THE IMPORTANCE OF WATER-HYDROCARBON PHASE EQUILIBRIA DURING RESERVOIR PRODUCTION AND DRILLING OPERATIONS

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NOUVEAUX DÉFIS LIÉS À LA PRÉSENCE D'ÉQUILIBRES EAU-HYDROCARBURES LORS DES OPÉRATIONS DE PRODUCTION ET DE FORAGE

La présence inévitable d'eau dans les réservoirs à hautes pression et température crée de nouveaux défis pour l'ingénieur pétrolier.

Un bref état de l'art des équilibres eau-hydrocarbures est présenté dans un premier temps. À haute température, de grandes quantités d'eau peuvent se trouver dans la phase hydrocarbonée (jusqu'à 10 % moles), et à haute pression, on trouvera des quantités non négligeables de gaz dissous dans l'eau. Des mesures de solubilités mutuelles ont donné lieu à un grand nombre de modèles. Étant donné les limites des données expérimentales, les restrictions des modèles sont soulignées. Des études récentes ont indiqué l'intérêt d'utiliser des constantes de Henry pour la prédiction de la solubilité d'hydrocarbures dans l'eau.

Les nouveaux défis sont abordés sur la base de quelques publications récentes. L'eau présente en phase hydrocarbonée peut conduire à des dépôts de sels autour du puits, et peut modifier l'estimation de la quantité de gaz en place. Elle peut également donner lieu à une modification des pressions de saturation. La présence d'eau dans les conduites de transport impose un traitement supplémentaire pour éviter la formation d'hydrates.

Les hydrocarbures dissous en phase aqueuse peuvent, de leur côté, modifier la composition du fluide, particulièrement lorsque la pression devient très faible. La toxicité de l'eau contenant du H_2S ou des aromatiques peut créer de réels problèmes lorsqu'il s'agit de nappes aquifères ou lorsqu'il est question de rejeter les eaux de production. Lors du forage, la présence de gaz dissous dans le fluide de forage (souvent à base d'eau) peut représenter un danger réel en causant des éruptions.

Une attention particulière doit être portée aux injections de gaz acides dans des réservoirs, car l'effet de ces fluides injectés peut être difficile à prédire.

En conclusion, au vu des besoins industriels présentés, des suggestions sont proposées pour des acquisitions de données supplémentaires ou pour améliorer les modèles actuels.

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THE IMPORTANCE OF WATER-HYDROCARBON PHASE EQUILIBRIA DURING RESERVOIR PRODUCTION AND DRILLING OPERATIONS

The inevitable presence of water in high pressure-high temperature reservoirs leads to a number of new challenges for petroleum engineers.

A brief state of the art on water-hydrocarbon phase equilibria is presented. It appears that large amounts of water may be present in the hydrocarbon phase (up to 10% molar), and non negligible amounts of gas can dissolve in water. Based on experimental data, a large number of models have been developed. However, concerning the limitations of the data, caution is expressed about the correctness of some models. Recent studies have proven the usefulness of Henry's constants to predict hydrocarbon solubilities in water.

The new challenges that are raised by this problem are discussed based on a number of recent publications. The water present in the hydrocarbon may lead to salt deposits downwell, and it must be taken into account in order to estimate the amount of gas in place. It can also result in modifications of the saturation pressure. Due to the presence of water, additional treatment is needed for pipe transport.

On the other hand, the large amount of hydrocarbons dissolved in the water phase may result in a modification of the hydrocarbon composition, especially when reservoir pressure becomes very low. The increased toxicity of the water, containing either H_2S or aromatics, can become a real burden for gas reservoirs in contact with aquifers or when disposing of production water. During drilling, large amounts of dissolved gas can become very hazardous, increasing the risk of eruption.

A particular attention must be paid to acid gas injection in reservoirs, as the true effect of the injected gas may not be straightforward to predict.

In conclusion, in light of the industrial importance of this information, some general guidelines are provided concerning additional data to be gathered and ideas for improving current models.

NUEVOS RETOS RELACIONADOS CON LA PRESENCIA DE EQUILIBRIOS AGUA - HIDROCARBUROS DURANTE LAS OPERACIONES DE PRODUCCIÓN Y DE SONDEO

La presencia inevitable de agua en los yacimientos en que reinan presiones y temperaturas elevadas, da origen a nuevos retos para los ingenieros de la industria del petróleo.

En primer lugar, se presenta la situación actual de la técnica en cuanto a los equilibrios agua-hidrocarburos. En caso de temperaturas elevadas, se pueden encontrar grandes volúmenes de agua en la fase hidrocarboinada (hasta 10 % moles) y en el caso de alta presión, se encontrarán cantidades nada insignificantes de gases en disolución en el agua. Las mediciones de solubilidades mutuas han dado lugar a un gran número de modelos. Habida cuenta de los límites de los datos experimentales, se hacen resaltar las restricciones de los modelos. Diversos estudios recientes han permitido precisar el interés de utilizar las constantes de Henry para la predicción de la solubilidad de los hidrocarburos en el agua.

Los nuevos retos se abordan según los fundamentos de algunas publicaciones recientes. El agua existente en la fase hidrocarbonada puede dar lugar a depósitos de sales en torno de los pozos, y puede así modificar las evaluaciones de la cantidad de gas in situ. También puede dar lugar a una modificación de las presiones de saturación. La presencia de agua en las canalizaciones de transporte impone un tratamiento suplementario para evitar la formación de hidratos.

Por su parte, los hidrocarburos disueltos en fase acuosa pueden llegar a modificar la composición del fluido, y básicamente cuando la presión llega a ser sumamente reducida. La toxicidad del agua que contiene H_2S o aromáticos puede llegar a crear serios problemas cuando se trata de acuíferos o cuando se trata de evacuar las aguas de producción. Durante el sondeo, la presencia de gas disuelto en el fluido de perforación (frecuentemente a base de agua), puede representar un peligro efectivo al provocar erupciones.

Se debe poner particular atención en cuanto a las inyecciones de gases ácidos en los yacimientos, puesto que el efecto de estos fluidos inyectados puede resultar difícil de predecir.

Como conclusión, y habida cuenta de las necesidades industriales existentes, se proponen soluciones para la adquisición de datos suplementarios o para mejorar los modelos actuales.

INTRODUCTION

Until recently, water and hydrocarbon fluids were considered as essentially immiscible, except for the water uptake of a gas. Even though water is permanently in contact with hydrocarbons in a reservoir, it was regarded, at best, as an inert fluid (only water level displacements and water compressibility were considered), at worst, as inexistent. The discovery of high pressure-high temperature reservoirs has changed the point of view of petroleum engineers on this subject. The reason is illustrated with Figures 1 and 2.

Figure 1 shows how the water content of a gas can behave as a function of pressure and temperature. It can reach, in the extreme conditions of high temperature and low pressure, up to 10 or 20% water. Under the currently common conditions of 170°C and 300 bar, the water content reaches 4 mole%.
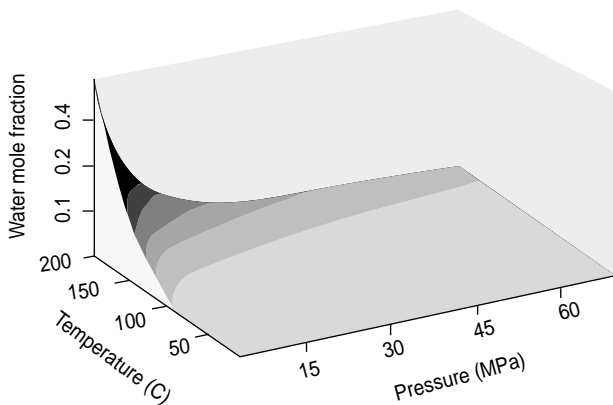

Figure 1

Water content of methane at various pressures and temperatures, as calculated with the Soreide and Whitson model (1992).

Figure 2, on the other hand, illustrates how high pressure conditions can result in non-negligible concentrations of hydrocarbons in water.

Both the water content of the hydrocarbon phase and hydrocarbon dissolution in water result in a number of particular challenges for petroleum engineers that can only be solved through improved predictive ability. For this purpose, the physical phenomena, and their determining conditions must first be reviewed.

