Aqueous Solubilities of Weathered Northern Crude Oils

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A knowledge of the aqueous solubility of crude oils is important in the assessment of the environmental effects of oil spills. Determinations of hydrocarbons in water or seawater extracts of crude oil have been reported by various authors. MCAULIFFE [1969, 1971] and MACKAY et al. [1975] used a vapour phase extraction technique to determine the hydrocarbons in water extracts whereas BOYLAN and TRIPP [1971] and LEE et al. [1974] used liquid extraction followed by injection of the concentrated solvent into a GC-MS system for identification. The former method has the advantage of greater sensitivity but some hydrocarbons such as the polynuclear aromatics may not be stripped from solution because of their low vapour pressures. In the latter method, the extracting solvent is normally subjected to evaporation and concentration before analysis thus the lower molecular weight hydrocarbons may be lost to a significant extent during evaporation. For example, LEE et al. [1974] found no hydrocarbon peaks lower than benzene and the small amount of benzene relative to toluene suggests that some benzene may have been lost by evaporation. We describe here a gas stripping method using helium as a carrier gas in which the hydrocarbons are collected in a liquid N_2 trap. The method is similar to that of SWINNERTON and LINNENBOM [1967] and SWINNERTON and LAMONTAGNE [1974] and can determine the aqueous concentrations of hydrocarbons of volatility greater than naphthalene. Hydrocarbons less volatile than napthalene are not efficiently stripped from the aqueous solution. It is thus, suggested that gas stripping and liquid extraction-evaporation are complementary in that the former method is applicable to low and medium molecular weight hydrocarbons whereas the latter method is applicable to medium and high molecular weight hydrocarbons. To obtain a total analysis of an aqueous solution both methods should be used. The application of the gas stripping method to the determination of the aqueous

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solubility of weathered crude oils is described here and some environmental implications discussed.

Experimental

Norman Wells and Prudhoe Bay crude oils were kindly supplied by Imperial Oil Ltd. and Atlantic Richfield respectively. The weathered samples were prepared by evaporation from a pan in a wind tunnel at 20°C, the sample being continuously weighed on a top loading balance.

A 200 ml cylindrical glass vessel with Teflon stopcocks at both ends was filled with 100 ml of doubly distilled water and 10 ml of crude oil. The vessel was shaken for about 5 minutes and was placed in a constant temperature both at 25°C to settle for at least 48 hours before analysis. The water phase was then drawn into the evacuated stripping apparatus.

The stripping apparatus consisted of a glass vessel into which helium was bubbled below water level. The helium was first passed through a cold molecular sieve trap before entering the stripping apparatus to prevent impurities reaching the sample loop. The helium stream from the stripper was first passed through a water absorber [a 10 cm length of glass tubing filled with ascarite] to prevent water blocking the sample loop. Tests showed that there was negligible hydrocarbon retention on the ascarite. The sample collection trap was a 30 cm by 1/8 inch stainless steel column with "Swagelok" quick connect fitting at each end. After stripping for 1 hour the sample trap was removed, connected to the gas chromatograph and was then immersed in a heated oil bath at 150°C. To ensure complete removal of hydrocarbons from the aqueous phase the procedure was repeated until the amount of hydrocarbon stripped as indicated by the peak area was less than .5% of the total area in the previous gas chromatograms. It was found that a crude oil water extract of about 50 ml required two hours of helium flow at 55 ml/min to remove over 99% of the hydrocarbon present.

