Volatile Organic Compounds – Biphenyl Thermodynamic Interactions

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***Abstract*—This work focused on the thermodynamic interactions involving volatile organic compounds (VOCs) and biphenyl. The solubility of 60 VOCs in biphenyl was studied using group contribution methods. The modified UNIFAC Dortmund and Lyngby were used to compute the required phase equilibrium in the form of infinite dilution activity coefficients. Six family groups were studied mainly alkanes, alkenes, alkynes, aldehydes, alcohols, and carboxylic acids. The Modified UNIFAC Dortmund performed better than the Modified UNIFAC Lyngby. Biphenyl showed excellent absorption affinity for all VOCs in particular for alkynes and aldehydes. The solubility decreased with increase in VOC molecular weight.**

***Index Terms*—Absorption, activity coefficient, interactions, phase equilibrium, thermodynamic**

I. INTRODUCTION

Volatile Organic Compounds are a large group of carbon-based compounds that easily evaporate at room temperature. Along with carbon, VOCs contain elements such as hydrogen, oxygen, fluoride, chloride, bromine, sulphur and nitrogen. They include both man-made and naturally occurring chemical compounds. Many VOCs are harmful to human health and the environment. Anthropogenic VOCs are regulated by law, especially indoors, where concentrations are the highest. VOCs are typically not acutely toxic, but instead have compounding long-term health effects, because their concentrations are usually low and the symptoms develop slowly. Emissions of VOCs originate from breathing and loading losses from storage tanks, venting of process vessels; leaks from piping and equipment, wastewater streams and heat exchange streams [1]. VOCs together with nitrogen oxides (NO_x) contribute to the formation of ground level smog and increasing tropospheric ozone pollution [2]. VOCs are largely found in the atmosphere because of their relatively high vapour pressure. However VOCs have been found to contaminate ground water, municipal drinking water and the subsurface soil. Consequently volatile organic compounds have a significant contribution to the cumulative exposure to pollution for human life and the environment [3]. Exposure can occur through ingestion, inhalation or by skin contact. Many VOCs may cause cancer to human beings and are known to contribute to global warming. The emissions of VOCs from chemical waste streams can be reduced and/or controlled using a number of abatement techniques. The reduction of volatile organic compounds released into the atmosphere is a major objective of chemical and industrial plants. Governments have also taken steps to help reduce volatile organic compounds released into the atmosphere through legislation which enforces industrial air pollution reduction [4] – [6]. This work, a continuation of our interest in volatile organic compounds – polymeric solvent interactions focuses on the phase equilibrium involving 60 VOCs and biphenyl. The objective is to investigate the potential of biphenyl as solvent for absorption of volatile organic compounds through physical absorption. The group contribution methods Modified UNIFAC Dortmund and Lyngby used in the computation of the required phase equilibrium have been previously discussed [7]-[10].

II. RESULTS AND DISCUSSION

Biphenyl is a molecule comprised solely of carbon and hydrogen atoms. It therefore does not contain any of the highly electronegative atoms (oxygen or nitrogen) which would render it a polar molecule. Furthermore biphenyl is a perfectly symmetrical molecule, and hence possesses no dipole moment. Thus biphenyl is a non-polar solvent which participates solely in van der Waals London dispersion interactions. Since the solubility rule states that like dissolves like, it is anticipated that nonpolar VOC solutes will be readily soluble in biphenyl, whilst highly polar VOCs will be practically insoluble in biphenyl.

Figs. 1 and 2 show the variation of activity coefficients with mole fraction for alkanes in biphenyl using UNIFAC-Dortmund and Lyngby respectively. The open chain nature of alkanes gives rise to larger molecular contact surface area and hence strong solute-solute van der Waals forces. Solubility decreases with molecular weight due to the increase in molecular surface areas and hence the van der Waals forces. The Lyngby over-estimate the infinite dilution activity coefficients. This could be attributed to the lack of UNIFAC – Lyngby parameters in the UNIFAC Consortium data bank. The combinatorial part also contributes to this over prediction as it does not account for the surface area as in the UNIFAC Dortmund.