Several research groups are working on data acquisition and modeling of the phenomena that are involved. As a matter of fact, due to the extreme
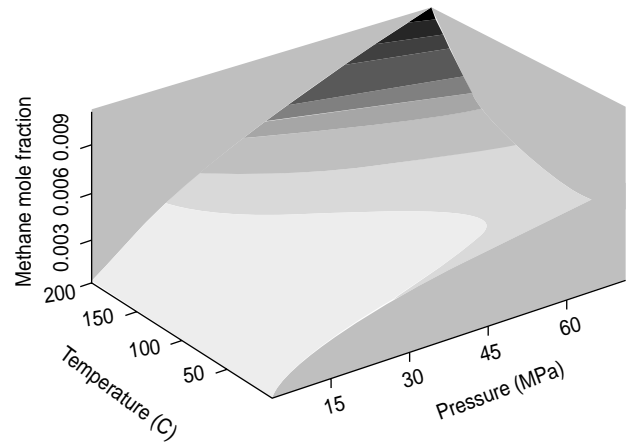

Figure 2

Methane content of water under various pressure and temperature conditions, as calculated with the Soreide and Whitson model (1992).

conditions of pressure and temperature, as well as the corrosivity of the fluids, and the small concentrations encountered, the usual PVT equipment and procedures cannot be used. Nevertheless, exploiting all available data and extrapolating when necessary, one can describe the phenomena with a reasonable degree of certitude. The first part of this paper tries to identify what is known and what still needs to be clarified.

In the second part of this paper, we will review a number of challenges that are encountered, due to the presence of water in reservoirs.

1 REVIEW OF THE PHENOMENA

In the first part of this paper, we will present a brief state of the art of the thermodynamic data concerning water-hydrocarbon mixtures. Our starting point is the availability of experimental data. In some areas, they are abundant, while in other areas, they are almost inexistent. Next, we will look at a number of models commonly used in the petroleum industry. Taking into account on which data the models are based will help us identify their limits.

1.1 Experimental Phase Equilibrium Data

Considering the different issues raised concerning water solubility in hydrocarbons and hydrocarbon solubility in water, we will handle the two cases separately.

1.1.1 Water Solubility in a Hydrocarbon Phase

It is generally observed, under identical pressure and temperature conditions, that water is much more soluble in hydrocarbons than hydrocarbons are in water. This solubility, however, varies greatly depending on whether the organic phase is liquid or gaseous.

A very clear picture of the solubility behavior of hydrocarbons in water is shown in Figure 3. This figure is given for the binary mixture water-pentane, but can be qualitatively extended to any water-hydrocarbon mixture.
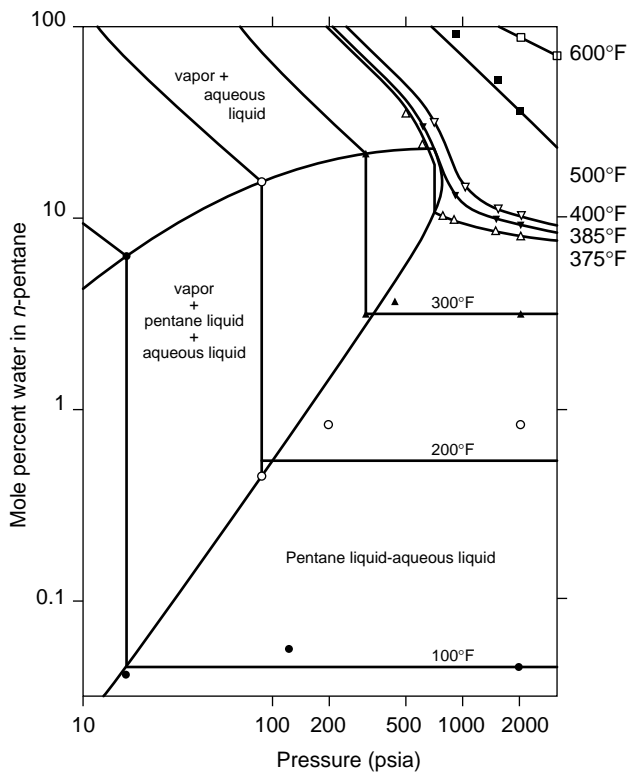

Figure 3

Water content of pentane as a function of pressure and temperature (redrawn from Gillespie and Wilson, 1982).

One recognizes the three phase region where the aqueous liquid coexists with the liquid pentane and the vapor phase. The upper part of the three phase region represents the vapor phase. Water solubility in a hydrocarbon vapor phase is large, as was already illustrated in Figure 1. At low pressure, Raoult's law can be used to estimate the water content of a vapor phase. When the pressure is increased above the three-phase region, the hydrocarbon becomes entirely liquid and its water content is much smaller. The figure indicates that pressure has almost no effect on solubility in the liquid-liquid region. The hydrocarbon critical point can readily be recognized in the figure (located at 385 °F (469 K) and 700 psia (4.8 MPa), approximately). Above this critical temperature, pressure variations do not induce any phase transition for the hydrocarbon phase. Its water content can, however, be significant.

Water solubility in a hydrocarbon gas generally follows a decreasing trend with pressure, as shown for supercritical pentane. This is well reproduced by the well-known correlation published by the *GPA* (most recent edition, 1994), shown in Figure 4. The gas hydrate formation temperature is visible. The solubility is considered independent of the gas composition, except for a correction term that is solely a function of the molecular weight (or gas gravity). A second correction term is given in case the water contains salts.

In a recent work (de Hemptinne, 1997a), we have evaluated the predictions from this graph for a number of experimental data, and it appears to perform at least as well as most other models.

This simple representation is no longer valid when acid gases are present in the fluid. Water solubility in acid gases is presented in Figure 5, using experimental data from Takenouchi and Kennedy (1964) and Selleck *et al.* (1952).

It appears that as pressure rises, the water content of the fluid increases. While this phenomenon is generally known, little experimental work has been found investigating the water uptake of gases containing various acid components.

The solubility of water in hydrocarbon liquids seems to be primarily affected by the aromatic/paraffinic characteristics of the hydrocarbons with very little effect due to the carbon number or molecular weight (Brady *et al.*, 1982). This is consistent with a solution of groups concept where the activity of water is primarily affected by the group environment. At low concentrations of water the group environment is determined by the paraffinic, olefinic, aromatic or naphthenic type of the hydrocarbons.

The solubility variations due to the group environment can clearly be seen in Figure 6 where the solubility is plotted at constant temperature versus a variable called the double bond index which is determined as follows:

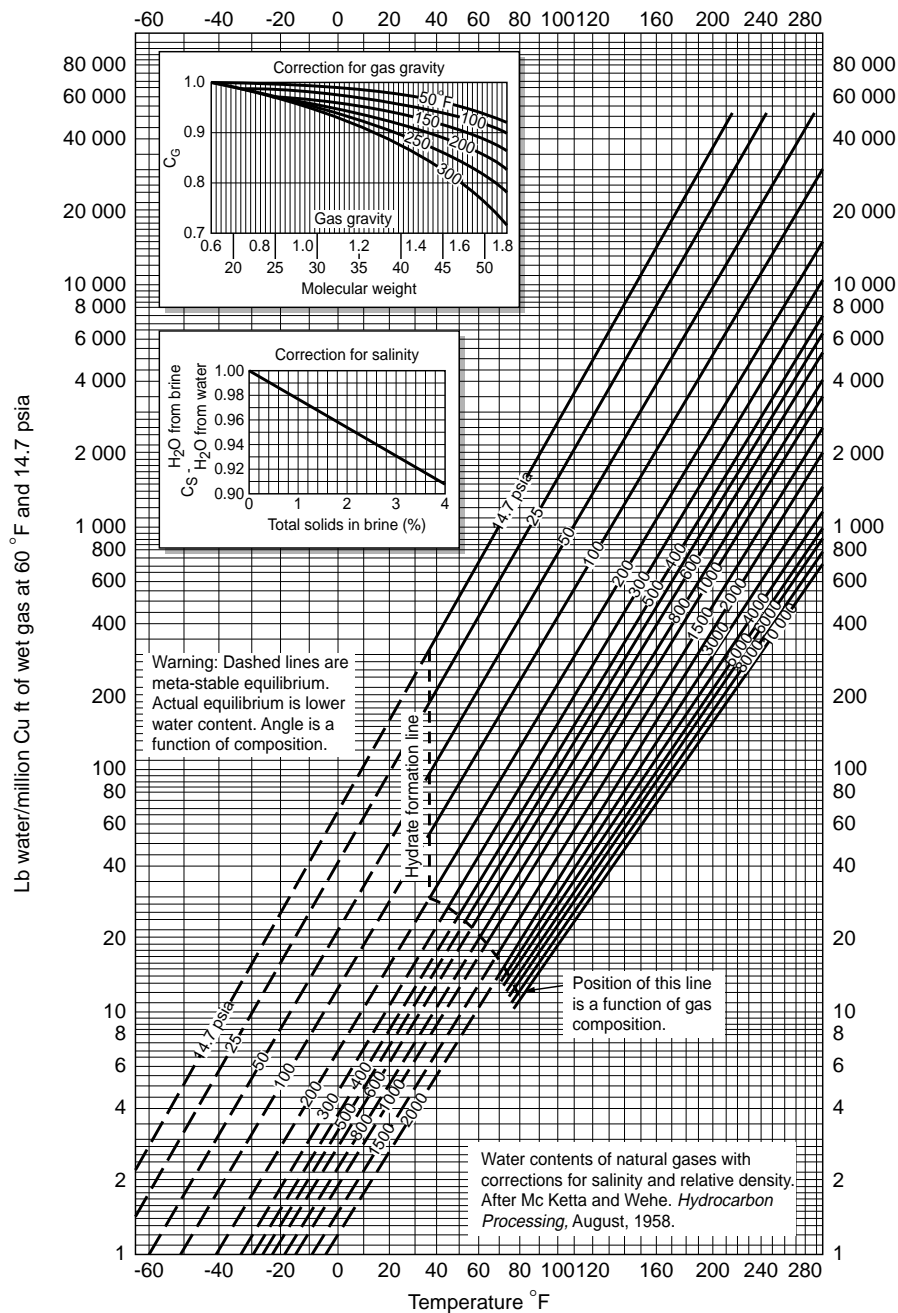$$\text{Double bond index} = 2\, n_D / n_C$$

