

## PREDICTING THE INTERFACIAL TENSION OF BRINE/GAS (OR CONDENSATES) SYSTEMS

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**Abstract :** This paper reviews the available literature data that can be used for estimating : (1) the surface tension of brines at ambient conditions, (2) the interfacial tension between a brine and a gas (or condensate) at reservoir conditions. When dealing with the first problem (surface tension of brines), the increase in surface tension due to the salts is often neglected, although there are enough available data to account for it. For the second problem, the paper reviews the literature data on the interfacial tension between water and hydrocarbons (gas, non polar liquids, or mixtures of both), and tries to improve an earlier correlation introduced by Firoozabadi *et al.* (1988). Still, the improved correlation does not handle properly mixtures of gas and neutral oils, and the need for more laboratory measurements is outlined. Salinity corrections similar to those for surface tensions are presented. The practical use of the predictive correlations is illustrated and compared with laboratory measurements at reservoir conditions on a real gas/brine case.

## INTRODUCTION

Capillary measurements are often used to check or calibrate the estimates of water saturations  $S_w$  derived from resistivity log interpretation. The routine methods most commonly employed are either the air/brine method (porous plate or centrifuge), or mercury porosimetry, both at ambient conditions and with no stress. Their results need to be converted into PC curves at reservoir conditions, by accounting for the effect of effective stress (outside the scope of this paper), and the effect of the different surface tensions  $\gamma$  and contact angles  $\theta$ . It is usually assumed that the latter effect is described by the Leverett conversion :

$$Pc_{res} = Pc_{lab} * (\gamma * \cos\theta)_{res} / (\gamma * \cos\theta)_{lab}$$

While the parameters  $\gamma$  and  $\theta$  are well known for the mercury/vacuum fluid pair, there is a need for a better estimation of them in all other cases.

A preliminary clarification of vocabulary should be made first. At ambient conditions, the tensions of a liquid against either its own vapor, or air saturated with its vapor, have practically the same value, because, at these conditions, the gas phase has a negligible density. This tension value is commonly referred to as the "surface tension". On the other hand, the tension between two liquids is called the "interfacial tension". At reservoir conditions, there is not such a general agreement on vocabulary : (1) "surface tension" is used by most specialists in Thermodynamics when dealing with the tension between an oil and the gas in equilibrium with it, while others prefer "interfacial tension" ; (2) in the case of gas versus brine, again both expressions are found in the literature, although in the writer's opinion, "interfacial tension" should be preferred, because the density of the gas phase (and a fortiori of a condensate) is not negligible. Consequently, throughout this paper, the writer will use :

- "surface tension" only for the case of gas/liquid at ambient conditions
- "interfacial tension" ("IFT") in all other cases, i.e. either oil/brine at ambient conditions, or any hydrocarbon/brine at reservoir conditions.

For natural crudes, the contact angle depends upon wettability and saturation history; moreover, the interfacial tension is very sensitive to small amounts of interfacially active components (organic anions, asphaltenes, porphyrins,...) which tend to concentrate at the brine/oil interface. Therefore the direct measurement of the IFT at reservoir conditions is to be preferred. For oils devoid of interfacially active components, i.e. having only saturates and aromatics fractions, it may be worth looking for a predictive correlation. Furthermore, in the case of gas or condensates, the hydrocarbon may be considered as perfectly non-wetting ( $\theta = 0$ ), and the only problem left is to estimate the ratio  $\gamma_{\text{res}} / \gamma_{\text{lab}}$ .

This paper thus addresses two problems :

- estimating the surface tension of brines at ambient conditions : the effect of salinity is often neglected,
- estimating the interfacial tension of gas (or condensates) / brine systems at reservoir conditions : it reviews an earlier paper by Firoozabadi *et al.* (1988) , adds other published literature data, emphasizes the need for more experimental and theoretical work on gas mixtures, and adds some data on the influence of salinity.

## SURFACE TENSION OF BRINES AT AMBIENT CONDITIONS

### Surface tension of pure water and temperature dependence

Several published results and equations are available in the literature, and in the temperature range 0 to 100 °C, they are in agreement only within  $\pm 0.3$  mN/m :

	<u>Technique</u>	<u>Temp. range</u>	<u>Reference</u>
$\gamma_0 = 76.24 - 0.1379 \cdot t - 0.3124 \cdot 10^{-3} \cdot t^2$	(Wilhelmy plate)	0 to 100 °C	Kayser (1976)
$\gamma_0 = 75.653 - 0.1379 \cdot t - 0.2717 \cdot 10^{-3} \cdot t^2$	(ring tensiometer)	0 to 50 °C	Cini <i>et al.</i> (1972)
$\gamma_0 = 75.668 - 0.1396 \cdot t - 0.2885 \cdot 10^{-3} \cdot t^2$	(Wilhelmy plate)	0 to 50 °C	Cini <i>et al.</i> (1972)

Figure 1 shows the corresponding values, compared with the data of the International Critical Tables (1928), Jasper (1972), and Vargaftik *et al.* (1983). Cini *et al.* (1972), Kayser (1976) and Vargaftik *et al.* (1983) give good reviews. In the temperature range 0 to 50 °C, the data of Cini *et al.*, the International Critical Tables, or Vargaftik *et al.*, should be preferred.

### Surface tension of brines at ambient temperature

The presence of common salts in the brine increases the surface tension, as compared to that of pure water at the same temperature :

$$\gamma \text{ (brine, } t, 1 \text{ atm.)} = \gamma_0 \text{ (pure water, } t, 1 \text{ atm.)} + \delta\gamma \text{ (salts)}$$

Several literature sources yield experimental results :

International Critical Tables :  $\delta\gamma = f(\text{molality } m)$  at 20 or 25 °C

Ralston *et al.* (1973) :  $\delta\gamma = f(\text{Molarity } c_M)$  at 21 °C

Aveyard *et al.* (1977) :  $\delta\gamma = f(\text{molality } m)$  at 20 °C

For 1-salt solutions, the coefficient  $b = \delta\gamma / m$  is often constant over a large range of molal concentrations : Figures 2 to 5 show the data of the 3 references above for KCl, NaCl, MgCl<sub>2</sub> and CaCl<sub>2</sub> brines, and the average lines. These lines are not strictly regression lines, and account for several details :

- the data of Aveyard *et al.* (1977) are more scattered
- because of a possible error on  $\gamma_0$ , the lines are not forced through the origin

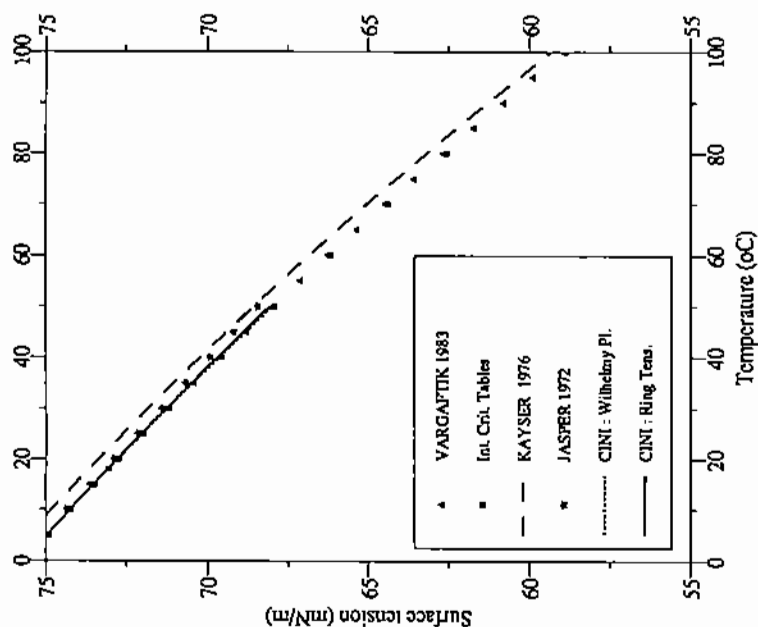


Fig 1 - Surface Tension of Pure water at 1 atm.

