

# Alkanes in Aqueous Systems. I. Exploratory Investigations on the Accommodation of C<sub>20</sub>-C<sub>33</sub> n-Alkanes in Distilled Water and Occurrence in Natural Water Systems<sup>1</sup>

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## Abstract

In order to understand more fully the mechanisms by which hydrocarbons may be mobilized for the ultimate formation of oil fields, the n-alkane content of several aqueous systems was measured. Both laboratory and natural systems were studied.

Exploratory measurements by gas liquid chromatography of total C<sub>20</sub> to C<sub>33</sub> n-alkanes accommodated in distilled water, alkaline solutions, and solutions containing surfactants fell in the range of 1 to 10 mg/l. Millipore filtration markedly reduced the alkane content with a filter of 0.05  $\mu$  pore size removing as much as 97% of the accommodated alkanes. Alkaline solutions accommodated higher quantities of alkanes than the distilled water, but the addition of surfactants had little further effect.

Natural waters had low total C<sub>20</sub> to C<sub>33</sub> n-alkane content. Samples of surface waters showed values of 0.2  $\mu$ g/l in sea water, 0.5  $\mu$ g/l in lake waters, and 1.5  $\mu$ g/l in a river water.

Coproduced oil field waters generally had a slightly higher n-alkane content with values of 1 to 1.4  $\mu$ g/l.

Waters expressed from recent lake sediments contained up to 50  $\mu$ g/l of total C<sub>20</sub>-C<sub>33</sub> n-alkanes. Addition of sodium bicarbonate and surfactants to the sediment prior to expressing water had little or no effect.

The data presented appear to be of geochemical significance as they indicate that water has the capacity to accommodate significant quantities of n-alkanes in a distribution remarkably similar to that of alkanes in the reference crude oil of A.P.I. Project 6.

## Introduction: Definition of Problems

Until recently, considerations of the origin of oil and the formation of oil fields have been in two areas of study: 1) the structure of rocks in which crude oil is known or expected to accumulate; and 2) the source of the hydrocarbons. Several comprehensive reviews have been recently published which show that the state of knowledge is quite well developed, particularly in the rock structure area (6,7,11,20).

The hydrocarbon source study of the origin of oil is developing rapidly, largely due to the advent of new analytical techniques. It is becoming apparent that the hydrocarbons of oil fields do not arise from special source rocks commonly referred to in classical geological literature, but rather arise from widely-disseminated hydrocarbons occurring in all sedimentary rocks. As a result, concepts of the origin and accumulation of crude oil are now changing to focus principally on the mechanisms by which the widely-

disseminated hydrocarbons give rise to oil fields. The concepts of oil field formation therefore involve source, mobilization, migration and accumulation as before, but with new meanings attached to each term.

The pioneering work of Smith (26) just over ten years ago showed the presence of disseminated hydrocarbons in recent sediments, and now it is agreed that virtually all sedimentary rocks contain hydrocarbons (5,27,15,16,23,24). Many igneous rocks also contain hydrocarbons, probably as natural contaminants carried by moving water (28).

Mobilization is a term recently applied to the process by which hydrocarbons move from the source or site of hydrocarbon generation. It is customary to refer to recent sediments as the source of hydrocarbons, but this is not necessarily the case, since much of the hydrocarbon material in the sediments was surely deposited with the major, inorganic, component of the sediments which had its origin elsewhere. Consequently the source of the hydrocarbons is probably the source of the organic component of the sediments. It seems reasonable to attribute such a source to at least three possibilities: 1) organic matter generated in the water overlying the recent sediments; 2) organic matter generated over and in the soil from which the sediments were formed; 3) organic matter present in the rocks from which the soil arose.

The major organic portion of recent sediments has been attributed to the first possibility with growing emphasis on the second. This change in emphasis is a result of carbon isotope measurements that indicate a close connection between the organic carbon of marine sediments and that of terrestrial plants (9). The third possibility is an obvious one which can be put into perspective by comparing the hydrocarbon content of terrestrial rocks with that of recent sediments. Generally it is clear that during the sedimentation cycle a marked enrichment of the sediments results from the deposition of plant remains.

*Migration* is not clearly defined but implies a movement of hydrocarbons from source to oil field site. *Accumulation* refers to the process by which hydrocarbons are "trapped" terminating migration.

Currently the migration operation is thought of as being merely an extension of the mobilization process (12,13). In the mobilization process hydrocarbons accompany the vast and continuous water-cycle, and in the accumulation process a small fraction of the mobilized hydrocarbons in a particular locality are left behind (12). If the abandoned hydrocarbons are adequate in bulk and if the operation occurs in a favorable rock structure, an oil field may result.

Much of the foregoing discussion is speculative, since supporting data for the hypotheses are inadequate. For example, few definitive data exist to test the mobilization concept pioneered by Baker in recent years (1-3). Baker proposed to study the solubility of hydrocarbons in water which led to a

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concept of surfactants increasing the "solubility" of hydrocarbons (1). The accumulation aspect was then linked to a breakdown in the efficacy of the surfactants. Oil field data supported this hypothesis (8,18), but two major questions arose: 1) Was such a method capable of accounting for the volumes of oil involved in a geological basin with its normal complement of oil fields? 2) Could such a system account for the distribution of individual hydrocarbons ultimately found in crude oil?

The first question might be rephrased to ask what level of hydrocarbon content in water would be required to account for the known oil accumulations in a typical basin? This was examined in some detail (12), with the conclusion that hydrocarbons would need to be mobilized to the extent of at least 1 ppm. (1 mg/liter of water) under conditions of water movement and accumulation that were assumed to be reasonable.

