

**PHYSICOCHEMICAL STUDIES OF LIQUID POLLUTANTS  
USING REVERSED FLOW GAS CHROMATOGRAPHIC  
TECHNIQUES**

**KHALISANNI KHALID**

**FACULTY OF SCIENCE  
UNIVERSITY OF MALAYA  
KUALA LUMPUR**

**2011**

**PHYSICOCHEMICAL STUDIES OF LIQUID POLLUTANTS  
USING REVERSED FLOW GAS CHROMATOGRAPHIC  
TECHNIQUES**

**KHALISANNI KHALID**

**DISSERTATION SUBMITTED IN FULFILLMENT OF THE  
REQUIREMENTS FOR THE DEGREE OF  
MASTER OF SCIENCE**

**DEPARTMENT OF CHEMISTRY  
FACULTY OF SCIENCE  
UNIVERSITY OF MALAYA  
KUALA LUMPUR**

**2011**

# UNIVERSITI MALAYA

## ORIGINAL LITERARY WORK DECLARATION

Name of Candidate: KHALISANNI BIN KHALID (I.C/Passport No:850617-08-6061)

Registration/Matric No: SGR080149

Name of Degree: MASTER OF SCIENCE

Title of Project Paper/Research Report/Dissertation/Thesis ("this Work"):

PHYSICO-CHEMICAL STUDIES OF LIQUID POLLUTANTS USING REVERSED FLOW GAS CHROMATOGRAPHIC TECHNIQUES

Field of Study: PHYSICAL/ ENVIRONMENTAL SCIENCE

I do solemnly and sincerely declare that:

- (1) I am the sole author/writer of this Work;
- (2) This Work is original;
- (3) Any use of any work in which copyright exists was done by way of fair dealing and for permitted purposes and any excerpt or extract from, or reference to or reproduction of any copyright work has been disclosed expressly and sufficiently and the title of the Work and its authorship have been acknowledged in this Work;
- (4) I do not have any actual knowledge nor do I ought reasonably to know that the making of this work constitutes an infringement of any copyright work;
- (5) I hereby assign all and every rights in the copyright to this Work to the University of Malaya ("UM"), who henceforth shall be owner of the copyright in this Work and that any reproduction or use in any form or by any means whatsoever is prohibited without the written consent of UM having been first had and obtained;
- (6) I am fully aware that if in the course of making this Work I have infringed any copyright whether intentionally or otherwise, I may be subject to legal action or any other action as may be determined by UM.

  
Candidate's Signature

Date 28/6/2011

Subscribed and solemnly declared before,

  
Witness's Signature

Name: ASSOCIATE PROFESSOR DR. RASHID ATTA KHAN

Designation:

Assoc. Prof. Dr. Rashid Atta Khan  
Lecturer, Department of Chemistry  
University of Malaya  
50603 Kuala Lumpur

Date 28/6/2011

  
Witness's Signature

Name: PROFESSOR DR. SHARIFUDDIN MOHD. ZAIN

Designation:

DR. SHARIFUDDIN M ZAIN  
Professor  
Department of Chemistry  
Faculty of Science, University of Malaya  
50603 Kuala Lumpur, Malaysia

Date 28/6/2011

## ABSTRACT

Evaporation of pollutant liquid is a vital ecological fate when the compounds are introduced into both freshwater and marine environments through industrial effluents, or introduced directly into the air from industrial unit processes such as bioreactors and cooling towers. In such cases, reversed-flow gas chromatography (RF-GC) method is needed to measure the physicochemical properties of the pollutant liquids. RF-GC sampling technique is an effortless, fast and accurate procedure. Since the earliest publication on RF-GC, the method has been used to study physicochemical quantities by measuring the value of one in the presence of another. The application of the method embraces the area of environmental sciences, food chemistry, chemical kinetics, catalyst and catalysis. In the present work, RF-GC was used to measure the diffusion coefficient of vapors from liquid into a carrier gas and at the same time to determine the rate coefficient for the evaporation of the respective liquid. The mathematical expression describing the elution curves of the samples peaks was derived and used to calculate the physicochemical parameters for the selected liquid pollutants such as, methanol, ethanol, 1-propanol, 1-butanol, *n*-pentane, *n*-hexane, *n*-heptane and *n*-hexadecane evaporating into the carrier gas, nitrogen. The values of diffusion coefficients found were compared with those calculated theoretically or reported in the literature, and the values of evaporation rate were used to determine the activation energy of respective samples using Arrhenius equation. An interesting finding of this work is, by using an alternative mathematical analysis based on equilibrium at the liquid-gas interphase, the comparison leads to profound agreement between the theoretical values of diffusion coefficients with the experimental values.

