

# New Solubility Data of Hydrocarbons in Water and Modeling Concerning Vapor–Liquid–Liquid Binary Systems

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Solubility data in water of ethane, propane, isobutane, n-butane, n-pentane, and n-hexane have been obtained as a function of temperature in vapor–liquid–liquid equilibrium (VLLE) conditions. The minimum temperature of experiments is 288 K, while the maximum temperature, for each system, is lower than the critical temperature of the corresponding hydrocarbon. New solubility vs temperature correlations are given herein for the studied hydrocarbons in water. Henry's law and activity coefficients at infinite dilution are deduced from the experimental solubility data. Good agreement is found with available literature data.

## 1. Introduction

The knowledge of equilibrium data between hydrocarbons and water is important for better understanding petroleum reservoir production behavior and for optimizing hydrocarbon processing units. It is also essential to estimate potential environmental contamination through wastewater treatment of wastewater coming from oils refineries, petrochemical plants, or natural gas processing plants and to optimize their treatment units. As a result of the very low concentrations to be measured, the determination of hydrocarbon solubility in water is rather difficult. However, the dissolved quantities have to be known accurately in order to design satisfactory industrial separation processes. Knowledge of hydrocarbon solubility data is required to design efficient wastewater wash processes.<sup>1</sup> Besides, during drilling, a large amount of dissolved gas inside drilling fluids can become very hazardous, increasing the risk of eruption.<sup>2</sup> On the other hand, the values of solubility and of volatility of hydrocarbons are needed for water pollution abatement.<sup>3</sup> Usually, water treatment processes are operated at various temperatures and pressures, and in some cases under vapor–liquid–liquid equilibrium conditions, consisting of water rich liquid phase, hydrocarbon rich liquid phase, and hydrocarbon rich vapor phase. This paper reports new solubility data for several hydrocarbons (ethane to hexane) in aqueous phases of three-phase systems. Corresponding work was motivated by considering drastic lack of data for those systems in the three phase equilibrium conditions. Solubility data, Henry's constants, and activity coefficients at infinite dilution are also presented by means of temperature-dependent correlations.

## 2. Literature Review

It is reported from many sources that, in general, binary "water–hydrocarbon" systems match a type III phase behavior according to van Konynenburg and Scott<sup>4</sup> classification due to the large immiscibility of the two species.<sup>5,6</sup> Although the solubility of hydrocarbons in water has been extensively studied by several authors, very few studies are available concerning the solubility in the three phase region. Apparently, no VLLE data were reported in the literature for the ethane–water system,

while the phase diagram for the propane–water system has been comprehensively studied by Harmens and Sloan<sup>7</sup> including the coexistence of the hydrate phase region. Kobayashi and Katz<sup>8</sup> have measured the solubility of propane in water in VLLE conditions from 285 to 369 K. VLLE of the isobutane–water system has not been investigated in the past. However, there are some VLLE data concerning the n-butane–water system, i.e., the data of Reamer et al.<sup>9</sup> and Wehe and McKetta.<sup>10</sup> Few VLLE data for n-pentane–water system were produced by Price<sup>11</sup> and Jou and Mather.<sup>12</sup> Price,<sup>11</sup> Jönsson et al.,<sup>13</sup> and Tsouopoulos and Wilson<sup>14</sup> have studied the n-hexane–water system and determined VLLE data.

To increase this solubility database we have measured the temperature dependent solubility of ethane (C2), propane (C3), isobutane (iC4), normal butane (nC4), normal pentane (nC5), and normal hexane (nC6) in water in the three phase region.

## 3. Experimental Section

**3.1. Materials.** Ethane and propane were purchased from Messer-Griesheim with a certified purity greater than 99.995 vol %. Isobutane and n-butane were purchased from Air Liquide with traces of impurities (H<sub>2</sub>O, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and C<sub>n</sub>H<sub>m</sub>) less than 500 ppm mol. n-Pentane is from Fluka with a certified GC purity greater than 99.5%, and n-hexane is from Merck with a certified GC purity greater than 99%. Helium (carrier gas) from Air Liquide is pure grade with only traces of water (3 ppm) and of hydrocarbons (0.5 ppm). Deionized water was used after careful degassing.

**3.2. Apparatus and Experimental Procedure.** The apparatus and experimental procedure used in this work have already been described in a previous paper.<sup>15</sup> Briefly, we can say it is based on a "static-analytic" method with vapor and/or liquid-phase samplings through online Rolsi samplers (see www.rolsi.com). Two 100 Ω platinum resistance thermometer devices (Pt 100) are used; they are periodically calibrated against a 25 Ω reference platinum resistance thermometer (TINSLEY precision instruments). The resulting uncertainty on temperature measurements is estimated within ±0.02 K. Pressures are measured by means of a Druck pressure transducer (0–0.3 MPa), which is maintained at constant temperature (higher than the maximum temperature of the study). The pressure transducer is calibrated against a dead-weight pressure balance (Desgranges & Huot 5202S, CP 0.3–40 MPa, Aubervilliers, France). Pressure measurement uncertainties are estimated to be within ±0.3 kPa.

