Estimating Acute Toxic Action of Sulfur Containing Compounds in the Petroleum

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***Abstract**: Sulfur being the third most abundant element next to carbon and hydrogen poses a serious threat in view of both economy and environment. Acute toxicity is one of a batch of tests used in environmental risk assessment to determine the safe use and disposal of organic chemicals. Estimation methods based on readily available chemical properties that can be correlated with acute toxicity are useful for identifying compounds likely to present the greatest environmental risk and for gaining an understanding of the mechanism of toxicity. It is necessary to distinguish between general toxicity (or narcosis) and specific (or reactive) toxicity. General toxicity occurs by non-specific disruption of the functioning of the cell membrane. Specific toxicity refers to chemicals that interact with or disrupt the function of a defined receptor site. The aim of this work is to define the acute toxic action of sulfur containing compounds which can be found in the petroleum.*

***Keywords:** acute toxicity, sulfur compounds, petroleum*

1. INTRODUCTION

Petroleum is one of the most complex mixtures known with respect to the number of individual species. The composition of crude oil can vary greatly from source to source. However, all crude oils are mainly composed of carbon and hydrogen in the form of alkanes, naphthenes and aromatics, i.e. hydrocarbons. In addition, minor amount of sulfur-, oxygen- and nitrogen-containing heterocycles, and trace amount of metals like vanadium and nickel are also found. The abundance of heteroatoms rises with increase in average molecular weight of the sample, which in turn is related to boiling point of distillation. Although heterocycles containing S, O and N represent a minor portion in most crude oils, they are of crucial importance for exploration, production and refining of petroleum. Generally, sulfur content in crude oils varies from 0.05 to 13.95 wt %. Oils containing, however, more than 1 wt % are considered as sulfur rich oils [8].

The trend for limits on sulfur content in transportation fuels, due to environmental pollution, is gradually declining. SOx, a major air pollutant causing acid rain, from petroleum-derived fuels also poses a serious threat to the environment. Sulfur compounds also affect the emission of NOx and hydrocarbons from automobile engines by reducing the activity of catalytic converters. Moreover, sulfur oxides have detrimental effects on human health, wildlife and agricultural productivity. Therefore, most countries have defined the limits on sulfur in transportation fuels, being the major source of SOx, in order to protect the environment [8].

The price of crude oil, the major backbone of a developed economy, is largely decided by the amount of sulfur in it. Moreover, sulfur being the most abundant hetero element in crude oil is of more concern than other heteroatoms. However, the source of such high amount of sulfur in fossil fuels still remains a mystery. Sulfur exists both in aliphatic and aromatic form in crude oil. All are collectively termed organic sulfur compounds (OSC) [8].

Sulfur is in the same column of the periodic table as oxygen, but being the third-period element means that sulfur is less electronegative and more polarizable than oxygen. Thus, thiols and sulfides bear an obvious resemblance to alcohols and ethers, respectively. Sulfides are easily oxidized; initially to produce sulfoxides, whereas further oxidation leads to the formation of sulfones. Sulfoxides and sulfones are typically represented as having sulfur–oxygen double bonds and thus an expanded octet around the sulfur. However, the sulfur-oxygen double bond is not a double bond in the same sense as a carbon–carbon or carbon-oxygen double bond. In the latter two cases, the “second bond” arises from -overlap of p-orbitals. Because sulfur has lower energy d-orbitals, it is thought that the sulfur–oxygen double bond is a result of an overlap of an oxygen p-orbital with a sulfur d-orbital. It was hypothesized that this atypical double bond may affect the toxicity of sulfur-containing compounds [10]. The aim of this work is to define the acute toxic action of sulfur containing compounds which can be found in the petroleum.

2. MATERIAL AND MEYHODS

Compounds. The organic sulfur compounds for acute toxicity (aquatic and terrestrial species) were collected. The name of compounds are presented (Table 1).

