CALCULATION OF WATER CONTENT IN WATER–METHANE SYSTEM

Petr VOŇKA[a1,*], Monika HUBKOVÁ[a2] and Vít MEISTR[a3,b]

[a] *Department of Physical Chemistry, Institute of Chemical Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic; e-mail: [1] petr.vonka@vscht.cz, [2] monika.hubkova@vscht.cz, [3] vit.meistr@vscht.cz*

[b] *RWE Plynoprojekt, s.r.o., U Plynárny 223/42, 140 21 Prague 4, Czech Republic*

Received September 30, 2009
Accepted November 16, 2009

Dedicated to Professor Ivo Nezbeda on the occasion of his 65th birthday.

Two methods to calculate the water content of water (1)–methane (2) system in the liquid–gas and ice–gas regions at temperatures from 253 to 373 K are proposed and tested in this work. Both are based on the assumption that the influence of methane solubility in liquid water on the calculated water content can be neglected (i.e., only pure water is considered in the liquid phase). A survey of experimental data is also given.
Keywords: Water; Methane; Water content; Dew point; Hydrates; Equation of state; Thermodynamics.

Many water–hydrocarbon systems occur in numerous industrial operations, so it is important to calculate the compositions of the coexisting phases at various temperatures and pressures. At moderate- and high-pressure regions a cubic equation of state (EOS) with the classical quadratic mixing rule for the attractive parameter a

$$a = a_{11} x_1^2 + 2a_{12} x_1 x_2 + a_{22} x_2^2 \qquad a_{12} = (1 - k_{12})\sqrt{a_{11} a_{22}} \tag{1}$$

is usually used for many types of binary systems. However, such a simple mixing rule cannot be used for water (1)–hydrocarbon (2) systems. The value of the cross term a_{12} (i.e., the value of the interaction parameter k_{12}) for the water-rich liquid phase differs significantly from the cross term a_{12} for the hydrocarbon-rich phase. The use of the mixing rule (*1*) does not enable the acceptable accurate calculation of both quantities, i.e., the water

Collect. Czech. Chem. Commun. 2010, Vol. 75, No. 3, pp. 257–274

doi:10.1135/cccc2009508

content in the (gaseous or liquid) hydrocarbon-rich phase and the solubility of hydrocarbon in the water-rich liquid phase.

Kabadi and Danner[1] proposed the empirical cross term

$$a_{12} = (1 - k_{12})\sqrt{a_{11}a_{22}} + \mathrm{l}_{12}x_1 \qquad (2)$$

where the interaction parameter l_{12} is equal to the difference between the cross term in the water-rich phase ($x_2 << x_1$) and the cross term in the hydrocarbon-rich phase ($x_1 << x_2$). The group contribution method is used for calculation of the parameter l_{12}. Percentage deviations between experimental and calculated compositions are in the wide interval of 4–104%.

Michel, Hooper and Prausnitz[2] reported another approach with the conclusion that the ordinary quadratic mixing rule (*1*) is adequate for dilute solutions of water in hydrocarbons but it fails for dilute solutions of hydrocarbons in water due to the significant change in the structure of water in the first coordination shell around the hydrocarbon molecule. They proposed an unconventional mixing rule

$$a = a_{11}x_1^2\varphi(x_2) + 2a_{12}x_1x_2 + a_{22}x_2^2 \qquad (3)$$

$$\varphi(x_2) = 1 + \beta_{12}x_2\exp(-10x_2) \quad \beta_{12} = \tau T^n$$

where the cross term a_{12} is defined in Eq. (*1*). It is possible to prove[3] that the calculated value of fugacity of the hydrocarbon in the water-rich phase depends significantly on the value of parameter β_{12}, but the influence of β_{12} on the calculated value of fugacity of water in the hydrocarbon-rich phase is neglectable. Therefore, it is possible to obtain good agreement between experimental and calculated compositions of both phases. Parameters k_{12}, τ and n were given for twelve liquid–liquid equilibrium data (water–C_nH_m, $n \geq 6$) in their work. It was shown[3] that the method is successfully applicable not only to liquid–liquid equilibrium data but also to vapor–liquid equilibrium data (water–C_nH_m, $n < 5$). Nasrifar and Moshfeghian[4] proposed function φ in the form

$$\varphi(x_2) = 1 + \delta_{12}x_1^9x_2 \quad x_1 = 1 - x_2 \quad \delta_{12} = \left(m_1 + \frac{m_2}{T}\right)\exp\left(-\frac{\Delta H^0}{RT}\right). \qquad (4)$$

Parameters k_{12}, m_1, m_2 and ΔH^0 were given for thirteen similar water– C_nH_m binaries where $n \geq 6$. In agreement with relation (*3*), the function φ differs significantly from unity only in water-rich phases ($x_2 << x_1$).

The previously described problems led to the need for describing the hydrocarbon-rich and water-rich phases differently[5–11]. An equation of state is usually used for the hydrocarbon-rich phase. To calculate the hydrocarbon solubility in the liquid water-rich phase, it is preferable to use Henry's law rather than an EOS.