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**Table 1.** CAS Numbers, Critical Temperature, Critical Pressures, and Acentric Factors of Studied Compounds According to Daubert et al.<sup>16</sup>

	CAS number	$T_C$ /K	$P_C$ /MPa	$\omega$
ethane	74-84-0	305.32	4.872	0.099
propane	74-98-6	369.83	4.247	0.152
isobutane	75-28-5	408.80	3.640	0.176
n-butane	106-97-8	425.15	3.800	0.193
n-pentane	109-66-0	469.70	3.369	0.251
n-hexane	110-54-3	507.40	3.014	0.296
water	7732-18-5	647.13	22.050	0.345

The analytical work was carried out using a gas chromatograph (Varian model CP-3800) equipped with two detectors in series: a thermal conductivity detector (TCD) and a flame ionization detector (FID). The TCD was used to quantify water contents in samples and FID in the hydrocarbon contents. Both detectors are calibrated by injecting known masses of each compound. Experimental uncertainties on mole numbers of each compound are estimated to be within  $\pm 2\%$  for water,  $\pm 2\%$  for ethane,  $\pm 2.5\%$  for propane,  $\pm 1.3\%$  for n-butane,  $\pm 2\%$  for isobutane,  $\pm 1.5\%$  for n-pentane, and  $\pm 1\%$  for n-hexane.

#### 4. Thermodynamic Considerations

**4.1. Pure Compound Properties.** The critical temperature ( $T_C$ ), critical pressure ( $P_C$ ), and acentric factor of each compound are provided in Table 1.

**4.2. Data Treatment.** For VLLE, three thermodynamic relations can be expressed, corresponding to equilibrium between each phase and for each compound  $i$

$$f_i^A = f_i^V; f_i^V = f_i^L; f_i^A = f_i^L$$

where  $f_i$  is the fugacity of species  $i$ , and superscripts A, V, and L refer to aqueous, vapor, and hydrocarbon liquid phases, respectively. Henry's law has been used to correlate the data obtained. For hydrocarbon species, the equilibrium between the vapor phase and the aqueous phase can be expressed by

$$\varphi_i^V y_i P \cong x_i^A H_i^A(T, P) \quad (1)$$

The fugacity coefficients in vapor phase are estimated using the Peng–Robinson equation of state. The partial pressure of hydrocarbons is calculated through

$$y_i P = P - P_w \quad (2)$$

where  $P_w$ , the partial pressure of water, is approximated by

$$P_w \cong P_w^{\text{sat}} \quad (3)$$

For the equilibrium between the water rich liquid phase and the hydrocarbon rich liquid phase, the following equation is used:

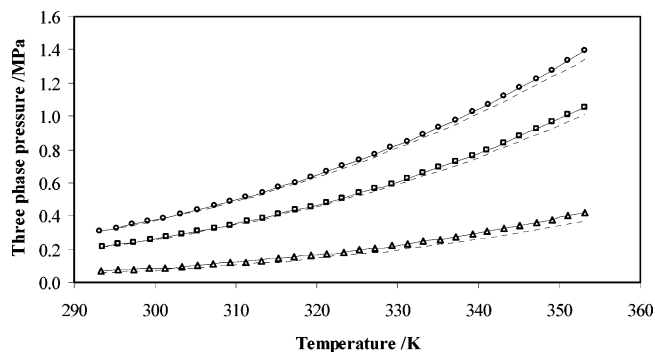
$$x_i^A \gamma_i^A = x_i^L \gamma_i^L \cong 1 \quad (4)$$

The hydrocarbon liquid is mainly composed of hydrocarbons, so composition and activity coefficient are close to unity.

As the aqueous phase can be represented either by Henry's law or one activity coefficient model, we write

$$x_i^A H_i^A(T, P) = x_i^A \gamma_i^A f_i^{A*} \quad (5)$$

With the system pressure being very close to the pure vapor pressure of the hydrocarbon, the liquid fugacity of the hydro-

**Figure 1.** Three phase equilibrium pressure for hydrocarbon–water systems: (○), isobutane (experimental); (□), n-butane (experimental); (△), n-pentane (experimental); solid line, calculated (eq 8); and dashed line, pure component vapor pressure.**Table 2.** Experimental and Calculated Three Phase Vapor Pressures of Ethane–Water and Propane–Water Systems

ethane				propane			
$T$ /K	$P_{\text{exp}}$ /MPa	$P_{\text{cal}}^a$ /MPa	$\delta P^b$ /%	$T$ /K	$P_{\text{exp}}$ /MPa	$P_{\text{cal}}^a$ /MPa	$\delta P^b$ /%
288.33	3.4122	3.3978	0.4	298.08	0.9846	0.9625	2.2
293.15	3.4122	3.4130	0.0	303.18	1.1010	1.0987	0.2
298.01	3.4122	3.4198	-0.2	313.11	1.3909	1.3997	-0.6
303.30	3.4122	3.4182	-0.2	323.15	1.7406	1.7547	-0.8
				333.16	2.1521	2.1612	-0.4
				343.18	2.6333	2.6208	0.5

<sup>a</sup> Calculated using eq 8. <sup>b</sup>  $\delta$ : relative deviation.

carbon can be approximated as follows (neglecting the Poynting correction factor):

$$f_i^{A*} \cong \varphi_i^{V,*}(T, P_i^{\text{sat}}) P_i^{\text{sat}} \quad (6)$$

Using eqs 4 and 6 eq 5 yields

$$x_i H_i^A(T) \cong \varphi_i^{V,*}(T, P_i^{\text{sat}}) P_i^{\text{sat}} \quad (7)$$

Both eqs 1 and 7 can be used to calculate Henry's law constants. Applied to water–hydrocarbon systems they give values that deviate from each other by less than 2%. This allows us to conclude that eq 4 is a convenient and satisfactory approximation.

