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# Establishment of Physicochemical Measurements of Water Polluting Substances via Flow Perturbation Gas Chromatography

(Menentusahkan Tentu-ukur Juzuk Fiziko-kimia Bahan-bahan yang
Mencemarkan Air Melalui Kromatografi Gas Aliran Terganggu)

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## ABSTRACT

*Spillage of water polluting substances via industrial disaster may cause pollution to our environment. Thus, reversed-flow gas chromatography (RF-GC) technique, which applies flow perturbation gas chromatography, was used to investigate the evaporation and estimate the diffusion coefficients of liquid pollutants. Selected alcohols (99.9% purity) and its mixtures were used as samples. The evaporating liquids (stationary phase) were carried out by carrier gas-nitrogen, 99.9% purity (mobile phase) to the detector. The findings of this work showed the physicochemical measurements may vary depending on the composition of water and alcohol mixtures, temperature of the mixtures, as well as the types of alcohol used. This study implies that there is a variation in the results based on the concentration, types and temperature of the liquids that may contribute in the references for future research in the area of environmental pollution analysis.*

*Keywords: Alcohol mixtures; evaporation rates; liquid-gas interphase; liquid pollutants; spillage; vapour pressure*

## ABSTRAK

*Limpahan bahan-bahan pencemaran melalui bencana industri boleh menyebabkan pencemaran kepada alam sekitar kita. Oleh itu, teknik gas kromatografi aliran berbalik (KTAB) yang mengaplikasikan teknik kromatografi gas aliran terganggu digunakan bagi menentu ukur kadar penyejatan dan menganggar pekali resapan bahan-bahan pencemar. Alkohol terpilih (99.9% darjah kepekatan) dan campuran telah digunakan sebagai sampel. Cecair menyejat (fasa penyebaran) telah diangkut oleh gas pengangkut iaitu nitrogen, 99.9% ketulenan (fasa persampelan) ke pengesan. Keputusan kajian ini menunjukkan ukuran fiziko-kimia mungkin berbeza bergantung kepada komposisi air dan alkohol di dalam campuran, suhu campuran dan jenis alkohol yang digunakan. Kajian ini menunjukkan bahawa terdapat perubahan keputusan berasaskan kepada kepekatan, jenis alkohol serta suhu campuran kajian, dan ia boleh menyumbang kepada rujukan untuk kajian akan datang dalam bidang analisis pencemaran alam sekitar.*

*Kata kunci: Campuran alkohol; cecair pencemar; fasa cecair-gas; kadar penyejatan; tekanan wap; tumpahan*

## INTRODUCTION

A substance or energy that enters the environment from different sources and has undesired effect or adverse effects on the usefulness of a resource is classified as pollutants. Pollutants from the atmosphere in the form of gaseous can diffuse into seawater by slow diffusion process that occurs in the air-water interphase. Pollution caused by alcohol is not a new phenomenon in the 21st century. The problem has increased and recognized more widely, simultaneously with the industrialization and growth of urban populations. The recent reported industrial accident of methanol spillage makes the study significant on the impact of alcohol to the environment (Mohammad et al. 2013). Evaporation emerges as an important process that happens in the air-water interphase and thus, encourages us to contribute to this particular field by acquiring data that can benefit the environmental researchers in the future. As a result, rate coefficients and diffusion coefficients in the gas phase play a major contribution on the transfer of pollutants from the air into water or vice versa.

There are two main categories of measuring the rate of evaporation in organic compounds, as reported in previous studies (Gavril et al. 2006), which involves the measurement of weight gain in vapour adsorbent above the liquid surface (Dilling 1977; Dilling et al. 1975; Mackay & Leinonen 1975; Mackay & Wolkolf 1973) and the rate of liquid loss into the moving gas stream flowing horizontally above the liquid surface (Beverley et al. 1999; Rusdi & Moroi 2004). The former allows the measurement of evaporation rates across a stagnant gas phase, while the latter measures the evaporation rates in perturbation gas flow. Most of the methods only measure the relative evaporation rates and evaporation halftimes which cannot portray the real physical properties of the evaporating organic compounds (Gavril et al. 2006).

Determination of the diffusion coefficients is really important for the area of basic and advanced research in engineering, as well as in chromatography (Karaiskakis & Gavril 2004). The data from the measurement of diffusion coefficient play a major role in the design of the reactors since the interaction between gas phases is involved. On the other hand, diffusion is also important in chemical reaction and should be considered when one wants to construct a column for chromatography purposes. Besides, diffusion is also applicable in the field of atmospheric chemistry, combustion science, studies of indoor air pollution and atmosphere-biosphere interaction (Karaiskakis & Gavril 2004). Diffusion is also important to investigate the major factors in chromatography, which is peak broadening (Grushka & Maynard 1972; Karaiskakis & Gavril 2004). Thus, the reliability and accuracy of diffusion coefficient is vital to proof the theory in chromatography.

Fuller-Schettler-Giddings (FGS) equation is used for this experiment because it is an easily applied method for determining binary gas-phase diffusivities. They successfully developed a successful equation in which atomic and structural volume increments and other parameters were obtained by a nonlinear least squares analysis of 153 different binary systems (340 measurements) (Fuller et al. 1966; Karaiskakis & Gavril 2004). The measurements show the best average percentage accuracy (3.40%) in predicting binary gas-phase diffusivities as compared with other methods (cf Table 2 of (Karaiskakis & Gavril 2004)) and provide the best practical combination of simplicity and accuracy.