Solving a practical operation, a good agreement either between the calculated and experimental solubility of the hydrocarbon in the water-rich liquid phase or between the calculated and experimental water content in the (liquid or gaseous) hydrocarbon-rich phase is usually required. For example, ecologists and environmentalists need a good description of the hydrocarbon solubility in liquid water, but they do not require any information on the composition of the coexisting hydrocarbon-rich phase (i.e., water content). On the contrary, the water content in gaseous hydrocarbon-rich phase is very important for predicting hydrate formation in pipelines during the transport of natural gas, but information on the solubility of hydrocarbons in liquid water is not important in this case. Therefore, calculation methods for either water content in the hydrocarbon-rich phase or solubility of hydrocarbons in liquid water are desirable. Calculation of water content in the water–methane system is the subject of this work.

Methane is the dominant component of natural gas (dry natural gas from Alaska or from Russia contains more than 99.5 or 98 mole % methane). The undesired formation of solid hydrates (risk of pipeline blockage during natural gas transport) is possible only in the case when the liquid water phase is present in the system. Therefore, knowing the temperature and pressure dependence of the (saturated) water content in the gaseous phase is important. Coexisting curves of the water–methane system ($P > 1$ MPa) are given in Fig. 1. Munck's[12] method was used to calculate the annotated points (Table I). In the first step we focused on the temperature interva1 273.15–373 K and the liquid–gas region (see Fig. 1), i.e., the region where the solid phase is not present. Experimental data[13–24] on the water content are given in Table II[+].

Chapoy, Coquelet and Richon[22,23] measured the water content in the gas phase of the water–methane system at temperatures from 283 to 318 K and

---

[+] Experimental data on water content measured by Avila et al.[25] are not given in Table II because only data from the ice–gas and hydrate–gas regions were measured.

pressures up to 34.5 MPa. They used a modified Peng–Robinson[26–28] EOS and Henry's law to calculate the fugacity of water and methane in the gaseous phase and the fugacity of both compounds in the aqueous phase, respectively. The NRTL model[29] was used to calculate the water activity. Folas et al.[24] measured (among other things) water content in the gas phase of the water–methane system at temperatures from 253 to 293 K and pressures up to 18 MPa. The CPA [9,10] (Cubic Plus Association) EOS was used to describe the vapor and liquid phases. The CPA EOS is equal to the Redlich–Kwong EOS but extended by an association term (water is considered as an associating component). Authors[30] of ISO 18453 used the modified Peng–Robinson EOS to describe the state behavior of both phases. Interaction parameters of 66 water–hydrocarbon/N_2/CO_2 binaries are given.

Two methods to calculate the water content of water (1)–methane (2) system in the liquid–gas region (extension for the ice–gas region is simple and will be done later) are proposed and tested in this work. Both of them are based on the assumption that the influence of methane solubility in liquid

TABLE I
Selected (*T*, *P*) points on the coexisting curve of the water–methane system

T, K	253	258	263	268	273	278	283	288	293	298
P, MPa	1.36	1.62	1.92	2.26	2.66	4.33	7.04	11.7	20.3	34.8

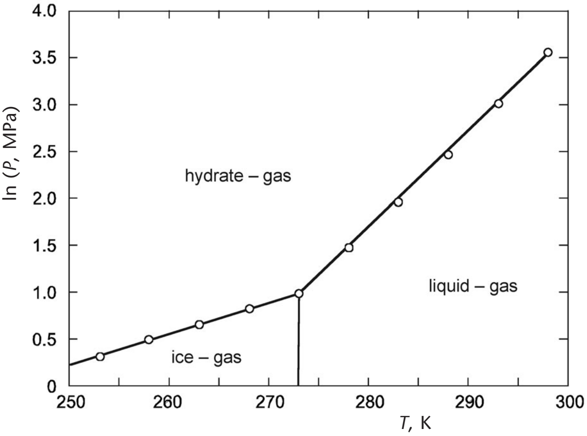

FIG. 1
Coexisting curves of the water–methane system

water on the calculated water content in the gaseous phase can be neglected (i.e., $x_2 = 0$ is considered). In the first method, the Redlich–Kwong–Soave (RKS) EOS[31] is applied for the calculation of fugacity of water in the gas phase. The vapor pressure, second virial coefficient and molar volume of liquid water are used to calculate the fugacity of pure liquid water. Calculation of the water content in the hydrocarbon-rich phase was discussed already in our previous works[32–36].

The second method is based on the derivation of an analytical explicit formula for the calculation of water content y_1. A sufficiently precise explicit formula is the simplest way to calculate the water content and also allows for an apriori analysis of the temperature and pressure dependence of the water content. Such an idea is not new, and a survey of empirical explicit formulas for the calculation of water content was given by Mohammadi et al.[37]. Our approach is based more on thermodynamic principles. The pressure in gas pipelines is usually less than 10 MPa, a condition under which the undesired formation of hydrates from liquid phase is possible in the temperature range from 273 to 288 K (see Table I and Fig. 1). Therefore we focus especially on this interval.