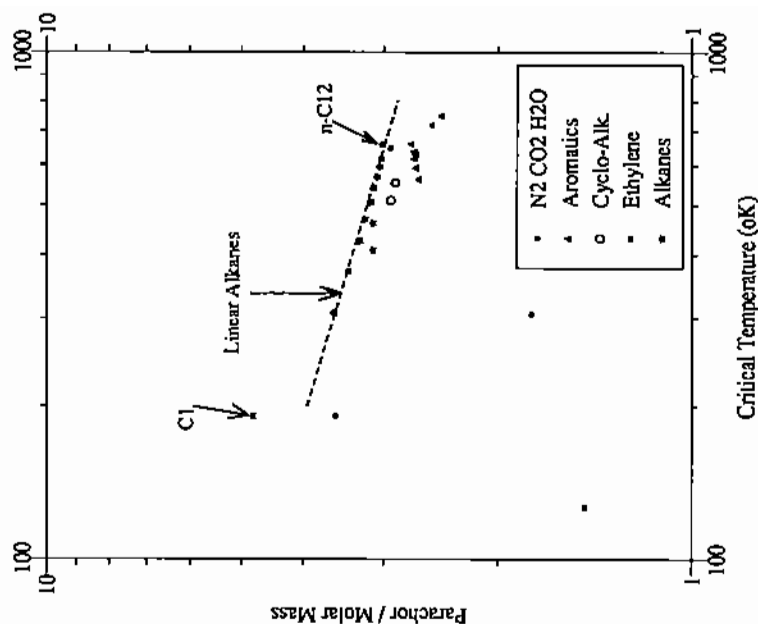


Fig 11 - P/M ratio versus Critical Temperature

- for some salts ( KCl, MgCl<sub>2</sub>, CaCl<sub>2</sub>), the variation is not linear over the whole range of molalities; for practical purposes, the dominant salt in formation brines is NaCl, and the concentrations of the others salts are rarely higher than 1.0 molal ; their lines were drawn only for this range of molalities.

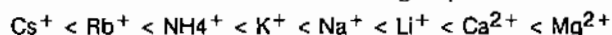
The slopes  $\delta\gamma/m$  (or "b" in the figure captions) obtained are given in Table 1 .

**TABLE 1 - Salt specific coefficients of increase in the surface tension of water**

Salt	$\delta\gamma/m$	Molality range	Temperature
LiCl	1.75	0 to 0.5	20°C
NaCl	1.63	0 to 6.0	20°C
KCl	1.48	0 to 2.	20°C
MgCl <sub>2</sub>	3.0	0 to 1.0	20°C
CaCl <sub>2</sub>	3.2	0 to 1.0	25°C
Na <sub>2</sub> SO <sub>4</sub>	2.68	0 to 1.0	20°C
MgSO <sub>4</sub>	3.00	0 to 1	20°C
Na <sub>2</sub> CO <sub>3</sub>	2.65	0 to 1.5	20°C

An undocumented point is whether, in a brine made with several salts, the increments of surface tension are additive.

The reason for the increase of surface tension due to dissolved salts, and for the different values found for different chlorides, is related to the structure of the Air/Water interface, and how the different cations concentrate there, as explained by Johansson *et al.* (1974) and Raiston *et al.* (1973). The cations tend to adsorb negatively at the interface, and the water molecules located at the interface "feel" more cation solvation towards the bulk of the water phase; this attraction increases as the ratio of cation charge  $z^+$  to cation surface area  $r^2$  increases; thus the effect on surface tension increases in the following sequence :



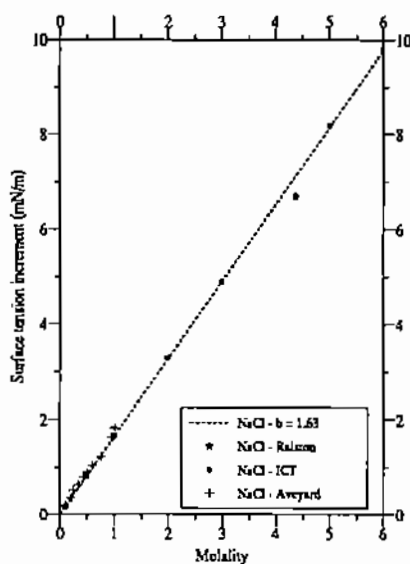


Fig 2 - Surface Tension of Brines - NaCl

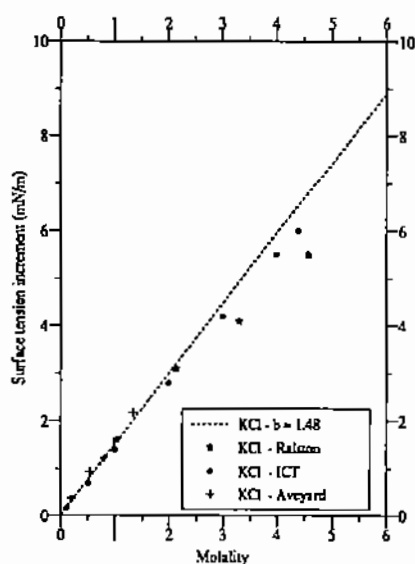
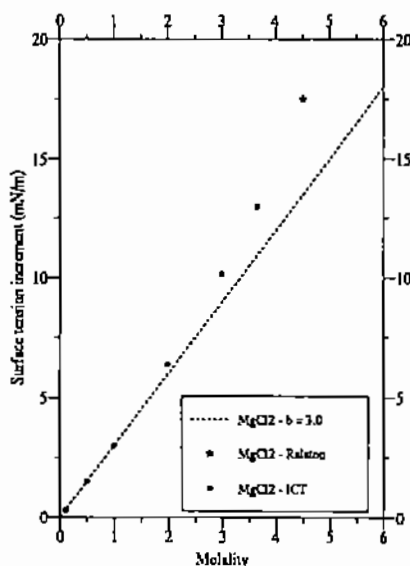
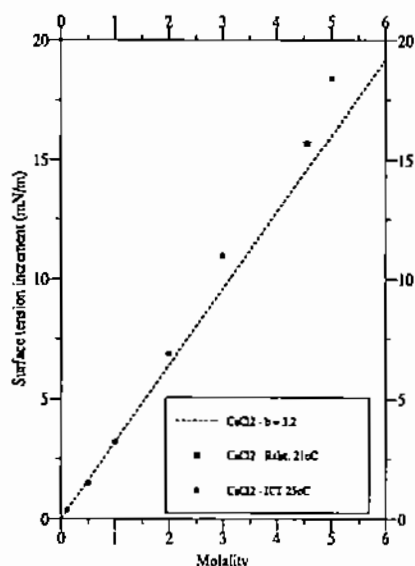


Fig 3 - Surface Tension of Brines - KCl

Fig 4 - Surface Tension of Brines -  $\text{MgCl}_2$ Fig 5 - Surface Tension of Brines -  $\text{CaCl}_2$

### Salt effect at higher temperatures

Several authors : Johansson *et al.* (1974), Aveyard *et al.* (1977), give theoretical expressions relating the increase in surface tension to various parameters (including temperature), either from electrostatic or thermodynamic considerations. They all suggest that, at a given salt concentration, the increase in surface tension  $\delta\gamma$  is proportional to the Kelvin temperature :

$$\delta\gamma \sim T (^{\circ}\text{K})$$

## INTERFACIAL TENSION BETWEEN WATER AND NEUTRAL OIL

### General comments

There are many published experimental data on interfacial tensions between water and hydrocarbons (gases, alkanes or aromatics), but they are not matched (different pressure and temperature conditions). Most of them were measured using the pendant drop technique. Most authors claim an experimental accuracy of  $\pm 0.1$  mN/m or better, which may be true for the resolution within a series of measurements by the same author on the same equipment, but not from one series to another. Some results may have been biased by experimental causes : using unrefined hydrocarbon products (Owens 1970) , pollution by some pieces of the equipment (Hough *et al.*, 1951), insufficient ageing time of the drop (Hassan *et al.* , 1953).

