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AQUEOUS SOLUBILITY OF HYDROCARBON MIXTURES

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SOLUBILITÉ DANS L'EAU DE MÉLANGES D'HYDROCARBURES

La solubilité de composés hydrocarbonés dans l'eau est d'une importance cruciale pour les sciences environnementales. Sa prévision est généralement basée sur la solubilité des constituants purs et de leur fraction molaire en mélange. La solubilité des composés purs est généralement bien connue, mais peu de données ont été publiées concernant les mélanges. L'utilisation d'une relation simple conduit à une sous-estimation de la solubilité réelle.

Cet article présente quelques données nouvelles de solubilités de mélanges hydrocarbonés simples. Une analyse thermodynamique rigoureuse permet de décrire la solubilité observée, aussi bien pour des mélanges modèles que pour des kérosènes. Les modèles de coefficient d'activité utilisés dans ce but sont NRTL, UNIQUAC et UNIFAC. Étant donné la faible concentration de certains constituants dans l'huile, leurs coefficients d'activité peut devenir important. Ceci explique une augmentation de la solubilité par rapport à celle proposée par le modèle simple d'un facteur supérieur à deux.

AQUEOUS SOLUBILITY OF HYDROCARBON MIXTURES

The solubility of hydrocarbon components in water is of great importance for the environmental sciences. Its prediction is usually based on using the pure component solubilities and the mole fraction of the components in the mixture. While the pure component solubilities are generally well known, few data exist on the solubility of mixtures. Using a simple relationship leads to an underestimation of the true solubility.

This paper presents some new data on the aqueous solubility of binary hydrocarbon mixtures. Using a rigorous thermodynamic analysis, we explain the observed behavior, as well as other data from the literature, including the solubility of jet fuel mixtures in water. The activity coefficient models used for this purpose are NRTL, UNIQUAC and UNIFAC. Considering the small concentration in oil of some very soluble substances, the activity coefficient can become significant and thus explain the fact that solubilities of some component may be as much as twice as large as expected.

SOLUBILIDAD EN EL AGUA DE LAS MEZCLAS DE HIDROCARBUROS

La solubilidad de los compuestos hidrocarbonados en el agua representa una importancia esencial para las ciencias medioambientales. Su predicción se funda, por lo general, en la solubilidad de los componentes puros y de sus fracciones molares en mezcla. La solubilidad de los componentes puros es perfectamente conocida pero se han publicado muy pocos datos

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acerca de las mezclas. La utilización de una relación simplificada conduce a subestimar la solubilidad real. En este artículo se presentan algunos nuevos datos de solubilidades de mezclas hidrocarbonadas simples. Un análisis termodinámico riguroso permite describir la solubilidad observada, tanto de las mezclas modelo como de los querosenos. Los modelos de coeficiente de actividad utilizados con este objeto son NRTL, UNIQUAC y UNIFAC. Habida cuenta de la reducida concentración de ciertos componentes en el petróleo, su coeficiente de actividad puede llegar a ser importante. Esto permite explicar un aumento de la solubilidad con respecto a aquella propuesta por el modelo simple de un factor superior a dos.

INTRODUCTION

Largely for environmental reasons, a great amount of work has been performed in order to determine the solubility of hydrocarbons in water at various temperatures. These solubility data have been compiled (Kertes, 1989a and 1989b) and correlated (Yaws, 1990, 1993a, 1993b, 1995).

In most cases, however, the water is in contact with a mixture of hydrocarbons, and the saturated water solubility must be corrected with the mole fraction of the component in the mixture. This is often taken for granted and very few experimental results have been published concerning water solubilities of hydrocarbon mixtures.

Leinonen (1972) first observed that the true concentration in water is larger than that predicted from binary data. A more detailed study of this effect has been presented by Leinonen and Mackay (1973). They analyze their results using an activity coefficient in the hydrocarbon phase, but conclude that it may be insufficient for explaining the increase in solubility. Burris and MacIntyre (1984) have similarly presented solubility measurements of two synthetic jet fuel mixtures, and related the increased solubility to the activity coefficient in the hydrocarbon phase.

More recently, Dhima *et al.* (1998) have discussed the water solubility of binary hydrocarbon gas mixtures under high pressure conditions. They use an equation of state (Peng-Robinson) for describing the hydrocarbon phase non-idealities.

The goal of the work presented in this paper is to contribute to the understanding and the modeling of the water solubility behavior of mixtures. To that end, additional experimental measurements have been performed to determine the solubility of a mixture of hydrocarbons in pure water. A rigorous thermodynamic treatment of the results and of other literature data including jet fuel mixtures indicates that the molar fraction approach may not be sufficient if accurate predictions are needed. On the contrary, the use of an activity coefficient model is required for that purpose.

