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## Standard state Gibbs energies of hydration of hydrocarbons at elevated temperatures as evaluated from experimental phase equilibria studies

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**Abstract**—Experimental results of phase equilibria studies at elevated temperatures for more than twenty hydrocarbon-water systems were uniformly correlated within the framework of the Peng-Robinson-Stryjek-Vera equation of state in combination with simple mixing rules. This treatment allows evaluation of the Gibbs energy of hydration for many alkanes, 1-alkenes, cycloalkanes (derivatives of cyclohexane) and alkylbenzenes up to 623 K at saturated water vapor pressure and up to 573 K at 50 MPa. Results for homologous series show regular changes with increasing carbon number, and confirm the applicability of the group contribution approach to the Gibbs energy of hydration of hydrocarbons at elevated temperatures. The temperature dependence of group contributions to the Gibbs energy of hydration were determined for CH<sub>3</sub>, CH<sub>2</sub>, and CH in aliphatic hydrocarbons; C=C and H for alkenes; c-CH<sub>2</sub> and c-CH in cycloalkanes; and CH<sub>ar</sub> and C<sub>ar</sub> in alkylbenzenes (or aromatic hydrocarbons). Close agreement between calculated and experimental results suggests that this approach provides reasonable estimates of Gibbs energy of hydration for many alkanes, 1-alkenes, alkyl cyclohexanes and alkylbenzenes at temperatures up to 623 K and pressures up to 50 MPa. Copyright © 2000 Elsevier Science Ltd

### 1. INTRODUCTION

Growing interest in the effects of organic compounds on a variety of geochemical and technological processes is influencing many areas of research concerned with

1. the formation and evolution of hydrocarbon deposits;
2. diagenesis of sediments;
3. design of process equipment in petrochemical plants;
4. use of a near-critical water for decomposition of hazardous wastes and as an environmentally benign medium for organic synthesis;
5. biogeochemistry;
6. support of high temperature and subsurface microbes; and
7. even the emergence of life.

Among the achievements of the last decade are the demonstrations, both theoretical (Shock, 1988; Shock, 1990; Helgeson et al., 1993) and experimental (Seewald, 1994), of the existence of metastable equilibrium states governing the distribution of organic compounds in hydrothermal systems. Complete stable chemical redox equilibrium is seldom achieved in the C-O-H system, at least at moderate temperatures. This circumstance makes possible the spectacularly rich organic chemistry of carbon, and eventually the very existence of life as on the Earth. However, the concept of metastable states in water-rock-organic systems (with a proper methodological framing) greatly enhances the possibilities for sound analysis of the distribution of organic compounds in hydrothermal solutions

as functions of temperature, pressure, and redox conditions using the well established apparatus of chemical thermodynamics.

Such considerations determine the main objective of this work, namely, to supply reliable values of the Gibbs energies of aqueous hydrocarbons at elevated temperatures and pressures. As experimental high-temperature heat capacity determinations for aqueous hydrocarbons are practically absent, we are forced to evaluate the Gibbs energies of these compounds from experimental studies of phase equilibria in water-hydrocarbon systems. First we discuss briefly the nature of the phase relations in binary water-hydrocarbon systems, then we use an equation-of-state approach to evaluate the fugacity/concentration ratios (or equilibrium constants,  $K_H$ , for hydration reactions) of dissolved hydrocarbons from experimental data. More than twenty mixtures involving water and hydrocarbons (alkanes, alkenes, cycloalkanes and alkylbenzenes) are treated uniformly to extract the Gibbs energy of hydration of hydrocarbons at elevated temperatures. The values of  $K_H$  obtained are used to describe the temperature dependence of hydration reaction constants at saturated water vapor pressure up to 623 K and at pressure  $P = 50$  MPa up to 573 K. Finally, we show that results for homologous series follow the linear dependence on carbon number, confirming the applicability of the group contributions approach at elevated temperatures. The numerical values of the Gibbs energy of hydration are evaluated for the CH<sub>3</sub>, CH<sub>2</sub>, CH, c-CH<sub>2</sub>, c-CH, CH<sub>ar</sub>, C<sub>ar</sub>, C=C and H groups at temperatures up to 623 K at saturated water vapor pressure and up to 573 K at  $P = 50$  MPa. These results allow estimates of the Gibbs energy of hydration for many hydrocarbons at elevated temperatures and pressures.

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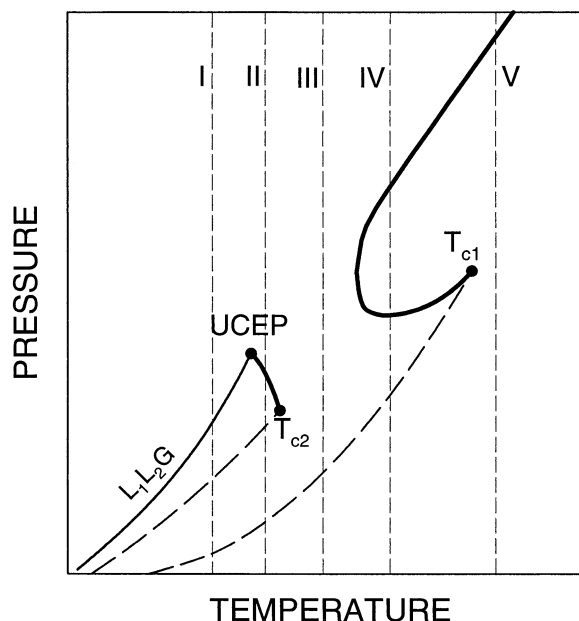


Fig. 1. A representative T-P projection of phase equilibria in hydrocarbon-water systems (see text for definitions of labels). Isothermal cross-sections indicated I-V are used to construct Fig. 2.

## 2. PHASE EQUILIBRIA IN WATER-HYDROCARBON SYSTEMS

In many practical applications water-hydrocarbon mixtures may be considered as completely immiscible at ambient conditions. However, as temperature increases, the picture of phase relations and mutual solubilities in these systems changes dramatically. After numerous experimental and theoretical studies the nature of phase relations between water and a hydrocarbon are well understood, at least qualitatively. Most experimentally studied hydrocarbon-water systems exhibit type III phase behavior according to the van Konynenberg and Scott (1980) classification of temperature-pressure (T-P) projections (see below). Important exceptions include polyaromatic compounds and, perhaps, “heavy” hydrocarbons that have critical temperatures higher than the critical temperature of pure water, and which were not considered in this study.

Based on experimental studies (Alwani and Schneider, 1967; Roof, 1970; De Loos et al., 1980; 1982; Tsonopoulos and Wilson, 1983; Heidman et al., 1985; Brunner, 1990; Yiling et al., 1991; Economou et al., 1997; and others) one can draw a representative T-P projection of phase equilibria in a hydrocarbon-water system, as shown in Figure 1. This projection is topologically correct for hydrocarbons with pure compound critical temperatures,  $T_{c2}$ , lower than the critical temperature of pure water,  $T_{c1}$ , and it is valid at moderate and elevated temperatures (i.e., above the temperatures of existence of ice or gas hydrates). Dashed curves show the T-P projections of the liquid-gas saturation curves of pure water and a pure hydrocarbon. The thin solid curve labeled  $G+L_1+L_2$  represents the T-P trajectory of the monovariant three phase equilibrium, i.e. the coexistence of the “water-rich”,  $L_1$ , “organic-rich”,  $L_2$ , and gaseous,  $G$ , phases. The three-phase equilibrium curve ends in the upper critical end point, UCEP, where compositions of the

“hydrocarbon-rich” and gaseous phases become identical. For hydrocarbon-water systems under consideration it has been shown experimentally that the pressure of the  $G+L_1+L_2$  equilibrium exceeds the vapor pressure of any of the pure compounds (and typically slightly exceeds the sum of vapor pressures of the pure compounds) and that the UCEP usually appears at a temperature that is lower than the critical temperature  $T_{c2}$  of the corresponding pure hydrocarbon. The bold solid curves in Figure 1 illustrate the two branches of the interrupted critical line of the mixture. (The critical line represents the limiting state for the existence of two phases. For example, crossing the critical line by approaching along an isobar from low temperatures represents the last instance of the coexistence of two phases). The lower branch of the critical line starts from the critical point of the pure hydrocarbon,  $T_{c2}$ , and goes to the UCEP. The upper branch of the critical line starts from the critical point of pure water,  $T_{c1}$ , first moves to lower temperatures and pressures, passes through a minimum and eventually goes to higher temperatures and pressures. Such behavior of the critical line of a mixture yields a type III phase diagram according to the Van Konynenberg and Scott (1980) classification.

Thin dashed vertical lines in Figure 1 represent temperatures of some isothermal cross-sections for pressure-composition (P-X) projections that illustrate the principal phase equilibria given in Figure 2. These diagrams are also useful because many experimental data are reported for isothermal conditions but at different pressures. The P-X projection of phase equilibria at temperatures below the temperature of UCEP is shown in Figure 2a. At pressures below the three-phase equilibrium pressure,  $P_{3ph}$ , the possible equilibria are  $G$ ,  $L_1$ ,  $L_2$ ,  $L_1+G$ , and  $L_2+G$ , depending on pressure and overall composition. The three phases coexist only at the fixed pressure  $P_{3ph}$ . At  $P > P_{3ph}$  the “water-rich” and “hydrocarbon-rich” liquid phases coexist. The solubility of  $H_2O$  in the liquid “hydrocarbon-rich”  $L_2$  phase decreases with pressure, and the solubility of the hydrocarbon in the “water-rich” liquid phase typically has a negligible pressure dependence at  $T < T_{c2}$ . As temperature rises, the compositions of the coexisting  $L_2$  and  $G$  phases at  $P = P_{3ph}$  become closer, and eventually identical at the UCEP, as shown in Figure 2b. This figure shows the last instance of the existence of the three phase,  $L_1+L_2+G$ , equilibrium. The P-X projection corresponding to cross-section II in Figure 1 is shown in Figure 2c. Here the temperature exceeds the temperature of the UCEP, but it is still below  $T_{c2}$ . For hydrocarbon-rich compositions the  $L_2+G$ -type equilibrium is realized, however, there is a continuous transition (without phase boundaries) from the “liquid-like” to “gas-like” phases. In order to escape terminological ambiguities associated with these gradual transitions, the large homogeneous field toward the hydrocarbon side of the diagram is labeled F (“fluid”), and the two-phase field starting from the vapor-liquid equilibrium point for the pure hydrocarbon in which “liquid-like” and “gas-like” phases are in equilibrium is labeled  $F_1+F_2$ . At temperatures higher than  $T_{c2}$ , but below the temperature minimum of the critical line (cross-section III in Fig. 1), a simple picture of F,  $L_1+F$ , and  $L_1$  equilibria is obtained as shown in Fig. 2d. Cross-section IV in Figure 1 intersects the upper branch of the critical line twice although it remains below the critical temperature of pure water,  $T_{c1}$ . The P-X projection given in Figure 2e shows that gas-liquid equi-

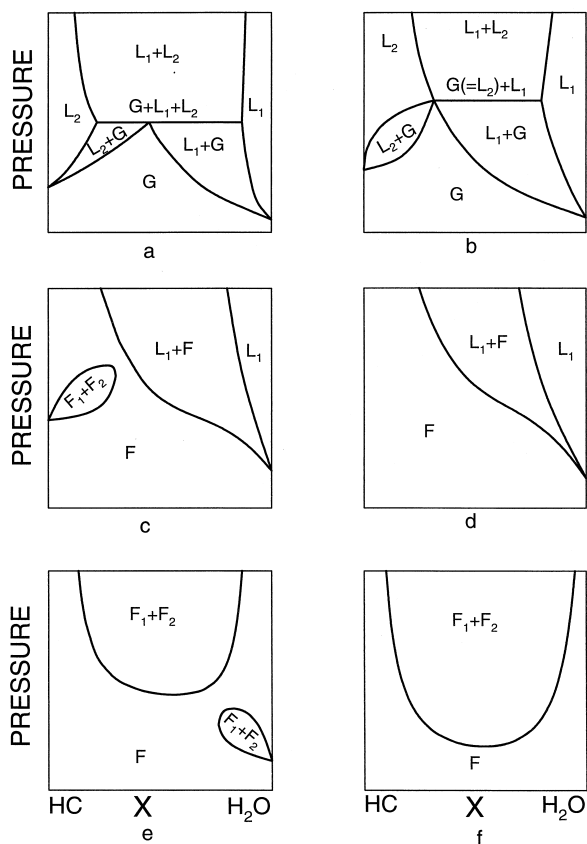


Fig. 2. Isothermal P-X projections of phase equilibria in hydrocarbon-water systems, corresponding to: a) cross-section I; b) temperature of the UCEP; c) cross-section II; d) cross-section III; e) cross-section IV; f) cross-section V.

libria are realized only for water-rich compositions. Again to escape terminological ambiguities due to gradual transitions from a “gas-like” phase to a “liquid-like” phase at the water corner, this “fluid” phase is labeled F. When crossing the critical line for the second time at higher pressures, the system goes from the homogeneous “fluid” state to the heterogeneous state  $F_1+F_2$ , where two “fluid” phases coexist. Historically, this equilibrium has been called a “gas-gas” equilibrium. At temperatures greater than  $T_{c1}$ , like cross-section V in Figure 1, the system may develop either a homogeneous “fluid” state F, or the heterogeneous  $F_1+F_2$  (“gas-gas”) state depending on pressure and overall composition, as depicted in Figure 2f.

The most extensive sets of experimental data for light hydrocarbons (carbon number  $\leq 4$ , which exist as gases at ambient temperatures and pressures) with low critical temperatures consist of compositions of coexisting phases for  $F+L_1$  equilibria, corresponding to conditions like those shown in Figure 2d. These results can be used to evaluate the equilibrium constant for a gas dissolution reaction, like  $\text{CH}_4(\text{g}) \rightleftharpoons \text{CH}_4(\text{aq})$ . As this reaction describes the transfer of a compound from a gaseous state to a state of aqueous solution, we call this reaction the hydration reaction, with equilibrium constant  $K_H$ . The standard state adopted in this study for a gas is one of unit fugacity of the hypothetical ideal gas state at pressure 0.1 MPa (1 bar) and any temperature. The standard state adopted for

aqueous species calls for unit activity of a hypothetical one molal solution referenced to infinite dilution at any T and P. The equilibrium constant for a reaction of hydration can be expressed as

$$K_H(T, P) = \frac{a_2(T, P)}{f_2(T, P)} = \frac{1000}{M_w} \cdot \frac{1}{k_H}, \quad (1)$$

where  $a_2(T, P)$  stands for the activity of the dissolved hydrocarbon in an aqueous solution;  $f_2(T, P)$  represents the fugacity of a hydrocarbon in an aqueous solution;

$$k_H = \lim_{x_2 \rightarrow 0} \left( \frac{f_2}{X_2} \right) \quad (1a)$$

is the Henry’s law constant (bar units);  $M_w = 18.0152 \text{ g} \cdot \text{mol}^{-1}$  stands for the molar mass of water. At elevated temperatures, when the solubility of water in the “hydrocarbon-rich” fluid phase becomes significant, accurate calculations of the fugacity of a hydrocarbon,  $f_2(T, P)$ , require use of an appropriate equation of state for a mixture (see, for instance, Fernandez-Prini and Crovetto, 1989).

For heavier hydrocarbons, which exist at ambient conditions as liquids, the most numerous and reliable experimental data are reported as compositions of the coexisting  $L_1$  (“water-rich”) and  $L_2$  (“hydrocarbon-rich”) phases for the  $L_1+L_2+G$  three-phase equilibria. Amend and Helgeson (1997) used this information at temperatures up to 500 K to calculate the standard Gibbs energy of solution,  $\Delta_s G^0(T, P)$ , of a hydrocarbon in water according to the relation:

$$\Delta_s G^0(T, P) = -RT \ln \frac{a_2(T, P)}{a_{HC}(T, P)}, \quad (2)$$

where  $a_{HC}(T, P)$  stands for the activity of a hydrocarbon in the “hydrocarbon-rich” phase. The simplest approximations were used by these authors:  $a_2(T, P) = m_{sat}$ , where  $m_{sat}$  stands for the saturation molality of a hydrocarbon in the “water-rich” phase, and  $a_{HC}(T, P) = 1$ . According to experimental data (Skripka, 1976; Tsonopoulos and Wilson, 1983; Anderson and Prausnitz, 1986; Chandler et al., 1998), the mole fraction of water in *n*-hexane at 473 K at the three-phase equilibrium pressure is about 0.10, and 0.18 in benzene. At these conditions the simplified approximation that  $a_{HC}(T, P) = 1$  (neglecting the solubility of water in a hydrocarbon) is satisfactory, resulting in the systematic shift in  $\Delta_s G^0(T, P)$  of only 0.4–0.8  $\text{kJ} \cdot \text{mol}^{-1}$  or less than 0.1 in  $\log K_H$ . However, this treatment can not be used at temperatures above the UCEP, where the  $L_2$  phase no longer exists. In addition, at temperatures above 473 K the solubility of water in the “hydrocarbon-rich” phase increases dramatically. As a consequence, corrections for the solubility of water in the “hydrocarbon-rich” phase, and non-ideality of the “hydrocarbon-rich” phase become necessary.

The greatest problems in estimating standard-state properties of aqueous hydrocarbons occur near the high-temperature field of “gas-gas” ( $F_1+F_2$ ) equilibria, see Figure 2e. In the low-pressure loop of this equilibrium, which starts at the point of liquid-gas equilibrium for pure water, compositions of the two coexisting fluid phases are so enriched in water that accurate calculation of the equilibrium fugacity of the hydrocarbon is difficult to perform. Another related problem is that the corre-

sponding equilibrium is reached in the vicinity of the critical point of pure water where cubic equations of state usually fail to perform accurately. Estimates, although semiquantitative, are possible for the high-pressure part of this equilibrium, corresponding to the upper  $F_1 + F_2$  field in Figure 2e.

Most phase equilibria in water-hydrocarbon systems can be used to obtain the hydration constants provided that reasonably accurate estimates of the fugacities of components in the coexisting phases can be obtained in the framework of a suitable equation of state.

### 3. EVALUATION OF HYDRATION CONSTANTS FOR HYDROCARBONS FROM HIGH-TEMPERATURE PHASE EQUILIBRIA DATA

#### 3.1. The Use of an Equation of State to Evaluate Hydration Constants for Hydrocarbons

Despite the complexity of phase relations in water-hydrocarbon systems, their principal picture is well reproduced in the framework of simple two-parameter cubic equations of state. However, problems with a quantitative reproduction of P-T-X relations, mainly for water-rich compositions, remain acute. Peng and Robinson (1976b); Peng and Robinson (1980) showed that their two-parameter EoS (Peng and Robinson, 1976a) in combination with simple van der Waals type mixing rules is able to describe quantitatively the compositions of "hydrocarbon-rich" gaseous, liquid and fluid phases for a number of light hydrocarbons at temperatures up to at least 523 K and pressures up to 1000 bar. However, the predicted hydrocarbon concentrations in the "water-rich" liquid phase were orders of magnitude lower than the experimental data. Only the introduction of a very strong temperature dependence in one of the model's parameters could improve the performance of the EoS for the aqueous compositions. An extensive analysis of high-temperature experimental data up to the UCEP for many hydrocarbon-water systems, both light and heavy (up to carbon number twelve), performed by Tsonopoulos, Wilson, and co-authors (Tsonopoulos and Wilson, 1983; Heidman et al., 1985; Economou et al., 1997) resulted in essentially the same conclusions: a number of simple equations of state, including the Peng-Robinson EoS, and modifications of the Redlich-Kwong EoS in combination with simple van der Waals mixing rules can successfully describe the compositions of the "hydrocarbon-rich" gaseous and liquid phases at temperatures from ambient to close to the UCEP (up to 590 K for the systems investigated), but fail to reproduce the compositions of the "water-rich" coexisting phases. This problem is attributed to the existence of strong hydrogen bonding in water. A large number of far more complicated EoS and/or mixing rules were proposed to address the problem (Tsonopoulos and Heidman, 1986; Michel et al., 1989; Anderko, 1991; Economou and Donohue, 1992; Wong and Sandler, 1992; Shinta and Firoozabadi, 1995; and many others), but most have only moderate success.

Nevertheless, for water-hydrocarbon mixtures the simple cubic equations of state allow accurate calculations of  $f_2(T,P)$ , the fugacity of a dissolved hydrocarbon relative to the fugacity of the pure hydrocarbon in the ideal gas state. The calculated values of  $f_2(T,P)$  can be used to evaluate the equilibrium constants for a hydration reaction according to a relation

$$K_H(T,P) = \frac{a_2(T,P)}{f_2(T,P)} = \frac{m_{sat}\gamma_2(T,P)}{f_2(T,P)} \approx \frac{m_{sat}}{f_2(T,P)}. \quad (3)$$

The only forced assumption is that the activity coefficient of a dissolved hydrocarbon in a "water-rich" phase equals one. This approximation is expected to be satisfactory for dilute aqueous solutions, except in the vicinity of critical points of a phase diagram. Several authors have used equations of state to calculate solute fugacities and evaluate Henry's law or hydration constants. Fernandez-Prini and Crovetto (1989) used this approach in their thermodynamic treatment of the solubility of apolar gases in high-temperature water, and Carroll and Mather (1997) and Carroll et al. (1997) used it to evaluate Henry's law constants for light hydrocarbons. A similar approach was employed by Tsonopoulos, Wilson, and coworkers (Tsonopoulos and Wilson, 1983; Heidman et al., 1985; Economou et al., 1997) to evaluate Henry's law constants for a large number of hydrocarbons (although these authors used correlations rather than an equation of state to estimate the fugacity coefficients of hydrocarbons in coexisting phases).