Figure 4

Water content of a hydrocarbon gas (redrawn from GPA).

where n_D is the number of double bonds in the molecule (three in benzene; five in naphthalene); and n_C is the number of carbon atoms. Paraffins and naphthenes have a double bond index of zero, while this index is one for benzene or naphthalene.

The plot shows that the solubility is a function of the double bond index at a given temperature. This simplified model doesn't account for everything, as it appears that the naphthenes systematically have a slightly lower solubility than the paraffins.

Griswold and Kasch (1942) present a study of mutual solubilities of several light oil fractions with water. Their results are best shown in Figure 7. The leftmost curve represents the solubility of water in
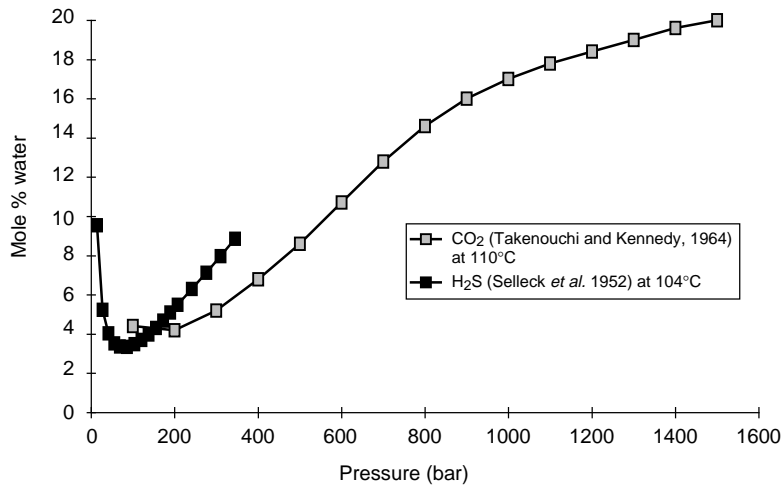
Figure 5

Water solubility in acid gases (mol %).

benzene while the other curve shows an average for the different petroleum products studied. Significant observations are:

– no regular trend of solubility with molecular weight exists,
– all data on petroleum fractions lie within 15°C of the curve.

It may therefore be concluded that the oil composition has a small influence on water solubility compared to the effect of temperature. A very aromatic fluid may contain more water, but the difference is not larger than a factor of two.

This behavior has been confirmed by Eubank *et al.* (1994) with *n*-alkanes. They also propose a simple relationship giving the water solubility as a function of temperature:

$$\ln(x_w) = -21.2632 + 5.9473 * 10^{-2} T - 4.0785 * 10^{-5} T^2$$

where x_w is the mole fraction of water and T is expressed in Kelvin. Since, according to the few data available, the water solubility in liquid oil is independent of pressure, this expression can be of great help when the water is pure (i.e. no salt).

1.1.2 The Effect of Water on Saturation Pressure

One particularly important issue is the effect of water on the hydrocarbon phase equilibrium. As already mentioned, most authors investigating water hydrocarbon equilibria perform their measurements at the three-phase pressure. This is nothing but the vapor pressure of the pure hydrocarbon component in the

presence of water. For water-*n*-alkane systems, the three-phase line is located above the pure component vapor pressure line. The three-phase pressure is normally the sum of the water vapor pressure and the hydrocarbon vapor pressure.

On the contrary, for water-CO_2 and water-H_2S binaries, the three-phase line lies below the vapor pressure of the pure acid gas. This is a consequence of the very large solubility of water in the liquid phase of these components.

Concerning the effect of water on the phase envelope of a binary hydrocarbon mixture, a very clear illustration is provided by Mc Ketta and Katz (1948), as shown in Figure 8. The bubble points are almost unchanged, while the dew points are shifted towards higher methane content.

Very few papers have been found investigating the effect of water on multicomponent hydrocarbon phase equilibria. The only significant effect that has been reported has been calculated by Zuo *et al.* (1996). They indicate a decrease of dew point pressure in the presence of water and an increase in bubble point pressure as a result of the presence of water. However, no experimental data could be found supporting this statement.

1.1.3 Hydrocarbon Solubility in Water

The solubility of single hydrocarbons in water has been extensively studied (Kertes, 1989a, 1989b; Hayduk, 1982, 1986). For gases, the domain investigated is that of high pressures (most often up to
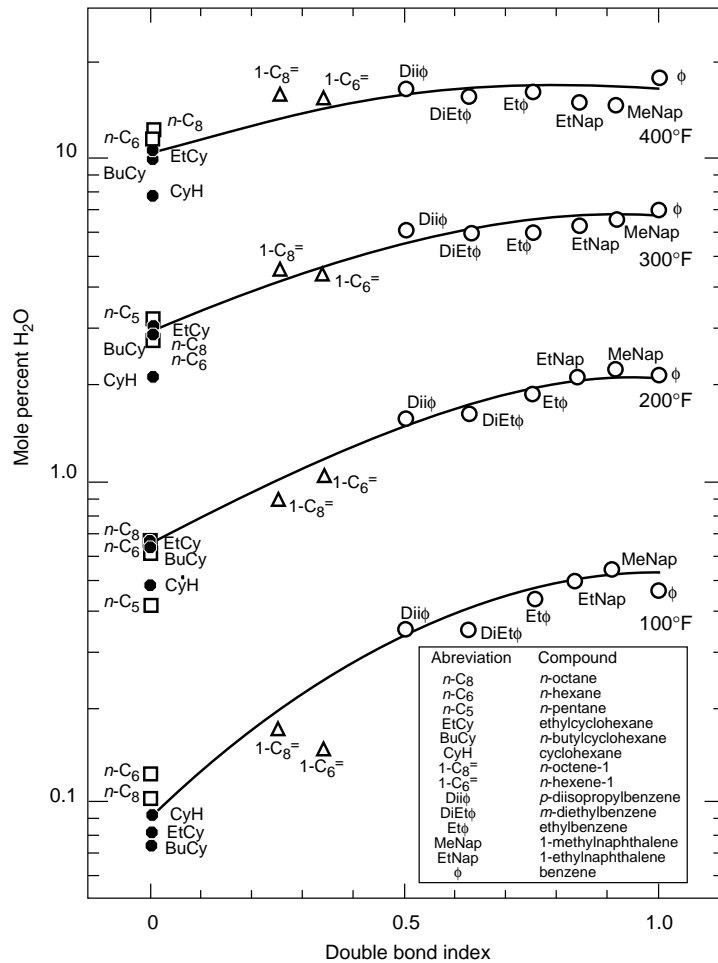
Figure 6

Solubility of water in hydrocarbons versus double bond index (redrawn from Brady *et al.*, 1982).

700 bar, but a few data exist at pressures above 1000 bar), and temperatures ranging from room temperature to the critical point of water. For liquids, most of the data have been measured around room temperature and at atmospheric pressure. They have been extensively reviewed by Yaws and co-workers (Yaws *et al.*, 1990, 1993a, 1993b, 1994, 1995).

The solubility of hydrocarbons generally increases with an increase in pressure, as is clearly illustrated for methane (Fig. 2). This pressure dependence becomes much less significant for liquid hydrocarbons. Bradley *et al.* (1973) observed that at very high pressures (between 1000 and 2000 bar), the solubility of toluene starts decreasing slowly. He is, however, the only investigator reporting such data.

With increasing temperature, the solubility of hydrocarbons shows a minimum. It is generally located between room temperature and 100°C. When the

molecular weight increases, the minimum in solubility decreases towards lower temperatures and for liquids the solubility increases monotonically with temperature. However, since most studies are limited to the boiling point of water at atmospheric pressure, the number of data for liquid hydrocarbons at high temperature is limited.