The idea of gas chromatographic method with periodic change (reversal) of the carrier gas flow (RFGC), which is related to the stopped-flow gas chromatography (SFGC) based on the works of Phillips et al. (1967) was proposed in 1980 by Katsonas (Karaiskakis et al. 1982). Initially, the RFGC method was designed for the measurement of the kinetic parameters of chemical reactions on the surface of the adsorbent-catalyst in chromatographic column-reactors (Karaiskakis et al. 1982). However, subsequently, the application of this method was greatly extended and RFGC was used to investigate the physiochemical properties of samples, such as the rate of coefficients (Karaiskakis & Katsanos 1984; Khalid et al. 2012), diffusion coefficients (Atta et al. 2002; Karaiskakis & Katsanos 1984; Khalid et al. 2011), mass transfer coefficients (Gavril & Karaiskakis 1997; Karaiskakis et al. 1986; Katsanos et al. 1988), activity coefficients (Agathonos & Karaiskakis 1989a, 1989b; Katsanos et al. 1985) and kinetic study of oxygen adsorption over supported catalysts (Dimitrios et al. 2012). Furthermore, this methods is also applied in separation for the growth phases of microbes (Lainioti et al. 2010) and surface studies (Gavril 2010; Metaxa et al. 2009).

The evaporation of pure liquids, as well as liquid mixtures has been studied in the past utilizing RF-GC (Karaiskakis & Katsanos 1984; Khalid et al. 2012; Mohammad et al. 2013). Previous works have intensively focused on the determination of the physiochemical measurement of the pure liquid pollutant while the current work, on the other hand also tries to investigate the effect of alcohol at different concentrations by using the same methodologies (Karaiskakis & Katsanos 1984; Khalid et al. 2011; Mohammad et al. 2013). There are quite a number of research studies on the evaporation of a binary low molecular weight alcohol mixture. Furthermore, studies on the evaporation rate and diffusion rate of low molecular weight alcohol are rare in literature. The aim of the present work were to investigate the effects of concentration of alcohol mixtures, the temperature being imposed, as well as the type of alcohol that influences the rate coefficients for evaporation and diffusion coefficients of that particular alcohol in the water environment.

## MATERIALS AND METHODS

### CHEMICALS

The alcohols used (methanol, ethanol, 1-propanol and 1-butanol) were purchased from Merck (Kuala Lumpur, Malaysia). The gases were purchased from MOX (Kuala Lumpur, Malaysia), which comprised the carrier gas; nitrogen of 99.99% purity, as well as the fuel gases for the FID; hydrogen of 99.99% purity and compressed air.

### PROCEDURES

The instruments used and the experimental procedures conducted are described (Karaiskakis & Katsanos 1984; Khalid et al. 2012; Mohammad et al. 2013). Reversed-flow gas chromatography (RF-GC) system, which is based on modified commercial gas chromatograph, comprises of six-port valve, sampling and diffusion columns and flame ionization detector (FID). A conventional gas chromatograph (Series GC-14B, Shimadzu, Japan) with an FID contained in its oven with two sections of $l'$ and $l$ in stainless-steel chromatographic column (57 + 57 cm × 4 mm I.D.), empty of any chromatographic material, is shown in Figure 1. The previous work had used the FID since its response factor was equal to unity, which definitely gives one to one response to the solute vapour in the sampling column (cf. Figure 1) during the sampling process (Katsanos et al. 1985).

The carrier gas supply and the detector via a six-port valve were connected to the sampling column via $D_1$ and $D_2$. The selection of nitrogen as the carrier gas was just because the gas accounts for 78% by volume of the air we breathe as dry atmosphere are mainly consists of nitrogen, oxygen and argon (> 99.9%), while carbon dioxide, krypton, neon, helium and xenon only contribute 0.1% (States & Gardner 2000). Furthermore, the problem of ethanol being a hygroscopic and easily absorbs moisture from the air, which arise from the previous study can be solved if nitrogen is used as the carrier gas, as manifested in previous investigations (O'Hare & Spedding 1992; O'Hare et al. 1993). The absorption rates of water by ethanol from the air has led to increased scatter in the pure ethanol data (O'Hare & Spedding 1992) even though the absorption rates are considered small in comparison with the evaporation rates. The fact directly indicates that nitrogen plays a major role in the atmosphere of air, plus the gas itself is non-reactive, easy to obtain and can be

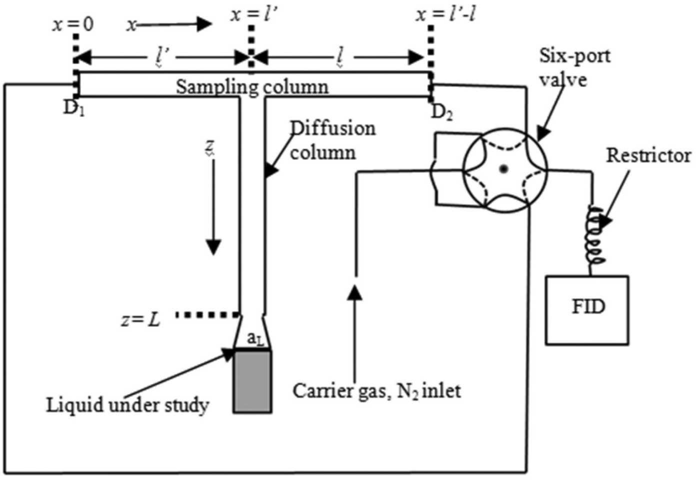

FIGURE 1. The set-up of reversed-flow gas chromatography technique for measuring rate coefficients and diffusion coefficients of water polluting substances

purchased at a reasonable cost (Goodman & Tipler 2009). By choosing the former gas as carrier gas, our work is proven to be significant for the environmental application to investigate the impact of liquid pollutants for studies on the environment.