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A. *Alkanes*

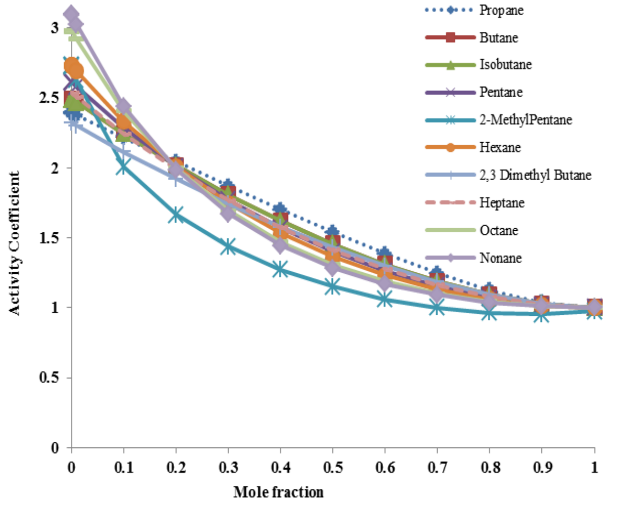

Fig. 1 Variation of activity coefficients with mole fraction for alkanes (UNIFAC Dortmund)

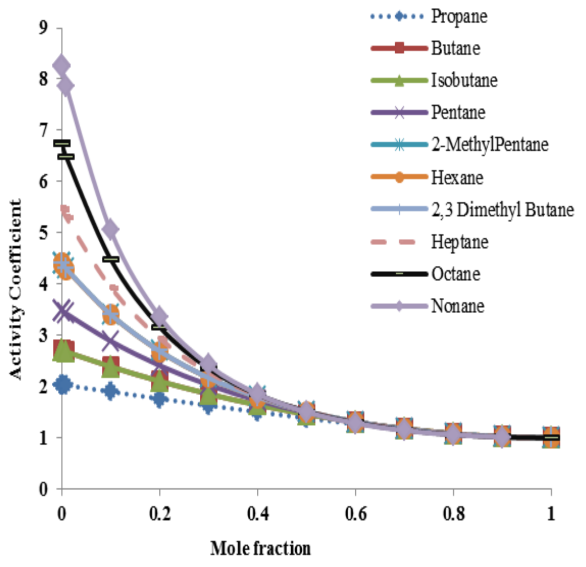

Fig. 2 Variation of activity coefficients with mole fraction for alkanes (UNIFAC Lyngby)

B. *Alkenes*

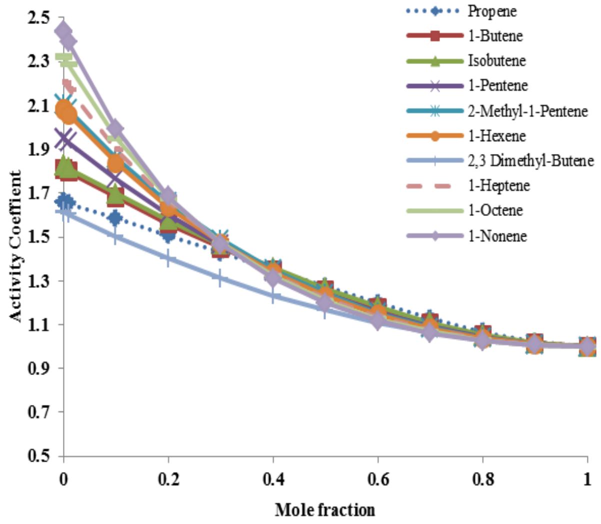

Fig. 3 Variation of activity coefficients with mole fraction for alkenes (UNIFAC Dortmund)

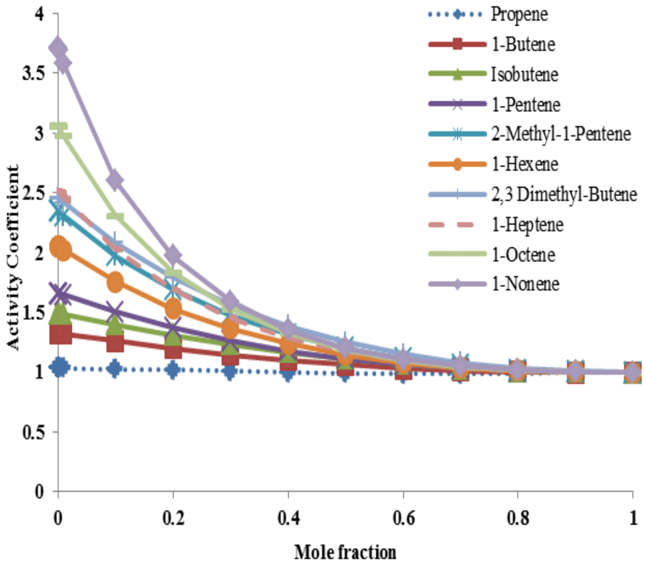

Fig. 4 Variation of activity coefficients with mole fraction for alkenes (UNIFAC Lyngby)