The second question is of particular scientific interest. The hydrocarbons generated in living organisms have an odd-carbon preference, evidently resulting from an even-carbon buildup of precursor fatty acids in plants. The odd-carbon preference persists in the n-alkanes of recent sediments. The n-alkanes of crude oil however show no odd-carbon preference; consequently, it is necessary to account for this change in hydrocarbon distribution in any process put forward to explain the mechanisms by which hydrocarbons are mobilized and accumulated.

It was the purpose of the present investigation to carry out exploratory measurements of hydrocarbons in water systems to obtain provisional answers to the foregoing questions of extent of mobilization and hydrocarbon selection as revealed by odd-carbon preference. While the analytical approaches yielded data for branched and cyclic hydrocarbons as well, principal attention was focussed on the occurrence and distribution of the n-alkanes. In the first instance the accommodation of  $C_{17}$ - $C_{33}$  alkanes in distilled water was studied and extended to include the effect of surfactants and filterability. From that point, analyses were made for the same hydrocarbons in natural water systems comprising selected samples of sediment waters, sea waters, river and lake waters, and finally oil field waters. While the data are exploratory and limited, they may be of value in establishing a better understanding of the mechanisms by which oil fields are formed.

#### n-Alkanes in Distilled Water

In an attempt to measure the solubility of n-alkanes in water, McAuliffe (21) equilibrated n-alkanes from  $C_4$  to  $C_8$  with distilled water at room temperature. Levels of 0.66 to 115 mg/l (ppm.) were determined. The content was inversely proportional to the molar volume of the individual hydrocarbons and the accommodation was assumed to be true solubility. Extrapolation of the data to the carbon range of  $C_{20}$  to  $C_{30}$ , of principal interest in the present investigations, indicated that the solubilities would be well below 10 - 4 mg/l for  $C_{20}$  and below 10 - 6 mg/l for  $C_{30}$ . Unpublished data of Baker (4) showed that levels of content well above the solubility extrapolation were observed; for example, water equilibrated with  $C_{18}$  showed 0.006 mg/l. Evidently some accommodation other than simple solubility was involved.

In the present investigations five n-alkanes,  $C_{20}$ ,  $C_{22}$ ,  $C_{24}$ ,  $C_{28}$  and  $C_{32}$ , were selected for equilibration with distilled water. These hydrocarbons were ob-

tained from the Aldrich Chemical Company Inc. Odd numbered n-alkanes in this range of carbon numbers were not available. Quantities of each, ranging from 100 mg to over 700 mg to give a marked excess of n-alkane, were added to two liters of distilled water which was then mechanically shaken at room temperature ( $22 \pm 2^\circ C$ ) for 16 hr and allowed to settle for 4 hr before sampling. Upon settling, the small flakes of alkane rapidly rose to the surface leaving a clear water phase.

To obtain a measure of the physical distribution of the hydrocarbons in the water, aliquots of samples were filtered through glass wool and millipore filters of pore sizes 5.0, 3.0, 0.45, 0.22 and 0.05  $\mu$ . Each aliquot was extracted with two successive 25 ml volumes of n-heptane, the extract was reduced in volume to 3 ml under nitrogen and the hydrocarbons determined by gas liquid chromatography. An alternative method of size distribution based on centrifugation was attempted. However, centrifugation resulted in large variation in sample temperature which made the results of little value.

A model 810 F&M gas chromatograph was used equipped with hydrogen flame detectors and compensating dual columns of  $\frac{1}{8}$  in. diameter stainless steel tubing 5 ft in length. Column packing was hexamethyl-disilazane treated chromosorb W containing 0.5-1% SE 30 silicone gum as the liquid phase. Helium was used as a carrier gas with a constant flow rate of 50 ml per minute as calculated from the input pressure and the flowmeter calibrated by the instrument manufacturer. A 1 to 100  $\mu$ l portion of the 3 ml of concentrated n-heptane extract was injected into the gas chromatograph. The oven was maintained at 100C for an interval of 10 min., following which it was programmed at 4°C per minute to 275C after which it was maintained at 275C until no more peaks appeared. Injection port temperature was set at 380C; detector temperature, 410C.

A number of precautions were taken to prevent extraneous materials from contaminating the columns. Silicone rubber septums used in the injection port were baked in the chromatograph oven before using and were allowed to stabilize for sixteen hours. All gases were passed through traps containing Linde 5A° molecular sieve, and a blank was run before each sample to demonstrate baseline stability and freedom from materials which would give interfering peaks. The n-heptane Eastman reagent grade used to extract the hydrocarbons was distilled twice through a 100 cm helix packed column before use.

The sensitivity of the detector calculated by the formula recommended by ASTM Committee 19,  $S = \frac{P}{M}$ , was  $2.8 \times 10^6$  mv/mole/min for n-tetracosane ( $C_{24}H_{50}$ ). This is in good agreement with  $1.34 \times 10^6$  mv/mole/min suggested by the manufacturer for unspecified compounds. Thus, the amount of tetracosane necessary to give a measurable peak, 0.05 mv  $\times$  1 min, i.e. the limit of detection, was 0.003  $\mu$ g. The equipment was calibrated using  $C_{16}$ ,  $C_{18}$ ,  $C_{20}$ ,  $C_{22}$ ,  $C_{24}$ ,  $C_{28}$ ,  $C_{32}$  and  $C_{36}$  n-alkanes. Measurements were based on peak areas. The corresponding detection limit for total hydrocarbons  $C_{20}$  to  $C_{33}$  was 0.05  $\mu$ g.