### The correlation of FIROOZABADI & RAMEY

In 1988, A. Firoozabadi and H. J. Ramey published a prominent and comprehensive review of the published data, and presented two predictive correlations based upon the density contrast  $\delta\rho$  between brine and hydrocarbon :

+ the first correlation (which will be referred to as the "correlation F&R1") applies to pure hydrocarbons, or binary mixtures of pure hydrocarbons, and involves the reduced temperature  $T_r$  of the hydrocarbon at the temperature of the measurement ; when plotting the "F&R1" function  $y_1$  :

$$y_1 = \gamma^{1/4} \cdot T_r^{.3125} / \delta\rho$$

versus  $\delta\rho$ , all the points fall on the same smooth continuous line. Here  $\delta\rho$  is not the true density contrast that would be observed between the water and the hydrocarbon in contact with each other, but the difference between the densities of the pure hydrocarbon (considered alone) and pure water (considered alone), i.e. this  $\delta\rho$  ignores the possible miscibility effects. The density of water was taken from the tables of Smith *et al.* (1934), which are in agreement with the Steam Tables of Baines (1964), and with the tables of Burnham (1969).

+ the second correlation ("correlation F&R2") applies to real crudes, and does not involve the reduced temperature; it uses the "F&R2" function :

$$y_2 = \gamma^{1/4} / \delta\rho$$

which, again plotted against  $\delta\rho$ , results in a smooth curve.

In this paper, we shall focus only on the first correlation, and investigate it along the following guidelines. First, it should be noted that the predicting variable  $\delta\rho$  is incorporated in the predicted function  $y_1$ , thus making the dependence between  $\gamma$  and  $\delta\rho$  not readily distinguishable. Secondly, in their paper Firoozabadi and Ramey selected some of the data of Hassan *et al.* (1953), and did not use the other data; they also mentioned that the data of Jennings & Newman (1971) for decane-methane mixtures do not satisfy the correlation very well, but did not plot them. Thirdly, we tried to incorporate other data published in the literature.

The data used, by both Firoozabadi & Ramey (1988), and this author, are listed in Table 2. Many of the data are given for series of fluid pressures at one or several temperatures, which are conveniently plotted as one or more "isotherms". Numerical data, when not directly listed in the papers, were prepared as follows :

- interfacial tensions were digitized from the figures
- hydrocarbon densities were computed by a computer program developed by F. Montel (1990), that uses the LKP model (cf Plocker *et al.*, 1978).
- the densities of pure water were computed from the program released by the US National Bureau of Standards (Gallagher 1985); a cross-check with data from the Steam Tables of Smith & Keyes (1934), or of Burnham (1969), at values of temperature and pressure selected over the whole range used (20 to 190 °C, 1 to 1500 bars), did not show any difference down to the 4th digit (0.0001 g/cm<sup>3</sup>).



**TABLE 2 - References of Experimental data  
on Hydrocarbon/Water Interfacial tension**

[1] References	[2] Hydrocarbon	[3] Temperatures (°C)	[4] Pressures (bar abs.)	[5] F&R's paper	[6] This paper
Jennings et al. (1971)	C1 C1-C10 mixt. C10	[3] 23.3-100 - 176.7 same temper. C1 weight fractions: 0.14-0.38-0.46-0.75-0.85 [3] 23.3 - 100 - 176.7	max[9] to 827 same press. range max[8] 1 to 827	YB YC YC	31 58 23
Hassan et al. (1953)	C3 n-C4 n-C5 n-C6 n-C8 i-C8 Benz.	[8] 26.6 - 37.7 - 48.8 - 59.8 - 71.0 - 82.1 [4] 26.6 - 37.7 - 48.8 - 59.9 [6] 28.6 - 37.7 - 48.8 - 59.8 - 71.0 - 82.1 [5] 28 - 48.8 - 59.9 - 71.0 82.1 [5] 26 - 48.8 - 59.9 - 71.0 82.1 [6] 26.6 - 37.7 - 48.8 - 59.9 - 71.0 - 82.1	max[8] 35 to 208 idem max[8] 35 to 208 max[8] 35 to 208 max[8] 35 to 208 max[8] 35 to 208	YBU <sup>a</sup> YBU <sup>b</sup> YBU <sup>c</sup> YBU <sup>d</sup> YU YU Ym	(42) (37) (24) (39) (33) (32) 42
Jennings (1967)	n-C10 Benz.	[3] 25 - 100 - 176 [4] 25 - 50 - 100 - 176.7	[8] 1 to 827 [8] 1 to 817	YC <sup>e</sup> YB	31 <sup>e</sup> 35
Mac Caffery (1972)	n-C8 n-C12	[3] 45 - 85 - 125 [4] 38 - 80 - 115 - 135	[4] 14-138-275-414 [3] 17-172-345	YB YB	12 12
Michaels et al. (1951)	n-C10 Benz.	[5] 23.6 - 50.2 - 80.9 - 110.8 - 131.7 [5] 23.3 - 45.9 - 66.7 - 89.2 - 89.3	[5] 1 to 709 [5] 1 to 678	Ym Ym	23 25
Matubayasi et al. (1977)	n-C6 n-C8 Benz.	[1] 30 [1] 30 [1] 30	[11] 78 to 1508 [8] 200 to 1385 [3] 302 to 1010	N N N	11 8 4
Mc Caffery et al. (1970)	n-C12 Benz.	[5] 20 to 90 [3] 24 - 52 - 83.5	[1] 1 [1] 1	N N	5 3
Mon et al. (1984)	n-C5 i-C5 n-C6	[3] 15 to 35 [4] 15 to 30 [5] 20 to 60	[1] 1 [1] 1 [1] 1	N N N	3 4 5
Ginfalco et al. (1957)	Cy-C8	[1] 20	[1] 1	N	1
Jho et al. (1978)	C1 C2 n-C4 i-C4 c2H4 CO2	[2] 25 - 50 [2] 25 - 48 [3] 25 - 37 - 50 [2] 25 - 36.8 - 48.1 [2] 25 - 38.4 [2] 25 - 45.2	[7] 11 to 72 [4] 11 to 42 [4] 1.5 to 3.0 [6] 1.5 to 4.0 [6] 11 to 62 [6] 11 to 52	N N N N N N	14 8 12 18 11 1

Next, Figure 7 shows the data of Jennings & Newman (1971) for C1, n-C10, and mixtures of both with varying compositions, as given in Table 3. These mixtures were prepared, according to Jennings & Newman, so as to simulate an ideal live oil. In fact, the "ideal" GOR of these mixtures (assuming a complete separation of C1 as gas phase, and C10 as liquid phase, at 1 atmosphere and 15°C) ranges from 176 to 6125 vol/vol, i.e. from an average live oil to a condensate. The densities were computed using the LKP model. In order to check the reliability of its prediction for

