A Review on Infinite Dilution Activity Co-Efficient (IDAC): A Tool for Environmental Pollution Assessment

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Abstract: IDAC values are the important physical property in environment field, from IDAC the partition co-efficient of the different substances can be predicted. In review of the methods different kind of experimental method like, GLC and Dilutor method and different kind of predictive methods Gibbs' Free Energy, NRTL Model, UNIFAC Method, UNIQUAC Method, ASOG Method are discussed. Importance of IDAC in environment is highlighted.

Index Terms: Infinite Dilution, Partition CO-efficient, GCT, Dilutor Method, UNIFAC

I. INTRODUCTION

We know that the ratio of activity to some convenient measure of the concentration in the liquid mixture is known as activity coefficient and it can be mathematically defined as,

$$\gamma_i = \frac{a_i}{x_i} = \frac{f_i}{x_i f_i^o} = \frac{y_i P}{x_i P_i^s}$$

Infinite dilution activity coefficients (γ^∞) characterize the behavior of a single solute molecule completely surrounded by solvent, thus it generally indicates a maximum non-ideality and provides incisive information regarding solute-solvent interactions in the absence of solute-solute interactions and is actually an excess property. It is a strictly dilute solution property, and can be directly used to determine the accurate equilibrium composition of a dilute mixture, which is very useful to many industrial processes such as high-purity extraction, azeotropic distillation and specialty chemical separation. [2]

II. IMPORTNCE OF IDAC IN ENVIRONMENTAL STUDIES

The distribution of a chemical is distributed in the environment depends upon how the chemical is released, how quickly it is degraded by microbes, and the mechanisms for its distribution throughout the environment. The persistent chemicals, such as DDT, polychlorinated biphenyls (PCBs), poly nuclear aromatic hydrocarbons (PAHs), etc., released into the environment over a period of years achieve a state of approximate phase equilibrium between the environmental compartments that include water, air, soil, sediment, suspended sediment, biota, and atmospheric particulates. Since the concentrations of pollutants in the environment are, thankfully, very low (usually in the parts per million or parts per billion range, or less), it is the infinite dilution behavior of the chemical that is important. In environmental studies it is common to define partition coefficients K based on concentration. For example, referencing all concentrations to that of the contaminant in water, we have

$$K_{AWi} = \frac{C_i^A}{C_i^W}, \; K_{BWi} = \frac{C_i^B}{C_i^W}, \; K_{SWi} = \frac{C_i^S}{C_i^W} \; and \; K_{SDWi} = \frac{C_i^{SD}}{C_i^W}$$

Here the superscripts A, W, B, S and *SD* indicate air, water, biota, soil and sediment, respectively, and C is concentration, typically in mg/m^3 or mmol/m^3. If the concentration of an environmental pollutant is known in one of the environmental compartments, its value in any or all other compartments can be computed provided the relevant partition coefficients are known. Of these partition coefficients, one can compute exactly is that between air and water which, at 25°C, is

$$K_{AW,i} = 7.262x10^{-9} \gamma_i^\infty P_i^s = 7.262x10^{-9} H_i$$

if the vapor pressure is expressed in Pa and the Henry's law constant in Pa/mol fraction. Given the variability of compositions of soil, sediment and biota, the other partition coefficients are obtained either by direct measurement or correlation; only correlations will be considered

here. A characteristic of most organic pollutants is that they are hydrophobic; in partitioning between an aqueous phase and an organic phase, they will be preferentially concentrated in the organic phase. One measure of this hydrophobic commonly used in environmental engineering is the octanol-water partition coefficient. This is determined by mixing n-octanol and water, adding a very small amount of solute, allowing the system to equilibrate, and then the concentration of the chemical in each of the phases is measured. The ratio of the concentrations of the species in the octanol-rich phase (27% water) to the water-rich phase (essentially pure water) is the octanol-water partition coefficient of the species K_{ow} values of the octanol-water partition coefficient range from less than unity (hydrophilic compounds) to values of the order of tens or hundreds of millions for very hydrophobic compounds. For this reason it is more common to report $Log_{10}K_{OW}$, since most organic pollutants are hydrophobic, they preferentially partition into the organic matter of soil and sediment or the lipids of the biota, and this is the basis of the correlations that are used for the partition coefficients. As a first estimate, the following correlations are used:

$$K_{BW,i} = f_B K_{OW,i} \quad K_{SW,i} = 0.62 f_i K_{OW} \quad and \quad K_{SDW,i} = 0.53 f_{SD} K_{OW}$$

