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Distribution of Hydrocarbons Among Oil, Water and Vapor Phases During Oil Dispersant Toxicity Tests

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A major consideration in determining the desirability of using dispersants as an oil spill countermeasure is the extent to which the dispersant alters the exposure of water column organisms to the oil. The role of the dispersing chemical is to reduce the oil-water interfacial tension and thus increase the tendency for oil droplets to shear from the slick and become incorporated in the water column. Aquatic biota will thus be exposed to higher concentrations of dispersed oil, possibly to higher concentrations of dissolved oil and they will also be exposed to the dispersant itself. The obvious approach to assessing the severity of the exposure increase is to undertake standard toxicity tests in which organisms are exposed to dispersed oil, then attempt to predict the environmental toxic effect by comparing test and environmental exposures. Even if this is impossible, the toxicity test is invaluable as a method of ranking organisms, oils and dispersants in order of vulnerability or toxicity and in investigating under controlled conditions the effect of variables such as temperature, oil concentration, exposure time and organism condition. This issue has been thoroughly reviewed and discussed in the text by BEYNON & COWELL [1974], a compendium of relevant literature has been assembled by DOE et al. [1978] and a standard test procedure has been described by BLACKMAN et al. [1977].

In this paper, we address the problem of calculating the distribution of specific hydrocarbons between the oil phase (slick or dispersed), the aqueous phase and the vapor phase during a toxicity test. It is suggested that this calculation is an essential component of interpreting the toxicity observations since, in many cases, the exposure of the organism to hydrocarbons depends on the relative volumes of these three phases. It is not immediately obvious, for example, that increasing the amount of oil used in the test can have a profound effect on the exposure to dissolved hydrocarbons, even at the same dispersed oil concentration. Further, it is believed that progress in understanding the fundamental toxicological effects of dispersed oil can only be made if the overall toxic effect is separated into the components of:-

(i) effect of dissolved hydrocarbon, which is presumably very dependent on the concentration and nature of the dissolved components,

(ii) effect of dispersed oil particles, which is presumably a function of particle size relative to the size or configuration of the receptor, and

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(iii) the effect of the dispersant chemicals.

Ideally, any toxicity assessment should include an investigation of which effect dominates. This is amenable to experimental determination since dissolved hydrocarbon solutions can be made up to simulate those existing in the text, dispersed concentrations of "non-toxic" oils can be prepared, and the dispersant itself can be readily tested for toxicity.

The approach taken here is to set out the equations describing hydrocarbon distribution in a hypothetical test, identify the controlling parameters, then illustrate the utility of the approach with an example. Although some of the physical-chemical concepts may be obscure to some biologists, this need not prevent the final equations being used since they are simple and do not require a knowledge of the derivation.

Theoretical

Consider a three-phase system consisting of oil (subscript o), water (w) and vapor (v) of volume V_o, V_w and V_v (m^3) at equilibrium and at the same temperature T(K). A hydrocarbon (such as benzene) will partition between these phases such that its chemical potential or fugacity (f atm) is equal in all phases. If we assume that dispersed oil and oil present in bulk form have identical compositions, we can ignore this difference in physical condition. The fugacity in each phase can be related to concentration as follows:

Vapor Phase

Equating fugacity to partial pressure P and using the gas law with constant R (atm m^3/gmol K) the concentration of the component C_v(gmol/m^3) becomes

$$C_v = P/RT = f/RT$$

Oil Phase

We assume Raoult's Law to apply in which the partial pressure is the mole fraction x times the pure component vapor pressure P^S. If the oil molar volume is v m^3/gmol, the concentration C_o becomes

$$C_o = x/v = f/vP^S \text{ since } f = xP^S$$

It should be noted that the correct vapor pressure here is that of the liquid hydrocarbon. It is thus necessary to estimate by extrapolation the vapor pressure of the subcooled liquid for those hydrocarbons (such as naphthalene) which are normally solid at the test temperature.

Water Phase

The simplest approach, i.e. to linearly reduce the pure component solubility in proportion to the mole fraction, tends to give low estimates and LEINONEN [1976] has proposed a correction or enhancement factor e which gives more accurate predictions of solubility in dilute solution. For a pure hydrocarbon, an e value of unity should be used but for dilute solutions, the values given in Table 1 should be used. It can be shown that concentration and fugacity are related through the Henry's law constant H (atm m^3/gmol) which is the ratio of the component vapor pressure P^S and aqueous solubility C_S (gmol/m^3) as follows

$$C_W = fe/H \text{ where } P^S = HC_S$$

For solid hydrocarbons, both C_S and P^S must refer to the same state, usually that of the solid.

