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ISSN: 0970-020 X; CODEN: OJCHEG
Oriental Journal of Chemistry
2011, Vol. 27, No. (2): Pg. 559-562

Evaluation of Rate Coefficients and Diffusion Coefficients of Evaporated *n*-Heptane using RF-GC Methodologies

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(Received: March 15, 2011; Accepted: April 29, 2011)

ABSTRACT

The cases of environmental contamination and toxicity originated from liquid pollutants are increasing from time to time. A fast and accurate technique is needed to study the physicochemical properties of respective liquid pollutants. Reversed-flow gas chromatography, which is a sub-technique of inverse gas chromatography, is an experimental arrangement simulating a simple model for the action of liquid pollutants in laboratory scale. By using a commercial gas chromatograph and an appropriate mathematical analysis, kinetic parameters such as rate coefficients, k_c and diffusion coefficients, D of analyzed liquid were calculated. These physicochemical properties of the liquid experimented will contribute to the references for future research in the area of environment, food, agriculture as well as physical sciences.

Key words: Chromatography, Diffusion Coefficients, Evaporation, Rate Coefficients.

INTRODUCTION

Evaporation of *n*-hexane is a vital ecological fate for compounds introduced into human, freshwater and marine environments by accidental spills, industrial effluents, or introduced directly into the air from industrial unit processes such as bioreactors and cooling towers¹. The *n*-hexane evaporates off to the atmosphere, contributes to the air pollution. The acute toxicity of *n*-heptane is relatively low, although it is a mild anesthetic. Inhalation of high concentrations produces first a state of mild euphoria, followed by somnolence with headaches and nausea. The long-

term toxicity of *n*-heptane in humans is well known; however the physicochemical properties (such as rate and diffusion coefficients) during transportation of the molecules to the environment are less described².

The application of RF-GC concerning on analysis of liquid pollutants was first reported by Karaiskakis³. In the research, *n*-heptane was one of the interest liquids under study but the diffusion coefficient values of the samples were not conformed to the theoretical ones which gave more than 20% deviations. The authors come to the conclusion that the equilibrium at the liquid-gas

interphase leads to profound disagreement with the experimental evidence. On the other hand, in 2004, Kwon has reported the diffusion coefficient values of *n*-heptane into air by using open-tube evaporation method⁴. The deviation between experimental and theoretical diffusion coefficient values gave less than 5%. However, the similarity of these reported research was the determination of diffusion coefficients of *n*-heptane were restricted within the temperature ranged of 20°C to 30°C, whilst in the industries itself, such as boilers, bioreactors and cooling towers, the activation temperatures might archived to 40°C and more.

Concerning to the case studies mentioned above, the aim of the research was to determine the rate and diffusion coefficients of *n*-heptane within the temperature ranged of 40°C to 90°C with 0.5% deviation (or less) assisted by RF-GC techniques.

EXPERIMENTAL

In this type of chromatography, the column was unfilled with any material and sampling process was carried out by reversing of the carrier gas from time to time producing sample peaks. Selected liquid pollutants of 99.99% purity (MERCK) will be used as solute, while carrier gas was nitrogen of 99.99% purity. After the injection of 1 cm³ s⁻¹ of liquid pollutant at atmospheric pressure and selected temperature, a continuous concentration–time curve was recorded passing through a maximum and then declining with time. By means of a six-port valve, the carrier gas flow direction is reversed for 5 s, which was a shorter time period than the gas hold-up time in both column sections *l* and *l*, and then the gas was again turned to its original direction.

This procedure creates extra chromatographic peaks (sample peaks) superimposed on the continuous elution curve. This was repeated many times during the experiment lasting a few hours. The height, *h* of the sample peaks from the continuous signal, taken as baseline, to their maximum was plotted as $\ln(h_{\infty}-h)$ versus time, giving a *diffusion band*, whose shape and slope both depend on vessel *L* which is empty, as well as on the geometric characteristics of the vessel and the temperature. In all experiments, the pressure drop along *l* + *l* will negligible, while the carrier gas flow-rate will keep constant (1.0 cm³ s⁻¹).