The effect of the molecular weight and hydrocarbon family on the solubility is clearly illustrated in Figure 9. The solubility decreases very fast with increasing molecular weight. The slope of the lines describing this behavior is independent of the chemical family. Brady *et al.* (1982) concluded that for each additional carbon atom, the solubility decreases by a factor of 1.87.

For *n*-alkanes, Table 1 gives the order of magnitude of the solubility under two different conditions and for various chain lengths.
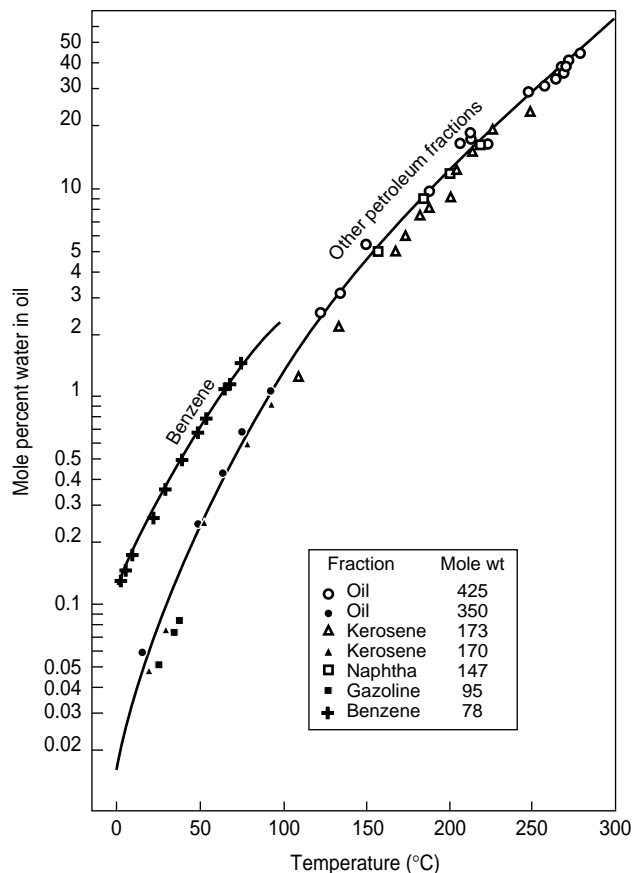
Figure 7

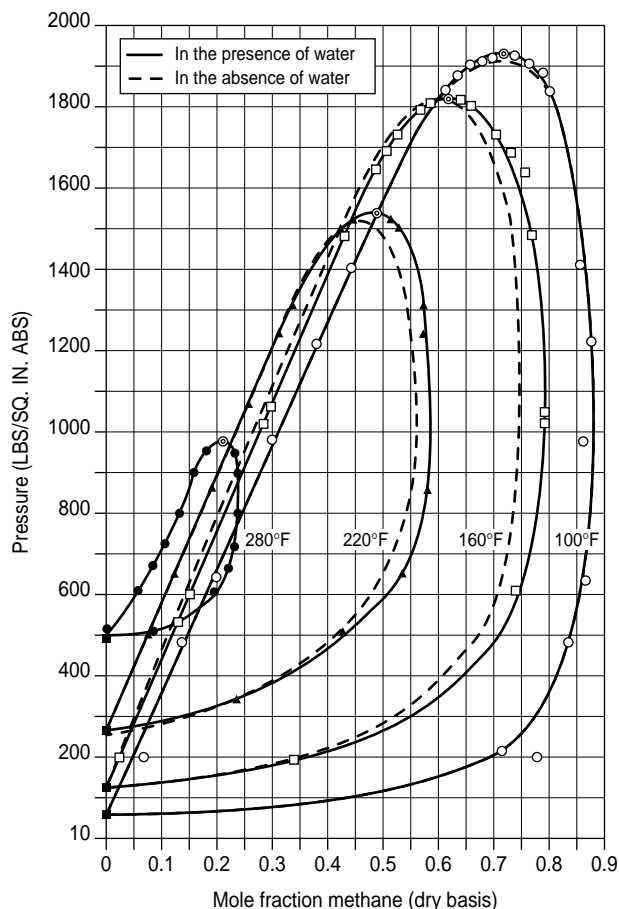Solubility of water in petroleum fractions (redrawn from Griswold and Kasch, 1942).

Figure 8

Effect of water on the vapor-liquid equilibrium of the methane-*n*-butane system (Mc Ketta and Katz, 1948).

TABLE 1

Solubility (in ppm molar) of some normal alkanes in water

Binary: water+	At 100 bar and 310 K	At high pressure and temperature (see footnotes)
Methane	2000	6990[1]
Ethane	1000	3300[1]
Propane	200	310[2]
n-Pentane	14	64[3]
n-Hexane	2	16[4]
n-Heptane	-	5.6[4]
n-Octane	0.1	2.4[4]

(1): Data point at 680 bar and 444 K
(2): Data point at 30 bar and 410 K
(3): Data point at 32 bar and 344 K
(4): At atmospheric pressure and 410 K

The effect of the chemical family and of the carbon number on the solubility of hydrocarbons in water has been investigated by Tsonopoulos and Wilson (1983), Heidman *et al.* (1985), Economou *et al.* (1997) and Brady *et al.* (1982). The relative solubility of various C_8 hydrocarbons is represented in Figure 10. Note that the data in the figure are given at the pressure of the three-phase line for each temperature. It increases with temperature as the low temperature point corresponds to the low pressure and thus to the lowest solubility, while the high temperature points correspond to the solubility at 1200 psi (87 bar). This doesn't affect the conclusion, as the solubility of these hydrocarbons is almost independent of pressure.

The conclusion to be drawn from this figure is that the solubility of aromatics in water is far larger than that of naphthenic components which is, in turn, higher than that of alkenes and alkanes. Suzuki *et al.* (1992) explain the high solubility of aromatics by the formation of hydrogen bonds.
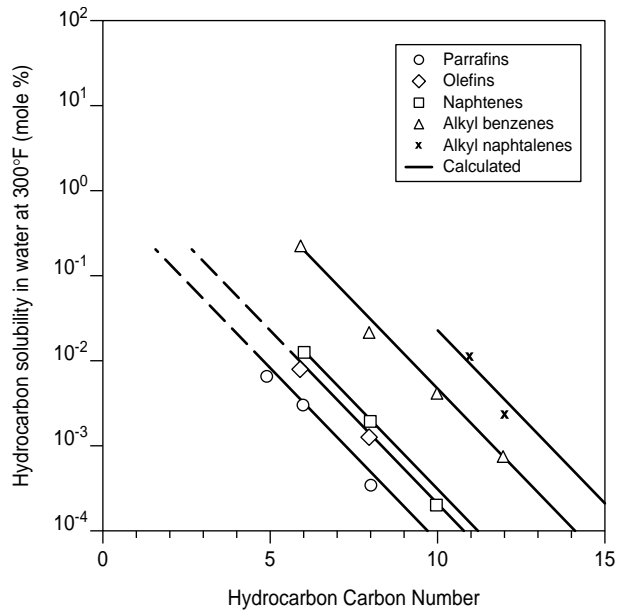
Figure 9

Generalized correlation for the solubility of hydrocarbons in water at 300°F (150°C), redrawn from Brady *et al.* (1982).
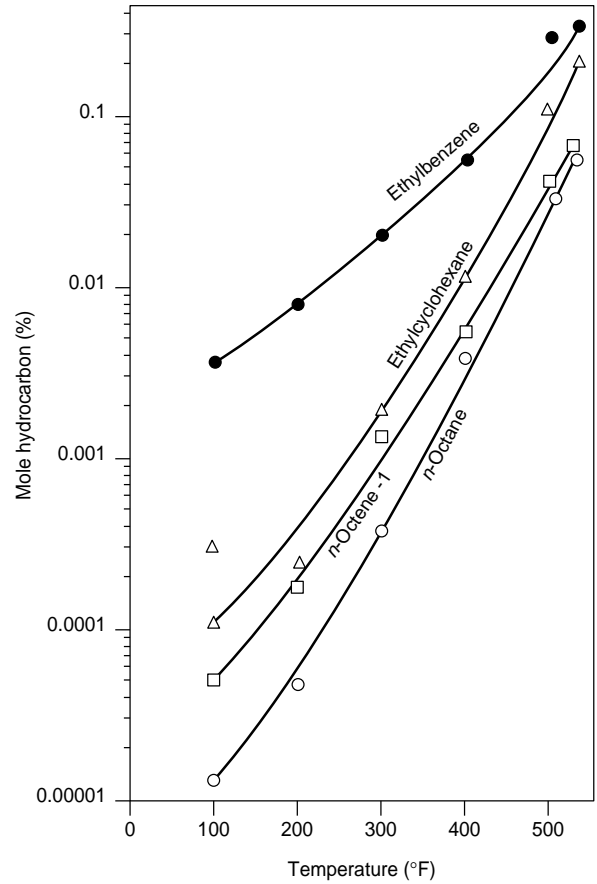

Figure 10

Solubility of C_8 hydrocarbons in water versus temperature, at three-phase equilibrium (redrawn from Brady *et al.*, 1982).