#### 3.2. The Peng-Robinson-Stryjek-Vera (PRSV) Equation of State

To calculate the fugacities of dissolved hydrocarbons we have chosen the Peng-Robinson equation of state (Peng and Robinson, 1976a; Peng and Robinson, 1976b). It is a computationally simple cubic equation of state, capable of accurate prediction of the compositions of "organic-rich" phases in water-hydrocarbon mixtures over wide ranges of temperatures and pressures. Stryjek and Vera (1986) proposed a modification of this equation, which notably improves the description of PVT-properties of pure compounds, particularly ones with large acentric factors (i.e. heavy hydrocarbons). In the literature this modification is called the Peng-Robinson-Stryjek-Vera (PRSV) equation of state.

The basic equations for the PRSV equation of state for pure compounds are given in the Appendix A, and below we give only relations relevant to a binary mixture:

$$P = \frac{RT}{V - b_m} - \frac{a_m}{V(V + b_m) + b_m(V - b_m)}, \quad (4)$$

where  $V$  stands for the molar volume of a mixture, and  $a_m$  and  $b_m$  represent the parameters in the PRSV equation of state. For the case of a binary mixture the following mixing rules are used:

$$a_m = X_1^2 a_1 + 2X_1 X_2 (a_1 a_2)^{0.5} (1 - \tau) + X_2^2 a_2,$$

$$b_m = X_1 b_1 + X_2 b_2,$$

where  $X_1$  and  $X_2$  stand for the mole fraction of water (subscript 1) and a hydrocarbon (subscript 2) in a (undefined) phase;  $a_1$ ,  $a_2$ ,  $b_1$ , and  $b_2$  designate the PRSV parameters for pure compounds (see Appendix A);  $\tau$  is the only mixture-specific parameter, and it is temperature-independent (Peng and Robinson, 1976b; Heidman et al., 1985; Tsonopoulos and Heidman, 1986; Economou et al., 1997).

The fugacity coefficient of a component  $i$  of a binary mixture

consisting of components  $i$  and  $j$  (if  $i = 1$  or  $2$  then  $j = 2$  or  $1$ , respectively),  $\psi_i$ , is given by:

$$\ln \psi_i = \frac{b_i}{b_m} (Z - 1) - \ln(Z - B) - \frac{A}{2^{1.5}B} \cdot \left\{ \frac{2(X_i a_{ij} + X_i a_i)}{a_m} - \frac{b_i}{b_m} \right\} \ln \left( \frac{Z + (1 + 2^{0.5})B}{Z + (1 - 2^{0.5})B} \right), \quad (5)$$

where

$$A = \frac{a_m P}{R^2 T^2};$$

$$B = \frac{b_m P}{RT};$$

and  $Z$  represents the compression factor of a mixture,

$$Z = \frac{PV}{RT}.$$

Calculation of hydrocarbon fugacities presupposes the solution of a system of four equations. Two of these are statements of the PRSV equation of state, Eqn. 4, for the “water-rich” phase and the “hydrocarbon-rich” phase, which establish the condition of mechanical stability of a mixture, or the equality of pressure in coexisting phases at isothermal conditions. The other two are statements of Eqn. 5 written in one case for water as a component and in the other for the hydrocarbon as a component in two coexisting phases, which establish the condition of chemical equilibrium of the mixture, or equality of the components’ fugacities in the coexisting “water-rich” and “hydrocarbon-rich” phases. As the solution of this system of equations one obtains compositions of two coexisting phases and their densities (or molar volumes, or compression factors); all other properties of interest can then be easily calculated.

### 3.3. The Parameterization of the PRSV Equation of State for Water-Hydrocarbon Mixtures

Parameters  $a_1$  and  $b_1$  for water and parameters  $a_2$  and  $b_2$  for hydrocarbons can be calculated from the critical properties and vapor pressure of pure compounds (see the Appendix A). However, the mixture-specific parameter,  $\tau$ , has to be evaluated from experimental results for the corresponding binary mixture. Its evaluation is possible from various sets of data: solubility of water in “hydrocarbon-rich” gaseous, liquid, or “fluid” phases, or from the values of the second cross (water-solute) virial coefficient,  $B_{12}(T)$ , in the latter case using the relation from Fernandez-Prini et al. (1992):

$$1 - \tau = \frac{RT}{(a_1 a_2)^{0.5}} \left[ \frac{b_1 + b_2}{2} - B_{12}(T) \right].$$

In agreement with the finding of Heidman et al. (1985) we found that estimates of  $\tau$  from compositions of liquid, “fluid” or gaseous phases are close, however, estimates of  $\tau$  from  $B_{12}(T)$  (given by Wormald and Lancaster (1988) for a number of aqueous hydrocarbons) are systematically higher (up to 0.08–0.16). The most probable reason is the known poor performance of the cubic equations of state for predicting second virial coefficients of pure polar substances and mixtures involv-

ing polar components. Therefore, to estimate values of the mixture-specific parameter  $\tau$  we employed data mainly on the compositions of  $L_2$  (“hydrocarbon-rich” liquid) and F (“hydrocarbon-rich fluid”) phases.

Literature data used to evaluate the mixture-specific parameter  $\tau$  are given in Tables 1–4. The optimal value of  $\tau$  was determined by a search of the minimum of the function

$$F = \Sigma \left( \frac{X_{w,\text{exp}} - X_{w,\text{calc}}}{\delta X_{w,\text{exp}}} \right)^2,$$

where  $X_{w,\text{exp}}$  and  $X_{w,\text{calc}}$  stand for the experimental and calculated values of the molar fraction of water in a “hydrocarbon-rich” phase;  $\delta X_{w,\text{exp}}$  is the expected uncertainty of the experimental  $X_w$  result. As a rule,  $\delta X_{w,\text{exp}}$  was set to 10% of the reported  $X_{w,\text{exp}}$  value. In a number of cases the discrepancies between data from different sources notably exceed 10%. To select the most reliable sets of data we employed the empirical finding of Economou et al. (1997) that the solubility of water in the hydrocarbons exhibits a negligible carbon number effect in homologous series. In addition, the solubility of water systematically increases from alkanes through alkenes to alkylbenzenes. Experimental results deviating from these regularities were given lower weights. Experimental points close to the UCEP of the phase diagram were not used in this procedure because of the known convergence problems for cubic equations of state around the critical points of the phase diagram. For 2-methylpentane (isohexane) there are no experimental  $X_w$  data at  $T > 298$  K, so, as a reasonable approximation, we used  $X_w$  data for  $n$ -hexane from Tsionopoulos and Wilson (1983). Similarly, we have used the high-temperature  $X_w$  data for  $m$ -xylene (Anderson and Prausnitz, 1986) as estimates of  $X_w$  in the “hydrocarbon-rich”  $L_2$  phase of the  $p$ -xylene-water mixture (*meta*- and *para*-xylenes, contrary to the *ortho*-isomer, have very similar physical properties). We believe that in most cases the evaluated  $\tau$  parameters have uncertainties within  $\pm 0.02$ . For  $n$ -butane we use the value of  $\tau$  evaluated by Carroll et al. (1997) who employed the PRSV equation of state in a careful consideration of all the relevant equilibria in the  $n$ -butane-water system.

Some values of  $\tau$  given in Tables 1–4 can be compared with literature estimates. For example, the value for the ethane-water system is equal to 0.52 as compared with 0.500 (Peng and Robinson, 1976b) and 0.525 (Carroll and Mather, 1997); for the  $n$ -octane-water system Table 1 gives  $\tau = 0.45$  compared with 0.48 (Peng and Robinson, 1976b) and 0.467 (Heidman et al., 1985); for the  $m$ -diethylbenzene-water binary  $\tau = 0.31$  compared with 0.300 (Economou et al., 1997), etc. Strictly speaking, these comparisons are not completely valid, because  $\tau$  from Tables 1–4 refer to the PRSV, and all other values to the original Peng-Robinson equation of state. Nevertheless, we expect that the difference between the values of  $\tau$  optimized for the PRSV and the PR equations of state will be small.

As one can see from data in Tables 1–4, the value of  $\tau$  depends mainly on a nature of a hydrocarbon and less on the carbon number inside a homologous series. In general  $\tau$  decreases from alkanes through cycloalkanes to alkenes and then to alkylbenzenes. In some sense the interaction parameter for a mixture reflects the “chemical” similarity of the components of that mixture. For a mixture of very similar compounds  $\tau$  will be

Table 1. Experimental data used for determination of  $\tau$  for various alkane-water systems.

Hydrocarbon	Reference	Equilibrium	Temperature range, K	Pressure range, MPa	N of points	Optimal $\tau$
Ethane C <sub>2</sub> H <sub>6</sub>	Coan and King (1971)	F + L <sub>1</sub>	298.2–373.2	2.3–3.6	18	0.52
	Anthony and McKetta (1967a)	F + L <sub>1</sub>	310.9–410.9	2.6–10.8	4	
	Anthony and McKetta (1967b)	F + L <sub>1</sub>	310.9–377.6	3.4–34.7	25	
	Danneil et al. (1967)	F + L <sub>1</sub>	473.2–573.2	20–100	9	
	Reamer et al. (1943)	F + L <sub>1</sub>	310.9–510.9	2.2–68.2	40	
Propane C <sub>3</sub> H <sub>8</sub>	Song and Kobayashi (1994)	G + L <sub>1</sub> + L <sub>2</sub>	282.0–299.7	0.62–0.9	4	0.53
	Kobayashi and Katz (1953)	G + L <sub>1</sub> + L <sub>2</sub>	287.8–367.7	0.74–4.2	16	
		L <sub>1</sub> + L <sub>2</sub>	310.9–360.9	5.6–19.3	13	
		F + L <sub>1</sub>	383.2–422.0	9.7–19.3	10	
Poetmann and Dean (1946)	G + L <sub>1</sub> + L <sub>2</sub>	288.8–359.3	0.8–3.8	9		
n-Butane C <sub>4</sub> H <sub>10</sub>	Gillespie and Wilson (1982)	G + L <sub>1</sub> + L <sub>2</sub>	311.5–423.4	0.12–2.1	3	0.54 <sup>a</sup>
n-Pentane C <sub>5</sub> H <sub>12</sub>		L <sub>1</sub> + L <sub>2</sub>	311.0–463.8	0.8–13.8	11	0.52
n-Hexane C <sub>6</sub> H <sub>14</sub>	Polak and Lu (1973)	F + L <sub>1</sub>	477.6–533.2	7.0–13.8	4	0.48
		L <sub>1</sub> + L <sub>2</sub>	273.2–298.2	0.1	2	
	Black et al. (1948)	L <sub>1</sub> + L <sub>2</sub>	278.7–298.2	0.1	3	
	Barrufet et al. (1996)	G + L <sub>1</sub> + L <sub>2</sub>	372.1–463.7	0.3–3.0	5	
	Brunner et al. (1993)	F + L <sub>1</sub>	573.2	20	1	
	Tsonopoulos and Wilson (1983)	G + L <sub>1</sub> + L <sub>2</sub>	310.9–473.2	0.1–3.5	7	
		L <sub>1</sub> + L <sub>2</sub>	473.2–493.2	3.6–78.5	19	
	Polak and Lu (1973)	L <sub>1</sub> + L <sub>2</sub>	273.2–298.2	0.1	2	
	Roddy and Coleman (1968)	L <sub>1</sub> + L <sub>2</sub>	298.2	0.1	1	
	Englin et al. (1965)	L <sub>1</sub> + L <sub>2</sub>	293.2–313.2	0.1	3	
Black et al. (1948)	L <sub>1</sub> + L <sub>2</sub>	293.2	0.1	1		
2-Methylpentane C <sub>6</sub> H <sub>14</sub>	Polak and Lu (1973)	L <sub>1</sub> + L <sub>2</sub>	273.2–298.2	0.1	2	0.49
	[Tsonopoulos and Wilson (1983) for n-hexane]	G + L <sub>1</sub> + L <sub>2</sub>	313–473	0.1–3.9	4	
n-Heptane C <sub>7</sub> H <sub>16</sub>	Polak and Lu (1973)	L <sub>1</sub> + L <sub>2</sub>	273.2–298.2	0.1	2	0.45
	O'Grady (1967)	F + L <sub>1</sub>	561.0–605.4	24.82	5	
	Englin et al. (1965)	L <sub>1</sub> + L <sub>2</sub>	273.2–313.2	0.1	6	
	Black et al. (1948)	L <sub>1</sub> + L <sub>2</sub>	283.2–298.2	0.1	3	
n-Octane C <sub>8</sub> H <sub>18</sub>	Rahman and Barrufet (1995)	G + L <sub>1</sub> + L <sub>2</sub>	366.5–449.8	0.12–1.3	5	0.45
	Heidman et al. (1985)	G + L <sub>1</sub> + L <sub>2</sub>	310.9–477.6	0.1–2.5	4	
	Skripka (1976)	L <sub>1</sub> + L <sub>2</sub>	498.2–538.2	3.5–78.5	26	
	Polak and Lu (1973)	L <sub>1</sub> + L <sub>2</sub>	273.2–298.2	0.1	2	
	Englin et al. (1965)	L <sub>1</sub> + L <sub>2</sub>	283.2–303.2	0.1	3	
	Black et al. (1948)	L <sub>1</sub> + L <sub>2</sub>	293.2	0.1	1	

<sup>a</sup>As determined by Carroll et al. (1997).

close to zero. So, qualitatively, the observed trend can be understood if the alkylbenzenes, which are more polarizable in water, are considered to be “more similar” to water than non-polar alkanes. Only for the propene-water system is the optimal

value of  $\tau$  out of the observed regularities. We believe that the experimental results of Li and McKetta (1963) on the solubility of water in liquid propene are in error. Indeed, in accordance with the finding of Economou et al. (1997), the solubilities of

Table 2. Experimental data used for determination of  $\tau$  for various alkene-water systems.

Hydrocarbon	Reference	Equilibrium	Temperature range, K	Pressure range, MPa	N of points	Optimal $\tau$
Ethene C <sub>2</sub> H <sub>4</sub>	Sanchez and Lentz (1973)	F + L <sub>1</sub>	439.2–573.2	10.0–94.5	12	0.35
	Anthony and McKetta (1967a)	F + L <sub>1</sub>	311.0–411.0	3.43–34.4	35	
	Diepen and Scheffer (1950)	F + L <sub>1</sub>	298.2	4–10	7	
Propene C <sub>3</sub> H <sub>6</sub>	Sanchez and Lentz (1973)	F + L <sub>1</sub>	441.2–603.2	12.6–97.0	16	0.48
	Li and McKetta (1963)	G + L <sub>1</sub> + L <sub>2</sub>	311.0–363.6	1.62–4.56	6	
		L <sub>1</sub> + L <sub>2</sub>	311.0–344.2	3.2–33.1	17	
		F + L <sub>1</sub>	377.6–411.0	7.2–34.0	17	
1-Butene C <sub>4</sub> H <sub>8</sub>	Wehe and McKetta (1961b)	G + L <sub>1</sub> + L <sub>2</sub>	310.9–410.9	0.43–3.85	6	0.37
	Leland et al. (1955)	G + L <sub>1</sub> + L <sub>2</sub>	310.9–410.9	0.44–3.87	4	
		L <sub>1</sub> + L <sub>2</sub>	310.9–410.9	13.8–69	20	
		F + L <sub>1</sub>	427.6	13.8–69	5	
		L <sub>1</sub> + L <sub>2</sub>	279.2–294.7	0.29–0.33	5	
1-Hexene C <sub>6</sub> H <sub>12</sub>	Economou et al. (1997)	G + L <sub>1</sub> + L <sub>2</sub>	310.9–475.3	0.2–3.9	4	0.41
	Irani and McHugh (1979)	F + L <sub>1</sub>	566.5	24.83	1	
1-Octene C <sub>8</sub> H <sub>16</sub>	Economou et al. (1997)	G + L <sub>1</sub> + L <sub>2</sub>	310.9–549.8	0.1–9.3	5	0.40

Table 3. Experimental data used for determination of  $\tau$  for various cycloalkane-water systems.

Hydrocarbon	Reference	Equilibrium	Temperature range, K	Pressure range, MPa	N of points	Optimal $\tau$
Cyclohexane C <sub>6</sub> H <sub>12</sub>	Tsonopoulos and Wilson (1983)	G + L <sub>1</sub> + L <sub>2</sub>	313.2–473.2	0.1–3.0	8	0.48
	Skripka (1976)	L <sub>1</sub> + L <sub>2</sub>	473–523.2	9.8–78.5	17	
	Goldman (1974)	L <sub>1</sub> + L <sub>2</sub>	283.2–313.2	0.1	7	
	Glaseo and Schultz (1972)	L <sub>1</sub> + L <sub>2</sub>	288.2–303.2	0.1	3	
	Roddy and Coleman (1968)	L <sub>1</sub> + L <sub>2</sub>	298.2	0.1	1	
	Rebert and Hayworth (1967)	G + L <sub>1</sub> + L <sub>2</sub>	516.4	6.58	1	
		F + L <sub>1</sub>	573.2–583.2	13.7–14.1	2	
		L <sub>1</sub> + L <sub>2</sub>	283.2–323.2	0.1	5	
	Tarassenkow and Poloshinzeva (1932)	L <sub>1</sub> + L <sub>2</sub>	283.2–326.2	0.1	6	
Ethylcyclohexane C <sub>8</sub> H <sub>16</sub>	Heidman et al. (1985)	G + L <sub>1</sub> + L <sub>2</sub>	310.9–552.8	0.1–8.8	6	0.48
n-Butylcyclohexane C <sub>10</sub> H <sub>20</sub>	Economou et al. (1997)	G + L <sub>1</sub> + L <sub>2</sub>	310.9–549.8	0.1–7.1	6	0.44

water in liquid 1-butene, 1-hexene and 1-octene are very similar, around  $(1.5\text{--}1.6) \cdot 10^{-3}$  in mole fraction at 311 K and moderate pressures (i.e. far from the UCEP for the corresponding systems), but equal to  $(0.8\text{--}0.9) \cdot 10^{-3}$  for the propene-water system at the same conditions. Such a low solubility is similar to the solubility of water in liquid propane, about  $(0.6\text{--}0.7) \cdot 10^{-3}$  at the same conditions. This hardly seems possible, because for other *n*-alkane-1-alkene pairs the solubility of water in the alkene is about twice the solubility of water in the alkane (all at 311 K and moderate pressures). So, we believe that  $\tau = 0.40$  is a more reasonable value for the propene-water binary, and this value was used in our treatment of data in the propene-water system. We expect that data from Tables 1–4 allow reasonable estimates of the interaction parameters for many hydrocarbon-water systems involving alkanes, cycloalkanes, alkenes or alkylbenzenes.

In accordance with observations of Peng and Robinson (1976b), Peng and Robinson (1980), Heidman et al. (1985), Carroll et al. (1997), and Economou et al. (1997), the solubility of water in “hydrocarbon-rich” phases can be accurately reproduced in the framework of the Peng-Robinson equation of state, or its PRSV variant, over a large temperature range, where  $X_w$  increases from 0.00n to 0.n. Typically the accuracy of predicted water solubilities are within 10–20% of the reported experimental values, which is often close to the scattering of data from different studies. Some experimental and calculated data on the solubility of water in the L<sub>2</sub> phase along G+L<sub>1</sub>+L<sub>2</sub> equilibria are shown in Figure 3 for three hydrocarbon-water systems.

### 3.4. Calculation of $K_H(T,P)$ from High-Temperature Phase Equilibria Data

To calculate the hydration constants for hydrocarbons we have collected experimental data from the literature on the compositions of the “water-rich” liquid L<sub>1</sub> and in a few cases “fluid” F<sub>1</sub> phases along the G+L<sub>1</sub>+L<sub>2</sub>, L<sub>1</sub>+L<sub>2</sub>, F+L<sub>1</sub> and F<sub>1</sub>+F<sub>2</sub> equilibria. As a rule, we did not include data points where the concentration of the hydrocarbon exceeds 1 mol · kg<sup>-1</sup> because of the potential problem that the activity coefficient of the solute in such concentrated aqueous solutions differs from one. This constraint places an upper temperature limit on many systems. Also we did not employ data within

5–15 K of the upper critical end point, UCEP, to escape potential divergence problems, and data at pressures in excess of 100 MPa because the Peng-Robinson equation of state was not tested at such high pressures. For G+L<sub>1</sub>+L<sub>2</sub> and L<sub>1</sub>+L<sub>2</sub> equilibria we used only data at temperatures in excess 370 K (for low-temperature results the standard Gibbs energy of hydration were calculated by combination of the standard Gibbs energies of solution and vaporization, see below). We did not include data from Kudchadker and McKetta (1961a,b); Kudchadker and McKetta (1962); or Guseva and Parnov (1963); Guseva and Parnov, (1964a,b) because of the consistent opinion in the later literature that they are not reliable (Heidman et al., 1985; Shaw, 1989).

