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Solubility of petroleum compounds in kerogen: implications for petroleum expulsion

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Abstract

Hildebrand solubility parameters, δ, have been calculated for the most common petroleum compounds, thus establishing a relative solubility scale of petroleum compounds in kerogen. The scale predicts that aromatics as a group are better retained in kerogen than saturates and that there exist large solubility differences within the aromatics. Within saturates, cycloalkanes are better retained than normal alkanes. In order to obtain a picture of direction and magnitude of fractionation, a polymer solution model was coupled with a petroleum generation model. Model results suggest fractionation in the expected direction but not the expected magnitude.

1. Introduction

Petroleum has long been known to undergo fractionation during migration (e.g. Tissot and Pelet, 1971). Processes that may affect different compound classes and compounds to a different extent during migration are adsorption on mineral surfaces (Barrer, 1989; Carlson and Chamberlain, 1986; Brothers et al., 1991), size exclusion in pelitic rocks (Krooss et al., 1991a), adsorption on organic matter (Lamberson and Busting, 1993), partitioning with the gas phase (Meulbroek et al., 1998, evaporative fractionation), partitioning with water (Lafargue and Barker, 1988, water washing), diffusion through organic matter and water (Krooss et al., 1991b; Thomas and Clouse, 1990a,b).

There seems to be broad agreement (e.g. Pepper and Corvi, 1995) that fractionation of petroleum components occurs in the sequence: asphaltenes > polars, resins > aromatics > branched alkanes > *n*-alkanes, the latter being preferentially expelled with respect to the former compound groups.

A critical review of the literature suggests that there is unequivocal evidence of fractionation of saturates and aromatics from a large number of field (summarised in Ritter, 2000), sequential extraction (Price and Wenger, 1992; Ropertz, 1994) and experimental studies (Lafargue et al., 1994; Ropertz, 1994; Rudkiewicz et al., 1994; Mishra et al., 1996.). One experimental study (Lafargue et al., 1994) yields saturate–aromatic fractionation only at high pressure and low temperature.

In addition, field and experimental evidence suggests either preferred expulsion of light *n*-alkanes (Sajgo et al., 1983; Leythaeuser et al., 1984; Price and Clayton, 1992), or preferred expulsion of heavier *n*-alkanes or their ambiguous behaviour (Mackenzie et al., 1987; Leythaeuser et al., 1988). The latter authors explain their observations with re-diffusion of light hydrocarbons into the source rock. Empirical evidence of fractionation of pristane and phytane with respect to *n*-C17 and *n*-C18 is even less strong (e.g. Lafargue et al., 1994; Leythaeuser et al., 1988; Price and Clayton, 1992).

It has been shown in recent years that coals are macromolecular systems which can be studied by techniques developed in polymer science (e.g. Takanohashi et al.,

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1996, 2000; Cody and Painter, 1997; Otake and Suuberg, 1997). Application of these techniques to primary migration (Sandvik et al., 1992) and kerogen (Larsen and Li, 1997a,b) has only recently been attempted.

The purpose of this paper is therefore to draw attention to polymer solution theory (Hildebrand, 1936; Hansen, 1967) as one possible process of differential retention of petroleum compounds in kerogen, and to demonstrate its effects by means of some simple applications.

2. The concept

The solubility of a compound in a polymer can be defined by a solubility parameter, δ, which in the literature is frequently referred to as the Hildebrand parameter (Hildebrand, 1936). The general rule is that the closer δ of two compounds the better their mutual solubility. As a first approach kerogen appears to have a δ between 9.5 and 10 $(\text{cal cm}^3)^{1/2}$ (Larsen and Li, 1997b). Hence hydrocarbon compounds closest to this value will be best retained by the kerogen.