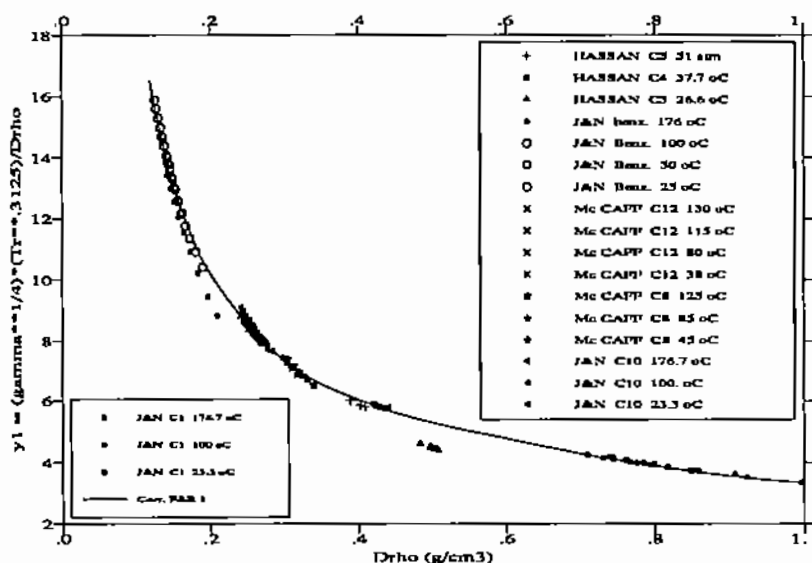


Fig 6 - Correlation F.R.1 - Data used by F-R - Pure HC

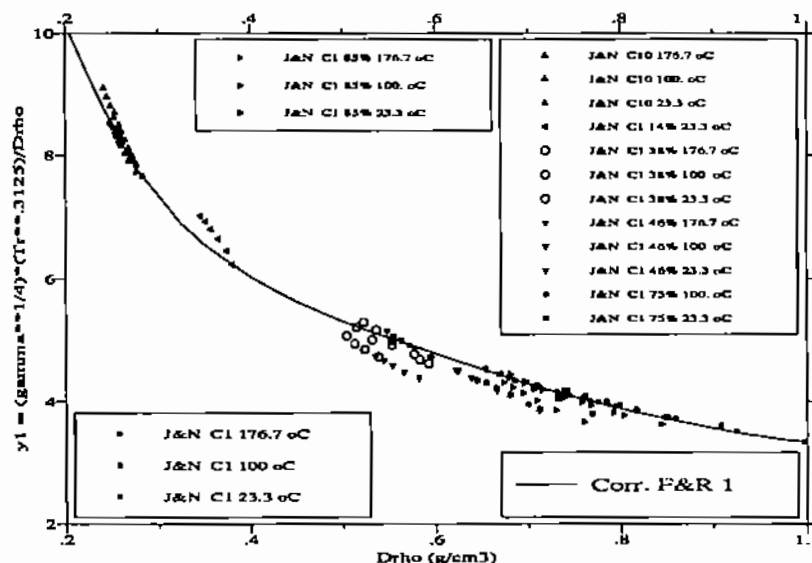


Fig 7 - Correlation F.R.1 - Mixtures C1-C10

the mixtures, we also used the LKP model to determine the densities of such mixtures as listed by Reamer *et al.* (1942), for each mixture, at 3 temperatures (37.8, 104.4 and 171.1 °C), and up to 5 pressures above the dew point pressure (2500, 3500, 5000, 7000 and 10000 psi a.) : the root mean square relative deviation, for a total number of 47 check points, is 1.20 %; the worst deviations are found when the pressure is less than 20 bars above the dew point. We computed the critical temperature for those mixtures as the mole fraction-weighted average of the individual critical temperatures of C1 and C10 (191.2 and 617.7 °K). This may seem arguable, because the LKP model would yield a different estimate, but is necessary *in order to be consistent with the approach of Firoozabadi and Ramey*. In their paper, they do not explicitly detail how they did estimate the critical temperature of the mixture, but this can be guessed from their Table 6. In this table, they compare measured and predicted IFT values for the mixture with 46 % weight fraction of C1, and give the reduced temperature they used, from which it is easily deduced that their critical temperature for the mixture was 240.65 °K. As a matter of fact, the mole fraction-weighted average is 241.05 °K, and the LKP model yields 277.1 °K. As shown on Figure 7, the data plot close to the FR1 correlation, but, in the detail, the isotherms again intersect the average trend slantwise, and generally the 100 °C isotherm plots above those at 23 °C and 177 °C.

**TABLE 3 - Data of Jennings & Newman (1971)  
Composition of the C1 / C10 mixtures**

C10 (wgt fr.)	C1 (wgt fr.)	C1 (mole fr.)	Apparent GOR (v/v)
1.00	0.00	0.0000	0.0
0.86	0.14	0.5908	176.
0.62	0.38	0.7712	411.
0.54	0.46	0.8831	921.
0.25	0.75	0.9638	3243.
0.15	0.85	0.9805	6125.
0.00	1.00	1.0000	inf.

We now incorporate stepwise all the data listed in Table 2. First, we include the data for typically "liquid" hydrocarbons : benzene, then all the "liquid" alkanes (carbon number > 3, and pressure high enough). Figure 8 shows an enlarged view of the diagram for benzene data : as observed by Firoozabadi & Ramey, all the data

are consistent. Figure 9 shows the data for benzene, "liquid" alkanes, and all the data of Hassan *et al.* (1953) for C3 to n-C6. The general trend for "liquid" alkanes intersects slantwise the correlation curve; the data of Hassan *et al.* (1953) for n-C4 to n-C6 show some scatter with respect to this curve, and all his data for C3 plot below the curve, more or less parallel to it. Thus we disagree with the use by Firoozabadi & Ramey of selected data from the Hassan *et al.* (1953) set for C3 : the entire data set for C3 has to be either deleted, or incorporated. Thus hereafter we delete all the data of Hassan *et al.* (1953).

Figure 10 shows the data for the "gases", i.e. C1 from Jennings (1967), and C1, C2, C3, n-C4, ethylene and CO2 from Jho *et al.* (1978) : because the pressures chosen by Jho *et al.* (1978) are less than the liquefaction pressures, the non-water phase is in the gaseous state. Jho *et al.* used the technique of capillary rise for measuring the IFTs, and not the pendent drop as Jennings (1967) did for the C1 data. Their data for C1 plot exactly on the correlation curve FR1, in conformity with the data from Jennings (1967), but their data for all the other gases, even the alkane gases (C2,C3,C4) definitely plot below that line. This means that the discrepancy observed between the correlation F&R1 and the data of Jho *et al.* (1978) on gases other than C1 cannot be ascribed to different techniques of measurement, but to the inability of this correlation to describe the behaviour of gases different from C1.

In order to explain the discrepancies observed for the gases, it is interesting to return to the physical meaning of the correlation function  $\gamma_1$  introduced by Firoozabadi & Ramey :

$$\gamma_1 = \gamma^{1/4} \cdot T_r^{-.3125} / \delta\rho$$

As explained by these authors, it originates from an assumed similarity between the water/liquid hydrocarbon IFT, and the surface tension  $\gamma_s$  of that hydrocarbon (tension between the liquid and its vapor); for pure hydrocarbons,  $\gamma_s$  is well described by the equation of McLeod (1923), reviewed by Fowler (1937) :

$$\gamma_s^{1/4} = P \cdot \delta\rho_{LV} / M \quad \delta\rho_{LV} = \text{density contrast liquid/vapor}$$

The parachor  $P$  is a temperature-independent and additive parameter : it is the sum of contributions from the atoms or specific chemical bonds. For linear alkanes,

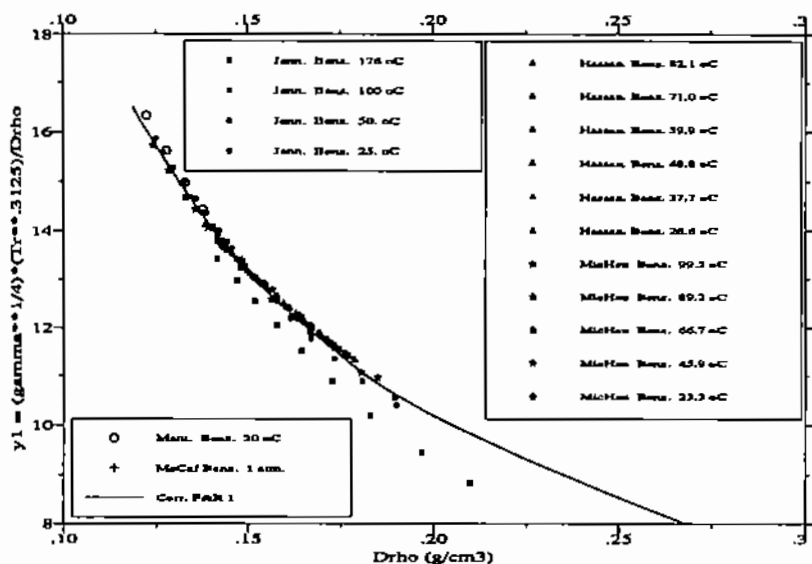


Fig 8 - Correlation F.R.1 - Data for Benzene

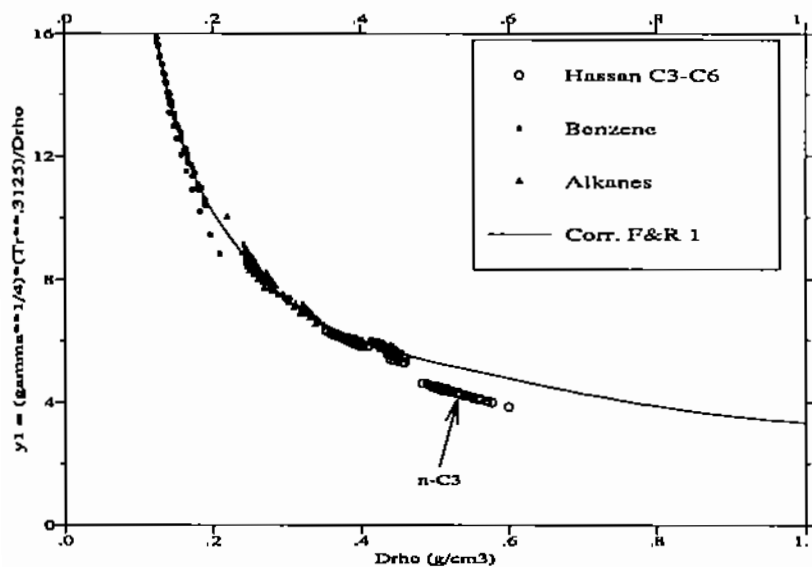


Fig 9 - Correlation F.R.1 : Benzene + Alkanes

the parachor and the molar mass increase linearly with the carbon number, and thus are themselves linearly correlated. Figure 11 shows the values of the ratio  $P/M$  (parachor/molar mass) plotted against the critical temperature  $T_c$  (°K) for various substances. From  $C_2$  to  $C_{10}$  the linear alkanes plot approximately on a trend with slope  $-1/4$ , well above the aromatics and ethylene, and  $C_1$  plots distinctly above that trend. Quite normally, the points for non-hydrocarbon substances ( $H_2$ ,  $N_2$ ,  $CO_2$ ,  $H_2O$ ) are far from the hydrocarbon points.