For each of the T-P-m experimental points referenced in Tables 5–8 we calculated compositions and the compression factors of two coexisting phases (i.e. for G+L<sub>1</sub>+L<sub>2</sub> equilibria compositions of only the L<sub>1</sub> and L<sub>2</sub> phases were determined), and then used calculated compositions of the “hydrocarbon-rich” phase to evaluate the fugacity coefficient of the hydrocarbon. The value of  $K_H(T,P)$  was then calculated according to Eqn.(3). There are two main contributions to the uncertainty in the log  $K_H$  value obtained in this way (besides a difficult-to-estimate contribution due to neglecting the possible deviation from one of the activity coefficient of a solute and the negligible  $\pm 0.02$  uncertainty in the  $\tau$  value): the error in the calculated fugacity coefficient of the hydrocarbon and the experimental error in the solubility value. The only feasible method to estimate the latter contribution is to compare solubility values from different laboratories, if available. The contribution due to the error in the fugacity of the hydrocarbon depends strongly on temperature, or to be more precise, on the solubility of water in the “hydrocarbon-rich” phase. At low temperatures, where the solubility of water,  $X_w$ , is less than, say, 0.05, even a large error in the calculated values of  $X_w$  (up to 20%) will result in only a small change in the fugacity of a hydrocarbon (less than 2%). However, at high temperatures, where  $X_w$  may be as high as 0.5–0.6, a 20% error in the calculated solubility of water in the “hydrocarbon-rich” phase causes a large error in the calculated hydrocarbon fugacity (up to 25% and more). This means that even without the possible contribution due to errors in the reported solubility values the minimum uncertainty in the calculated log  $K_H(T,P)$  values at T > 500 K is about 0.1 log unit.

Table 4. Experimental data used for determination of  $\tau$  for various alkylbenzene-water systems.

Hydrocarbon	Reference	Equilibrium	Temperature range, K	Pressure range, MPa	N of points	Optimal $\tau$		
Benzene C <sub>6</sub> H <sub>6</sub>	Chandler et al. (1998)	G + L <sub>1</sub> + L <sub>2</sub>	473.2–536.7	2.7–8.8	4	0.28		
	Wormald and Slater (1996)	F + L <sub>1</sub>	548.2	9.5–17/2	2			
		L <sub>1</sub> + L <sub>2</sub>	503–521	16.4	2			
	Chen and Wagner (1994a)	F + L <sub>1</sub>	544–560	16.4	2			
		L <sub>1</sub> + L <sub>2</sub>	303.2–373.2	0.1–0.3	8			
	Anderson and Prausnitz (1986)	G + L <sub>1</sub> + L <sub>2</sub>	374.2–477.0	0.3–5.2	8			
	Tsonopoulos and Wilson (1983)	G + L <sub>1</sub> + L <sub>2</sub>	313.2–473.2	0.1–5.0	6			
	Skripka (1976)	L <sub>1</sub> + L <sub>2</sub>	498.2–523.2	9.8–78.5	10			
	Goldman (1974)	L <sub>1</sub> + L <sub>2</sub>	283.2–313.2	0.1	7			
	Karlsson (1973)	L <sub>1</sub> + L <sub>2</sub>	288.2–308.2	0.1	9			
	Polak and Lu (1973)	L <sub>1</sub> + L <sub>2</sub>	273.2–298.2	0.1	2			
	Roddy and Coleman (1968)	L <sub>1</sub> + L <sub>2</sub>	298.2	0.1	1			
	Moule and Thurston (1966)	L <sub>1</sub> + L <sub>2</sub>	282.6–322.6	0.1	9			
	Thompson and Snyder (1964)	L <sub>1</sub> + L <sub>2</sub>	311.0–477.6	6.9–34.5	12			
	Rebert and Kay (1959)	G + L <sub>1</sub> + L <sub>2</sub>	500.7–515.7	5.0–6.4	2			
	Pavia (1958)	L <sub>1</sub> + L <sub>2</sub>	283.4–338.2	0.1	7			
Toluene <sup>a</sup> C <sub>7</sub> H <sub>8</sub>	Staveley et al. (1943)	L <sub>1</sub> + L <sub>2</sub>	297.9–344.2	0.1	7	0.30		
	Tarassenkow and Poloshinzeva (1932)	L <sub>1</sub> + L <sub>2</sub>	278.2–346.2	0.1	9			
	Chandler et al. (1998)	G + L <sub>1</sub> + L <sub>2</sub>	473.2–523.2	2.5–5.8	2			
	Chen and Wagner (1994b)	L <sub>1</sub> + L <sub>2</sub>	523.2–548.2	17.2	2			
		L <sub>1</sub> + L <sub>2</sub>	303.2–373.2	0.1–0.2	8			
	Brunner et al. (1993)	F + L <sub>1</sub>	573.2	20.0	1			
	Stephenson (1992)	L <sub>1</sub> + L <sub>2</sub>	273.2–363.4	0.1–0.2	9			
	Anderson and Prausnitz (1986)	G + L <sub>1</sub> + L <sub>2</sub>	372.5–473.5	0.16–2.4	6			
	Polak and Lu (1973)	L <sub>1</sub> + L <sub>2</sub>	273.2–298.2	0.1	2			
	Glasoe and Schultz (1972)	L <sub>1</sub> + L <sub>2</sub>	288.2–303.2	0.1	3			
	Englin et al. (1972)	L <sub>1</sub> + L <sub>2</sub>	273.2–323.2	0.1	6			
	Tarassenkow and Poloshinzeva (1932)	L <sub>1</sub> + L <sub>2</sub>	283.7–366.2	0.1	10			
	Ethylbenzene C <sub>8</sub> H <sub>10</sub>	Chen and Wagner (1994c)	L <sub>1</sub> + L <sub>2</sub>	303.2–373.2	0.1–0.2		8	0.30
		Heidman et al. (1985)	G + L <sub>1</sub> + L <sub>2</sub>	311.0–536.1	0.1–6.5		5	
		Polak and Lu (1973)	L <sub>1</sub> + L <sub>2</sub>	273.2–298.2	0.1		2	
		Englin et al. (1972)	L <sub>1</sub> + L <sub>2</sub>	283.2–303.2	0.1		3	
<i>m</i> -Xylene <sup>b</sup> C <sub>8</sub> H <sub>10</sub>	Jones and Monk (1963)	L <sub>1</sub> + L <sub>2</sub>	298.2–308.2	0.1	3	0.30		
	Anderson and Prausnitz (1986)	G + L <sub>1</sub> + L <sub>2</sub>	373.6–473.3	0.15–2.0	6			
	Chernoglazova and Simulin (1976)	L <sub>1</sub> + L <sub>2</sub>	293.2–343.2	0.1	3			
	Polak and Lu (1973)	L <sub>1</sub> + L <sub>2</sub>	273.2–298.2	0.1	2			
<i>p</i> -Xylene <sup>c</sup>	Englin et al. (1972)	L <sub>1</sub> + L <sub>2</sub>	283.2–303.2	0.1	3	0.31		
	Chen and Wagner (1994c)	L <sub>1</sub> + L <sub>2</sub>	303.2–373.2	0.1–0.2	8			
	[Anderson and Prausnitz (1986) as for <i>m</i> -xylene]	G + L <sub>1</sub> + L <sub>2</sub>	373.6–473.3	0.15–2.0	6			
	Polak and Lu (1973)	L <sub>1</sub> + L <sub>2</sub>	298.2	0.1	1			
<i>m</i> -Diethylbenzene <sup>d</sup> C <sub>10</sub> H <sub>14</sub>	Economou et al. (1997)	G + L <sub>1</sub> + L <sub>2</sub>	310.9–549.8	0.1–7.1	6	0.31		
<i>p</i> -Diisopropylbenzene <sup>e</sup> C <sub>12</sub> H <sub>18</sub>	Economou et al. (1997)	G + L <sub>1</sub> + L <sub>2</sub>	310.9–549.8	0.1–6.5	6	0.30		

IUPAC names: <sup>a</sup> methylbenzene; <sup>b</sup> 1,3-dimethylbenzene; <sup>c</sup> 1,4-dimethylbenzene; <sup>d</sup> 1,3-diethylbenzene; <sup>e</sup> 1,4-bis(1-methylethyl)benzene.

As a result of the data treatment described above we accumulated a large array of hydration constants at different temperatures and pressures. As a first step in the data reduction, we extrapolated isothermal  $K_H(T, P)$  to the saturated water vapor pressure,  $P_w$ , by means of:

$$\ln K_H(T, P_w) = \ln K_H(T, P) + \frac{1}{RT} \int_{P_w}^P V_2^0(T, P) dP, \quad (6)$$

where  $V_2^0(T, P)$  stands for the infinite dilution partial molar volume of a solute. For temperatures below 473 K this was accomplished through a least-squares method employing the simplified relation:

$$\ln K_H(T, P_w) = \ln K_H(T, P) + \frac{V_2^0(P - P_w)}{RT},$$

i.e., assuming that at these temperatures one can neglect the pressure dependence of the infinite dilution partial molar volume of a solute (the Krichevskii-Kazarnovskii approximation). At higher temperatures we estimated  $V_2^0(T, P)$  at different temperatures and pressures using the procedures proposed in Plyasunov et al. (2000), for which the expected error is within 10–15%. As a result, we have values of the hydration constants along the water vapor saturation curve for all hydrocarbons under consideration. In cases where it was possible, we have also selected hydration constants for hydrocarbons at pressure  $P = 50$  MPa and different temperatures. For benzene, toluene, *n*-hexane and cyclohexane there are direct measurements of  $V_2^0(T, P)$  from V. Majer's laboratory (Degrange, 1998), which we used to calculate  $K_H(T, P)$  at  $P = 50$  MPa for these solutes by means of Eqn. 6.

High-temperature values of hydration constants evaluated in

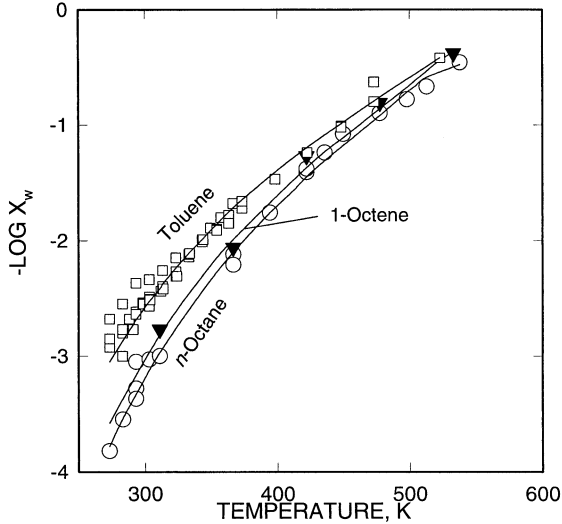


Fig. 3. Experimental values (symbols) of water concentrations in the “hydrocarbon-rich” phases along the G+L<sub>1</sub>+L<sub>2</sub> equilibrium for binary mixtures involving water, and either toluene, or 1-octene, or n-octane, together with values correlated with the PRSV EoS (solid curves).

this study were combined with the available literature data referring to temperatures below 373 K at 0.1 MPa (these results are marked as “ $K_H$ ” in Tables 5–8). In addition, numerous literature data on the solubility of liquid hydrocarbons in water at  $T < 373$  K (marked in Tables 5–8 as “L<sub>1</sub>+L<sub>2</sub>” equilibria) were converted to the values of  $K_H(T,P)$ . This was done as described in Plyasunov and Shock (2000): a reaction  $\text{HC}(g) \rightleftharpoons \text{HC}(aq)$  is represented by the sum of two reactions:  $\text{HC}(g) \rightleftharpoons \text{HC}(l)$  and  $\text{HC}(l) \rightleftharpoons \text{HC}(aq)$ , where HC stands for the generalized hydrocarbon, and the subscripts  $g, l, aq$  designate the gaseous, liquid, and aqueous state of the hydrocarbon, respectively. A proper thermodynamic treatment results in the following relation:

$$\Delta_h G^0 = \Delta_{sol} G^0 - \Delta_{vap} G^0 \approx -RT \ln m_{sat} + RT \ln \frac{\psi P_s}{P^\phi}, \quad (7)$$

where  $\Delta G^0$  designates the change of the standard Gibbs energy in some process; subscripts  $h, sol,$  and  $vap$  define the processes of hydration, solution and vaporization, respectively;  $m_{sat}$  stands for the saturation molality of a hydrocarbon in the  $L_1$  phase;  $P_s$  designates the saturation pressure of a pure hydrocarbon at temperature  $T$ ;  $P^\phi$  represents the reference pressure of the ideal gas state, 0.1 MPa;  $\psi$  stands for the fugacity coefficient of a pure hydrocarbon in the gaseous state at temperature  $T$  and pressure  $P_s$  (calculated from the virial EoS truncated at the second virial coefficient,  $B_{HC}$ , of the pure hydrocarbon:

$$\ln \psi = \frac{B_{HC} P_s}{RT}.$$

The sign “ $\approx$ ” is needed because Eqn. 7 neglects the solubility of water in the coexisting “hydrocarbon-rich” phase and the deviation from one of the activity coefficient of a hydrocarbon in the saturated aqueous solution. Errors due to both simplifications make negligible contributions to the values of the

standard Gibbs energy of hydration at  $T < 373$  K. The corresponding equation for the hydration constant is given by

$$\ln K_H(T,P) \approx \ln m_{sat} - \ln \frac{\psi P_s}{P^\phi}.$$

#### 4. TEMPERATURE DEPENDENCE OF $K_H(T,P)$ IN THE SUBCRITICAL REGION

A description of the temperature dependence of hydration constants is plagued by two main problems: a small number of  $K_H$  data points at elevated temperatures, and their low accuracy at  $T > 500$  K. In light of these difficulties we decided to reduce the dimension of the fitting task (i.e. the number of adjustable parameters) to the possible minimum. To treat hydration constants referring to the saturated vapor water pressure we selected the equation proposed by Harvey (1996) for the Henry’s law constants. His equation, converted to the definitions and concentration units accepted in this study, see Eqn.(1), can be written as:

$$\ln K_H(T, P_w) = -\ln P_w + \frac{A}{T} + \frac{B}{T} (T_c - T)^{n_1} + C \exp\left(1 - \frac{T}{T_c}\right) \cdot T^{n_2} + \ln\left(\frac{1000}{M_w}\right), \quad (8)$$

where  $A, B,$  and  $C$  represent three fitting parameters;  $n_1 = 0.355$  and  $n_2 = -0.41$  designate two universal constants of the Harvey (1996) model;  $T_c = 647.14$  K stands for the critical temperature of pure water; and  $P_w$  represents the temperature-dependent saturated water vapor pressure. Among the various proposed three-parameters models, the Harvey equation is the fortunate one in terms of accuracy. It can be used for  $K_H$  interpolation in the temperature range between 273.15 K and close to the critical point of pure water. More importantly for the purposes of the present study it can be applied for reliable extrapolation of  $K_H$  data towards higher temperatures. Harvey (1996) showed for nitrogen that the fit based on constants at  $T < 450$  K allows an accurate prediction of  $\log K_H$  at temperatures up to 630 K. We checked and confirmed this claim using methane (a non-polar solute) and ammonia (a polar solute) as examples.

To reduce the number of fitting parameters in the Harvey equation we employed two additional constraints, namely the fixed numerical values of the Gibbs energy of hydration,  $\Delta_h G^0$ , and the enthalpy of hydration,  $\Delta_h H^0$ , of a hydrocarbon, both at 298.15 K and 0.1 MPa. The required values of  $\Delta_h G^0$  (298.15, 0.1) and  $\Delta_h H^0$ (298.15, 0.1) are taken from Plyasunov and Shock (2000), or estimated, where necessary, using the group contributions values from the same source. The analytical statements for the temperature dependence of  $\Delta_h G^0$  and  $\Delta_h H^0$ , consistent with the Harvey (1996) model, are given by:

$$\frac{\Delta_h G^0}{R} = -T \ln K_H = T \ln P_w - A - B(T_c - T)^{n_1} - C \exp\left(1 - \frac{T}{T_c}\right) T^{n_2+1} - T \ln\left(\frac{1000}{M_w}\right) \quad (9)$$

and

Table 5. Experimental data used for determination of  $\Delta_h G^0$  for various alkanes.

Hydrocarbon	Reference	Equilibrium	Temperature range, K	Pressure range, MPa	N of points	
Ethane C <sub>2</sub> H <sub>6</sub>	Dhima et al. (1998)	F + L <sub>1</sub>	344.3	50	1	
	Fernandez-Prini and Crovetto (1989)	K <sub>H</sub>	348.2–473.2	0.1–1.6	6	
	Cosgrove and Walkley (1981)	K <sub>H</sub>	283.2–303.2	0.1	3	
	Rettich et al. (1981)	K <sub>H</sub>	273.2–333.2	0.1	7	
	Danneil et al. (1967)	F + L <sub>1</sub>	573.2–623.2	30–100	3	
Propane C <sub>3</sub> H <sub>8</sub>	Culberson and McKetta (1950)	F + L <sub>1</sub>	310.9–444.3	50	5	
	Hayduk (1986)	K <sub>H</sub>	273.2–343.2	0.1	8	
	De Loos et al. (1980)	F <sub>1</sub> + F <sub>2</sub>	623.2	28.7–95	3	
	Wehe and McKetta (1961a)	G + L <sub>1</sub>	344.3	0.77–1.25	7	
	Azarnoosh and McKetta (1958)	G + L <sub>1</sub>	288.7–344.3	0.10–2.66	45	
		F + L <sub>1</sub>	377.6–410.9	0.26–3.53	26	
	Kobayashi and Katz (1953)	G + L <sub>1</sub> + L <sub>2</sub>	285.3–360.9	0.50–3.8	5	
n-Butane C <sub>4</sub> H <sub>10</sub>		L <sub>1</sub> + L <sub>2</sub>	285.4–360.9	3.0–19.2	19	
		F + L <sub>1</sub>	383.2–422.0	1.5–19.2	20	
	Dhima et al. (1998)	L <sub>1</sub> + L <sub>2</sub>	344.3	50	1	
	Carroll et al. (1997)	K <sub>H</sub>	273.2–523.2	0.1–4.0	10	
	Yiling et al. (1991)	F <sub>1</sub> + L <sub>1</sub>	618	41.9	1	
	Hayduk (1986)	K <sub>H</sub>	273.2–353.2	0.1	9	
	Danneil et al. (1967)	F <sub>1</sub> + F <sub>2</sub>	628	59.0–72.5	2	
	Reamer et al. (1952)	L <sub>1</sub> + L <sub>2</sub>	310.9–410.9	50	3	
	n-Pentane C <sub>5</sub> H <sub>12</sub>	Gillespie and Wilson (1982)	F + L <sub>1</sub>	444.3–510.9	50	4
			G + L <sub>1</sub> + L <sub>2</sub>	311.5–423.4	0.12–2.1	3
		L <sub>1</sub> + L <sub>2</sub>	311.0–463.8	0.8–13.8	6	
		F + L <sub>1</sub>	477.6–533.2	7.0–13.8	15	
Jönsson et al. (1982)		K <sub>H</sub>	288.2–308.2	0.1	4	
Price (1976)		L <sub>1</sub> + L <sub>2</sub>	313.3–422.7	0.1–2.1	6	
Polak and Lu (1973)		L <sub>1</sub> + L <sub>2</sub>	273.2	0.1	1	
Nelson and De Ligny (1968)		L <sub>1</sub> + L <sub>2</sub>	277.2–303.2	0.1	4	
Connolly (1966)		F + L <sub>1</sub>	278.7–298.2	15–70	12	
n-Hexane C <sub>6</sub> H <sub>14</sub>		Barrufet et al. (1996)	G + L <sub>1</sub> + L <sub>2</sub>	373.2–463.7	0.3–3.0	5
		Brunner et al. (1993)	F + L <sub>1</sub>	573.2	20	1
		Bittrich et al. (1983)	L <sub>1</sub> + L <sub>2</sub>	313.2–333.2	0.1	2
		Tsonopoulos and Wilson (1983)	G + L <sub>1</sub> + L <sub>2</sub>	313.2–473.2	0.1–3.5	7
		Jönsson et al. (1982)	K <sub>H</sub>	288.2–308.2	0.1	4
		Price (1976)	L <sub>1</sub> + L <sub>2</sub>	313.0–425.0	0.1–1.3	9
	Polak and Lu (1973)	L <sub>1</sub> + L <sub>2</sub>	273.2	0.1	1	
	Nelson and De Ligny (1968)	L <sub>1</sub> + L <sub>2</sub>	277.2–328.2	0.1	5	
	Price (1976)	L <sub>1</sub> + L <sub>2</sub>	313.3–422.7	0.1–1.4	6	
	Polak and Lu (1973)	L <sub>1</sub> + L <sub>2</sub>	273.2	0.1	1	
2-Methylpentane C <sub>6</sub> H <sub>14</sub>	O'Connellly (1966)	F + L <sub>1</sub>	573.2–603.2	15.4–70.0	11	
	n-Heptane C <sub>7</sub> H <sub>16</sub>	Jönsson et al. (1982)	K <sub>H</sub>	288.2–308.2	0.1	4
		Price (1976)	L <sub>1</sub> + L <sub>2</sub>	313.3–423.6	0.1–0.9	6
Polak and Lu (1973)		L <sub>1</sub> + L <sub>2</sub>	273.2	0.1	1	
n-Octane C <sub>8</sub> H <sub>18</sub>	Nelson and De Ligny (1968)	L <sub>1</sub> + L <sub>2</sub>	277.2–318.2	0.1	4	
	O'Grady (1967)	F + L <sub>1</sub>	561.0–605.4	24.82	5	
	O'Connellly (1966)	F + L <sub>1</sub>	568.2–605.4	17.0–70.0	14	
	Rahman and Barrufet (1995)	G + L <sub>1</sub> + L <sub>2</sub>	394.3–449.9	0.3–1.3	4	
	Burriss and MacInture (1985)	L <sub>1</sub> + L <sub>2</sub>	293.2–343.2	0.1	3	
n-Octane C <sub>8</sub> H <sub>18</sub>	Heidman et al. (1985)	G + L <sub>1</sub> + L <sub>2</sub>	310.9–536.1	0.1–7.03	5	
		F + L <sub>1</sub>	552.8	8.86	1	
	Jönsson et al. (1982)	K <sub>H</sub>	288.2–308.2	0.1	4	
	Price (1976)	L <sub>1</sub> + L <sub>2</sub>	313.3–422.7	0.1–0.7	6	
	Polak and Lu (1973)	L <sub>1</sub> + L <sub>2</sub>	273.2	0.1	1	
	Nelson and De Ligny (1968)	L <sub>1</sub> + L <sub>2</sub>	278.2–318.2	0.1	2	

$$\frac{\Delta_h H^0}{R} = -T^2 \left( \frac{\partial}{\partial T} \left[ \frac{\Delta_h G^0}{RT} \right] \right)_p = -T^2 \left( \frac{\partial \ln P_w}{\partial T} \right)_p \quad \ln(P_w/\text{bar}) = A_w + \frac{B_w}{T + C_w}, \quad (11)$$

$$- A - B(T_c - T^{n_1-1})\{T_c + T(n_1 - 1)\}$$

$$- C \exp\left(1 - \frac{T}{T_c}\right) T^{n_2-1} \left\{ \frac{T}{T_c} - n_2 \right\} \quad (10)$$

As an analytical approximation for the temperature dependence of the water vapor pressure we employed the Antoine equation:

where the numerical values of the fitting parameters  $A_w$ ,  $B_w$ , and  $C_w$  were determined by the least-squares method using  $P_w$  values generated from the international formulation (Saul and Wagner, 1987) for the vapor pressure of water between 273.15 and 643.15 K:  $A_w = 11.866 \pm 0.028$ ;  $B_w = -3945.3 \pm 21.0$ ;  $C_w = -40.503 \pm 0.934$ . Equation 11 describes the recom-

Table 6. Experimental data used for determination of  $\Delta_h G^0$  for various alkenes.

