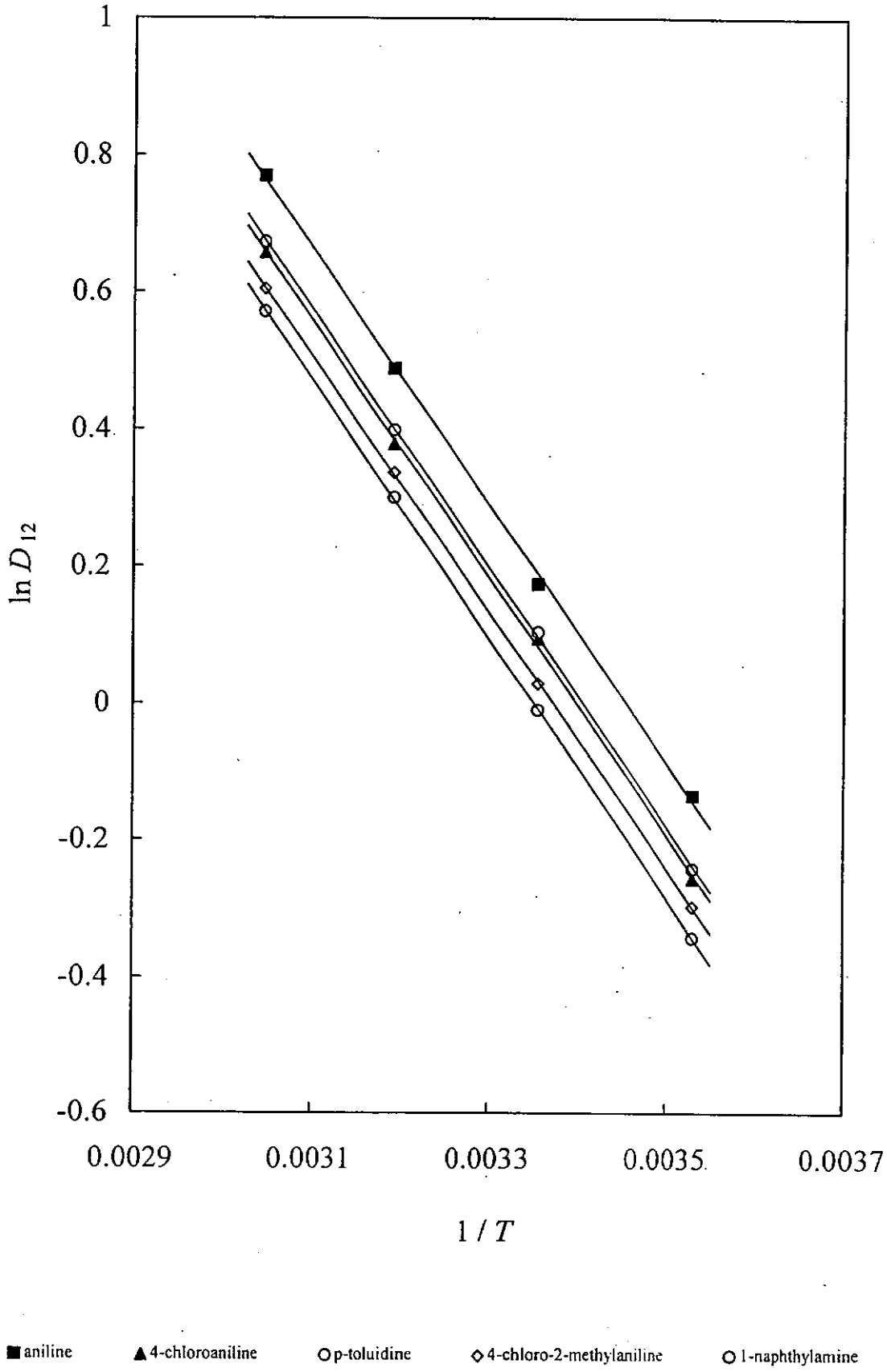

Fig. 19 Plot of ln D_{12} *vs*. $1/T$ for aromatic amines

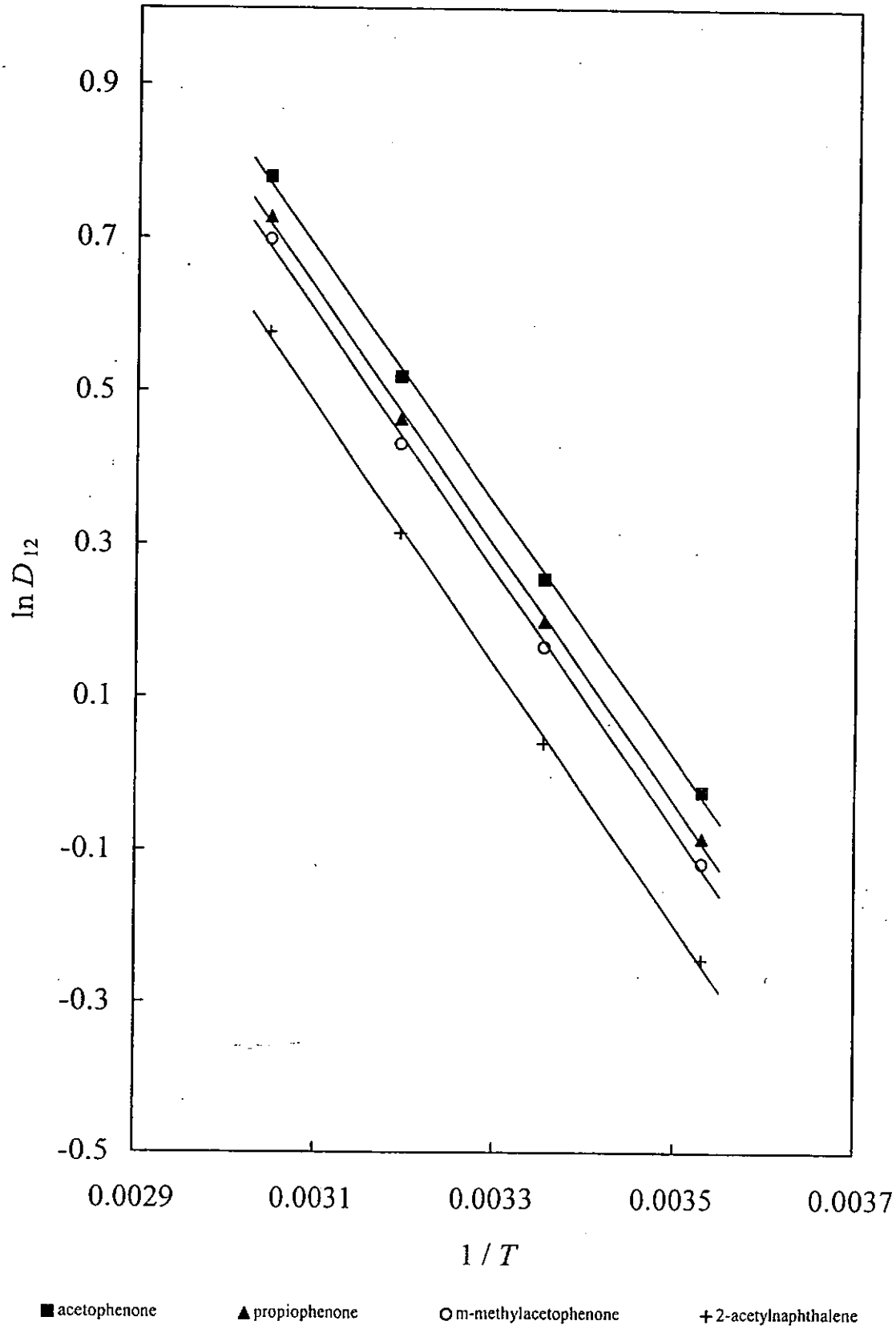

Fig. 20 Plot of ln D_{12} *vs*. $1/T$ for aromatic ethers

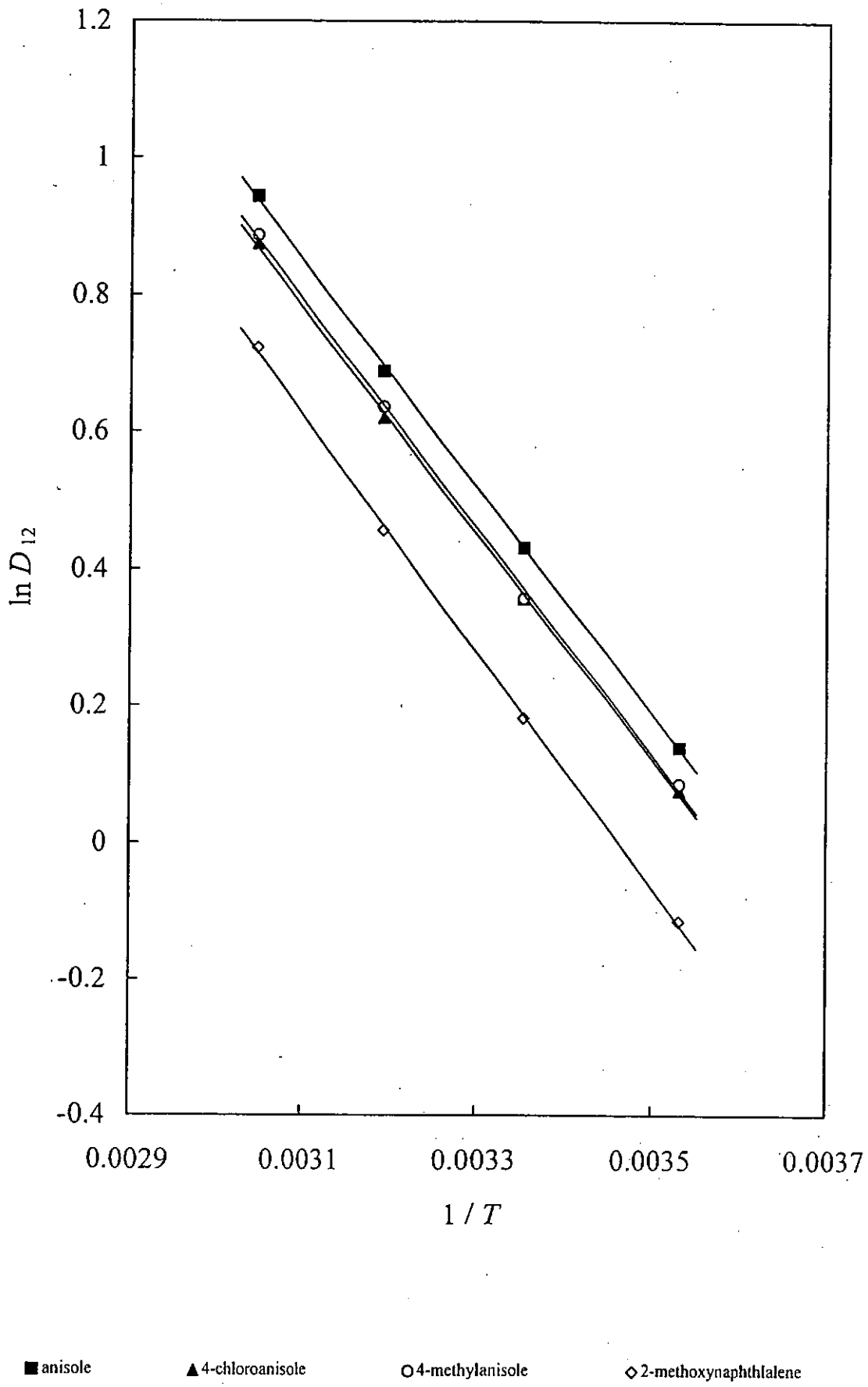

Fig. 21 Plot of ln D_{12} *vs* . $1/T$ for aromatic ethers

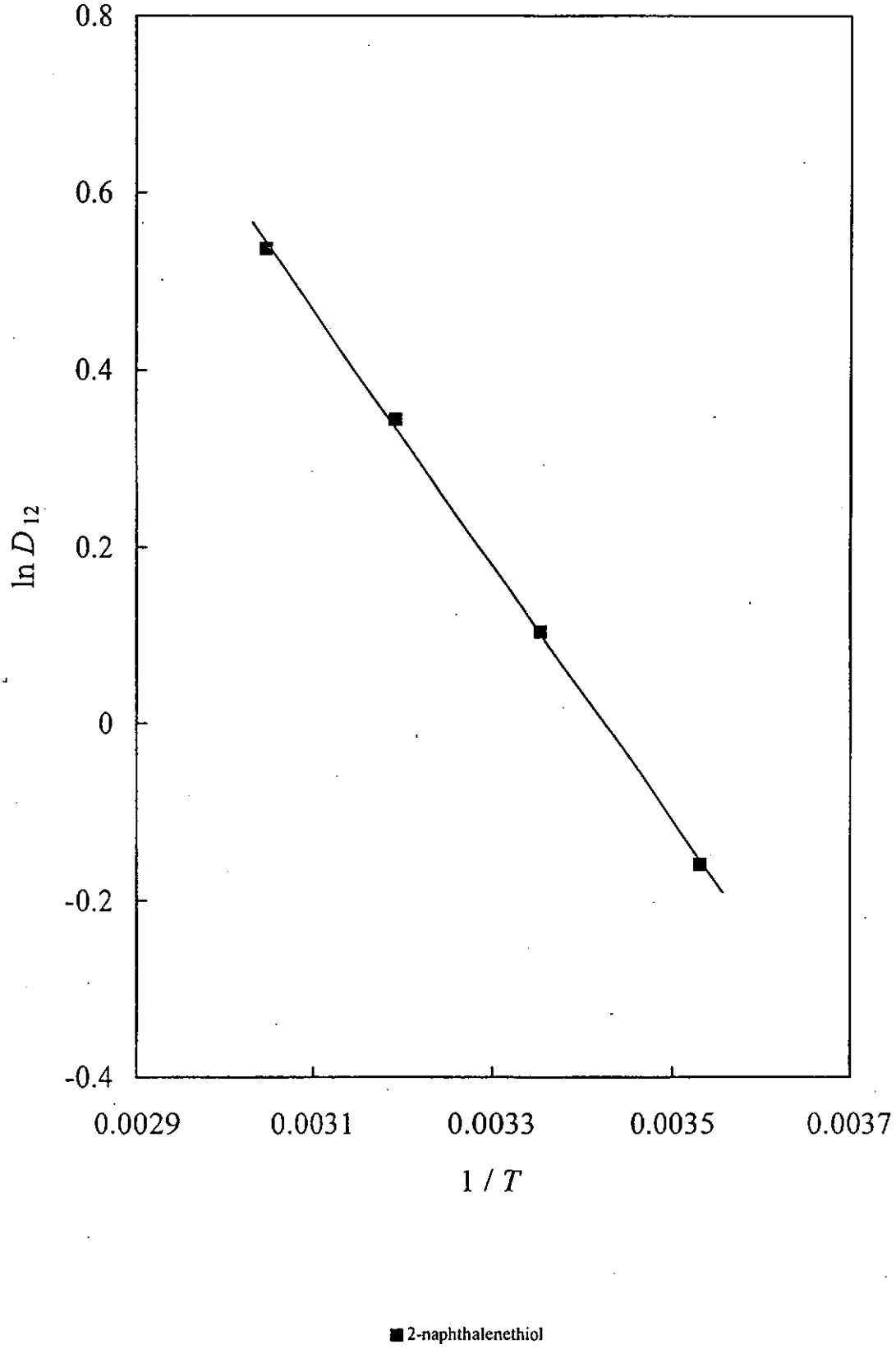

Fig. 22 Plot of ln D_{12} *vs*. $1/T$ for 2-naphthalenethiol

Arrhenius equation. From the Arrhenius-type relationship and the plots of ln D_{12} against $1/T$, the slope of each plot is the activation energy of the solute molecules divided by the gas constant, *i.e.*, $-E_D/R$. Thus, the activation energy of each solute molecule can be obtained by multiplying the gas constant