Acute Aquatic Toxicity Data. Toxicity values of sulfur compounds to *Tetrahymena pyriformis* were obtained from the literature [10] and reported in Table 1. Population growth impairment was assessed after 40h with the common ciliate *T. pyriformis*.

Acute Terrestrial Toxicity Data. The experimental data for rat (oral LD_{50} values) were collected from the literature [3].

EcoSAR software. EcoSAR is a user-friendly computer programme developed and routinely applied by the US EPA for predicting aquatic toxicity to fish, daphnids and algae [4]. This software was used for grouping of the chemicals.

Log P. Data for the logarithm of the 1-octanol-water partition coefficient (log P) were obtained from the KOWWIN software [5]. Where possible measured log P values were verified and used in preference to calculated values.

Baseline models. In this study several models were used for non-polar compounds to aquatic and terrestrial species to determine the acute toxicity of organic sulfur compounds (Tables 1).

Baseline model (saturated alcohols and ketones) of *Tetrahymena pyriformis* [2]:

(1) $\log(1/IGC_{50})=0.78*\log P–2.01$

n = 87 R^2 = 0.96 s = 0.20 F = 2131

Baseline model (saturated alcohols and ketones) of Rat (oral LD_{50}) [6]:

(2) $\log(1/LD_{50}) = 0.805*\log P – 0.971*\log(0.0807*10^{\log P}+1) + 0,984$

n = 54 R^2 = 0.824 s = 0.208 F = 35.3

Excess toxicity. The property - excess toxicity - was used to define the toxicity of chemicals (reactive or nonrective) [6]. The extent of excess toxicity was determined as the toxic ratio (TR), which was calculated by the following equations 3-4 [6, 7]:

(3) $TR = \log(1/C)exp – \log (1/C)calc$

(4) TR=(predicted baseline toxicity)/(observed toxicity)

Mode of action. For environmental toxicants four broad classes of mode of action have been identified – from class I to class IV [9, 11].

3. RESULTS AND DISCUSSION

There are several modes of action for acute toxicity. The sulfur compounds were classified as neutral organics, thiols (mercaptans), thiophenes, vinyl/allyl sulfones from the EcoSAR software. For the organic sulfur compounds mode(s) of toxic action, where toxicity is observed to be (or not to be) in excess of narcosis, the possible mechanism is (ir)reversible, i.e. the toxicity is (not) observed to be related to hydrophobicity and is (not) in excess of baseline toxicity for the compounds (Fig. 1).

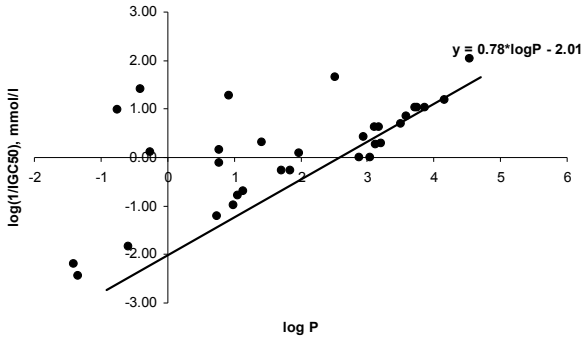

Fig. 1: Plot of toxicity to *Tetrahymena pyriformis* vs log P for sulfur compounds showing baseline toxicity.

Therefore, among sulfur compounds are recognized narcotics and reactive chemicals.