Impurities in the n-heptane constituted a major source of error in determining the n-alkanes below  $C_{20}$ . Blank values for 50 ml of n-heptane were typically:

C <sub>16</sub>	0.27 $\mu\text{g}$
C <sub>17</sub>	0.36
C <sub>18</sub>	0.13
C <sub>19</sub>	0.05
above C <sub>19</sub>	<0.02

The other major source of error was loss during handling and evaporation of the solvent. To test the procedure, known amounts of approximately 1  $\mu\text{g}$  of n-alkanes (C<sub>16</sub>, C<sub>20</sub>, C<sub>22</sub>, C<sub>24</sub>, C<sub>28</sub> and C<sub>32</sub>) were added to 10 ml of n-heptane which was then evaporated to dryness under a stream of filtered nitrogen at room temperature. The residue was dissolved in 10  $\mu\text{l}$  of benzene and half of the resulting solution was injected into the gas chromatograph to determine the loss of the hydrocarbons. To test the loss attributed to the evaporation phase of the process, the procedure was repeated with the modification that evaporation was halted when the solution reached 0.5 ml. The results in Table I show clearly that evaporating to dryness resulted in almost complete loss of the C<sub>16</sub> alkane. The arrested evaporation method restricted the losses to only 30%, and evidently most of this was to be attributed to handling losses. For the higher alkanes the losses were less serious, and the adoption of the arrested evaporation method permitted recoveries of 75% or more of C<sub>20</sub> and higher alkanes.

The hydrocarbon content of the distilled water-hydrocarbon system was surprisingly high when compared with the McAuliffe values for the C<sub>4</sub> to C<sub>8</sub> alkanes. For the aliquots passed through the simple glass wool filters the content of C<sub>20</sub> was 350  $\mu\text{g}/\text{l}$ , compared with only 660  $\mu\text{g}/\text{l}$  for n-octane as determined by McAuliffe (21). The corresponding levels of alkane content for the other four n-alkanes to C<sub>32</sub> were progressively lower, falling to 42  $\mu\text{g}/\text{l}$  for C<sub>32</sub> in Figure 1 along with those of McAuliffe show a substantial difference from what might be expected through a simple extrapolation of the C<sub>4</sub> to C<sub>8</sub> data, for example 350  $\mu\text{g}/\text{l}$  for C<sub>20</sub> compared with about  $5 \times 10^{-5}$   $\mu\text{g}/\text{l}$ . This was in keeping with Baker's observation (4), and it strongly suggests a different kind of accommodation for the higher hydrocarbons in distilled water from the simple solubility attributed to the C<sub>4</sub> to C<sub>8</sub> alkanes. The straight line relation of accommodation to molar volume however suggests that it is of a nonrandom character. This is particularly evident when the observed n-alkane content of the distilled water systems is related to the starting n-alkane content of the individual systems as illustrated in Figure 2. There is no direct relationship between the starting levels and the equilibrated values.

To gain some understanding of the mode of accommodation of the n-alkanes in the water, the data for the filtered systems is of value. The largest millipore filter, with 5  $\mu\text{pores}$ , produced reductions in hydrocarbon content of about 75% from the glass wool filtrate value. Again the data fell in a straight

TABLE I  
Evaluation of Losses due to Handling and Evaporation

n-Alkane	Loss, % of starting amount	
	Method I Evaporation to dryness	Method II Arrested evaporation
C <sub>16</sub>	100	30
C <sub>20</sub>	65	25
C <sub>22</sub>	40	20
C <sub>24</sub>	35	18
C <sub>28</sub>	22	10
C <sub>32</sub>	25	0

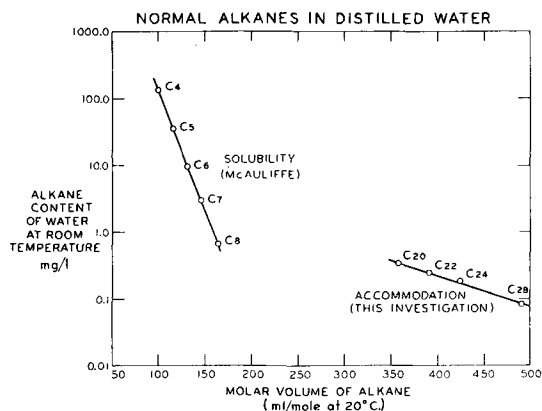


FIG. 1. Difference between solubility and accommodation in distilled water of C<sub>4</sub> to C<sub>8</sub> and C<sub>20</sub> to C<sub>28</sub> n-alkanes at room temperature. Solubility data reported by McAuliffe (21); accommodation data, results of this investigation.

line and the line was nearly parallel to that for glass wool filtrate. The other three lines of Figure 2 representing the alkane contents of the filtrates from the finer filters were parallel to the 5  $\mu\text{m}$  line. The finest filter, 0.05  $\mu\text{m}$ , reduced the C<sub>24</sub> content from 170  $\mu\text{g}/\text{l}$  of the glass wool filtrate to 3.5  $\mu\text{g}/\text{l}$ , i.e. by about 98%. Figure 3 illustrates the relationship between alkane content of the filtered water and the pore size of the filter. The distribution of the points for the various hydrocarbons suggests a micellar type of accommodation. The break in the distribution curve as shown in Figure 3 would fit the concept of two types of micelles put forward by Baker who discussed small ionic micelles of mean size 6.4  $\text{m}\mu$  and large neutral micelles of 500  $\text{m}\mu$  mean size (3).