#### 5. Results and Discussion

**5.1. Three Phase Vapor Pressure.** The three phase vapor pressure  $P_3$  is the pressure at which all three phases are at equilibrium. It is slightly above the vapor pressure of the pure hydrocarbon (nearly the sum of the pure vapor pressures). For each system (except water–n-hexane),  $P_3$  was measured as a function of temperature; corresponding measurements are reported in Tables 2 and 3. As the degree of freedom is one (three phase system), the pressure is only a function of temperature. The  $P$ – $T$  data are correlated using eq 8:

$$\ln P_3 = A_i + B_i/T + C_i \ln(T) \quad (8)$$

The  $A_i$ ,  $B_i$ , and  $C_i$  parameters are adjusted on experimental data by minimizing an objective function based on pressure.  $A_i$ ,  $B_i$ , and  $C_i$  parameter values are given in Table 4.

Deviations between experimental and calculated pressures (using eq 8) are less than 1% except for propane (2%). Figure 1 presents the three phase loci for the water–isobutane, water–n-butane, and water–n-pentane systems. As seen in

**Table 3. Experimental and Calculated Three Phase Vapor Pressures of Isobutane–Water, n-Butane–Water, and n-Pentane–Water Systems**

isobutane				n-butane				n-pentane			
T/K	$P_{\text{exp}}/\text{MPa}$	$P_{\text{cal}}/\text{MPa}$	$\delta P^b/\%$	T/K	$P_{\text{exp}}/\text{MPa}$	$P_{\text{cal}}/\text{MPa}$	$\delta P^b/\%$	T/K	$P_{\text{exp}}/\text{MPa}$	$P_{\text{cal}}/\text{MPa}$	$\delta P^b/\%$
293.33	0.3059	0.3049	0.3	293.35	0.2195	0.2176	0.9	293.34	0.0690	0.0683	1.0
295.36	0.3251	0.3244	0.2	295.37	0.2336	0.2320	0.7	295.45	0.0739	0.0736	0.4
297.22	0.3436	0.3430	0.2	297.34	0.2481	0.2469	0.5	297.31	0.0787	0.0785	0.2
299.27	0.3648	0.3645	0.1	299.31	0.2633	0.2625	0.3	299.26	0.0840	0.0840	0.0
301.21	0.3860	0.3857	0.1	301.24	0.2790	0.2785	0.2	301.21	0.0896	0.0898	-0.3
303.31	0.4098	0.4097	0.0	303.28	0.2963	0.2961	0.1	303.25	0.0957	0.0962	-0.5
305.26	0.4328	0.4329	0.0	305.25	0.3139	0.3140	0.0	305.19	0.1021	0.1027	-0.5
307.26	0.4576	0.4579	-0.1	307.29	0.3329	0.3333	-0.1	307.21	0.1090	0.1097	-0.7
309.26	0.4835	0.4838	-0.1	309.24	0.3520	0.3526	-0.2	309.23	0.1162	0.1172	-0.8
311.25	0.5102	0.5108	-0.1	311.24	0.3724	0.3733	-0.2	311.20	0.1240	0.1250	-0.8
313.28	0.5386	0.5392	-0.1	313.21	0.3934	0.3946	-0.3	313.18	0.1324	0.1331	-0.6
315.26	0.5676	0.5683	-0.1	315.22	0.4158	0.4171	-0.3	315.21	0.1422	0.1420	0.1
317.29	0.5986	0.5992	-0.1	317.21	0.4391	0.4405	-0.3	317.25	0.1521	0.1513	0.5
319.37	0.6317	0.6324	-0.1	319.32	0.4640	0.4662	-0.5	319.33	0.1622	0.1614	0.5
321.24	0.6623	0.6631	-0.1	321.28	0.4887	0.4911	-0.5	321.31	0.1723	0.1715	0.4
323.22	0.6961	0.6971	-0.1	323.23	0.5141	0.5169	-0.5	323.27	0.1828	0.1821	0.4
325.28	0.7326	0.7337	-0.1	325.30	0.5425	0.5454	-0.5	325.33	0.1945	0.1938	0.4
327.22	0.7682	0.7693	-0.1	327.22	0.5699	0.5728	-0.5	327.23	0.2057	0.2050	0.3
329.19	0.8061	0.8071	-0.1	329.22	0.5998	0.6024	-0.4	329.22	0.2182	0.2174	0.4
331.20	0.8459	0.8469	-0.1	331.21	0.6307	0.6330	-0.4	331.21	0.2312	0.2305	0.3
333.21	0.8875	0.8881	-0.1	333.23	0.6637	0.6653	-0.2	333.23	0.2451	0.2444	0.3
335.16	0.9290	0.9294	0.0	335.19	0.6965	0.6978	-0.2	335.19	0.2589	0.2586	0.1
337.15	0.9731	0.9733	0.0	337.16	0.7309	0.7316	-0.1	337.16	0.2734	0.2735	0.0
339.22	1.0202	1.0205	0.0	339.22	0.7681	0.7682	0.0	339.22	0.2893	0.2899	-0.2
341.14	1.0654	1.0656	0.0	341.14	0.8041	0.8035	0.1	341.13	0.3051	0.3057	-0.2
343.19	1.1161	1.1155	0.1	343.19	0.8438	0.8425	0.2	343.13	0.3227	0.3232	-0.2
345.16	1.1659	1.1651	0.1	345.12	0.8828	0.8805	0.3	345.10	0.3408	0.3412	-0.1
347.19	1.2197	1.2181	0.1	347.18	0.9261	0.9224	0.4	347.16	0.3605	0.3609	-0.1
349.11	1.2714	1.2695	0.1	349.14	0.9685	0.9636	0.5	349.12	0.3803	0.3806	-0.1
351.06	1.3260	1.3236	0.2	351.06	1.0118	1.0054	0.6	351.04	0.4003	0.4007	-0.1
353.16	1.3866	1.3836	0.2	353.14	1.0603	1.0522	0.8	353.09	0.4226	0.4231	-0.1

