

Alkanes in Aqueous Systems. II. The Accommodation of C₁₂-C₃₆ n-Alkanes in Distilled Water¹

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Abstract

The accommodation of n-alkanes in the C₁₂ to C₃₆ range in distilled water was measured as a function of hydrocarbon supply, settling time, filtration pore-size, and mode of introduction. Accommodation levels for individual hydrocarbons generally fell in the range of 0.01 to 100 mg/liter; liquids were accommodated to a greater extent than solids. Settling times of many days sharply reduced the measured accommodation, as did millipore filtration. The accommodation of a given n-alkane showed a strong dependence on the supply of the n-alkane in the equilibrating aqueous system.

Binary mixtures showed a limited effect of one alkane on another except in the case of mixtures of a liquid alkane and a solid alkane, in which the presence of the liquid greatly enhanced the accommodation of the solid. Similarly, supply ratios were reproduced for accommodated liquid alkanes except in those systems where the supply alkanes separated into co-existing liquid and solid phases with compositions as determined by the phase rule for the particular hydrocarbon system. The accommodated alkane composition was the same as that of the liquid hydrocarbon phase. The same pattern was observed for fused mixtures of n-alkanes in the C₁₂ to C₃₆ range, and on long-term settling there was an over-all, clear-cut tendency for preferential accommodation of n-alkanes in the C₁₆ to C₂₀ range at the expense of alkanes with both higher and lower carbon numbers.

Introduction

HYDROCARBONS ARE NOW KNOWN to occur widely in recent sediments (6,11,15,19-20), thus the problem of the origin of crude oil is no longer that of the source of the petroleum hydrocarbons but rather that of the process by which dispersed hydrocarbons may be collected to form crude oil (10). Of the 16,200 cubic miles of hydrocarbons estimated to exist in sedimentary basins throughout the world, only about 173 cubic miles are thought to be contained in reservoir rocks (11,21). The fact that only 1% of the earth's oil occurs in oil fields indicates that a specific combination of circumstances is required for the formation of an oil field. Obviously, geological factors, such as suitable structures, are of prime importance, but the mode of hydrocarbon movement is also clearly of great significance (9,10,17,22). It is this aspect of oil-field formation that is least understood.

Subsurface water may be of importance in the mobilization and migration of petroleum hydrocarbons (14). Basin-wide movements of subsurface waters are known to occur, and recent isotopic evidence indicates that a formation may be flushed many times during its geological history (7). Past dis-

cussions on the role of these waters in moving hydrocarbons have been largely speculative as chemical data describing hydrocarbon-water systems have been limited. By using tritiated hydrocarbons, E. G. Baker studied the solubility of the higher n-alkanes C₁₀, C₁₈, and C₃₆ and developed an hypothesis on the formation of petroleum (1-5). McAuliffe (13) recently reported the solubility of 65 hydrocarbons, including n-alkanes C₁ to C₉ inclusively, and Franks (8) investigated the solubility behavior of n-alkanes C₁₀, C₁₂, C₁₄, and C₁₆. Subsurface waters may experience a wide variety of chemical conditions while in contact with the many possible geological environments, and certainly a great many compounds exist in petroleum.

The purpose of the present series of communications is to report data describing the hydrocarbon-water relationship; however it is possible to consider only a small portion of this large topic within its scope. Therefore this series (16) is limited to the accommodation in distilled water of n-alkanes, one of the major constituent groups of crude oils as outlined recently by Smith in a comprehensive examination of the over-all composition of petroleum (18).

Whenever water is considered as an agent in petroleum migration, three basic questions arise: a) can water accommodate sufficient quantities of hydrocarbons to effect the mass transfer required for oil-field formation; b) will the transported hydrocarbons have a distribution similar to that found in crude oils; and c) what mechanism can release accommodated hydrocarbons?

In Part I preliminary data were obtained leading to tentative answers to the first two questions. Under the conditions, the limited data indicated that n-alkanes could be accommodated in the required quantities in distilled water with a modified distribution. The purpose of the present study is to expand the data presented in Part I and to inquire more comprehensively into the mode of hydrocarbon accommodation in distilled water. Thus the accommodation of single hydrocarbons, simple mixtures, and finally more complex mixtures was examined as a function of hydrocarbon supply, settling time, filtration pore-size, and mode of introduction. The results show that hydrocarbons are accommodated in water to a large degree in direct proportion to the availability of the hydrocarbons, and there are interactions between individual hydrocarbons such that, in some instances, the addition of a second hydrocarbon to an equilibrating system will greatly enhance the accommodation of the first hydrocarbon.