It is now possible to give in Table 2 some solubility values as a function of both carbon number and chemical family. Solubility data for single hydrocarbons in water may be plentiful, but information concerning hydrocarbon mixtures is very limited. An exhaustive review of gas mixture solubilities has recently been published by Dhima *et al.* (1997), but it appears that some inconsistencies remain. In particular, some authors indicate that the solubility of a hydrocarbon mixture is greater than the solubility of the pure components at the same temperature and pressure (Amirijafari and Campbell, 1972). This phenomenon has been investigated by Dhima *et al.* (1997) with various mixtures, and found to be untrue.

Similarly, the solubility of liquid hydrocarbon mixtures has been investigated by a number of authors, Burris and McIntyre, 1984, 1985; Leinonen and McKay, 1973). We have shown (de Hemptinne *et al.*, 1997c) that the so-called solubility enhancement could be explained, within these mixtures, as a non-ideality in the hydrocarbon phase. This non-ideality can be important because the molar fraction of any one hydrocarbon within the mixture is small. Its effect is very clearly demonstrated in Figure 11 for the ternary mixture methane-butane-water, where the butane

solubility, x, is computed as a function of the hydrocarbon phase fugacity f

$$x = \frac{f}{f^*} x^*$$

where the asterisk stands for the values of molar fraction and fugacity in the case of pure butane solubility in water, for the same pressure and temperature conditions (Dhima *et al.*, 1997).

TABLE 2

Estimated solubilities of various chemical hydrocarbon families in water at 200°F (93°C) and at the three-phase pressure (in ppm molar)

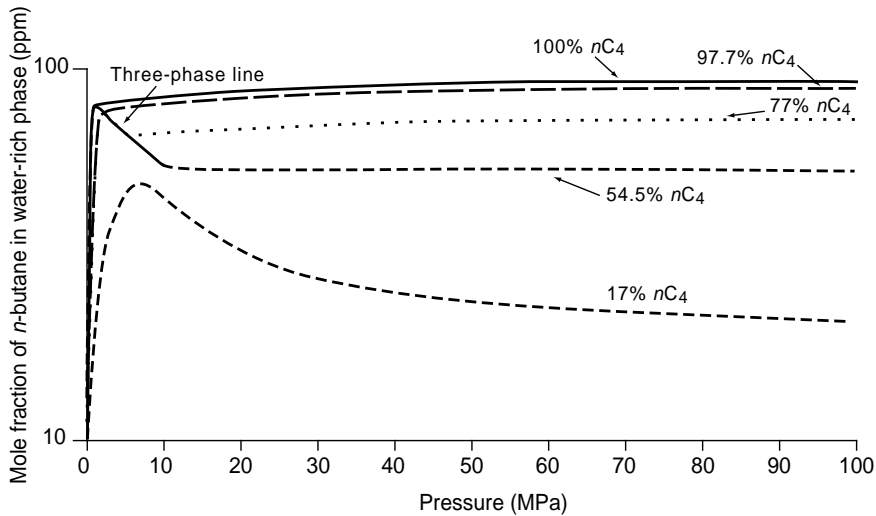| Carbon number	*n*-Alkanes	Naphthenes	Monoaromatics
6	6	50	950
8	0.5	2.4	86
10	0.12	0.2	10

Figure 11

Calculated n-butane solubility in water as a function of pressure in the methane-n-butane-water system at 71°C (160°F), and for different concentrations of butane in the hydrocarbon phase (concentrations are given on a water-free basis).

The figure shows the solubility of pure n-butane as a function of pressure. Up to the butane-water three-phase pressure (close to the butane vapor pressure), the solubility increases with pressure as for a gas; above this pressure, the increase becomes very small as is the case with a liquid. When methane is added to the mixture (first, 4.3%, i.e. 95.7% butane), the solubility logically decreases as the concentration is lower. This decrease, however, is not proportional to the butane content. When methane is added at the given temperature, methane and butane form a liquid-vapor equilibrium, as shown in Figure 8. When a three-phase system occurs in a ternary system, the phase rule imposes that all compositions be fixed at a given pressure and temperature. In Figure 11, the three-phase line is shown and gives an identical n-butane solubility, independently of the n-butane content of the hydrocarbon. As a result, along this line, when pressure increases, the liquid phase is enriched in methane and the total n-butane solubility decreases! This same phenomenon remains visible outside the three-phase region, when the total concentration of butane becomes very small. The butane fugacity in the mixture increases and subsequently decreases; the solubility in water follows the same pattern. Hence, it is clear that the total solubility is not proportional to the mole fraction of butane. However, the solubility is always a monotonic function of the concentration.

Despite this observation, still other experimental data concerning the aqueous solubility of mixtures containing a gas (methane) and a liquid hydrocarbon remain difficult to explain. Using the data of Ng et al.

(1995), the solubility as a function of the concentration is no longer monotonic, and an enhancement factor of the order of three is observed.

When the water contains salts, it is well-known (Price, 1976; Groves, 1988; Keeley et al., 1988) that the solubility of hydrocarbons decreases. Figure 12 illustrates this "salting-out" effect on the solubility of benzene with NaCl. However, Bradley et al. (1973), indicate that some ions (Ag^+ and K^+ in particular) form complexes with benzene and toluene. Thus, their presence in the aqueous phase can significantly increase the solubility of these aromatics, resulting in a "salting-in" effect.
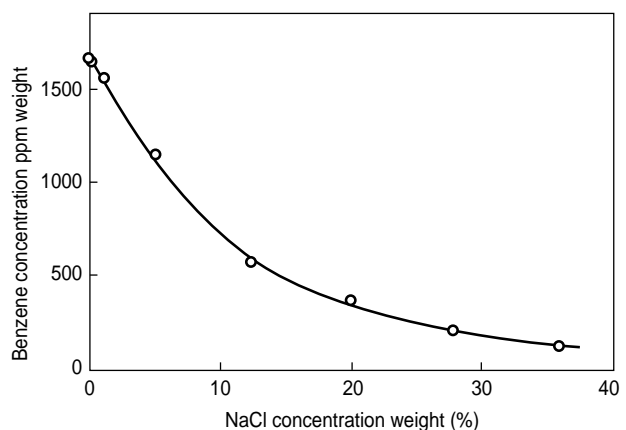

Figure 12

Salting out effect of NaCl on benzene (redrawn from Price, 1976).

Although a large number of gas (CH_4, CO_2 and H_2S) solubility data exist in the presence of salt water, very few of these data are measured at pressures above 100 bar (Ye, 1996).

1.2 Models

Phase equilibrium calculations are based on the identity of the fugacity in all phases:

$$f_i^{HC} = f_i^{aq}$$

The fugacity is often computed using equations of state; and in the petroleum industry, the equations most often used are cubic equations of state.

Water, however, differs from organic molecules due to its polar structure. The question may therefore be raised whether these cubic equations are appropriate for treating systems that contain water. First, we will investigate this issue. The problem related to the presence of salts can be treated separately by activity coefficient methods. This question is raised as a second point. Other equations of state have been developed recently for taking into account the behavior of water molecules. They will be mentioned very briefly. Finally, we will present some recent work at *IFP* that proposes to use a simple Henry's law approach for describing water-hydrocarbon equilibria.

1.2.1 Cubic Equations of State

The use of cubic equations of state for modeling water-hydrocarbon equilibria is possible on the condition that two modifications be applied to their conventional form.

The first modification concerns the functional form of the attractive parameter of water as a function of temperature. The usual Soave approach is no longer valid. Peng and Robinson (1976) propose a procedure that appears to give acceptable results when calculating the water content in the liquid/vapor hydrocarbon-rich phase:

$$\alpha^{1/2} = 1.0085677 + 0.82154(1 - T_r^{1/2})$$

This formulation ensures a correct representation of the water vapor pressure in the entire temperature range.

The second issue concerns the mixing rule for the attractive parameter. The usual quadratic mixing rule with a single binary interaction parameter is:

$$a(T) = \sum_i \sum_j x_i x_j a_{ij} = \sum_i \sum_j x_i x_j \sqrt{a_i a_j}\,(1 - k_{ij})$$

Michel *et al.*, (1989) state that such a simple mixing rule is not appropriate for water-hydrocarbon equilibrium calculations. Several authors therefore suggest composition-dependent mixing rules (Daridon *et al.*, 1993; Kabadi and Danner, 1985; Mollerup and Clark, 1989). This approach is essential for describing phase equilibria when the phases have similar compositions. Li *et al.* (1997) use an MHV2-type mixing rule, combined with the UNIFAC method for activity coefficients.

