INEXPENSIVE AND SIMPLE BINARY MOLECULAR DIFFUSION EXPERIMENTS

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Three chemical engineering laboratory classes are taught at Tuskegee University: one for junior students and two for senior students. The Junior Unit Operations laboratory class consists mainly of fluid-mechanics and heat-transfer experiments. The Senior Unit Operations laboratory class consists mainly of mass-transfer, thermodynamics, and chemical-reaction experiments. The third laboratory consists of process-control experiments.

The senior laboratory course was designed for students to obtain experimental data by conducting various experiments through laboratory-scale unit operations, to statistically interpret these data, to write technical reports on the basis of statistical interpretations of experimental data, and to design a flow reactor, a distillation column, and a fluidized-bed decontamination vessel under the desired operating conditions. Final composite grades were based on laboratory reports, design reports, final examinations, and attendance.

We added a binary molecular diffusion experiment to the senior laboratory course to improve its course contents and to satisfy ABET 2000 criteria. The experiment was designed as an extension of the mass transfer course and the transport phenomena course (offered to seniors) and the engineering mathematics course (offered to juniors). Acetone and methylene chloride, in addition to n-heptane, were used for the diffusion experiment. The first choice for the diffusion experiment was n-heptane since it is almost odorless and is less toxic and stabler than the others. The objectives of this experiment were for our students to design and conduct the diffusion experiment, to analyze and interpret diffusion experimental data by applying knowledge of mathematics and science to diffusion experimental data, and to write laboratory reports with computer software.

Setup of an experimental apparatus is simple and inexpensive, since only an electronic balance and a test tube are needed as the major equipment. The binary molecular diffusion experiment provides an opportunity for students to apply mathematical and computational skills to analyzing statistically experimental data and to write a report using computer software. The experiment also familiarizes students with the concept of mass transfer, which they learned in the mass transfer and transport phenomena courses.

Binary diffusion coefficients of vapors of liquids diffused into stagnant air are determined at room temperature and atmospheric pressure. Experimental data on binary diffusion coefficients are obtained from the steady-state open-tube evaporation method modified for this study. Experimental binary diffusion coefficients are obtained by applying experimental data of mass loss of volatile liquids vs. evaporation duration to the developed diffusion equation. Predicted binary diffusion coefficients are calculated with the Wilke-Lee method and compared with experimental values obtained from this study.

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INTRODUCTION

Molecular mass transfer of toxic gases and vapors of industrial solvents into air are widely investigated in the study of air pollution control and environmental emissions of volatile vapors. Rates of absorption, adsorption, drying, distillation, and condensation occurring in various industrial processes (such as chemical, petroleum and gas industries) are dependent on diffusion of processed gaseous chemicals.[1] The extensive use of the term *diffusion* in the chemical engineering literature refers to the net transport of material within a single phase in the absence of mixing. Binary diffusion coefficients, a property of the binary system, are dependent on temperature, pressure, and the nature of the binary components. Both experiment and theory have shown that the driving forces of diffusion are pressure gradients, temperature gradients, and concentration gradients.[2] Diffusion coefficients of compounds used in industrial applications are important in understanding transport mechanisms in industrial processes.[3]

Many experimental methods[1,4,5] have been employed in determining binary diffusion coefficients of both gases and vapors. The following experimental methods have been used frequently.

Binary diffusion coefficients of the vapor of a volatile liquid diffused into air are most conveniently determined by the open-tube evaporation method.[6] In this method, a volatile liquid is partially contained in a narrow-diameter vertical tube, is maintained at a constant temperature, and an air stream is passed over the top of the tube.[4] This method is widely used to determine binary diffusion coefficients of vapors of various liquids dispersed into a stagnant gas, which fills the rest of the tube. The diffusion coefficient is determined from experimental data of slow losses of the liquid in the tube at a constant temperature and pressure. The mass transfer takes place from the surface of a liquid by molecular diffusion alone[7] at constant temperature and pressure. Slow losses of a liquid by evaporation are obtained by the change in the tube's liquid level.[7]

Determination of diffusion coefficients by the closed-tube method is usually quite reliable. The essential characteristic is a variation of mixture composition with time and position throughout a long tube closed at both ends. The gases of the mixture are initially separated in the closed tube, then are interdiffused at constant temperature and pressure.[5] The diffusion time is controlled by an opening mechanism in the middle of the tube.