1 EXPERIMENTAL SETUP

The hydrocarbon + water two-phase mixture was stirred during two days using a magnetic stirrer. The cell, sketched in Figure 1, had a volume of 250 cm³. A water + glycol mixture was circulated through the

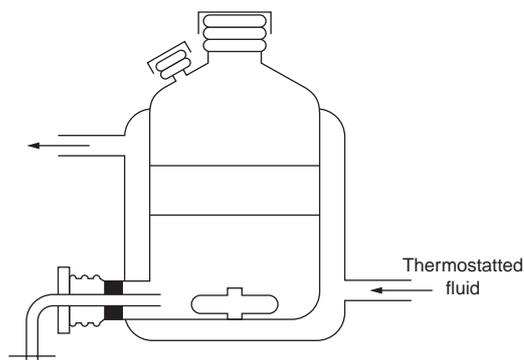


Figure 1
Experimental setup.

external envelope providing a temperature control to $\pm 0.1^\circ\text{C}$. A pipe at the bottom of the cell relied on gravity to draw off the aqueous phase.

Aqueous phase sampling is carried out as follows:

- the hydrocarbon + water mixture is allowed to stand for 24 hours;
- 4 ml of a paraxylene + *n*-octane mixture at 500 mass ppm of *n*-octane, providing the internal standard, are introduced into a 10 ml volumetric flask;
- the liquid level is brought to the mark by adding the aqueous phase drawn from the experimental cell;
- the mixture is vigorously shaken during 2 minutes;
- the emulsion is let stand for 12 hours;
- finally, the organic phase is analyzed by gas phase chromatography (GPC) using a semi-capillary column (stationary phase: OV1, 0.15 μm film, 0.53 mm ID, 25 m length).

We have verified that a single liquid-liquid extraction allows a quantitative recovery of benzene and cyclohexane dissolved in water. The paraxylene used as an extracting solvent has been purified on a 40 plate adiabatic column in order to remove the traces of volatile impurities that could possibly interfere with benzene, cyclohexane or *n*-octane during the gas chromatographic analysis.

2 EXPERIMENTAL RESULTS

The uncertainty in the solubility in the aqueous phase is estimated to be ± 4 molar ppm for benzene and ± 0.2 molar ppm for cyclohexane.

Solubilities of both benzene and cyclohexane in water, at different temperatures, are reported in Tables 1 and 2, and in Figures 2 and 3. Good agreement is observed with data found in the literature.

TABLE 1

Experimental solubility of benzene in water (mole fraction $\times 10^6$) at different temperatures, comparison with data found in the literature (Sorensen *et al.*, 1980)

Temperature ($^\circ\text{C}$)	x_{exp}^{aq}	x_{lit}^{aq}
5.6	397	*
10.1	387	378.9
20.0	379	366.6
30.0	402	392.5
40.3	422	410.2
50.1	446	434.4

* No data have been found.

TABLE 2

Experimental solubility of cyclohexane in water (mole fraction $\times 10^6$) at different temperatures, comparison with data found in the literature (Kertes *et al.*, 1989a)

Temperature ($^\circ\text{C}$)	x_{exp}^{aq}	x_{lit}^{aq}
1.1	13.5	*
16.1	13.0	13.2
21.1	12.6	14.9; 21.4
25.6	12.8	12.4
29.1	13.0	*
35.0	14.1	19.0
40.2	14.0	*
50.0	15.4	*

* No data have been found.

Solubilities of the organic compounds in the aqueous phase, at various temperatures, are reported in Tables 3 through 6, and in the Figures 4 through 8, for the ternary mixture benzene-cyclohexane-water.

TABLE 3

Experimental solubility of benzene and cyclohexane in water (mole fraction $\times 10^6$) at different temperatures for organic phase: $x^{org}(\text{benzene}) = 0.3281$

Temperature ($^\circ\text{C}$)	x_{exp}^{aq} (benzene)	x_{exp}^{aq} (cyclohexane)
9.8	168	9.0
21.5	169	8.4
30.0	169	8.5
41.3	174	8.8
49.7	178	9.5

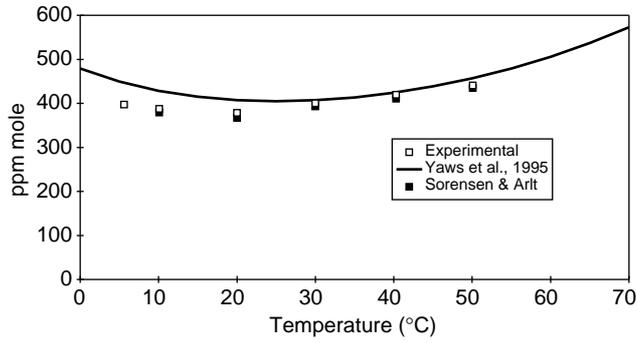


Figure 2
Solubility of benzene in water.