C. *Alkynes*

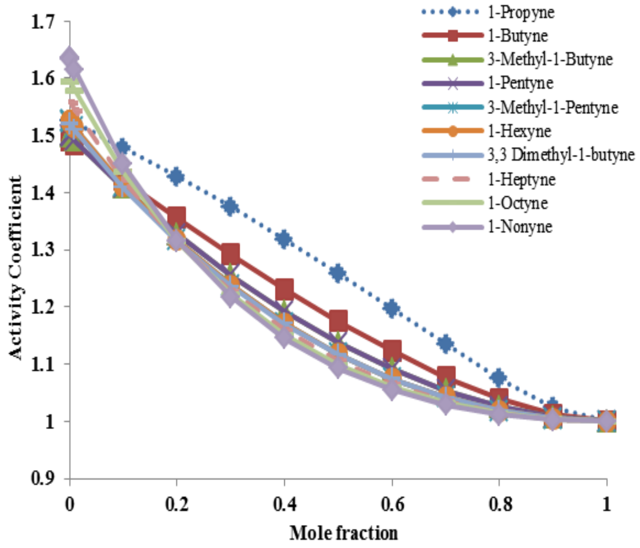

Fig. 5 Variation of activity coefficients with mole fraction for alkynes (UNIFAC Dortmund)

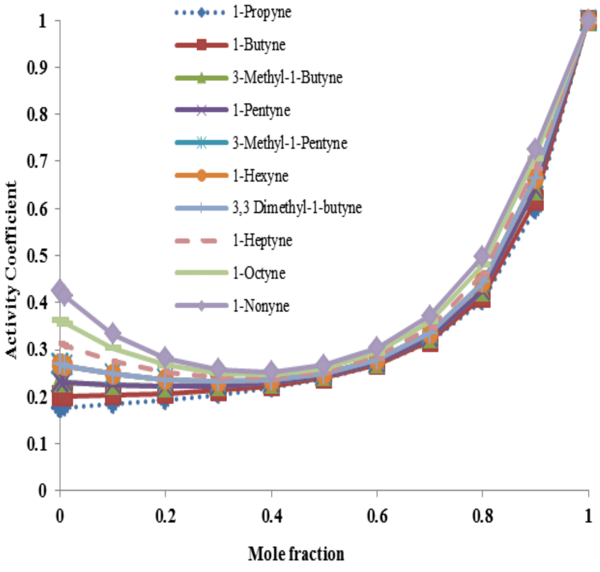

Fig. 6 Variation of activity coefficients with mole fraction for alkynes (UNIFAC Lyngby)

Alkynes are non-polar and thus dissolve in non-polar solvents such as biphenyl. Due to their linear structure alkyne-alkyne intermolecular bonding is more compact than similar alkene and alkane interactions, resulting in stronger solute-solute London dispersion interactions that would be expected for alkane and alkene interactions. It would therefore be expected that alkynes would be less soluble in biphenyl. However the triple bonds of alkynes are highly polarisable because the electrons constituting the double pi-bonds are not confined to the regions around the centres of the two carbon atoms which form the triple bond. The delocalised electron clouds above the biphenyl rings presumably results in greater ease in the formation of temporary dipoles in comparison to non-aromatic molecules. This leads to a greater mutual attraction between alkynes and biphenyl compared to those involving alkanes and alkenes as the induced dipoles resulting from solvent interactions polarise the alkyne solutes.