In the two-bulb method, the apparatus consists of two glass bulbs with volumes V_1 and V_2 connected by a capillary of cross-sectional area A and length L whose volume is small compared to V_1 and V_2. Pure gas A is added to V_1 and pure gas B to V_2 at the same pressures. The valve is opened, diffusion proceeds for the given time, and then the valve is closed and the mixed contents of each chamber are sampled separately.[8]

Gas chromatography[3,9] is a method in which a trace amount of gas is injected as a pulse in a carrier gas flowing through a long hollow tube. The combined action of molecular diffusion and the parabolic velocity profile of the carrier gas causes the dispersion of the pulse. As the pulse emerges from the tube outlet, measurements of the dispersion lead to values of D_{AB}.

In the interferometric method, a barrier separates the liquid from the gas prior to diffusion. At the instant of removing the barrier, unsteady-state evaporation begins in an open cylinder. Shifts of interference bands with time are photographed with a high-speed camera and a neon lamp. The main advantage of this method is that it eliminates the need to measure the rates of mass transfer. The main limitation is caused by the diffusion cell, which allows one to measure binary diffusion coefficients of vapors of volatile liquids diffused only into air at atmospheric pressure and room temperature.[1]

The point-source method[5] was developed especially for determining diffusion coefficients at high temperatures. A trace amount of gas is introduced through a fine hypodermic tube into a carrier gas flowing in the same direction. The tracer spreads by diffusion through the carrier gas, which has characteristics of steady-state laminar flow with a flat velocity profile. The mixture composition is measured by means of a sample probe located at various distances downstream from the inlet. Electrical heat allows the temperature to increase to 1200 K.

The methods mentioned above have served as experimental methods for scientists to obtain binary diffusion coefficients of volatile liquids into air for many years. A novel experimental method and a newly developed diffusion equation suitable for this method are presented in this paper.

It is difficult to recognize the change in the liquid level in the tube in the conventional evaporation method for short evaporation duration. A novel open-tube evaporation method was developed to overcome the limitation of the conventional open-tube evaporation method. The method is used for this study to determine experimentally binary diffusion coefficients of the vapor of a volatile liquid diffused into air. Experimental diffusion coefficients of the vapor of the liquid into air in this study, however, are obtained from experimental data of loss amounts of the liquid due to its evaporation vs. evaporation durations rather than changes in the liquid level in a tube vs. evaporation durations without passing air over the top end of a diffusion path.

Surprisingly, this method has proven to be not only reliable and accurate, but also convenient for this diffusion study. Nonetheless, the method is restricted to narrow ranges of temperatures and is strongly dependent on the volatility of the substance being tested.[5]

THEORY

Diffusion coefficients of a vapor can be experimentally measured in a tube. The tube is partially filled with a volatile liquid A at a constant temperature and atmospheric pressure. The inside and the outside of the tube, partially filled with the volatile liquid A, is surrounded with a gas B having a negligible solubility in the liquid A. The component A vaporizes and diffuses through the stagnant gas phase B in the diffusion path of the tube. The vaporization rate of the liquid A is described in the following equation, based on Fick's first law in which diffusion of A through stagnant or non-diffusing B occurs at steady state.[10]

$$N_{Az} = \frac{PD_{AB}}{RT} \ln\left(\frac{1}{1-y_{Ao}}\right) \quad (1)$$

A pseudo-steady-state diffusion of the component A through the stagnant gas B is assumed, since the length of the diffusion path does not change significantly over a short period of time. The molar flux of the component A, N_{Az} is also described in terms of the amount of the liquid component A vaporized, as shown in

$$N_{Az} = \frac{\rho_A}{M_A} \frac{dz}{dt} \quad (2)$$

Substituting Eq. (1) into Eq. (2) and integrating the combined equation produces

$$t = \frac{\rho_A RT}{2PD_{AB}M_A \ln\left(1/(1-y_{Ao})\right)}\left(z^2 - z_o^2\right) \quad (3)$$