Hydrocarbon	Reference	Equilibrium	Temperature range, K	Pressure range, MPa	N of points
Propene C <sub>3</sub> H <sub>6</sub>	Serra et al. (1998)	K <sub>H</sub>	293.2–323.2	0.1	6
	Sanchez and Lentz (1973)	F + L <sub>1</sub>	441.2–603.2	12.6–94.0	15
	Li and McKetta (1963)	G + L <sub>1</sub> + L <sub>2</sub>	311.0–344.3	1.62–3.23	2
		L <sub>1</sub> + L <sub>2</sub>	311.0–344.2	3.2–32.2	15
		F + L <sub>1</sub>	377.6–411.0	8.7–32.2	14
1-Butene C <sub>4</sub> H <sub>8</sub>	Wehe and McKetta (1961b)	G + L <sub>1</sub> + L <sub>2</sub>	310.9–377.6	0.43–2.07	3
	Leland et al. (1955)	G + L <sub>1</sub> + L <sub>2</sub>	310.9–410.9	0.44–3.87	4
		L <sub>1</sub> + L <sub>2</sub>	310.9–410.9	13.8–69	39
		F + L <sub>1</sub>	427.6	13.8–69	9
1-Hexene C <sub>6</sub> H <sub>12</sub>	Economou et al. (1997)	G + L <sub>1</sub> + L <sub>2</sub>	310.9–494.3	0.2–5.4	5
	Irani and McHugh (1979)	F + L <sub>1</sub>	566.5	24.83	1
1-Octene C <sub>8</sub> H <sub>16</sub>	Economou et al. (1997)	G + L <sub>1</sub> + L <sub>2</sub>	310.9–549.8	0.1–9.3	6

mended  $P_w$  data with an accuracy of about 1% or better between 273.15 and 623.15 K and better than 3% at 643.15 K, which is sufficient for the purposes of this study.

From the three parameters of the Harvey model only the  $B$  parameter was determined by the least-squares fit of hydration constants. Parameters  $A$  and  $C$  are unambiguously defined by the numerical values of  $\Delta_h G^0(298.15, 0.1)$ ,  $\Delta_h H^0(298.15, 0.1)$  and the  $B$  parameter. For convenience we give in Table 9 (upper line for each solute) all the corresponding values.

Hydration constants referring to  $P = 50$  MPa,  $K_H(T, 50$  MPa), were fitted using the following equation:

$$\ln K_H(T, 50 \text{ MPa}) = -\frac{\Delta_h G^0(T_r, 50 \text{ MPa})}{RT_r} + \frac{\Delta_h H^0(T_r, 50 \text{ MPa})}{R} \cdot \left( \frac{1}{T_r} - \frac{1}{T} \right) + D \left[ \frac{T_r}{T} - 1 + \ln \left( \frac{T}{T_r} \right) \right], \quad (12)$$

where  $T_r = 298.15$  K is the reference temperature,  $\Delta_h G^0(T_r, 50$  MPa) and  $\Delta_h H^0(T_r, 50$  MPa) stand for the Gibbs energy of hydration and enthalpy of hydration, respectively, at  $T = T_r$  and  $P = 50$  MPa. The necessary values of  $\Delta_h G^0(T_r, 50$  MPa) and  $\Delta_h H^0(T_r, 50$  MPa) were evaluated as follows:

$$\Delta_h G^0(T_r, 50 \text{ MPa}) = \Delta_h G^0(T_r, 0.1 \text{ MPa}) + \int_{0.1}^{50} V_2^0 dP \approx \Delta_h G^0(T_r, 0.1 \text{ MPa}) + 50V_2^0(T_r, 0.1 \text{ MPa})$$

and

$$\Delta_h H^0(T_r, 50 \text{ MPa}) = \Delta_h H^0(T_r, 0.1 \text{ MPa}) + \int_{0.1}^{50} \left( V_2^0 - T \left( \frac{\partial V_2^0}{\partial T} \right)_P \right) dP \approx \Delta_h H^0(T_r, 0.1 \text{ MPa}) + 50V_2^0(T_r, 0.1 \text{ MPa}),$$

where values of the infinite dilution Gibbs energy of hydration, enthalpy of hydration, and partial molar volume of solutes at 298.15 K and 0.1 MPa were taken from Plyasunov and Shock (2000) or estimated using group contribution values from the same source. The physico-chemical basis of Eqn. 12 is the assumption that the heat capacity of hydration of a solute at  $P = 50$  MPa is constant. As this assumption certainly becomes unsatisfactory at near-critical conditions, we suggest that Eqn. 12 is not to be used at  $T > 523$ – $573$  K. The parameters of Eqn. 12 are given in Table 9 in *italics*.

In Figure 4a–d we show “experimental” (different symbols) and fitted (solid curves) values of hydration constants for a number of hydrocarbons, together with the predictions (dotted curves) of the revised HKF-model (Shock and Helgeson, 1990). In general, the HKF-predictions of  $K_H$  are satisfactory for aqueous hydrocarbons, typically being within 0.1 log unit at temperatures up to 473 K and 0.2–0.3 log unit up to 623 K.

## 5. RETRIEVAL OF GROUP CONTRIBUTION VALUES AT ELEVATED TEMPERATURES

It is known that plots of the Gibbs energy of hydration at 298.15 K for homologous series show linear dependences on

Table 7. Experimental data used for determination of  $\Delta_h G^0$  for various cycloalkanes.

Hydrocarbon	Reference	Equilibrium	Temperature range, K	Pressure range, MPa	N of points
Cyclohexane C <sub>6</sub> H <sub>12</sub>	Dewulf et al. (1999)	K <sub>H</sub>	275.2–291.2	0.1	4
	Kolb et al. (1992)	K <sub>H</sub>	313.2–353.2	0.1	4
	Ashworth et al. (1988)	K <sub>H</sub>	283.2–303.2	0.1	4
	Tsonopoulos and Wilson (1983)	G + L <sub>1</sub> + L <sub>2</sub>	313.2–482.2	0.1–3.6	6
	Tucker et al. (1981)	K <sub>H</sub>	308.2–315.7	0.1	2
	Rebert and Hyaworth (1967)	F + L <sub>1</sub>	563.2–573.2	13.9–18.9	2
Ethylcyclohexane C <sub>8</sub> H <sub>16</sub>	Heidman et al. (1997)	G + L <sub>1</sub> + L <sub>2</sub>	311.5–552.8	0.1–8.8	6
n-Butylcyclohexane C <sub>10</sub> H <sub>20</sub>	Economou et al. (1997)	G + L <sub>1</sub> + L <sub>2</sub>	366.5–549.8	0.1–7.1	5

Table 8. Experimental data used for determination of  $\Delta_{\mu}G^0$  for various alkylbenzenes.

Hydrocarbon	Reference	Equilibrium	Temperature range, K	Pressure range, MPa	N of points	
Benzene C <sub>6</sub> H <sub>6</sub>	Chandler et al. (1998)	G + L <sub>1</sub> + L <sub>2</sub>	473.2–523.2	2.7–7.2	3	
		L <sub>1</sub> + L <sub>2</sub>	523.2	17.2	1	
		F + L <sub>1</sub>	548.2	17.2	1	
	Peng and Wan (1997)	K <sub>H</sub>	288.2–313.2	0.1	6	
	Zou et al. (1997)	L <sub>1</sub> + L <sub>2</sub>	303.2–313.2	0.1	3	
	Alaee et al. (1996)	K <sub>H</sub>	277.2–308.1	0.1	7	
	Dewulf et al. (1995)	K <sub>H</sub>	275.2–291.4	0.1	4	
	Chen and Wagner (1994a)	L <sub>1</sub> + L <sub>2</sub>	303.2–373.2	0.1–0.3	8	
	Khalifaoui and Newsham (1994)	K <sub>H</sub>	293.2–303.2	0.1	4	
	Stevenson et al. (1994)	L <sub>1</sub> + L <sub>2</sub>	472.5–523.2	3.5–7.7	3	
	Perlinger et al. (1993)	K <sub>H</sub>	283.2–303.2	0.1	4	
	Robbins et al. (1993)	K <sub>H</sub>	303.2–323.2	0.1	4	
	Cooling et al. (1992)	K <sub>H</sub>	293.2–323.2	0.1	4	
	Ashworth et al. (1988)	K <sub>H</sub>	283.2–303.2	0.1	5	
	Anderson and Prausnitz (1986)	G + L <sub>1</sub> + L <sub>2</sub>	374.2–477.0	0.3–3.2	8	
	Bittrich et al. (1983)	L <sub>1</sub> + L <sub>2</sub>	313.2–333.0	0.1	2	
	May et al. (1983)	L <sub>1</sub> + L <sub>2</sub>	273.4–343.0	0.1	8	
	Tsonopoulos and Wilson (1983)	G + L <sub>1</sub> + L <sub>2</sub>	423.2–473.2	1.1–3.0	2	
	Dutta-Chudhury et al. (1982)	L <sub>1</sub> + L <sub>2</sub>	281.2–306.2	0.1	3	
	Sanemasa et al. (1982)	K <sub>H</sub>	278.2–318.2	0.1	4	
	Tucker et al. (1981)	K <sub>H</sub>	288.2–318.2	0.1	6	
	Green and Frank (1979)	K <sub>H</sub>	283.2–303.2	0.1	7	
	Price (1976)	L <sub>1</sub> + L <sub>2</sub>	328.5–347.9	0.1	2	
	Brown et al. (1974)	L <sub>1</sub> + L <sub>2</sub>	277.7–293.3	0.1	9	
	Bradley et al. (1973)	L <sub>1</sub> + L <sub>2</sub>	318.2–328.2	0.1	2	
	Polak and Lu (1973)	L <sub>1</sub> + L <sub>2</sub>	273.2	0.1	1	
	Connolly (1966)	F + L <sub>1</sub>	533.2	10–80	4	
	Thompson and Snyder (1964)	L <sub>1</sub> + L <sub>2</sub>	311.0–477.6	6.9–34.5	8	
	Franks et al. (1963)	L <sub>1</sub> + L <sub>2</sub>	290.2–336.2	5.0–6.4	12	
	Alexander (1959)	L <sub>1</sub> + L <sub>2</sub>	274.0–338.6	0.1	11	
	Bohon and Claussen (1951)	L <sub>1</sub> + L <sub>2</sub>	278.4–316.0	0.1	6	
	Arnold et al. (1958)	L <sub>1</sub> + L <sub>2</sub>	278.1–342.2	0.1	20	
	Toluene C <sub>7</sub> H <sub>8</sub>	Dewulf et al. (1999)	K <sub>H</sub>	275.2–291.2	0.1	4
Chandler et al. (1998)		G + L <sub>1</sub> + L <sub>2</sub>	473.2–548.2	2.5–8.6	3	
		L <sub>1</sub> + L <sub>2</sub>	523.2–548.2	17.2	2	
Peng and Wan (1997)		K <sub>H</sub>	288.2–308.2	0.1	6	
Dewulf et al. (1995)		K <sub>H</sub>	275.2–291.4	0.1	4	
Chen and Wagner (1994b)		L <sub>1</sub> + L <sub>2</sub>	303.2–373.2	0.1–0.2	8	
Brunner et al. (1993)		F + L <sub>1</sub>	573.2	20.0	1	
Ettre et al. (1993)		K <sub>H</sub>	318.2–353.2	0.1	4	
Perlinger et al. (1993)		K <sub>H</sub>	283.2–303.2	0.1	4	
Robbins et al. (1993)		K <sub>H</sub>	303.2–323.2	0.1	4	
Stephenson (1992)		L <sub>1</sub> + L <sub>2</sub>	273.2–363.4	0.1–0.2	11	
Smith et al. (1989)		L <sub>1</sub> + L <sub>2</sub>	278.2–318.2	0.1	4	
Ashworth et al. (1988)		K <sub>H</sub>	283.2–303.2	0.1	4	
Anderson and Prausnitz (1986)		G + L <sub>1</sub> + L <sub>2</sub>	372.5–473.5	0.16–2.4	6	
Bittrich et al. (1983)		L <sub>1</sub> + L <sub>2</sub>	313.2–333.2	0.1	2	
Dutta-Choudhury et al. (1982)		L <sub>1</sub> + L <sub>2</sub>	283.2–306.2	0.1	2	
Sanemasa et al. (1982)		K <sub>H</sub>	288.2–318.2	0.1	3	
Brown and Wasik (1974)		L <sub>1</sub> + L <sub>2</sub>	277.7–293.3	0.1	9	
Bradley et al. (1973)		L <sub>1</sub> + L <sub>2</sub>	318.2–328.2	0.1	2	
Polak and Lu (1973)		L <sub>1</sub> + L <sub>2</sub>	273.2	0.1	1	
O'Connell (1966)		F + L <sub>1</sub>	553.2	15–60	4	
Bohon and Claussen (1951)		L <sub>1</sub> + L <sub>2</sub>	273.6–318.5	0.1	11	
Ethylbenzene C <sub>8</sub> H <sub>10</sub>		Dewulf et al. (1995)	K <sub>H</sub>	275.2–291.4	0.1	4
		Chen and Wagner (1994c)	L <sub>1</sub> + L <sub>2</sub>	303.2–373.2	0.1–0.2	8
		Perlinger et al. (1993)	K <sub>H</sub>	283.2–303.2	0.1	4
		Robbins et al. (1993)	K <sub>H</sub>	303.2–313.2	0.1	2
		Ashworth et al. (1988)	K <sub>H</sub>	283.2–303.2	0.1	4
		Owens et al. (1986)	L <sub>1</sub> + L <sub>2</sub>	283.2–318.2	0.1	15
		Heidman et al. (1985)	G + L <sub>1</sub> + L <sub>2</sub>	311.0–552.8	0.1–8.6	6
		Sanemasa et al. (1982)	K <sub>H</sub>	288.2–318.2	0.1	3
		Brown and Wasik (1974)	L <sub>1</sub> + L <sub>2</sub>	277.7–293.3	0.1	9
		Polak and Lu (1973)	L <sub>1</sub> + L <sub>2</sub>	273.2	0.1	1
		Bohon and Claussen (1951)	L <sub>1</sub> + L <sub>2</sub>	273.6–316.0	0.1	6
	<i>m</i> -Xylene C <sub>8</sub> H <sub>10</sub>	Dewulf et al. (1995)	K <sub>H</sub>	275.2–291.4	0.1	4
		Robbins et al. (1993)	K <sub>H</sub>	303.2–323.2	0.1	4
		Ashworth et al. (1988)	K <sub>H</sub>	283.2–303.2	0.1	4

(Continued)

Table 8. (Continued).

Hydrocarbon	Reference	Equilibrium	Temperature range, K	Pressure range, MPa	N of points
<i>p</i> -Xylene C <sub>8</sub> H <sub>10</sub>	Anderson and Prausnitz (1986)	G + L <sub>1</sub> + L <sub>2</sub>	373.6–473.4	0.2–2.0	6
	Sanemasa et al. (1982)	K <sub>H</sub>	288.2–318.2	0.1	3
	Chernoglazova and Simulin (1976)	L <sub>1</sub> + L <sub>2</sub>	293.2–343.2	0.1	3
	Polak and Lu (1973)	L <sub>1</sub> + L <sub>2</sub>	273.2	0.1	1
	Pryor and Jentoft (1961)	L <sub>1</sub> + L <sub>2</sub>	344–540	0.1–6.8	7
	Bohon and Claussen (1951)	L <sub>1</sub> + L <sub>2</sub>	273.6–312.8	0.1	7
	Dewulf et al. (1995)	K <sub>H</sub>	275.2–291.4	0.1	4
	Knauss and Copenhaver (1995)	L <sub>1</sub> + L <sub>2</sub>	325–422	0.1–0.69	11
	Chen and Wagner (1994c)	L <sub>1</sub> + L <sub>2</sub>	303.2–373.2	0.1–0.2	8
	Hansen et al. (1993)	K <sub>H</sub>	300.2–319.1	0.1	3
	Ashworth et al. (1998)	K <sub>H</sub>	283.2–303.2	0.1	4
	Sanemasa et al. (1982)	K <sub>H</sub>	288.2–318.2	0.1	3
	Polak and Lu (1973)	L <sub>1</sub> + L <sub>2</sub>	273.2	0.1	1
	Pryor and Jentoft (1961)	L <sub>1</sub> + L <sub>2</sub>	360.4–556	0.1–8.8	5
	Bohon and Claussen (1951)	L <sub>1</sub> + L <sub>2</sub>	273.6–316.0	0.1	10
<i>m</i> -Diethylbenzene C <sub>10</sub> H <sub>14</sub>	Economou et al. (1997)	G + L <sub>1</sub> + L <sub>2</sub>	310.9–549.8	0.1–7.1	6
<i>p</i> -Diisopropylbenzene C <sub>12</sub> H <sub>18</sub>	Economou et al. (1997)	G + L <sub>1</sub> + L <sub>2</sub>	310.9–549.8	0.1–6.1	6

the carbon number except for the lowest members of series. McAuliffe (1966) presented extensive evidence of these relations based on his solubility measurements for a large number of hydrocarbons. These empirical facts form the basis for group additivity methods used to describe available data and predict the thermodynamic properties of organic compounds not studied experimentally. In this respect, one of the major results of our study is a confirmation of the applicability of the group contribution method to the Gibbs energy of hydration of hydrocarbons at elevated temperatures. In Figure 5a we show the fitted values of  $\log K_H$  for normal alkanes versus temperature along the saturation curve of pure water. The numbers above the curves denote the numbers of methylene, CH<sub>2</sub>, groups in each of the compounds: zero for ethane, C<sub>2</sub>H<sub>6</sub> or CH<sub>3</sub>-CH<sub>3</sub>; three for *n*-pentane, C<sub>5</sub>H<sub>12</sub> or CH<sub>3</sub>-(CH<sub>2</sub>)<sub>3</sub>-CH<sub>3</sub>; six for *n*-octane, C<sub>8</sub>H<sub>18</sub> or CH<sub>3</sub>-(CH<sub>2</sub>)<sub>6</sub>-CH<sub>3</sub>; etc. It is apparent in Figure 5(a) that the values of  $\log K_H$  vary in a regular fashion with the increase of the number of the CH<sub>2</sub>-groups in the compounds. The simplest explanation of this fact is the assumption that each of the alkanes can be considered as built-up from the CH<sub>3</sub> and CH<sub>2</sub> groups, which have constant energetic contributions (at fixed T and P) independently of the nature of a particular normal alkane. In Figure 5b we show the values of the Gibbs energy of hydration for *n*-alkanes (circles) and 1-alkenes (triangles) at 523.15 K and  $P_{sat}$  versus the number of CH<sub>2</sub> groups in the compounds (note that in *n*-octane there are six CH<sub>2</sub> groups and in 1-octene there are five CH<sub>2</sub> groups). The two groups of data have nearly identical slopes confirming that the energetic contribution of the CH<sub>2</sub> group is very similar in both *n*-alkanes and 1-alkenes (remember that at 523 K an uncertainty of  $\pm 0.05$  log units in  $K_H$  corresponds to an uncertainty  $\pm 0.5$  kJ · mol<sup>-1</sup> in the value of the Gibbs energy of hydration,  $\Delta_h G^0$ ).