A much simpler approach that has been chosen by other authors (Erbar *et al.*, 1980; Soreide and Whitson, 1992) is to use two different sets of binary interaction parameters. A temperature-dependent set of interaction parameters for the aqueous liquid phase should be estimated on the basis of the existing binary water solubility. For the non-aqueous liquid and/or vapor phase, most authors consider that constant interaction parameters are sufficient. They base their observations on the fitting of three-phase pressure measurements. Eubank *et al.* (1994), however, use the water solubility in the hydrocarbon phase and show that their relationship does not degrade the prediction of three-phase equilibria. They suggest the following relationship (for the Peng-Robinson equation):

$$k_{ij}^{HC} = A - BT_r - C/T_r$$

Very few authors take into consideration the effect of salts. Soreide and Whitson (1992) deal with this issue by adapting the attraction parameter of water and the binary interaction parameters between water and any other component in the aqueous phase as follows:

$$\alpha^{1/2} = 1 + 0.4530\left[1 - T_r(1 - 0.0103 c_{sw}^{1.1})\right]$$
$$+ 0.0034(T_r^{-3} - 1)$$

and

$$k_{ij}^{Aq} = A_0(1 + \alpha_0 c_{sw}) + A_1 T_{ri}(1 + \alpha_1 c_{sw})$$
$$+ A_2 T_{ri}^2(1 + \alpha_2 c_{sw})$$

where c_{sw} is the salt content, expressed in 10^3 molal concentration. The parameters A_k, and α_k are

coefficients given by the authors and T_{ri} is the hydrocarbon reduced temperature.

All the above methods are fitted on the available binary equilibrium data, meaning that they are essentially focused on gas-water equilibria at high pressures (up to 700 bar) and up to 200°C. The results are very sensitive to the fitted parameters. One can, therefore, not really look upon these methods as predictive. In particular, extrapolation to heavy hydrocarbons is very hazardous.

1.2.2 Models Using Electrolyte Activity Coefficients

Except for the very empirical method of Soreide and Whitson (1992), cubic equations of state are generally not suited for describing electrolyte phases. On the other hand, a large number of well-documented equations exist that are adapted to electrolytes (Zemaitis *et al.*, 1986). Several authors (Aasberg-Petersen *et al.*, 1991; Zuo and Guo, 1991) manage to combine the equation of state approach to the electrolyte models in order to obtain powerful prediction tools:

$$f_i^{aq} = \gamma_i f_i^{aq,\ eos}$$

The following assumptions are thus implicitly made:
– The concentration of hydrocarbons in the aqueous phase is too small to affect the calculation of the activity coefficient of water, γ_i. The conventional electrolyte models are therefore applicable.
– The equation of state calculation of the fugacity in pure water, $f_i^{aq,\ eos}$, is accurate.

These assumptions are applicable as long as the gas solubility remains small, which is generally the case. They are appropriate for fluid-phase equilibria calculations, but may not be sufficient when species equilibrium is required, especially in the presence of dissolved CO_2 or H_2S. This issue is, however, outside the scope of the present review.

Almost all activity coefficient models are based on the relationship first developed by Debye and Hückel (1923a and 1923b). It shows the average activity coefficient of a salt ($\gamma_{\pm}^{D-H}$) as a function of the ionic strength:

$$\ln \gamma_{\pm}^{D-H} = \alpha |z_+ z_-| \frac{\sqrt{I}}{1 + b\sqrt{I}}$$

where:
α is a constant that depends on the solvent
$|z_+ z_-|$ is the product of the valences of the ions
I is the ionic strength, defined as:

$$I = \frac{1}{2} \sum_i z_i^2 m_i$$

when m_i is the molality of ion i and z_i its valence.

The Debye-Hückel law is not adapted to highly concentrated salt solutions. Several additional corrections have been proposed for improving this law (Zemaitis *et al.*, 1986; Rafal *et al.*, 1994). The most well-known model is the empirical model of Pitzer (1973). Its equation looks as follows:

$$\frac{G^E}{n_w RT} = f(I) + \sum_i \sum_j \lambda_{ij}(I) m_i m_j + \sum_i \sum_j \sum_k \mu_{ijk} m_i m_j m_k$$

where I is the ionic strength of the solution; m_i, m_j and m_k are the molalities of the species i, j and k. The first term, $f(I)$ corresponds to the Debye-Hückel expression; the second term refers to binary interactions and the third to ternary interactions. A major advantage of the Pitzer model is that it allows for the calculation of the activity coefficient of non-ionic species, which are needed in order to describe the salting-out effect. However, it is purely empirical and only to be used in the range where the parameters have been fitted.

The alternative approach for calculating the activity coefficient of neutral species is the method first introduced by Setchenow (1889):

$$\ln\left(\gamma_i^{aq}\right) = KC_s$$

where:
C_s is the molar concentration of salt
K is the Setchenow constant.

In order to obtain a predictive equation, Weisenberger and Schumpe (1996) propose to write the Setchenow constant as a sum over all ions in the solution:

$$K = \sum \left(h_i + h_G\right) n_i$$

where:
h_i is the contribution of ion i
h_G is the contribution of gas G
n_i is the index of the ion in the salt formula.

Values for h_i and h_G are published by Weisenberger and Schumpe for a large number of ions and gases.

The strength of electrolyte activity coefficients is their ability to describe the effect of any ionic species in water. However, the empirical parameters have generally been obtained at atmospheric pressure (mostly) or at the water vapor pressure (above 100°C). The effect of pressure, however, is neglected. This effect is known to be (if the reference state is taken at the pressure of the system):

$$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{T,N_{i,j}} = \frac{\bar{v}_i^E}{RT}$$

where $\bar{v}_i^E$ is the excess partial molar volume of species i in the electrolyte mixture. Very few data are available for estimating this quantity. Lown *et al.* (1968) and Owen and Brinkley (1941) have investigated the modification of the ionic dissociation constants due to pressure. Their observations indicate that at very high pressure (1000 bar), the activity coefficients are a function of pressure. This issue is however badly documented.

1.2.3 Non-Cubic Equations of State

As we have seen, conventional mixing rules are not appropriate for cubic equation of state calculations of water-hydrocarbon equilibria. Some alternative mixing rules are density dependent (Aasberg-Petersen *et al.*, 1991). This results in a mixing rule without discontinuity, but the simplicity of the cubic equation is lost.

Fürst and Renon (1993) have developed the MSA (Mean Spherical Approximation) for the description of an aqueous electrolyte. Their equation of state is based on an expression of the excess Helmholtz energy for a cubic equation of state. They add short and long range interaction terms to the free energy expression of SRK in order to adapt it to the presence of electrolytes. However, the added terms are density dependent, and as a result the equation is no longer cubic. The method is available with parameters for several salts (NaCl, LiCl, KCl, CsCl, $MgCl_2$, $CaCl_2$, $SrCl_2$), but only light gases are considered (CO_2, N_2 and CH_4).

A large number of other equations have been developed taking into account the self-associating character of water (Economou and Donohue, 1992; Economou and Tsonopoulos, 1997; Anderko, 1992). Their main strength is a good description of the phase envelope closures at high temperature and pressure. However, they are usually rather complex, don't allow for the presence of salts and don't bring any clear improvement in the prediction of solubilities compared with the cubic equations of state. As a result, they are rarely used in reservoir engineering calculations.

1.2.4 The Henry's Law Approach

Henry's law is generally used for calculating the solubility of almost insoluble solutes. In the case of water-hydrocarbon mixtures, this is particularly the case.

An indirect method of describing solubilities of liquids, considering that pressure has a negligible effect, is to use correlations that provide the solubility as a function of temperature. The expression developed by Yaws *et al.* (1990, 1993a, 1993b, 1994, 1995) can thus be used:

$$\log[S] = A + B / T + C / T^2$$

Where the solubility, S, is given in ppm weight. The authors have tabulated the coefficients A, B and C for a very large number of hydrocarbons, including paraffins, naphthenes and aromatics. Furthermore, they give a general correlation to estimate water solubility data for hydrocarbons C_{5+} at 25°C as a function of T_b, the normal boiling temperature (expressed in K):

$$\log[S(\text{ppm(wt}))] = -7.861 + 103.032 \cdot 10^{-3} T_b$$

$$+ -315.247 \cdot 10^{-6} T_b^2 + 262.558 \cdot 10^{-9} T_b^3$$

For predicting gas solubilities at high pressure, the full Henry's law expression must be used:

$$x_{i,w} = \frac{f_i^{gas}(P,T,y_{(y_i + y_w = 1)})}{H_{i,w}(P,T)}$$

The validity of this equation is confirmed by the high pressure solubility data for methane, ethane, *n*-butane and CO_2 in pure water as measured at *IFP* by Dhima *et al.* (1997).