The middle of the sampling column, *l*' + *l* was connected perpendicularly at its upper end with a stainless steel diffusion column of length *L* (28.5 cm × 4 mm I.D.). A 0.25 in. Swagelok tee union was used for the connection at the T-junction *x* = *l*'. A 2 cm tube containing 4 $cm^3$ of a pure liquid or a liquid mixture was connected to the lower end of the diffusion column, *L* by Swagelok 0.25 in. union. The sampling cell, which consists of diffusion column and sampling column, was placed in the oven. The restrictor was placed before the detector to curb the flame of FID being extinguished when the perturbation process of the carrier gas was being carried out. The pressure drop along the sampling column, *l*' + *l* was negligible. The temperature for the studies was restricted in the range of 313.15-373.15 K and the volumetric carrier gas flow-rate, was 1.00 $cm^3\,s^{-1}$.

After placing the glass tube containing liquid polluting substance, all joints in the sampling cell were tested with liquid leak detector for any leakage. Any formation of bubbles indicated that there was leakage at that particular joint. The automatic six-port valve was activated via LabSolutions CS software by Shimadzu from Personal Computer (PC) once the monotonously rising concentration-time (µV/s) curve for the vapour of the liquid mixture appeared on the monitor after a long time. The detector and PC were connected via CBM-102 Bus Module integrator. The sampling process was started by reversing the flow of carrier gas for an exact time period of 6 s. The reversal period was ensured to be shorter than the time in both sections *l*' and *l*. When the carrier gas flow was restored in its original direction, sample peaks like those in Figure 2, which 'seat' on the baseline of the curve, were recorded, corresponding to various times $t_0$ from the beginning of the experiment. The theoretical basis and the calculation of evaporation rates, $K_G$ and diffusion rates, *D* have been discussed intensively in the previous papers (Karaiskakis & Katsanos 1984; Khalid et al. 2012). Readers can always consult those papers if they are interested in the theoretical part of the current work.

## QA/QC OF RF-GC METHODS

The uncertainty in the determination of rate coefficients for evaporation mostly depends on the accuracy of the temperature control. The uncertainty of the chromatograph oven is ± 0.1 K for all experiments. The error in the determination of the diffusion coefficient may come from the measurement of the diffusion column, *L*. Since *D* is proportional to $L^2$ (Gavril et al. 2006; Karaiskakis & Gavril 2004), small error while measuring the length of the column may contribute to the inaccuracy of the diffusion coefficients determination. We measured the column, *L*, directly and used a solute of accurately known for the diffusion coefficients in the given carrier gas (such as $C_2H_6O$ in $N_2$[23]) and carry out a calibration experiment for *L*. The value of *L*, which was determined at 28.5 cm, was used to estimate unknown diffusion coefficients based on the data from the previous work (Khalid et al. 2012) (c.f. rate coefficients for evaporation and diffusion coefficients values for methanol and 1-propanol (100% *v*/*v*) in Table 1). The determination of the evaporation rate depends also on the accuracy of the length of the diffusion column, *L*.

The nitrogen gas that was used in this experiment was filtered via carrier gas trap and filter (Z-Pure Glass Indicating Moisture Trap, CRS, USA) so that there was no moisture carried in the carrier gas. Furthermore, after running a particular sample, for example, 90% *v*/*v* methanol, the experiment was run with an empty bottle by increasing the temperature of the column up to 200°C in order to eliminate any dead volumes at any column junctions of the previous sample. This was to ensure that the columns were empty of any solute remaining from the

TABLE 1. The rate coefficients for the evaporation of the alcohol component at various volume percent (% *v*/*v*) from alcohol-water mixtures, and diffusion coefficients of the alcohol vapour into nitrogen at 1 atm pressure