The following groups are present in the compounds considered in this study: CH<sub>3</sub>, CH<sub>2</sub>, and CH for aliphatic hydrocarbons; c-CH<sub>2</sub> and c-CH in cycloalkanes (for example, ethylcyclohexane consists of five c-CH<sub>2</sub> groups, one c-CH group as well as one CH<sub>2</sub> and one CH<sub>3</sub> group); CH<sub>ar</sub> and C<sub>ar</sub> in alkylbenzenes (or aromatic hydrocarbons, where, for example, toluene is composed of five CH<sub>ar</sub> groups, one C<sub>ar</sub>, and one CH<sub>3</sub>

group). Compounds with double bonds are supposed to be composed of the C = C group and a number of attached H groups, i.e. ethene, C<sub>2</sub>H<sub>4</sub>, is considered as the sum of one C = C group and four H groups, and propene, C<sub>3</sub>H<sub>6</sub>, for example, is considered to be built-up from one C = C group and three H groups in addition to one CH<sub>3</sub> group. This selection of groups was first proposed by Cabani et al. (1981), and was accepted in our treatment of the thermodynamic properties of many aqueous hydrocarbons at 298.15 K and 0.1 MPa (Plyasunov and Shock, 2000).

The group contributions were retrieved in the following order: first we treated the numerous and probably most reliable data for *n*-alkanes to extract values for the CH<sub>3</sub> and CH<sub>2</sub> groups at different temperatures by the least-squares method. In further retrieval the values obtained from the *n*-alkanes were fixed. Values for the CH group were evaluated from  $\Delta_h G^0$  of only one compound, 2-methylpentane (isohexane). A treatment of data for propene, 1-butene, 1-hexene and 1-octene gave four estimates for a linear combination of C = C + 3H groups, which were averaged. Results for ethene (for ethene the values of hydration constants at  $P = P_{sat}$  were taken from Harvey et al. (1991), and recalculated to  $P = 50$  MPa using equations and parameters from Plyasunov et al., 2000) allow evaluation of the sum of C = C + 4H groups, which can be combined with the results for of C = C + 3H groups to separate contributions of C = C and H groups. Numerical values for the CH<sub>ar</sub> group were obtained from the Gibbs energy of hydration for benzene. Evaluations for the C<sub>ar</sub> group were accepted as averaged from corresponding values obtained from  $\Delta_h G^0$  for toluene, ethylbenzene, *m*- and *p*-xylenes, 1,3-diethylbenzene and *m*-diisopropylbenzene, which turned out to be in reasonable agreement. Values of c-CH<sub>2</sub> were obtained from  $\Delta_h G^0$  for cyclohexane, and results for ethylcyclohexane and *n*-butylcyclohexane were used to evaluate values for the c-CH group.

We expect that the uncertainty in estimates of the contribution of the CH<sub>2</sub> group is within 0.10 kJ · mol<sup>-1</sup> up to 473 K, and gradually increases to 0.25 kJ · mol<sup>-1</sup> at 573 K. The expected uncertainties of the CH<sub>3</sub>, CH<sub>ar</sub>, and C<sub>ar</sub> groups are within 0.15–0.20 kJ · mol<sup>-1</sup> up to 473 K increasing to 0.40 kJ · mol<sup>-1</sup> at 573 K. For compounds with a double bond only

Table 9. The parameters of the Harvey model, Eqn. 8, for the description of the temperature dependence of hydration constant along the saturation curve of water, and Eqn. 12 at P = 50 MPa (second line, in *italics*).

Compound	$\Delta_h G^0$ <sup>a,b</sup>	$\Delta_h H^0$ <sup>a,b</sup>	A <sup>c</sup>	$\frac{B^d}{D^f}$	C <sup>e</sup>	T <sub>max</sub>
Alkanes						
Ethane, C <sub>2</sub> H <sub>6</sub>	15.57 <i>18.15</i>	-19.40 <i>-16.83</i>	13325	-319.5 ± 6.9 28.3	-300.7	623 573
Propane, C <sub>3</sub> H <sub>8</sub>	16.09	-22.90	16491	-330.2 ± 32.0	-369.1	623
n-Butane, C <sub>4</sub> H <sub>10</sub>	16.58 <i>20.73</i>	-25.90 <i>-21.76</i>	18905	-271.4 ± 27.7 38.7	-423.8	628 511
n-Pentane, C <sub>5</sub> H <sub>12</sub>	17.40	-28.65	21486	-247.4 ± 14.2	-481.9	623
n-Hexane, C <sub>6</sub> H <sub>14</sub>	18.12 <i>23.81</i>	-31.60 <i>-25.79</i>	24084	-224.5 ± 39.2 44.0	-539.8	573 573
2-Methylpentane, C <sub>6</sub> H <sub>14</sub>	18.51 <i>24.17</i>	-33.28 <i>-27.56</i>	24981	-183.4 ± 24.3 45.7	-565.6	603 573
n-Heptane, C <sub>7</sub> H <sub>16</sub>	18.85	-36.17	27763	-176.6 ± 52.9	-623.8	623
n-Octane, C <sub>8</sub> H <sub>18</sub>	19.57	-39.92	31623	-168.7 ± 26.4	-704.9	553
Alkenes						
Ethene, C <sub>2</sub> H <sub>4</sub>	<i>15.58</i>	<i>-14.17</i>		21.9		573
Propene, C <sub>3</sub> H <sub>6</sub>	12.85 <i>15.85</i>	-21.60 <i>-18.60</i>	13146	-318.6 ± 17.4 27.6	-290.6	603 573
1-Butene, C <sub>4</sub> H <sub>8</sub>	13.81 <i>17.36</i>	-24.19 <i>-28.30</i>	15877	-301.7 ± 112.4 32.4	-350.9	428 428
1-Hexene, C <sub>6</sub> H <sub>12</sub>	15.26	-31.71	22877	-257.8 ± 52.7	-503.1	567
1-Octene, C <sub>8</sub> H <sub>16</sub>	16.71	-39.23	29301	-192.5 ± 58.4	-647.1	550
Cycloalkanes						
Cyclohexane, C <sub>6</sub> H <sub>12</sub>	13.00 <i>17.80</i>	-33.10 <i>-28.30</i>	20839	-201.7 ± 19.2 38.5	-465.5	573 573
Ethylcyclohexane, C <sub>8</sub> H <sub>16</sub>	15.45	-42.82	32173	-213.2 ± 59.9	-698.8	553
n-Butylcyclohexane, C <sub>10</sub> H <sub>20</sub>	16.90	-50.34	38479	-143.4 ± 160.0	-841.1	550
Alkylbenzenes						
Benzene, C <sub>6</sub> H <sub>6</sub>	4.29 <i>8.44</i>	-31.70 <i>-27.55</i>	14397	-273.3 ± 16.5 28.0	-302.4	533 533
Toluene, C <sub>7</sub> H <sub>8</sub>	4.52 <i>9.38</i>	-36.30 <i>-31.38</i>	17373	-217.6 ± 30.3 32.4	-372.2	553 553
Ethylbenzene, C <sub>8</sub> H <sub>10</sub>	5.24	-39.26	20135	-196.1 ± 130.1	-433.3	553
<i>m</i> -Xylene, C <sub>8</sub> H <sub>10</sub>	4.94	-38.71	19874	-214.6 ± 41.7	-424.3	540
<i>p</i> -Xylene, C <sub>8</sub> H <sub>10</sub>	4.94	-38.71	19218	-190.0 ± 32.0	-415.0	556
<i>m</i> -Diethylbenzene, C <sub>8</sub> H <sub>16</sub>	6.39	-46.23	25808	-130.9 ± 45.4	-561.3	550
<i>p</i> -Diisopropylbenzene, C <sub>12</sub> H <sub>18</sub>	8.63	-55.49	33015	-18.0 ± 53.1	-730.2	550

<sup>a</sup> 298.15 K, 0.1 MPa (upper line) or 50 MPa (second line, in *italics*).

<sup>b</sup> kJ · mol<sup>-1</sup>.

<sup>c</sup> K.

<sup>d</sup> K<sup>0.645</sup>.

<sup>e</sup> K<sup>0.41</sup>.

<sup>f</sup> Dimensionless.

linear combinations of groups are meaningful, namely C = C + 3H for 1-alkenes and C = C + 4H for ethene, and their uncertainties are believed to be within 0.20 kJ · mol<sup>-1</sup> up to 373 K, 0.30 kJ · mol<sup>-1</sup> up to 473 K, and 0.60 kJ · mol<sup>-1</sup> up to 573 K. The same uncertainties are expected for the c-CH<sub>2</sub> group. Results for the CH and c-CH groups are based on a few experimental studies (at T > 373 K on only one data source) and their uncertainties can not be evaluated without additional experimental measurements. All these estimates of uncertainties refer to the saturation water vapor pressure, uncertainties at P = 50 MPa are expected to be larger.

Following the approach taken in our study of the values of group contributions for thermodynamic properties of hydration of hydrocarbons at 298.15 K and 0.1 MPa (Plyasunov and Shock, 2000) we assume that the Gibbs energy of hydration of a compound can be written as:

$$\Delta_h G^0 = Y_0 + \sum_i n_i Y_i \quad (13)$$

where n<sub>i</sub> stands for the number of times the *i*-th Y<sub>i</sub> group is present in the compound, and the term Y<sub>0</sub> is equal the Gibbs energy of hydration of an imaginable compound without any groups at all, i.e. for a material point. The value of Y<sub>0</sub> is given by theory (see, for instance, Pierotti, 1976) as:

$$Y_0 = RT \ln \frac{RT}{V_1^0} - RT \ln \frac{1000}{M_w}, \quad (14)$$

where V<sub>1</sub><sup>0</sup> stands for the molar volume of pure water at the specified T and P; M<sub>w</sub> represents the molar mass of water; the first term is the so-called "standard state conversion term"; the second term is needed when the molality concentration scale is employed. So, Y<sub>0</sub> can be calculated from the PVT properties of pure water independently of any experimental data for hydrocarbons.

The temperature dependence of group contribution values can be represented by an empirical polynomial expression:

$$Y = a_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4, \quad (15)$$

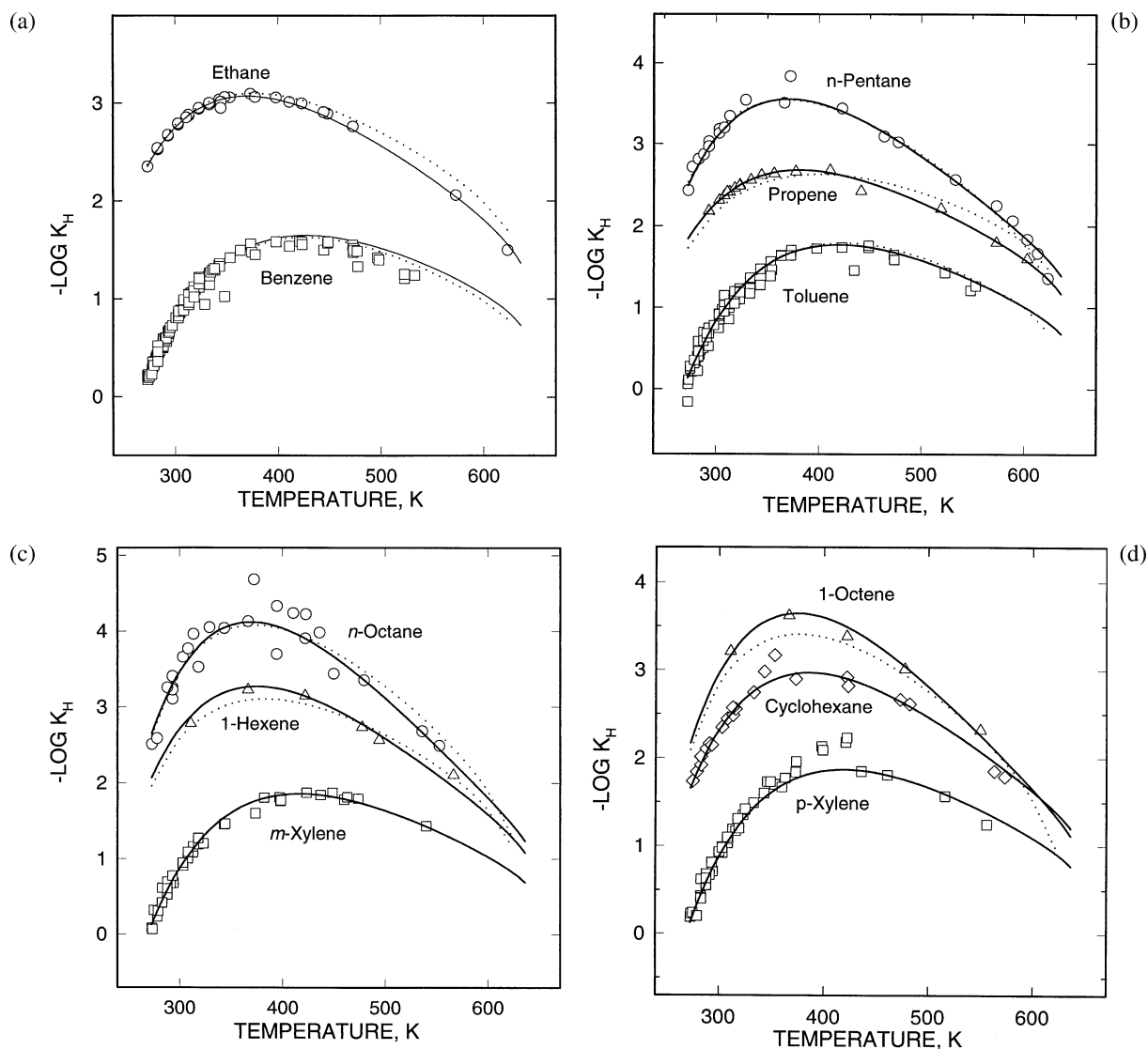


Fig. 4. Experimental (symbols) and correlated (solid curves) values of the hydration constants for a number of hydrocarbons at different temperatures along the vapor-liquid saturation curve of pure water. The HKF predictions are shown as dotted curves.

where the number of terms was chosen to provide an accurate reproduction of results at different temperatures evaluated in this study. Values of the parameters  $a_j$  at both the saturated water pressure and  $P = 50$  MPa are given in Table 10. Resulting values of  $\Delta_h G^0$  for various groups at the saturation water vapor pressure are shown in Figure 6. We expect that these numerical values of group contributions allow reasonably accurate estimations of the Gibbs energy of hydration, or Henry's law constants, for hundreds of alkanes, 1-alkenes, cycloalkanes (derivatives of cyclohexane) and alkylbenzenes at temperatures up to 623 K and pressures up to 50 MPa.

## 6. DISCUSSION

This work is concerned with the evaluation of the hydration constants for aqueous hydrocarbons from the results of phase

equilibria studies at elevated temperatures and pressures. Experimental data for more than twenty water-hydrocarbon systems were uniformly correlated within the framework of the Peng-Robinson-Stryjek-Vera equation of state in combination with simple mixing rules. In this way we determined hydration constants (or the Gibbs energy of hydration) for many hydrocarbons up to 623 K and 50 MPa. Results for homologous series show regular change with increasing carbon number confirming the applicability of the group contribution approach to the Gibbs energy of hydration of hydrocarbons at elevated temperatures. The temperature dependence of the Gibbs energy of hydration was determined for the following groups that constitute the hydrocarbons under consideration in this study:  $\text{CH}_3$ ,  $\text{CH}_2$ , and  $\text{CH}$  in aliphatic hydrocarbons;  $\text{C}=\text{C}$  and  $\text{H}$  for alkenes;  $\text{c-CH}_2$  and  $\text{c-CH}$  in cycloalkanes;  $\text{CH}_{\text{ar}}$  and  $\text{C}_{\text{ar}}$  in alkylbenzenes (or aromatic hydrocarbons).

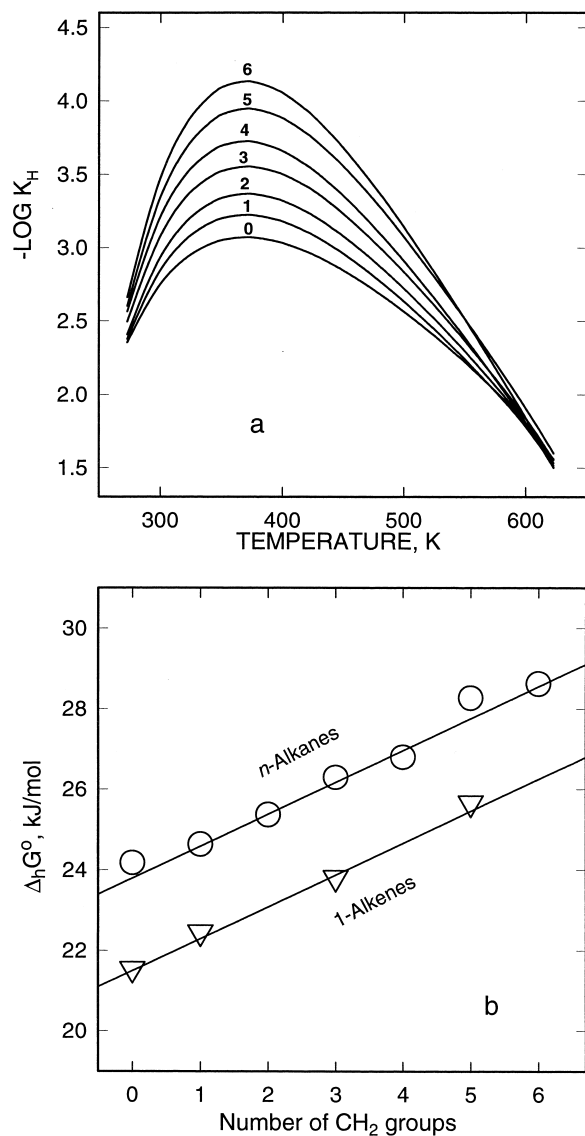


Fig. 5. (a) Calculated values of the hydration constants for normal alkanes as a function of temperature at saturated water vapor pressure labeled by the numbers of methylene groups (for example 6 for *n*-octane). (b) Calculated values of the Gibbs energy of hydration for normal alkanes and 1-alkenes at 523 K and saturated water vapor pressure.

How could these results be employed for geochemical applications?

First, many computer codes used for thermodynamic modeling typically require values of the standard partial molar Gibbs energy of a solute,  $G_2^0$ , as input information. Results of the present work supply values of the standard Gibbs energy of hydration of a solute,  $\Delta_h G^0(T, P)$ . The following relation provides the connection between these properties:

$$\Delta_h G^0(T, P) = G_2^0(T, P) - G_{ig}^0(T), \quad (16)$$

where  $G_{ig}^0(T)$  stands for the Gibbs energy of a hydrocarbon in the ideal gas state at any temperature,  $T$ , and the ideal gas

Table 10. The parameters of Eqn. 15 for the description of the temperature dependence of the Gibbs energy of hydration, in  $\text{kJ} \cdot \text{mol}^{-1}$ , of the groups considered in this work at the saturation water vapor pressure, and at  $P = 50 \text{ MPa}$  (second line, in *italics*).