where is the fraction of the biota that is lipids (typically 5% for aquatic biota), and are the fractions of soil and sediment that are organic matter, typically 2 wt % and 5 wt %, respectively. Note that there is a many order of magnitude variation in the concentration of the chemical, benzopyrene, between the air, water, soil and biota, and this is at least qualitatively predicted from this simple model. This large increase in composition is the result of phase equilibrium! Given the heterogeneity of the environment, and the simplicity of the model, this order of magnitude agreement is rather remarkable. Higher level models take into account mass transport and biodegradation effects, and lead to more accurate predictions.

Table I. Distribution of Benzo[a]pyrene in Southern Ontario [18]

Compartment	Concentrations ng/m³	
	calculated	reported
water	2.82x10⁴	2.82x10⁴
air	0.55	1.3, 4.7, 7.1
soil	3.3x10⁸	1.5x10⁸, 4.5 to 7.5x10⁸
sediment	7.1x10⁸	1 to 4x10⁸
fish	1.3x10⁹	1.4x10⁸

An important observation is that such food chain accumulation of chemicals does not occur until the value of $LogK_{ow}$, exceeds about 4, and then increases rapidly with values of this parameter until the molecules become so big as to be not easily transported across the gut. The insecticide DDT has a value of Log K_{ow}, of 6.19 ($K_{ow,..}=1,550,000$) and bio accumulated to such an extent as to seriously harm eagles and other birds of prey. The octanol-water partition coefficient is central to ascertaining the distribution of a chemical in the environment, both as a result of the equilibrium phase behavior, and by food chain bioaccumulation. Therefore, let us return to the question of determining the octanol-water partition coefficient. The direct way of measuring K_{wo}, can be a very difficult to do accurately since very hydrophobic chemicals adsorb from the aqueous phase onto various surfaces after phase disengagement and before analysis giving unrealistically low octanol-water partition coefficients, or microscopic emulsions may form resulting in an incorrect large value of the octanol-water partition coefficient. To avoid these problems, simple correlation for the octanol-water partition coefficient of a species may be used

$$\log_{10} K_{OW}, i = -0.65 + 0.91 \log_{10} \gamma_i^{w,\infty} - 0.911 \log_{10} \gamma_i^{O,\infty}$$

where $\gamma_i^{W,\infty}$ and $\gamma_i^{O,\infty}$ are the infinite dilution activity coefficients of the chemical in pure water and in pure octanol, respectively. The advantage of this correlation is that instead of performing a difficult octanol-water partitioning measurement, one can instead use the methods that have been discussed, such as the relative gas chromatographic method, to do two infinite dilution activity coefficient measurements, and from these data determine how a long-lived chemical will partition in the environment, and whether it will food chain bioaccumulate. For the very hydrophobic organic chemicals on the Environmental Protection Agency Priority Pollutant List, the infinite dilution activity coefficients of the chemicals in water can be very large, while the values in octanol are frequently of the order of unity. Therefore, to almost the same degree of accuracy, the simpler correlation requiring only the infinite dilution activity coefficient of the component in water (1).

$$\log_{10} K_{OW,i} = -0.486 + 0.806 \log_{10} \gamma_i^{W,\infty}$$

III. IMPORTANCE OF THE PARTION COEFFICIENT IN THE ENVIRONMENT

The term partition coefficient commonly refers to the equilibrium distribution of a single substance between two solvent phases separated by a boundary. The phases may be pure substances or solutions. One or both solvents are condensed phases. Partition coefficients are sometimes called distribution coefficients. A few well-known examples may be mentioned. When one phase is a gas above its critical temperature and the other is a liquid, the partition coefficient is known also as Henry's constant or simple solubility. It is tacitly assumed here that solute concentration is low and is effectively at "infinite dilution". In vapor-liquid equilibrium, the corresponding quantity is the activity coefficient at infinite dilution.

The continuous usage and the disposal of the polluted chemicals contaminated the environment. The characterization of pollutants is of growing interest as concerns about the environment increase. One parameter useful in predicting the fate of a chemical in the environment, the infinite dilution activity coefficient, has been determined here for several EPA priority pollutants in l-octanol at 25 C using a relative gas-liquid chromatographic measurement technique. A simple correlation has been developed relating the limiting activity coefficients of a species in pure water and in pure 1-octanol to its octanol/water partition coefficient. Agreement between the experimental results and published values is very good. The method developed here of computing the octanol/water partition coefficient from gas chromatographic measurements of its infinite dilution activity coefficients is an improvement over traditional partition coefficient determination methods in that it is easier and quicker, without a loss of accuracy. Furthermore, we show that this method is applicable to chemicals covering a large range of hydrophobicities.