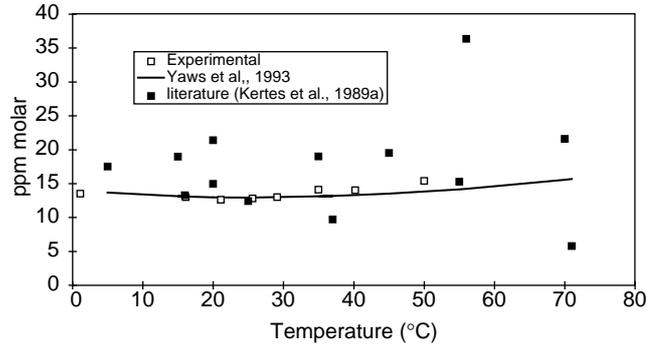


Figure 3
Solubility of cyclohexane in water.

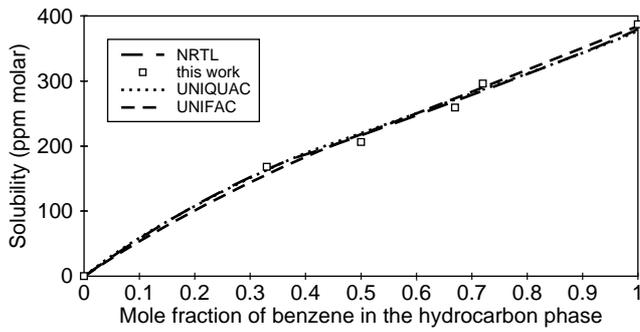


Figure 4a
Benzene solubility in water at 10°C for the ternary mixture water-benzene-cyclohexane.

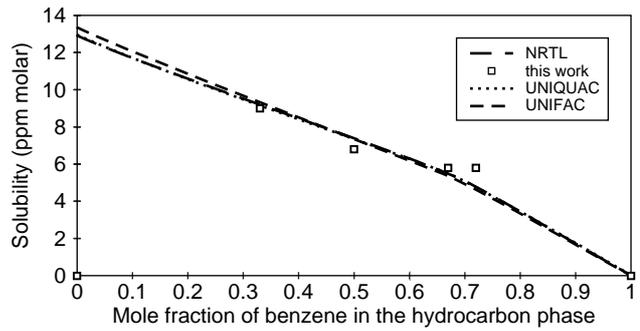


Figure 4b
Cyclohexane solubility in water at 10°C for the ternary mixture water-benzene-cyclohexane.

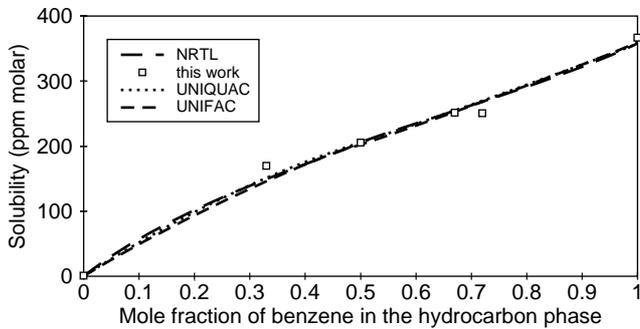


Figure 5a
Benzene solubility in water at 20°C for the ternary mixture water-benzene-cyclohexane.

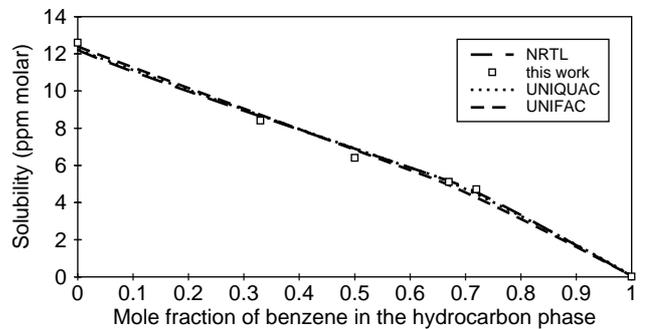


Figure 5b
Cyclohexane solubility in water at 20°C for the ternary mixture water-benzene-cyclohexane.

