ORGANOPHILIC PORES AS PROPOSED PRIMARY MIGRATION MEDIA FOR HYDROCARBONS IN ARGILLACEOUS ROCKS

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ABSTRACT

A chemical model for the structure of the double layer in the presence of organic ions and molecules in the vicinity of clay surfaces is postulated. The validity of this model is examined in the light of known literature on the interaction between clay minerals and organic compounds. The probability of the penetration of organic ions and molecules into the inner Helmholtz layer is discussed.

The effect of migrating water on the migration of hydrophilic and hydrophobic organic compounds through a rock is discussed. The rate of migration of organic compounds depends on their chemical nature as well as the nature of the rock. From the model on the stability of the double layer it may be concluded that amphipathic molecules (soaps) are carried with migrating water from pores where their surface density is low to pores where their surface density is high. There is a probability of a complete saturation of several of the pores with organic ions or polar molecules. Such a pore is defined as an "organo-pore" and is shown to be hydrocarbon permeable. Organo-pores may become the paths for primary migration of hydrocarbon in the argillaceous source rock.

INTRODUCTION

The physical and geological processes which are associated with the primary migration of oil from clay source rocks have been the subject of many investigations (see e.g., Chapman, 1972; Cordell, 1972; Johns and Shimoyama, 1972). In most studies the primary migration of the hydrocarbons was considered to be dependent on the dehydration stages of the clay minerals and on the hydrostatic liquid pressures associated with burial depth of sediment. Recently, Cordell (1973) pointed out that intergranular primary migration of oil globules or droplets would be quite difficult in argillaceous source beds because of small average pore size and predominance of extremely small pores. Pore size analysis suggests that pore diameters in general are less than 50 Å. According to Cordell the primary migration is associated with enhancement of hydrocarbon solubility. This may occur in the presence of "soaps" which may form micelles. Cordell himself points out a few facts which conflict with this proposal. The quantity of soap required for hydrocarbon solubilization is many times greater than that of the hydrocarbon.
This contradicts geochemical observations. Furthermore the size of the micelle containing the hydrocarbon molecules would be too great to migrate through the small pore spaces.

Much laboratory work has recently been done on the interaction of clay minerals with organic compounds and on the structures of organo-clay complexes and has been well reviewed by Theng (1974). It seems that most of those polar organic compounds which may be classified as "soaps" interact with clay minerals. In general, pores in clay sediments are water permeable, but not hydrocarbon permeable. In the present communication, the formation of organophilic pores is discussed. These pores are obtained by the interaction of the surfaces of hydrophilic pores with organic polar molecules and ions. If such pores are obtained, even in small amounts, they may become the paths for primary migration of hydrocarbons.

In the present communication we shall differentiate between three categories of organic compounds in sediments:

**Category 1:** Compounds containing a large proportion of oxygen, nitrogen, sulphur and aromatic rings. These are polar hydrophilic compounds.

**Category 2:** Compounds having a small number of functional polar groups which can be non-ionic, zwitterionic or ionic, and long highly saturated aliphatic straight or branched tails. These may be considered as "soaps" or "amphipathic molecules" having both hydrophilic or organophilic poles. These compounds are very important in converting organophobic pores into organophilic ones.

**Category 3:** Hydrocarbons (petroleum-like paraffins) which are hydrophobic in their character.

**The electric charge of the pore surface**

For simplicity we shall limit our discussion to the mica type expanding layer silicates. Clays may be compacted after their sedimentation from either a dispersed or a flocculated suspension. In the dispersed suspension the particles are present as single plates or as tactoids of several parallel plates. After sedimentation the plates are parallel. In such a sediment we may differentiate between "interlayer space" pores with negatively charged surfaces and pores limited by the edges of the plates, which are usually positively charged, but sometimes also negatively charged.

In the flocculated suspension, a card-house structure is obtained with edge to face interaction between the plates. The most probable shape of such a floc is a sphere, within which liquid is immobilized. The net charge of such a sphere is negative. After sedimentation this floc shrinks but it preserves its spherical structure. The surface charge of these pores is negative. In addition to this type of pores, highly compacted clays of flocculated suspensions contain "interlayer space" pores and "edge-of-plate" pores.