The idea is then to use the ratio  $P/M$  of parachor to molar mass as a corrective factor to the correlation function  $\gamma_1$  of Firoozabadi & Ramey; namely we introduce a new function  $z_1(\alpha)$ , with  $\alpha$  as an exponent :

$$z_1(\alpha) = \gamma_1 / [P/M]^\alpha = [\gamma^{1/4} * T_r^{.3125}] / [\delta\rho * (P/M)^\alpha]$$

Figure 12 shows the results of this correction with  $\alpha = 0.5$ , for the gases; the agreement is better for  $C_2$  and ethylene, slightly better for  $C_4$ . Figure 13 shows the effect of the same correction for the whole set of data, in arithmetic scale : the isotherms are now more parallel to the average trend, especially for the  $C_1 - C_{10}$  mixtures (for those mixtures, the average parachor and molar mass are the mole fraction-weighted averages of the respective values for  $C_1$  and  $C_{10}$ ). The hyperbolic shape of this average trend suggests the use of log-log plots. Figures 14 and 15 show the same data (correction with  $\alpha=0.5$  and  $\alpha=0.625$  respectively) : there are two domains :

- for  $\delta\rho < 0.5$  g/cm<sup>3</sup> (typical liquid hydrocarbons) , the points plot along a linear axis of slope  $-0.95$  ; the  $\delta\rho$  dependence of the IFT can then be explicitly described as :

$$\gamma \sim [P/M]^{4\alpha} * \delta\rho^{0.20} * T_r^{-5/4}$$

- for  $\delta\rho > 0.7$  g/cm<sup>3</sup> (gases), the average slope is approximately  $-0.75$  ; the  $\delta\rho$  dependence of the IFT can then be explicitly described as :

$$\gamma \sim [P/M]^{4\alpha} * \delta\rho * T_r^{-5/4}$$

In brief, the density contrast  $\delta\rho$  between water and hydrocarbon is not the only predictive variable to be used for IFT prediction. It accounts for the effect of pressure (different compressibilities between water and hydrocarbon, especially

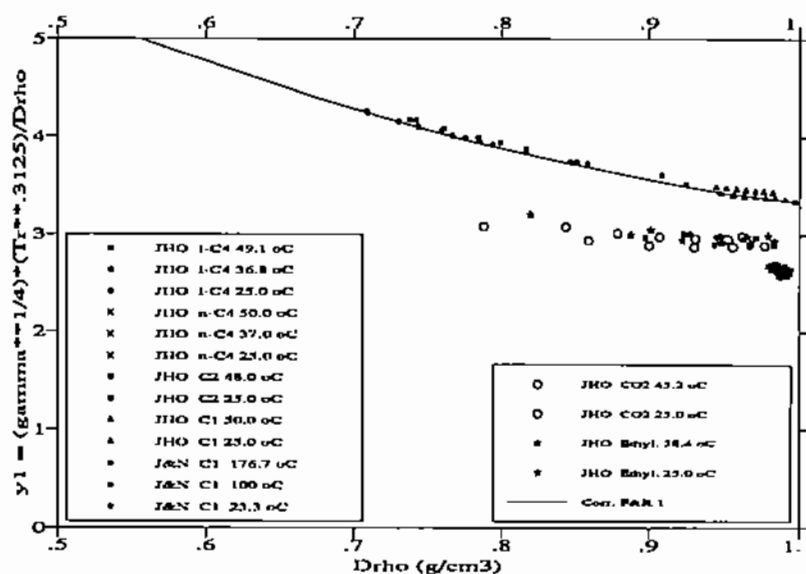


Fig 10 - Correlation F.R.1 : Data for gases

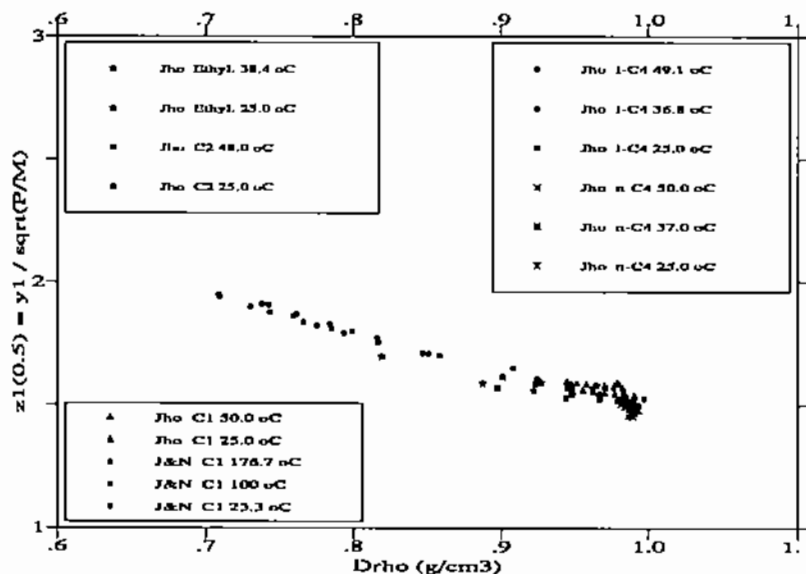


Fig 12 - Correlation z1(0.5) - Gases



when this hydrocarbon is a gas), and only partially for the difference in chemical structure. A complementary information has to be sought from the chemical structure of the hydrocarbon, related to the parachor, i.e. related to its surface tension. As a matter of fact, one may recall the formula of Fowkes (1964), relating hydrocarbon/water IFT  $\gamma_{hw}$  and surface tension  $\gamma_h$  (for liquid alkanes only) :

$$\gamma_{hw} = \gamma_h + \gamma_w - 2 \sqrt{\gamma_h' \gamma_w'}$$

where  $\gamma_w$  is the surface tension of water, and  $\gamma_h'$  and  $\gamma_w'$  are the respective contributions of the dispersion forces to the surface tensions of hydrocarbon and water.

So far, this correction concerns only pure hydrocarbons. What about mixtures ? Two different cases have to be considered, whether none of the components of the hydrocarbon mixture is miscible with water, or any one (e.g. gas) is soluble in water. For the first case, there are no data in the literature concerning such mixtures of liquid hydrocarbons immiscible with water, so we made some tests using Benzene-Decane mixtures. The data are given in Table 4. Unfortunately they are not very accurate : the lab temperature was not controlled ( $21 \pm 1^\circ\text{C}$ ), the technique used was the ring tensiometer ; benzene was MERCK's high purity-assay quality benzene, and the IFT measured : 33.66 mN/m, fits with literature data ; decane however was standard medium quality PROLABO decane, and the IFT measured : 47.95 mN/m, is lower than that for pure decane. Table 4 also gives the densities computed with the LKP model : in the benzene-rich domain, they may differ from the measured ones by up to 0.01 g/cm<sup>3</sup>.