Experimental Procedure

The experimental procedure in the present study differed little from that of the earlier work (16). The basic experiment was to equilibrate a measured amount of n-alkane (as received, supplied by the Aldrich Chemical Company Inc.) with distilled water by mechanical shaking, followed by a settling period

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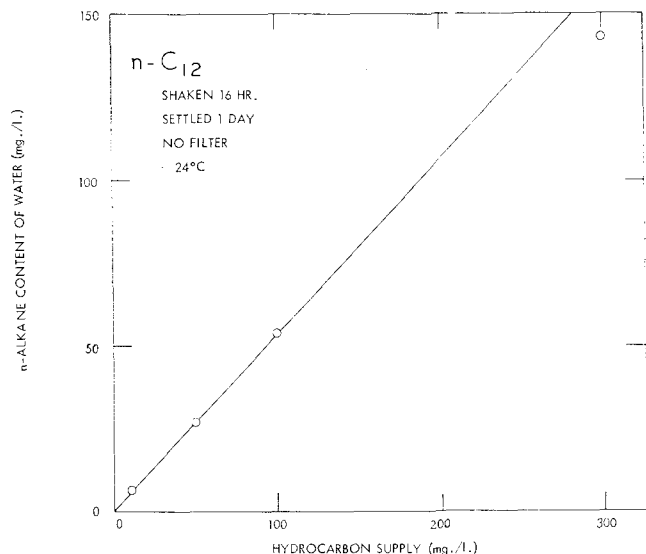


Fig. 1. Accommodation of C₁₂ n-alkane in distilled water as a function of the alkane supply. The level of accommodation is directly proportional to supply in this range.

and filtration step. Subsequent extraction with n-heptane recovered the accommodated alkane, which was analyzed by gas chromatography. The settling step differed from the one described in Part I in that in the present study it was more fully controlled, being carried out in a vertical, 4-cm diameter, glass tube from which aliquot samples were obtained by inserting a hypodermic needle through a septum held in a joint at the bottom of the tube.

Results

Single-n-Alkanes

Each of a series of single n-alkanes C₁₂, C₁₄, C₁₆, C₂₀, and C₂₄ showed similar accommodation behavior in experiments which were conducted under fixed but somewhat arbitrary conditions of shaking, settling, and filtering. A number of experiments were carried out to establish the effect of shaking and settling under

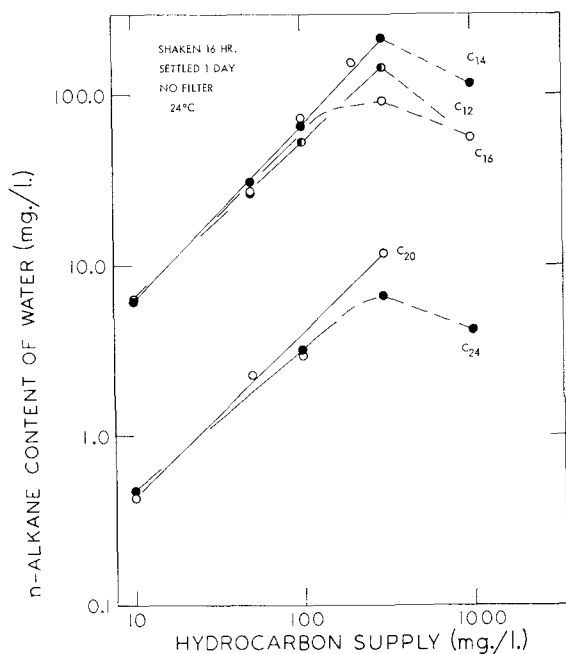


Fig. 2. Accommodation of individual n-alkanes in distilled water. The liquids C₁₂, C₁₄, and C₁₆ are accommodated to a greater extent than the solids C₂₀ and C₂₄.

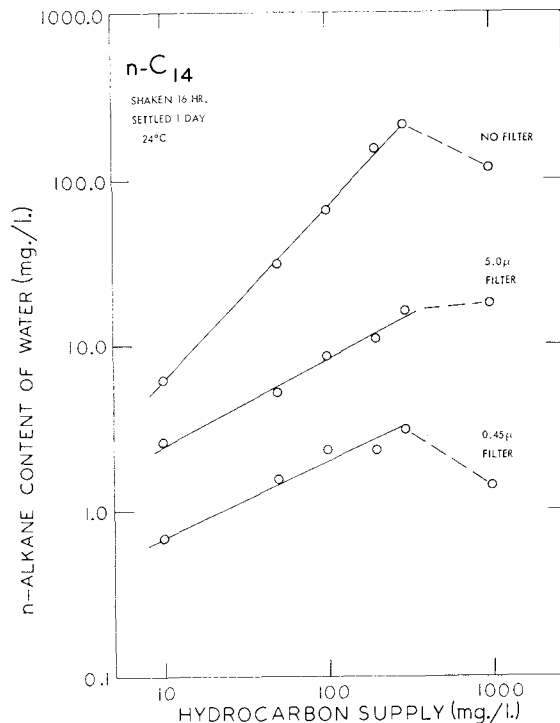


Fig. 3. Dependence of C₁₄ n-alkane accommodation on alkane supply before and after filtration.

the conditions in the laboratory as a guide for the systematic accommodation measurements.

