

Solubility of Organics in Water and Silicon Oil: A Comparative Study

Edison Muzenda

Abstract—The aim of this study was to compare the solubility of selected volatile organic compounds in water and silicon oil using the simple static headspace method. The experimental design allowed equilibrium achievement within 30 – 60 minutes. Infinite dilution activity coefficients and Henry's law constants for various organics representing esters, ketones, alkanes, aromatics, cycloalkanes and amines were measured at 303K. The measurements were reproducible with a relative standard deviation and coefficient of variation of 1.3×10^{-3} and 1.3 respectively. The static determined activity coefficients using shaker flasks were reasonably comparable to those obtained using the gas liquid - chromatographic technique and those predicted using the group contribution methods mainly the UNIFAC. Silicon oil chemically known as polydimethylsiloxane was found to be better absorbent for VOCs than water which quickly becomes saturated. For example the infinite dilution mole fraction based activity coefficients of hexane is 0.503 and 277 000 in silicon oil and water respectively. Thus silicon oil gives a superior factor of 550 696. Henry's law constants and activity coefficients at infinite dilution play a significant role in the design of scrubbers for abatement of volatile organic compounds from contaminated air streams. This paper presents the phase equilibrium of volatile organic compounds in very dilute aqueous and polymeric solutions indicating the movement and fate of chemical in air and solvent. The successful comparison of the results obtained here and those obtained using other methods by the same authors and in literature, means that the results obtained here are reliable.

Keywords—Abatement, Absorbent, Activity coefficients, Equilibrium, Henry's Law Constant

I. INTRODUCTION

ESTIMATING the performance of absorbers or strippers in the abatement of volatile organic compounds from contaminated air streams requires knowledge of the equilibrium concentrations of the solute and the solvent. These are available in most cases as Henry's law constants, vapour pressures or vapour – liquid equilibrium ratios or infinite dilution activity coefficients. Henry's law constants and their corresponding infinite dilution activity coefficients in water and other solvents are of great interest due to the emphasis on the pollutants' environmental fate and risk assessment. The growth in environmental legislations, the increasing influence of public opinion and the inception of the "permit to operate" principle are playing increasing pressure

on industry to avoid and minimize gaseous emissions such VOCs. Scrubbing of the waste gases using selective high boiling solvents is a reversible technique, which allows both the cleaning of the waste gas and recovery of VOC. Infinite dilution studies are crucial in that environmental concern focus on the entirely dilute regions, parts per million. In most separation processes, this is the most difficult and expensive part of separation. Also the greatest deviation from ideal behaviour is exhibited. Infinite dilution studies are also crucial in obtaining high purity products. In this paper the following dimensional form of H is used (1).

$$H_{pc} = \frac{y_i P_T}{C_L} \left[\frac{kPam^3}{mole} \right] \quad (1)$$

Henry's law constant is expressed in many different ways and the six commonly encountered definitions are related as outlined in [1].

The infinite dilution activity coefficient of the VOC in the solvent is obtained (2)

$$\gamma_i^\infty = \frac{H}{p_i^{sat}} \quad (2)$$

In this paper a simple headspace chromatographic technique [1] was used to measure H and γ of VOCs in dilute aqueous and polymeric mixtures. The organic compounds studied here exhibit the following combination of characteristics in water and silicon oil: high solubility (easier to absorb and difficult to strip) or low solubility (easier to strip and difficult to strip) with high, moderate or low volatility. The static headspace method developed [1] was used in this study. Volatile organic compounds can be abated using both recovery and destruction techniques. It is the aim of this paper to present the essential equilibrium design data for absorption and stripping towers.

II. PROCEDURE

A. Solutes

A total of thirteen volatile organic compounds were used in this work. The chemicals were of high purity (larger than 99%). These chemicals were purchased from Merck Ltd or Sigma Aldrich Company Ltd. For simplicity, the VOCs in this work are coded as follows pentane (1), hexane (2), heptane (3), triethyl amine (4), toluene (5), xylene (6), cyclohexane (7), butylacetate (8), diethyl ether (9), chloroform (10), acetone (11), ethyl methyl ketone (12) and isobutyl methyl ketone (13).