to the slope of each plot. The so-called 'activation' energy, E_D, and the correlation coefficient of the least-squared straight line for each of the aromatic pseudoplanar solutes are presented in Table 18. All correlation coefficients indicate a very good linear relationship between ln D_{12} and $1/T$ for all solutes diffusing in ethanol. From Table 18, one can see that the activation energies of a given class of solutes are about the same. It is worthy to note that our calculated activation energy value for benzene is exactly the same as the previous result of Tominaga *et al.* [73] This lends confidence in our experimental results. The data also indicate that the activation energies are of the following order: phenols > aromatic amines > phenones > aromatic ethers > nonassociated solutes > 2-naphthalenethiol. This result thus suggested that the activation energy is dependent on the polar group attached for aromatic solutes diffusing in ethanol. It should be noted that 2-naphthalenethiol has the lowest activation energy. The reason of this anomalous result is still not clear.

Table 18 Activation energies (E_D) for aromatic solutes in this study

Solutes	Slope/10^3	E_D, kJmol^{-1}	Correlation Coefficients
Nonassociated			
Benzene	1.62	13.5	1.00
Chlorobenzene	1.63	13.6	1.00
Toluene	1.61	13.4	1.00
Ethylbenzene	1.65	13.7	0.999
Naphthalene	1.69	14.1	0.999
1,2,4-trichlorobenzene	1.66	13.8	1.00
Propylbenzene	1.64	13.6	0.999