Tab. 1: Experimental and predicted values of organic sulfur compounds

Name of compound	logP	Exp. T. pyriformis log(1/IGC_{50}), Mmol/l	Pred. T. pyriformis log(1/IGC_{50}), Mmol/l /TR	Exp. oral Rat LD_{50} Mmol/Kg	Pred. oral Rat LD_{50} Mmol/Kg / TR
Cycloheanethiol	3.05[b]	-0.004	0.369/-0.37		
1-Heptanethiol	3.72[b]	1.02	0.892/0.13		
Hexane-1,6-dithiol	3.18[b]	0.63	0.470/0.16		
Octane-1,8-dithiol	4.16[b]	1.19	1.235/-0.04		
1,4-Dithiane	0.77[a]	-0.11	-1.409/1.30	23.02	27.54/1.20
2,2'-Bithiophene	3.75[a]	1.04	0.915/0.13		
Propyl sulfide	2.88[b]	-0.003	0.236/-0.24		
n-Butyl sulfide	3.87[b]	1.04	1.009/0.03	15.18	25.25/1.66
Sulfurous acid, diethyl ester	0.99[b]	-0.99	-1.238/0.25		
Di-n-propyl sulphite	1.97[b]	0.09	-0.473/0.56		
Diethylsulfate	1.14[a]	-0.70	-1.121/0.42	5.71	38.55/6.75
Sulfuric acid, dibutyl ester	3.11[b]	0.62	0.416/0.20		
Dimethyl sulfoxide	-1.35[a]	-2.44	-3.063/0.62	185.59	0.79/0.004
Dipropyl sulfoxide	0.74[b]	-1.22	-1.423/0.21	3.72	26.60/7.14
1,1'-sulfinylbisbutane	1.72[b]	-0.26	-0.668/0.41		
Dimethyl sulfone	-1.41[a]	-2.20	-3.110/0.91	53.12	0.70/0.013
Diethyl sulphone	-0.59[a]	-1.84	-2.470/0.63		

1,1'-sulfonylbis butane	1.84[b]	-0.26	-0.575/0.31		
Vinyl sulfone	-0.40[b]	1.41	-2.32/3.73	0.27	4.45/16.44
Methyl vinyl sulfone	-0.75[b]	0.99	-2.59/3.59	5.37	2.37/0.44
Ethyl vinyl sulfone	-0.26[b]	0.11	-2.213/2.32		
Thiophenol	2.52[a]	1.66	-0.044/1.70	0.42	40.89/97.51
Thianaphthene	3.12[a]	0.26	0.424/-0.16		
Phenoxathiin	4.54[a]	2.04	1.531/0.51		
(Ethythio)benzene	3.20[a]	0.30	0.486/-0.19		
Benzene, (propylthio)- (9CI)	3.58[b]	0.86	0.782/0.08		
(Allylthio)benzene	3.51[a]	0.69	0.728/-0.04		
Phenyl vinyl sulphide	2.95[b]	0.42	0.291/0.129		
Phenyl vinyl sulphoxide	0.78[b]	0.16	-1.402/1.56		
(Ethylsulphonyl)benzene	1.05[b]	-0.79	-1.191/0.40		
Allyl phenyl sulfone	1.41[b]	0.31	-0.910/1.22		
Phenyl vinyl sulphone	0.92[b]	1.28	-1.292/2.57		

[a]Experimental value of logP; [b]Calculated value of logP.

A number of reliable baseline equations are available for different organisms (aquatic (*Tetrahymena pyriformis*) and terrestrial (Rat)) and endpoints (IGC_{50}, LD_{50}). Baseline models (eqs 1-2) for different species (aquatic and terrestrial) were applied to organic sulfur compounds (Table 1). On the basis of calculated and experimental values for acute toxicity, the toxicity ratio (TR) as the ratio of the calculated baseline toxicity over the experimentally determined value was calculated. A TR-value less than one could indicate rapid hydrolysis and/or biotransformation of the parent compound by the organism to non-toxic metabolites [1].

4. CONCLUSION

A series of aliphatic and aromatic sulfur-containing compounds were evaluated in the *T. pyriformis* population growth impairment assay (IGC_{50}) and oral Rat (LD_{50}) for acute toxicity. The endpoints are a result of different

routes of exposure in various species. The effect of a chemical is dependent on the species, route of exposure, and dose. The structure of sulfur compounds is varied, suggesting a different reactivity (non-covalent and covalent interactions).

5. REFERENCES

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