| Alcohol | T (K) | $\dot{V}$ (cm$^3$ s$^{-1}$) | Volume percent (% *v*/*v*) | $10^2 K_G$ (cm s$^{-1}$) | | | $10^3 D$ (cm$^2$s$^{-1}$) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Present work | Reference 1 | Reference 2 | Present work | Reference 1 | Theoretical | Precision[#] (%) | Accuracy (%) |
| Methanol | 313.15 | 1.00 | 100 | 96.69 ± 0.20[a] | 140.87 ± 0.11 | 3.30[b] | 181.86 ± 0.04[a] | 184.30 ± 0.70 | 184.31 | 1.34 | 1.35 |
| | | | 95 | 47.10 ± 0.13[a] | - | - | 182.86 ± 0.04[a] | - | 184.31 | - | 0.80 |
| | | | 90 | 61.91 ± 0.15[a] | - | - | 181.86 ± 0.03[a] | - | 184.31 | - | 0.20 |
| Ethanol | 313.15 | 1.00 | 100 | 175.58 ± 0.07[a,*] | 175.58 ± 0.07 | 2.79[c] | 140.40 ± 0.09[a] | 140.04 ± 0.90 | 140.30 | 0.00 | 0.06 |
| | | | 95 | 70.92 ± 0.15[a] | - | - | 113.28 ± 0.07[a] | - | 140.33 | - | 5.29 |
| | | | 90 | 47.51 ± 0.89[a] | - | - | 146.88 ± 0.09[a] | - | 140.33 | - | 4.46 |
| 1-propanol | 313.15 | 1.00 | 100 | 190.94 ± 0.15[a,*] | 190.94 ± 0.15 | 3.64[d] | 116.90 ± 0.02[a] | 119.90 ± 0.20 | 116.90 | 2.57 | 0 |
| | | | 95 | 70.79 ± 0.16[a] | - | - | 116.21 ± 0.01[a] | - | 116.94 | - | 0.63 |
| | | | 90 | 74.12 ± 0.04[a] | - | - | 116.31± 0.01[a] | - | 116.94 | - | 0.53 |
| 1-butanol | 313.15 | 1.00 | 100 | 54.51 ± 0.19[a] | 208.68 ± 0.08 | 2.68[e] | 101.00 ± 0.03[a] | 102.00 ± 0.50 | 102.03 | 0.98 | 1.02 |
| | | | 95 | 50.23 ± 0.09[a] | - | - | 101.55 ± 0.03[a] | - | 102.03 | - | 0.48 |
| | | | 90 | 61.77 ± 0.15[a] | - | - | 101.71 ± 0.01[a] | - | 102.03 | - | 0.31 |

[a] Uncertainty obtained from the standard error of the $K_G$ and *D* values from the slopes of the linear plots of (20) and (21) of (Karaiskakis & Katsanos 1984), respectively. Number of the observations being made for each point, *n*=3

[*] This measurement is done by using 0.5 cm$^3$ solute in the glass bottle while the rest of the experiments, the volume of the solute was 4.0 cm$^3$. The former volume of the solute being used to calibrate the diffusion column, *L*. (cf. QA/QC OF RF-GC METHODOLOGY section)

Reference1 : (Khalid et al. 2012)

Reference 2 : The rate coefficient for evaporation is measured at 322.5 K[b], 336.8 K[c], 342.3 K[d], and 358.1 K[d], respectively. The length of diffusion column, *L* = 116.2 cm with the flow of the carrier gas is in the range 0.290-0.674 cm$^3$ s$^{-1}$ is used for the experiment.(Karaiskakis & Katsanos 1984)

[#] Precision has been defined as ( $|D_{\text{present work}} - D_{\text{reference/literature}}|/D_{\text{present work}}$)*100 (Karaiskakis & Gavril 2004) previous experiment. We ensured that the chromatogram achieved a stable baseline before conducting the reversal process. Plus, every rate coefficients data for this experiment were compared with the FSG theoretical value and one finds that the values' accuracy was less than 5%, which is considered as accepted tolerance value.

## RESULTS AND DISCUSSION

In the present paper, the rate coefficients for the evaporation of the liquid mixtures methanol-water, ethanol-water, 1-propanol-water and 1-butanol-water, as well as the diffusion of those liquids into carrier gas nitrogen, were determined.

Table 1 shows the results obtained with all the pure alcohol, as well as their mixtures being studied at constant temperature and various alcohol concentrations. The rate coefficient for evaporation of the current work is listed in the fifth column of Table 1. Previous works (Karaiskakis & Katsanos 1984; Khalid et al. 2012) measured the rate coefficients for evaporation for pure liquid alcohol in carrier gas helium and nitrogen, respectively.

Comparison of the results for the evaporation of pure ethanol and 1-propanol 100% *v*/*v*, with the literature, shows relatively good accuracy. We used the same volume of ethanol and 1-propanol, which was 0.5 cm$^3$ as used in the previous work (Khalid et al. 2012) in order to calibrate the diffusion column, *L*, whereby the procedure is elaborated in the previous section. For the rest of the experiment, we used 4.0 cm$^3$ of alcohol to measure the rate coefficient for evaporation and the diffusion coefficient of alcohols into carrier gas nitrogen. The rate coefficient for evaporation calculated for methanol and 1-butanol was less than the amount used in the previous work (Khalid et al. 2012) because the liquid coverage area, $a_L$ for both experiments was different (cf. Figure 1). When less liquid was poured in the glass bottle, the coverage area of the liquid was bigger since the liquid was deposited at the bottom of the bottle. In the present work, we used 4.0 cm$^3$ of alcohol and the liquid almost filled the whole bottle and the liquid level was at the neck of the bottle, which is shown in Figure 1. Thus, the liquid coverage area, $a_L$ was smaller as compared to when less liquid was poured into the bottle.

On the other hand, when all the $K_G$ values of pure alcohol found in the work was compared with the literature, as shown in the seventh column of Table 1 (Karaiskakis & Katsanos 1984), the values of $K_G$ for the former was higher than the latter. This was due to the bigger size of carrier gas nitrogen's molecules, employed in this work, compared with carrier gas helium, used in the literature work. The variation in $K_G$ value seemed to be logical, as the temperature conditions, as well as carrier gas were different in the literature. Otherwise, the values of $K_G$ were higher for the former than the latter. Besides, the value of $K_G$ found in this work for pure alcohols was between the afore-mentioned literature values (Karaiskakis & Katsanos 1984; Khalid et al. 2012).