The above equation can only be used in a predictive manner if an appropriate equation of state exists for the vapor phase and if an expression for Henry's constant as a function of pressure, temperature and composition is found.

Based on experimental low pressure solubility data many authors give expressions of the temperature dependence of the solubility or of the Henry's constants (Wilhelm *et al.*, 1977; Yamamoto *et al.*, 1976; Rettich *et al.*, 1981; Crovetto *et al.*, 1982, 1984; Prini and Crovetto, 1989). Pierotti (1965) and Schulze and

Prausnitz (1981) obtained the temperature dependence of Henry's constant applying scaled-particle theory while the other references give a polynomial dependence on T (K) or $(1/T)$ of the solubility or Henry's constant.

Harvey (1996) gives the Henry's constant as a semi-empirical function of the water saturated vapor pressure, $P_w^{sat}(T)$ and of its reduced temperature $T_r = T/T_{c,w} = T(K)/647.14$:

$$\ln H_{i,w}(MPa) = \ln P_w^{sat} + \frac{A_{i,w}}{T_r} + \frac{B_{i,w}(1-T_r)^{0.355}}{T_r}$$
$$+ \frac{C_{i,w}\exp(1-T_r)}{T_r^{-0.41}}$$

where, in this case, the coefficients A, B, C are obtained by fitting solubility data from the literature for 13 solutes in water. No expression was found providing Henry's constant as a predictive function of the hydrocarbon component.

To illustrate different expressions giving the temperature dependence of Henry's constant we give in Figure 13 the results for the case of methane.

The effect of pressure on Henry's constant is given by the Krychevsky-Kasarnovsky (1935) equation:

$$\lim_{x_i \to 0} \ln \frac{f_i}{x_i} = \ln H_{i,w} = \ln H_{i,w}^{(P_w^{sat})} + \frac{\bar{v}_i^\infty (P - P_w^{sat})}{RT}$$

where the Henry's constant at the saturated water vapor pressure is calculated by one of the methods given above, while the partial molar volume at infinite dilution, $\bar{v}_i^\infty$, can be calculated in different ways as given in the literature (Lyckman *et al.*, 1965; Brelvi and O'Connell, 1972; Lee, 1983). Application of the Krychevsky-Kasarnovsky equation should be used with caution for the solubility of CO_2, especially at temperatures higher than 100°C (Parkinson and De Nevers, 1969; Gibbs and Van Ness, 1971; Malinin, 1974; Carroll and Mather, 1992).

2 THE NEW CHALLENGES

As a result of the increased mutual solubilities of water and hydrocarbons, a number of new challenges are raised. Even though most issues are closely related, we will separately consider the problems due to the presence of water in the hydrocarbon phase and those resulting from the solubility of reservoir fluids in an aqueous phase.

2.1 Issues Related to the Presence of Water in the Hydrocarbon Fluid

2.1.1 Scale Formation Due to Evaporation of Water in or near the Well

During production, a pressure drop occurs within the reservoir close to the well, and subsequently within the
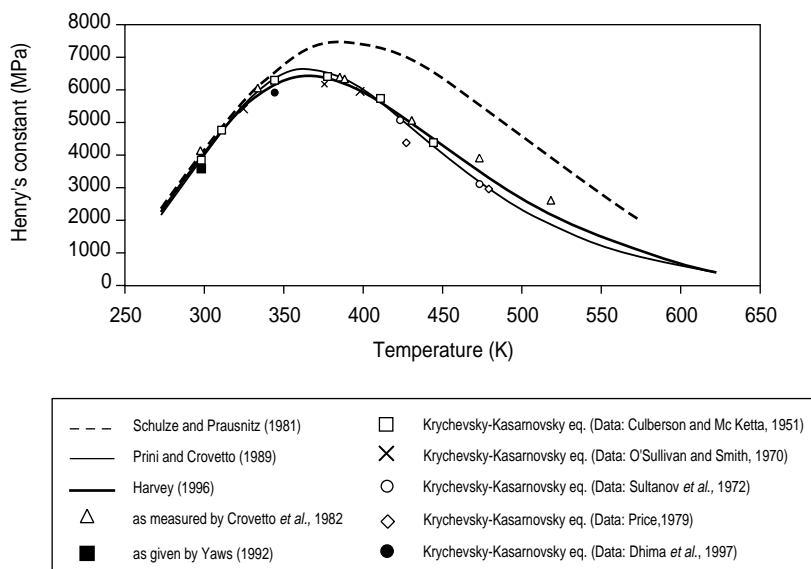

Figure 13

Temperature dependence of the Henry's constant of methane, according to different authors.
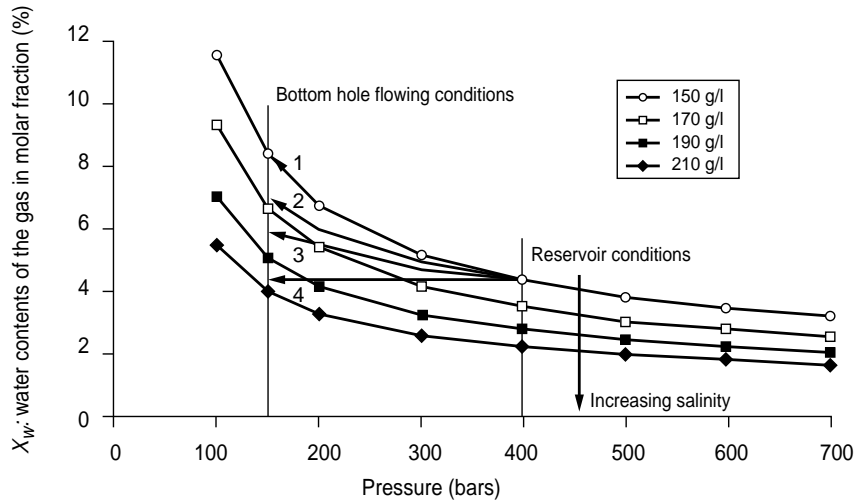
Figure 14

The water content of a reservoir fluid as a function of pressure and salinity (redrawn from Morin and Montel, 1996).

well. Figure 14 shows how the water content of a gas increases when pressure decreases (1), for a given salt content. The same figure also indicates how the water content of the gas decreases with increasing salinity. When water near the well is vaporized, the salt remains and the salinity of the remaining aqueous phase increases. As a result, the water content of the gas is reduced (2 and 3) until the salinity profile compensates exactly for the enhanced water saturation (4). At that point, no more water vaporization can take place (Morin and Montel, 1996).

This salinity increase could result in scale formation, but the risk is even higher within the well, where no connate water is present, but where water can be mechanically entrained. Figure 15 illustrates the pressure versus temperature variation of a fluid within the well.

The bottom-hole conditions used as an example are 100 bar and 150°C, in the top right corner of the figure. The diagonal lines represent constant water content of the fluid in the presence of excess water. In this example, the fluid under reservoir conditions contains 46 g/Sm^3 of water. When traveling up the well, however, the fluid will not remain on the same line of constant water content. If the conditions follow the bold dotted line, the water content of the fluid decreases, and water is deposited from the vapor phase. No salt deposit can form under these conditions, but the existing water droplets are diluted. However, if the fluid pressure-temperature profile runs along the continuous bold line (calculated as the isenthalpic limit), the water content of the fluid will continuously increase, and any entrained
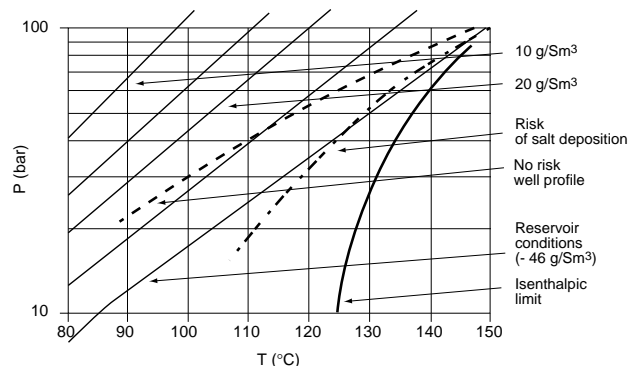

Figure 15

Schematic representation of the risk of scale formation within the well.

droplets may entirely vaporize, thus leaving solid scale behind. The more plausible intermediate solution is presented as a bold dash-dot line. In the first section of the curve, above and to the left of the line representing 46 g/Sm^3, the water content is lower and that water will condense from the gas. However, as soon as the curve crosses the 46 g/Sm^3 iso-content line, vaporization will occur with risk of scale formation. Two conditions are thus required for scale formation: entrainment of connate water droplets and vaporization resulting from pressure and temperature changes.