The Hildebrand solubility parameter, δ, is defined as:

$$\delta = \left[\frac{\Delta E - R \cdot T}{V_m}\right]^{1/2} (\text{cal/ cm}^3)^{1/2} \quad (1)$$

where ΔE is the energy of vaporisation, R is the gas constant, T is absolute temperature; and V_m the molar volume. The energy of vaporisation is the energy necessary to vaporise a liquid, i.e. it is the energy corresponding to the van der Waals forces that hold the molecules of the liquid together. The same intermolecular attractive forces have to be overcome when dissolving a liquid since the molecules of a liquid are physically separated by the molecules of the solvent. Fig. 1 shows the Hildebrand solubility parameters for a number of individual petroleum compounds calculated using Eq. (1). Here the energy of vaporisation has been approximated according to Gallant (1984). Also indicated is the range of the most likely δ values for kerogen. This diagram suggests that

1. Aromatics as a group are better retained in kerogen than saturates.
2. Within aromatics, benzene, phenol, cresol, toluene, are better retained in kerogen than ethylbenzene and xylenes.
3. Methylnaphthalene and diphenyl are better retained than anthracene, methylphenanthrene and phenanthrene.
4. Within saturates, cycloalkanes tend to be better retained than the respective normal alkanes.
5. Heavy *n*-alkanes are less well retained than intermediate n-alkanes (*n*-C6–*n*-C9).
6. There is no difference in retention capacity between iso- and *n*-alkanes.
7. Dry gas is more easily expelled than wet gas at temperatures around 150 °C.
8. The solubility differences of pristane, phytane, *n*-C17 and *n*-C18 are small.

Most polymers exhibit smaller or larger amounts of swelling in response to the uptake of solvents. The swelling process results from the incorporation of solvent molecules in the polymer structure. The swelling ratio, Q_v, is defined as

$$Q_v = V_s / V_i \quad (2)$$

where V_s is the volume of the swollen sample and V_i the volume of the initial sample.

Generally, the swelling ratio of a polymer is related to the solubility of its structural units (polymer chains) in a given solvent. Thus, measuring the swelling ratios of a polymer with different solvents provides a means to assess its solubility parameter δ. This procedure can also be applied to kerogens.

A plot of the measured Q_v-values over the δ values of the corresponding solvents yields a distribution that can usually be matched by a bell-shaped curve, the maximum of which represents the solubility parameter of the kerogen.

Published Q_v values range from about 1.0 to 2.4 for Argonne coals (Otake and Suuberg, 1997; Yun and Suuberg, 1998; Takanohashi et al., 2000), and from 1.5 to 3 for Green River and Rundle oil shale (Larsen and Li, 1997a,b). There are indications that Q_v decreases with increasing maturity (Larsen and Li, 1997b).

3. Modelling of expulsion

In order to test their impact on petroleum expulsion, Hildebrand parameters for individual compound classes (Table 1) were combined with a petroleum generation model and an empirical relationship between Q_v and δ for specific kerogen types. The computations were performed for two source rocks with high, and intermediate to low initial generation potentials respectively. Kinetic parameters for petroleum generation were the same for both source rocks. No secondary cracking has been modelled since it was the objective of this paper to investigate compositional changes caused by expulsion. The generation model is derived from confidential data and comprises the compound groups C1, C2–C5, C6–C14 saturates and aromatics, C15–C35 saturates and aromatics and NSO compounds. All results are given for a modelled maturity of 0.69% Ro, using the vitrinite reflectance model of Burnham and Sweeney (1989).

An empirical Q_v can be modelled using the fact that the relationship usually approaches a bell-shaped curve.

The following equation is therefore used to match a curve to available Q_v and δ couples:

$$Q_v = S_c \cdot \frac{1}{\sqrt{2 \cdot \pi}} \cdot \frac{1}{d} \cdot \exp\left[-0.5 \cdot \left(\frac{\delta_c - \delta_k}{d} \right)^2 \right] \quad (3)$$

where d is a distribution factor that corresponds to the standard deviation of the curve. δ_c and δ_k are the Hildebrand parameters for the hydrocarbon compounds and the kerogen respectively, and S_c is a scaling factor. Once calibrated by adjusting S_c and d, this function assigns a retention threshold to each compound group. In this paper, d is set at 15% of δ_k [9.5 $(cal/cm^3)^{1/2}$] and S_c is varied according to the Q_v required. Modelling was conducted in order to explore the general sensitivity of the parameters δ and Q_v. All results are shown in terms of expulsion efficiency (EEF) and expulsion gas/oil ratio