## ABSTRAK

Penyejatan cecair pencemar adalah suatu keadaan pengakhiran ekologi yang berbahaya di mana bahan dialirkan ke kawasan aliran air tawar dan air masin melalui bahan buangan industri, atau dialirkan secara terus ke udara dari pemprosesan unit industri seperti reaktor-bio dan menara penyejuk. Dalam kes yang sedemikian, kaedah Gas Kromatografi Aliran-Berbalik (RF-GC) diperlukan untuk mengkaji sifat fisikokimia cecair-cecair pencemar. RF-GC adalah kaedah yang mudah, cepat dan tepat. Semenjak penerbitan terawal berkenaan RF-GC, kaedah ini telah digunakan untuk kajian kuantiti fisikokimia dengan mengukur nilai di antara suatu sama lain. Penerapan kaedah ini merangkumi bidang ilmu sains persekitaran, kimia makanan, kimia kinetik, pemangkinan dan katalisis. Dalam kajian ini, RF-GC telah digunakan untuk mengukur pemalar penyebaran wap dari cecair ke dalam gas pembawa dan dalam masa yang sama menentukan pemalar kadar bagi proses penyejatan bagi cecair yang terlibat. Ungkapan matematik yang menjelaskan puncak lengkungan elusi sampel yang diterbitkan dan digunakan untuk menaakul parameter fisikokimia bagi cecair pencemar yang terpilih seperti metanol, etanol, 1-propanol, 1-butanol, *n*-pentana, *n*-heksana, *n*-heptana dan *n*-heksadekana yang tersejat ke dalam gas pembawa nitrogen. Nilai pemalar penyebaran eksperimen dibandingkan dengan nilai-nilai teori yang didapati secara kaedah teori atau nilai-nilai yang telah dilaporkan di dalam jurnal, dan seterusnya nilai-nilai pemalar penyejatan ini digunakan bagi menentukan tenaga pengaktifan bagi setiap sampel menggunakan persamaan Arrhenius. Suatu penemuan yang menarik dalam penyelidikan ini ialah dengan menggunakan analisis matematik alternatif berdasarkan keseimbangan di fasa perantara cecair-gas, nilai-nilai teori pemalar penyebaran adalah selari dengan nilai eksperimen.

## ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to all people who in different ways have contributed to this thesis. I am very grateful to you all, and especially:

My supervisor, Associate Professor Dr. Rashid Atta Khan for his never-ending enthusiasm, devoting his utmost time, encouragement with generosity and patience to think big and be open minded. We made it!

My co-supervisor, Professor Dr. Sharifuddin Mohd. Zain who contributes his knowledge of expertise, supports and always there when needed.

My parents, Mr. Khalid and Madam Rohani, who give me courage when times were rough, telling me to work less when I worked too much and believing in me. I know you always want the best for me! My sister, Khalizani for making time at work as well as time off-work and for the love and giving me lots of joy and support during this study.

The deepest appreciation to National Science Fellowship (NSF) - Ministry of Science and Technology (MOSTI) for giving me the scholarship.

The staffs of Department of Chemistry, Faculty of Science, University of Malaya, for providing all the requirements used in this work.

I would also like to extend my appreciation to my fellow friends who helped me with this Masters' dissertation project.

Finally, and most of all, I would like to praise God Almighty for his consent to make it happened.