**TABLE 4 - Densities and IFTs for benzene-decane mixtures at 21°C**

C10 (mole fr)	Benzene (mole fr)	$\rho_h$ meas. (g/cm <sup>3</sup> )	$\rho_h$ LKP (g/cm <sup>3</sup> )	$\delta\rho$ (g/cm <sup>3</sup> )	IFT (mN/m)	$z_1(0.5)$
0.0	1.0	0.877	0.8608	0.121	33.66	9.999
0.2	0.8	0.821	0.8249	0.177	36.20	6.766
0.3	0.7	0.802	0.8094	0.196	36.52	6.052
0.4	0.6	0.782	0.7950	0.216	37.60	5.474
0.5	0.5	0.776	0.7818	0.222	40.80 ?	5.385 ?
0.6	0.4	0.763	0.7695	0.235	39.96	5.017
0.7	0.3	0.754	0.7580	0.244	40.62	4.813
0.8	0.2	0.748	0.7472	0.250	42.14	4.706
1.0	0.0	0.728	0.7276	0.270	47.95	4.440

The measured densities are used to plot the data on Figure 14 : in the decane-rich region, they plot below the  $z1(0.5)$  correlation, because the decane used is not pure ; but the important point is that the data plot *linearly*. Consequently, we believe that this  $z1(0.5)$  correlation can be used to predict the IFT's of mixtures of liquid hydrocarbons, when none of the component is soluble in water.

The second case (one at least of the hydrocarbon compound soluble in water) is illustrated by the C1-C10 mixtures of Jennings & Newman (Figures 13, 14, 15) : introducing the P/M correction makes the isotherms more parallel to the average trend, but the 100°C isotherm plots above the isotherms at 23.3 and 176.7°C. Using the critical temperature from the LKP model, instead of the molar fraction-weighted average, would not change the situation. Differential solubility effects (of C1 in water) might explain this relative location of the isotherms (F. Montel, 1991).

### Influence of water salinity

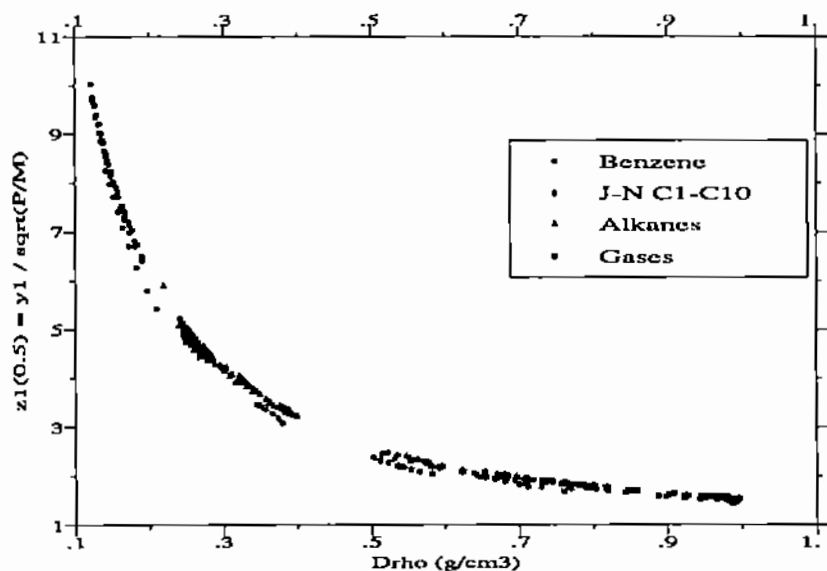
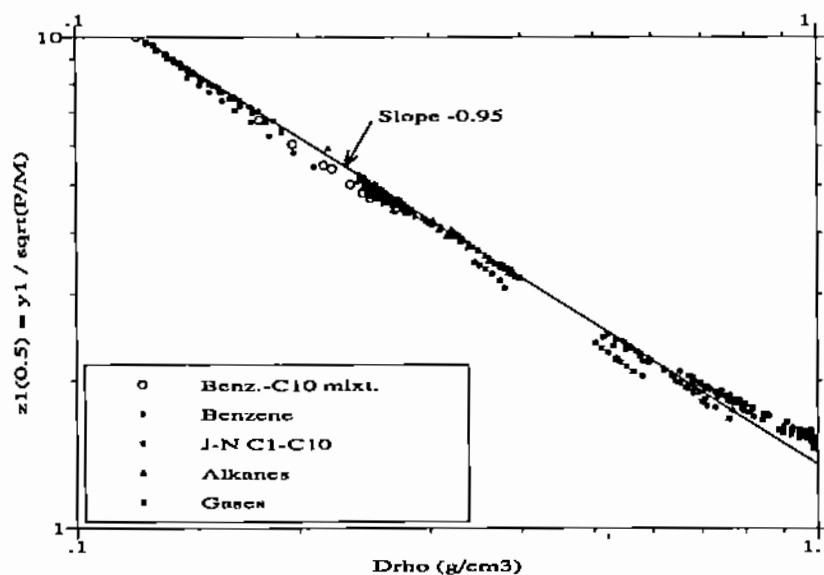
As for the surface tension of water, the salinity increases the IFT between a **Neutral oil** and a brine. It is important to note this restriction to the case of a neutral oil, i.e. an oil having only paraffins and light aromatics fractions, and devoid of polar fractions (resins and asphaltenes): these latter fractions may include interfacially active compounds bearing acid or base groups, which tend to concentrate at the interface, and which are more or less dissociated depending upon the salinity, pH and cation-type of the brine : for instance,  $\text{Ca}^{2+}$  often decreases the IFT.

Aveyard *et al.* (1977) measured the increments of interfacial tension due to brine salinity, with that of distilled water at the same temperature (20 °C) as a reference, at atmospheric pressure :

$$\delta\gamma' = \gamma(\text{Alkane/Brine}) - \gamma_0(\text{Alkane/Pure water})$$

The salts employed were: LiCl , NaCl , KCl , and  $\text{Na}_2\text{SO}_4$  ; the alkane was n-dodecane in each case, and additionally n-decane with NaCl brine : in the latter case, the change from n-C12 to n-C10 did not significantly change the increments.

The results, as  $\delta\gamma'$  increments of IFT plotted against molalities, are shown on Figures 16 and 17 . The "b' " or  $\delta\gamma'/m$  coefficients determined by non-forced linear regression, are given in Table 5, and compared with those determined for the

Fig 13 - Correlation  $z_1(0.5)$  - All dataFig 14 - Correlation  $z_1(0.5)$  - All data

surface tension of the brine : the latter values are not exactly those determined in Table 1, because they were determined on a broader molality range. The salt-specific coefficient is slightly less for the IFT alkane/brine than for the surface tension of that brine, the ratio ranging from 0.84 to 0.95.

**TABLE 5 - Salt specific coefficients of increase in the interfacial tension alkane / water and comparison with surface tension**

Salt	b' (IFT)	b (Surface t.)	b'/b
LiCl	1.45	1.53	0.95
NaCl	1.42	1.68	0.84
KCl	1.36	1.56	0.87
Na <sub>2</sub> SO <sub>4</sub>	2.35	2.60	0.91

Because, for the alkane/brine IFT, the effect is very similar to that for the surface tension of the brine, Aveyard *et al.* (1977) conclude that the alkane/brine interface (on the brine side) has the same structure as that of the air/brine interface : existence of a surface layer with a lower cation content than in the bulk brine.

