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Origin and Migration of Oil

Oil may consist of hydrocarbons that collected from waters containing natural solubilizers.

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Although much progress has been made in the past decade, a generally acceptable understanding of the origin of oil is still lacking. Insight into the mechanism of the migration of oil has proved to be even more elusive (*1*). Although the problems of the origin and migration of oil are usually treated as separate subjects, they are, nonetheless, intimately related.

Ever since Smith (*2*) demonstrated the presence of paraffinic, naphthenic, and aromatic hydrocarbons in recent marine sediments, the connection of these hydrocarbons with crude oil deposits has been debated (*3*). However, the main problem is still that of understanding how these highly dispersed sediment hydrocarbons collect to form an oil accumulation (*4*). This is usually referred to as the problem of oil migration, but it is also the problem of the origin of oil. A solution is proposed here—namely, that crude oil deposits consist of sediment hydrocarbons that have migrated in, and collected from, waters containing natural solubilizers. This hypothesis can be evaluated in the light of our growing knowledge of crude oil composition.

Migration in Aqueous Solution

Whatever the mechanism of oil formation, it must be closely associated with the evolution of a sedimentary basin. To investigate this relationship, an experimental program was initiated several years ago by Esso Research and Engineering Company (*5*) to learn whether the hydrocarbons known to be present in Recent sediments could dissolve in and move with the waters expelled from compacting sediments (*6*). Such a process, if hydrocarbons are sufficiently soluble, would enable the highly dispersed hydrocarbons in clay sediments to become concentrated in the more permeable and porous sands and, hence, to form the deposits known as crude oils. In addition to requiring adequate solubilities, this mechanism would require that the hydrocarbons come out of solution and be trapped in the reservoir rock.

Our initial work on hydrocarbon solubilities in ordinary water was expanded by a study of solubilities in dilute colloidal electrolyte solutions. The latter work, by demonstrating greatly increased solubilities, by providing a reasonable mechanism for unloading oil from solution, and—perhaps most significantly—by indicating that a relationship exists between crude oil composition and hydrocarbon solubility, has led to the hypothesis set forth in this article.

Crude Oil Composition

If crude oil did form from hydrocarbons that dissolved in water and then came out of solution, the composition of oil should be related to the solubility in water of the individual hydrocarbons comprising the oil. The logical step is to consider whether the composition of crude oil reflects such a solution mechanism of origin.

Although our knowledge of the composition of crude oil is far from adequate, it is becoming increasingly apparent that crude oil is a far more simple and uniform collection of hydrocarbons than one would have previously imagined. Its simplicity is revealed by the fact that not all of the statistically possible isomers are present in the distillate fractions of oil. The results of an exhaustive fractionation of a representative petroleum by research project No. 6 of the American Petroleum Institute (API) show, for example, that 159 different hydrocarbons account for the lower-boiling 44.5 percent of the original petroleum (*7*). This is truly a remarkable result when it is considered that at least some hundreds of thousands of different hydrocarbons could have appeared in this distillate fraction of the crude oil.

More recently, A. Hood *et al.* (*8*) suggested that a single picture of simplicity applies to the entire distillate range of petroleum and that a predominant portion of the higher-boiling fractions of petroleum also consists of a relatively few simple isomeric molecules. Meinschein (*9*) finds a similar simplicity in the hydrocarbons dispersed in marine sediments. Thus, the simplicity of the composition of crude oil reflects the fact that there were a limited number of different hydrocarbons available in the sediments for collection.

The uniformity in crude oil composition is disclosed by the fact that within a given class of hydrocarbons—say the alkylaromatics or the normal paraffins—the relative amounts of the individual hydrocarbons occur in nearly the same proportions in different crude oils (*10*).