Mesitylene	1.64	13.6	1.00
Biphenyl	1.67	13.9	1.00
		Avg.= 13.7±0.2	
Phenols			
Phenol	1.91	15.9	1.00
p-Chlorophenol	1.86	15.5	0.999
p-Cresol	1.9	15.8	0.999
1-Naphthol	1.93	16.0	1.00
2-Naphthol	1.92	16.0	1.00
Biphenyl-2-ol	1.93	16.0	1.00
		Avg.= 15.9±0.2	
Aromatic Amines			
Aniline	1.88	15.6	1.00
p-Chloroaniline	1.88	15.6	1.00
p-Toluidine	1.89	15.7	1.00
4-Chloro-2-methylaniline	1.87	15.5	1.00
1-Naphthylamine	1.89	15.7	1.00
		Avg.= 15.6±0.1	
Aromatic Thiol			
2-Naphthalenethiol	1.44	12.0	1.00
Phenones			
Acetophenone	1.65	13.7	1.00
Propiophenone	1.67	13.9	1.00
m-Methylacetophenone	1.68	14.0	0.999
2-Acetylnaphthalene	1.69	14.1	1.00
		Avg.= 13.9±0.1	
Aromatic Ethers			
Anisole	1.65	13.7	1.00
p-Chloroanisole	1.65	13.7	1.00
p-Methylanisole	1.66	13.8	1.00
2-Methoxynaphthalene	1.73	14.4	1.00
		Avg.= 13.9±0.2	

VII. CONCLUSION

We have demonstrated in this study that experimental measurements of diffusion coefficients can provide straightforward and useful information regarding the effects of solute-solvent interaction on diffusion. The findings of this project can be summarized as follows:

1. Our results have indicated that there exists a linear relationship between the reciprocal of the diffusion coefficient and van der Waals volume for both pseudoplanar nonassociated and associated solutes having the same polar group in ethanol, methanol and acetone at 298.2K. Similar results are also obtained in ethanol at other 283.2K, 313.2K and 328.2K.