The behavior of n-alkane C₁₂ (Fig. 1) shows the level of accommodation as a function of the supply of the hydrocarbon. Up to an alkane supply of about 300 mg/liter the accommodation level is directly proportional to the supply; slightly more than half of the supply is accommodated by 16 hours of mechanical shaking, one-day settling, and no filtration. At supply levels above about 300 mg/liter the accommodation response falls off sharply (Fig. 2). Corresponding data for n-alkanes C₁₄, C₁₆, C₂₀, and C₂₄ over a supply range of 10 to 1,000 mg/liter gave similar curves (Fig. 2).

Grouping of the results was evident; those hydrocarbons which are liquid at the temperature of the experiments, i.e., C₁₂, C₁₄, and C₁₆, were char-

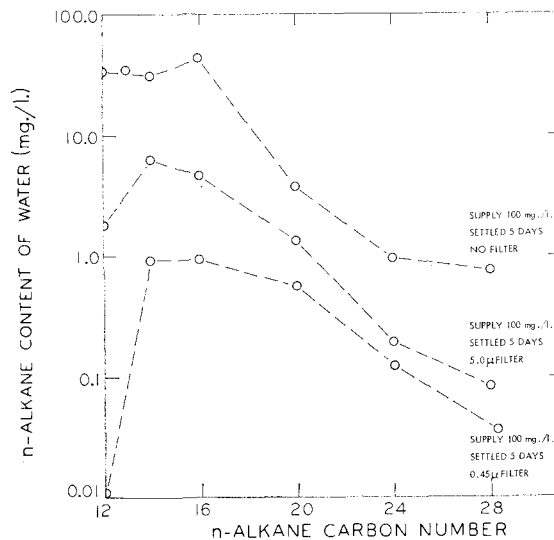


Fig. 4. The effect of small pore-filtration upon individually accommodated n-alkanes, showing the marked disaccommodation of C₁₂.

TABLE I
Simultaneous Accommodation of Two Liquid Alkanes as a Function of Supply Ratio

Supply mg/liter		Ratio C ₁₄ :C ₁₃	C ₁₄ :C ₁₃ Ratio Accommodated						Average
C ₁₄	C ₁₃		One-Day settling			Five-Day settling			
			No filter	5.0 μ filter	0.45 μ filter	No filter	5.0 μ filter	0.45 μ filter	
10	20	0.5:1	0.48	0.47	0.48	0.48	0.53	0.61	0.54
100	200	0.5:1	0.54	0.52	0.54	0.59	0.65	0.96	
100	200	0.5:1	0.48	0.47	0.48	0.62	0.48	0.53	
100	100	1:1	1.05	1.10	1.23	0.99	1.05	1.04	1.08
200	100	2:1	1.97	1.97	1.73	1.82	2.07	2.29	1.89

acterized by "high" accommodation levels whereas the others, the solid hydrocarbons, were accommodated to a much lower degree. The n-alkanes up to and including C₁₇ were free-flowing liquids; C₁₈ to C₂₂ were oily solids; alkanes above C₂₂ were dry, loosely-packed crystals. The liquid hydrocarbons were accommodated, at moderate supply levels, to about 60% of the supply whereas the solid hydrocarbons were marked by an accommodation corresponding to only about 4% of the supply.

Study of a single n-alkane C₁₄ gives an insight into the effect of filtration on the accommodation process. Aliquots of water containing previously accommodated n-alkanes were filtered by vacuum through 5.0 μ and 0.45 μ millipore filters before extraction with heptane. The data for C₁₄ (Fig. 3) are typical of the group of hydrocarbons, and it is clear that the dependence of accommodation on the supply persisted. Although filtration had little effect on the pattern of alkane accommodation, it did however have a profound effect on the amount of hydrocarbon accommodated. The accommodation level was reduced by 90 to 99% in the finer filter.

Another aspect of the filtration effect is shown in Fig. 4, which presents a few of the data covering a number of the settling-filtration patterns investigated. The most striking feature is the marked susceptibility to filtration exhibited by the liquid alkanes, particularly the C₁₂ n-alkane, the accommodation of which dropped from 35 mg/liter with no filtration to about 0.01 mg/liter in the 0.45 μ filtrate. This behavior was evident in all of the systems studied.

The mechanism of the ultrafiltration step of course is not clearly understood. Although there is no evidence to suggest that anything other than simple particle filtration is involved, care must nevertheless be taken in interpreting the results in these terms. Thus, in summary, the single alkane systems showed: a) a direct relationship between accommodation and supply up to a supply of about 300 mg/liter; b) liquid alkanes are accommodated to a much greater extent than solids; c) liquid alkanes are more susceptible to filtration than solids.