The uniformity in the distribution of homologous hydrocarbons is illustrated in Fig. 1 for the single-ring aromatic hydrocarbons. The amounts of benzene, toluene, ethylbenzene, and *n*-propylbenzene in three widely different crude oils (*11*) are shown as a function of hydrocarbon size, or molar volume. It can be seen that there is always more toluene than benzene in crude oil—even though the oil may be called a paraffinic base crude (the Bradford oil), because paraffin hy-

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Table 1. Comparison of predicted and observed composition of crude oil.

Paraffin	Measured solubilities (vol. parts per billion)		Concentrations in crude oil (vol. parts per thousand)	
	Micelle solution*	Water	Predicted†	Observed‡
n-Decane	34.6	22.0	17.9	18.0
n-Octadecane	11.3	7.75	5.0	5.0
n-Hexatriacontane	2.31	2.09	0.31	0.32

* Micelle solution is composed of Na laurate (0.13 wt percent) plus NaCl (1.0 percent).
† From Eq. 1, with $k = 1.42 \times 10^6$ and $m = 1$.
‡ From data of American Petroleum Institute project No. 6.

drocarbons are predominant, or a naphthenic base crude (the Conroe oil), because cyclic hydrocarbons are predominant.

Because a remarkable similarity within a given homologous series of hydrocarbons exists among various crude oils, even though the hydrocarbons have been produced from widely different environments, it is evident that some common, universal process must have operated that selectively removed hydrocarbons from the source sediments and deposited them in the right proportions in the reservoirs. I suggest that this selective process is the solution and migration of sediment hydrocarbons in waters containing natural solubilizers.

In contrast to this hypothesis of the migration of hydrocarbons in aqueous solution, it has been postulated that hydrocarbons may move en masse from source to reservoir rock. If sediment hydrocarbons could move in a nonaqueous state into the reservoir rock by compaction, the distribution of hydrocarbons in the reservoir, particularly the distribution of the saturated hydrocarbons, would be similar to their distribution in the source sediments. Insofar as the normal paraffin hydrocarbons are concerned, this is not the case. The normal paraffins in sediments, unlike those in crude oil, exhibit a strong preference for odd-carbon-number paraffins (*12*). As is shown below, differences in the distribution of hydrocarbons in sediments and in crude oils are easily understood in terms of the selective nature of the solution mechanism by which the sediment hydrocarbons become concentrated to form oil deposits.

Hydrocarbon Solubility

Our studies of hydrocarbon solubilities in ordinary water and in dilute colloidal electrolyte solutions, such as formation waters, indicate that a relationship exists between crude oil composition and hydrocarbon solubility. For example, the equation

$$C_i = k(S_i - mS_i^\circ) \qquad (1)$$

(where C_i is the volume ratio of the *i*th hydrocarbon in petroleum, S_i and S_i° are the volume ratio solubilities of the *i*th hydrocarbon in the colloidal electrolyte solution and in pure water, respectively, and k and m are constants for a given petroleum and colloidal electrolyte solution) relates the concentration of individual hydrocarbons in crude oil to their solubilities in dilute colloidal electrolyte solutions and in pure water. The equation suggests that the abundance of any hydrocarbon in crude oil is determined primarily by its micellar solubility ($m = 1$) and by the effect of subsequent leaching by water ($m > 1$). The constant k is just the reciprocal of the micellar solubility of oil in water containing solubilizers. The dependence of crude oil composition on the micellar solubilities of hydrocarbons is perhaps best illustrated by Fig. 2, which shows the solubility data obtained for benzene, toluene, and *n*-propylbenzene in a dilute sodium naphthenate solution.

It will be recalled that the distribution of single-ring aromatics in crude oil shows that toluene is always the most abundant hydrocarbon. Figure 2 illustrates that it is not the total solubility of hydrocarbon in the soap solution (upper curve) or the solubility of hydrocarbon in ordinary water (lower curve) that predicts the excess of toluene over benzene in crude oil but, rather, the solubility in soap micelles—the difference between the upper and lower curves.