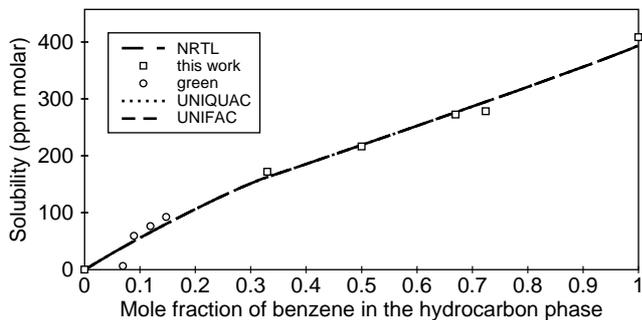


Figure 6a
Benzene solubility in water at 30°C for the ternary mixture water-benzene-cyclohexane.

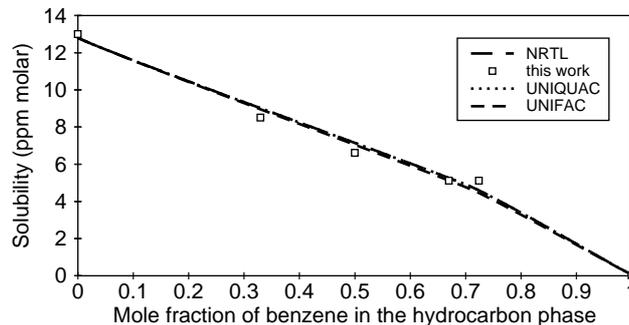


Figure 6b
Cyclohexane solubility in water at 30°C for the ternary mixture water-benzene-cyclohexane.

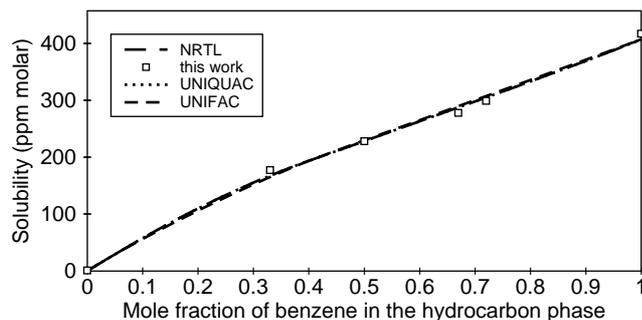


Figure 7a
Benzene solubility in water at 40°C for the ternary mixture water-benzene-cyclohexane.

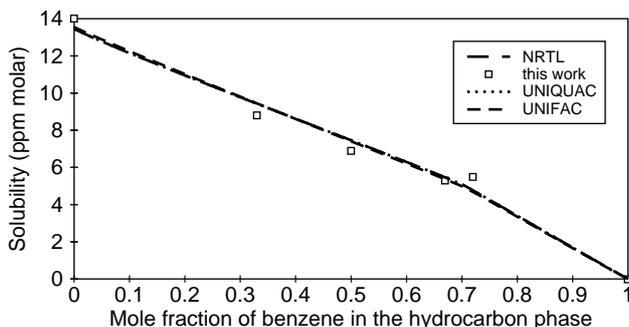


Figure 7b
Cyclohexane solubility in water at 40°C for the ternary system water-benzene-cyclohexane.

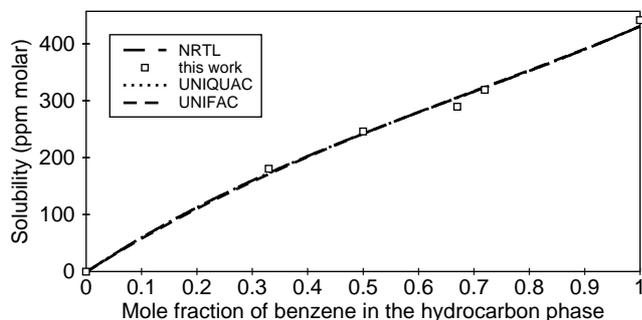


Figure 8a
Benzene solubility in water at 50°C for the ternary system water-benzene-cyclohexane.

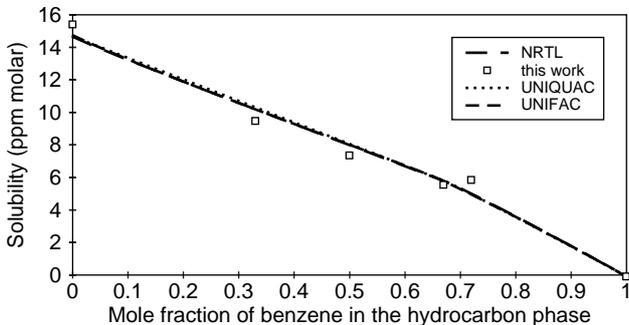


Figure 8b
Cyclohexane solubility in water at 50°C for the ternary system water-benzene-cyclohexane.