Once again, thanks to all....

# TABLE OF CONTENTS

	page
<b>ABSTRACT</b>	<b>ii</b>
<b>ABSTRAK</b>	<b>iii</b>
<b>ACKNOWLEDGEMENTS</b>	<b>iv</b>
<b>TABLE OF CONTENTS</b>	<b>v</b>
<b>LIST OF TABLES</b>	<b>viii</b>
<b>LIST OF FIGURES</b>	<b>x</b>
<b>LIST OF ABBREVIATIONS</b>	<b>xii</b>
<b>CHAPTER 1: INTRODUCTION</b>	
1.1 Background	1
1.2 Objectives of research	5
<b>CHAPTER 2: LITERATURE REVIEW</b>	
2.1 Pollutant liquids	6
2.1.1 Alcohols	7
2.1.2.1 Alcohol pollution effects	8
2.1.2 Alkane	9
2.1.2.1 Alkane pollution effects	11
2.2 Evaporation	12
2.3 Gas Chromatography	15
2.3.1 Reversed Flow-Gas Chromatography	18
2.3.1.1 Historical Review	20
2.3.1.1.1 Measurement of diffusion coefficients	21

2.3.1.1.2	Conventional techniques	22
2.3.1.1.3	FSG equation in RF-GC	24
2.3.1.2	Empirical equation	29
2.3.1.3	The methodology potential of RF-GC	31
<b>CHAPTER 3:</b>	<b>THEORY</b>	
3.1	Mathematical Theory	32
<b>CHAPTER 4:</b>	<b>EXPERIMENTAL SETUP</b>	
4.1	Chemicals	38
4.2	Experimental arrangement	38
<b>CHAPTER 5:</b>	<b>RESULTS AND DISCUSSION</b>	
5.1	Determination of theoretical diffusion coefficient values	41
5.1.1	Application of FSG equation	41
5.1.1.1	Molar volume	43
5.1.1.2	Atomic weights	43
5.1.2	Theoretical diffusion coefficients values	44
5.1.3	Relation between temperature and diffusion coefficients	48
5.2	Determination of experimental diffusion coefficient values	52
5.2.1	Plotting height ( $h$ ) versus time (minutes)	54
5.2.2	Plotting $\ln(h_{\infty}-h)$ versus time (minutes)	55
5.2.3	Plotting $\ln[h(1/2t_0^{1/2}+k_c t_0^{1/2})]$ versus 1/time (minutes <sup>-1</sup> )	55
5.3	Determination of activation energy	60



<b>CHAPTER 6:</b>	<b>CONCLUSION</b>	
6.1	Conclusion	62
<b>REFERENCES</b>		65
<b>APPENDICES</b>		
<b>LIST OF PUBLICATIONS/ PROCEEDINGS/ CONFERENCES</b>		

## LIST OF TABLES

Table		Page
2.1	List of alkanes	10
2.2	List of various elements and compounds for FSG equation	30
5.1	Atomic volumes, $V_A$ ( $\text{cm}^3 \text{mol}^{-1}$ ) of various elements and compounds	43
5.2	Atomic weights of various elements	43
5.3	Theoretical diffusion coefficients values for methanol at various temperatures	44
5.4	Theoretical diffusion coefficients values for ethanol at various temperatures	44
5.5	Theoretical diffusion coefficients values for propanol at various temperatures	45
5.6	Theoretical diffusion coefficients values for butanol at various temperatures	45
5.7	Theoretical diffusion coefficients value for <i>n</i> -pentane at selected temperature	46
5.8	Theoretical diffusion coefficients values for <i>n</i> -hexane at various temperatures	46
5.9	Theoretical diffusion coefficients values for <i>n</i> -heptane at various temperatures	47
5.10	Theoretical diffusion coefficients values for <i>n</i> -hexadecane at various temperatures	47