RESULTS AND DISCUSSION

The results obtained from the preliminary experiments were evaluated for physicochemical quantities of *n*-heptane.

In Figure 1, the height, *h* of the sample peaks as a function of the time *t*₀, when the flow reversal was made, was plotted on a semilogarithmic scale⁵. It shows the steep rise and then the leveling off with time of the sample peak height. As an example using equations,

$$\ln(h_{\infty} - h) = \ln h_{\infty} - [2(k_c L + D) / L^2] t_0 \dots (1)$$

$$\ln[h(L/2t_0)^2 + k_c t_0^2] = \ln[4k_c c_0 / v(D/\pi)] - (L^2/4D)(1/t_0) \dots (2)$$

Where

h_{∞}	=	maximum height of peak (cm)
<i>h</i>	=	peak height (cm)
k_c	=	rate coefficient (cms ⁻¹)

Table 1: Rate coefficients for evaporation of pure liquid and diffusion coefficients of vapors into nitrogen at 1atm

Liquid	T, K	k_c , cm s ⁻¹	Present work D , cm ² s ⁻¹	Theoretical D , cm ² s ⁻¹	Deviation (%)
<i>n</i> -Heptane	313.15	279.40±0.16	0.0798±0.0009	0.0799	0.04
	323.15	293.39±0.17	0.0846±0.0004	0.0844	0.20
	333.15	308.57±0.12	0.0890±0.0004	0.0890	0
	343.15	324.94±0.17	0.0937±0.0007	0.0937	0
	353.15	342.01±0.18	0.0986±0.0003	0.0986	0
	363.15	362.22±0.12	0.1035±0.0016	0.1035	0

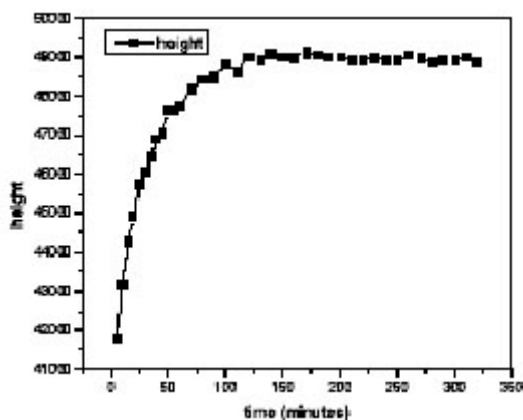


Fig. 1: The rise of the sample peak height with time for the diffusion of *n*-heptane vapor into nitrogen ($v=1\text{cm}^3\text{ s}^{-1}$), 313.15K and 1 atm

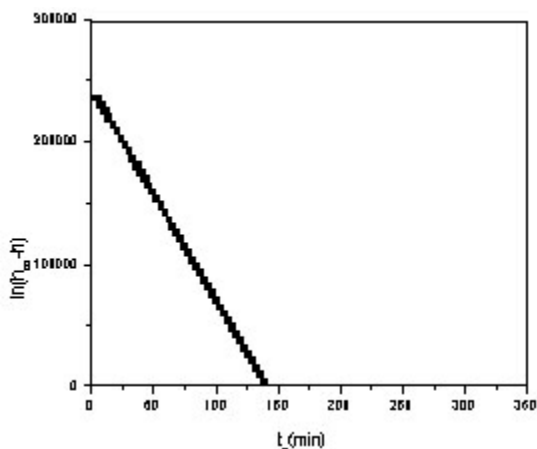


Fig. 2: Diffusion of *n*-heptane vapor into nitrogen ($V=1\text{cm}^3\text{ s}^{-1}$), at 313.15K and 1atm