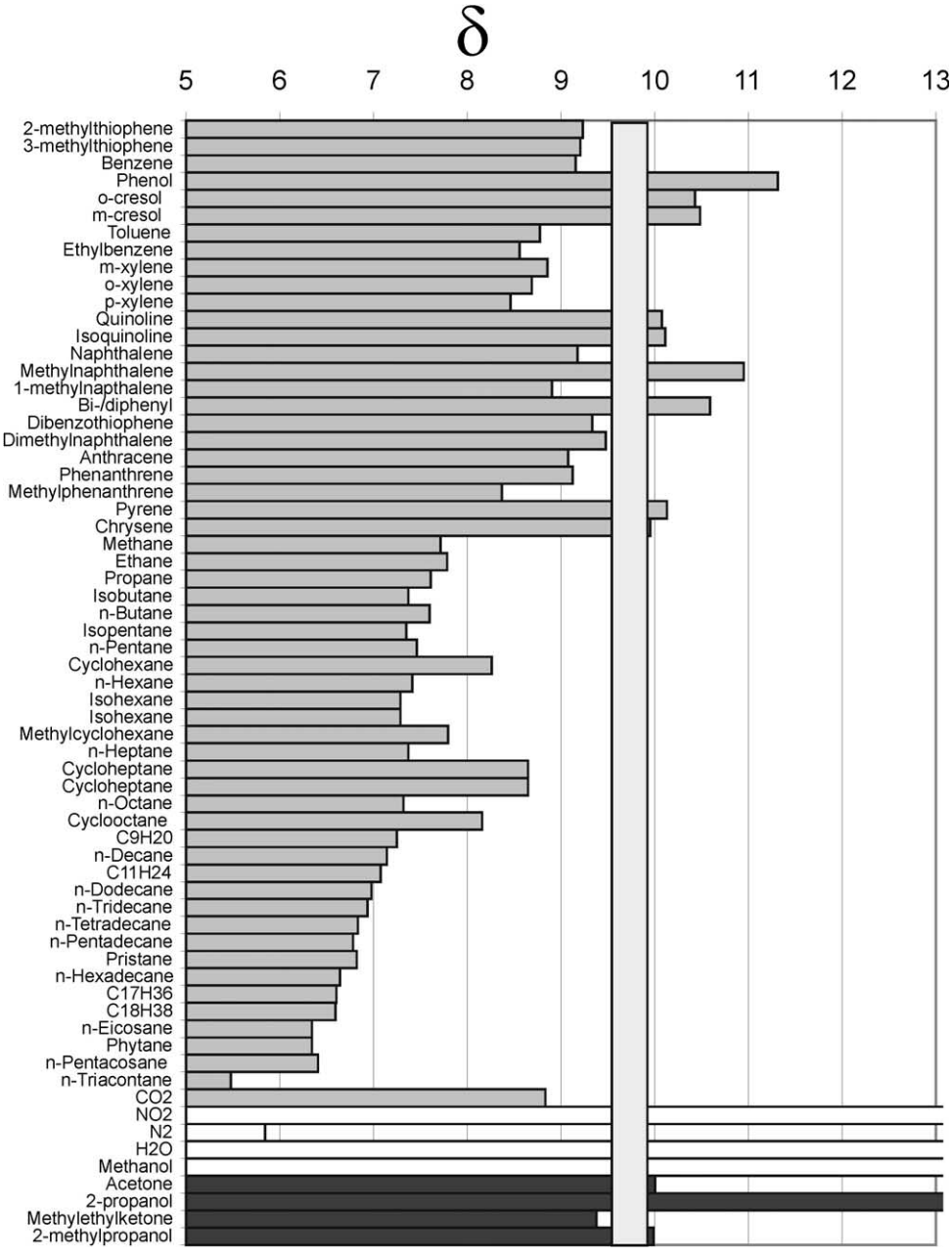

Fig. 1. Solubility parameter δ calculated for typical petroleum compounds using Eq. (1). The average δ of kerogen is between 9.5 and 10. Aromatics tend to be closer to δ of the kerogen and thus more soluble than aliphatics. δ In $(cal\ cm^3)^{1/2}$. Delta values are calculated for a temperature of 0 K.