Thus it is clear that hydrocarbons in the C<sub>20</sub>-C<sub>30</sub> range are accommodated in distilled water in amounts much greater than would be expected by simple solubility considerations, and that millipore filtration reduces the degree of accommodation in a systematic fashion while maintaining a clear-cut relation between alkane content and carbon number.

It is pertinent to observe that the foregoing data are in agreement with one of the major requirements for oil field formation, that of selective mobilization. The accommodation of given alkanes in distilled water is evidently a function of the properties of the alkane, rather than of the supply of the alkane. That is, an odd carbon preference in the source material would not persist into the mobilizing water system.

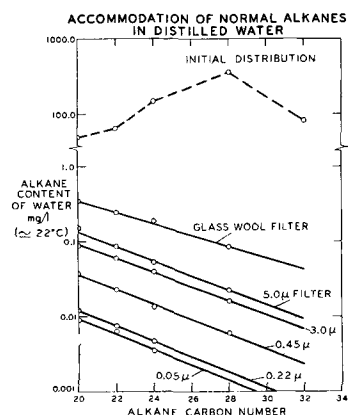


FIG. 2. Accommodation of C<sub>20</sub> to C<sub>30</sub> n-alkanes in distilled water as a function of filtration pore size and alkane carbon number. Filtrate hydrocarbons appear to be independent of initial distribution.

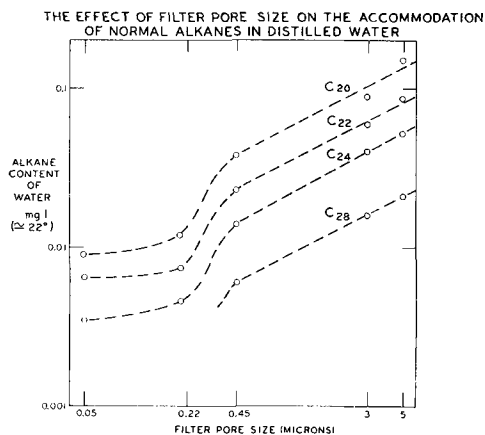


FIG. 3. The relationship between the normal alkane content of filtered distilled water solutions and pore size, indicating micellar accommodation.

It is desirable to calculate the total content of n-alkanes to be expected for hydrocarbons in the  $C_{20}$  to  $C_{33}$  range. This may be done by plotting the alkane contents as in Figure 2 and summing the individual values for the entire range, including both the determined values and the interpolated values. This was done for the various filtrates and the data are summarized in Table II, typical values for the total n-alkanes being 1.9 mg/l for the glass wool filtrate and 0.04 mg/l for the 0.05  $\mu$  filtrate.

These data suggest that the levels of hydrocarbon content required for oil field formation through the methods previously discussed (12) are probably well within reach. But it is wise to make actual measurements on natural waters before assuming such a conclusion. Since principal natural water systems are generally slightly alkaline, the foregoing analytical approach was extended to the accommodation of n-alkanes in distilled water to which sodium bicarbonate had been added.

Thus two liters of distilled water containing 1000 mg/l of sodium bicarbonate was equilibrated with the same five standard n-alkanes, in random amounts as follows:  $C_{18}$ , 43.9 mg/l;  $C_{20}$ , 11.5 mg/l;  $C_{22}$ , 73.0 mg/l;  $C_{24}$ , 22.4 mg/l;  $C_{28}$ , 15.4 mg/l; and  $C_{32}$ , 79.0 mg/l. The solution was allowed to settle and aliquots were filtered as before, filters of glass wool, 5  $\mu$  and 0.45  $\mu$  being used. The data are shown in Figure 4, and the most significant feature was that the n-alkane content of each filtrate was significantly higher than in the distilled water system. In general, the alkaline system accommodated three or four times the amount of n-alkanes accommodated in the distilled water.

Further, there seemed to be a clear-cut departure from the straight-line logarithmic relation between n-alkane content and molar volume, or carbon number, with some reflection of the relative amounts of the individual hydrocarbons added. This appeared to be the case in all three filtrates.

Thus, it appears that waters containing sodium bicarbonate are capable of accommodating greater

TABLE II

Estimated Accommodation of n-Alkanes in Distilled Water

Filter	Total n-alkane content $C_{20}-C_{33}$ , <sup>a</sup> mg/l
Glass wool	1.9
5 $\mu$	0.64
3 $\mu$	0.45
0.45 $\mu$	0.17
0.22 $\mu$	0.05
0.05 $\mu$	0.04

<sup>a</sup> Based on measured values for  $C_{20}$ ,  $C_{22}$ ,  $C_{24}$  and  $C_{28}$ .

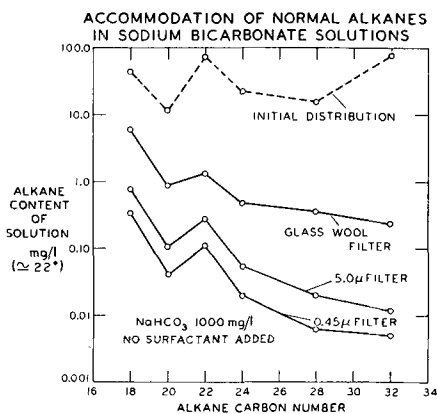


FIG. 4. The effect of initial individual alkane content on the distribution of normal alkanes accommodated in a distilled water system containing sodium bicarbonate.

amounts of n-alkanes than distilled water, but are not so effective in controlling distribution patterns. The next step in the overall examination was to explore the effect of potential surfactants, since it is agreed that natural surfactants are probably present in most natural waters.