D. *Alcohols*

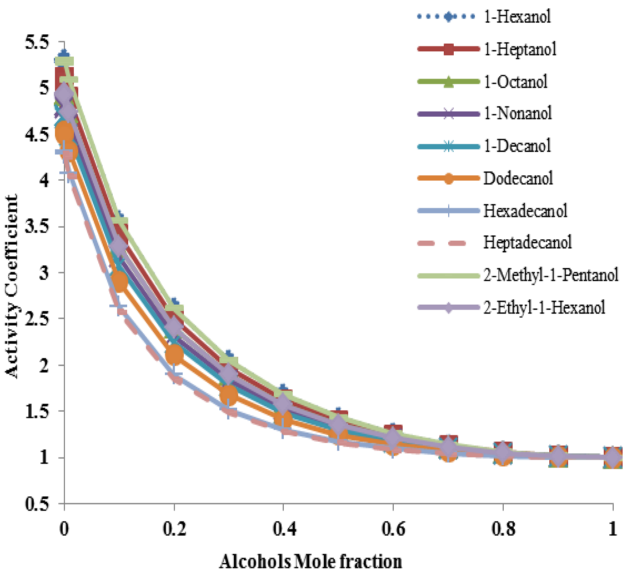

Fig.7 Variation of activity coefficients with mole fraction for alcohols (UNIFAC Dortmund)

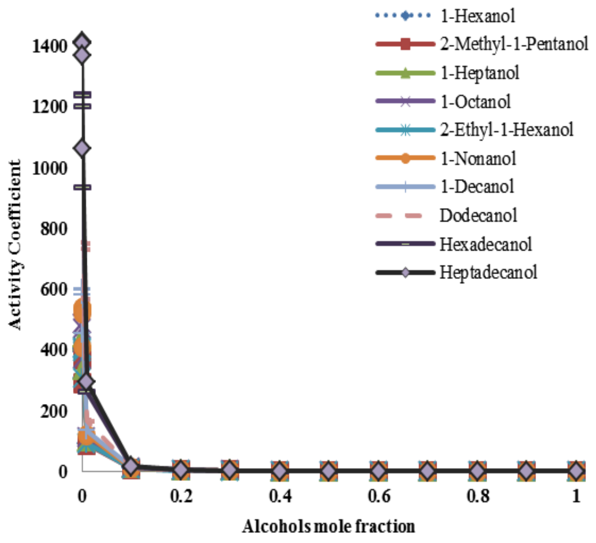

Fig. 8 Variation of activity coefficients with mole fraction for alcohols (UNIFAC Lyngby)

Figs. 7 and 8 show the variation of infinite dilution activity coefficients of alcohols in biphenyl. Alcohols are highly polar because they act as both hydrogen bond donors and acceptors, and are thus much less soluble in biphenyl than the nonpolar alkane, alkene and alkyne VOC solutes. The energy requirements for breaking the strong solute-solute hydrogen bonds and the relatively strong solvent-solvent London bonds in order to form solute-solvent bonds are very high, and little energy would be released in forming solute-solvent bonds. Thus alcohol-biphenyl intermolecular attractions would generally tend not to occur. The UNIFAC – Lyngby overestimate the phase equilibrium under study.

E. *Aldehydes*

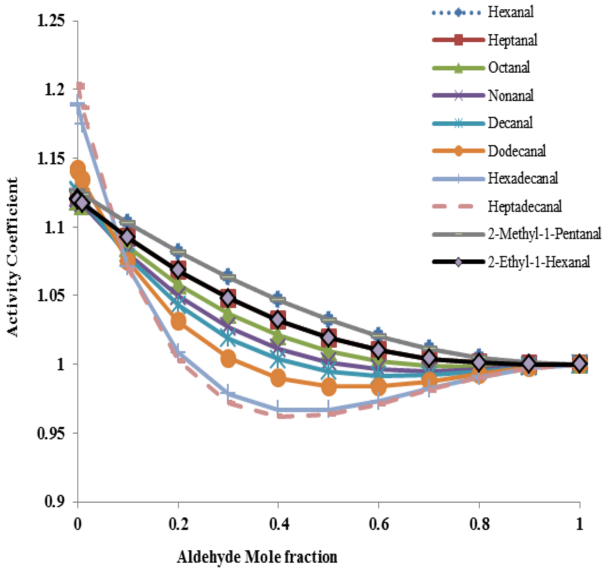

Fig. 9 Variation of activity coefficients with mole fraction for aldehydes (UNIFAC Dortmund)