**A model for the structure of the double layer in the presence of organic ions of the second category**

The distribution of organic ions with a charge opposite to that of the
solid phase, within the double layer, may be speculated from a model of the distribution of inorganic ions. For simplicity, the organic ion will be considered to consist of two distinct moieties, a hydrophilic head, where the electric charge is concentrated, and a hydrophobic tail. The clay surface will be considered to be flat with a uniform charge density. The aqueous phase is divided into four regions A, B, C and D of distinct dielectric behavior (Bell and Levine, 1972). These are the inner and outer “Helmholtz” layers, the diffuse layer and the bulk water with dielectric constants \( \varepsilon_1 < \varepsilon_2 < \varepsilon_3 < \varepsilon_4 \) respectively.

The penetration of the organic ions into the double layer, is predominantly due to “long range” electrostatic attraction. This is minimized by the three following reactions:

1. Dimers or micelles must dissociate before organic ions pass from the
bulk into the double layer. The free energy change during this dissociation process $\Delta F_d$ depends on the ratio of the surface area of the monomeric ion to that of the polymeric form. For aliphatic tails it increases with increasing number of carbons (Mukerjee, 1967).

(2) Ions must be completely or partly dehydrated before they may penetrate into the double layer. The free energy change during this process, $\Delta F_h$, depends mainly on the polarization and charge of the hydrophilic group, and to some extent also on the structure and composition of the non-charged hydrophobic moiety of the ion. Bodenheimer et al. (1966a) showed that in the clay interlayers amines display their true basicity, unaffected by solvating molecules, while in the bulk aqueous solution hydration shells have great influence on the basicity of the amine.

(3) Polarized water molecules are repelled from the double layer by the penetrating organic ions. The change in free energy is given by equation (1).

$$\Delta F_s = \frac{1}{8\pi} \left(1 - \frac{1}{\varepsilon}\right)x^2v$$

where $x$ is the intensity of the electric field at the point where the center of the ion is located in the double layer and $v$ is the volume of the organic ion together with its hydrophobic and hydrophilic hydration shells.

Water in the vicinity of the non-charged moiety of the organic ion will have the "hydrophobic hydration" structure. There may be repulsion forces resulting from the self atmosphere potentials of the organic and inorganic ions present in the double layer, and also from the electric field induced by the clay surface (arrows in Fig. 1). Due to these repulsion forces in the diffuse and the Helmholtz layers, the hydrophobic alkyl tail will point away as far as possible from the clay surface towards regions with low intensities of the electric field.

When the concentration of organic ions in the double layer increases, the possibility of hydrophobic moieties contacting each other will occur even if this requires that the angle which develops between the oxygen sheet and the long axis of the tail is non-perpendicular (Weiss, 1963; Walker, 1967). The free energy change as a result of this association is defined as the double layer association energy, $\Delta F_a$.

Since this kind of association, which tends to increase the penetration of organic ions into the double layer, increases with increasing concentration, it is expected that the selectivity of the double layer for the organic ion increases with the increased occupancy of the exchange sites by organic cations. This was shown by Theng (1971) for the adsorption of alkylammonium cations by Na-montmorillonite. As will be seen in a later stage, this is an important factor in the mechanism of the formation of the organophilic pore, due to the selective sorption of organic ions.

Because of the low polarizability of the hydrophobic chain, the electric field induced by the clay surface may be screened by the tilted hydrophobic part of the organic ion. This increases the ease of dehydration of organo-
clay complexes.

The increase in the number of carbon atoms in the alkyl group is paralleled by an increase in the adsorption energy. The size of the increment is approximately 400 cal/CH$_2$ group (Cowan and White, 1958). In the earlier literature the increase of free energy with the chain length of the alkylammonium ion was attributed to the effect of increasing van-der-Waals forces. Recently, Vansant and Uytterhoeven (1972) showed that the van-der-Waals interactions are negligible and that hydration and the coulombic interaction between the cation and the clay are more important.

“Short range” forces can occur when ions penetrate into region A. These forces are characterized by a strong dependency upon distance and comprise van-der-Waals forces, $H$ and chemical bonds and $\pi$ interactions. For surfaces at the edges of the clay plates, the effect of short range forces is more critical than long range forces.