#### Effect of Surfactants on n-Alkanes in Alkaline Water Systems

Three compounds were selected to illustrate the effects to be expected from the presence of surface active agents such as naphthenic acids, fatty acids, and aromatic acids. The surfactants, cyclohexane carboxylic acid, n-nonadecanoic acid, and benzoic acid, were introduced to alkaline water systems containing the five standard n-alkanes in amounts given in Table III ranging from 660 to 685 mg/l, for the acids, and from amount 20 to 150 mg/l for the alkanes. The three systems were equilibrated and filtered as before.

To recover the hydrocarbons from the individual filtrates, they were acidified and extracted successively with two 20 ml portions of n-heptane. In each case, the extracts were reduced in volume to approximately 3 ml, and the n-alkanes separated from the surfactants by silica gel column chromatography using a 200  $\times$  12 mm column prepared from a slurry of activated silica gel (10) in n-heptane, prewashed with 50 ml of n-heptane to remove any contaminating alkanes. The 3 ml extract was placed on the column and eluted with 40 ml of n-heptane. The eluate, containing the alkanes, was collected and reduced under nitrogen at room temperature to a volume in the range of 0.5 to 3 ml for analysis by gas chromatography.

The data for the three systems are shown in Figures 5, 6 and 7. Considering first the aliquots filtered through glass wool, the presence of cyclohexane carboxylic acid and n-nonadecanoic acid resulted in a reduction of the n-alkane content of the aqueous sys-

TABLE III

The Composition of Alkaline Water Systems Surfactants and n-alkanes added to solutions containing 1,000 mg/l sodium bicarbonate

Surfactant	mg/l	n-Alkanes, mg/l					
		$C_{18}$	$C_{20}$	$C_{22}$	$C_{24}$	$C_{28}$	$C_{32}$
Cyclohexane carboxylic acid	660	52.5	15.4	65.2	31.2	22.0	43.9
n-Nonadecanoic acid	670	19.9	58.5	71.5	40.4	26.8	80.1
Benzoic acid	685	148	41.9	84.6	41.5	38.1	103.0

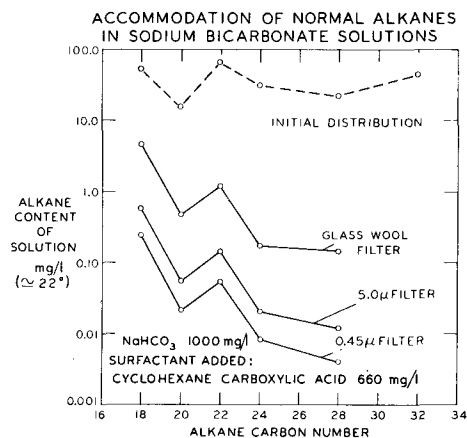


FIG. 5. Distribution of *n*-alkanes accommodated in an alkaline solution containing 660 mg/l cyclohexane carboxylic acid illustrating the lack of effect of the surfactant.

tem, while benzoic acid produced little or no change. The millipore filtrates however showed a somewhat different pattern in which the cyclohexane carboxylic acid and benzoic acid brought about a reduction in alkane accommodation, while the *n*-nonadecanoic acid increased the alkane accommodation. This is perhaps better illustrated in Table IV where the summed measured and interpolated accommodation values for  $C_{20}$ - $C_{33}$  *n*-alkanes are presented. In solutions filtered through glass wool only the indicated  $C_{20}$ - $C_{33}$  sums for systems containing cyclohexane carboxylic acid and nonadecanoic acid were reduced from 7.2 mg/l for the straight alkaline system, to 3.6 and 3.0 mg/l, respectively. The benzoic acid change was only 7.2 to 7.0 mg/l. After filtration through the  $0.45 \mu$  filter the solution containing *n*-nonadecanoic acid showed a projected sum for  $C_{20}$ - $C_{33}$  in the amount of 1.36 mg/l, a marked increase over the corresponding figure of 0.36 mg/l for the sodium bicarbonate solution with no added surfactants.

The *n*-alkane distribution pattern as shown in Figure 6 for the *n*-nonadecanoic acid system showed little reflection of the starting quantities of the standard hydrocarbons. The other two surfactant systems showed a distribution which was obviously influenced by the quantities initially available, as is clear in Figures 5 and 7.

These surfactant data are difficult to interpret, but there seems to be some justification for concluding that the distribution of *n*-alkanes in alkaline systems

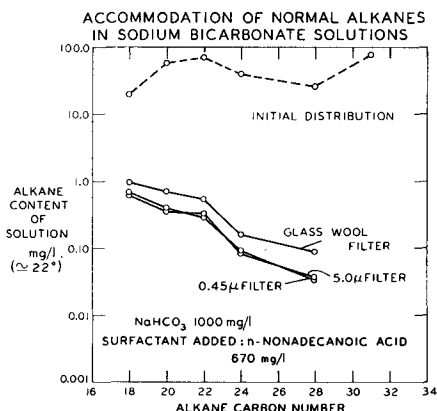


FIG. 6. The effect of filtration on the alkane content of an alkaline solution containing 670 mg/l *n*-nonadecanoic acid equilibrated with normal alkanes  $C_{18}$  to  $C_{33}$ , indicating the effect of the surfactant on micelle size.