<sup>a</sup> Calculated using eq 8. <sup>b</sup>  $\delta$ : relative deviation.

**Table 4. Values of Parameters for Calculating the Three Phase Vapor Pressure of Water–Hydrocarbon Systems Using Eq 8**

hydrocarbon	parameter				temp range/K	data used
	A	B/K	C			
ethane	73.82	-2598.16	-8.79		288–30	this work
propane	47.13	-3492.86	-3.80		298–34	this work
isobutane	14.02	-2246.77	1.11		298–36	this work
n-butane	18.61	-2633.00	0.46		298–35	this work
n-pentane	-5.82	-1843.89	4.09		298–34	this work
n-hexane	-367.98	-16128.65	52.82		313–42	ref 14

**Table 5. Ethane Solubility Data in Water**

T/K	$P_{\text{exp}}/\text{MPa}$	$x_{\text{exp}} \text{C}2 \times 10^3$	$x_{\text{cal}} \text{C}2 \times 10^3$	rel dev/%	$\delta x^a \times 10^6$
288.33	3.4122	1.090	1.099	-0.8	5
293.15	3.7883	1.034	1.022	1.2	7
298.01	4.1982	0.956	0.958	-0.2	12
303.30	4.6146	0.901	0.903	-0.2	3

<sup>a</sup> Repeatability of sequential analyses of the aqueous phase.

Figure 1, the three phase pressure loci are close to pure hydrocarbon vapor pressures.

**5.2. Solubility.** Tables 5–10 present the experimental solubility results for water with ethane, propane, isobutane, n-butane, n-pentane, and n-hexane, respectively. The repeatability of sequential analyses of the aqueous phase is also displayed in the last columns of the tables ( $\delta x$ ). As the pressure in the equilibrium cell must be greater than 0.3 MPa in order to allow convenient samplings through Rolsi samplers, it has been increased to about 0.5 MPa by adding helium each time the three phase equilibrium pressure was below 0.3 MPa. We have checked, for the

**Table 6. Propane Solubility Data in Water**

T/K	$P_{\text{exp}}/\text{MPa}$	$x_{\text{exp}} \text{C}3 \times 10^4$	$x_{\text{cal}} \text{C}3 \times 10^4$	rel dev/%	$\delta x^a \times 10^7$
298.08	0.9846	2.151	2.150	0.0	7
303.18	1.1010	2.095	2.096	-0.1	10
313.11	1.3909	2.034	2.033	0.0	10
323.15	1.7406	2.016	2.020	-0.2	10
333.16	2.1521	2.062	2.056	0.3	4
343.18	2.6333	2.141	2.143	-0.1	3

<sup>a</sup> Repeatability of sequential analyses of the aqueous phase.

**Table 7. Isobutane Solubility Data in Water**

T/K	$P_{\text{exp}}/\text{MPa}$	$x_{\text{exp}} \text{iC}4 \times 10^4$	$x_{\text{cal}} \text{iC}4 \times 10^4$	rel dev/%	$\delta x^a \times 10^6$
298.23	0.3544	0.96	0.96	0.2	2
303.33	0.4105	0.97	0.97	-0.3	1
313.30	0.5398	0.99	0.99	0.1	1
323.21	0.6972	1.00	1.00	-0.2	1
333.24	0.8901	1.02	1.02	0.3	1
343.19	1.1201	1.03	1.03	0.0	1
353.14	1.3910	1.04	1.04	-0.1	1
363.19	1.7117	1.05	1.05	0.0	1

<sup>a</sup> Repeatability of sequential analyses of the aqueous phase.

n-butane–water system, that adding helium has a negligible effect on hydrocarbon solubility, within experimental uncertainty.

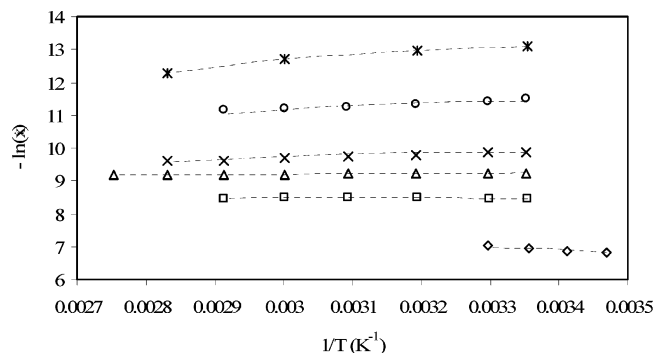
The evolution of solubility (mole fractions of hydrocarbons in water) as a function of temperature ( $-\ln(x_i)$  vs  $1/T$ ) is displayed in Figure 2.