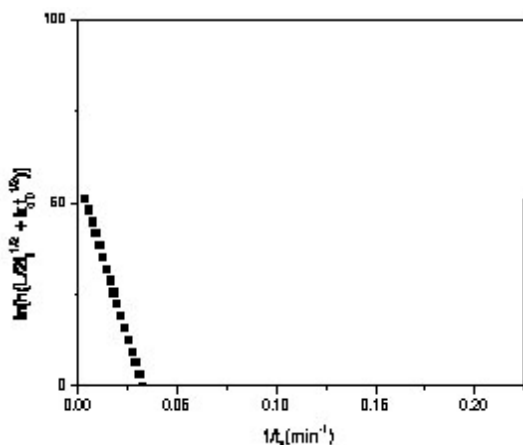


Fig. 3: Data from evaporation of *n*-heptane into nitrogen ($V=1\text{cm}^3\text{ s}^{-1}$), at 313.15K and 1atm

- D = diffusion coefficient (cm^2s^{-1})
- L = length of column (cm)
- t_0 = initial time (minute)
- c_0 = initial concentration (moldm^{-3})
- v = carrier gas flow rate (cm^3s^{-1})

The equations above were derived from Katsanos⁶ to analyze the experimental findings; the data on Figure 1 were treated as follows. Iterated some points, which correspond to small times, the rest of the experimental points were plotted according to Equation 1, as shown in Figure 2.

As infinity value h_∞ was taken the mean of the values found in the time interval, which differed little from one another. From the slope of this plot, which was equal to $-2(k_c L + D)/L^2$, according to Equation 1, using the theoretically calculated value of $0.0799\text{ cm}^2\text{ s}^{-1}$, and the actual value of L (28.5cm), a value of 279.40 cm s^{-1} for k_c , was calculated. This approximate value was used to plot all but the few point closed to h_∞ according to Equation 2 as shown in Figure 3

From the slope of this latter plot, a value of $0.0798\text{ cm}^2\text{ s}^{-1}$ for D was found. If this is combined with the slope of the previous plot (Figure 2), a second value for $k_c = 279.40\text{ cm s}^{-1}$ was calculated and further used to re-plot the data according to Equation 2. The new value for D found coincides with the previous one ($0.0799\text{ cm}^2\text{ s}^{-1}$), and thus the iteration procedure must be stopped.

Table 1 summarizes the results obtained with the pure liquid studied. In the same table, the diffusion coefficients determined here were compared with those calculated theoretically. As one can see from the Table 1, the D values determined in this work were very close to the theoretical ones. The deviation given in the last column was the accuracy of the experimental values from those calculated theoretically⁷:

$$\text{Deviation (\%)} = 100[(D_{\text{found}} - D_{\text{theory}})/D_{\text{found}}]$$

With no exception, this accuracy is better than 0.5% in all cases and indicated that investigation of liquid pollutants using reversed-flow gas chromatography (RF-GC) is of great significance in environmental science⁸. However, the

comparison of experimental and literature values is impossible because the experimental temperatures, column length, gas flow rate and pressure are varies⁹. The findings of these evaporated liquid were unattainable for the experimental temperature $\geq 100^{\circ}\text{C}$ because the boiling temperature of this liquids is merely more than 90°C .

Evaporation of chemicals from water bodies to the atmosphere can be an important environmental pathway for certain pollutant liquids. The transfer rate of pollutants from the air onto the sea surface depends on rate coefficients and diffusion coefficients in the gas phase. The chemical interaction involves measurement of the rate of liquid loss into a gas stream flowing horizontally across the liquid surface. In the majority of these techniques relative evaporation rates, which cannot be related to the physical properties of the evaporating species, as well as evaporation halftimes are measured. Thus, this relative new technique of reversed-flow

gas chromatography (RF-GC) is suitable to study various physicochemical measurements, such as of rate coefficients and diffusion coefficients for the evaporation of pure liquid¹⁰.

CONCLUSIONS

From the findings of this research, it can be concluded that the equilibrium at the liquid-gas interphase leads to profound agreement with the experimental evidence

ACKNOWLEDGEMENTS

The author is indebted to University Malaya, who supported the research project and Ministry of Science and Technology Malaysia (MOSTI) for the scholarship. Last but not least, special thanks to the staff of the Department of Chemistry, University of Malaya for their technical support.

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