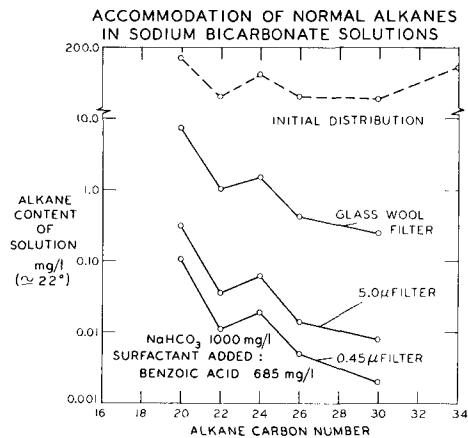


FIG. 7. The distribution of normal alkanes accommodated in an alkaline solution containing 685 mg/l benzoic acid, showing the lack of effect of the surfactant.

containing *n*-nonadecanoic acid is such that greater quantities will pass the small-pore filters. This may be interpreted by saying that the hydrocarbon micelles are significantly smaller in the *n*-nonadecanoic system than in all the others. If this is so, it might be speculated that ground waters carrying hydrocarbons in the presence of long chain fatty acids would be expected to carry hydrocarbons through sediment and rock formations where systems containing other surfactants would quickly lose their hydrocarbons.

Having considered the foregoing exploratory data, it is now of interest to determine *n*-alkanes in waters associated with recent sediments.

#### *n*-Alkanes in Water Expressed from Recent Sediments

Recent sediments contain dispersed hydrocarbons in quantities of several hundred parts per million (5,26,27), and it is generally believed that small portions of such hydrocarbons, given the right conditions ultimately become accumulated as petroleum in oil fields. In the present investigation exploratory data were sought to measure the mobilization of the sediment hydrocarbons during a simulated natural compaction process. First the hydrocarbon contents of samples of recent sediments were established.

Secondly, a major proportion of the sediment water was expressed by centrifuging, and this was examined for *n*-alkane content. Finally the effect of added surfactants was explored in the same system.

#### Recent Sediments

The analytical procedure used for determining *n*-alkanes in wet sediments was as follows. A sample of the sediments of about 10 g was shaken with about 30 ml of methanol and benzene (30-70 v/v) for several hours. The resulting emulsion was centri-

TABLE IV  
Effect of Added Surfactants on the Accommodation of *n*-Alkanes in Distilled Water Systems

	<i>n</i> -Alkane content, mg/l <sup>a</sup>		
	Glass wool filter	5 $\mu$ filter	0.45 $\mu$ filter
Distilled water	1.9	0.65	0.17
Sodium bicarbonate added	7.2	0.98	0.36
Cyclohexane carboxylic acid and sodium bicarbonate added	3.6	0.52	0.19
<i>n</i> -Nonadecanoic acid and sodium bicarbonate added	3.0	1.56	1.36
Benzoic acid and sodium bicarbonate added	7.0	1.26	0.09

<sup>a</sup> Values for total *n*-alkane content  $C_{20}$  to  $C_{33}$  based on measured values for  $C_{20}$ ,  $C_{22}$ ,  $C_{24}$ ,  $C_{28}$ .

fuged, the liquid drawn off and a further 25 ml of solvent added to the sediment prior to a second shaking. After several such extractions, the combined extracts were evaporated under nitrogen at 20°C until two distinct liquid layers developed. The benzene layer was removed and the aqueous layer was further extracted with benzene to remove any residual alkanes. To transfer the alkanes from the benzene layer to n-heptane for liquid chromatography, the combined benzene extracts were reduced to 10 ml under nitrogen, and 20 ml of n-heptane was added. The mixed solvent solution was evaporated to 10 ml, and a further 20 ml of n-heptane added, followed by a further evaporation reduction to 10 ml. This procedure was repeated three times to reduce the benzene content to a level which would not interfere with subsequent chromatography on silica gel, in which n-heptane elution separated the alkanes from the bulk of the extracted organic material. Contamination from the solvents used contributed insignificant amounts of alkanes. The silica gel n-heptane eluate was examined as before for n-alkanes using gas liquid chromatography.

The sediment samples were selected to relate to three widely different environments of deposition. One was from Lake Wabamun, a fresh-water lake near Edmonton, Alberta which had been included in earlier investigations (14); the second was from the Atlantic sea floor off the coast of Nova Scotia (19); and the third was an arctic delta sediment from the Mackenzie river near Inuvik, N.W.T., in northern Canada (17).

The gas chromatograms of the alkanes extracted from the three sediments are shown in Figure 8. Each shows a strong odd carbon preference in the n-alkanes in keeping with the results of other investigators (5,27). The n-alkane contents of the sediments in the C<sub>20</sub>-C<sub>33</sub> range were 27, 9 and 66 µg/g, dry weight basis, for the lake, marine and delta sediments respectively. If the lake sediment n-alkanes were reported on an as-received, i.e. wet, basis the level would be about 3.8 µg/g. As the sediments were over 80% water it might be expected that a significant proportion of these hydrocarbons were actually accommodated in the water phase rather than in the solid matrix.