Group	$a_0$	$a_1 \cdot 10^1$	$a_2 \cdot 10^4$	$a_3 \cdot 10^7$	$a_4 \cdot 10^{10}$	$T_{\text{max}}$
$Y_0$	-10.701	1.2487	-3.6084	6.3377	-4.1598	623
	<i>-0.756</i>	<i>0.215</i>	<i>0.364</i>	<i>-0.336</i>		573
$\text{CH}_3$	-48.817	3.8899	-10.356	12.750	-6.6081	623
	<i>-25.716</i>	<i>1.7430</i>	<i>-2.7070</i>	<i>1.0377</i>		573
$\text{CH}_2$	-13.685	0.9309	-1.8375	1.1218		623
	<i>-8.542</i>	<i>0.5886</i>	<i>-0.9980</i>	<i>0.4856</i>		573
$\text{CH}$	8.150	-0.5297	0.6562			623
	<i>5.476</i>	<i>-0.3781</i>	<i>0.4790</i>			573
$\text{C} = \text{C}$	12.827	-1.2411	1.5659			623
	<i>6.768</i>	<i>-0.8484</i>	<i>0.8864</i>			573
$\text{H}$	-11.170	0.7981	-0.9817			623
	<i>-9.287</i>	<i>0.7046</i>	<i>-0.7959</i>			573
$\text{CH}_{\text{ar}}$	-8.133	0.3854	-0.4479			623
	<i>-8.125</i>	<i>0.4152</i>	<i>-0.4725</i>			573
$\text{C}_{\text{ar}}$	6.152	-0.5323	0.6577			623
	<i>5.196</i>	<i>-0.4791</i>	<i>0.5943</i>			573
<i>c</i> - $\text{CH}_2$	-16.779	1.0595	-1.8623	0.9474		623
	<i>-10.235</i>	<i>0.5965</i>	<i>-0.6754</i>			573
<i>c</i> - $\text{CH}$	-15.401	0.9946	-2.0866	1.2240		623

reference pressure, 0.1 MPa. The values of  $G_2^0(T, P)$  for the selected groups are calculated in Appendix B.

Second, we suggest that the results of this work can be used for calculating distributions of species in aqueous solutions, which are unsaturated with respect to liquid or "fluid" hydrocarbon. If calculations involving hydrocarbon phases are to be performed at temperatures in excess of approximately 450 K one should consult Figure 2 to determine the nature of the expected phase equilibria and "hydrocarbon-rich" phases, so that modeling topologically impossible relations or compositions can be avoided. A special problem is the reliable evaluation of the chemical potential of a hydrocarbon in naturally-

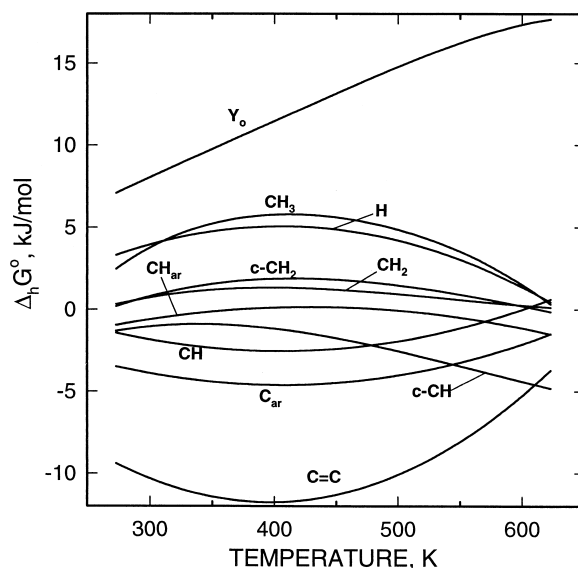


Fig. 6. The temperature dependence of the group contributions to the Gibbs energy of hydration at saturated water vapor pressure.

occurring "hydrocarbon-rich" phases due to their multicomponent character, and particularly the solubility of water in "hydrocarbon" phases.

Another possible application of the results of this study is for planning and design of experimental investigations of thermodynamic properties of organic compounds in high-temperature aqueous solutions. Rigorous thermodynamic interpretations of results from phase equilibria studies ("solubility" determinations) at temperatures above 500–550 K are not easy due to high mutual solubilities, which make it difficult to evaluate accurately the chemical potentials of organic compounds in coexisting phases. An approach based on studies of reactions ("equilibrium constants") in dilute homogeneous solutions unsaturated with respect to an "organic-rich" phase is a better alternative at  $T > 500$  K (see: Seewald, 1994). Finally, heat capacity and density determinations of dilute solutions of organic compounds at elevated temperatures should have the highest priority.

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#### REFERENCES

- Alaee M., Whittall R. M., and Strachan W. M. J. (1996) The effect of water temperature and composition on Henry's law constants for various PAH's. *Chemosphere* **32**, 1153–1163.
- Alexander D. M. (1959) The solubility of benzene in water. *J. Phys. Chem.* **63**, 1021–1022.
- Alwani Z. and Schneider G. (1967) Druckeinfluss auf die Entmischung flüssiger Systeme. VI. Phasengleichgewichte und kritische Erscheinungen im System Benzol-H<sub>2</sub>O zwischen 250 und 368°C bis 3700 bar. *Ber. Bunsenges. Phys. Chem.* **71**, 633–638.
- Amend J. P. and Helgeson H. C. (1997) Group additivity equations of state for calculating the standard molal thermodynamic properties of aqueous organic species at elevated temperatures and pressures. *Geochim. Cosmochim. Acta* **61**, 11–46.
- Anderko A. (1991) Phase equilibria in aqueous systems from an equation of state based on the chemical approach. *Fluid Phase Equil.* **65**, 89–110.
- Anderson F. E. and Prausnitz J. M. (1986) Mutual solubilities and vapor pressures for binary and ternary aqueous systems containing benzene, toluene, m-xylene, thiophene and pyridine in the region 100–200°C. *Fluid Phase Equil.* **32**, 63–76.
- Anthony R. G. and McKetta J. J. (1967a) Phase equilibrium in the ethylene-water system. *J. Chem. Eng. Data* **12**, 17–20.
- Anthony R. G. and McKetta J. J. (1967b) Phase equilibrium in the ethylene-ethane-water system. *J. Chem. Eng. Data* **12**, 21–28.
- Arnold D. S., Plank C. A., Ericson E. E., and Pike F. P. (1958) Solubility of benzene in water. *Chem. Eng. Data Ser.* **3**, 253–256.
- Ashworth R. A., Howe G. B., Mullins M. E., and Rogers T. N. (1988) Air-water partitioning coefficients of organics in dilute aqueous solutions. *J. Hazard. Mat.* **18**, 25–36.
- Azarnooosh A. and McKetta J. J. (1958) The solubility of propane in water. *Petrol. Refin.* **37**, No.11, 275–278.
- Barrufet M. A., Liu K., Rahman S., and Wu C. (1996) Simultaneous vapor-liquid-liquid equilibria and phase molar densities of a quaternary system of propane + pentane + octane + water. *J. Chem. Eng. Data* **41**, 918–922.
- Bittrich H.-J., Fahl A., and Hartwig F. (1983) Zur Löslichkeitsbeeinflussung von Kohlenwasserstoffen in Wasser. II. Der Einfluss von quaternären Ammoniumsalzen. *Z. phys. Chem. (Leipzig)* **264**, 891–895.
- Black C., Joris G. G., and Taylor H. S. (1948) The solubility of water in hydrocarbons. *J. Chem. Phys.* **16**, 537–543.
- Bohon R. L. and Claussen W. F. (1951) The solubility of aromatic hydrocarbons in water. *J. Amer. Chem. Soc.* **73**, 1571–1578.
- Boublik T., Fried V., and Hala E. (1984) The vapour pressures of pure substances. Elsevier.
- Bradley R. S., Dew M. J., and Munro D. C. (1973) The solubility of benzene and toluene in water and aqueous salt solutions under pressure. *High Temp.-High Press.* **5**, 169–176.
- Brown R. L. and Wasik S. P. (1974) A method of measuring the solubilities of hydrocarbons in aqueous solutions. *J. Res. NBS* **78A**, 453–460.
- Brunner E. (1990) Fluid mixtures at high pressures. IX. Phase separation and critical phenomena in 23 (n-alkane + water) mixtures. *J. Chem. Thermodyn.* **22**, 335–353.
- Brunner G., Steffen A., and Dohrn R. (1993) High pressure liquid-liquid equilibria in ternary systems containing water, benzene, toluene, n-hexane and n-hexadecane. *Fluid Phase Equil.* **82**, 165–172.
- Burris D. R. and MacIntyre W. G. (1985) Water solubility behavior of binary hydrocarbon mixtures. *Environ. Toxicol. Chem.* **4**, 371–377.
- Cabani S., Gianni P., Mollica V., and Lepori L. (1981) Group contributions to the thermodynamic properties of non-ionic organic solutes in dilute aqueous solution. *J. Solut. Chem.* **10**, 563–595.
- Carroll J. J. and Mather A. E. (1997) A model for the solubility of light hydrocarbons in water and aqueous solutions of alkanolamines. *Chem. Eng. Sci.* **52**, 545–552.
- Carroll J. J., Jou F.-Y., and Mather A. E. (1997) Fluid phase equilibria in the system n-butane + water. *Fluid Phase Equil.* **140**, 157–169.
- Chandler K., Eason B., Liotta C. L., and Eckert C. A. (1998) Phase equilibria for binary aqueous systems from a near-critical water reaction apparatus. *Ind. Eng. Chem. Res.* **37**, 3515–3518.
- Chen H. and Wagner J. (1994a) An apparatus and procedure for measuring mutual solubilities of hydrocarbons + water: benzene + water from 303 to 373 K. *J. Chem. Eng. Data* **39**, 470–474.
- Chen H. and Wagner J. (1994b) An efficient and reliable gas chromatographic method for measuring liquid-liquid mutual solubilities in alkylbenzene + water mixtures: toluene + water from 303 to 373 K. *J. Chem. Eng. Data* **39**, 475–479.
- Chen H. and Wagner J. (1994c) Mutual solubilities of alkylbenzene + water systems at temperatures from 303 to 373 K: ethylbenzene, p-xylene, 1,3,5-trimethylbenzene, and butylbenzene. *J. Chem. Eng. Data* **39**, 679–684.
- Chernoglazova F. S. and Simulin Yu. N. (1976) Mutual solubility in the system m-xylene-water. *Zh. Fiz. Khim.* **50**, 809 (in Russian).
- Coan C. R. and King A. D. (1971) Solubility of water in compressed carbon dioxide, nitrous oxide, and ethane. Evidence for hydration of carbon dioxide and nitrous oxide in the gas phase. *J. Amer. Chem. Soc.* **93**, 1857–1862.
- Connolly J. F. (1966) Solubility of hydrocarbons in water near the critical solution temperature. *J. Chem. Eng. Data* **11**, 13–16.
- Cooling M. R., Khalfouli B., and Newsham D. M. T. (1992) Phase equilibria in very dilute mixtures of water and unsaturated chlorinated hydrocarbons and of water and benzene. *Fluid Phase Equil.* **81**, 217–229.
- Cosgrove B. A. and Walkley J. (1981) Solubilities of gases in H<sub>2</sub>O and <sup>2</sup>H<sub>2</sub>O. *J. Chromatogr.* **216**, 161–167.
- Cox J. D., Wagman D. D., and Medvedev V. A. (1989) CODATA Key Values for Thermodynamics, HPC.
- Culberson O. L. and McKetta J. J., Jr. (1950) Phase equilibria in hydrocarbon-water systems. II. The solubility of ethane in water at pressures to 10,000 psi. *Petroleum Trans., AIME* **189**, 319–322.
- Danneil A., Tödheide K., and Franck E. U. (1967) Verdampfungs-gleichgewichte und kritische Kurven in den Systemen Äthan/Wasser und n-Butan/Wasser bei hohen Drücken. *Chemie Ing. Techn.* **30**, 816–822.
- Daubert T. E. and Danner R. P. (1996) Physical and thermodynamic properties of pure chemicals. Data compilation. Parts I–V. Taylor and Francis.
- Degrange S. (1998) Nouvelle procedure de determination simultanee des proprietes enthalpiques et volumiques des systemes fluides: Application a l'etude des solutions aqueuses d'hydrocarbures jusqu'au domaine critique de l'eau. Ph.D. dissertation, Univ. Blaise Pascal, France.

- De Loos Th. W., Pender W. G., and Lichtenthaler R. N. (1982) Phase equilibria and critical phenomena in fluid (n-hexane + water) at high pressures and temperatures. *J. Chem. Thermodyn.* **14**, 83–91.
- De Loos Th. W., Wijen A. J. M., and Diepen G. A. M. (1980) Phase equilibria and critical phenomena in fluid (propane + water) at high pressures and temperatures. *J. Chem. Thermodyn.* **12**, 193–204.
- Dewulf J., Drijvers D., and Langenhove H. V. (1995) Measurement of Henry's law constants as function of temperature and salinity for the low temperature range. *Atmosph. Chem.* **29**, 232–331.
- Dewulf J., Langenhove H. V., and Everaert P. (1999) Determination of Henry's law coefficients by combination of the equilibrium partitioning in closed systems and solid-phase microextraction technique. *J. Chromatogr. A* **830**, 353–363.
- Dhima A., de Hemptine J.-C., and Moracchini G. (1998) Solubility of light hydrocarbons and their mixtures in pure water under high pressure. *Fluid Phase Equil.* **145**, 129–150.
- Diepen G. A. M. and Scheffer F. E. C. (1950) The solubility of water in supercritical ethene. *Rec. Trav. Chim.* **69**, 604–609.
- Domalski E. S. and Hearing E. D. (1996) Heat capacities and entropies of organic compounds in the condensed phase. Volume III. *J. Phys. Chem. Ref. Data* **25**, 1–402.
- Domalski E. S. and Hearing E. D. (1993) Estimation of the thermodynamic properties of C-H-N-O-S-halogen compounds at 298.15. *J. Phys. Chem. Ref. Data* **22**, 805–1159.
- Dutta-Choudhury M. K., Miljevic N., and Van Hook W. A. (1982) Isotope effects in aqueous systems. 13. The hydrophobic interaction. Some thermodynamic properties of benzene/water and toluene/water solutions and their isotope effects. *J. Phys. Chem.* **86**, 1711–1721.
- Economou I. G. and Donohue M. D. (1992) Equation of state with multiple associating sites for water and water-hydrocarbon mixtures. *Ind. Eng. Chem. Res.* **31**, 2388–2394.
- Economou I. G., Heidman J. L., Tsonopoulos C., and Wilson G. M. (1997) Mutual solubilities of hydrocarbons and water: III. 1-Hexene, 1-octene, C<sub>10</sub>-C<sub>12</sub> hydrocarbons. *AIChE J.* **43**, 535–546.
- Englin B. A., Plate A. F., Tugolukov V. M., and Pryanishnikova M. A. (1965) Solubility of water in individual hydrocarbons. *Khimiya i Tekhnologiya Topliv i Masel* **10**, 42–46 (in Russian).
- Ettre L. S., Welter C., and Kolb B. (1993) Determination of gas-liquid partition coefficients by automatic equilibrium headspace-gas chromatography utilizing the phase ratio variation method. *Chromatographia* **35**, 73–84.
- Fernandez-Prini R. and Crovetto R. (1989) Evaluation of data on solubility of simple apolar gases in light and heavy water at high temperature. *J. Phys. Chem. Ref. Data* **18**, 1231–1243.
- Fernandez-Prini R., Corti H. R., and Japas M. L. (1992) High-temperature aqueous solutions: thermodynamic properties. CRC Press.
- Franks F., Gent M., and Johnson H. H. (1963) The solubility of benzene in water. *J. Chem. Soc.*, 2716–2723.
- Frenkel M., Kabo G. J., Marsh K. N., Roganov G. N., and Wilhoit R. C. (1994) Thermodynamics of organic compounds in the gas state. Vol. I,II. TRC Data Series.
- Glaseo P. K. and Schultz S. D. (1972) Solubility of H<sub>2</sub>O and D<sub>2</sub>O in carbon tetrachloride, toluene, and cyclohexane at various temperatures. *J. Chem. Eng. Data* **17**, 66–68.
- Gillespie P. C. and Wilson G. M. (1982) Vapor-liquid and liquid-liquid equilibria: water-methane, water-carbon dioxide, water-hydrogen sulfide, water-n-pentane, water-methane-n-pentane. Research Report, RR-48, Gas Processor Association.
- Goldman S. (1974) The determination and statistical mechanical interpretation of the solubility of water in benzene, carbon tetrachloride, and cyclohexane. *Can. J. Chem.* **52**, 1668–1680.
- Green W. J. and Frank H. S. (1979) The state of dissolved benzene in aqueous solution. *J. Solut. Chem.* **8**, 187–196.
- Guseva A. N. and Parnov E. I. (1963) The solubility of cyclohexane in water. *Russ. J. Phys. Chem.* **37**, 1494.
- Guseva A. N. and Parnov E. I. (1964a) Isothermal sections in the systems cyclanes-water. *Vestn. Mosk. Univ., Ser.II, Khim.* **19**, 77–78 (in Russian).
- Guseva A. N. and Parnov E. I. (1964b) Isothermal sections of monocyclic arene-water binary systems at 25°, 100°, and 200°. *Russ. J. Phys. Chem.* **38**, 439–440.
- Hansen K. C., Zhou Z., Yaws C. L., and Aminabhavi T. M. (1993) Determination of Henry's law constants of organics in dilute aqueous solutions. *J. Chem. Eng. Data* **38**, 546–550.
- Harvey A. H. (1996) Semiempirical correlation for Henry's constants over large temperature ranges. *AIChE J.* **42**, 1491–1494.
- Harvey A. H., Levelt Sengers J. M. H., and Tanger IV J. C. (1991) Unified description of infinite-dilution thermodynamic properties for aqueous solutes. *J. Phys. Chem.* **95**, 932–937.
- Hayduk W. (1986) Volume Editor. Solubility data series. Propane, butane and 2-methylpropane. Vol.24. Pergamon Press.
- Heidman J. L., Tsonopoulos C., Brady G. J., and Wilson G. M. (1985) High-temperature mutual solubilities of hydrocarbons and water. Part II: Ethylbenzene, ethylcyclohexane, and n-octane. *AIChE J.* **31**, 376–384.
- Helgeson H. C., Knox A. M., Owens C. E., and Shock E. L. (1993) Petroleum, oil field waters, and authigenic mineral assemblages: Are they in metastable equilibrium in hydrocarbon reservoirs? *Geochim. Cosmochim. Acta* **57**, 3295–3339.
- Helgeson H. C., Owens C. E., Knox A. M., and Richard L. (1998) Calculation of the standard molal properties of crystalline, liquid, and gas organic molecules at high temperatures and pressures. *Geochim. Cosmochim. Acta* **62**, 985–1081.
- Irani C. A. and McHugh D. J. (1979) High pressure ternary equilibrium in aqueous—hydrocarbon systems. *High Press. Sci. Tech. I, 6th AIRAPT Conf.*, **1**, 600–608.
- Jones J. R. and Monk C. B. (1963) Determination of the solubility of water in some organic liquids by means of tritium. *J. Chem. Soc.* 2633–2635.
- Jönsson J. A., Vejrosta J., and Novak J. (1982) Air/water partition coefficients for normal alkanes (n-pentane to n-nonane). *Fluid Phase Equil.* **9**, 279–286.
- Karlsson R. (1973) Solubility of water in benzene. *J. Chem. Eng. Data* **18**, 290–292.
- Khalfaoui B. and Newsham D. M. T. (1994) Determination of infinite dilution activity coefficients and second virial coefficients using gas-liquid chromatography. I. The dilute mixtures of water and unsaturated chlorinated hydrocarbons and of water and benzene. *J. Chromatogr. A* **673**, 85–92.
- Kobayashi R. and Katz D. L. (1953) Vapor-liquid equilibria for binary hydrocarbon-water systems. *Ind. Eng. Chem.* **45**, 440–451.
- Kolb B., Welter C., and Bichler C. (1992) Determination of partition coefficients by automatic equilibrium headspace gas chromatography by vapor phase calibration. *Chromatographia* **34**, 235–240.
- Kudchadker A. P. and McKetta J. J. (1961a) Solubility of hexane in water. *Hydrocarb. Process. Petrol. Refiner* **40**, 231–232.
- Kudchadker A. P. and McKetta J. J. (1961b) Solubility of cyclohexane in water. *AIChE J.* **7**, 707.
- Kudchadker A. P. and McKetta J. J. (1962) Solubility of benzene in water. *Hydrocarb. Process. Petrol. Refiner* **41**, 191–192.
- Leland Th. W., Jr., McKetta J. J., Jr., and Kobe K. A. (1955) Phase equilibrium in 1-butene-water system and correlation of hydrocarbon-water solubility data. *Ind. Eng. Chem.* **47**, 1265–1271.
- Li C. C. and McKetta J. J. (1963) Vapor-liquid equilibrium in the propylene-water system. *J. Chem. Eng. Data* **8**, 271–275.
- Majer V. and Svoboda V. (1985) Enthalpies of vaporization of organic compounds. Blackwell Scientific Publications.
- May W. E., Wasik S. P., Miller M. M., Tewari Y. B., Brown-Thomas J. M., and Goldberg R. N. (1983) Solution thermodynamics of some slightly soluble hydrocarbons in water. *J. Chem. Eng. Data* **28**, 197–200.
- McAuliffe C. (1966) Solubility in water of paraffin, cycloparaffin, olefin, acetylene, cycloolefin, and aromatic hydrocarbons. *J. Phys. Chem.* **70**, 1267–1275.
- Michel S., Hooper H. H., and Prausnitz J. M. (1989) Mutual solubilities of water and hydrocarbons from an equation of state. Need for an unconventional mixing rule. *Fluid Phase Equil.* **45**, 173–189.
- Moule D. C. and Thurston W. M. (1966) A method for the determination of water in nonpolar liquids; the solubility of water in benzene. *Can. J. Chem.* **44**, 1361–1367.
- Nelson H. D. and De Ligny C. L. (1968) The determination of the solubilities of some n-alkanes in water at different temperatures, by means of gas chromatography. *Rec. Trav. Chim.* **87**, 528–544.
- O'Grady T. M. (1967) Liquid-liquid equilibria for the benzene-n-