It has been found, over a wide range of soap concentrations and soap types, that the ratio of the solubility of toluene to that of benzene in soap micelles varies between 2.6 and 5.7. This is an important finding, since analyses of the benzene and toluene content of 27 widely different crude oils (*13*) showed that the ratio of toluene to benzene varied between 2.0 and 11.3 but that the average value was 4.6 ± 2.3, even though the absolute amount of benzene in these different oils varied by a factor of 600, from 0.00091 to 0.557 volume parts per hundred.

Similar analyses carried out by the U.S. Bureau of Mines (*14*) showed that in 21 domestic crude oils the average ratio of toluene to benzene was 4.1 and the average ratio in 11 foreign crude oils was 4.8.

To illustrate further the dependence of crude oil composition on the micellar solubilities of individual hydrocarbons, Eq. 1 has been used to predict the amounts of the very slightly soluble *n*-paraffin hydrocarbons that were isolated from one representative petroleum (*7*). A comparison of predicted and observed hydrocarbon abundances in API crude oil is shown in Table 1. The equation utilizes solubility data that were ob-

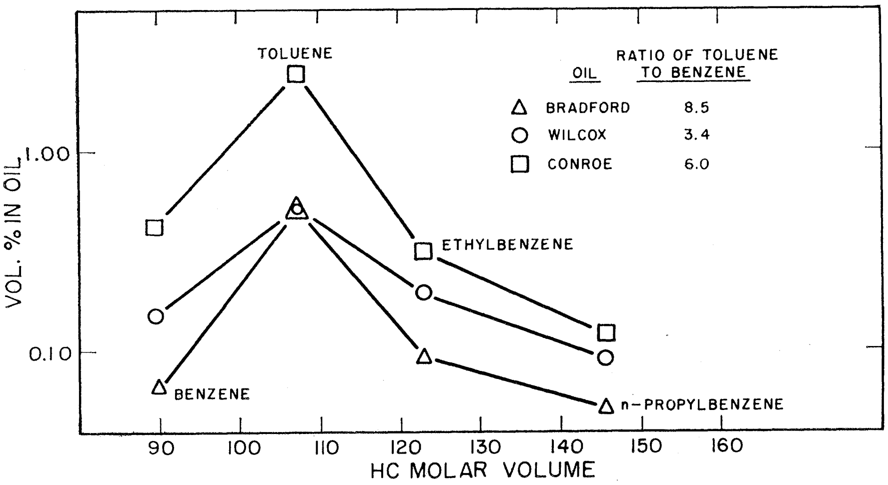

Fig. 1. Graph showing similarity of distribution of single-ring aromatics in various crude oils.

tained from dilute sodium laurate solutions. It may be noted that micellar solubilities of *n*-paraffin hydrocarbons decrease with increasing hydrocarbon size, just as the concentration of these hydrocarbons in crude oil decreases with increasing size.

Thus, the fact that the distribution of *n*-paraffin hydrocarbons in petroleum is different from that in sediments is easy to understand. If the composition of crude oil is determined primarily by hydrocarbon solubility in soap micelles, the distribution of hydrocarbons in oil need not bear any relationship to their distribution in the sediments. All the mechanism requires is that the sediments contain the necessary hydrocarbons in excess of the amount required to saturate the interstitial waters. Since hydrocarbons still are found widely scattered throughout ancient, highly compacted, nonreservoir rocks (*15*), an excess of sediment hydrocarbons over the amount which can be dissolved by the formation waters is clearly indicated.