The probability of the penetration of organic ions into region A is given by

$$
\nu = g \exp\left(-\frac{(Z_i\varphi + \Delta F_s + \Delta F_d - \Delta F_h - \Delta F_a - \Delta F_{\pi})}{kT}\right)
$$

(2)

where $Z_i$ is the charge of the ion, $\varphi$ the electric potential in region A, $\Delta F_s$ is the “short range” energy, $k$ is the Boltzmann constant and $g$ is a statistical factor which depends on the concentration of the organic ion. Since $\Delta F_s$ greatly increases with increasing concentration, it follows that the probability of penetration of organic ions into region A also increases. This can be supported by the study of Yariv and Lurie (1971) of the sorption of a cationic dye molecule (methylene-blue) by montmorillonite. According to these investigators, metachromasy of aromatic dyes in montmorillonite results due to their penetration into region A followed by effects of the lone pair electrons of the oxygen on the amplitude of the $\pi$ electrons of the aromatic rings. From their study it can be concluded that the fraction of the dye reaching region A per total dye added, increases with increasing concentration.

Sorption of organic anions at the flat unit-layer surface

From equation 2 it is to be expected that anionic species will be negatively sorbed by a double layer having a negative potential. Only if the short range energy $\Delta F_s$ exceeds the sum of hydration energies $\Delta F_h$ and $\Delta F_{\pi}$, micelle dissociation energy $\Delta F_d$ and coulombic repulsion $Z_i\varphi$ will anions be positively adsorbed. Negative adsorption of anionic herbicides by montmorillonite was observed by Frissel and Bolt (1962). In the presence of polyvalent metallic cations, benzoate anions were adsorbed due to short range interaction of benzoate and the metallic cations (Yariv, Russell and Farmer, 1966). Anions may be sorbed from aqueous solutions by clay minerals if they are able to form stable coordination species which are positively charged (Yariv et al., 1964a, b).
Sorption of organic polar molecules of the second category

Since the dielectric constant of the solvent in the double layers is lower than that in the bulk, proton transfer reactions in the double layer are faster than in the bulk solution. Strong bases are protonated to give positively charged ions. The extent of this reaction depends on the basicity of the organic compounds and polarizability of the metallic cation (see e.g., Bodenheimer et al., 1966b and Yariv and Heller, 1970). The organic ion thus obtained may reach region A.

With decreasing basicity of the organic compounds or acidity of metallic cations, association species are obtained with hydrogen bonding, wherein a water molecule acts as a porton donor (Yariv et al., 1968). Transition metals and organic bases form coordination compounds in the clay surface (Bodenheimer et al., 1962, 1963, 1966).

Proton donors may interact with two different sites: (1) basic sites in the oxygen sheet; (2) negative poles of water molecules in the hydration spheres of cations (Sofer et al., 1969; Yariv et al., 1969).

The conclusions drawn in the preceding section concerning the structure of the double layer and the probability of sorption of organic ions are also valid for polar molecules.

Sorption of fatty acids by clays

It has been proposed that fatty acids are transformed into paraffins during burial of sediments (Kvenvolden and Weiser, 1967) and that this conversion is catalyzed by clay surfaces (Shimoyama and Johns, 1971; Waples, 1972). Sorption of organic acids by the double layer of the flat unit layer surface is affected by the exchangeable inorganic cations. The carboxylic group is bound to the cation through a water bridge (Yariv, Russell and Farmer, 1966).

Sorption of fatty acids from aqueous solution is predominantly due to their interaction with the edges of the clay plates. This sorption depends on the pH of the system. There is an optimal pH value at which the surface charge is still positive and the concentration of the carboxylate anion is sufficiently high for a maximum sorption to occur. At higher pH values, at which the positive surface charge decreases, and may even become negative, sorption decreases although the concentration of the anionic species increases. At a lower pH value a decrease in the concentration of the negative species leads to a decrease in sorption of the acid. According to Hingston et al. (1967) for inorganic weak acids there is a convincing correlation between pK of the acid and pH of maximum adsorption.