(GOR, Figs. 2 and 3). The delta values used for modelling (Table 1) have been calculated for 150 °C and an unweighted average of the compound groups. The effects of temperature on delta are moderate [0.5 to 1.0 $(cal/cm^3)^{0.5}$] for a temperature between 0 and 673 K, except for light *n*-alkanes, where the difference is up to 2 $(cal/cm^3)^{0.5}$. Note that most delta values in the literature seem to be given for a temperature of 0 K. Q_v is calculated from δ in Eq. (3). The model allows for calibration of this curve [(3), Fig. 4] to experimental data (2) such that the calculated Q_v corresponds to the observed Q_v in the best possible way. By convention, polymer chemists regard the delta of the peak of the distribution (1) as the delta of the polymer to be investigated. Q_v defines an expulsion threshold for each compound group. Expulsion occurs once cumulative generation is higher than the respective retention capacity. No compound group may occupy possibly unused retention capacity of another compound group. A more detailed description of the numerical model is beyond the scope of this paper.

Model results are shown for two source rocks that have different initial generation potential. Source Rock 1 provides 538 mg petroleum/g TOC and source Rock 2 215 mg petroleum/g TOC. All other modelling parameters are the same.

Fig. 3 shows gas/oil ratios and expulsion efficiencies against the swelling ratio, Q_v. The expulsion efficiency is:

$$\mathrm{EEF}_i = \sum_{i=0}^{n} P_e / \sum_{i=0}^{n} P_g \quad (4)$$

where P_e is expelled-and P_g generated petroleum, and i is time step.

Table 1
δ Values $(cal\ cm^3)^{1/2}$ used for modelling

Compound group	δ
Kerogen	9.50
C1	6.00
Gw	7.00
SATl	7.20
AROl	7.80
SATh	7.00
AROh	8.00
NSO	7.00

Explanations: C1: methane; G_w: wet gas; C2–C5, SAT: saturates, C6–C14; AROl: aromatics, C6–C14; SATh: saturates, C15+; AROh: aromatics, C15+; NSO: C15+ non-hydrocarbons. δ Values shown here are calculated for a temperature of 150 °C.

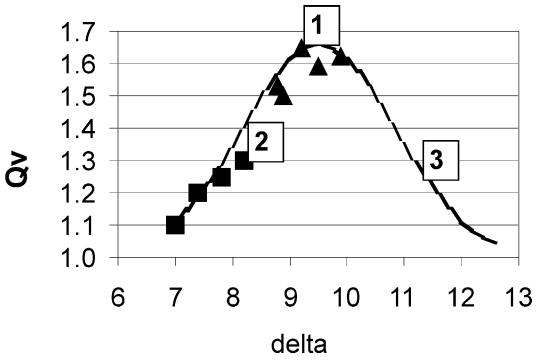

Fig. 2. Relationship of delta and swelling ratio. A normal distribution (3) is fitted to measured Q_v–δ couples of different compounds (2). The maximum of the curve represents the δ of the polymer.

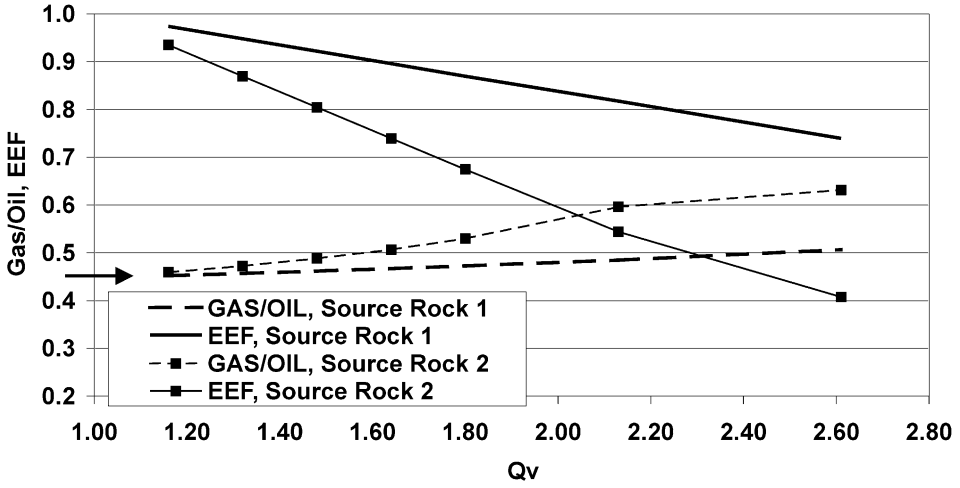

Fig. 3. Gas/oil ratios and expulsion efficiencies (EEF) for two source rocks with different initial potentials. Modelled at vitrinite reflectance 0.69%. Initial potential Source Rock 1: 538 mg/g TOC. Source Rock 2: 215 mg/g TOC.