- heptane-water system in the critical solution region. *J. Chem. Eng. Data* **12**, 9–12.
- Owens J. W., Wasik S. P., and DeVoe H. (1986) Aqueous solubilities and enthalpies of solution of n-alkylbenzenes. *J. Chem. Eng. Data* **31**, 47–51.
- Pavia R. A. (1958) The solubility of water in benzene. M.S. Thesis, North Carolina State College, Raleigh, N.C., USA (quoted from Shaw, 1989).
- Pedley J. B., Naylor R. D., and Kirby S. P. (1986) *Thermochemical Data of Organic Compounds* Second Edition, Chapman and Hall.
- Peng D.-Y. and Robinson D. B. (1976a) A new two-constant equation of state. *Ind. Eng. Chem. Fundam.* **15**, 59–64.
- Peng D.-Y. and Robinson D. B. (1976b) Two and three phase equilibrium calculations for systems containing water. *Can. J. Chem. Eng.* **54**, 595–599.
- Peng D.-Y. and Robinson D. B. (1980) Two- and three-phase equilibrium calculations for coal gasification and related processes. In *Thermodynamics of aqueous systems with industrial applications* (eds. S. A. Newman et al.), ACS Symposium Series 133, pp. 393–414.
- Peng J. and Wan A. (1997) Measurement of Henry's constants of high-volatility organic compounds using a headspace autosampler. *Environ. Sci. Technol.* **31**, 2998–3003.
- Perlanger J. A., Eisenreich S. J., and Capel P. D. (1993) Application of headspace analysis to the study of sorption of hydrophobic organic chemicals to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. *Environ. Sci. Technol.* **27**, 928–937.
- Pierotti R. A. (1976) A scaled particle theory of aqueous and nonaqueous solutions. *Chem. Rev.* **76**, 717–726.
- Plyasunov A. V. and Shock E. L. (2000) Thermodynamic functions of hydration of hydrocarbons at 298.15 K and 0.1 MPa. *Geochim. Cosmochim. Acta* **64**, 439–468.
- Plyasunov A. V., O'Connell J. P., and Wood R. H. (2000) Infinite dilution partial molar properties of aqueous solutions of nonelectrolytes. I. Equations for partial molar volumes at infinite dilution and standard thermodynamic functions of hydration of volatile nonelectrolytes over wide range of conditions. *Geochim. Cosmochim. Acta* **64**, 495–512.
- Poetmann F. H. and Dean M. R. (1946) Water content of propane. *Petrol. Refiner* **25**, 125–128.
- Polak J. and Lu B. C.-Y. (1973) Mutual solubilities of hydrocarbons and water at 0 and 25°C. *Can. J. Chem.* **51**, 4018–4023.
- Price L. G. (1976) Aqueous solubility of petroleum as applied to its origin and primary migration. *Bull. Amer. Ass. Petrol. Geol.* **60**, 213–244.
- Proust P. and Vera J. H. (1989) PRSV: the Stryjek-Vera modification of the Peng-Robinson equation of state. Parameters for other pure compounds of industrial interest. *Can. J. Chem. Eng.* **67**, 170–173.
- Pryor W. A. and Jentoft R. E. (1961) Solubility of m- and p-xylene in water and in aqueous ammonia from 0° to 300°C. *J. Chem. Eng. Data* **6**, 36–37.
- Rahman S. and Barrufet M. A. (1995) A new technique for simultaneous measurement of PVT and phase equilibria properties of fluids at high temperatures and pressures. *J. Petrol. Sci. Eng.* **14**, 25–34.
- Reamer H. H., Olds R. H., Sage B. H., and Lacey W. N. (1943) Phase equilibria in hydrocarbon systems. Composition of dew-point gas in ethane-water system. *Ind. Eng. Chem.* **35**, 790–794.
- Reamer H. H., Sage B. H., and Lacey W. N. (1952) Phase equilibria in hydrocarbon systems. n-butane-water system in the two-phase region. *Ind. Eng. Chem.* **44**, 609–615.
- Rebert C. J. and Hayworth K. E. (1967) The gas and liquid solubility relations in hydrocarbon-water systems. *AIChE J.* **13**, 118–121.
- Rebert C. J. and Kay W. B. (1959) The phase behavior and solubility relations of the benzene-water system. *AIChE J.* **5**, 285–289.
- Reid R. C., Prausnitz J. M., and Poling B. E. (1987) *The properties of gases & liquids*. McGraw-Hill Book Company.
- Rettich T. R., Handa Y. P., Battino R., and Wilhelm E. (1981) Solubility of gases in liquids. 13. High-precision determination of Henry's law constants for methane and ethane in liquid water at 275 to 328 K. *J. Phys. Chem.* **85**, 3230–3237.
- Robbins G. A., Wans S., and Stuart J. D. (1993) Using the static headspace method to determine Henry's law constants. *Anal. Chem.* **65**, 3113–3118.
- Roddy J. W. and Coleman C. F. (1968) Solubility of water in hydrocarbons as a function of water activity. *Talanta* **15**, 1281–1286.
- Roof J. G. (1970) Three-phase critical point in hydrocarbon-water systems. *J. Chem. Eng. Data* **15**, 301–303.
- Sanchez M. and Lentz H. (1973) Phasengleichgewichte der Systeme Wasser-Propen und Wasser-Äthen bei hohen Drücken und Temperaturen. *High Temp.-High Pres.* **5**, 687–699.
- Sanemasa I., Araki M., Deguchi T., and Nagai H. (1982) Solubility measurements of benzene and the alkylbenzenes in water by making use of solute vapor. *Bull. Chem. Soc. Jpn.* **55**, 1054–1062.
- Saul A. and Wagner W. (1987) International equations for the saturation properties of ordinary water substances. *J. Phys. Chem. Ref. Data* **16**, 893–901.
- Seewald J. S. (1994) Evidence for metastable equilibrium between hydrocarbons under hydrothermal conditions. *Nature* **370**, 285–287.
- Serra M. C. C., da Fonseca M. M. R., Calado J. C. G., and Palavra A. M. F. (1998) Solubility of propene in water and in a mineral medium for the cultivation of a *Xanthobacter* strain. *J. Solut. Chem.* **27**, 455–461.
- Shaw D. G., Volume Editor (1989) Solubility data series. Hydrocarbons with water and seawater. Part I: Hydrocarbons C<sub>5</sub> to C<sub>7</sub>. Vol.38. Pergamon Press.
- Shinta A. A. and Firoozabadi A. (1995) Equation of state representation of aqueous mixtures using an association model. *Can. J. Chem. Eng.* **73**, 367–379.
- Shock E. L. (1988) Organic acid metastability in sedimentary basins. *Geology* **16**, 886–890.
- Shock E. L. (1990) Do amino acids equilibrate in hydrothermal fluids? *Geochim. Cosmochim. Acta* **54**, 1185–1189.
- Shock E. L. and Helgeson H. C. (1990) Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Standard partial molal properties of organic species. *Geochim. Cosmochim. Acta* **54**, 915–945.
- Skripka V. G. (1976) Vaporization of hydrocarbons into water vapor and solubility of water in hydrocarbons at high temperatures. *Tr. Vses. Neftegazov. Nauchno-Issled. Inst.* **61**, 139–151 (in Russian).
- Smith R. R., Charon N. W., and Canady W. J. (1989) Thermodynamics of solution of aromatic hydrocarbons in water and in water-ethanol solutions: comparison of some methodologies. *J. Phys. Chem.* **93**, 5938–5943.
- Song K. Y. and Kobayashi R. (1994) The water content of ethane, propane and their mixtures in equilibrium with liquid water or hydrates. *Fluid Phase Equil.* **95**, 281–298.
- Staveley L. A. K., Jeffes J. H. E., and Moy J. A. E. (1943) The hydrogen bond and the hydration of organic molecules. *Trans. Faraday Soc.* **39**, 5–13.
- Steele W. V. and Chirico R. D. (1993) Thermodynamic properties of alkenes (mono-olefins larger than C<sub>4</sub>). *J. Phys. Chem. Ref. Data* **22**, 377–430.
- Stephenson R. M. (1992) Mutual solubilities: water-ketones, water-ethers, and water-gasoline-alcohols. *J. Chem. Eng. Data* **37**, 80–95.
- Stevenson R. L., LaBracio D. S., Beaton T. A., and Thies M. C. (1994) Fluid phase equilibria and critical phenomena for the dodecane-water and squalane-water systems at elevated temperatures and pressures. *Fluid Phase Equil.* **93**, 317–336.
- Stryjek R. and Vera J. H. (1986) PRSV: an improved Peng-Robinson equation of state for pure compounds and mixtures. *Can. J. Chem. Eng.* **64**, 323–333.
- Tarassenkow D. N. and Poloshnizewa E. N. (1932) Löslichkeit des Wassers in Benzol, Toluol und Cyclohexan. *Chem. Ber.* **65**, 184–186.
- Thompson W. H. and Snyder J. R. (1964) Mutual solubilities of benzene and water. Equilibria in the two phase liquid-liquid region. *J. Chem. Eng. Data* **9**, 516–520.
- Tsonopoulos C. and Heidman J. L. (1986) High-pressure vapor-liquid equilibria with cubic equations of state. *Fluid Phase Equil.* **29**, 391–414.
- Tsonopoulos C. and Wilson G. M. (1983) High-temperature mutual solubilities of hydrocarbons and water. Part I: Benzene, cyclohexane and n-hexane. *AIChE J.* **29**, 990–999.
- Tucker E. E., Lane E. H., and Christian S. D. (1981) Vapor pressure studies of hydrophobic interactions. Formation of benzene-benzene and cyclohexane-cyclohexanol dimers in dilute aqueous solution. *J. Solut. Chem.* **10**, 1–20.
- Van Konyenburg P. H. and Scott R. L. (1980) Critical lines and phase

- equilibria in binary van der Waals mixtures. *Phil. Trans. Roy. Soc. A298*, 495–540.
- Wehe A. H. and McKetta J. J. (1961a) Method for determining total hydrocarbons dissolved in water. *Anal. Chem.* **33**, 291–293.
- Wehe A. H. and McKetta J. J. (1961b) n-Butane-1-butene-water system in the three-phase region. *J. Chem. Eng. Data* **6**, 167–172.
- Wong D. S. H. and Sandler S. I. (1992) A theoretically correct mixing rule for cubic equations of state. *AIChE J.* **38**, 671–680.
- Wormald C. J. and Lancaster N. M. (1988) Excess enthalpies and cross-term second virial coefficients for mixtures containing water vapour. *J. Chem. Soc., Faraday Trans. I* **84**, 3141–3158.
- Wormald C. J. and Slater J. (1996) Excess enthalpies for (water+benzene) in the liquid and supercritical regions at T = 503 K to T = 592 K and p = 16.4 MPa. *J. Chem. Thermodyn.* **28**, 627–636.
- Yiling T., Michelberger Th., and Franck E. U. (1991) High-pressure phase equilibria and critical curves of (water+n-butane) and (water+n-hexane) at temperatures to 700 K and pressures to 300 MPa. *J. Chem. Thermodyn.* **23**, 105–112.
- Zou L., Han B., Liu R., and Yan H. (1997) Solubilities of benzene and diphenyl in (t-butyl alcohol+water) and hydrophobic interaction. *J. Chem. Thermodyn.* **29**, 1289–1299.

#### APPENDIX A. THE PENG-ROBINSON-STRYJEK-VERA EQUATION OF STATE

The basic equation is given by:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b) + b(V-b)}, \quad (\text{A1})$$

where  $V$  stands for the molar volume,  $b$  represents a temperature-independent parameter (sometimes called an “excluded volume”), given by the relation:

$$b = 0.07780 \frac{RT_c}{P_c}, \quad (\text{A2})$$

where  $T_c$  and  $P_c$  stand for the critical temperature and pressure of a pure compound, respectively;  $a$  indicates a temperature-dependent term (also called an “attractive” parameter):

$$a = 0.45724 \frac{R^2 T_c^2}{P_c} \cdot \alpha(T), \quad (\text{A2})$$

where  $\alpha(T)$  represents a function of temperature and the acentric factor  $\omega$  (an individual characteristic of a pure compound related to its vapor pressure, see Reid et al., 1987):

$$\alpha(T) = [1 + \kappa(1 - T_r^{0.5})]^2, \quad (\text{A4})$$

where the  $T_r$  designates the reduced temperature,

$$T_r = \frac{T}{T_c};$$

and

$$\kappa = \kappa_0 + \kappa_1(1 + T_r^{0.5})(0.7 - T_r), \quad (\text{5})$$

where  $\kappa_1$  is an adjustable parameter specific for each pure compound, and  $\kappa_0$  stands for a universal function of the acentric factor  $\omega$ :

$$\kappa_0 = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3. \quad (\text{A6})$$

For pure water Eqn. (A5) applies up to the critical temperature, however for hydrocarbons at  $T_r > 0.7$  the value of  $\kappa_1$  should be set to zero. We used values of the parameter  $\kappa_1$  tabulated for many pure compounds by Stryjek and Vera (1986) and Proust and Vera (1989) or, where necessary, evaluated values of  $\kappa_1$  from the published data on the saturated vapor pressure. The set of the PRSV equation of state parameters for pure compounds used in this work is given in Table A1.

#### APPENDIX B. THE STANDARD PARTIAL MOLAR GIBBS ENERGIES OF THE SELECTED GROUPS AT ELEVATED TEMPERATURES AND PRESSURES

In this work we evaluated values of the standard partial molar Gibbs energy of hydration,  $\Delta_h G^0(T, P)$ , for a number of groups constituting hydrocarbons, up to 623 K and 50 MPa. As many computer codes used for geochemical modeling require values of the standard partial molar Gibbs energy of aqueous compounds,  $G_{ig}^0(T, P)$ , it was decided to calculate these properties.

The following relation connects  $\Delta_h G^0(T, P)$  and  $G_{ig}^0(T, P)$ :

$$G_{ig}^0(T, P) = \Delta_h G^0(T, P) + G_{ig}^0(T), \quad (\text{B1})$$

where  $G_{ig}^0(T)$  stands for the standard Gibbs energy of a compound in the ideal gas state at any temperature,  $T$ , and the ideal gas reference pressure,  $P_r = 0.1$  MPa. The temperature dependence of  $G_{ig}^0(T)$  is given by:

$$G_{ig}^0(T) = \Delta_f G_{ig}^0(T_r) - (T - T_r) \cdot S_{ig}^0(T_r) + \int_{T_r}^T C_{p_{ig}}^0(T) dT - T \int_{T_r}^T \frac{C_{p_{ig}}^0(T)}{T} dT, \quad (\text{B2})$$

where  $S_{ig}^0(T)$  and  $C_{p_{ig}}^0(T)$  represent the entropy and heat capacity of a compound in the ideal gas state;  $\Delta_f G^0(T_r)$  is the standard Gibbs energy of formation of a compound in the ideal gas state from the elements in their stable form at the reference temperature,  $T_r = 298.15$  K, and the reference pressure.  $\Delta_f G_{ig}^0(T_r)$  is calculated by means of

$$\Delta_f G_{ig}^0(T_r) = \Delta_f G^0(T_r, P_r) + \Delta_{vap} G^0(T_r) = \Delta_f H^0(T_r, P_r) - T_r \cdot \Delta_f S^0(T_r, P_r) + \Delta_{vap} G^0(T_r), \quad (\text{B3})$$

where  $\Delta_f G^0(T_r, P_r)$ ,  $\Delta_f H^0(T_r, P_r)$  and  $\Delta_f S^0(T_r, P_r)$  stand for the standard molar Gibbs energy, enthalpy and entropy of formation of a compound in the liquid or solid state from the elements in their stable form at the reference temperature and pressure;

$$\Delta_{vap} G^0(T_r) = -RT_r \ln \frac{P_s \Psi}{P_r}$$

is the standard molar Gibbs energy of vaporization of a compound at the reference temperature; here  $P_s$  and  $\Psi$  represent the saturated vapor pressure and the gaseous phase fugacity coefficient of a compound, respectively. Values of  $\Delta_f H^0(T_r, P_r)$  are typically available from enthalpy of combustion measurements. For a hydrocarbon of a composition  $C_p H_q$  the value of  $\Delta_f S^0(T_r, P_r)$  is calculated as

$$\Delta_f S^0(T_r, P_r) = S^0(T_r, P_r) - p \cdot S^0(C(cr)) - \frac{q}{2} \cdot S^0(H_2(g)), \quad (\text{B4})$$

where  $S^0(T_r, P_r)$  represents the standard molar entropy of a compound in the liquid or solid state at the reference temperature and pressure (often available from low-temperature heat capacity measurements);  $S^0(C(cr)) = 5.74 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  and  $S^0(H_2(g)) = 130.680 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  stand for the standard molar entropies of the elements carbon and hydrogen in their stable forms at 298.15 K and 0.1 MPa, as recommended by CODATA (Cox et al., 1989).

The entropy of a compound in the ideal gas state,  $S_{ig}^0(T_r)$ , can be calculated using the methods of statistical thermodynamics based on spectral data, or obtained by means of

$$S_{ig}^0(T_r) = S^0(T_r, P_r) + \frac{1}{T_r} (\Delta_{vap} H^0(T_r) - \Delta_{vap} G^0(T_r)), \quad (\text{B5})$$

where  $\Delta_{vap} H^0(T_r)$  stands for the standard enthalpy of vaporization of a compound at the reference temperature (which can be measured calorimetrically or evaluated from the temperature dependence of the saturated vapor pressure).

So, in order to calculate the standard partial molar Gibbs energy of a compound at elevated  $T$  and  $P$ , one needs to know:  $\Delta_f H^0$ ,  $S^0$ ,

Table A1. The set of the Peng-Robinson-Stryjek-Vera EoS parameters for pure compounds.

Compound	T <sub>c</sub> , K	P <sub>c</sub> , MPa	ω	κ <sub>a</sub>
Water, H <sub>2</sub> O	646.281 <sup>a</sup>	22.0898 <sup>a</sup>	0.34380 <sup>a</sup>	-0.06635 <sup>a</sup>
		Alkanes		
Ethane, C <sub>2</sub> H <sub>6</sub>	305.43 <sup>a</sup>	4.8798 <sup>a</sup>	0.0978 <sup>a</sup>	0.0267 <sup>a</sup>
Propane, C <sub>3</sub> H <sub>8</sub>	369.82 <sup>a</sup>	4.2495 <sup>a</sup>	0.1542 <sup>a</sup>	0.0314 <sup>a</sup>
n-Butane, C <sub>4</sub> H <sub>10</sub>	425.16 <sup>a</sup>	3.7966 <sup>a</sup>	0.2010 <sup>a</sup>	0.0344 <sup>a</sup>
n-Pentane, C <sub>5</sub> H <sub>12</sub>	469.70 <sup>a</sup>	3.3690 <sup>a</sup>	0.2514 <sup>a</sup>	0.0395 <sup>a</sup>
n-Hexane, C <sub>6</sub> H <sub>14</sub>	507.30 <sup>a</sup>	3.0124 <sup>a</sup>	0.3008 <sup>a</sup>	0.0510 <sup>a</sup>
2-Methylpentane, C <sub>6</sub> H <sub>14</sub>	497.5 <sup>b</sup>	3.01 <sup>b</sup>	0.278 <sup>b</sup>	0.0379 <sup>c</sup>
n-Heptane, C <sub>7</sub> H <sub>16</sub>	540.10 <sup>a</sup>	2.7358 <sup>a</sup>	0.3502 <sup>a</sup>	0.0465 <sup>a</sup>
n-Octane, C <sub>8</sub> H <sub>18</sub>	568.76 <sup>a</sup>	2.4865 <sup>a</sup>	0.3982 <sup>a</sup>	0.0446 <sup>a</sup>
		Alkenes		
Ethene, C <sub>2</sub> H <sub>4</sub>	282.35 <sup>d</sup>	5.042 <sup>d</sup>	0.0865 <sup>d</sup>	0.0419 <sup>d</sup>
Propene, C <sub>3</sub> H <sub>6</sub>	365.57 <sup>d</sup>	4.6646 <sup>a</sup>	0.1408 <sup>a</sup>	0.0440 <sup>a</sup>
1-Butene, C <sub>4</sub> H <sub>8</sub>	419.53 <sup>d</sup>	4.023 <sup>d</sup>	0.1941 <sup>d</sup>	0.0222 <sup>d</sup>
1-Hexene, C <sub>6</sub> H <sub>12</sub>	504.0 <sup>b</sup>	3.17 <sup>b</sup>	0.285 <sup>b</sup>	0.020 <sup>c</sup>
1-Octene, C <sub>8</sub> H <sub>16</sub>	567.5 <sup>e</sup>	2.675 <sup>e</sup>	0.388 <sup>e</sup>	0.006 <sup>f</sup>
		Cycloalkanes		
Cyclohexane, C <sub>6</sub> H <sub>12</sub>	553.64 <sup>a</sup>	4.075 <sup>a</sup>	0.2088 <sup>a</sup>	0.0702 <sup>a</sup>
Ethylcyclohexane, C <sub>8</sub> H <sub>16</sub>	609.2 <sup>b</sup>	3.00 <sup>b</sup>	0.243 <sup>b</sup>	0.140 <sup>c</sup>
n-Butylcyclohexane, C <sub>10</sub> H <sub>20</sub>	667.0 <sup>b</sup>	3.15 <sup>b</sup>	0.362 <sup>b</sup>	0.010 <sup>c</sup>
		Alkylbenzenes		
Benzene, C <sub>6</sub> H <sub>6</sub>	562.16 <sup>a</sup>	4.898 <sup>a</sup>	0.2093 <sup>a</sup>	0.0702 <sup>a</sup>
Toluene, C <sub>7</sub> H <sub>8</sub>	591.80 <sup>a</sup>	4.106 <sup>a</sup>	0.2632 <sup>a</sup>	0.0385 <sup>a</sup>
Ethylbenzene, C <sub>8</sub> H <sub>10</sub>	617.20 <sup>a</sup>	3.606 <sup>a</sup>	0.3027 <sup>a</sup>	0.0399 <sup>a</sup>
<i>m</i> -Xylene, C <sub>8</sub> H <sub>10</sub>	617.05 <sup>d</sup>	3.536 <sup>d</sup>	0.3257 <sup>d</sup>	0.0161 <sup>d</sup>
<i>p</i> -Xylene, C <sub>8</sub> H <sub>10</sub>	616.23 <sup>a</sup>	3.511 <sup>a</sup>	0.3214 <sup>a</sup>	0.0128 <sup>a</sup>
<i>m</i> -Diethylbenzene, C <sub>8</sub> H <sub>16</sub>	663.0 <sup>g</sup>	2.88 <sup>g</sup>	0.350 <sup>g</sup>	0.153 <sup>g</sup>
<i>p</i> -Diisopropylbenzene, C <sub>12</sub> H <sub>18</sub>	689.0 <sup>g</sup>	2.45 <sup>g</sup>	0.390 <sup>g</sup>	0.110 <sup>h</sup>

<sup>a</sup> Stryjek and Vera (1986).