Recently, Meyers and Quinn (1971, 1973) studied the sorption of long chain fatty acids with various clay minerals from aqueous solutions. Their results are in a good agreement with the above model of the sorption mechanism and the structure of the double layer. The pK of the acids they studied was about 5. For systems of pH > 5 they found that fatty acid sorption by clay decreased as the pH became more basic. They found that the
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sorption increased with increasing concentration and chain length or decreasing temperature. These phenomena are in agreement with equation (2). These investigators studied the effect of NaCl salinity on heptadecanoic acid adsorption by bentonite and found it to increase with increasing salt concentration. This might also be a result of the increase of "double-layer association energy". If we assume that an increase of the salt concentration leads to a compression of the diffuse counter ion atmosphere, then it is to be expected that the probability of organic chains associating and dehydrating will increase.

The effect of migrating water on the migration of the organic compounds

Migrating water in the saturated source rocks serves as the chief carrier for the organic soluble compounds. The adsorbing clay tends to lower the rate of migration. The chemical reaction occurring during this process may be formulated as follows:

\[
\text{(A)} \quad \text{Clay}^1 \cdot \text{OC} + (x+y)\text{H}_2\text{O} \overset{\frac{u_1}{u'_1}}{\rightarrow} \text{Clay}^1 \cdot (\text{H}_2\text{O})_{x+y} \cdot \text{OC} + \text{H}_2\text{O} \\
\text{(B)} \quad \text{Clay}^2 \cdot (\text{H}_2\text{O})_{x+y} \cdot \text{OC} \overset{\frac{u'_2}{u_2}}{\rightarrow} \text{Clay}^2 \cdot \text{OC} + (x+y)\text{H}_2\text{O}
\]

OC denotes an uncharged organic compound, l and s denote liquid and solid phases respectively and Clay\(^1\) denotes a solid phase in a position below Clay\(^2\). \(u_1\), \(u'_1\), \(u_2\) and \(u'_2\) are the reaction rates. With increase of \(u_1\) and \(u_2\) and decrease of \(u'_1\) and \(u'_2\) the rate of the migration of the organic molecule increases.

\(u_1\) and \(u_2\) depend on the availability of water molecules to exchange all functional groups in the organic molecule which form bonds with various sites in the clay, either as electron donors or acceptors. This depends on the site of the functional group, whether it is at the edge or inside the molecule. The probability of exchanging all functional groups for water molecules decreases with increasing number of functional groups, aromatic character and molecular weight. Hence, the migration of compounds of the first category is extremely low, approaching zero, even when they are hydrophilic.

Molecules of the second category. From our discussion of the "double layer association energy", it appears that sorption energy increases with increasing interface concentration of the organic material. It follows that \(u'_1/u_1\) and \(u'_2/u_2\) of equations (A) and (B) increase with increasing interface concentration of the organic material. Migrating water will carry these organic compounds from pores where their surface density is low to pores where their surface density is high. This results in a probability \(\alpha\) of a complete saturation of a pore with organic ions or polar molecules. If \(p\) is the total number of pores in the source rock, then \(\alpha p\) is the number of saturated pores obtained some time after compaction. Such a pore may be defined as
an "organo-pore". The distribution of the aqueous soluble organic material in a clay rock will not be homogeneous. This material tends to be concentrated along some of the pores. In a certain stage during the compaction of the rock, the formation of a continuous network of organo-pores is probable.

**Molecules of the third category.** Hydrocarbons are formed in buried sediments on the surfaces of clays (Shimoyama and Johns, 1971). Isolated hydrocarbon molecules are extracted by the migrating water and join this phase in upwards migration. As a result of diffusive flow, and due to migration near newly formed hydrocarbons, regions of supersaturation of hydrocarbons in water will be formed, leading to the separation of hydrocarbon droplets. When two droplets of dispersed paraffins are near each other, molecules of the intervening water are simultaneously subject to being pulled away by the homogeneous water-water attraction forces emanating from the medium. Since the heterogeneous paraffin-water attraction is weaker than the homogeneous water-water attraction, the intervening liquid will retract and the two droplets of paraffin will come together and coalesce (Ross, 1973).

The driving force for migration of drops of hydrocarbon through a porous rock is \(\Delta P = P_2 - P_1\) where \(P_1\) and \(P_2\) are the hydrostatic liquid pressures at two horizontal parallel planes, the distance between which is \(d\).