**Temperature Dependence of Hydrocarbon Solubility.** The temperature derivative of the solubility is related to the partial molar enthalpy of the solute in the solvent. The relationship

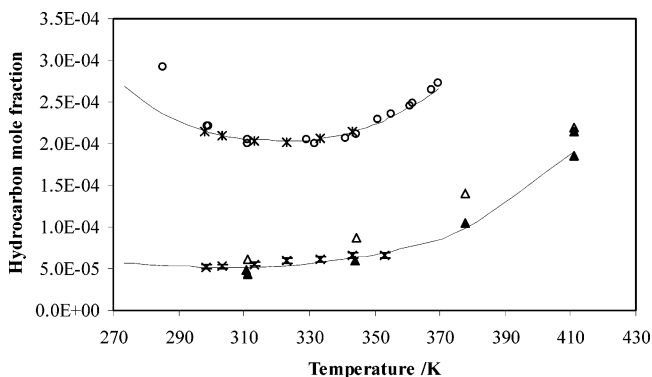
**Table 8. n-Butane Solubility Data in Water**

T/ K	$P_{exp}/$ MPa	$x_{exp}$ nC4 $\times 10^5$	$x_{cal}$ nC4 $\times 10^5$	rel dev/%	$\delta x^b$ $\times 10^7$
298.29	0.5311 <sup>a</sup>	5.20	5.09	2.1	7
303.31	0.5669 <sup>a</sup>	5.27	5.09	3.4	6
313.24	0.3868	5.53	5.18	6.3	6
323.15	0.5079	5.93	5.40	8.9	6
333.28	0.6599	6.17	5.76	6.6	7
343.16	0.8399	6.55	6.28	4.2	7
353.14	1.0585	6.59	6.99	-6.1	9

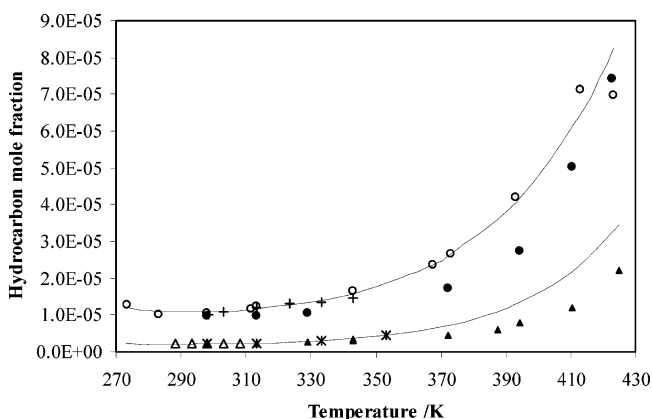
<sup>a</sup> Total pressure adjusted with helium in order to allow convenient sampling. <sup>b</sup> Repeatability of sequential analyses of the aqueous phase.



**Figure 2.** Solubility of hydrocarbons in water: ( $\diamond$ ), ethane; ( $\square$ ), propane; ( $\Delta$ ), isobutane; ( $\times$ ), n-pentane; and ( $*$ ), n-hexane. Dashed line: eq 10.



**Figure 3.** Experimental solubility data for hydrocarbons in water. Comparison of literature data with our results: ( $*$ ), propane (this work); ( $\circ$ ), propane (ref 8); ( $\times$ ), n-butane (this work); ( $\blacktriangle$ ), n-butane (ref 10); and ( $\Delta$ ), n-butane (ref 9). Solid lines are determined with eq 10.



**Figure 4.** Experimental solubility data for hydrocarbons in water. Comparison of literature data with our results: ( $*$ ), n-hexane (this work); ( $\blacktriangle$ ), n-hexane (ref 11); ( $\Delta$ ), n-hexane (ref 13); ( $+$ ), n-pentane (this work); ( $\bullet$ ), n-pentane (ref 11); ( $\circ$ ), n-pentane (ref 12). Solid lines are determined with eq 10.

**Table 9. n-Pentane Solubility Data in Water**

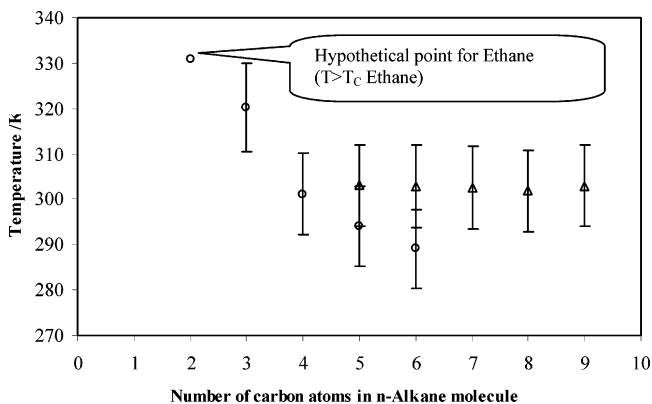
T/ K	$P_{exp}^a/$ MPa	$x_{exp}$ nC5 $\times 10^5$	$x_{cal}$ nC5 $\times 10^5$	rel dev/%	$\delta x^b$ $\times 10^7$
298.28	0.4978	1.00	1.08	-7.9	4
303.31	0.5085	1.10	1.10	0.0	4
313.19	0.4961	1.21	1.15	5.0	3
323.34	0.5480	1.32	1.25	4.9	3
333.21	0.5102	1.35	1.39	-3.4	3
343.15	0.5078	1.45	1.59	-9.7	4

<sup>a</sup> Total pressure adjusted with helium in order to allow convenient sampling. <sup>b</sup> Repeatability of sequential analyses of the aqueous phase.