**TABLE 6 - Salt specific IFT increments as a function of temperature  
Data of Aveyard & Haydon (1965)  
n-C14 / NaCl Brine (3 molal)**

Temperature	(°C)	20	25	30
Temperature	(°K)	293.2	298.2	303.2
IFT n-C14 / Pure water	(mN/m)	53.32	52.92	52.46
IFT n-C14 / NaCl Brine	(mN/m)	57.61	57.26	56.86
IFT increment $\delta\gamma$	(mN/m)	4.29	4.34	4.40
$\delta\gamma$ (1°C) / $\delta\gamma$ (20°C)		1.000	1.012	1.026
T (°K) / 293.2 (°K)		1.000	1.017	1.034

Aveyard *et al.* (1965) provide other data on the IFT between n-C14 and NaCl brines of molarities either 0.1M or 3M, at 3 temperatures. The data for 0.1M molarity suggest a salt-specific "b'" coefficient of 1.33 at 20°C, whereas for 3M molarity (molality = 2.82), that coefficient would have a value of 1.52. Those two values average close to 1.42, the value given in Table 5. Moreover, the data at 3 temperatures for the highest brine molarity (3M) indicate that the "b'" coefficient

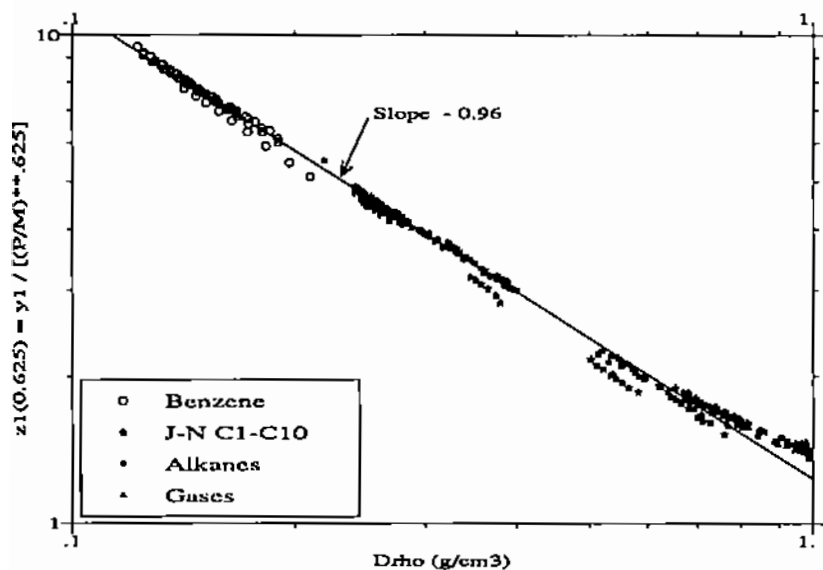
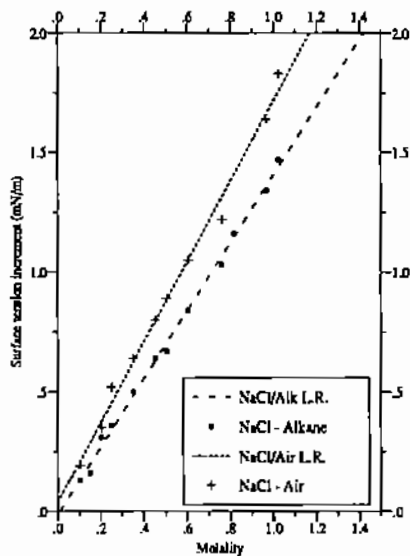
Fig 15 - Correlation  $z_1(0.625)$  - All data

Fig 16 - IFT (Alk./Br.) and Surface Tension of NaCl brines (AVEYARD-SALEEM)

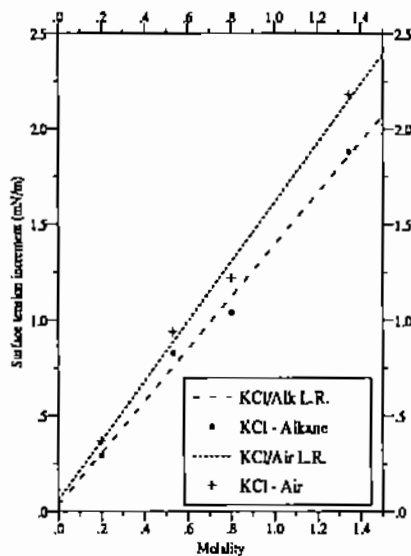


Fig 17 - IFT (Alk./Br.) and Surface Tension of KCl brines (AVEYARD-SALEEM)

increases as temperature increases, yet not as much as a linear dependence upon the Kelvin temperature would indicate (cf Table 6).

### EXAMPLE OF A REAL CASE

Four measurements of the Gas / Brine IFT were made, using the drop-volume method, at several slightly different reservoir conditions : temperatures 120°C and 130°C, pressures 353 and 453 bars abs. The molar composition of the gas was :  $C_1 = 0.97$  ;  $CO_2 = 0.03$  . The brine had a total salt content of 161.5 g/l at ambient conditions, its detailed composition is given in Table 7, with the calculated contributions in surface tension increase due to the salts : the total increase at ambient conditions (298 °K) is 4.78 mN/m. The four IFTs measured at reservoir conditions have closely related values : 42 to 45 mN/m (cf Table 9).

**TABLE 7 - Real case - Brine composition and Surface Tension increments at 22°C**

Salt	Molality	Spec. Coeff. "b"	$\delta\gamma$ at 22°C (mN/m)
NaCl	2.217	1.63	3.61
KCl	0.021	1.48	0.03
CaCl <sub>2</sub>	0.301	3.00	0.90
MgCl <sub>2</sub>	0.073	3.20	0.23
Total			4.78

In order to predict the IFT values, we proceed as follows. The densities for the gas mixture are computed using the LKP model (the LKP critical temperature used is then 180.45 °K), and the densities of the pure water (not in contact with the gas) are derived from the Steam Tables of Bain (1964). The density contrasts are then used to interpolate the values of the  $\gamma_1$  function (Table 8). We use only the  $\gamma_1$  function, and not the ratio of parachor to molar mass, because  $CO_2$  is not a hydrocarbon (thus the use of a Parachor is not good), and is in such a low percentage that the gas is nearly pure methane (no mixing rule required). The critical temperature used to compute  $Tr^{0.3125}$  is 194.59 °K, the result of a simple molar fraction-weighted average, instead of 180.45 °K. Table 8 shows the values predicted for the IFT value between pure water and the gas. In Table 9, we add the increases in tension due to salinity, derived from the value at 298 °K by assuming proportionality to Kelvin

temperature. The predicted values agree with the measured values within  $\pm 2$  mN/m, but, in the detail, the prediction is not entirely satisfactory : it predicts correctly that, as pressure is increased, the tension decreases; and incorrectly that, as temperature is increased, the tension should decrease, whereas the measurements seem to show the reverse trend.

**TABLE 8 - Real case - Prediction of IFT for Pure Water/ Gas  
at reservoir conditions**

Pressure (bar a.)	Temp (°C)	Densities (g/cm <sup>3</sup> )			Tr	$\gamma_1$	$\gamma_0$ (mN/m)
		Pure water	Gas	Contrast			
353	120	0.9597	0.1713	0.7884	2.021	3.922	37.94
353	130	0.9519	0.1660	0.7859	2.072	3.931	36.64
453	120	0.9639	0.2038	0.7601	2.021	4.030	36.54
453	130	0.9563	0.1981	0.7582	2.072	4.038	35.35

**TABLE 9 - Real case - IFT for Brine/Gas at reservoir conditions  
(predicted + measured)**

Pressure (bar a.)	Temp. (°C)	$\gamma_0$ (mN/m)	$\delta\gamma$ (mN/m)	$\gamma$ predicted (mN/m)	$\gamma$ measured (mN/m)
353	120	37.94	6.41	44.35	44.7
353	130	36.64	6.57	43.21	45.3
453	120	36.54	6.41	42.95	41.7
453	130	35.35	6.57	41.92	42.7

## CONCLUSIONS

1) The salinity of the brine increases the IFT between the brine and either a gas, or a non polar oil. Specific salt coefficients are available for estimating this effect, which is linearly related to the molality of the salt. The coefficients for gas/brine and oil/brine have closely related values. Some references indicate that the effect is proportional to the Kelvin temperature.

2) The correlation no 1 presented by Firoozabadi & Ramey (1988) does not predict well the IFTs at low pressures for light gaseous alkanes other than methane.

Another drawback of it is that the predicting variable (density contrast  $\delta\rho$ ) is incorporated in the predicted function.

3) This correlation can be improved by introducing the ratio of Parachor/ Molar mass of the hydrocarbon; it can then be split into 3 different domains :

3a - typical gases (C1, C2) with  $\delta\rho$  values above 0.7 g/cm<sup>3</sup> : the IFT is roughly proportionnal to the density contrast; the change in density with varying pressure dominates.

3b - ungassed, typically "liquid" hydrocarbons, with  $\delta\rho$  values below 0.5 g/cm<sup>3</sup>, insoluble in water: benzene, decane, hexane, etc... ; either pure, or as mixtures; the IFT against water depends only slightly on the density contrast  $\delta\rho$  ; it seems possible to generalize some kinds of mixing rules.