The amount of the liquid component A vaporized for the vaporization duration t is obtained from (see Figure 1)

$$z = z_o + \frac{(m_o - m)}{S\rho_A} \quad (4)$$
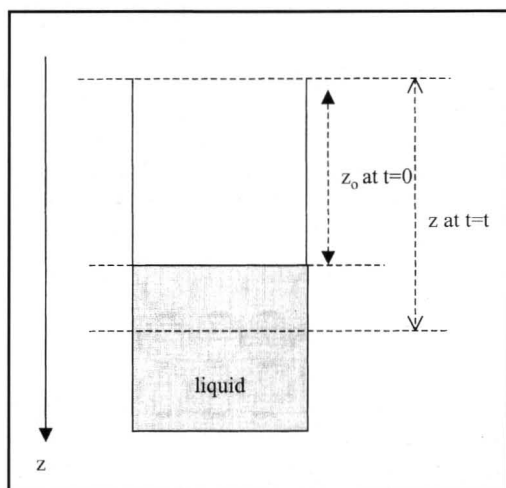
Substituting Eq. (4) into Eq. (3) produces

Figure 1. Diffusion tube with moving liquid level.

$$t = \frac{\rho_A RT}{2PD_{AB}M_A \ln\left(1/(1-y_{Ao})\right)}\left(\frac{m_o - m}{S\rho_A}\right)\left(2z_o + \frac{m_o - m}{S\rho_A}\right) \quad (5)$$

To predict diffusion coefficients of both gases and vapors of volatile liquids, several models[11-13] were developed. The Wilke-Lee method[14] (see Eq. 6) is chosen to predict diffusion coefficients of the chosen binary systems in this study. This method is exclusively recommended for mixtures of nonpolar gases or polar gas with a nonpolar gas.

$$D_{AB} = \frac{10^{-4}\left(1.084 - 0.249\sqrt{\frac{1}{M_A} + \frac{1}{M_B}}\right)T^{\frac{3}{2}}\sqrt{\frac{1}{M_A} + \frac{1}{M_B}}}{P(r_{AB})^2 f\left(\frac{kT}{\varepsilon_{AB}}\right)}$$

$$(6)$$

EXPERIMENTAL PROCEDURE

The setup of the novel diffusion experiment is simple and inexpensive since most laboratories already have the equipment necessary for diffusion experimentation. An air circulation system is not required with the novel open-tube diffusion experiment. Numerous diffusion data can be continuously obtained for the 3-hour laboratory class. The experimental setup (see Figure 2) consists of a test tube, a balance,[15] a caliper, and a thermometer.