Attention might be drawn to the predominant alkanes in the three sediments. The Atlantic sample showed a clear-cut predominance of the C<sub>31</sub> and C<sub>29</sub> n-alkanes. The northern lake sample showed a pre-

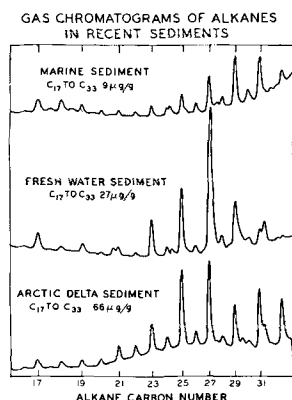


FIG. 8. Carbon number distribution in gas chromatograms of alkanes from recent sediments from (a) the Atlantic off the south eastern coast of Nova Scotia (b) a shallow fresh water lake in the Edmonton, Alberta area (c) the delta of the Mackenzie River near Inuvik, N.W.T.

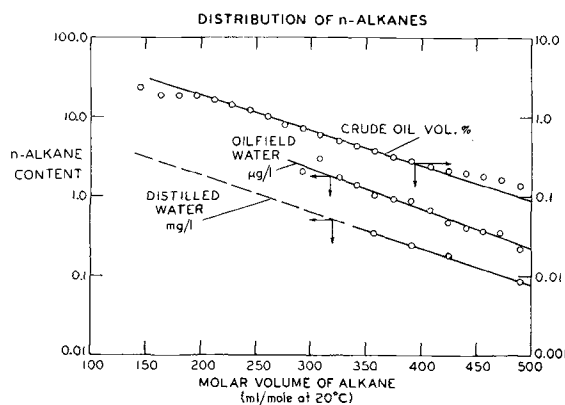


FIG. 9. Similarities among the distribution of normal alkanes in (a) A.P.I. Project 6 reference crude oil (b) Joffre Nisku oil field water and (c) distilled water after shaking for 24 hr with an excess of normal alkanes.

dominance of C<sub>27</sub> and the arctic sample indicated that the C<sub>27</sub> dominance was shifting to that of C<sub>25</sub>. While the sediments came from different environments and it may be unwise to attribute much significance to these data, they nevertheless do fit into a north-south pattern of latitude control of carbon number preferences such as that suggested by Meinschein (22), based upon his data and those of Oró who found a predominance of C<sub>31</sub> in whole plants from Texas (25).

#### n-Alkanes in Expressed Waters

Sediments from Lake Wabamun and North Cooking Lake were centrifuged (1050 g, 30 min) to simulate a natural compaction. The expressed water amounted to about 50% of the water originally present. It was filtered through a wad of glass wool and centrifuged a second time (1050 g, 1 hr) to settle traces of suspended substances. The water was then extracted in the same manner as the foregoing alkaline systems. n-Alkanes in the C<sub>20</sub>-C<sub>33</sub> range were determined as before.

The n-alkane content was surprisingly low, with only 0.029 mg/l of C<sub>20</sub>-C<sub>33</sub> in one sample of water expressed from Wabamun Lake sediments. A second sample showed 0.016 mg/l. The sediment water from the other lake showed slightly higher values, at 0.043 and 0.056 mg/l. The distribution of n-alkanes in both reflected the strong odd carbon preference of the parent sediments. This was not unexpected since (a) the alkaline nature of the waters would be expected to give much the same effect as that of the sodium bicarbonate distilled water systems which reflected parent hydrocarbon availability, and (b) the suspension of inorganic particles of <1 µ in size surviving the centrifuging operations would be carrying hydrocarbons of a distribution similar to that of hydrocarbons in the bulk of the sediments. These hydrocarbons would contain alkanes with a strong odd carbon number preference, and in the extraction stage would be included with those accommodated directly in the water. Further the system was somewhat more complex since the hydrocarbons present in the sediments were not simply suspended as in the distilled water systems but rather were adsorbed and integral components of the solid matrix. Hence, the availability of the source hydrocarbons for accommodation in water would be reduced. Secondly, the composition of the water with its dissolved salts and organic matter would be expected to have a noticeable effect upon the amount of alkane accommodated.

**n-Alkane in Expressed Waters with Added Surfactants**

One of the more significant components of the sediment system was expected to be the natural surfactants or solubilizers present, and an attempt was made to define this effect to some degree by adding additional surfactants prior to the compaction centrifuging.

To make an exploratory test of the effect of added surfactants in the lake sediments, the following systems were made up, involving added sodium bicarbonate and the surfactants used before in the distilled water systems:

	Lake water	Wet lake sediments	NaHCO <sub>3</sub>	Surfactant
a)	500 ml	1 kg		
b)	500 ml	1 kg	1 g	
c)	500 ml	1 kg	1 g	Cyclohexane carboxylic acid 0.5 g
d)	500 ml	1 kg	1 g	n-Nonadecanoic acid, 0.5 g
e)	500 ml	1 kg	1 g	Benzoic acid, 0.5 g

In each case, after being shaken for 24 hr, the semi-liquid mixture was centrifuged (30 min, 1050 *g*), and the liquid layer from the first centrifugation recentrifuged (one hour, 1050 *g*). The supernatant liquid was divided into two aliquots, one for filtration through glass wool, and the other through a 5  $\mu$  millipore filter. Both filtrates were extracted as before with n-heptane. Stable emulsions were formed which could be broken only through repeated freezing and thawing. The n-heptane extracts were analyzed in the usual manner for alkanes in the C<sub>20</sub>-C<sub>33</sub> range. The results are shown in Table V.

The presence of the sodium bicarbonate approximately doubled the mobilization of the C<sub>20</sub>-C<sub>33</sub> n-alkanes. The addition of cyclohexane carboxylic acid and benzoic acid suppressed the mobilization and the addition of n-nonadecanoic acid had no effect. The effect of filtering through the 5  $\mu$  filter was a minor reduction in the n-alkane accommodation, this reduction being most pronounced in the unaltered sediment system wherein the n-alkane content was reduced by one half.