These measurements were useful in establishing an exploratory understanding of both the nature and extent of the accommodation of n-alkanes in water. The levels of accommodation were much higher than those given by Franks for the solubility of hydrocarbons in water (8). For example, the solubility of

n-C₁₂ was reported by Franks to be about 10⁻⁹ mole fraction, i.e., about 0.01 mg/liter, compared with accommodation levels in the present study at 10–100 mg/liter. The accommodation mechanism is clearly something more than true solution, and the data are useful in establishing reference points for the examination of the accommodation of mixtures of hydrocarbons.

Binary Mixtures

Binary mixtures are the simplest, and three such pairs of alkanes were selected to explore the interaction between such components in an accommodation system. Two short-chain alkanes, C₁₃ and C₁₄, were chosen to examine interactions between hydrocarbons in the liquid state; similarly C₁₉ and C₂₀ were selected for the solid state. The third pair, C₁₄ and C₂₀, represented a liquid and a solid alkane.

Measurements of accommodated alkanes were made for equilibrations at two levels of supply, roughly 10 mg/liter and 100 mg/liter. To test the interaction between members of each pair, a wide range of supply ratios was employed, from 10:1 to 1:10 in some instances. To allow comparison with some of the single alkane data, the shaking period was set at 16 hours with settling periods of one and five days, followed by 5.0 μ and 0.45 μ filtrations. Each of the n-alkanes was introduced to the water independently of the other, and the results therefore should reflect any interactions that took place between the alkanes during the equilibration step.

The results are best described in each of two ways: as a comparison of absolute amounts and as a comparison of supply ratios with accommodated ratios.

The absolute amounts of individual alkanes accommodated were affected to some degree by the presence of the second alkane. In general, in the C₁₃–C₁₄ system, the presence of C₁₃ suppressed the accommodation of C₁₄, and C₁₄ enhanced the accommodation of C₁₃. In the C₁₉–C₂₀ system the presence of C₁₉ slightly enhanced the accommodation of C₂₀. Similarly, for C₂₀ and C₁₄, the addition of C₂₀ slightly increased the accommodation of C₁₄, but a profound enhancement of the accommodation of C₂₀ resulted from the addition of C₁₄ to the system. In general, the increase was in the range of two to eight-fold.

These data are presented in the ratio form in Tables I, II, and III, wherein the relationship between member pairs is examined in the context of the odd-

TABLE II
Simultaneous Accommodation of Two Solid Alkanes as a Function of Supply Ratio

Supply mg/liter		Ratio C ₂₀ :C ₁₉	C ₂₀ :C ₁₉ Ratio Accommodated						Average
C ₂₀	C ₁₉		One-Day settling			Five-Day settling			
			No filter	5.0 μ filter	0.45 μ filter	No filter	5.0 μ filter	0.45 μ filter	
20	6.7	3.0:1	1.99	1.98	2.02	1.88	1.98	2.01	1.98
200	100	2.0:1	1.41	1.66	1.60	1.72	1.49	1.61	1.58

TABLE III
Simultaneous Accommodation of a Solid and a Liquid Alkane as a Function of Supply Ratio

Supply mg/liter		Ratio C ₂₀ :C ₁₄	C ₂₀ :C ₁₄ Ratio Accommodated						Average
C ₂₀	C ₁₄		One-Day settling			Five-Day settling			
			No filter	5.0μ filter	0.45μ filter	No filter	5.0μ filter	0.45μ filter	
10.3	100	0.1:1	0.11	0.12	0.11	0.11	0.12	0.16	0.12
100	200	0.5:1	0.52	0.32	0.41	0.44	0.46	0.58	0.46
100	100	1.0:1	0.95	0.81	0.92	0.96	1.16	1.05	0.98
200	100	2.0:1	0.95	0.80	1.07	0.96	1.13	1.05	0.99
97	10	9.7:1	1.07	0.55	1.06	0.98	0.93	1.07	0.94

carbon preference phenomenon in the relation between petroleum source-material and the alkane distribution in petroleum. The basic question is whether the alteration of the known odd-carbon preference of biologically derived hydrocarbons to a uniform alkane distribution in petroleum is related to accommodation phenomena.

The results for the liquid-liquid pair show clearly that the ratio of accommodated alkanes is essentially identical with the supply ratio, lending no support to the above suggestion. The solid-solid data however were somewhat different; the 2:1 and 3:1 supply ratios were reduced to about 1.6:1 and 2.0:1 respectively. The more striking data were those for the C₁₄-C₂₀ n-alkane pair, in which the supply ratio persisted in those instances in which the liquid (C₁₄) was predominant in the alkane supply but died out completely when C₂₀ was predominant. The C₁₄ to C₂₀ ratios did not reflect the results of the single n-alkane experiments, which showed that accommodation levels of the liquid C₁₄ were several times greater than those of the solid C₂₀.