TABLE.4

Experimental solubility of benzene and cyclohexane in water (mole fraction $\times 10^6$) at different temperatures for organic phase: x^{org} (benzene) = 0.5093

Temperature (°C)	x_{exp}^{aq} (benzene)	x_{exp}^{aq} (cyclohexane)
10.0	206	6.8
20.0	205	6.4
31.3	213	6.6
40.3	224	6.9
49.4	242	7.4

TABLE.5

Experimental solubility of benzene and cyclohexane in water (mole fraction $\times 10^6$) at different temperatures for organic phase: x^{org} (benzene) = 0.6692

Temperature (°C)	x_{exp}^{aq} (benzene)	x_{exp}^{aq} (cyclohexane)
9.7	259	5.8
21.4	251	5.1
29.8	268	5.1
41.0	273	5.3
49.5	285	5.6

TABLE 6

Experimental solubility of benzene and cyclohexane in water (mole fraction $\times 10^6$) at different temperatures for organic phase: x^{org} (benzene) = 0.7243

Temperature (°C)	x_{exp}^{aq} (benzene)	x_{exp}^{aq} (cyclohexane)
9.9	296	5.8
20.4	250	4.7
29.8	274	5.1
40.1	294	5.5
50.0	314	5.9

3 THERMODYNAMIC ANALYSIS

In their recent work, Dhima *et al.* (1998) have proposed an original method for evaluating the non-ideality of the solubility in the aqueous phase. A summary of the approach is given here.

Equilibrium between two phases is established when the fugacity of each component i is identical in both phases:

$$f_i^{aq} = f_i^{HC} \quad (1)$$

In our case, we consider an aqueous and a hydrocarbon phase, denoted by the superscripts aq and HC , respectively.

The fugacity of a component within any phase is written as:

$$f_i = f_i^o(P, T, \bar{x}^o) x_i \gamma_i(P, T, \bar{x}^o) \quad (2)$$

where f_i^o is the fugacity of component i for a phase composition \bar{x}^o that is chosen as reference. The activity coefficient γ_i is defined by this equation. Both f_i^o and γ_i depend on pressure (P) and temperature (T). Pressure is taken at 1 atmosphere throughout this work.

For the hydrocarbon phase, the reference composition for Equation (2) is generally taken as the pure component i . As a result, $\gamma_i = 1$ for the pure component. Equation (2) then becomes:

$$f_i^{HC} = f_i^*(T) x_i^{HC} \gamma_i^{HC}(T) \quad (3)$$

where the asterisk indicates the pure component property. The activity coefficient defined in this way is a well-know quantity that can be readily determined from low pressure vapor-liquid equilibrium measurements. Many models exist for describing it, provided that the water dissolved in the hydrocarbon phase is negligible. This point is verified later on.

A rigorous description of the aqueous phase, as was done by Dhima *et al.* (1998), would require the use of a separate activity coefficient for this phase. However, as Dhima *et al.* have shown, and as we will show further in this paper, the very low solubility of hydrocarbons in water allows us to consider this coefficient to be a constant. Equation (2) then becomes:

$$f_i^{aq} = k_i^{aq}(T) x_i^{aq} \quad (4)$$

where k_i^{aq} can be identified as the Henry's constant of solute i in water. It is a function of temperature. The relation that needs to be satisfied for thermodynamic equilibrium is thus found by combining Equations (1), (3) and (4):

$$k_i^{aq}(T) x_i^{aq} = f_i^*(T) x_i^{HC} \gamma_i^{HC}(T) \quad (5)$$

The pure component solubility is found when $x_i^{HC} = \gamma_i^{HC} = 1$. In that case the water concentration is:

$$x_i^{aq,*}(T) = \frac{f_i^*(T)}{k_i^{aq}(T)} \quad (6)$$

The value of $x_i^{aq,*}(T)$ can readily be determined from binary solubility data as they were compiled in *IUPAC's Solubility Data Series* (e.g. Kertes, 1989a and 1989b). Hence, we find a convenient expression for the

solubility of a component i in the water phase as a function of its solubility as a pure component:

$$x_i^{aq}(T) = x_i^{HC} x_i^{aq,*}(T) \gamma_i^{HC}(T) \quad (7)$$

In this last expression we find:

- x_i^{HC} The molar fraction of component i in the hydrocarbon mixture.
- $x_i^{aq,*}(T)$ The pure component solubility of i in water. This is often available through correlations or from literature values.
- $\gamma_i^{HC}(T)$: The activity coefficient of component i in the hydrocarbon phase. This coefficient is often neglected, while it can easily reach a factor 2, as will be seen in the discussion (its value is one for the pure hydrocarbon). Indeed, the molar fraction of each individual component in the hydrocarbon mixture is relatively small. Generally, the smaller the molar fraction, the larger the activity coefficient. In the discussion below, we will use different activity coefficient models in order to interpret our results and those of other authors.