2. The experimental data have shown that neither strong solute-solvent nor solute-solute interactions exist when monosubsitituted polar aromatic solutes diffuse in nonpolar *n*-hexane. This implies that the effects of hydrogen bonding on diffusion in more polar solvents systems studied here are due to solute-solvent interactions only. The data also confirm the previous finding that the mutual diffusion coefficients are approximately equal for solutes with the same size and shape regardless of the mass of solute, i.e., the mutual diffusion coefficients are generally insensitive to the molecular mass of the solutes.

3. It is found that the effects of solute-solvent association on diffusion are approximately equal for solutes containing the same polar group. The effects are

nonetheless different for different functional groups. Our present results indicate that the order of the effects are generally such that -OH > $-NH_2$ > SH > -C(O)-. However, aromatic ethers practically act like nonassociated solutes in all solvent systems studied. It is also found that for a given solute, the effects of hydrogen bonding are greater in alcohols than those in acetone. This is expected as -OH can form stronger hydrogen bonds than -C(O)-.

4. The solvation numbers which indicate the degree of molecular association have been determined for various solutes by comparing the diffusion coefficients of associated and nonassociated solutes. The trends of the solvation numbers are similar to those of the effects of hydrogen bonding on diffusion.

5. The temperature dependence of the diffusion coefficients indicated that the data obey the Arrhenius equation. The activation energies thus calculated from this equation are found to depend on the type of polar group attached in the aromatic solutes studied. The activation energies have the following order: phenols > aromatic amines > phenones > aromatic ethers > nonassociated solutes > 2-naphthalenethiol.

In this work, only solutes containing one polar group have been investigated. In the future, it would be of interest to find out the effects of molecular association on mutual diffusion for solutes capable of strong solute-solvent interactions at multi-sites. Finally, the possibility of enhancing diffusion theory by modifying the existing theories for nonassociated molecules to incorporate the effects of molecular association should be explored.

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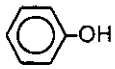
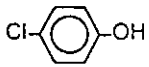
Appendix Structures of the Associated Aromatic Compounds Investigated

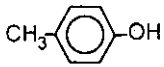
Phenols



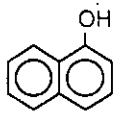
phenol



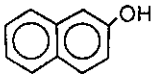
p-chlorophenol



p-cresol



1-naphthol



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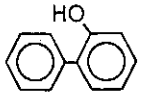
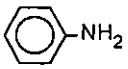
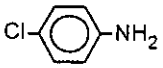


biphenyl-2-ol

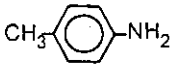
Aromatic amines



aniline



p-chloroaniline



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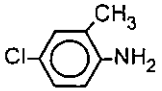
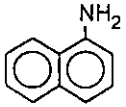
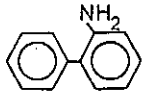


4-chloro-2-methylaniline

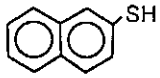


1-naphthylamine



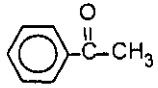
2-biphenylamine

Aromatic thiol

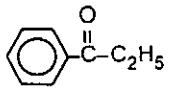


2-naphthalenethiol

Phenones



acetophenone



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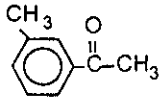
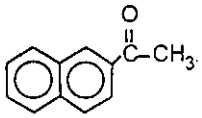
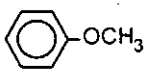


m-methylacetophenone

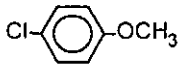


2-acetylnaphthalene

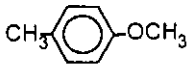
Aromatic ethers



anisole



p-chloroanisole



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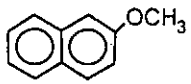

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