The rate of flow of the hydrocarbons across the rock is

\[
\overline{U} = (\mu_2 - \mu_1)/r = \dot{v} \Delta P/r \tag{3}
\]

where \(\dot{v}\) is the molar volume of the hydrocarbon, \(\mu\) is the appropriate chemical potential and \(r\) is the resistance to flow. The major resistance to flow is offered by the rock, and \(r = d/D_{\text{eff}}\) where \(D_{\text{eff}}\) is a modified diffusion coefficient for the hydrocarbons in the rock analogous to the Fick diffusion coefficient.

\(D_{\text{eff}}\) is conventionally related to a constant \(D_0\) which may be considered to be a modified form of the bulk diffusivity in a non-disturbed environment by

\[
D_{\text{eff}} = D_0 \theta K_{\text{p}} K_r / \tau \tag{4}
\]

where \(\theta\) is the pore volume fraction, \(\tau\) is the tortuosity, \(K_{\text{p}}\) is the equilibrium partition coefficient (that is, the ratio of concentration inside the pore to concentration outside the pore at equilibrium), and \(K_r\) is the fractional reduction in diffusivity within the pore which results as the diameters of the droplets and those of pores are of comparable size.

If hydrocarbon drops enter into the field of polar surfaces of a non-organic pore, then the films which surround these drops will become unstable and drops will coalesce. Since their size increases, there will be more geometric disturbances and \(\overline{U}\) will decrease. If there is a strong chemical interaction between the paraffin molecules and the surface of the pore, the water in the surrounding film will be repelled when a hydrocarbon drop approaches this surface. The drop of paraffin molecules will disintegrate.
$D_0$, $K$, and $K_p$ will depend on the size of the single molecule of hydrocarbon. $U$ will greatly increase. This in fact occurs in the organo-pores. When such pores are saturated with hydrocarbons, water can be present only in the form of droplets surrounded by hydrocarbons. The migration rate of water in such pores is very low since $D_0$, $K$, and $K_p$ will depend on the size of the water drops and not on the size of the water molecule.

We may conclude that pores with organophilic surface are hydrocarbon permeable and water impermeable while pores with hydrophilic surfaces are the reverse.

CONCLUSIONS

1. From the preceding discussion it follows that if there are aqueous soluble organic compounds in the source rock which may be considered as "soaps", they may be sorbed by clay minerals, and there is a probability that they will be concentrated on the surfaces of some of the pores only. Thereby, pores may become permeable to hydrocarbons (organo-pores). The formation of continuous network of organo-pores in an oil source bed is probable.

A pore does not become organophilic immediately after the sedimentation and compaction of the clay. The time required for a pore to become organophilic depends on the supply and rate of migration of the organic ions or polar molecules which are water soluble. Very dilute aqueous solutions are obtained and it is to be expected that a great amount of water will pass through the rock before the adsorption by the pore is high enough to make it organophilic.

2. Hydrocarbons generated at lower depths, migrate through these organo-pores. Since in saturated clay-organic complexes organophilicity depends on the charge density of the silicate layer, it is expected that permeability of the rock to hydrocarbons will increase with increasing time of diagenesis of the clay minerals. The transformation of montmorillonite into illite leads to an increase in charge density. This transformation should be a stepwise process. Since illite with non-expandable interlayer may not serve as an easy path for the migration of hydrocarbons, one expects optimal time for highest migration which will be sufficiently long for an increase in charge density but insufficient for shrinkage of the interlayer space to take place.

The organic saturated pores serve as the principal stationary phase in the separation and sorting of organic molecules in the source rock. It was found from gas chromatographic studies of montmorillonite saturated with alkyl quaternary ammonium ions (Mortimer and Gent, 1964) that these clays exhibit a selective retention of aromatics relative to paraffins, depending on organophilicity and steric effects. The rates of migration of the hydrocarbons through the pores in the rock depend on their length and on their isomeric structure.

3. With further sedimentation above the source rock, the temperature of
the discussed bed becomes high enough for the "soap" molecules to decompose and give petroleum. The lowest edge of the organo-pore decomposes first and the newly formed hydrocarbons migrate through the rest of the organo-pore.

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REFERENCES


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