2.1.2 Gas In Place Prediction

In a recent SPE paper (de Hemptinne *et al.*, 1996 and 1997b), we discussed how the often used *P/Z* (pressure over compressibility factor) relationship for estimating

the amount of gas in place (Cossé, 1988) is modified as a result of the presence of water. The relationship is a simple mass balance between the initial conditions, marked with an index *i*, and the condition at any given time. The fraction of gas, *Q*, that is produced at that time (expressed in mole fraction) is found from the expression:

$$\frac{P}{Z(P)} = \frac{P_i}{Z_i}(1-Q)$$

which is a linear relationship between *P/Z* and *Q*. A deviation from linearity is observed when water is present, as shown in Figure 16.

This deviation can be expressed as follows if water is taken into consideration:

$$\frac{P(1-x_{H_2O})}{Z^s(P)} = \frac{P_i(1-x_{i,H_2O})}{Z^s{}_i}(1-Q)$$
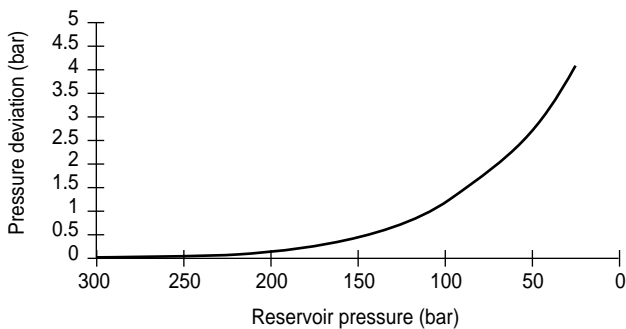

Figure 16

Pressure deviation from the simple *P/Z* relationship of a gas reservoir near 140°C, due to water-gas exchanges.

Here, the water content is explicitly stated as a mole fraction, x_{i,H_2O}, and the exponents *s* indicate that the compressibility factor must be taken at saturation, or in the presence of excess water.

2.1.3 Modification of the Saturation Pressure

It is easy to conceive how the presence of several percent of a light molecule in the hydrocarbon fluid could affect the saturation pressure. Unfortunately, very few experimental measurements have been found in the open literature on this subject. We have measured one data point (de Hemptinne *et al.*, 1996), and have not seen any measurable evidence of a modification of the

dew point under high temperature (190°C) and medium pressure (300 bar) conditions for a paraffinic fluid. However, it is possible that the fluid composition (in particular its aromaticity) may affect the conclusions.

2.2 Issues Related to the Solubility of Hydrocarbons in Water

2.2.1 Hydrocarbon Loss in Water

As was mentioned above, acid gases (H_2S and CO_2) are very soluble in water. Paux and Zhou (1997) give an example of how this solubility may result in a significant modification of the hydrocarbon phase composition over time, without any hydrocarbon phase transition. Figure 17 shows the H_2S content of a reservoir gas as a function of the reservoir pressure.

It appears that during most of the life of the reservoir, the H_2S remained approximately constant at 15% mole. Very recently, as a result of the decrease in reservoir pressure, the H_2S content has increased significantly. According to water-hydrocarbon equilibria models, this phenomenon can be explained by the degassing of the connate water. It is striking how this phenomenon sets in very suddenly. This may have very serious consequences on future operations on this reservoir.
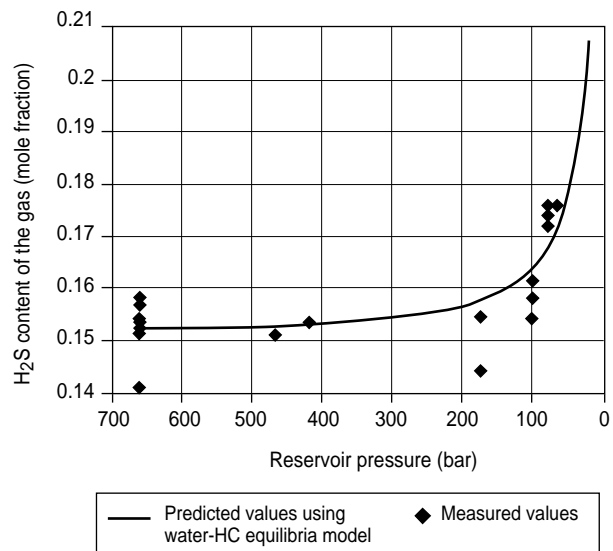

Figure 17

Evolution of the H_2S content of a reservoir fluid as a function of pressure (Paux and Zhou, 1997).

It is very likely that other similar instances exist but have not been detected as degassing has not yet begun.

2.2.2 Consequences of Acid Gas Injection

Up to now, the H_2S acid gas originating from a reservoir, was treated by a Claus plant to form elemental sulfur. The sulfur market is decreasing, and as a result new options for the H_2S removal are being investigated. One of these options is acid gas reinjection. However, as was mentioned above, acid gases are very good solvents for water in reservoir conditions; and their solubility in water is non-negligible. Their presence may therefore affect the phase equilibria and enhance the effect of water in all problems mentioned here.

2.2.3 Interactions with Drilling Fluids

Almost all drilling muds contain variable amounts of water. When drilling, the mud and the reservoir fluid are brought in close contact with one another. As a result, issues relating to the solubility behavior of the mud and the reservoir fluid should be considered.

The first issue is the risk of gas kicks. This phenomenon occurs when free gas bursts out at the well-head. It can be detected because this gas has a large specific volume and as a result the mud flow rate increases significantly when a large bubble travels along the well. However, as long as the gas remains in solution, only a small effect is visible at the surface of the well. A significant hazard can thus result.

The gas content of the mud can be used to determine the reservoir fluid composition down the well. The interpretation of the results will, however, vary significantly depending on whether the gas dissolves in the mud (in which case it travels at the same rate) or not (gas bubbles will travel faster).

2.2.4 Environmental Problems Resulting from Gas Storage

When hydrocarbon gases are stored in reservoirs that are in contact with fresh water aquifers, the potential pollution of the aquifer becomes an important issue. The need for solubility data to estimate the potential damage is very different from the need cited for other reservoir engineering issues. Even very small concentrations can result in serious problems. For this reason, high-pressure, high-temperature (probably lower than in the case of HP/HT reservoirs) data on aromatics in the presence of gases are needed. As was mentioned above, these data are scarce in the open literature.

2.2.5 Prediction of Compositional Modifications Due to Fluid Migration Within Basins

In order to determine whether different fluids have similar origins, the phase behavior of the fluids in their natural environment must be closely investigated. In particular, the presence of very large amounts of water that migrate differently than the hydrocarbon fluids may result in substantial compositional modifications of the fluid. Understanding the thermodynamics of this process, known as water-washing, is important for petroleum geochemistry.

2.3 Other Issues

Only challenges resulting from the high-pressure/high-temperature behavior of water-hydrocarbon mixtures have been mentioned in this presentation. Many other issues could be cited, for example those related to the fact that at low temperature a hydrate phase is formed. The presence of hydrates has many consequences, for example the need to use additives in pipe transport.

Finally, water, since it is a vital resource for all life on earth, the potential environmental consequences of the coexistence of hydrocarbons and water require in-depth studies of low (atmospheric) pressure equilibria. These issues, however, are beyond the scope of the present review.

CONCLUSIONS

As applied research is the fruit of a combination of industrial need and scientific ignorance, we are able, at the end of our presentation, to identify some large trends for future research.

In order of priority, experimental investigations always appear most crucial, models being indispensable for extrapolating and generalization.

In our view, experimental data are lacking in the following fields:
– High pressure and high temperature solubility measurements of water in reservoir fluids are too scarce to allow reliable modeling.

– The influence of the presence of water on the saturation pressure of a reservoir fluid has not been thoroughly established. The few measurements known indicate no major effect, but in light of the potential importance of this parameter, it should be confirmed by additional measurements

– The high temperature (above 100°C) solubility data for heavy hydrocarbons in water are often questionable. Either they are inexistent (paraffins, in particular) or in contradiction with one another.

The effect of pressure on the activity coefficient of water in electrolytes has been very poorly investigated. Before any model can take this into account, additional measurements are needed. The current cubic equations of state are generally well-adapted to the prediction of hydrocarbon phase behavior. However, in our view, for polar substances, additional efforts are needed:

– A simple and correct description of the fugacity of non-hydrocarbons in the hydrocarbon phase is essential. The present-day empirical k_{ij} parameters are in that sense useful but insufficient for a predictive approach

– Cubic equations of state are not designed to describe an aqueous phase. Again, empirical k_{ij} parameters can provide reasonable answers, but are necessarily linked to experimental data. No predictive method exists so far.

– In order to describe the effect of the high pressure solubility of acid gases in brines on the species equilibria, specific models could be used. More work is needed to predict three-phase gas-water-salt equilibria.

ACKNOWLEDGMENTS

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Final manuscript received in April 1998