4 DISCUSSION

In the discussion that follows, three excess Gibbs free energy models have been used: NRTL, UNIQUAC and UNIFAC. Both the NRTL model (Renon and Prausnitz, 1968) and the UNIQUAC model (Abrams and Prausnitz, 1975) accurately describe the non-idealities of the systems for which binary interaction parameters exist. The parameters have been taken from the PRO II library (version 3.33). These two models have been used in order to verify whether the differences between models could modify the conclusions. The UNIFAC model (Fredenslund *et al.*, 1975) is used when no binary interaction parameters exist for either NRTL or UNIQUAC. Again, the parameters are taken from the PRO II library.

In no case the water dissolved in the hydrocarbon phase is taken into consideration. Indeed, the water content always remains very low. The highest value that we may have encountered is the water content of pure benzene at 50°C. According to Kertes (1989) the molar fraction of water is 0.67%. It could be argued that considering its polarity, a small amount of water could have a non-negligible effect on the hydrocarbon

phase activity coefficient. This argument will be invalidated by both our high temperature results, and the results of Leinonen and Mackay.

4.1 The Binary System Benzene-Cyclohexane in Equilibrium with Water

Our experimental results are compared with the theoretical Equation (7) in the Figures 4 through 8. Each figure shows the results at one temperature, part a concerns the solubility of benzene, while part b is for cyclohexane. The solubility of the pure hydrocarbon, $x_i^{aq,*}$ has been fitted independently at each temperature in order to best describe the experimental data. The standard deviation has been calculated using the function:

$$\sigma_i = \sqrt{\frac{\sum_j^N (x_i^{exp,j} - x_i^{cal,j})^2}{N}} \quad (8)$$

where:

- $x_i^{exp,j}$ is the j^{th} experimental solubility value of component i ;
- $x_i^{cal,j}$ is the calculated solubility value of component i , using Equation (7) and corresponding to the j^{th} experimental solubility value;
- N is the number of experimental data points at a given temperature.

A summary of the numerical results of this analysis is given in Tables 7 and 8.

It appears that all models give very similar results that are much better than the straight line that result, when no activity coefficient is taken into account. The UNIFAC method is almost as accurate as the other models, and has the major advantage that it is fully predictive for molecules whose molecular structure is known.

The standard deviations are slightly larger than the experimental uncertainties mentioned above. This can be explained by the fact an uncertainty exists on the mole fraction of the organic phase, and that the temperature of the measurements at different mole fractions is not identical.

At higher temperature (50°C), when more water is dissolved in the hydrocarbon phase, we see no degradation of the standard deviation. This would indicate that the presence of water has no significant effect on the activity coefficient.

TABLE 7

Pure component solubilities (mole fraction $\times 10^6$) and standard deviations of the aqueous solubility of pure benzene, as calculated from all the solubility data of the cyclohexane-benzene mixture, by minimizing Equation (8), and using different activity coefficient models

Temperature	NRTL		UNIQUAC		UNIFAC	
	$x_i^{aq,*}$	σ_i	$x_i^{aq,*}$	σ_i	$x_i^{aq,*}$	σ_i
10°C	379	10	378	11	383	10
20°C	357	13	356	13	359	14
30°C	387	13	387	13	388	14
40°C	400	9	400	9	402	9
50°C	425	9	425	9	426	9

TABLE 8

Pure component solubilities (mole fraction $\times 10^6$) and standard deviations of the aqueous solubility of pure cyclohexane, as calculated from all the solubility data of the cyclohexane-benzene mixture, by minimizing Equation (8), using different activity coefficient models

Temperature	NRTL		UNIQUAC		UNIFAC	
	$x_i^{aq,*}$	σ_i	$x_i^{aq,*}$	σ_i	$x_i^{aq,*}$	σ_i
10°C	12.9	0.6	12.9	0.6	13.3	0.7
20°C	12.2	0.4	12.2	0.4	12.4	0.3
30°C	12.8	0.4	12.9	0.4	12.9	0.5
40°C	13.4	0.6	13.4	0.6	13.5	0.6
50°C	14.7	0.8	14.7	0.8	14.7	0.7

In Figure 6a, at 30°C, the data of Green and Frank (1979) have been added to the figure. They are in agreement with the measured data and with the results of the activity coefficient models. These authors also present measurements at 15°C that fit to the activity coefficient model. Arich *et al.* (1975) propose data for the same system at 25°C. They have not been investigated here.