The tube is partially filled with a volatile liquid. The initial length of the diffusion path (the initial distance between the top end of the tube and the liquid level in the tube) is measured. The top window of the balance remains open for the natural convection of air without passing air over the balance. The tube, partially filled with a known amount of the
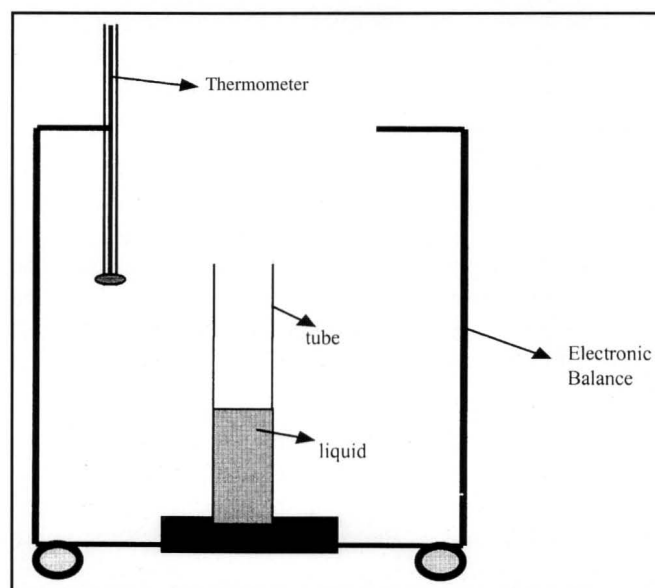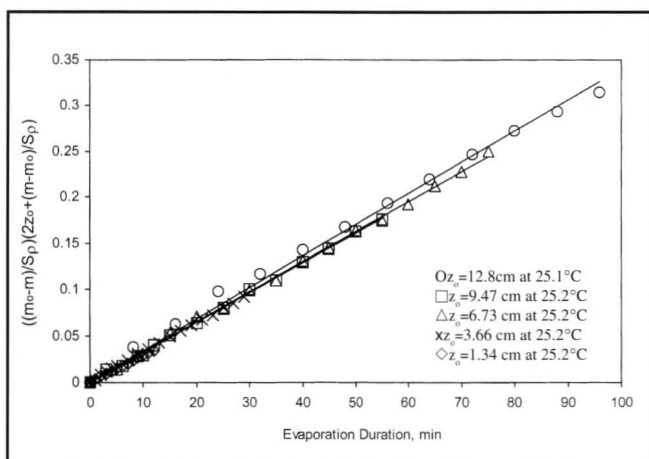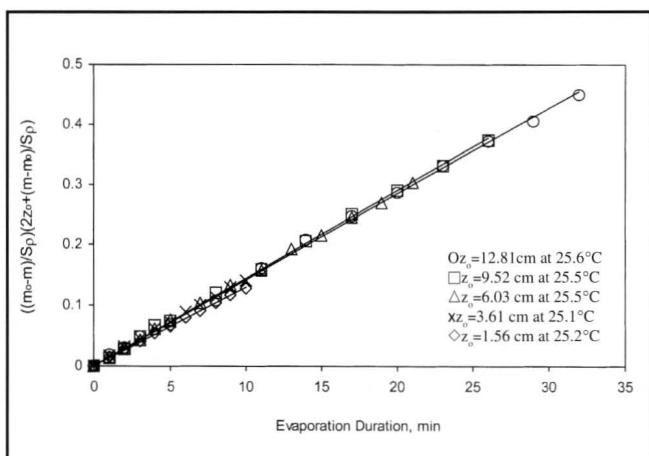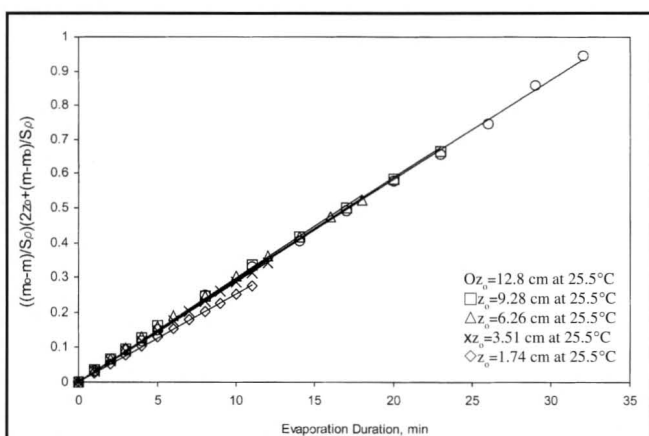

Figure 2. Schematic diagram of an experimental setup.

Figure 3. *Loss amounts of liquid n-heptane due to evaporation into air at various evaporation durations and various initial lengths of diffusion path (z_o) under atmospheric pressure.*

Legend in figure:
Oz_o=12.8cm at 25.1°C
$\Box z_o$=9.47 cm at 25.2°C
$\triangle z_o$=6.73 cm at 25.2°C
xz_o=3.66 cm at 25.2°C
$\diamond z_o$=1.34 cm at 25.2°C

Figure 4. *Loss amounts of liquid acetone due to evaporation into air at various evaporation durations and various initial lengths of diffusion path (z_o) under atmospheric pressure.*

Legend in figure:
Oz_o=12.81cm at 25.6°C
$\Box z_o$=9.52 cm at 25.5°C
$\triangle z_o$=6.03 cm at 25.5°C
xz_o=3.61 cm at 25.1°C
$\diamond z_o$=1.56 cm at 25.2°C

Figure 5. *Loss amounts of liquid methylene chloride due to evaporation into air at various evaporation durations and various initial lengths of diffusion path (z_o) under atmospheric pressure.*

Legend in figure:
Oz_o=12.8 cm at 25.5°C
$\Box z_o$=9.28 cm at 25.5°C
$\triangle z_o$=6.26 cm at 25.5°C
xz_o=3.51 cm at 25.5°C
$\diamond z_o$=1.74 cm at 25.5°C

liquid to a known initial level in the tube, is placed on the balance. The balance is reset and a stopwatch is started after the inside wall of the tube is dried for approximately 5 minutes. The temperature and the pressure are recorded. Loss amounts of the liquid due to its evaporation are recorded at random time intervals for 10 to 100 minutes.