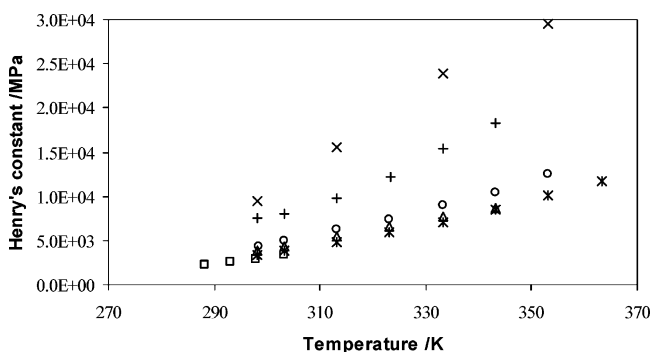
**Table 10. n-Hexane Solubility Data in Water**

T/ K	$P_{exp}^a/$ MPa	$x_{exp}$ nC6 $\times 10^6$	$x_{cal}$ nC6 $\times 10^6$	rel dev/%	$\delta x^b$ $\times 10^8$
298.09	0.4997	2.08	2.08	0.0	9
313.15	0.5028	2.33	2.33	0.0	6
333.15	0.5012	3.08	3.08	0.0	5
353.15	0.5028	4.58	4.58	0.0	13

<sup>a</sup> Total pressure adjusted with helium in order to allow convenient sampling. <sup>b</sup> Repeatability of sequential analyses of the aqueous phase.



**Figure 5.** Temperature of minimum solubility ( $T_{min}$ ) of different n-alkanes in water (VLE equilibrium): ( $\circ$ ), determined through our correlation eq 10 and ( $\Delta$ ), calculated with the correlation of Tsionopoulos.<sup>19</sup>



**Figure 6.** Henry's constants for hydrocarbons in water as a function of temperature: ( $\square$ ), ethane; ( $\Delta$ ), propane; ( $*$ ), isobutane; ( $\circ$ ), n-butane; ( $+$ ), n-pentane; and ( $\times$ ), n-hexane.

between solubility and heat of solution is given by

$$\left( \frac{\partial \ln x_i^A}{\partial (1/T)} \right)_P \cong -\frac{\Delta \bar{h}_i}{R} \quad (9)$$

According to Prausnitz et al.,<sup>17</sup> the heat of solution (or the partial molar excess heat) includes two effects: a positive heat of cavitation (condensation) and a negative heat due to the hydrophobic interactions between hydrocarbon and water. At low temperatures, the hydrophobic interaction effect predomi-

**Table 11. Solubility of Hydrocarbons in Water, Parameter Values for Eq 10, Temperature Validity Ranges, and References of Data Used for Fitting**

hydrocarbon	parameter					
	$A_i$	$B_i/K$	$C_i$	$D_i/K^{-2}$	temp range/K	data used and references
ethane	94.85	7.05	-19.24	87.94	288-303	this work
propane	56.79	5.70	-12.40	60.36	298-343	this work + ref 9
isobutane	-49.25	1199.06	6.49	-10.99	298-363	this work
n-butane	12.99	1201.34	-5.54	52.56	298-353	this work + ref 10
n-pentane	-226.60	9612.60	32.05	3.68	298-343	this work + ref 11 + ref 12
n-hexane	-301.57	12510.60	43.27	-0.02	298-353	this work + ref 12 + ref 13

nates and the heat of solution is endothermic. As the temperature increases, the cavitation effect increases, but the solubility and the slope also continue to decrease. These two effects cancel each other at  $T_{\min}$ , the temperature at which the hydrocarbon solubility goes through a minimum. If temperature increases over  $T_{\min}$ , the cavitation effect predominates, and the resulting heat of solution is exothermic, leading to a solubility increase.

The analysis of the new measurements data was carried out using a simple correlation:

$$\ln x_i^A = A_i + B_i/T + C_i \ln(T) + D_i T^2 \quad (10)$$

The thermodynamic basis of eq 10 comes from eq 9, in which the heat of solution is temperature dependent:<sup>18</sup>

$$\Delta \bar{h}_i(T) = \Delta \bar{h}_i(T_o) + \int_{T_o}^T \Delta \bar{C}p_i(T) dT \quad (11)$$

In eq 11, the heat capacity of solution can be expressed as a polynomial function of temperature<sup>18</sup> ( $\Delta \bar{C}p_i = f(T)$ ).

The fitting of parameters contained in eq 10 has been performed on our data associated with some literature data in order to determine as accurately as possible the minimum of solubility.

The values of  $A_i$ ,  $B_i$ ,  $C_i$ , and  $D_i$  for the six hydrocarbons are listed in Table 11.

The relative deviation between experimental and calculated solubilities through eq 10 is less than 10%.