Another property useful for the characterization of pollutant behavior in the environment is the octanol/water partition coefficient, K_{Ow} defined for a species i as

$$K_{ow} = C_i^{op} / C_i^{w}$$

where C_i^{oP} and C_i^{w} are the concentrations of the species in an octanol-rich phase and in a water-rich phase, respectively, when l-octanol, water, and a small amount of the species are allowed to come to equilibrium. It should be noted that in octanol/water partitioning a t 25 °C, the water-rich phase is essentially pure water (99.99 mol % water) while the octanol- rich phase is a mixture of l-octanol and water (79.3 mol % l-octanol). Utilizing liquid molar volumes and liquid-liquid equilibrium relationships at 25 °C, the octanol/water partition coefficient of a species may be related to its infinite dilution activity coefficients in each of the phases by, [3]

$$K_{OW} = 0.1508 \, \gamma_i^{\infty,w} / \gamma_i^{\infty,op}$$

$\gamma_i^{\infty,w}$ =IDAC of spices I in water

$\gamma_i^{\infty,op}$ = IDAC of spices I in 1-octanol

Some Equation of the Partition co-efficient [3]
1. The relation between $\tilde{a}8$ and distribution coefficient K_{aw} can be presented as follows.

$$K_{aw} = \frac{\gamma_i^{\infty} P_i^s v_w^L}{RT}$$

K_{aw} distribution coefficient

P_i^s saturation vapour pressure of the pure solute i (Pa)

v_w^L liquid molar volume of pure solvent

T temperature of the cell (K)

2.

$$K_D = \left(\gamma_w^{\infty} / \gamma_B^{\infty} \right)\left(V_w / V_B \right)$$

γ_w^{∞} =IDAC of solute in water

$\gamma_\bullet^{\infty}$ = IDAC of solute in solvent

V_w=molar volume of water

V_B= molar volume of solvent

3. Ginger and co-workers correlate IDAC and K_{ow} the following equation (1)

$$\log K_{ow} = -0.65 + 0.91\left(\log \gamma_i^{w,\infty} - \log \gamma_i^{o,\infty}\right)$$

γ^{∞} = Infinite dilution activity co-efficient

4. MacKay represent the K_{ow} in the following equation (1)

$$K_{ow} = 0.115 \left(\gamma_i^{w} / \gamma_i^{o} \right)$$

γ_i^{w} = IDAC in water

γ_i^o = IDAC in octanol

5. K_{ow} can be found out by following equation also [1]

$$K_{ow} = 0.138\left(\frac{\gamma_i^{w,\infty}}{\gamma_i^{o,\infty}}\right)$$

IV EXPERIMENTAL METHOD FOR FINDING IDAC

(1) Dilutor Method:

The dilutor technique used to determine the activity coefficients at infinite dilution. The principle of the measurement is that a highly diluted component is stripped from the solvent by a constant inert gas flow. The variation of the solute concentration in the vapor phase is recorded using gas chromatography, whereby the flow of the inert gas, helium, is controlled and measured using a digital mass flow controller Bronkhorst. Before helium enters the equilibrium cell it is saturated with the solvent or solvent mixture in a pre saturation cell. [4]   Figure 1 explains the equipment.
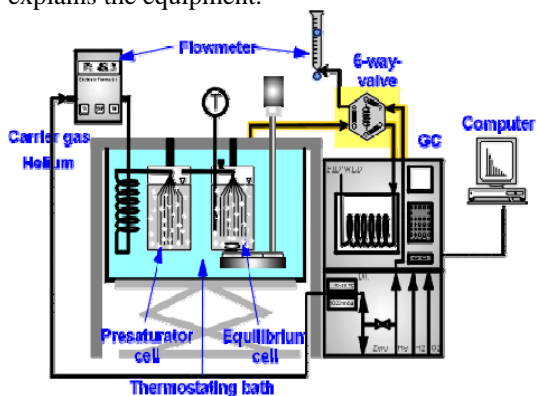

Fig 1 Gas Chromatograph for Dilutor Method

(2) Gas Liquid Chromatography (GLC) [6]