CALCULATIONS

Equation 5 is rearranged to obtain Eq. (7) with evaporation durations as an independent variable and left-side values of Eq. (7) containing loss amounts of a volatile liquid as a dependent variable.

$$\left(\frac{m_o-m}{S\rho_A}\right)\left(2z_o+\frac{m_o-m}{S\rho_A}\right)=\frac{2PD_{AB}M_A\ln\left(\frac{1}{(1-y_{Ao})}\right)}{\rho_A RT}t \quad (7)$$

Loss amounts of a liquid due to its evaporation are recorded at random evaporation durations. These experimental data are applied to Eq. (7) to obtain the value of a slope through the linear least squares method, as shown in Figures 3 through 5 and Figure 7. Binary diffusion coefficient values can be calculated from slope values obtained through the linear least squares method. The density ρ_A and the molecular weight M_A[16] and the mole fraction y_{Ao} of the component A at the liquid surface of the component A in a tube are also used in calculating binary diffusion coefficient values. The vapor pressure of the component A is obtained from the Antonie equation[17,18] to calculate the mole fraction y_{Ao} of the component A at the liquid surface of the component A in a tube. Predicted diffusion coefficients for vapors of volatile liquids in air are calculated with Eq. (6) and compared with experimental diffusion values obtained from this study, as shown in Table 1.

RESULTS AND DISCUSSION

The main purposes of this diffusion experiment are to obtain diffusion values of vapors into air with the novel open-tube evaporation method and the diffusion equation, to compare diffusion values from this experimental method with those predicted from the theoretical diffusion model, and to find diffusion values independent of diffusion-path length and diffusion area. The outcomes of this experiment are for our students to be able to design and conduct the diffusion experiment, to analyze and interpret diffusion experimental data by applying their knowledge of mathematics and science, and to write laboratory reports with computer software.

Experimental and predicted binary diffusion coefficients of n-heptane, acetone, and methylene chloride at atmospheric pressure are shown in Table 1. Experimental binary diffusion coefficients from this study are compared with those predicted from the model.[14]

Several series of experiments with liquid n-heptane, ac-

etone, and methylene chloride are conducted to find out effects of initial lengths of diffusion path on its binary diffusion coefficients into atmosphere, as shown in Figures 3 through 5 and Figure 7. These results indicate that binary diffusion coefficients of n-heptane, acetone, and methylene chloride diffused into air are independent of initial length of the diffusion path.

Diffusion coefficients appear to be almost independent of diffusion paths above 4 cm of the initial diffusion path length (see Figure 6). Errors of diffusion values increase with decreased diffusion-path lengths because mole fractions of a vapor at the top end of the diffusion path are neglected in this study (see Table 1). Errors of diffusion values may increase with decreased boiling points of volatile liquids at a given diffusion-path length.

The diffusion values of the vapors of n-heptane, acetone, and methylene chloride into air are calculated with the diffusion equation, neglecting mole fractions of the vapors at the top end of a diffusion tube. The calculated diffusion values are plotted against the diffusion lengths. The diffusion values of vapors of n-heptane, acetone, and methylene chloride appear to be not affected significantly with the lengths of diffusion path above around 4-cm length of diffusion path, although evaporation rates of the liquids increase exponentially with diffusion-path lengths at room temperature.

Higher experimental errors will be expected with smaller evaporation areas in obtaining diffusion data due to relatively consistent magnitudes of experimental errors such as caliper readings, balance readings, and thermometer readings (see Table 1). A series of experiments with liquid n-heptane are conducted to find out effects of evaporation areas on its binary diffusion coefficients into atmosphere, as shown in Figures 7 and 8.