A Hewlett-Packard Model 5750 Gas Chromatograph equipped with a flame ionization detector was used. A 10 ft. long by 1/8" diameter stainless steel column packed with 10% SE 30 ultra phase on Chromosorb P, 60/80 mesh was used to analyze the samples. The temperature of the column was programmed from 30°C to 280°C at a rate of 15°/min, one minute after injection of sample. Peak areas were determined by a

TABLE I

Composition of Northern Crude Oils
[normalised to C_1 to C_{24} as 100%]

Percentage Peak Areas of Hydrocarbon Groups

Percentage Evaporated	C_1-C_5	$>C_5$-C_6	$>C_6$-C_7	$>C_7$-C_8	$>C_8$-C_{10}	$>C_{10}$-C_{12}	$>C_{12}$-C_{16}	$>C_{16}$-C_{24}
Norman Wells								
0	7.1	4.4	8.5	10.3	14.6	10.6	20.8	23.8
6	3.1	3.3	7.7	10.3	16.08	12.3	20.5	26.6
12	1.0	1.7	5.2	8.5	14.76	12.4	23.9	32.4
20.4	.098	2.7	1.6	3.7	11.40	13.8	28.9	40.3
29	-	-	-	.21	7.39	13.6	31.1	47.6
36.7	-	-	-	-	1.43	9.1	36.1	53.3
43.2	-	-	-	-	-	2.1	36.3	61.6
Prudhoe Bay								
0	2.5	1.6	4.5	7.0	11.7	12.1	24.3	36.2
9.8	-	-	0.1	0.86	9.9	13.3	28.7	47.0
18.2	-	-	-	-	0.1	6.1	32.9	60.8
24.1	-	-	-	-	-	2.3	28.5	70.2

TABLE II

Aqueous Solubility [mg/l] of Northern Crude Oils

Percentage Evaporated	Benzene	Toluene	Ethylbenzene Xylenes and Cumene	Others	Total
Norman Wells					
0	12.0	7.6	2.3	10.3	32.3 ±.8
6	8.8	7.8	3.9	6.5	23.18±.22
12	5.3	5.5	2.3	1.5	14.59±.51
20.4	1.8	2.3	1.8	1.4	7.33±.27
29	0.20	0.11	0.071	1.9	2.77±.07
36.7	0.13	0.033	0.012	.5	.33±.008
43.2	0.026	0.037	0.024	.053	.140±.005
Prudhoe Bay					
0	11.1	8.3	3.7	6.2	29.25±.45
9.8	0.41	1.6	1.9	1.0	4.89±.074
18.2	0.020	0.025	0.024	.084	.153±.004
24.1	0.040	0.051	.0021	.009	.056±.001

Hewlett-Packard Model 3371B Electronic Integrator.

Results and Discussion

Both fresh and weathered crude oils were studied. The oil compositions as identified up to C_{24} are given in Table 1. Although Norman Wells crude oil is lighter than Prudhoe Bay, their aqueous solubilities are comparable. The solubility data are tabulated in Table II. As expected, solubilities fall as the oil weathers because of the loss of the more volatile hydrocarbons which also tend to be the more soluble.

Gas chromatograms of water extract of fresh Norman Wells and Prudhoe Bay crude oils are shown in Fig. 1 and 2. Compounds were identified from n-pentane to naphthalene as shown. The chromatogram of the 24.1% evaporated Prudhoe Bay crude is also shown in Fig. 3. It is interesting to note that benzene, toluene and xylenes are still the major dissolved hydrocarbons in the water phase, despite as indicated in Table I, there are only trace amounts of C_1 to C_{10} hydrocarbons remaining in the oil. It is also noteworthy that although benzene and toluene make up approximately 2% of the fresh crude oil they constitute about 50% of the total dissolved hydrocarbon concentration. Interpretation of the peaks after naphthalene is less reliable because of the lower stripping efficiency, the difficulties of identification and the presence of some column bleeding. Peaks in this region will probably be mainly polynuclear aromatics which have a low solubility and low vapour pressures and thus a low stripping efficiency.