The expelled gas/oil ratio is:

$$\mathrm{GOR} = \frac{C1 + Gw}{C6+} \ \mathrm{(g/g)} \qquad (5)$$

where *C1* is expelled methane, G_w is wet gas (C2–C5) and *C6+* all petroleum compounds with C numbers of 6 and higher.

For Source Rock 1, which corresponds to a good type II kerogen, EEF is high even at very high Q_v values. For Source Rock 2, which corresponds to a relatively poor source rock, EEF is also high at low Q_v. values but becomes much poorer at high Q_v. values. If we assume a Q_v. of about 1.6 for both source rocks, EEF is 0.7 and 0.9 respectively.

The expelled gas/oil ratio is hardly affected in Source Rock 1, and only to a minor extent in Source Rock 2. All other parameters being the same, the expelled gas/oil ratio is a function of EEF. This is easily explained. Since the δ values of aromatics and NSO compounds are closer to 9.5 $(\mathrm{cal\ cm^3})^{1/2}$ than the ones for aliphatic hydrocarbons, more of the latter will be expelled than of the former. Since all dry and wet gas compounds are aliphatic, more gas will be expelled than heavier compounds. At the same time a smaller proportion of the total generated petroleum, for any give Q_v, will be retained of a rich rock than of a poor one. Hence low EEF entails a higher expulsion gas/oil ratio. This is what we observe in Fig. 3.

The model may also explain the triangular SAT–ARO–NSO trend frequently observed when comparing source rock extracts and reservoired petroleum derived from these source rocks (Fig. 4). The exact trend-direction will depend on the relative magnitude of the Hildebrand parameters of aromatics and NSO compounds. In the present case (Table 1) δ NSO is somewhat smaller than δ ARO, and aromatics are therefore more strongly depleted than NSO compounds. The overall trend is, however, one of saturate-enrichment.

4. Discussion and conclusions

Polymer solution theory seems to provide a viable basis to model retention and fractionation of petroleum compounds in a kerogen. The calculated Hildebrand parameters largely confirm the observed sequence of fractionation observed in nature with the exception of branched alkanes, which do not show any δ values different from the respective *n*-alkanes (Fig. 1). On the other hand cycloalkanes seem to have a higher δ value than the respective *n*-alkanes, yet no systematic fractionation effects seem to have been reported in the literature.

Some uncertainty exists with respect to the delta value of NSO compounds. Published δ values of asphaltenes reaches about 6–9 $(\mathrm{cal/cm^3})^{0.5}$, with larger aggregates having lower delta values than smaller aggregates (see