5.11	Binary gaseous diffusion coefficients, $D_{AB}$ ( $\text{cm}^2\text{s}^{-1}$ ) of alcohols (A: trace solute, B: carrier gas), measured by the reversed flow-gas chromatographic techniques ( $v = 1\text{cm}^3\text{s}^{-1}$ )	57
5.12	Binary gaseous diffusion coefficients, $D_{AB}$ ( $\text{cm}^2\text{s}^{-1}$ ) of hydrocarbons (A: trace solute, B: carrier gas), measured by the reversed flow-gas chromatographic techniques ( $v = 1\text{cm}^3\text{s}^{-1}$ )	58
5.13:	The activation energy values of respective samples calculated using Arrhenius equation and measured by the reversed flow-gas chromatographic techniques ( $v = 1\text{cm}^3\text{s}^{-1}$ )	61

## LIST OF FIGURES

Figure		Page
2.1	The layout of the modern gas chromatography	17
3.1	Schematic arrangement showing the diffusion column $L$ connected to the chromatographic column $l' + l$ through which carrier gas flows from $D_2$ to $D_1$ or vice versa.	33
4.1	Shimadzu GC-14B	38
4.2	Instrumentation of the reversed flow gas chromatography technique for the simultaneous measurement of the diffusion coefficients and rate transfer coefficients of the evaporating liquids.	39
4.3	Internal close-up of the RF-GC system	40
5.1	The rise of theoretical diffusion coefficient values of methanol at various temperatures	48
5.2	The rise of theoretical diffusion coefficient values of ethanol at various temperature	49
5.3	The rise of theoretical diffusion coefficient values of propanol at various temperatures	49
5.4	The rise of theoretical diffusion coefficient values of butanol at various temperatures	50
5.5	The rise of theoretical diffusion coefficient values of $n$ -hexane at various temperatures	50
5.6	The rise of theoretical diffusion coefficient values of $n$ -heptane at various temperatures	51

5.7	The rise of theoretical diffusion coefficient values of <i>n</i> -hexadecane at various temperatures	51
5.8	Reversed flow gas chromatogram showing two sample peaks for the adsorption of liquid pollutant at 312.15K and 1atm ( $v=1.0\text{cm}^3 \text{s}^{-1}$ )	53
5.9	The rise of the sample peak height with time for the diffusion of liquid vapor into nitrogen ( $v=\text{cm}^3 \text{s}^{-1}$ ) at 1 atm.	54
5.10	Example of plotting Eq. 20 for the diffusion of liquid vapor (ethanol) into carrier gas at 313.15K and 1atm ( $v=1.0\text{cm}^3 \text{s}^{-1}$ )	55
5.11	Data from evaporation of liquid vapor (ethanol) into carrier gas at 313.15K and 1atm ( $v=1.0 \text{cm}^3 \text{s}^{-1}$ ), plotted according to Eq 21.	56

## LIST OF ABBREVIATIONS

$\gamma$	obstructive factor
atm	atmosphere
°C	Degree Celcius
CH <sub>3</sub> OH	methanol
C <sub>2</sub> H <sub>5</sub> OH	ethanol
cm	centimeter
CO <sub>2</sub>	carbon dioxide
Co <sub>3</sub> O <sub>4</sub> -	cobalt oxide ion
$D_{AB}$	Diffusion coefficient
e.g	for example
EPA	Environment Pollution Agency
erfc	complimentary error function
et. al.,	and friends
exp	exponential funtion
FSG	Fuller-Schettlar-Giddings
g/mol	gram per mol
GC	Gas Chromatography
$H$	height
Hg	mercury
IGC	Inverse Gas Chromatography
K	Kelvin
LD <sub>50</sub>	Lethal Dose 50%
$M$	molecular weight

ml	milliliter
NO <sub>x</sub>	nitrogen oxide
-OH	hydroxyl
<i>p</i>	Pressure
Pa	Pascal
ppm	part per million
psig	pound/square inch [gauge]
RF-GC	Reversed-Flow Gas Chromatography
<i>T</i>	Temperature
TRI	Toxic Release Inventory
<i>v</i>	velocity
<i>V</i>	molar volume