Comparisons with literature data have been carried out, and they are shown in Figures 3 and 4. These figures demonstrate that the solubility is highly dependent on both the temperature and the number of carbon atoms in the hydrocarbon molecule. They also display a nonmonotonic behavior, i.e., the solubility goes through a minimum, as mentioned by Tsonopoulos<sup>19</sup> and Tsonopoulos and Wilson.<sup>14</sup> This is obvious for the solubility of propane in water. Our results seem to be in good agreement with those of Kobayashi and Katz<sup>8</sup> (propane-water) and Jou and Mather<sup>12</sup> (n-pentane-water). However, significant dispersions between the different experimental data are noted. Up to 30% of deviation between data is pointed out for n-butane in water. Likewise, the results of Jou and Mather<sup>12</sup> and Price<sup>11</sup> for the n-pentane-water system are too scattered beyond 370 K (about 50% of deviation between their data).

**Solubility Minimum.** Equation 10 predicts (by derivation) the temperature at which the solubility goes through a minimum ( $T_{\min}$ ) value for each system. Figure 5 presents the calculated  $T_{\min}$  versus the number of carbon atoms in the hydrocarbon molecule. The maximum uncertainty on calculating  $T_{\min}$  is estimated to  $\pm 3\%$ . In Figure 5, we have compared our results with those obtained from Tsonopoulos's correlation. A maximum uncertainty of  $\pm 3\%$  is observed for the common calculated points (C5 and C6). This uncertainty corresponds to  $\pm 10$  K deviation on the calculation of the minimum temperature of solubility. The results obtained from the correlation of Tsonopoulos match almost a constant progression of the minimum

**Table 12. Henry's Constants for Hydrocarbons in Water, Parameters of Eq 12, and Temperature Validity Ranges**

hydrocarbon	parameter			
	$A_i$	$B_i/K$	$C_i$	temp range/K
ethane	-40.51	0.04	8.51	288-303
propane	189.86	-10156.70	-25.90	298-343
isobutane	46.37	-3620.39	-4.59	298-363
n-butane	37.71	-3064.86	-3.34	298-353
n-pentane	-28.33	0.36	6.53	298-343
n-hexane	347.74	-17990.73	-48.83	298-353

**Table 13. Activity Coefficients for Hydrocarbons in Water, Parameters of Eq 13, and Temperature Validity Ranges**

hydrocarbon	parameter			
	$A_i$	$B_i/K$	$C_i$	temp range/K
ethane	-15.02	0.63	3.86	288-303
propane	176.32	-7934.32	-24.79	298-343
isobutane	4.24	364.92	0.66	298-363
n-butane	-6.58	1205.94	2.18	298-353
n-pentane	-136.01	7623.21	21.40	298-343
n-hexane	301.56	-12510.68	-43.27	298-353

solubility temperature, while our results show a decreasing of  $T_{\min}$  with a carbon atoms number. We believe that our result is consistent because of the condensation effect (condensation part of the heat of solution) which is more important for heavier hydrocarbons. Therefore, the change of the slope of solubility with temperature, due to the increase of the cavitation effect (condensation) in the detriment of the hydrophobic effect, begins earlier when going from a heavy to a less heavy hydrocarbon. Furthermore, the hydrophobic effect should be in the same order of magnitude for each hydrocarbon-water system because of the nature of the polar-nonpolar bond which provides the same type of hydrophobic interactions. This is what asserts the leading part of the condensation effect and explains the behavior of the temperature of minimum solubility with a carbon atoms number. Although,  $T_{\min}$  is calculated for the ethane-water system and seems to respect the observed trend, this value (about 330 K) has no physical significance because at this temperature ethane is supercritical and cannot be found in the liquid state. This value is then rejected.

**5.3. Henry's Constant.** Henry's constants are needed for "vapor-liquid" and "vapor-liquid-liquid" equilibrium calculations. In this work, Henry's constants for each measured system have been calculated using eq 1. The data are fitted with the following simple equation

$$\ln H_i = A_i + B_i/T + C_i \ln(T) \quad (12)$$

where  $H_i$  is expressed in MPa. The coefficients for each hydrocarbon are reported in Table 12. The maximum relative deviation between Henry's constant calculated with eq 12 and those obtained with eq 1 is 0.3%.

As can be shown in Figure 6, Henry's law constant is not only temperature dependent but also a function of number of carbon atoms.

**5.4. Activity Coefficient at Infinite Dilution.** The activity coefficient of a solute is nearly independent of the solute's mole fraction provided the latter is sufficiently small. Our data are used to produce correlations for an activity coefficient as a function of temperature only:  $\gamma_i^A \cong 1/x_i^A$  (according to eq 4).

The correlation is expressed as follows:

$$\ln \gamma_i^A = A_i + B_i/T + C_i \ln(T) \quad (13)$$

The coefficients for each hydrocarbon are reported in Table 13. The maximum relative deviation generated with this correlation is 0.2% in comparison with activity coefficient calculated with eq 4.

## 6. Conclusion

New data have been measured using a "static-analytic" method based apparatus. These data concern the solubility of several alkanes (from C2 to C6) in water in vapor-liquid-liquid equilibrium conditions. Globally, good agreement with the literature data is observed, although important dispersions are found between them due to the low level of solubility values which are quite difficult to measure. New correlations for representing mole fractions, Henry's law constants, and activity coefficients at infinite dilution versus temperature are provided thanks to thermodynamic data treatment. It is demonstrated that the hydrophobic interactions and condensation phenomenon play an important role in the solubility behavior with respect to temperature and number of carbon atoms.