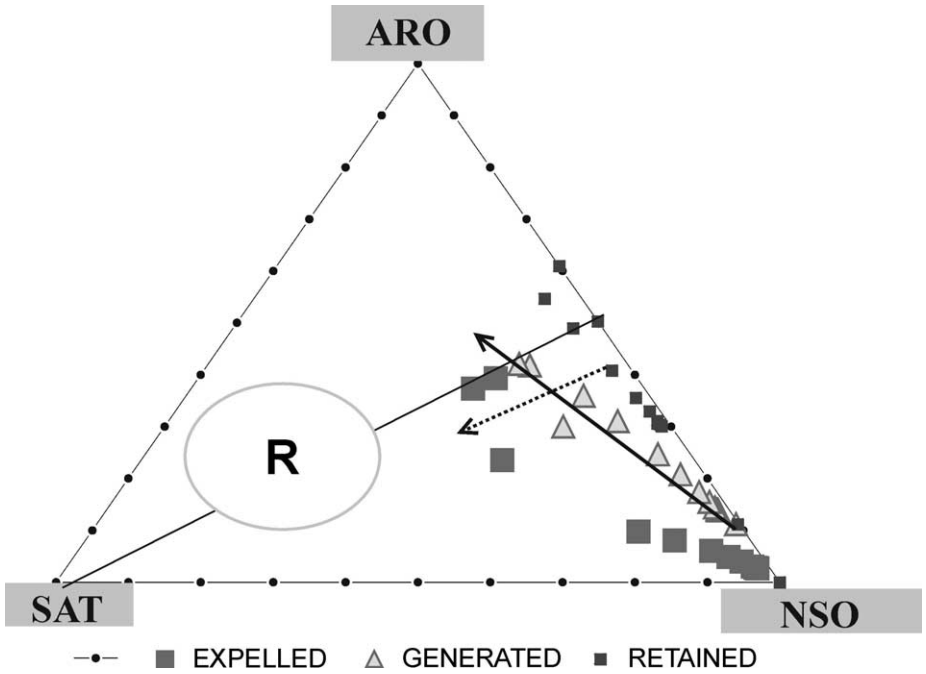

Fig. 4. SAT–ARO–NSO fractionation caused by differential retention in kerogen, and by maturation. Apices denote 100%. Dashed arrow denotes fractionation trend. Solid arrow denotes direction of increasing maturity. R indicates the general composition of reservoired petroleum.

Rogel, 1995, and references therein). Which of these values are the most "realistic" is difficult to say. To get the trend in Fig. 4 pointing to the saturate apex, the delta values of NSO compounds have to be slightly lower than those of heavy aromatics, the absolute magnitude of the values depending on the composition of the compound group and temperature. On the other hand, aggregation of asphaltenes seems to be primarily an effect of the interaction of asphaltenes, resins and aromatic hydrocarbons in the fluid phase. In the kerogen structure, where it is restricted by the average cross link density, one would expect asphaltenes to display the smallest possible aggregate size, and hence the higher range of possible delta values to be effective.

Fig. 4 was calibrated to simulate the trend observed in the Brae Field by Leythaeuser et al. (1988) between strongly depleted and less depleted source rock as well as reservoir extracts. Other field relationships may require somewhat different relationships between delta aromatic and delta NSO which would all be in agreement with the possible delta values.

To be consistent, all other delta values used for modelling, and in Fig. 1, are calculated using an empirical relationship between the energy of vaporisation and critical temperature, critical pressure and boiling temperature (Gallant, 1984). His equation is supposed to have an error of ± 1–2%. For some compounds, different publications or data bases quote different values of the critical parameters due to different experimental settings and methods. Most of these deviations are small and do not affect the results significantly.

Used in a proper way the theory may aid the petroleum geochemists to interpret extraction data, and explorationists to use appropriately calibrated models to estimate the amount and composition of expelled petroleum. More research seems to be necessary regarding the retention capacity of different kerogens and/or maceral types. Ideally this research should concentrate on swelling by representative petroleum compounds, and compare this with extraction by different methods:

- what are the δ- and Q_v values of different kerogen types at different maturities?
- to what extent are different extraction methods representative of the total absorbed petroleum?

Today's swelling experiments are mainly carried out in order to obtain structural information on kerogen. Alkylbenzenes appear to make up about 80% of the C6–C14 aromatics of generated petroleum in experiments (SINTEF Petroleum Research, internal information, 2001). Hence xylenes or toluene for example would be a more representative measure of the absorption capacity of a kerogen for petroleum.

Polymer solution theory and the present model do *not* explain the magnitude of fractionation between source rock and reservoir that has been observed in known petroleum systems such as in the North Sea (e.g. Horsfield, 1997, his Fig. 6.15). It also fails to explain the presence of large accumulations of aliphatic petroleum sourced from coals (Petersen and Brekke, 2001) as heating experiments do not indicate that Jurassic coals generate less aromatics than other Jurassic source rocks of the North Sea (e.g. Monin et al., 1990; Behar et al., 1997).

Apart from fractionation during secondary migration, there are a variety of processes that could complement or enhance the effects of polymer retention: Strongly hydrogen-bonding solvents enhance the uptake of non-hydrogen bonding solvents (Yun and Suuberg, 1998). Organic acids have high hydrogen-bonding capacity and frequently precede the generation of petroleum. If present in large amounts, they could strongly enhance sorption capacity for the subsequently generated petroleum.

Another process arises from the nature of vitrinite, which usually has a high proportion of nano-pores (e.g. Parkash and Chakrabartty, 1986). This would contribute much to the internal surface area at which adsorption occurs, and may act as sites for capillary condensation and molecular sieving. Preliminary modelling of *adsorption* in vitrinite suggests a retention capacity several times that of polymer solution.

In conclusion, petroleum retention in source rocks based on polymer solution theory is probably one contributing factor to petroleum fractionation during expulsion. In kerogen containing no or few land plant-derived macerals, it may even be the dominant process. Adsorption and capillary condensation will also mainly affect asphaltenes, resins and aromatics and thus enhance the effects caused by polymer solution.