Values of molecular weight, P^S, C_S, H and e are given for selected hydrocarbons at 25°C in Table I for both fresh and seawater [MACKAY & SHIU 1975]. The two P^S values for naphthalene are of the solid (S) and subcooled liquid (L). If the original amount of oil introduced is V_1, (which will usually be very close to V_O) and the concentration of the component in that oil was C_1, then a mass balance gives

$$V_1C_1 = V_VC_V + V_OC_O + V_WC_W$$

We ignore here sorption on the apparatus or uptake by test organisms. Substituting fugacity for the concentration terms and rearranging gives

$$f = V_1C_1/\left\{V_V/RT + V_O/vP^S + V_We/H\right\} = V_1C_1/A$$

The fractions of the component in each phase are thus

$$\text{In the vapor} = V_VC_V/V_1C_1 = V_V/RTA$$

$$\text{In the oil} = V_OC_O/V_1C_1 = V_O/vP^SA$$

$$\text{In the water} = V_WC_W/V_1C_1 = V_We/HA$$

where

$$A = V_V/RT + V_O/vP^S + V_We/H$$

The dissolved aqueous concentration C_W is of interest and is given by

$$C_W = fe/H = V_1C_1e/HA$$

Also of interest is a comparison of the aqueous phase concentration of the component with the maximum or equilibrium value which would exist if a large amount of oil was present. This is a measure of the extent to which the concentration of the component in the aqueous phase is lowered by virtue of the relatively low oil volume which may be used in the test. If a significant fraction of the component is dissolved, the concentration in the oil is

TABLE 1

PHYSICAL PROPERTIES OF SELECTED HYDROCARBONS AT 25°C

Hydrocarbons	Molecular wt. g/mole	Vapor pressure atm	Solubility in Water		Solubility in Seawater		Henry's Law Constant H atm.m^3/mole		e
			g/m^3	mole/m^3	g/m^3	mole/m^3	Water	Seawater	
n-pentane	72.15	0.675	38.5	0.534	27.6	0.383	1.26	1.765	1.4
n-hexane	86.17	0.205	9.5 12.3	0.110 0.143	8.06	0.0935	1.86 1.436	2.192	1.4
n-octane	114.23	0.0186	0.66	0.0058			3.19		1.4
n-decane	148.28	1.73×10^{-3}	0.052	3.51×10^{-4}			4.93		1.4
n-dodecane	170.33	1.55×10^{-4}	0.0037	2.17×10^{-5}	0.0029	1.703×10^{-5}	7.135	9.104	1.4
benzene	78.11	0.125	1780	22.79	1391	17.80	5.49×10^{-3}	7.02×10^{-3}	2.2
toluene	92.13	0.353	515	5.59	392	4.26	6.31×10^{-3}	8.30×10^{-3}	2.2
e-xylene	106.17	8.71×10^{-3}	175	1.648	110.9	1.045	5.28×10^{-3}	8.34×10^{-3}	2.2
cumene	120.2	6.03×10^{-3}	50	0.416	42.5	3.536	1.45×10^{-2}	1.705×10^{-2}	2.2
naphthalene	128.17	s. 1.16×10^{-4} l. 3.20×10^{-4}	31.7	0.247	22.0	0.172	4.43×10^{-4}	6.76×10^{-4}	2.2

reduced, thus the dissolved concentration must be correspondingly reduced below the equilibrium value. This complicated and not immediately obvious (and difficult to express) point is most important for hydrocarbons which partition most into the water and thus tend to control the toxic effect of the dissolved oil. These tend to be the aromatics which are the most toxic components.

The ratio of the actual concentration C_w to the maximum achievable concentration C_{wm} is:

$$C_w/C_{wm} = C_o/C_1 = V_1/vP^sA$$

Examination of the equations shows that the partition properties are controlled by the relative magnitudes of the terms (V_v/RT), (V_o/vP^s) and (V_we/H) which respectively are proportional to the amounts of the component in the vapor, oil and water phases and which in total are the term "A". Calculation of these quantities is illuminating in that the overall distribution becomes apparent. Since H, P^s and e are the dependent on the properties of the specific hydrocarbon, the distribution differs from component to component.

A hydrocarbon of high P^s (volatile) and low C_s (insoluble) will have a high H thus the vapor term (V_v/RT) may dominate. This is likely for the lower alkanes which partition into the vapor. For this reason, these compounds are ideal for "head-space" or gaspurging analysis.

Hydrocarbons of high solubility (low H) such as the aromatics will tend to partition into the aqueous phase and the term (V_we/H) will dominate. This occurs especially if the ratio of water to oil volumes is large.

Finally for hydrocarbons of low P^s and low solubility, the term V_o/vP^s dominates, indicating that the component remains in the oil phase. Most hydrocarbons of high molecular weight are in this class.

In summary, to calculate the partition of a specific hydrocarbon, one first assembles values of V_1, V_o (which can be assumed to equal V_1), V_w and V_v, the properties P^s, H (possibly from P^s/C_s), e and v which can be estimated from the oil density ρ (g /cm^3) and its mean molecular weight M (g/mol) as:

$$v = 10^{-6}\ M/\rho$$

For example an oil of mean molecular weight 240 and density 0.8 will have a molar volume of 300 x 10^{-6}m^3/mol (equivalent to 300 cm^3/mol). The gas constant R has a value of 82 x 10^{-6} atm m^3/gmol. C_1 can be estimated from a gas chromatograph of the oil using standard procedures.