4.2 Other Binary C₆ Mixtures

Investigations of a number of other binary mixtures have been reported in the literature. Leinonen and MacKay (1973) thus describe a number of experimental solubility measurements performed on mixtures of C₆ hydrocarbons. They analyze their results using an expression that is similar to Equation (7), using a Redlich-Kister activity coefficient model. The pure component solubility value, however, was not fitted as in our case, by minimization of Equation (8), but the experimental value was taken. The possible experimental error on that one measurement thus influences the total analysis. They conclude that the solubility enhancement related to the calculated hydrocarbon

activity coefficient is not sufficient for predicting the total solubility.

Unfortunately, the only experimental data given in their paper must be read from a graph. They concern the benzene-2-methylpentane mixture. When the same analysis is performed as above using these data, Table 9 is found.

TABLE 9

Pure component solubilities (mole fraction $\times 10^6$) and standard deviations of the aqueous solubility of pure benzene and 2-methylpentane, as calculated from all the solubility data of the 2-methylpentane-benzene mixture at 25°C (data from Leinonen and MacKay), by minimizing Equation (8), using different activity coefficient models

Temperature	$x_i^{aq,*}$	NRTL		UNIQUAC		UNIFAC	
		$x_i^{aq,*}$	σ_i	$x_i^{aq,*}$	σ_i	$x_i^{aq,*}$	σ_i
25°C	measured						
Benzene	410.2	434.1	17.1	433.15	17.0	443.2	19.0
2-methylpentane	2.97	3.20	0.10	3.20	0.10	3.23	0.12

In opposition to the trend observed in Tables 2 and 3, the measured pure component solubility is smaller than that obtained from the fitting of Equation (7). This is what brought Leinonen and Mackay to conclude that there is solubility enhancement. However, the difference for benzene is less than 5%, while they indicate an experimental uncertainty of 7%. For 2-methylpentane, the authors announced an uncertainty of 10%, while the observed difference is 8%. Even though all their measurements (unfortunately unavailable) indicate the same trend, it is hazardous to conclude that the effect is real.

4.3 Binary Alkane-Aromatic Mixtures

Burris and MacIntyre (1987) have used Equation (7) in order to determine the hydrocarbon phase activity coefficient directly from their experimental data. The solubility of a large number of binary aromatic-alkane mixtures have thus been measured. The raw data are unfortunately unavailable. From their graphical presentation, we could extract the values presented in Table 10. These results are compared with modeling results for these same binaries. In most cases, no binary interaction coefficients were available for the UNIQUAC and NRTL models. We have therefore only presented the results of the UNIFAC model. Interestingly, for the two systems where binary information was available, the UNIFAC results are closer to the observed activity coefficient values than those obtained with NRTL or UNIQUAC.

TABLE 10

Activity coefficients of the aromatic component in binary mixtures as measured by Burris and MacIntyre at 20°C; comparison with the UNIFAC activity coefficient model

Binary mixture	Aromatic component mole fraction	Observed activity coefficient of the aromatic	UNIFAC activity coefficient of the aromatic
Toluene + <i>n</i> -octane	0.1	1.29	1.403
	0.2	1.21	1.318
	0.3	1.15	1.244
Ethylbenzene + <i>n</i> -octane	0.1	1.38	1.359
	0.2	1.30	1.282
	0.3	1.12	1.216
<i>n</i> -butylbenzene + <i>n</i> -octane	0.1	1.38	1.311
	0.2	1.30	1.234
	0.3	1.25	1.172
1,3,5-triethylbenzene+ <i>n</i> -octane	0.1	1.25	1.207
	0.2	1.20	1.145
	0.3	1.15	1.100
Tetralin + <i>n</i> -octane	0.1	1.70	1.522
	0.2	1.52	1.393
	0.3	1.40	1.288
2-éthyl-naphthalene + <i>n</i> -octane	0.1	2.21	1.915
	0.2	1.83	1.654
	0.3	1.60	1.459
1,4-dimethyl-naphthalene + <i>n</i> -octane	0.1	2.37	1.965
	0.2	2.05	1.661
	0.3	1.75	1.448
1-methylnaphthalene + <i>n</i> -octane	0.1	2.5	2.116
	0.2	2.05	1.800
	0.3	1.75	1.563
1-methylnaphthalene + <i>n</i> -decane	0.1	2.06	2.066
	0.2	1.91	1.806
	0.3	1.72	1.594
1-methylnaphthalene + <i>n</i> -dodecane	0.1	2.02	1.982
	0.2	1.86	1.774
	0.3	1.64	1.593
1-methylnaphthalene + <i>n</i> -tetradecane	0.1	1.87	1.887
	0.2	1.71	1.723
	0.3	1.58	1.573
1-methylnaphthalene + <i>n</i> -hexadecane	0.1	1.66	1.791
	0.2	1.58	1.664
	0.3	1.52	1.542

From Table 10, it appears that the observed activity coefficients of the aromatic component, although systematically larger, are close to those predicted by the UNIFAC model. One can therefore conclude that UNIFAC correctly predicts the activity coefficients.