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References

Barrer, R.M., 1989. Shape-selective sorbents based on clay minerals: a review. Clays and Clay Minerals 37, 385–395.

Behar, F., Vandenbroucke, M., Tang, Y., Marquis, F., Espitalie, J., 1997. Thermal cracking of kerogen in open and closed systems: determination of kinetic parameters and stoichiometric

coefficients for oil and gas generation. Organic Geochemistry 26, 321–339.

Brothers, L., Engel, M.H., Krooss, B.M., 1991. The effects of fluid flow through porous media on the distribution of organic compounds in a synthetic crude oil. Organic Geochemistry 17, 11–24.

Burnham, A.K., Sweeney, J.J., 1989. A chemical kinetic model of vitrinite maturation and reflectance. Geochimica et Cosmochimica Acta 53, 2649–2657.

Carlson, R.M.K., Chamberlain, D.E., 1986. Steroid biomarker—clay mineral adsorption free energies: implications to petroleum migration indices. Organic Geochemistry 10, 163–180.

Cody, G.D., Painter, P.C., 1997. Modulus of swollen coal gels. Energy & Fuels 11, 1044–1047.

Gallant, R.W., 1984. Physical Properties of Hydrocarbons, Vol. 2. Gulf Publishing, Houston.

Hansen, C.M., 1967. The three dimensional solubility parameter- key to paint component affinities: iii. independent calculations of the parameter components. Journal of Paint Technology 3, 511.

Hildebrand, J.H., 1936. The Solubility of Non-electrolytes. Reinhold, New York.

Horsfield, B., 1997. The bulk composition of first-formed petroleum in source rocks. In: Welte, D.H., Horsfield, B., Baker, D.R. (Eds.), Petroleum and Basin Evolution. Springer, Berlin, Heidelberg, New York, pp. 335–402.

Krooss, B.M., Brothers, L., Engel, M.H., 1991a. Geochromatography in Petroleum Migration: A Review. Petroleum Migration. Geological Society of London Special Publication No. 59, pp. 149–163.

Krooss, B.M., Hanebeck, D., Leythaeuser, D., 1991b. Experimental measurement of the molecular migration of light hydrocarbons in source rocks at elevated temperatures. In: Dore, A. et al. (Eds.), Basin Modelling: Advances and Applications, Vol. 3. Norwegian Petroleum Society Special Publication, Stavanger, pp. 277–291.

Lafargue, E., Barker, C., 1988. Effect of water washing on crude oil compositions. Bulletin of American Association of Petroleum Geologists 72, 263–276.

Lafargue, E., Espitalie, J., Broks, T.M., Nyland, B., 1994. Experimental simulation of primary migration. Organic Geochemistry 22, 575–586.

Lamberson, M.N., Bustin, R.M., 1993. Coalbed methane characteristics of Gates Formation coals, Northeastern British Columbia: effect of maceral composition. Bulletin of American Association of Petroleum Geologists 77, 2062–2076.

Larsen, J.W., Li, S., 1997a. Changes in the macromolecular structure of a type I kerogen during maturation. Energy & Fuels 11, 897–901.

Larsen, J.W., Li, S., 1997b. An initial comparison of the interactions of Type I and Type III kerogens with organic liquids. Organic Geochemistry 26, 305–309.

Leythaeuser, D., Mackenzie, A., Schaefer, R.G., Bjorøy, M., 1984. A novel approach for recognition and quantification of hydrocarbon migration effects in shale-sandstone sequences. Bulletin of American Association of Petroleum Geologists 68, 196–219.

Leythaeuser, D., Schaefer, R.G., Radke, M., 1988. Geochemical effects of primary migration of petroleum in Kimmeridge source rocks from Brae field area, North Sea. I: gross composition and C15+-soluble organic matter and molecular composition of C15+-saturated hydrocarbons. Geochimica et Cosmochimica Acta 52, 701–713.

Mackenzie, A.S., Price, I., Leytheauser, D., Mueller, P., Radke, M., Schaefer, R.G., 1987. The expulsion of petroleum from Kimmeridge clay source-rocks in the area of the Brae oilfield, UK continental shelf. In: 3rd Geological Society of London Conference: Petroleum Geology of NW Europe, Proceedings, London, pp. 865–877.