## Nomenclature

$A_i, B_i, C_i, D_i$  = correlation parameters

$f_i$  = fugacity of species  $i$

$\varphi_i$  = fugacity coefficient of species  $i$

$H_i$  = Henry's law constant of species  $i$

$\Delta h_i$  = heat of solution ( $\text{J}\cdot\text{mol}^{-1}$ )

$\Delta Cp_i$  = heat capacity of solution ( $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ )

$\gamma_i$  = activity coefficient of species  $i$

$P$  = pressure (MPa)

$R$  = gas constant ( $\text{J}\cdot\text{mol}^{-1}\text{K}^{-1}$ )

$T$  = temperature (K)

$x$  = liquid mole fraction

$y$  = vapor mole fraction

### Superscripts

A = related to aqueous phase

V = related to vapor phase

sat = at saturation

\* = related to pure component property

H = related to hydrocarbon liquid phase

### Subscripts

C = critical properties

3 = related to three phase point

$i, j$  = molecular species

w = water

cal = calculated

exp = experimental

min = minimum value

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## Literature Cited

(1) de Hemptine, J.-C.; Dhima, A.; Shakir, S. The Henry constant for 20 hydrocarbons, CO<sub>2</sub> and H<sub>2</sub>S in Water as a function of pressure and temperature. Paper presented at the Fourteenth symposium on Thermophysical Properties, June 25–30, 2000, Boulder, CO, U.S.A.

(2) de Hemptine, J.-C.; Dhima, A.; Zhou, H. The importance of Water–Hydrocarbon phase equilibria during reservoir production and drilling operations. *Rev. Inst. Fr. Pet.* **1998**, *53*, 283.

(3) Tsonopoulos, C. Thermodynamic analysis of the mutual solubilities of normal alkanes and Water. *Fluid Phase Equilib.* **2001**, *186*, 185.

(4) Van Konynenburg, P. H.; Scott, R. L. Critical Lines and Phase Equilibria in Binary van der Waals Mixtures. *Philos. Trans. R. Soc. London, Ser. A* **1980**, *298*, 495.

(5) Brunner, E. Fluid mixtures at high pressures. IX. Phase separation and critical phenomena in 23 (n-alkane + Water) mixtures. *J. Chem. Thermodyn.* **1990**, *22*, 335.

(6) Plyasunov, A. V.; Shock, E. L. Standard state Gibbs energies of hydration of hydrocarbons at elevated temperatures as evaluated from experimental phase equilibria studies. *Geochim. Cosmochim. Acta* **2000**, *64*, 2811.

(7) Harmens, A.; Sloan, E. D. The phase behaviour of the Propane–Water system: A review. *Can J. Chem. Eng.* **1990**, *68*, 151.

(8) Kobayashi, R.; Katz, D. L. Vapor-liquid equilibria for binary hydrocarbon–Water systems. *Ind. Eng. Chem.* **1953**, *45*, 440.

(9) Reamer, H. H.; Sage, B. H.; Lacey, W. N. Phase equilibria in hydrocarbon systems. *Ind. Eng. Chem.* **1952**, *44*, 609.

(10) Wehe, A. H.; McKetta, J. J. Method for determining total hydrocarbons dissolved in Water. *Anal. Chem.* **1961**, *33*, 291.

(11) Price, L. C. *Am. Assoc. Petrol. Geol. Bull.* **1976**, *60*, 213.

(12) Jou, F. Y.; Mather, A. E. Vapor–liquid–liquid locus of the system Pentane + Water. *J. Chem. Eng. Data* **2000**, *45*, 728.

(13) Jönsson, J. A.; Vejrosta, J.; Novak, J. Air/Water partition coefficients for normal alkanes (n-Pentane to n-nonane). *Fluid Phase Equilib.* **1982**, *9*, 279–286.

(14) Tsonopoulos, C.; Wilson, G. M. High-temperature mutual solubilities of hydrocarbons and Water. *AIChE J.* **1983**, *29*, 990.

(15) Chapoy, A.; Mokraoui, S.; Valtz, A.; Richon, D.; Mohammadi, A. H.; Tohidi, B. Solubility measurement and modeling for the system Propane–Water from 277.62 to 368.16 K. *Fluid Phase Equilib.* **2004**, *226*, 213.

(16) Daubert, T. E.; Danner, R. P.; Sibel, H. M.; Stebbins, C. C. *Physical and thermodynamic properties of pure chemicals, Data Compilation*; Taylor & Francis: Washington, DC, 1997.

(17) Prausnitz, J. M.; Lichtenthaler, R. N.; Azevedo, E. G. *Molecular thermodynamics of fluid-phase equilibria*, 3rd ed.; Prentice Hall PTR: Upper Saddle River, NJ, 1999.

(18) Perry, R. H.; Chilton, C. H.; Green, D. W. *Perry's Chemical Engineers Handbook*, 7 rev ed.; McGraw-Hill Publishing Co.: New York, 1997.

(19) Tsonopoulos, C. Thermodynamic analysis of the mutual solubilities of normal alkanes and Water. *Fluid Phase Equilib.* **1999**, *156*, 21.

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