As before the hydrocarbons in the expressed waters retained their odd-carbon preference with the added surfactants having no effect. Thus, under the particular conditions existing, the three potentially surface active agents produced no noticeable increase in n-alkane content of the expressed water and no change in the n-alkane distribution.

**n-Alkanes in Surface Waters**

Attention was then directed to the n-alkanes occurring in some surface waters, specifically in some lake, ocean and river waters.

Lake waters were collected from three local lakes, including those from which the foregoing lake sediments were taken. Five-gallon water samples were collected, in the winter time through holes augered in

the ice and transported promptly in carefully cleaned pyrex glass carboys to the laboratory where they were filtered through glass wool plugs to remove large particulate matter.

Sea water samples were collected in similar containers off the Atlantic coast near Halifax and in the Strait of Georgia near Victoria, British Columbia. They were analysed within a few days of being collected. The one local river sample was collected in the same manner as the lake samples.

After filtration through glass wool four-liter aliquots of each sample were acidified with a few drops of 12N hydrochloric acid and extracted with two 40 ml portions of n-heptane by shaking vigorously in large separatory funnels. To complete the extraction of each 5-gallon sample of water, subsequent 4-liter portions of the samples were extracted with the same n-heptane portions. At the conclusion of the 4-liter extractions, the separatory funnels were washed with a further 25 ml of n-heptane. The combined extracts for each water sample were reduced to approximately 3 ml by evaporation under nitrogen. The alkanes were separated from other organic matter by chromatography on silica gel and analyzed by gas chromatography as before.

The n-alkanes in the C<sub>20</sub>-C<sub>33</sub> range found in surface waters were appreciably less abundant than in the waters expressed from sediments. They ranged from less than 0.2  $\mu$ g/l in the sea waters to 3.8  $\mu$ g/l in one of the lake waters, as shown in Table VI. Only one sample showed a strong odd carbon preference. This was a sample taken from Cooking Lake in the fall of the year and it showed the highest n-alkane content at 3.8  $\mu$ g/l. A second sample taken five months later showed only 0.3  $\mu$ g/l with a less pronounced odd carbon preference. Both observations may be attributed to the remains of plant life which flourishes in this shallow autochthonous lake during the ice-free season, rather than to the basic accommodation of hydrocarbons in the water of this lake.

The most significant feature of the occurrence of n-alkanes in the various surface water samples is the very low content, roughly three orders of magnitude lower than the accommodation of the n-alkanes in distilled water.

It is now of interest to turn to the occurrence of high-molecular weight n-alkanes in subsurface oil field waters.

**n-Alkanes in Oil Field Waters**

It would seem reasonable to expect water associated with crude oil to be in equilibrium with the hydrocarbons of the oil, especially when considering the intimate contact between the petroleum and water during crude oil production.

Three samples of coproduced water from oil and gas fields of western Canada were examined. The samples were collected from the wellhead to avoid

TABLE V  
Effect of Added Sodium Bicarbonate and Surfactants on the Mobilization of n-Alkanes from Recent Lake Sediments

	Total n-alkanes C <sub>20</sub> to C <sub>33</sub> in $\mu$ g/l of expressed water	
	Glass wool filter	5 $\mu$ Filter
Unaltered sediments	14	7
Sodium bicarbonate added	27	20
Cyclohexane carboxylic acid and sodium bicarbonate added	19	16
n-Nonadecanoic acid and sodium bicarbonate added	26	19
Benzoic acid and sodium bicarbonate added	21	13

TABLE VI  
n-Alkane Content of Surface Waters

Sample	Total C <sub>20</sub> to C <sub>33</sub> , $\mu$ g/l	Odd carbon preference
Lake water		
Cooking Lake, Oct.	3.8	Strong
Cooking Lake, Mar.	0.3	Weak
Lake Wabamun	0.2	None
Pigeon Lake	0.7	None
Sea water		
Victoria, B.C.	0.2	None
Dartmouth, N.S.	<0.2	None
River water		
North Saskatchewan River	1.6	None

contamination from the separator or treater and allowed to stand in a closed container for several weeks to allow a good gravity separation of coproduced oil and water. In each case, the water was carefully transferred to a separatory funnel and allowed to stand for 1 hr, after which it was drained off into a second funnel in which it was extracted with n-heptane. As before the extracts were chromatographed on silica gel and the alkanes determined by gas chromatography.

Very low levels of solvent contamination, which had not previously been attained, permitted the measurement of normal alkanes C<sub>16</sub> and above.

The content of n-alkanes in the C<sub>20</sub>-C<sub>33</sub> range as shown in Table VII is low, being only slightly higher than in the surface waters discussed in the preceding section. Significantly, they were appreciably lower than in the expressed waters of the sediments, and were 2.6 μg/l, 14 μg/l and 1.1 μg/l for the Joffre and Judy Creek oil-fields and the Countess gas field waters, respectively. Again as in most of the water samples examined, the distribution was logarithmic with a slope nearly the same as that of n-alkanes in distilled water. There was no odd carbon preference.

TABLE VII  
n-Alkane Content of Oilfield Waters

Field	Stratigraphic unit	Total C <sub>16</sub> -C <sub>33</sub> μg/l	pH
Joffre	Upper Devonian, Nisku formation	5.1	6.5
Judy Creek	Upper Devonian, Beaverhill Lake formation	14	6.9
Countess	Lower Cretaceous, Bow Island formation	1.1	8.0

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