<sup>b</sup> Reid et al. (1987).

<sup>c</sup> Our estimation from P<sub>s</sub> values from Reid et al. (1987).

<sup>d</sup> Proust and Vera (1989).

<sup>e</sup> Steele and Chirico (1993).

<sup>f</sup> Our estimation from P<sub>s</sub> values from Steele and Chirico (1993).

<sup>g</sup> Daubert and Danner (1996).

<sup>h</sup> Our estimation from P<sub>s</sub> values from Boublik et al. (1984).

$\Delta_{vap}H^0$ ,  $\Delta_{vap}G^0$  for the compound at the reference temperature and pressure; the heat capacity of the compound in the ideal gas state at different temperatures,  $Cp_{ig}^0(T)$ ; and the values of the Gibbs energy of hydration of this compound at different  $T$  and  $P$ ,  $\Delta_h G^0(T, P)$ .

It was decided, wherever possible, to provide consistency with the results of Helgeson et al. (1998), which give the values of the thermodynamic properties of several groups constituting organic compounds in the liquid, crystalline and gaseous states over a wide range of temperatures. The obvious problem here is the different stoichiometry of groups (besides CH<sub>3</sub> and CH<sub>2</sub>) selected in our work and in that of Helgeson et al. (1998). We selected for hydrocarbons the groups CH<sub>3</sub>, CH<sub>2</sub>, CH, CH<sub>ar</sub>, C<sub>ar</sub>, c-CH<sub>2</sub>, c-CH, C = C and H. On the other hand, Helgeson et al. selected CH<sub>3</sub>, CH<sub>2</sub>, CH(CH<sub>3</sub>)<sub>2</sub>, CH(CH<sub>3</sub>), C<sub>6</sub>H<sub>5</sub>, and tabulated data for cyclohexane and methylcyclohexane, however, they did not consider alkenes. As a necessary compromise to find common ground, it was decided to tabulate the properties of the following groups, which can be considered as linear combinations of the results of this work and that of Helgeson et al. (1998): CH<sub>3</sub>, CH<sub>2</sub> (common in both studies); CH(CH<sub>3</sub>)<sub>2</sub> and CH(CH<sub>3</sub>), which for the case of the functions of hydration are equal to the sum of CH+2CH<sub>3</sub> and CH+CH<sub>3</sub> groups, respectively; C<sub>6</sub>H<sub>5</sub>, which for the case of the functions of hydration is equal to the sum of 5CH<sub>ar</sub>+C<sub>ar</sub> groups; CH<sub>ar</sub>, equal to 1/6 of the properties of benzene; C<sub>ar</sub>, which is equal to C<sub>6</sub>H<sub>5</sub> minus 5/6 times the thermochemical properties of benzene; c-CH<sub>2</sub> as equal to 1/6 of the thermochemical properties of cyclohexane; c-CH, which is equal to the thermochemical properties of liquid methylcyclohexane minus that of the CH<sub>3</sub> group and minus 5/6 of the thermochemical properties of cyclohexane. Note that because properties of c-CH<sub>2</sub> and c-CH groups are entirely based on properties of derivatives of cyclohexane, we call for caution when applying these results for

estimation of thermochemical properties of derivatives of other cycloalkanes. In addition, not all of these groups are linearly independent, for example, the group C<sub>6</sub>H<sub>5</sub> is identical to the sum of groups 5CH<sub>ar</sub>+C<sub>ar</sub>. Sources of experimental data for the Gibbs energies and enthalpies of vaporization, used to derive the necessary values for the selected groups, are given elsewhere (Plyasunov and Shock, 2000).

The properties of C = C and H groups, not considered by Helgeson et al. (1998), were determined from the available information, assuming that thermochemical properties of groups CH<sub>3</sub>, CH<sub>2</sub>, CH(CH<sub>3</sub>)<sub>2</sub> and CH(CH<sub>3</sub>) are identical in both alkanes and alkenes. The evaluation of  $\Delta_r H^0(T_r, P_r)$  for C = C and H groups in the liquid state is based on the values of the enthalpy of formation of 31 liquid alkenes with carbon number from 3 to 10, as recommended by Pedley et al. (1986). The evaluation of  $S^0(T_r, P_r)$  for C = C and H groups in the liquid state was done by considering experimental data for 12 alkenes with carbon number from 3 to 10, which received a high quality rating (A) in the compilation of Domalski and Hearing (1996). Values of the Gibbs energy and enthalpy of vaporization of C = C and H groups were determined using the experimental results for 15 alkenes with carbon number from 5 to 9 (Majer and Svoboda, 1985; Reid et al., 1987; Steele and Chirico, 1993). In all cases results for *cis*-isomers were not used. Heat capacities of C = C and H groups in the ideal gas state were determined from  $Cp_{ig}^0(T)$  values for 6 alkenes with carbon number from 2 to 5 as given in Frenkel et al. (1994). Data at temperatures 273–900 K were fitted by an equation in the form accepted by Helgeson et al. (1998):

$$Cp_{ig}^0(T) = a + bT + cT^2. \quad (\text{B6})$$

Finally, the temperature dependence of the standard partial molar Gibbs energy of a compound is given by

Table B1. Standard molar thermodynamic properties and the coefficients of the heat capacity equation in the ideal gas state for the selected groups.

Group	Properties in the liquid state			Vaporization properties		Heat capacity in the ideal gas state		
	$\Delta_f H^0(T_r, P_r)^a$	$S^0(T_r, P_r)^b$	$\Delta_f S^0(T_r, P_r)^b$	$\Delta_{vap} G^0(T_r)^a$	$\Delta_{vap} H^0(T_r)^a$	$a^b$	$b \cdot 10^{3c}$	$c \cdot 10^{5d}$
CH <sub>3</sub>	-47.61 <sup>e</sup>	83.30 <sup>e</sup>	-118.46	-3.82 <sup>f</sup>	5.96 <sup>f</sup>	3.33 <sup>e</sup>	84.52 <sup>e</sup>	-2.644 <sup>e</sup>
CH <sub>2</sub>	-25.73 <sup>e</sup>	32.38 <sup>e</sup>	-104.04	2.91 <sup>f</sup>	4.96 <sup>f</sup>	-2.25 <sup>e</sup>	97.07 <sup>e</sup>	-4.590 <sup>e</sup>
CH(CH <sub>3</sub> ) <sub>2</sub>	-104.34 <sup>e</sup>	143.02 <sup>e</sup>	-331.58	1.07 <sup>g</sup>	14.08 <sup>g</sup>	-3.06 <sup>e</sup>	278.48 <sup>e</sup>	-10.255 <sup>e</sup>
CH(CH <sub>3</sub> )	-54.56 <sup>e</sup>	59.51 <sup>e</sup>	-213.33	5.07 <sup>h</sup>	8.25 <sup>h</sup>	-8.94 <sup>e</sup>	199.22 <sup>e</sup>	-8.004 <sup>e</sup>
C <sub>6</sub> H <sub>5</sub>	60.47 <sup>e</sup>	139.83 <sup>e</sup>	-221.31	11.59 <sup>i</sup>	31.19 <sup>i</sup>	-32.78 <sup>e</sup>	432.63 <sup>e</sup>	-20.803 <sup>e</sup>
CH <sub>ar</sub>	8.16 <sup>j</sup>	28.87 <sup>j</sup>	-42.21	0.85 <sup>k</sup>	5.65 <sup>k</sup>	-5.43 <sup>j</sup>	75.10 <sup>j</sup>	-3.596 <sup>j</sup>
C <sub>ar</sub>	19.67 <sup>l</sup>	-4.52 <sup>l</sup>	-10.26	7.34 <sup>m</sup>	2.94 <sup>m</sup>	-5.63 <sup>e</sup>	57.13 <sup>l</sup>	-2.838 <sup>l</sup>
C = C	85.7 <sup>n</sup>	-58.6 <sup>n</sup>	-70.08	19.38 <sup>p</sup>	8.46 <sup>p</sup>	-2.0 <sup>q</sup>	119.0 <sup>q</sup>	-6.00 <sup>q</sup>
H	-11.0 <sup>n</sup>	57.4 <sup>o</sup>	-7.94	-6.97 <sup>p</sup>	0.44 <sup>p</sup>	2.4 <sup>q</sup>	3.3 <sup>q</sup>	0.35 <sup>q</sup>
c-CH <sub>2</sub>	-26.03 <sup>r</sup>	34.06 <sup>r</sup>	-102.36	0.84 <sup>s</sup>	5.52 <sup>s</sup>	-9.09 <sup>r</sup>	101.53 <sup>r</sup>	-3.990 <sup>r</sup>
c-CH	-7.51 <sup>t,u</sup>	-7.19 <sup>t,u</sup>	-78.27	6.52 <sup>t,v</sup>	1.88 <sup>t,v</sup>	-8.30 <sup>t,w</sup>	115.76 <sup>t,w</sup>	-6.568 <sup>t,w</sup>

<sup>a</sup> kJ · mol<sup>-1</sup>.<sup>b</sup> J · K<sup>-1</sup> · mol<sup>-1</sup>.<sup>c</sup> J · K<sup>-2</sup> · mol<sup>-1</sup>.<sup>d</sup> J · K<sup>-3</sup> · mol<sup>-1</sup>.<sup>e</sup> Helgeson et al. (1998).<sup>f</sup> From experimental results for n-alkanes with carbon number 5–14.<sup>g</sup> From experimental values for 2-methylalkanes with carbon number 5–11.<sup>h</sup> From experimental values for 3-methylalkanes with carbon number 6–11.<sup>i</sup> As the sum of 5CH<sub>ar</sub> + C<sub>ar</sub>.<sup>j</sup> As 1/6 of the value for benzene from Helgeson et al. (1998).<sup>k</sup> As 1/6 of the experimental value for benzene.<sup>l</sup> As the sum C<sub>6</sub>H<sub>5</sub>–5CH<sub>ar</sub>.<sup>m</sup> From experimental values for 11 alkylbenzenes with carbon number 7–12.<sup>n</sup> From values for 31 liquid alkenes with carbon number 3–10, as recommended in Pedley et al. (1986).<sup>o</sup> From values for 12 liquid alkenes with carbon number 3–10 as given in Domalski and Hearing (1996).<sup>p</sup> From experimental values for 15 alkenes with carbon number 5–9.<sup>q</sup> From values for 6 alkenes with carbon number 2–5 as given in Frenkel et al. (1994).<sup>r</sup> As 1/6 of the value for cyclohexane from Helgeson et al. (1998).<sup>s</sup> As 1/6 of the experimental value for cyclohexane.<sup>t</sup> As the sum of methylcyclohexane–5c-CH<sub>2</sub>–CH<sub>3</sub>.<sup>u</sup> Value for methylcyclohexane as calculated from algorithms given by Domalski and Hearing (1993).<sup>v</sup> From the experimental value for methylcyclohexane.<sup>w</sup> Value for methylcyclohexane from Helgeson et al. (1998).Table B2. Calculated values of the standard partial molar Gibbs energies,  $G_r^0(T, P)$ , in kJ · mol<sup>-1</sup>, of the selected groups as function of temperature at the saturated water vapor pressure and at P = 50 MPa (second line, in *italics*).

Group	Temperature, K														
	273.15	298.15	323.15	348.15	373.15	398.15	423.15	448.15	473.15	498.15	523.15	548.15	573.15	598.15	623.15
Y <sub>o</sub>	7.09	7.96	8.82	9.67	10.51	11.36	12.21	13.05	13.88	14.69	15.45	16.15	16.77	17.27	17.63
	<i>7.15</i>	<i>8.00</i>	<i>8.86</i>	<i>9.72</i>	<i>10.59</i>	<i>11.45</i>	<i>12.31</i>	<i>13.17</i>	<i>14.01</i>	<i>14.83</i>	<i>15.64</i>	<i>16.43</i>	<i>17.20</i>		
CH <sub>3</sub>	-10.76	-12.44	-14.48	-16.84	-19.49	-22.39	-25.52	-28.86	-32.40	-36.12	-40.04	-44.16	-48.49	-53.05	-57.87
	<i>-9.43</i>	<i>-11.17</i>	<i>-13.20</i>	<i>-15.49</i>	<i>-18.04</i>	<i>-20.83</i>	<i>-23.86</i>	<i>-27.11</i>	<i>-30.58</i>	<i>-34.25</i>	<i>-38.11</i>	<i>-42.16</i>	<i>-46.38</i>		
CH <sub>2</sub>	9.48	8.91	8.19	7.33	6.34	5.23	4.01	2.70	1.30	-0.18	-1.71	-3.31	-4.94	-6.60	-8.28
	<i>10.24</i>	<i>9.62</i>	<i>8.89</i>	<i>8.05</i>	<i>7.09</i>	<i>6.04</i>	<i>4.88</i>	<i>3.64</i>	<i>2.30</i>	<i>0.88</i>	<i>-0.61</i>	<i>-2.18</i>	<i>-3.81</i>		
CH(CH <sub>3</sub> ) <sub>2</sub>	3.71	1.12	-2.15	-6.02	-10.41	-15.27	-20.55	-26.20	-32.22	-38.57	-45.26	-52.31	-59.74	-67.59	-75.90
	<i>6.53</i>	<i>3.93</i>	<i>0.80</i>	<i>-2.85</i>	<i>-6.99</i>	<i>-11.60</i>	<i>-16.66</i>	<i>-22.15</i>	<i>-28.05</i>	<i>-34.34</i>	<i>-40.99</i>	<i>-47.99</i>	<i>-55.32</i>		
CH(CH <sub>3</sub> )	16.88	15.98	14.76	13.27	11.53	9.59	7.46	5.17	2.72	0.11	-2.64	-5.54	-8.62	-11.88	-15.35
	<i>18.36</i>	<i>17.51</i>	<i>16.42</i>	<i>15.08</i>	<i>13.50</i>	<i>11.70</i>	<i>9.69</i>	<i>7.47</i>	<i>5.06</i>	<i>2.47</i>	<i>-0.30</i>	<i>-3.23</i>	<i>-6.31</i>		
C <sub>6</sub> H <sub>5</sub>	134.88	131.05	126.86	122.31	117.39	112.11	106.46	100.45	94.07	87.33	80.23	72.77	64.95	56.77	48.23
	<i>138.10</i>	<i>134.51</i>	<i>130.53</i>	<i>126.17</i>	<i>121.42</i>	<i>116.29</i>	<i>110.76</i>	<i>104.85</i>	<i>98.55</i>	<i>91.86</i>	<i>84.79</i>	<i>77.34</i>	<i>69.50</i>		
CH <sub>ar</sub>	21.76	20.97	20.10	19.14	18.10	16.98	15.76	14.47	13.08	11.61	10.06	8.42	6.70	4.90	3.01
	<i>22.40</i>	<i>21.65</i>	<i>20.81</i>	<i>19.89</i>	<i>18.88</i>	<i>17.78</i>	<i>16.59</i>	<i>15.32</i>	<i>13.95</i>	<i>12.50</i>	<i>10.96</i>	<i>9.33</i>	<i>7.61</i>		
C <sub>ar</sub>	26.10	26.20	26.36	26.59	26.88	27.23	27.64	28.12	28.66	29.26	29.92	30.65	31.44	32.29	33.20
	<i>26.12</i>	<i>26.26</i>	<i>26.46</i>	<i>26.71</i>	<i>27.02</i>	<i>27.39</i>	<i>27.80</i>	<i>28.27</i>	<i>28.80</i>	<i>29.38</i>	<i>30.01</i>	<i>30.70</i>	<i>31.45</i>		
C = C	114.17	115.72	117.40	119.22	121.17	123.27	125.50	127.88	130.39	133.05	135.85	138.79	141.88	145.11	148.49
	<i>113.77</i>	<i>115.33</i>	<i>116.93</i>	<i>118.59</i>	<i>120.31</i>	<i>122.07</i>	<i>123.89</i>	<i>125.77</i>	<i>127.70</i>	<i>129.69</i>	<i>131.74</i>	<i>133.84</i>	<i>136.01</i>		
H	-10.24	-11.70	-13.29	-15.01	-16.86	-18.84	-20.95	-23.19	-25.56	-28.05	-30.68	-33.43	-36.31	-39.32	-42.46
	<i>-9.53</i>	<i>-10.96</i>	<i>-12.49</i>	<i>-14.13</i>	<i>-15.88</i>	<i>-17.74</i>	<i>-19.70</i>	<i>-21.76</i>	<i>-23.94</i>	<i>-26.22</i>	<i>-28.60</i>	<i>-31.09</i>	<i>-33.69</i>		
c-CH <sub>2</sub>	6.75	6.10	5.28	4.30	3.18	1.91	0.52	-1.00	-2.63	-4.36	-6.19	-8.10	-10.09	-12.15	-14.27
	<i>7.57</i>	<i>6.87</i>	<i>6.05</i>	<i>5.11</i>	<i>4.05</i>	<i>2.86</i>	<i>1.55</i>	<i>0.11</i>	<i>-1.45</i>	<i>-3.14</i>	<i>-4.95</i>	<i>-6.88</i>	<i>-8.93</i>		
c-CH	20.45	21.29	21.97	22.50	22.88	23.12	23.25	23.27	23.19	23.02	22.78	22.48	22.13	21.74	21.32

$$\begin{aligned}
G_2^0(T,P) &= \Delta_f G^0(T,P) + \Delta_f H^0(T_r,P_r) - T_r \Delta_f S^0(T_r,P_r) \\
&+ \Delta_{\text{vap}} G^0(T_r) - (T - T_r) S^0(T_r,P_r) \\
&- \frac{T - T_r}{T_r} (\Delta_{\text{vap}} H^0(T_r) - \Delta_{\text{vap}} G^0(T_r)) \\
&+ a \left( T - T_r - T \ln \frac{T}{T_r} \right) - \frac{b}{2} (T - T_r)^2 - \frac{c}{6} \\
&\cdot (T^3 + 2T_r^3 - 3TT_r^2).
\end{aligned} \tag{B7}$$

The necessary parameters for the selected groups are given in Table B1, and the calculated values of  $G_2^0(T,P)$  for groups are given in Table B2. As an example we calculate the value of the standard state partial molar Gibbs energy of 2-methylbutane (isopentane) at 473.15 K and saturated water vapor pressure. This compound consists of three groups:  $\text{CH}(\text{CH}_3)_2$  ( $G_2^0(T,P) = -32.22 \text{ kJ} \cdot \text{mol}^{-1}$ ),  $\text{CH}_2$  ( $G_2^0(T,P) = +1.30 \text{ kJ} \cdot \text{mol}^{-1}$ ), and  $\text{CH}_3$  ( $G_2^0(T,P) = -32.40 \text{ kJ} \cdot \text{mol}^{-1}$ ), however, the value of  $Y_o = 13.88 \text{ kJ} \cdot \text{mol}^{-1}$  (the Gibbs energy of hydration of a material point at the temperature and pressure of interest) must be added to the sum to satisfy Eqn. (13) for a correct calculation of the Gibbs energy of hydration of an individual species. The result is  $G_2^0(T,P) = -49.44 \text{ kJ} \cdot \text{mol}^{-1}$ .