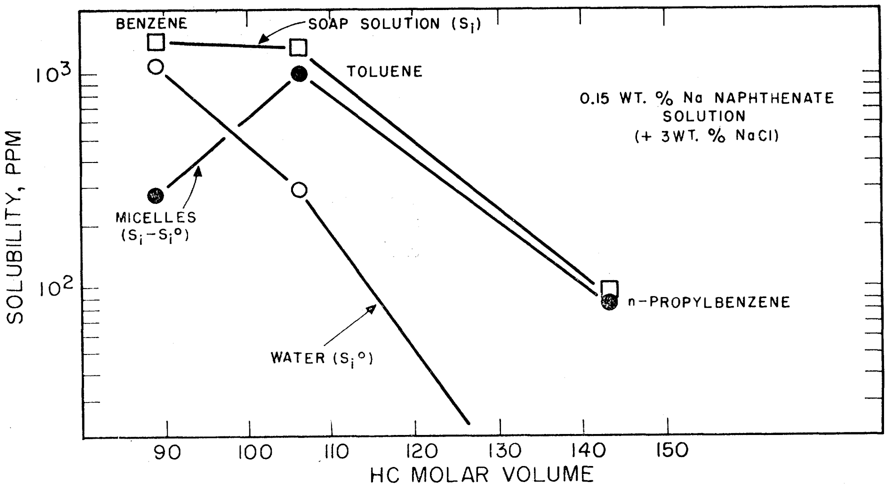

Fig. 2. Observed values for micellar solubility of single-ring aromatics, from which relative abundance of hydrocarbons in oil may be predicted.

Factors Which Affect Crude Oil Composition

If all crude oil deposits collected from ordinary water, one might logically expect them to have nearly the same composition; this, of course, they do not have. Although the distribution of individual homologs is similar from one oil to the next, crude oils do differ in the extent to which different classes of hydrocarbons occur—that is, there are paraffinic, naphthenic, and mixed-base crude oils, depending upon the type of hydrocarbons predominantly present.

Studies of hydrocarbon solubilities in dilute colloidal electrolyte solutions suggest that the variation in the composition of crude oils with respect to the predominant hydrocarbon type present may be due, in part, to variation in the types of colloidal electrolytes that were available to solubilize the sediment hydrocarbons.

In support of this viewpoint, studies of the solubility of normal paraffins and a naphthenic hydrocarbon in the micelles formed by sodium naphthenate show that the solubility of the paraffin hydrocarbons decreases with increasing size or molar volume, as one might expect (*16*). However, the micellar solubility, in a sodium naphthenate solution, of the naphthenic hydrocarbon 2-methyldecalin, which has almost the same volume as decane, is about 5 times greater than one would have predicted from considerations of size alone.

The data on micellar solubility are presented in Table 2. This table also shows that in sodium stearate micelles (a normal paraffinic soap containing 18 carbon atoms), the naphthenic hydrocarbon is no longer unusually soluble, but that octadecane, which has the same number of carbon atoms as the individual soap monomers, is about 16 times more soluble than one would have expected. If oil collected from waters containing sodium stearate as the main solubilizer, one might predict that the normal paraffin distribution curve of the unloaded oil would show a strong peak at carbon number 18. Such peaks between carbon numbers 16 and 18 have been observed in 12 oils that have been investigated in detail; these include samples from both the East Texas and the Big Horn basins (*17*).

It would seem, then, that colloidal electrolyte solutions show a greater solubilizing action toward hydrocarbons having the same general molecular structure as the soap molecules themselves, and hence that the presence of different natural solubilizers may account for the variation that is known to exist in crude oil types. Predominantly fatty acid salts might be expected to produce paraffinic oils, and naphthenic acid salts might be expected to produce naphthenic oils.

It is obvious, however, that variation in the types of natural solubilizers available is not the only factor that can influence the composition of crude oil. Our studies have shown, for example, that if sodium chloride is present in dilute fatty acid soap solutions, the solubility of paraffin hydrocarbons is markedly increased but that the solubility of the aromatic hydrocarbons is decreased. This suggests that crude oils collecting from saline waters will be relatively more paraffinic than oils collecting from fresh water. As a rule the older, more paraffinic, oils are associated with the more saline formation waters, whereas the younger, more cyclic, oils are associated with less saline waters. It should be kept in mind that the words *old* and *young* have to do only with the age of the reservoir rock in which the oil is now found.