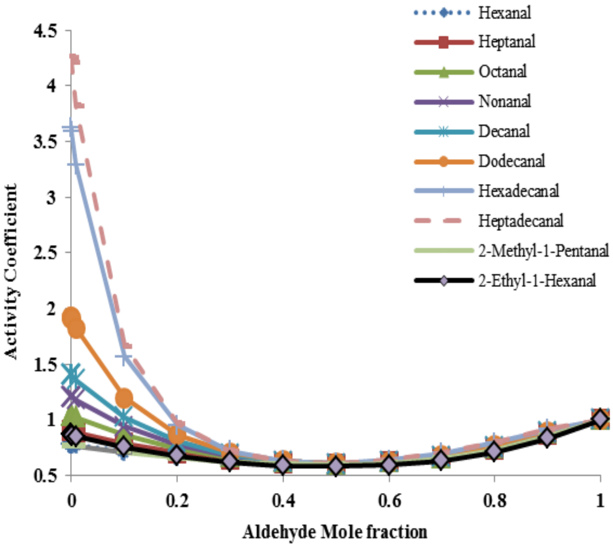

Fig. 10 Variation of activity coefficients with mole fraction for aldehydes (UNIFAC Lyngby)

Aldehydes have permanent dipoles due to the polarized carbonyl groups However unlike alcohols aldehydes do not possess a hydrogen atom attached to the strongly electronegative oxygen atom and can therefore only act as hydrogen bond acceptors – thus no hydrogen bonding occurs in an aldehyde-biphenyl solution. The aldehydes investigated are only slightly polar and interactions between aldehydes and biphenyl intermolecular are predominantly dipole-induced dipole (Debye) van der Waals interactions. The polarity of the aldehydes decreases with increasing aldehyde molecular chain length. Thus Debye interactions dominate with small-sized aldehyde-biphenyl interactions but as the aldehyde molecule becomes increasingly nonpolar with increasing chain length London dispersion forces dominate. The longer the aldehyde unsaturated alkane chain becomes; the more energy is required to break the London interactions between VOC solute molecules to allow solute-solvent bonding to occur. Thus the solubility of aldehydes in biphenyl decreases with increase in VOC size.

F. *Carboxylic Acids*

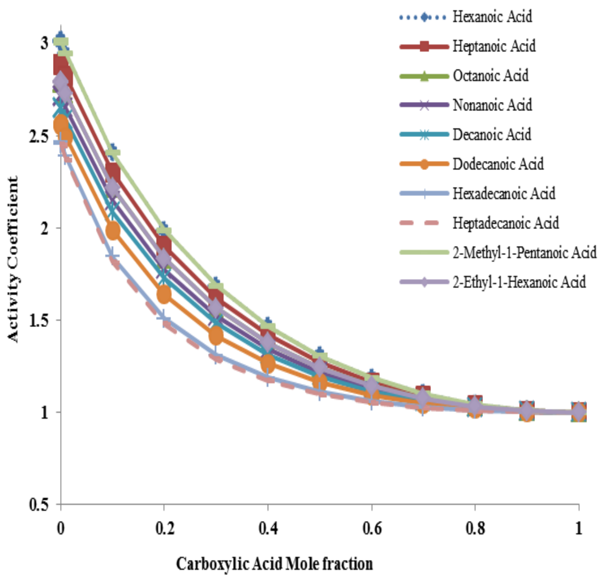

Fig. 11Variation of activity coefficients with mole fraction for carboxylic acids (UNIFAC Dortmund)

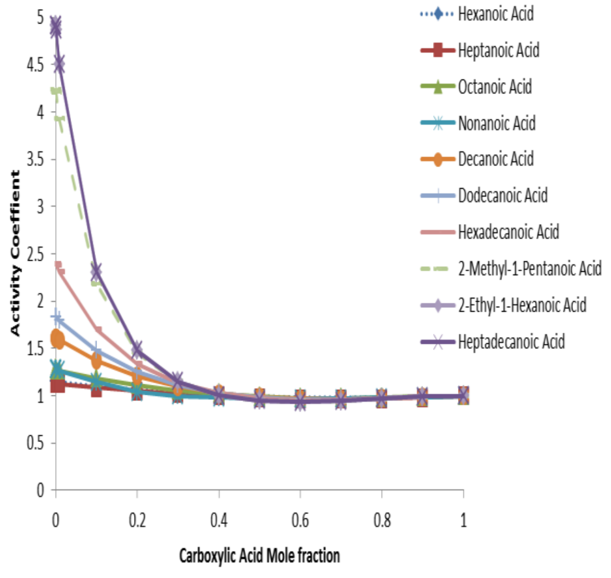

Fig. 12 Variation of activity coefficients with mole fraction for carboxylic acid (UNIFAC Lyngby)