The equilibrium concentrations of individual hydrocarbons in the oil and water phases can be predicted approximately by equating the fugacities or chemical potentials, leading to the following expression [LEINONEN and MACKAY, 1973],

$$x_h \gamma_h = x_a \gamma_a$$

where x_a and x_h are the mole fractions of a component in the aqueous and oil phase respectively, and γ_a and x_h are the activity coefficients [on a Raoult's Law Basis] in the aqueous and oil phase respectively. Since γ_h is approximately unity and γ_a is the reciprocal of the mole fraction solubility of the pure hydrocarbon [LEINONEN et al. 1971] the value of x_a can be calculated if x_h is known. Thus if an oil analysis is available and a mean oil molecular can be estimated then x_h can be estimated approximately. Table III

TABLE III

Observed and Predicted Aqueous Solubilities of Selected Components of Norman Wells Crude Oil

Component	γ_a	Analysis of Crude Oil		Analysis of Aqueous Phase	Predicted Aqueous Phase
		Mass Fraction	Mole Fraction	Mole Fraction	Mole Fraction
Benzene	2.43×10^{3}	0.0040	0.0077	1.8×10^{-6}	3.2×10^{-6}
Toluene	9.9×10^{3}	0.016	0.026	1.1×10^{-6}	2.6×10^{-6}
Xylenes	3.09×10^{4}	0.017	0.024	3.7×10^{-7}	7.7×10^{-8}
Cumene	1.3×10^{5}	0.0034	0.0042	2.1×10^{-8}	3.2×10^{-8}
n-Pentane	1.04×10^{5}	0.011	0.022	2.8×10^{-7}	2.1×10^{-7}
n-Hexane	5.0×10^{5}	0.011	0.018	5.2×10^{-8}	3.6×10^{-8}
n-Octane	9.6×10^{6}	0.011	0.021	1.7×10^{-9}	2.2×10^{-9}
n-Decane	1.5×10^{8}	0.016	0.017	not detected	1.1×10^{-10}