Meulbroek, P., Whelan, J., Cathles, L., 1998. Phase fractionation at South Eugene Island Block 330. Organic Geochemistry 29, 223–239.

Mishra, C.S., Samanta, U., Gupta, A., Thomas, N.J., Misra, K.N., 1996. Hydrous pyrolysis of a Type III source: fractionation effects during primary migration in natural and artificially matured samples. Organic Geochemistry 25, 489–505.

Monin, J.C., Connan, J., Oudin, L., Durand, B., 1990. Qualitative and quantitative experimental approach of oil and gas generation: application to the North Sea source rocks. Organic Geochemistry 16, 133–142.

Otake, Y., Suuberg, E.M., 1997. Temperature dependence of solvent swelling and diffusion processes in coals. Energy & Fuels 11, 1155–1164.

Parkash, S., Chakrabartty, S.K., 1986. Microporosity in Alberta Plains coals. Journal of Coal Geology 6, 55–70.

Pepper, A.S., Corvi, P.J., 1995. Simple kinetic models of petroleum formation. Part III: modelling an open system. Marine and Petroleum Geology 12, 417–452.

Petersen, H.I., Brekke, T., 2001. Source rock analysis and petroleum geochemistry of the Trym discovery, Norwegian North Sea: a Middle Jurassic coal-sourced petroleum system. Marine and Petroleum Geology 18, 889–908.

Price, L.C., Clayton, J.L., 1992. Extraction of whole versus ground source rocks: fundamental petroleum geochemical implications including oil-source rock correlation. Geochimica et Cosmochimica Acta 56, 1213–1222.

Price, L.C., Wenger, L.M., 1992. The influence of pressure on petroleum generation and maturation as suggested by aqueous pyrolysis. Organic Geochemistry 19, 141–159.

Ritter, U., 2000. Compound class fractionation during migration: how much is due to primary migration? In: 7th Norwegian Meeting on Organic Geochemistry, Stavanger, June 2000, Abstract P14.

Rogel, E., 1995. Studies on asphaltene aggregation via computational chemistry. Colloids and Surfaces A: Physicochemical and Engineering Aspects 104, 85–93.

Ropertz, B., 1994. Eine Untersuchung der Porennetze, Klüfte und Kerogennetzwerke als Leitbahnen für den Kohlenwasserstoff-Transport. Dissertation, Fakultät für Bergbau und Hüttenwesen, RWTH, Aachen.

Rudkiewicz, J.L., Brevart, O., Connan, J., Montel, F., 1994. Primary migration behaviour of hydrocarbons: from laboratory experiments to geological situations through fluid flow models. Organic Geochemistry 22, 631–639.

Sajgo, C., Maxwell, J.R., Mackenzie, A.S., 1983. Evaluation of fractionation effects during the early stages of primary migration. Organic Geochemistry 5, 65–73.

Sandvik, E.I., Young, W.A., Curry, D.J., 1992. Expulsion from hydrocarbon sources: the role of organic absorption. Organic Geochemistry 19, 77–87.

Takanohashi, T., Nakamura, K., Terao, Y., Iino, M., 2002. Computer simulation of solvent swelling of coal molecules: effects of different solvents. Energy & Fuels 24, 393–399.

Takanohashi, T., Yanagida, T., Iino, M., 1996. Extracttion and swelling of low rank coals with various solvents at room temperature. Energy & Fuels 10, 1128–1132.

Thomas, M.M., Clouse, J.A., 1990a. Primary migration by diffusion through kerogen: pt.1: model experiments with organic-coated rocks. Geochim. et Cosmochim. Acta 54, 2775–2779.

Thomas, M.M., Clouse, J.A., 1990b. Primary migration by diffusion through kerogen: pt. 2: hydrocarbon diffusivities in kerogen. Geochimica et Cosmochimica Acta 54, 2781–2792.

Tissot, B., Pelet, R., 1971. Nouvelles donnees sur les mechanismes de genese de migration du petrole. Simulation matematique et application a la prospection. 8th World Petroleum Congress, Proceedings 2, 35–46.

Yun, Y., Suuberg, E.M., 1998. Cooperative effects in solvent swelling of a bituminous coal. Energy & Fuels 12, 798–800.