The explanation for the particular changes in the hydrocarbon ratios probably lies in the observation, a) that alkanes in the liquid state are accommodated in water much more fully than those in the solid state so that the observed accommodation is owing almost solely to the supply of alkanes in the liquid state and b) that the composition of the liquid hydrocarbon supply is determined by the phase behavior of the particular hydrocarbon system. The n-alkanes C₁₄ and C₂₀ are completely miscible in both the liquid and solid state. Liquid and solid phases exist simultaneously in some C₁₄-C₂₀ mixtures at room temperature.

The phase behavior would be similar to that outlined by Mazee et al. (12) for alkanes in the C₂₀-C₃₆

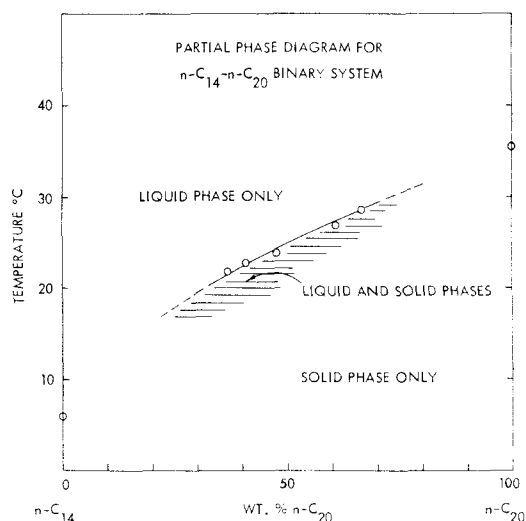


FIG. 5. Partial phase diagram for C₁₄-C₂₀ alkane binary mixtures, showing composition of liquid phase when both solid and liquid phases are present.

range. The composition of the liquid in contact with the water would either be the same as that of the variable alkane supply for compositions above the liquidus line or would be a composition given by the liquidus line when both liquid and solid phases were present at the temperature of the experiment. The data in Table III for C₂₀-C₁₄ binary systems are consistent with this suggestion. The liquidus line is encountered at supply ratios above 1.0, as indicated by the fixed composition of accommodated hydrocarbons for increasing supply ratios beyond the 1.0 point.

To test this interpretation of the accommodation data, an attempt was made to determine the position of the liquidus line for the C₂₀-C₁₄ system in the region pertinent to the accommodation measurements. This was done by determining the freezing point of a series of C₂₀-C₁₄ mixtures and by measuring the composition of the liquid phase for the same mixtures as a function of temperature. The results are plotted in Figure 5, and it is clear that the interpretation is indeed supported.

Fused n-Alkane Mixtures

Experiments similar to those for the binary mixtures were carried out with more complex mixtures. Instead of two components there were now several, seven in one mixture, 20 in another, and 14 in a third mixture. Instead of the components being introduced independently, they were mixed in a stock supply through melting. Appropriate liquid aliquots were taken from the melted stock supply.

The seven-component, fused mixture was a microcrystalline solid at room temperature and consisted of n-alkanes C₁₂, C₁₆, C₂₀, C₂₄, C₂₈, C₃₂, and C₃₆. Figure 6 shows a gas chromatogram of the starting mixture along with that of the alkanes accommodated in water after the mixture was shaken 16 hours and settled one-half hour. It is obvious that there is

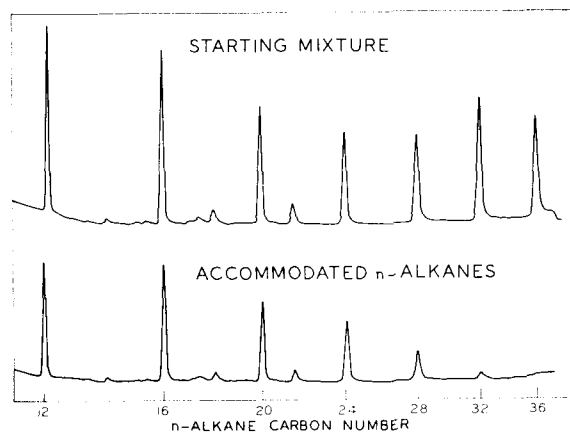


FIG. 6. Gas chromatograms of a fused mixture of seven n-alkanes before and after accommodation in distilled water. The higher-molecular-weight alkanes are the least readily accommodated.