This phenomenon was described in Figure 6. Figure 6 shows the attractive force between the alcohol's molecules at the interface of liquid bulk and the vapour phase of the alcohol. When the molecules were exposed to the larger liquid coverage area, $a_L$ more molecules were exposed at the interface and increased the probability of the molecules to be ejected from the liquid bulk (Birdi et al. 1989; Jozsef 2009; Rowan et al. 1995). The attractive forces between the molecules at the interface and the molecules in the liquid bulk became weaker and the molecules at the interface escaped into vapour phase (Davies & Rideal 1961). Thus, the rate coefficient for evaporation of methanol and 1-butanol was higher in the larger liquid coverage area, $a_L$.

The diffusion coefficients were compared with those calculated theoretically using Fuller-Schettler-Giddings (FSG) equation (cf. supplementary material) (Fuller et al. 1966), permits the calculation of the method's accuracy, which is defined as,

$$\text{Accuracy (\%)} = [(D_{\text{present work}} - D_{\text{theoretical}})/D_{\text{present work}}]*100. \tag{1}$$

The results are tabulated in the last column of Table 1. The table shows that the $K_G$ values increased with increasing the alcohol's volume percent (% *v*/*v*) generally. The evaporation rate of the alcohol increased as the alcohol's volume percent (% *v*/*v*) increased, as pictured in Figure 3. The results applied for all alcohols for this study, except for 1-butanol. The equilibrium of liquid-vapour phase is established in the diffusion column (cf. Figure 1), between 130-330 min, since the intensity-time graph (cf. Figure 2) reaches plateau in this period. The fact that 1-butanol had negative gradient, as depicted in Figure 3 (decreasing evaporation rate as composition of 1-butanol in water is increasing) because 1-butanol possessed the lowest vapour pressure as compared with others. Thus, there was a small deviation of evaporation in pure 1-butanol and its mixture (90-95% *v*/*v* in water). The previous study also showed that the evaporation of the alcohol components, comprising a binary mixture with water, could be predicted in terms of vapour pressure (O'Hare & Spedding 1992). The investigators believe that the vapour pressure acted as a driving force in a similar way as the pure component (alcohol) evaporation. The vapour pressure exerted by the alcohol became significant as compared to the water component in the mixture in the range of 30-100% *w*/*w*.

The rate coefficients for the evaporation of the alcohols (90% *v*/*v*) at various temperatures, ranging from 313.15-373.15 K, as well as the diffusions coefficients of the alcohol vapours into nitrogen at these temperatures, are compiled in Table 2. The conclusion can be drawn from this table is that the $K_G$ values increased with the increase of the temperature in accordance with the Arrhenius equation (Karaiskakis et al. 1986), as depicted in Figure 4, when the $K_G$ values are plotted against reciprocal of their temperatures. From the Arrhenius equation,

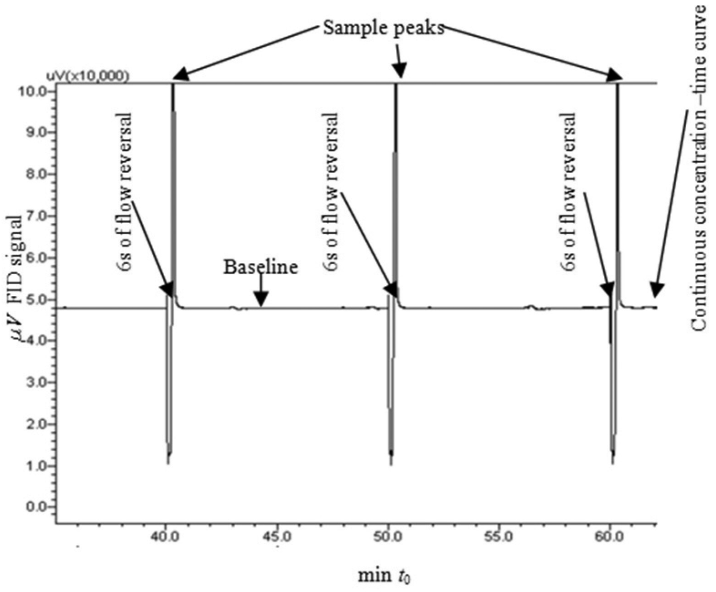

FIGURE 2. Three sample peaks for the diffusion of liquid mixture vapours into carrier gas nitrogen at 323.15 K and 101325 Pa (volumetric flow rate = 1 $cm^3 min^{-1}$) extracted from a reversed-flow chromatogram