3c - mixtures of typical "liquid" and "gaseous" hydrocarbons : neither the original F&R1 correlation, nor the improved one using the ratio of Parachor to Molar Mass, accounts properly for the observed values, possibly because partial and selective solubility effects may be involved ; more experimental and theoretical research is needed in this domain, so far unexplored, yet crucial for Reservoir Engineering.

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## SYMBOLS

$C_M$	= molarity (mole number/1000 ml of solution)
$m$	= molality (mole number/1000 g of pure water)
$M$ (g)	= molar mass
$p$ (bars)	= pressure
$P$	= Parachor
$P_c$ (bar)	= capillary pressure
$t$ (°C)	= Celsius temperature
$T$ (°K)	= Kelvin temperature



$T_c$ (°K)	= critical temperature
$T_r = T / T_c$	= reduced temperature
$\gamma$ (mN/m)	= surface or interfacial tension
$\theta$ (degrees)	= contact angle
$\rho$ (g/cm <sup>3</sup> )	= density
$\delta\rho$ (g/cm <sup>3</sup> )	= density contrast hydrocarbon/brine
$\delta\gamma$ (mN/m)	= increment in surface or interfacial tension due to salinity (pure water as the reference)

## Subscripts :

h	= hydrocarbon
o	= pure water (as opposed to brine)
w	= water (as opposed to hydrocarbon)

## REFERENCES

- AVEYARD, R. and HAYDON, D.A. (1965). Thermodynamic properties of aliphatic Hydrocarbon/Water interfaces. *Trans. Faraday Soc.*, **61**, 2255-2261
- AVEYARD, R. and SALEEM, S.M. (1977). Interfacial tensions at Alkane - Aqueous electrolytes interfaces. *J. C. S. Faraday*, **73**, 1609-1617
- BAIN, W.R. (1964). *Steam Tables 1964*. Nat. Engineering Lab., Edinburgh, Her Majesty's Stationery Office
- BURNHAM, C.W., HOLLYDAY, J.R., DAVIS, N.F. (1969). *Thermodynamic properties of water to 1000°C and 10000 Bars*. The Geological Society of America
- CINI, R., LOGLIO, G., and FICALBI, A. (Nov. 1972). Temperature dependence of the surface tension of water by the equilibrium ring method. *Journal of Coll. & Interface Science*, **41**, 2, 287-297
- FIROOZABADI, A. and RAMEY, H.J. (May 1988). Surface tension of water-hydrocarbon systems at reservoir conditions. *Journal of Canad. Petrol. Technology*, **27**, 3, 41-48
- FOWKES, F.F. (1964). Attractive forces at interfaces. *Ind. Eng. Chem.*, **56**, 12, 40-52

- FOWLER, R.H. (1937). A tentative statistical theory of MacLeod's equation for surface tension and the parachor. *Proc. Roy. Soc. of London - Series A*, 229-246
- GALLAGHER, J.F. (1985). *Steam Tables 1985*. National Bureau of Standards, Ref. Database 10
- GIRIFALCO, L.A. and GOOD, R.J. (1957). A theory for the estimation of surface and interfacial energies. I. Derivation and application to interfacial tension. *J. Phys. Chem.*, **61**, p 904
- HASSAN, M.E., NIELSEN, R.F. and CALHOUN J.C. (1953). Effect of pressure and temperature on oil-water interfacial tensions for a series of hydrocarbons. *Petr. Trans. AIME*, **198**, 299-306
- HOCOTT, C.R. (1939). Interfacial tension between water and oil under reservoir conditions. *Petrol. Trans. AIME*, **132**, 184-190
- HOUGH, E.W., RZASA, M.J., and WOOD B.B. (1951). Interfacial tensions at reservoir pressures and temperatures : apparatus, and the Water-Methane system. *Petrol. Trans. AIME*, **192**, 57-60
- International Critical Tables of Numerical Data, Physics, Chemistry and Technology* (1928). **4**, 463-466. Mc Graw Hill
- JASPER, J.J. (1972). Surface tension of pure liquid compounds. *J. Phys. Chem. Ref. Data*, **1**, **4**, 841-1009
- JENNINGS, H.Y. (July 1967). The effect of temperature and pressure on the interfacial tension of Benzene-Water and Normal Decane-Water. *J. Coll. Interf. Sci.*, **24**, **3**, 323-329
- JENNINGS, H.Y. and NEWMAN, G.H. (1971). The effect of temperature and pressures on the interfacial tensions of Water against Methane-Normal Decane mixtures. *Soc. Petr. Eng. J.*, **11**, 171-175
- JHO, C., NEALON, D., SHOGBOLA, S. and KING, A.D. (June 1978). Effect of pressure on the surface tension of water : Adsorption of Hydrocarbon gases and Carbon dioxide on water at temperatures between 0 and 50 °C. *Journal of Coll. & Interface Science*, **65**, **1**, 141-154

- JOHANSSON, K. and ERIKSSON, J.C. (Sept. 1972). Determination of  $d\gamma/dT$  by means of a differential technique. *Journal of Coll. & Interface Science*, **40**, 3, 398-405
- JOHANSSON, K. and ERIKSSON, J.C. (Dec. 1974).  $\gamma$  and  $d\gamma/dT$  measurements on aqueous solutions of 1,1 -electrolytes. *Journal of Coll. & Interface Science*, **49**, 3, 469-480
- KAYSER, K.W. (Sept. 1976). Temperature dependence of the surface tension of water in contact with its saturated vapor. *Journal of Coll. & Interface Science*, **56**, 3, 622-627
- F.G. Mac CAFFERY, F.G. and MUNGAN, N. (July-Sept. 1970). Contact angle and Interfacial tension studies of some Hydrocarbon-Water-Solid systems. *J. Can. Petr. Techn.*, **9**, 185-196
- Mac CAFFERY, F.G. (July-Sept. 1972). Measurement of Interfacial tensions and contact angles at high temperature and pressure. *J. Can. Petr. Techn.*, 26-32
- Mac LEOD, D.B. (1923). On a relation between surface tension and density. *Trans. Farad. Soc.*, **19**, 38-43
- MATUBAYASI, N., MOTOMURA, K., KANESHINA, S., NAKAMURA, M. and MATUURA, R. (Febr. 1977). Effect of pressure on interfacial tension between oil and water. *Bull. Chem. Soc. Japan*, **50**, 2, 523-524
- MICHAELS, S.A. and HAUSER, E.A. (1951). Interfacial tension at elevated pressure and temperature- II - Interfacial properties of Hydrocarbon-Water systems. *J. Phys. Chem.*, **55**, 648, 408-421
- MONTEL, F. (1991). Personal communications
- MORI, Y., TSUI, N. and KIYOMIYA, M. (1984). Surface and interfacial tensions and their combined properties in seven binary, immiscible liquid-liquid-vapor systems. *J. Chem. Eng. Data*, **29**, 407-412
- NIEDERHAUSER, D.O. and BARTELL, F.E. (1948-1949). A corrected table for the calculation of boundary tensions by the pendent drop method. In *Fundamental Research on Occurrence and Recovery of Petroleum*, API, Lord Baltimore Press

- OWENS, D.K. (1970). Comments on determination of interfacial tension of hydrocarbons against water. *J. Phys. Chem.*, 74, 17, 3305-3306
- PLOCKER, U.J., KNAPP, H. and PRAUSNITZ, J.M. (1978). Calculation of high-pressure vapor-liquid equilibria from a corresponding-states correlation with emphasis on asymmetric mixtures. *Ind. Eng. Chem. Proc. Des. Dev.*, 17, 3, 324-322
- RALSTON, J. and HEALY, T.W. (March 1973). Specific cation effects on water structure at the air/octadecanol monolayer/water interfaces. *Journal of Coll. & Interface Science*, 42, 3, 629-644
- REAMER, H.H., OLDS, R.H., SAGE, G.H. and LACEY, W.N. (1942). Phase equilibrium in hydrocarbons systems, Methane-Decane systems. *Ind. Eng. Chem. Fund.*, 34, 1526-1532
- SMITH, L.B. and KEYES, F.G. (April 1934). The volumes of unit masses of liquid water and their correlation as a function of pressure and temperature. *Proceed., Amer. Acad. of Arts & Sci.*, 285-312
- VARGAFTIK, N.B., VOLKOV, B.N. and VOLJAK, L.D. (1983). International tables of the surface tension of water. *J. Phys. Chem. Ref. Data*, 12, 3, 817-820

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