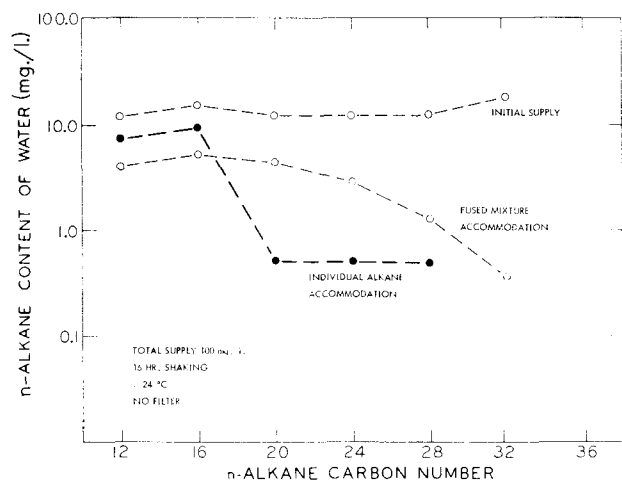


Fig. 7. A comparison of n-alkane accommodation with n-alkanes supplied either individually or as a fused mixture.

preferential accommodation of the lighter alkanes. The conclusion is that the accommodation mechanism is something other than a simple dispersion of the fused mixture. Also the accommodation mechanism is not a simple accommodation of each of the component n-alkanes, as is evident from Figure 7, in which the accommodated alkane contents are related to the starting mixture.

The liquid alkanes seem to have enhanced the accommodation of the solid alkanes, as was the case in the liquid-solid binary system. When the solid alkanes, C_{20} , C_{24} , and C_{28} , were introduced into the water as part of the fused mixture rather than as individual alkanes, their levels of accommodation were greatly increased. A related experiment, in Part I of this series, by using no liquid alkanes, had produced much lower accommodation levels than found in the present solid-liquid study. In both cases the alkanes were not all accommodated to the same extent, and solid alkanes above C_{20} showed a systematic decrease in accommodation. The fused seven-component mixture was a microcrystalline solid at room temperature, but, after shaking for 16 hours with distilled water, both liquid and solid hydrocarbon phases were visible. The systematic decrease in accommodation with increasing n-alkane molecular weight may have been caused by preferential accommodation of the liquid

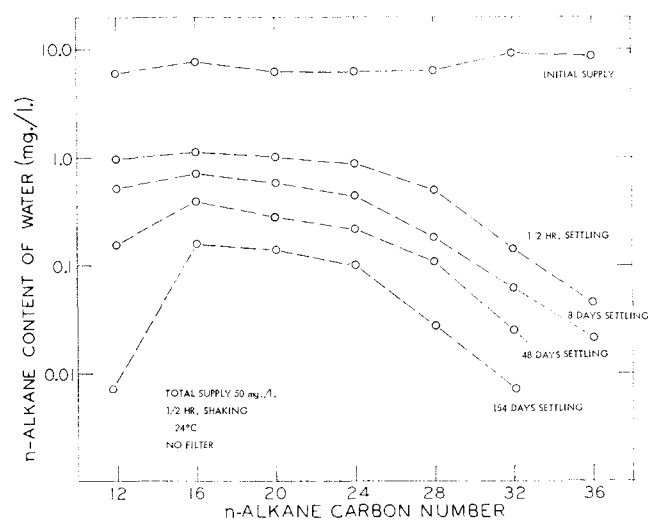


Fig. 8. Changes in the distribution pattern of a fused seven-component n-alkane mixture as a result of accommodation and settling.

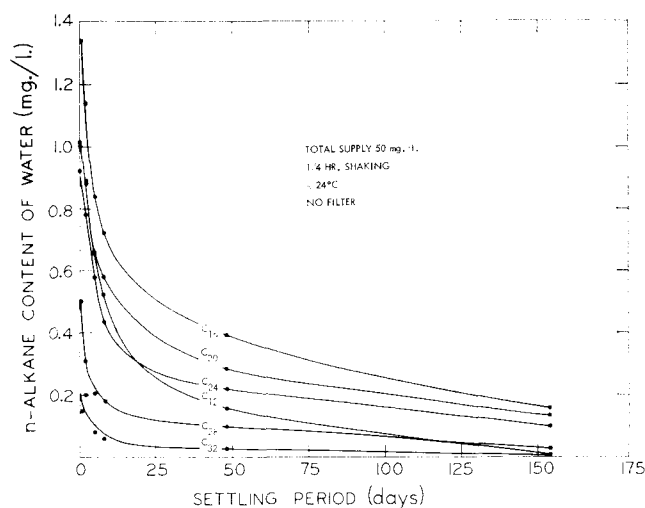


Fig. 9. The effect of settling period upon the accommodation of the components of a simple fused mixture. The n-alkane C_{12} settles most rapidly.

n-alkane layer, composed of both lower-molecular-weight liquid n-alkanes and solid n-alkanes to the limit of their miscibility with the liquids at room temperature.