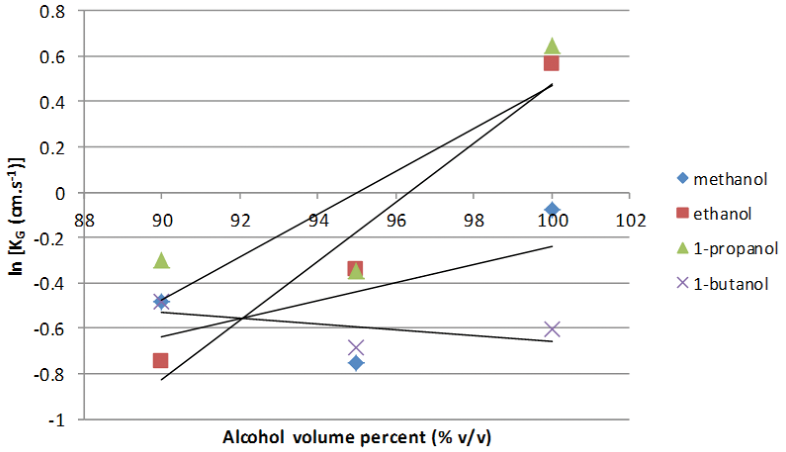

FIGURE 3. Volume percent (% *v*/*v*) dependence of $K_G$ for the evaporation of the alcohol from the alcohol-water mixtures at 313.15 K

$$\ln k = \ln A - \frac{E_a}{RT}, \tag{2}$$

where $k$ is the rate coefficients for evaporation (cm $s^{-1}$); $E_a$ is the activation energy of the alcohol (J $mol^{-1}$); $T$ is temperature of the liquid (Kelvin); $R$ is the constant (8.3145 J $mol^{-1}$ $K^{-1}$) and $A$ is an arbitrary constant, one can calculate the activation energy, $E_a$ of the selected alcohol. Previous works (Karaiskakis et al. 1986; Khalid et al. 2012) have calculated the activation energy, $E_a$ of the pure alcohols and they found that the values were smaller than 40 kJ $mol^{-1}$(Katsanos 1988). This was expected since $K_G$ values were rate coefficients for evaporation, which is a physical phenomenon (Karaiskakis et al. 1986). Besides, we obtained a linear Arrhenius plot with negative slope, which portrays that the activation energy, $E_a$ of the selected alcohols changed with temperature (Khalid et al. 2012) and the type of alcohols. The differences of the slope in the plot were expected since different types of alcohols possess different activation energy, $E_a$. The steeper the slope means the higher the activation energy and the stronger the temperature dependence of the rate coefficients for evaporation of one particular alcohol (Peter & De 2006). Based on the plot in Figure 4, methanol (90% *v*/*v*) has the steepest slope among the alcohols, which indicates that methanol (90% *v*/*v*) possesses the highest activation energy and the strongest temperature dependence of the rate coefficients for evaporation.

The temperature dependence of the rate coefficients for evaporation can be described as follows: The kinetic energy, i.e. the tendency of the alcohol's molecules to escape from the liquid surface is governed by the temperature. A certain fraction of the molecules possess

TABLE 2. The rate coefficients for the evaporation of the alcohol component from alcohol-water mixtures at constant alcohol volume percent (% *v*/*v*) and various temperatures and diffusion coefficients of the alcohol vapour into nitrogen at 1 atm pressure

| Alcohol | Volume percent (% v/v) | $\dot{V}$ (cm$^3$ s$^{-1}$) | T (K) | $10^2 K_G$ (cm s$^{-1}$) | $E_a$ (kJ mol$^{-1}$) | $10^3 D$ (cm$^2$s$^{-1}$) | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | Present work | Theoretical | Accuracy (%) |
| Methanol | 90 | 1.00 | 313.15 | $61.91 \pm 0.15^a$ | 36.4 | $181.86 \pm 0.03^a$ | 184.31 | 0.20 |
| | | | 323.15 | $138.81 \pm 0.46^a$ | | $198.13 \pm 0.04^a$ | 194.74 | 1.71 |
| | | | 333.15 | $142.34 \pm 0.88^a$ | | $208.79 \pm 0.18^a$ | 205.41 | 1.62 |
| Ethanol | 90 | 1.00 | 313.15 | $47.51 \pm 0.89^a$ | 27.7 | $146.88 \pm 0.09^a$ | 140.33 | 4.46 |
| | | | 323.15 | $71.01 \pm 0.12^a$ | | $149.17 \pm 0.01^a$ | 148.27 | 0.50 |
| | | | 333.15 | $94.49 \pm 0.07^a$ | | $159.87 \pm 0.02^a$ | 156.39 | 0.84 |
| | | | 343.15 | $141.77 \pm 0.44^a$ | | $167.43 \pm 0.01^a$ | 164.70 | 1.62 |
| | | | 353.15 | $170.68 \pm 0.07^a$ | | $172.73 \pm 0.01^a$ | 173.19 | 0.26 |
| | | | 363.15 | $199.44 \pm 0.12^a$ | | $180.12 \pm 0.02^a$ | 181.86 | 0.84 |
| 1-propanol | 90 | 1.00 | 313.15 | $74.12 \pm 0.04^a$ | 10.9 | $116.31 \pm 0.01^a$ | 116.94 | 0.53 |
| | | | 323.15 | $83.36 \pm 0.02^a$ | | $123.65 \pm 0.02^a$ | 123.35 | 0.08 |
| | | | 333.15 | $92.17 \pm 0.68^a$ | | $130.03 \pm 0.02^a$ | 130.32 | 0.22 |
| | | | 343.15 | $104.40 \pm 0.02^a$ | | $138.37 \pm 0.02^a$ | 137.24 | 0.60 |
| | | | 353.15 | $125.61 \pm 0.04^a$ | | $143.12 \pm 0.02^a$ | 144.32 | 0.83 |
| | | | 363.15 | $126.58 \pm 0.27^a$ | | $150.70 \pm 0.03^a$ | 151.54 | 0.56 |
| 1-butanol | 90 | 1.00 | 313.15 | $61.77 \pm 0.15^a$ | 8.4 | $101.71 \pm 0.01^a$ | 102.03 | 0.31 |
| | | | 323.15 | $71.44 \pm 0.19^a$ | | $107.00 \pm 0.02^a$ | 107.80 | 0.75 |
| | | | 333.15 | $72.56 \pm 0.04^a$ | | $113.28 \pm 0.01^a$ | 113.71 | 0.37 |
| | | | 343.15 | $82.52 \pm 0.03^a$ | | $117.40 \pm 0.01^a$ | 119.75 | 2.00 |
| | | | 353.15 | $91.33 \pm 0.02^a$ | | $124.56 \pm 0.01^a$ | 125.92 | 1.09 |
| | | | 363.15 | $97.14 \pm 0.09^a$ | | $133.74 \pm 0.02^a$ | 132.22 | 1.13 |
| | | | 373.15 | $104.54 \pm 0.12^a$ | | $136.27 \pm 0.03^a$ | 138.66 | 1.75 |