In headspace gas chromatography, phase equilibrium is first achieved between the volatile components of a prepared liquid sample and the vapor phase in a sealed vessel. A sample of the vapor phase is then removed for gas chromatographic analysis. From the prepared concentration of the VOC in the liquid phase, and its measured vapor phase concentration, its activity coefficient can be calculated. Doubly distilled water is to be used in all measurements. The equipment is described in figure 2.
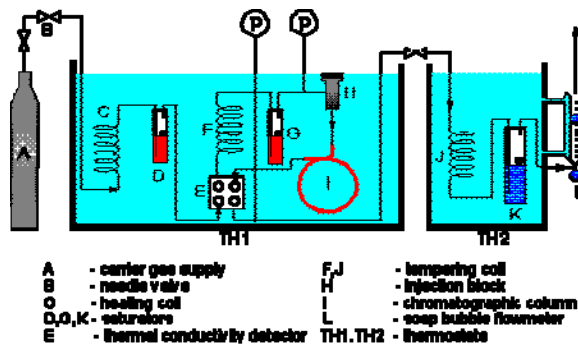

A	- carrier gas supply	F,J	- tempering coil
B	- needle valve	H	- injection block
O	- heating coil	I	- chromatographic column
D,O,K	- saturators	L	- soap bubble flowmeter
E	- thermal conductivity detector	TH1,TH2	- thermostats

Fig 2. Gas Chromatograph for GLC Method

V PREDICTIVE METHODS FOR THE ESTIMATION OF THE IDAC

(1) Activity Coefficients From Gibbs Free Energy [8]

Activity-coefficient equations often have their basis in Gibbs free-energy models. For a non-ideal solution, the molar Gibbs free energy, *g*, is the sum of the molar free energy of an ideal solution and an excess molar free energy g^E for non-ideal effects. The partial excess molar free energy is related by classical thermodynamics to the liquid-phase activity coefficient by the Equation.

(2) NRTL Model [7]

The nonrandom, two-liquid (NRTL) equation developed by Renon and Prausnitz. The NRTL equation is applicable to multi component vapor–liquid, liquid–liquid, and vapor–liquid–liquid systems. For multi component vapor–liquid systems, only binary-pair constants from the corresponding binary-pair experimental data are required

(3) UNIQUAC Model [6]

In an attempt to place calculations of liquid-phase activity coefficients on a simple, yet more theoretical basis, Abrams and Prausnitz used statistical mechanics to derive an expression for excess free energy. Their model, called UNIQUAC (universal quasichemical), generalizes a previous analysis by Guggenheim. However, rather than local volume fractions or local mole fractions, UNIQUAC uses the local area fraction θ_{ij} as the primary concentration variable.

(4) UNIFAC Model [6]

Liquid-phase activity coefficients must be estimated for non-ideal mixtures even when experimental phase equilibrium data are not available and when the assumption of regular

solutions is not valid because polar compounds are present. For such predictions, Wilson and Deal and then Derr and Deal, in the 1960s, presented methods based on treating a solution as a mixture of functional groups instead of molecules. In practice, about 50 functional groups are used to represent literally thousands of multi component liquid mixtures. To estimate the partial molar excess free energies, $\bar{g}_i^E$ and then the activity coefficients, size parameters for each functional group and binary interaction parameters for each pair of functional groups are required.

Advantages over other group-contribution methods:
(1) It is theoretically based on the UNIQUAC method; (2) The parameters are essentially independent of temperature; (3) Size and binary interaction parameters are available for a wide range of types of functional groups; (4) Predictions can be made over a temperature range of 275–425 K and for pressures up to a few atmospheres; and (5) Extensive comparisons with experimental data are available. All components in the mixture must be condensable.

(5) ASOG Method [6]

ASOG is widely applied to predict the liquid-phase activity coefficients. The activity coefficient of component *i* is given as

$$\ln \gamma_i = \ln \gamma_i^{FH} + \ln \gamma_i^{G}$$

Where the first term of right-hand side is the combinatorial part due to the entropy of mixing, which is given by the Flory–Huggins (FH) equation and the second term is interaction part between group pairs (G). The detailed mathematical representation of above methods is presented elsewhere [6]

VI Summary

In the present review work some key uses of IDAC are highlighted and methods to determine IDAC and predict the same have been listed. These methods are helpful in estimating the fate of any pollutants in the environmental impact.

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