Figs. 11 and 12 show the interaction involving carboxylic acids and biphenyl. Carboxylic acids are highly polar due to the presence of carbonyl and hydroxyl groups which provide two sites for hydrogen bonding to occur. Like the alcohols, carboxylic acids act as both hydrogen bond donors and acceptors. Carboxylic acids exist as dimeric pairs in non-polar solvents such as biphenyl due to their tendency to "self-associate". This tendency, along with the fact that carboxylic acids have two hydrogen bonding sites in comparison to the alcohol family's one site, results in the short chain carboxylic acids being even more insoluble than the short chain alcohols in biphenyl. As for the alcohols, the breaking of solute-solute and solvent-solvent intermolecular bonds to allow for solute-solvent bonds is energetically not viable and thus such bonding tends not to occur.

III. CONCLUSION

This work attempted to model thermodynamic molecular interactions involving selected 60 volatile organic compounds with biphenyl. The Modified UNIFAC Dortmund was found to perform better compared to the Lyngby. Biphenyl showed good absorption affinity for most of the organics studied. Biphenyl has high solvency, flash point, chemical stability, boiling point as well as low reactivity and polarity. Since the melting point of biphenyl is between 69 – 71°C, the absorption system would have to be operated at a temperature of around 75°C (viscosity permitting).

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REFERENCES

[1] F. I. Khan and A. K. Ghoshal, "Removal of volatile organic compounds from polluted air," *Journal of Loss Prevention in the Process Industries,* vol. 13, pp. 527-545, 2000.

[2] S. Vigneron, S. Hermia and J. Chaouki, *Characterization and Control of Odours and VOC in the Process Industries.* Elservier Science, 1994, pp. 11-14.

[3] W. Wang, J. A. Schnoor and J. Doi, *Volatile Organic Compounds in the Environment*, West Conshohocken, ASTM International, 1996, pp. 7-9.

[4] B. V. *EU Legislation: Volatile Organic Compounds (VOC's)*. CBI, Ministry of Foreign Affairs of the Netherlands, 2000, pp.1-4.

[5] T. Y. Joseph, Update on Federal & State VOC Regulations, *ISSA Regulatory Forum*, 2009, pp. 2-11.

[6] *Government Gazette: Republic of South Africa. No.33064*, Pretoria: Government Printer, 2010, pp. 8-11 and 28-29.

[7] E. Muzenda, "Volatile organic compounds – Polydimethylsiloxane Interactions: A Thermodynamic Study Part 1," *in Proc. 3rd Biennial Engineering Conference*, Minna, Nigeria, 2013, pp. 276-280.

[8] J. J. Scheepers and E. Muzenda, "Glycerol – A viable solvent for absorption of high polar solutes 1: Behaviour of molecular interactions," Journal of Clean Energy Technologies, vol. 3, no. 4, pp. 282-286, July 2014.

[9] J. J. Scheepers, E. Muzenda and M. Belaid, "Influence of Temperature and Molecular Structure on Organics-Biodiesel Interactions using Group Contribution Methods," ufacturing Engineering and Engineering Management, IAENG, London, UK, 4-6 July *In Proc. World Congress on Engineering, London,* 2012, vol 3, pp. 1411-1416.

[10] J. J. Scheepers, E. Muzenda and M. Belaid**,** "Influence of structure on fatty acid ester – alkane interactions," *In Proc. International Conference Proceedings of the Planetary Scientific Research Centre,* Bangkok, 2012, pp. 93-102.

[11] J. J. Scheepers, E Muzenda and M Belaid**,** "Influence of structure on fatty acid ester – alkane interactions" International Conference on Chemical Engineering and its Applications, Bangkok, September 8-9, *In International Conference Proceedings of the Planetary Scientific Research Centre,* pp. 93-102, 2012.