E. Muzenda is with the Department of Chemical Engineering, Faculty of Engineering and the Built Environment, University of Johannesburg, Doornfontein, Johannesburg 2028, Tel: +27115596817, Fax: +27115596430, Email: emuzenda@uj.ac.za.

B. Procedure

The enclosed system consisted of a conical flask with a glass side arm. The flask was sealed by a rubber bung. The initial VOC injection and gas sampling were done through the side arm subseal. At start up a fixed volume of silicon oil (200ml) and a desired volume of the volatile organic compound were added into the flask. The flask was then subjected to manual shaking for a minute. Afterwards, the flask was placed in a water bath shaker for an hour. This ensured good mixing of the flask contents and also the temperature could easily be maintained. Two flasks were used for each VOC concentration and three injections were made from each flask. Therefore the resultant value was a mean of six measurements.

C. Sample analysis

Gas samples were analyzed by Perkin Elmer – Gas Chromatography. An air tight syringe was used to take a sample from the flask. A gas sample volume of 0.5ml was injected into the GC. The conditions were as follows; flame ionization detector (FID), helium carrier gas at 35ml/min flow rate, injector and detector temperatures at 250°C, column diameter of 1/8 inch of stainless steel packed with 30% Carbowax P60 – 80 mesh.

D. Calibration curves

The shaker flasks were thoroughly cleaned and then oven dried. The flask was sealed from the atmosphere by a rubber bung. VOC injection and sampling were done through the sidearm subseal. This procedure minimizes contamination by pollutants in the lab air. Known volumes of VOC corresponding to the required parts per million were injected into the flasks. The VOCs were allowed to vaporize in water shaker bath at 303K. Gas samples were withdrawn using a gas tight syringe and injected into the GC. This procedure was repeated for all concentrations of interest. Calibration curves were obtained by plotting concentration kg/m^3 against peak area in units.

III. RESULTS AND DISCUSSION

The reliability and basis of simple headspace method was discussed by [1]. Ref [1] studied the effect of liquid depth and shaking time, and established conditions for equilibrium. Calibration curves were produced for all thirteen compounds. The shaker flasks produced curves with high degree of linearity and the calibration data was characterized by high degree of reproducibility. In all cases the R^2 values were greater than 0.99 as shown in Table 1.

TABLE I
VOLATILE ORGANIC COMPOUNDS CALIBRATION CURVES

VOC	Calibration Eqn	R ² Values
1	Y=0.00012x-0.00005	0.9998
2	Y = 0.00011x-0.00001	0.9997
3	Y=0.00013x-0.00042	0.9999
4	Y=0.00012x-0.00041	0.9995
5	Y=0.00014x -0.00150	0.9993
6	Y=0.00016x-0.00049	0.9997
7	Y=0.00007x-0.0001	1
8	Y=0.00010x-0.0001	0.9994
9	Y=0.00020x -0.0004	1
10	Y=0.00020x -0.0014	0.9996
12	Y=0.00013x-0.00156	0.999
13	Y=0.00012x-0.0003	0.9998

Table II shows the Static and GLC solute mole and weight fraction based activity coefficients in 10cs silicon with corresponding average molecular weight of 1000. The results obtained using this method compare very well with those obtained using the accurate glc technique [2]. Compared to the glc technique, the internal agreement of the simple static headspace measurements is a factor of three lower. A mean of ten measurements for each concentration was used in the calculation.

TABLE II
COMPARISON OF STATIC AND GLC SOLUTE MOLE AND WEIGHT - FRACTION BASED ACTIVITY COEFFICIENTS AT INFINITE DILUTION (10CS PDMS)

VOC	Static headspace		GLC Technique	
	Mole	Weight	Mole	Weight
1	0.388	5.384	0.384	5.323
2	0.503	5.833	0.458	5.317
3	0.539	7.34	0.539	5.382
4	0.525	5.187	0.392	3.878
5	0.56	6.08	0.585	6.354
6	0.805	7.587	0.617	5.808
7	0.397	4.72	0.399	4.378
8	0.86	7.401	0.748	4.35
9	0.624	8.413	0.359	4.489
10	0.425	3.557	0.374	3.133
11	1.026	17.669	0.865	14.895
12	0.532	7.381	0.739	10.245
13	1.096	10.941	0.841	8.396