[a] Uncertainty obtained from the standard error of the $K_G$ and $D$ values from the slopes of the linear plots of (20) and (21) of (Karaiskakis & Katsanos 1984), respectively. Number of the observations being made for each point, $n$=3

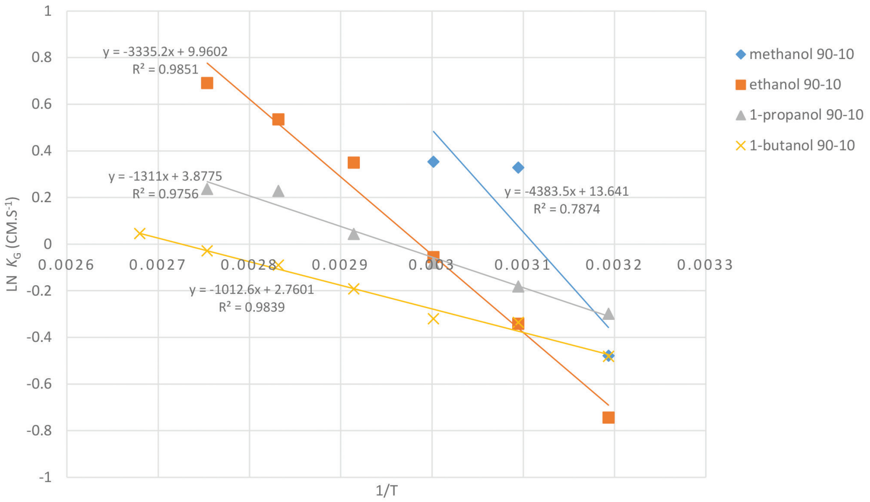

FIGURE 4. Temperature dependence of $K_G$ for the evaporation of the alcohol from the alcohol-water mixtures in volume percent (% *v*/*v*)

enough kinetic energy to overcome the forces of attraction of the surrounding molecules and to escape from the surface of the liquid at each temperature (Jozsef 2009). When higher temperature is exposed to the alcohols, the alcohol's particles with higher average kinetic energy will populate on the surface of the liquid. Some particles will have higher kinetic energy than the average kinetic energy and tends to escape from the liquid surface, while some others possess lower kinetic energy than the average and remains on the liquid surface.

The accuracy of the diffusion coefficients of the methanol 90% *v*/*v* into nitrogen gas were found to be less than 2% and this means that the experimental values of the coefficients are closed to the theoretical values predicted by Fuller-Schettlar-Giddings (FSG)(Fuller et al. 1966). To the best of our knowledge, only Khalid et al. (2012) managed to get less than 0.2% in all the diffusion coefficients measurement of organic liquid using the reversed-flow gas chromatography methods.

Table 3 shows the rate coefficients for the evaporation of the alcohol component from alcohol-water mixtures at constant alcohol volume percent (90% *v*/*v*) and various types of the low molecular weight alcohol vapour into nitrogen at 1 atm pressure. From the table, we can conclude that the evaporation rate of the alcohol increased as the molecular weight of the alcohol decreased, as depicted by the graph in Figure 5. Since there was no other works measuring the diffusion coefficients of methanol at 90% v/*v*, the value of the coefficients were compared with the theoretical calculation from the FSG equation and the accuracy of the coefficients was less than 2% for this case. The results in the fifth column show that the evaporation process was highly dependent on the structure, the molecule weight of the alcohol, as well as the concentration percentage of the selected alcohol. The light molecule and high volatile liquid were easier to evaporate compared with the heavier ones (Hofmann 1932). The present experiment also supports the previous study (Brown et al. 1969; Hu et al. 2010; O'Hare et al. 1993), which concludes that ethanol seems to possess lower evaporation rates as compared to 1-propanol due to the hydrogen bonding that makes the hydroxyl ion of ethanol being 'trapped' in a fluctuation clathrate structure. The current study only focused on the straight chain, low molecular weight alcohol as evaporate liquid since it is widely used as bio fuel in vehicles (Cheng & Timilsina 2011). Thus, the rate of coefficient for evaporation increased based on the following trends:

1-butanol < Ethanol < 1-propanol < Methanol

$$\xrightarrow{\hspace{12em}}$$

Rate coefficient for evaporation increases

## CONCLUSION

The findings provide a useful data for estimating the evaporation, as well as diffusion rates of water polluting substances at different concentration, temperatures and types of alcohols being used towards environmental science application. The accuracy of diffusion rates calculated from the experiments based on FSG equation with no exception is better than 5% in all cases and falls between the diffusion coefficients values calculated by the previous work. The uniqueness of the method is because of its simplicity which makes the measurement of physicochemical much simpler since the time taken to acquire the data was less than 3 h. Furthermore, this method enables us to measure the rate coefficients, as well as the diffusion coefficients of the liquids simultaneously. Future work should focus on retarding the evaporation of the dangerous polluted liquid to the environment since it may cause devastating effect on the human health.

TABLE 3. The rate coefficients for the evaporation of the alcohol component from alcohol-water mixtures at constant alcohol volume percent (% *v*/*v*) and various types of the low molecular weight alcohol vapour into nitrogen at 1 atm pressure

| Alcohol | T (K) | ($cm^3 s^{-1}$) | Volume percent (% v/v) | $10^2 K_G$ ($cm\ s^{-1}$) | $10^3 D$ ($cm^2 s^{-1}$) | | |
|---|---|---|---|---|---|---|---|
| | | | | | Present work | Theoretical | Accuracy (%) |
| Methanol | 323.15 | 1.00 | 90 | 138.81 ± 0.46[a] | 198.13 ± 0.04[a] | 194.74 | 1.71 |
| Ethanol | 323.15 | 1.00 | 90 | 71.01 ± 0.12[a] | 149.17 ± 0.01[a] | 148.27 | 0.50 |
| 1-propanol | 323.15 | 1.00 | 90 | 83.36 ± 0.02[a] | 123.65 ± 0.02[a] | 123.35 | 0.08 |
| 1-butanol | 323.15 | 1.00 | 90 | 71.44 ± 0.19[a] | 107.00 ± 0.02[a] | 107.80 | 0.75 |

[a] Uncertainty obtained from the standard error of the $K_G$ and $D$ values from the slopes of the linear plots of Eqs. 20 and 21 of (Karaiskakis & Katsanos 1984), respectively. Number of the observations being made for each point, $n$=3

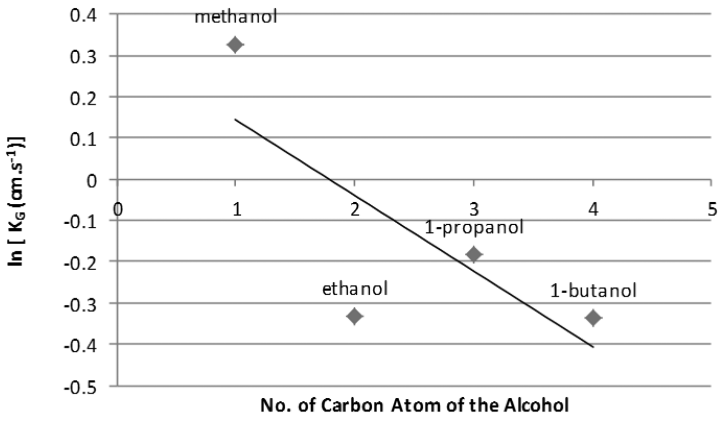

FIGURE 5. Types of alcohol dependence of $K_G$ for the evaporation of the alcohol from the alcohol-water mixtures at 323.15 K

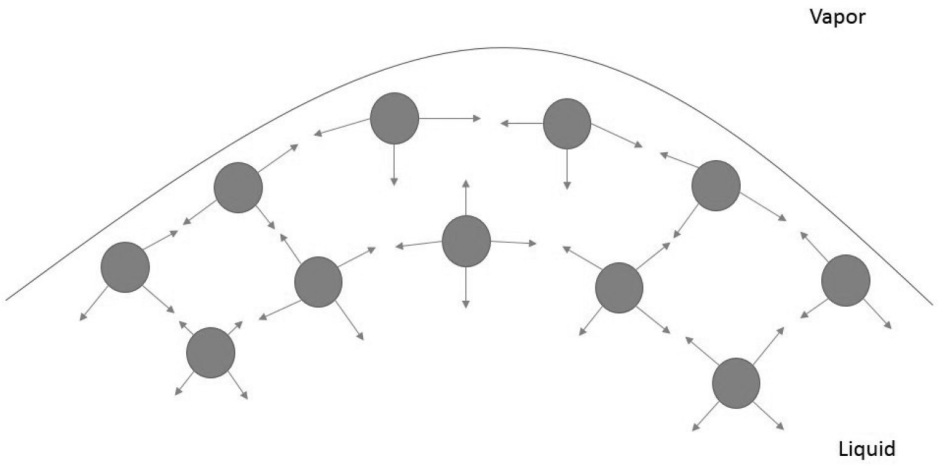

FIGURE 6. Attractive forces (represented by arrows) between alcohol's molecules (show as spheres) at the surfaces and in the interface of a liquid. (FIGURE 6 adapted from (Davies & Rideal 1961))

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