Diffusion values of vapor of n-heptane into air appear to be not significantly affected with cross-sectional areas of diffusion path, although slight radial temperature distributions and axial temperature distributions may be expected in large evaporation areas such as 11.22 cm^2 and 4.26 cm^2 in comparison with small evaporation areas such as 0.52 cm^2 and 0.97 cm^2. These results indicate that diffusion coefficients of n-heptane diffused into air appear to be independent of evaporation areas.

The results suggest that the experimental technique gives reasonable agreement between the experimental values and the predicted values. Although the results from this method are rather precise, as shown in Table 1, it is also important to notice the limitations on this particular experimental diffusion method. Disturbance of air surrounding the evaporation apparatus should be minimized to obtain good agreement between experimental diffu-sion coefficients and predicted diffusion coefficients.

CONCLUSION

An inexpensive diffusion experiment was developed to determine molecular diffusion coefficients of vapors of volatile liquids into air. A diffusion equation suitable for the inexpensive diffusion experiment was developed to determine diffusion coefficients of vapors into air with experimental data. This laboratory experiment introduces chemical engineering students to the concept of molecular diffusion for the mass transfer, the heat transfer, and the transport phenomena courses. This experiment also provides opportunities for students to carry out experiments for the acquisition of experimental data, to apply their mathematical and computational skills as well as statistical analysis to interpreting experimental data with the aid of computer software, to compare diffusion coefficients from diffusion experiments with those predicted from the theoretical model, and to write their laboratory report using a word processor.

NOMENCLATURE

D_{AB} diffusivity
$f(kT/\varepsilon_{AB})$ collision function
k Boltzmann's constant
M_A molecular weight of a liquid A
M_B molecular weight of a gas B
m_o initial amount of liquid A in a diffusion tube
m amount of liquid A in a diffusion tube at evaporation duration t
$m_o - m$ loss amount of liquid A due to evaporation for the evaporation duration t
N_{Az} flux of the vapor of liquid A at steady state

TABLE 1
**Experimental and predicted binary diffusion coefficients of vapors into air at atmospheric pressure.**