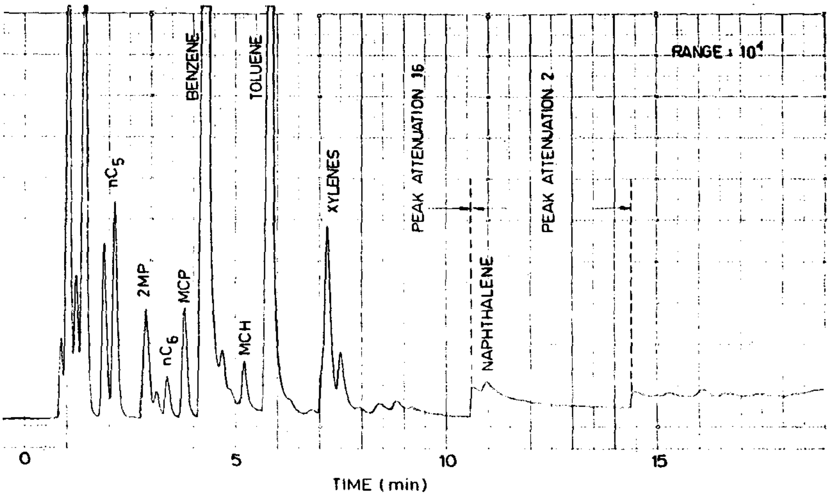

FIG. 1 GAS CHROMATOGRAM OF HYDROCARBONS FROM WATER EXTRACT OF FRESH NORMAN WELLS CRUDE OIL

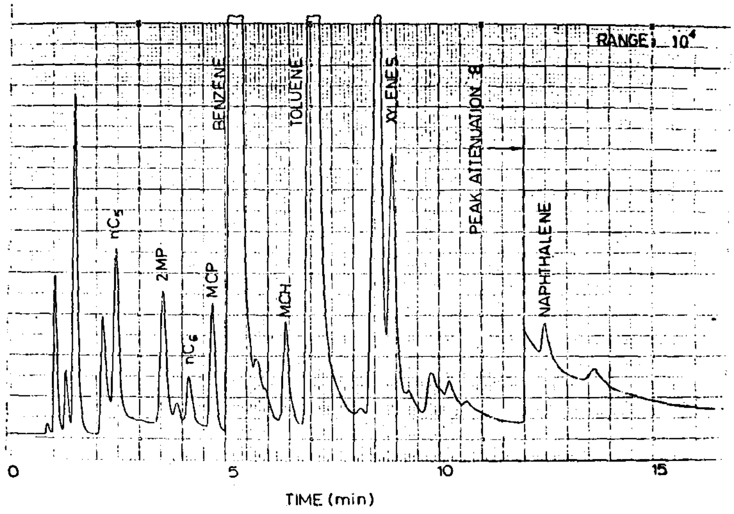

FIG. 2 GAS CHROMATOGRAM OF HYDROCARBONS FROM WATER EXTRACT OF FRESH PRUDHOE BAY CRUDE OIL

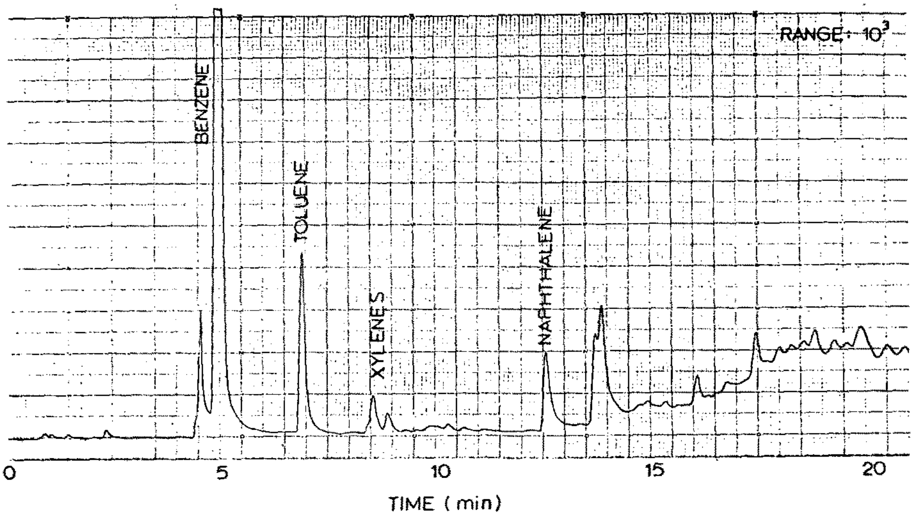

FIG. 3 GAS CHROMATOGRAM OF HYDROCARBONS FROM WATER EXTRACT OF 24.1% EVAPORATED PRUDHOE BAY CRUDE OIL

gives the observed and predicted aqueous solubilities for an assumed mean oil molecular weight of 150. The results are in good agreement in that the maximum error is a factor of about 2 in concentrations differing by a factor of 10^6. If better values for x_h and γ_h were available, the accuracy would no doubt be improved. Similar calculations on the solubility of other oils and weathered oils indicate the reliability of this approach in providing an approximate aqueous solubility for an oil from only the oil analysis.

In conclusion, it is suggested that gas stripping is the best method of determining the aqueous solubility of the lighter components of crude oils. These components, especially benzene and toluene, constitute the bulk of the dissolved material. As weathering or evaporation proceeds the solubility falls considerably as the more volatile and soluble compounds are lost. An approximate estimate of the total and component solubilities of crude oil in water can be made from the oil analysis alone.

The environmental implications are that aquatic biota may be exposed to relatively high concentrations of dissolved aromatic hydrocarbons in the first few hours after a crude oil spill but as the oil weathers, its solubility, and presumably the toxic effects, are reduced. A knowledge of the response of biota to concentration of dissolved hydrocarbons, particularly aromatics, when coupled to an estimate of the solubility of a weathering oil and an estimate of the rate of diffusion of dissolved hydrocarbons from the oil slick could lead to a more quantitative estimate of the toxic effects of crude oil spill on water. Only when the three factors; solubility as a function of weathering; diffusion rates; and specific toxicity can be quantified and combined can the full environmental impact of oil spills be assessed.

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