The groups (V_v/RT), (V_o/vP^s) and (V_we/H) can then be calculated and summed to give A. The fraction in each phase can then be calculated as each term divided by A. The water phase concentration C_w and the fraction which this is of the maximum value can also be calculated if desired. The concentration in gmol/m^3 if multiplied by the molecular weight (g/gmol) gives the concentration in g/m^3 which is equivalent to mg/litre or parts per million. The procedure can be repeated for as many components as required but it is simpler and may be preferable to lump all the single ring aromatics (which are the dominant compounds in solution) into one pseudo-component and assign it mean properties such as those of toluene.

DISCUSSION

Using this procedure, the implications of changing the test procedure can be readily explored. If vapor losses are too high, it will be desirable to reduce V . Increasing the amount of oil will tend to increase C_w to its maximum value which occurs when

$$V_o/vP^s \approx A$$

and thus $C_w \approx C_1 evP^s/H \approx C_1 evC_s$

The group (evC_s) is thus an effective oil-water partition coefficient.

An interesting and important aspect of dispersed oil toxicity testing is the effect of oil weathering or evaporation. Weathered oils usually have lower toxicities because of the loss of volatile, soluble aromatics [MACKAY & SHIU 1976]. From the equations, it is possible to calculate the dissolved hydrocarbon content for various degrees of weathering (provided that corresponding oil analyses are obtained). Comparison of these concentrations with the toxicities should reveal the relative toxic contributions of the dissolved and particulate oil.

The effect of test temperature on concentration and partition can be readily assessed if data are available for the temperature dependence of P^s and C_s. Vapor pressure data for hydrocarbons are available from WILHOIT & ZWOLINSKI [1971]. Generally, the effect of temperature on C_s is small and can be ignored in all but the most accurate work.

A useful approach in elucidating the relative toxic contributions of dissolved and particulate oil and of individual hydrocarbons may be to prepare and test synthetic solutions of hydrocarbons in water similar to those which occur during dispersed oil test conditions. It may also be desirable to prepare dispersed solutions of "insoluble" oils such as long chain alkanes to investigate the effect of the dispersed oil alone.

Finally, it must be emphasised that calculation of aqueous concentration is no substitute for actual measurement. It is recommended that rather than rely entirely on calculation, the dissolved and particulate oil be separated by centrifuging or filtration and analysed individually by standard techniques.

Conclusions

A set of equations has been derived which permit the calculation of the partition of a hydrocarbon or group of hydrocarbons between oil, water and vapor phases as may occur during dispersed oil toxicity testing. It is hoped that these equations will be useful in designing and interpreting the results from dispersed oil toxicity tests, especially in elucidating the relative toxic contributions of dissolved and particulate oil.

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Appendix

This example is based on the conditions used by FOY [1978] to test the toxicity of dispersed Prudhoe Bay crude oil to four Arctic marine invertebrates. The phase volumes were: oil 0.3 ml, water 1500 ml and vapor 800 ml.

The mole fractions used for n-hexane, toluene and naphthalene are in the concentration range reported by MACKAY & SHIU [1976] for Prudhoe Bay crude oil. From these data, the distributions shown in Table 2 were calculated. The most striking finding is, that under these test conditions, most (84.9%) of the hexane partitions into the vapor and does not thus contact the organism. Other lower molecular weight alkanes will behave similarly. Most of the naphthalene remains in the oil and will only contact the organism if the oil particles are ingested. Most of the toluene dissolves in the water; thus the lower aromatics are probably responsible for the toxic effect of the dissolved oil. Increasing the amount of oil in the test would increase the dissolved toluene concentration almost in proportion but would only slightly increase the dissolved naphthalene concentration since the toluene is only at 5.6% of the maximum value whereas the naphthalene is at 98.5% of its maximum. The dispersed and dissolved oil to which the organism is exposed differ markedly from the original oil; thus interpretation of the test results must recognise these differences. Copies of the detailed calculations are available on request from the authors.

Table 2

CALCULATED DISTRIBUTION OF HYDROCARBONS DURING TOXICITY TEST
(Temperature 25°C. Concentrations in mol/m^3)

Hydrocarbon	Toluene	Naphthalene	Hexane
Mole fraction in oil (x)	0.029	0.00606	0.021
Original Concentration (C)	96.7	20.2	70.3
Concentration in oil (C_O)	5.5	19.9	8.9
Concentration in water (C_W)	0.017	6.2×10^{-5}	0.00035
Concentration in vapor (C_V)	0.0025	7.8×10^{-7}	0.0224
Percent in oil	5.7	98.4	12.6
Percent in water	87.4	1.5	2.5
Percent in vapor	6.9	0.01	84.9