Liquid Vapor	Diffusion Path, cm	Evaporation Area, cm^2	Temp. ℃	Binary Diffusion Coefficient cm^2/s		Deviation % from Predicted Values
				Experimental	Predicted	
Acetone	1.56	1.5690	25.2	0.0993	0.1104	-10.1
Acetone	3.61	1.5690	25.1	0.1102	0.1104	-0.1
Acetone	6.03	1.5690	25.5	0.1084	0.1107	-2.0
Acetone	9.52	1.5690	25.5	0.1088	0.1107	-1.7
Acetone	12.81	1.5690	25.6	0.1060	0.1107	-4.3
n-Heptane	4.10	11.2221	24.6	0.0729	0.0725	0.6
n-Heptane	4.10	4.2638	26.0	0.0727	0.0734	-0.9
n-Heptane	4.10	1.4957	25.7	0.0726	0.0730	-0.5
n-Heptane	4.10	0.9677	25.5	0.0744	0.0726	2.4
n-Heptane	4.10	0.5217	25.6	0.0768	0.0729	5.3
n-Heptane	1.34	1.5690	25.2	0.0651	0.0728	-10.5
n-Heptane	3.66	1.5690	25.2	0.0712	0.0728	-2.2
n-Heptane	6.73	1.5690	25.2	0.0716	0.0728	-1.6
n-Heptane	9.47	1.5690	25.2	0.0724	0.0728	-0.6
n-Heptane	12.80	1.5690	25.1	0.0760	0.0728	4.3
Methylene chloride	1.74	1.5690	25.5	0.0945	0.1078	-12.3
Methylene chloride	3.51	1.5690	25.5	0.1074	0.1078	-0.3
Methylene chloride	6.26	1.5690	25.5	0.1118	0.1078	3.7
Methylene chloride	9.28	1.5690	25.5	0.1101	0.1078	2.2
Methylene chloride	12.80	1.5690	25.5	0.1081	0.1078	0.4
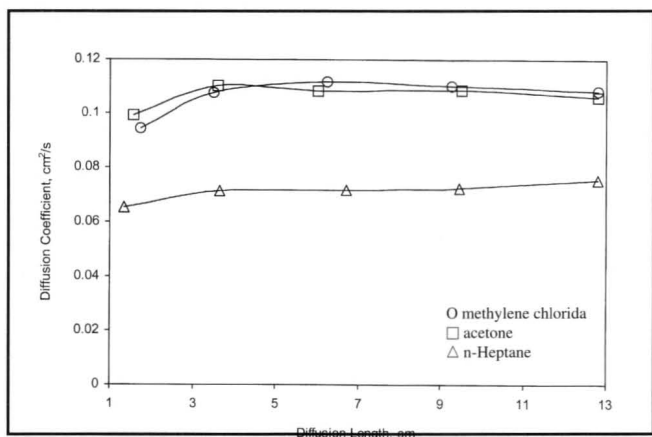
Figure 6. *Effects of diffusion-path length on diffusion of vapors into stagnant air in the temperature range of 24.7 to 25.7°C.*
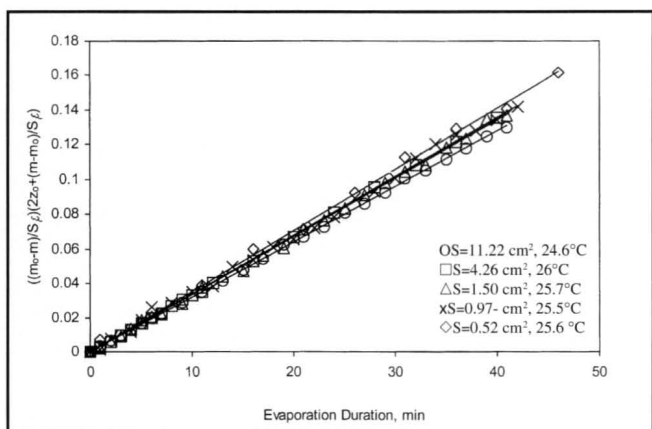
Figure 7. *Loss amounts of liquid n-heptane due to evaporation into air with various evaporation areas (S) and the initial 4.1-cm diffusion path length (z_o) at atmospheric pressure.*
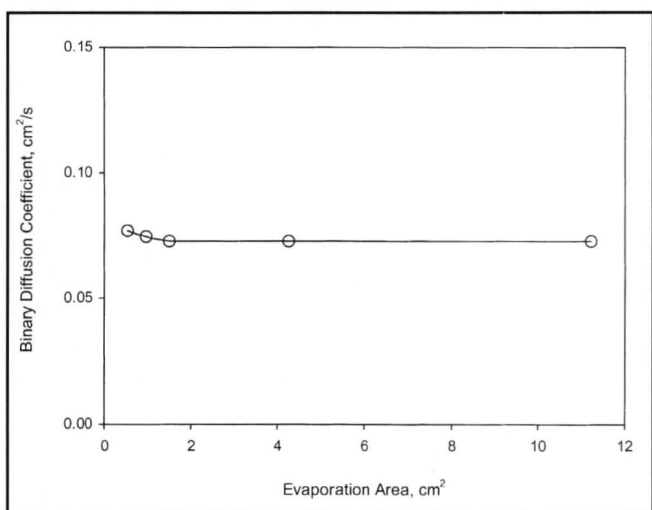
Figure 8. *Binary diffusion coefficients on n-heptane into air with various evaporation areas at room temperature and atmospheric pressure.*

P   atmospheric pressure
R   ideal gas constant, 82.0545 atm-cm³/g-mole-K
r_{AB} molecular separation at collision, $r_{AB} = (r_A + r_B)/2$
S   cross-sectional areas of diffusion tube
T   absolute vaporization temperature
t   diffusion duration
y_{Ao} mole fraction of the vapor A at the liquid surface in a diffusion tube at T and P
z   length of diffusion path
z_o initial length of diffusion path
ε_{AB} energy of molecular attraction = $\sqrt{\varepsilon_A \varepsilon_B}$
ρ_A density of a liquid A at T

ACKNOWLEDGMENTS

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