The variation of the infinite dilution activity coefficients in silicon oil and water obtained in this study and those in literature are shown Tables 3 and 4 respectively. The results compare very well with those found by other workers using

experimental and predictive methods. This shows that when full attention is paid to the experimental set up and procedures, the simple headspace method can be of value in phase equilibrium studies. Based on the successful comparison, the activity coefficients of triethyl amine, butyl acetate, diethyl ether, acetone, ethyl methyl ketone, isobutyl methyl ketone and xylene in silicon oil were considered to be correct as they are not reported anywhere in literature.

TABLE III
VARIATION OF SIMPLE HEADSPACE SOLUTE WEIGHT FRACTION
BASED ACTIVITY COEFFICIENTS IN 10cs PDMS AT 303K

VOC	Activity Coefficients			
	This work	Lit	% Variation	Source
1	5.384	6.066 (static)	11.2	[3]
		6.092 (GLC)	11.6	[3]
		5.523 (GCLF -EOS)	2.5	[4]
		6.134 (UNIFAC)	12.2	[4]
2	5.833	6.003 (static)	2.8	[3]
		6.023 (GLC)	3.2	[3]
		5.679 (GCLF -EOS)	2.7	[4]
		5.932 (UNIFAC)	1.7	[4]
3	7.34	6.109	20.2	[3], [4]
		6.135	19.6	[3]
		5.895	24.5	[4]
4	5.187			
5	6.08	5.363 (static)	13.4	[3]
		6.457 (GLC)	5.8	[3]
6	7.587			
7	4.72	5.378 (GLC)	12.2	[3]
		5.363 (GCLF -EOS)	11.9	[4]
		4.245 (UNIFAC)	11.2	[4]
8	7.401			
9	8.413			
10	3.557	3.366	5.6	
11	17.669			
12	7.381			
13	10.942			

TABLE IV
VARIATION OF SIMPLE MODIFIED HEADSPACE MOLE FRACTION
BASED ACTIVITY COEFFICIENTS IN WATER AT 303K

VOC	Activity Coefficients			Source
	This work	Lit	% Variation	
1	6700			
2	277			
	000			
3	607			
	000			
4	56			
5	8800	10 400 (exp)	14.5	[5]
	5187	7 000 (UNIFAC)	27	[5]
6	16 500			
7	18 500	20 400 (exp)	9.3	[5]
		4 960 (UNIFAC)		[5]
8	75			
9	77	72.9 (exp), 163 (UNIFAC)	5.6; 52.3	[5]
10	611	821 (exp)	25.5	[6]
11	7			
12	109			
13	86			

TABLE V
SOLUTE HENRY'S LAW CONSTANTS IN WATER

VOC	Henry's Law Constants		
	This work, Hpx	Lit Values	Sources
1	100	128	[10]
2	115	130.6	[7], [10]
3	88	95.7	[7], [10]
4	0.73		
5	0.828	0.768	[10]
6	0.915	0.981, 0.529, 0.560	[7],[8], [9]
7	7.481	18.5, 16.6	[7], [10]
8	0.00425	0.0202	[7]
9	0.12	0.095	[7]
10	0.649	0.57, 0.814	[10], [11]
11	0.00428	0.0031, 0.00441, 0.00269	[7],[8]
12	0.035	0.003946	[7]
13	0.00541	0.0456	[7]

A comparative study of Henry's law constants of volatile organic compounds in water and those reviewed from literature is presented in Table 5. There was a close agreement especially for acetone, diethyl ether, toluene, xylene and pentane, with variations from literature findings of 1.2%, 5.6%, 6%, 6.7%, and 8% respectively. All literature values reported in this paper were measured at 303 K with the exception of [5], [12] at 293K and [13] at 298K. For a comprehensive comparative study temperature regression of literature values is recommended

V. CONCLUSION

Henry's law constants and infinite dilution activity coefficients of thirteen volatile organic compounds of environmental significance were measured with the aim of designing a gas treatment process with silicon oil or water. Silicon oil was found to be a better abatement medium for organic compounds compared to water. The phase equilibrium data reported in this work is close to literature values. It is recommended to continue vapour – liquid equilibrium studies of additional binary systems of volatile organic compounds in water or silicon oils.