The distribution pattern of the accommodated n-alkanes was distorted to some degree when settling effects were considered (Fig. 8). As noted during millipore filtration studies on the single-component systems, some alkanes are more readily disaccommodated than others. Similarly, settling over a long period resulted in a reduction in the content of the lower-molecular weight-alkanes, in this mixture, C_{12} . The differences in settling rates which brought about the changes in distribution are illustrated in Fig. 9. Settling effects are most pronounced during the first few days; only minor changes occurred beyond 10 days. Thus the initial distribution of alkanes is changed both during accommodation, as the lower-molecular-weight components, C_{12} to C_{24} , are preferentially accommodated, and during settling, when C_{12} was most rapidly disaccommodated. After 154 days of settling these combined effects resulted in an apparent preferential accommodation of alkanes C_{16} and C_{24} .

To test for any effect of biological activity on alkane accommodation, hydrocarbons were equilibrated with

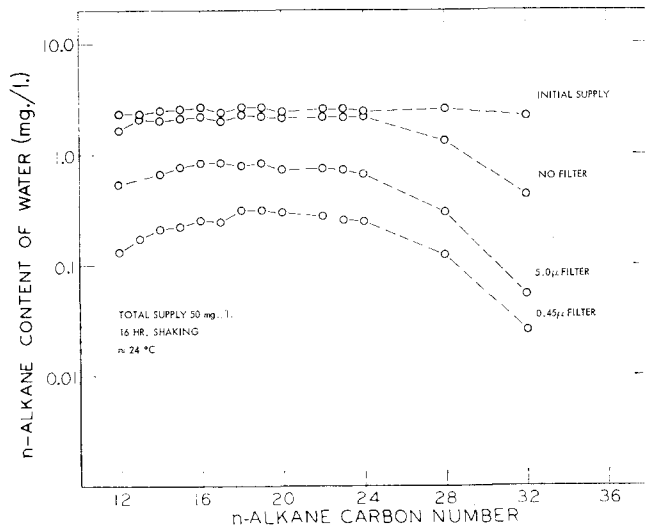


Fig. 10. The accommodation of the components of a fused mixture of 20 n-alkanes, illustrating the effect of filtration upon the distribution.

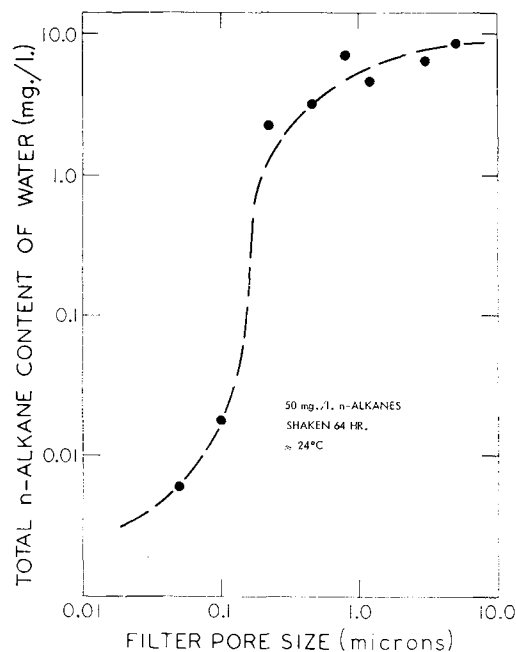


FIG. 11. The effect of filtration upon the total alkane accommodation level for a 20-component, fused mixture.

two solutions, one of which contained 0.01% HgCl_2 to inhibit bacterial growth. After 121 days of settling, under identical laboratory conditions, there was no evidence of bacterial decomposition in the untreated solution.

In the course of the experiments, information was obtained relating to the effect of the time of shaking. In all cases the degree of accommodation was directly dependent upon the length of the shaking period until periods of 12 to 24 hours were reached. In turn, the settling effects were dependent upon the initial period of shaking. In general, the longer the shaking period the slower was the rate of settling. Thus the levels of alkane accommodation were variable, but the distribution pattern in all cases showed that C_{12} was the most rapidly disaccommodated alkane of the seven alkanes present in the fused mixture.

In summary, the data for the fused seven-component system thus demonstrate that the fused alkanes do not behave as a single unit during accommodation but rather as liquid and solid phases. The change in distribution pattern during accommodation and settling results in a predominance in the water of n-alkanes in the range of C_{16} to C_{24} .

A similar series of experiments was carried out by using a fused mixture of roughly equal quantities of 20 n-alkanes in the C_7 to C_{36} range. The mixture resolved into both a liquid and solid phase upon standing at room temperature for several days. When accommodated in distilled water, the n-alkanes showed a distribution similar to that of the accommodated seven n-alkane fused mixture with steadily decreasing amounts of n-alkanes above C_{20} . Analysis of the liquid phase of the hydrocarbon mixture showed a similar n-alkane distribution.

The effect of filtration on the accommodated n-alkane is shown in Fig. 10. The changes brought about by filtration were similar to those produced in the seven-component mixture by prolonged settling. The n-alkanes with carbon numbers of less than 18 were most greatly affected by filtration, and extension of the measurements to C_9 showed a continuing steady decline in content beyond C_{12} down to C_9 .