Table 2. Selective solubilizing action of colloidal electrolyte solutions at 25°C.

Hydrocarbon	Molar vol. (ml/mole)	Micellar solubility*	
		Na naphthenate† (0.12 wt %)	Na stearate (0.15 wt %)
n-Decane	195	187	179
n-Octadecane	328	63.3	1008‡
n-Hexatriacontane	621	6.38	8.34
2-Methyldecalin	189	846	137

* $S_i - S_i^\circ$, expressed in volume parts per billion.
† Saturated with crude oil.
‡ The predicted value from a log ($S_i - S_i^\circ$) vol./vol. versus a molar volume plot is 64.0.

Formation of Crude Oil Deposits

Our studies have demonstrated that significant amounts of hydrocarbons can move out of fine-grained sediments, having been solubilized in the waters squeezed from the sediments during compaction, provided that the waters contain about 0.05 percent soap (*18*). Since the water that moves out of the compacting basin will be directed toward those sediments that offer the least resistance to water movement, disproportionately large volumes of water will pass through the sediments of greatest transmissibility, and these, consequently, play a dominant role in draining the compacting basin. Accordingly, large quantities of hydrocarbons, solubilized in soap solution, will be brought into particular beds (potential reservoir rocks) and given the opportunity to collect therein.

Although the mechanism by which the solubilized hydrocarbons come out of solution to form discrete oil droplets has not yet been determined, it is known that mere dilution of a soap solution will bring about the release of some of the solubilized hydrocarbons by destruction of the soap micelles. Such dilution would occur if meteoric water should enter the more permeable strata and mix with the water being expressed from the adjacent compacting sediments. While this is a reasonable mechanism, there are other factors, such as adsorption, salt concentration, and temperature, which may be involved in the unloading process. Once the oil droplets have formed in the more porous and permeable sandstones or limestones, they will continue to grow in size and, in response to the forces of buoyancy, will collect finally in the highest parts of the reservoir, where the oil saturation will increase significantly. The rate of final collection of dispersed oil droplets will depend upon the inclination of the reservoir strata; the greater the dip, the faster the rate of collection. During the time of final accumulation the oil droplets will be leached by the moving waters; they will be depleted in the more soluble hydrocarbons as well as in the accompanying nonhydrocarbons. Consequently, a given oil will become progressively enriched in the more paraffinic hydrocarbons if the time of final accumulation is long; it will not be so enriched if the final accumulation occurs soon after the oil droplets appear.

Summary

A relationship exists between the composition of crude oil and the solubility of the component hydrocarbons in dilute colloidal electrolyte solutions, suggesting that crude oil consists of hydrocarbons that were once solubilized in formation waters. It is not solubility in ordinary water or solubility in complete soap solution that correlates with the composition of oil but, rather, solubility in soap micelles. Because it implies a possible unloading mechanism, this concept is attractive, for it follows that when a soap solution is diluted with water, the soap micelles disperse and the hydrocarbons solubilized therein appear as discrete, filterable oil droplets.

Thus, it would seem that crude oil originates during the compaction of a sedimentary basin by virtue of the fact that sediment hydrocarbons dissolve in waters containing natural solubilizers and then come out of solution as oil droplets. The composition of crude oil as now understood is consistent with this hypothesis. And—most important—it is now possible to formulate meaningful questions, the answers to which, upon investigation in both field and laboratory, will go far toward enabling us to assess the validity of the mechanism presented here.

In addition to the implications regarding the composition of crude oil that are inherent in the hypothesis that crude oil collects from aqueous colloidal electrolyte solutions, there are several interesting implications from the geological viewpoint. To mention one, such a mechanism would lend credence to the suggestion that the source beds of petroleum are not necessarily unique accumulations of hydrocarbons in a limited area but, rather, may generally be coincident with the area from which water is expressed into the porous strata that eventually form the reservoirs.

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