equilibrium measurement and computation, energy, environment, separation processes as well waste minimization and utilization. He has published more than 60 international peer reviewed papers in international scientific journals and conferences. He serves as reviewer of a number of reputable international conferences and journals. He has also chaired several sessions at International Conferences. The author is a member of the International Scientific Committee, Scientific and Technical Committee & Editorial Review Board of Natural and Applied Sciences, Africa Representative and International Scientific Secretariat for the World Academy of Science Engineering and Technology; Water Institute of SA; International Association of Engineers; AMIChemE.

REFERENCES

- [1] E. Muzenda and A. S Afolabi "A Simple Static Headspace Method for Phase Equilibrium Measurement" World Congress on Engineering and Computer Science, IAENG, San Francisco, USA, October 19 -21, 2011, Unpublished
- [2] E. Muzenda, M. Belaid, and F. Ntuli, "Measurement of Infinite Dilution Activity Coefficients of Selected Environmentally Important Volatile Organic Compounds in Polydimethylsiloxane using Gas – Liquid Chromatography," Kor. J. Chem. Eng., vol. 27, no. 5, pp. 1509 – 1512, 2010
- [3] A. J. Ashworth , C. F. Chien, D. L. Furio., D. M. Hooker, M. M. Kopečni, R. J. Laub and G. J. Price, "Comparison of static with gas – chromatographic solute infinite-dilution activity coefficients with poly(dimethylsiloxane) solvent," Macro., vol. 17, no. 5, pp. 1090-1094, 1984.
- [4] H. Hand, "A note on the prediction of phase equilibria in siloxane polymer systems using a Group Constant Lattice Fluid Equation of State," (a) Experimental – Sorption method (b) GCLF_EOS (c) UNIFAC – FV' Report number 1994 – 10000 – 39527, pp. 2 – 20, 1994.
- [5] F. Nielsen and E. Olsen, "Henry's law constants and infinite dilution activity coefficients for volatile organic compounds in water by a validated air stripping method"
- [6] R. S. Barr and D. M. T. Newsham, "Phase equilibria in very dilute mixtures of water and chlorinated hydrocarbons. Part 1 – Experimental results," Fluid Phase Equilib., vol. 35, pp. 189-205, 1987.
- [7] J. Staudinger and P. V. Roberts, "A critical compilation of Henry's law constant temperature dependence relations for organic compounds in dilute aqueous solutions" Chemosphere, vol. 44, pp. 561 – 576, 2001.
- [8] P. Chatkun Na Ayuttaya, T. N. Rogers, M. E. Mullins and A. A. Kline, "Henry's law constants derived from equilibrium static cell measurements for dilute organic–water mixtures" Fluid Phase Equilibria, 185, 359 – 377, 2001.
- [9] K. C. Hansen, Z. Zhou, C. L. Yaws, and T. M. Aminabhavi, "A laboratory method for the determination of Henry's law constants of volatile organic chemicals," J. Chem. Educ., vol. 72, pp. 93-96, 1995.
- [10] C. L. Yaws, J. R. Hopper, S. D. Sheth, M. Han and R. W. Pike, "Solubility and Henry's law constant for alcohols in water. Waste Management, vol. 17, pp. 541 – 547.
- [11] P. Warneck P, "A review of Henry's law coefficients for chlorine-containing C1 and C2 hydrocarbons," Chemosphere, vol. 69, pp. 347-361, 2007.



Edison Muzenda is the Research and Postgraduate Coordinator and Head of Environmental and Process Systems Engineering Research Unit in the School of Mining, Metallurgy and Chemical Engineering at the University of Johannesburg. Dr Muzenda holds a BSc Hons (NUST, ZIM, 1994) and a PhD, Chemical Engineering (Birmingham, UK, 2000). He has more

than 15 years experience in academia which he gained at different Institutions: National University of Science and Technology Bulawayo, University of Birmingham, Bulawayo Polytechnic, University of Witwatersrand and University of Johannesburg. He is a recipient of several awards and scholarships for academic excellence. His research interests in phase