An extension of the filter examination of the twenty-component mixture was made, as with single alkanes in Part I, with a series of filters, producing the dependence of accommodation on filter pore-size (Fig. 11). The S-shaped curve reported previously was confirmed; the inflection point occurred at a nominal filter pore-size of about 0.2μ . Thus the 5μ and 0.45μ filters used routinely in the present experimental work represented the larger of the two populations of alkane particles, which were indicated in the water by the bimodal curve of Fig. 11.

The results arising from the study of simple mixtures and the equal-abundance, many-component mixtures yielded some support for the suggestion that the odd-carbon preference in n-alkanes from a biological source would be suppressed in an accommodation in water. Yet the fact remains that the accommodation of a given n-alkane is a function of the supply of that hydrocarbon, and an odd-carbon preference in the supply should therefore persist. Further, the liquid-phase, phase-rule distribution would be expected to operate if both liquid and solid phases exist in the hydrocarbon supply. Thus transmission of an odd-carbon preference from supply to water is indicated under these conditions. This was confirmed by the data of Fig. 12, which were obtained from an experiment by using a fused n-alkane mixture with a strong odd-carbon preference. As was expected, analysis of the liquid component of this two-phase hydrocarbon mixture showed a composition closely resembling that of the accommodated n-alkanes.

Accommodation Levels

The results of the series of experiments outlined in this paper have been reported mainly in terms of distribution patterns rather than absolute accommodation values. Various factors which affect absolute values have been mentioned from time to time. These factors include hydrocarbon supply, shaking period, settling period, and filter pore-size. To these could be added temperature effects and the effects of dissolved gases. It is apparent that the accommodated alkanes are not in equilibrium with the water; in order to assign a value to the accommodation level of a single alkane or fused mixture of alkanes, conditions must be carefully defined.

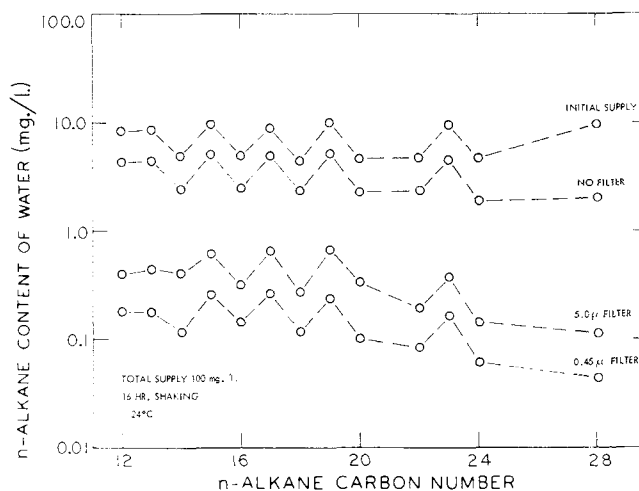


FIG. 12. The accommodation of the components of a mixture containing a predominance of odd-carbon alkanes. The ratio of odd to even alkanes is not significantly changed by accommodation in this experiment.

TABLE IV
Typical Accommodation Levels of Individual n-Alkanes and n-Alkane Mixtures Illustrating the Effects of Settling and Filtration

Hydrocarbon	Total Supply mg/liter	Shaking Period hr	Settling Period days	Filter Pore-Size microns	Total Hydrocarbons Accommodated mg/liter
C ₁₂	100	16	1	58
C ₁₂	100	16	5	5.0	4.0
C ₁₂	100	16	5	0.45	1.8
C ₂₀	100	16	1	4.0
7 components	50	½	0.02	4.7
7 components	50	½	154	0.4
7 components	50	40	154	8.5
20 components	100	23	4	24.6
20 components	100	23	200	8.8
20 components	100	16	10	5.0	5.3
20 components	100	16	5	0.45	1.8

Such factors as the energy imparted to the system during shaking are not easily calculated, therefore the importance of the values shown in Table IV must not be over-emphasized. These data have been chosen to illustrate points previously discussed. Similarly, unless the conditions are precisely known and all previously mentioned factors are considered, a valid comparison of accommodation levels of individual alkanes, as reported herein, and alkane solubility as determined by Baker (1,2), McAuliffe (13) and Franks (8) is not possible. It is clear however that it is possible to accommodate hydrocarbons in water at levels much higher than solubility levels and that these systems are stable over long periods of time.

The extent of the accommodation is determined by the intensity of hydrocarbon introduction to the water on the one hand, and by the depletion on the other. For mixtures of hydrocarbons, there is deep involvement of hydrocarbon-phase behavior in the accommodation step. The depletion step is different; evidence suggests that C₁₂ and lower n-alkanes are more readily disaccommodated, even from mixtures. These two factors appear to give rise to a surprising net preferential accommodation of alkanes in the C₁₆-C₂₀ range.

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