4.4 Synthetic Jet Fuel Mixtures

The same authors (Burris and MacIntyre, 1987), use the same approach to describe the solubility of

synthetic jet fuels in water. The activity coefficients of the various components in the complex mixture was determined directly from the binary mixture measurements. The assumption is made that the activity coefficient is only a function of the mole fraction of the component, and does not depend on the composition of the mixture. Using the UNIFAC method, it is possible to take into account the global composition. This has been done in Tables 11a and 11b with the two jet fuels presented in the paper.

A number of observations can be made from Tables 11a and 11b:

- The activity coefficient of the heavy aromatics can become significant in oil mixtures. As a consequence, aqueous solubility can be enhanced by a factor 2. The UNIFAC method gives a reasonable estimate of this effect.
- The activity coefficient is slightly smaller for the second jet fuel which is much more paraffinic (75% mole) than the first one. The presence of a non negligible amount of a naphthene (methylcyclohexane) increases the activity coefficients and thus the aqueous solubility.

CONCLUSION

The question has been raised whether the aqueous solubility of hydrocarbon mixtures could be described using activity coefficient models, assuming that:

- no interaction between hydrocarbons must be considered within the aqueous phase;
- the water content of the hydrocarbon phase is sufficiently small not to influence the activity coefficient of the hydrocarbons.

For that purpose, we have presented some novel solubility data for benzene-cyclohexane mixtures at various temperatures from 10°C to 50°C. In addition,

TABLE 11a

Aqueous solubility at 20°C for the jet fuel JP4, as measured by Burriss and MacIntyre, and as predicted from the UNIFAC activity coefficients

Component name	Mole fraction	Activity coefficient (UNIFAC)	Pure component solubility (mg/l)	Predicted solubility (mg/l)	Measured solubility (mg/l)
Toluene	0.0431	1.221	567	29.84	28.3
Ethylbenzene	0.0479	1.197	180	10.32	10.6
<i>n</i> -butylbenzene	0.0388	1.181	13.3	0.609	0.624
Tetralin	0.0292	1.333	45	1.752	1.9
1-methylnaphthalene	0.0267	1.854	30.2	1.495	1.8
1,4-dimethylnaphthalene	0.0261	1.744	-	-	-
Methylcyclohexane	0.2123	0.975	16.6	3.435	3.5
<i>n</i> -octane	0.183	1.028	0.884	0.166	0.173
<i>n</i> -decane	0.1377	1.021	-	-	-
<i>n</i> -undecane	0.1033	1.003	-	-	-
<i>n</i> -dodecane	0.0819	0.980	-	-	-
<i>n</i> -tridecane	0.07	0.948	-	-	-

TABLE 11b

Aqueous solubility at 20°C for the jet fuel JP8, as measured by Burriss and MacIntyre, and as predicted from the UNIFAC activity coefficients

Component name	Mole fraction	Activity coefficient (UNIFAC)	Pure component solubility (mg/l)	Predicted solubility (mg/l)	Measured solubility (mg/l)
<i>n</i> -butylbenzene	0.0386	1.138	13.3	0.584	0.613
1,3,5-triethylbenzene	0.042	1.103	3.47	0.161	0.164
Tetralin	0.0374	1.265	45	2.129	2.25
1-methylnaphthalene	0.0366	1.778	30.2	1.966	2.11
1,4-dimethylnaphthalene	0.0335	1.719	9.47	0.545	0.629
2-ethylnaphthalene	0.0436	1.654	9.21	0.664	0.682
<i>n</i> -decane	0.0923	1.019	-	-	-
<i>n</i> -undecane	0.1497	1.026	-	-	-
<i>n</i> -dodecane	0.1864	1.030	-	-	-
<i>n</i> -tridecane	0.1742	1.018	-	-	-
<i>n</i> -tetradecane	0.1069	1.006	-	-	-
<i>n</i> -pentadecane	0.0586	0.990	-	-	-

we have analyzed data from the literature on the aqueous solubility of mixtures.

It appears that the nonidealities in the hydrocarbon phase can be important and result—in the systems considered—in activity coefficients up to 2.5. As a result, the proposed approach uses a well-established activity coefficient model, UNIFAC, that has the great advantage of being fully predictive, while giving activity coefficients that are accurate enough for the present purpose.

The nonidealities in the aqueous phase, on the other hand, can be neglected considering the very small concentrations of dissolved hydrocarbons.

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