TABLE II
Experimental data on water content of the water–methane system; N is the number of experimental points from the liquid–gas region included into the fit

Literature	Date	T_{min}/T_{max}, K	P_{min}/P_{max}, MPa	N
Olds[13]	1942	311/378	1.4/20.7	27
Gillespie[14]	1948	323/348	1.4/13.8	6
Culberson[15]	1951	311/311	5.2/35.8	5
Rigby[16]	1968	298/373	2.4/9.4	12
Sharma[17]	1969	311/344	1.5/14.4	15
Kosyakov[18]	1982	273/283[a]	1/6.1	5
Yarym-Agaev[19]	1985	313/338	2.5/12.5	10
Yokoyama[20]	1988	298/323	3/8	5
Althaus[21]	1999	273/293[a]	0.5/10	17
Chapoy[22,23]	2005	283/318	1/34.6	39
Folas[24]	2007	273/293[a]	1/18	8

[a] Data on water content from ice–gas or hydrate–gas regions were also measured.

THEORY

An equation of state is applied in the first method. With the above mentioned assumption, that the influence of methane solubility in liquid water on the calculated water content can be neglected, the equilibrium conditions for the given fixed values of temperature T, $T = \hat{T}$, and pressure P, $P = \hat{P}$, are based on only two equations and have the following form

$$f_1^{\text{gas}}(\hat{T}, v^{\text{gas}}, y_1) = f_1^{0,\text{liq}}(\hat{T}, \hat{P}) \quad P(\hat{T}, v^{\text{gas}}, y_1) = \hat{P}. \tag{5}$$

The condition for satisfying equality of fugacities of water in both phases is contained in the first equation. The second equation corresponds to the EOS. The equality of fugacities of methane in both phases is replaced by the relation $x_2 = 0$. Relation (*5*) is a set of two equations for two unknowns: the molar volume of the gaseous phase v^{gas} and the molar fraction of water in gaseous phase y_1 (water content).

The fugacity of pure liquid water $f_1^{0,\text{liq}}$ is determined from basic thermodynamic relations for a pure component

$$\left(\frac{\partial \ln f}{\partial P}\right)_T = \frac{v}{RT} \quad \lim_{P \to 0} \frac{f^{0,\text{gas}}}{P} = 1 \quad f^{0,\text{liq}}(T, P^{\text{sat}}) = f^{0,\text{gas}}(T, P^{\text{sat}}). \tag{6}$$

It follows from (*6*) that

$$f^{0,\text{liq}}(T,P) = f^{0,\text{liq}}(T, P^{\text{sat}}) \exp\left(\frac{1}{RT} \int_{P^{\text{sat}}}^{P} v^{0,\text{liq}}\, \mathrm{d}P\right) = \tag{7}$$

$$= P^{\text{sat}}(T) \exp\left(\frac{1}{RT}\left[\int_{P^{\text{sat}}}^{P} v^{0,\text{liq}}\, \mathrm{d}P + \int_{0}^{P^{\text{sat}}} \left(v^{0,\text{gas}} - \frac{RT}{P}\right) \mathrm{d}P\right]\right).$$

The dependence of the molar liquid volume on the pressure can be neglected. Since the vapor pressure of water P^{sat} is less than the atmospheric pressure ($T < 373$ K), the virial EOS $v^{\text{gas}} = RT/P + B(T)$ can be used. Incorporating these assumptions, relation (*7*) can be rewritten into the final form

$$f^{0,\text{liq}}(T,P) = P^{\text{sat}}(T) \exp\left(\frac{v^{0,\text{liq}}(P - P^{\text{sat}}) + BP^{\text{sat}}}{RT}\right). \tag{8}$$

Fugacity f_1^{gas} is determined from the thermodynamic relation[38]

$$\ln f_1(T,v,y_1) = \ln\frac{y_1 RT}{v} + \frac{1}{RT}\int_V^{\infty}\left[\left(\frac{\partial P}{\partial n_1}\right)_{T,V,n_2} - \frac{RT}{V}\right]\mathrm{d}V \qquad v = \frac{V}{n_1 + n_2}. \tag{9}$$

The RKS equation of state[31]

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)} \tag{10}$$

with the classical quadratic mixing rules

$$b = b_{11}y_1 + b_{22}y_2 \qquad a = a_{11}y_1^2 + 2a_{12}y_1y_2 + a_{22}y_2^2 \qquad a_{12} = (1-k_{12})\sqrt{a_{11}a_{22}} \tag{11}$$

is used to describe the state behavior of the gaseous phase. Based on (*9*), (*10*) and (*11*), the formula for the fugacity of water in gaseous phase is

$$\ln f_1^{\mathrm{gas}}(T,v,y_1) = \ln\frac{y_1 RT}{v-b} + \frac{b_{11}}{v-b} - \frac{ab_{11}}{RTb(v+b)} - \frac{b\bar{a}_1 - y_2 a(b_{11}-b_{22})}{RTb^2}\ln\frac{v+b}{v} \tag{12}$$

$$\bar{a}_1 = a + y_2\frac{\mathrm{d}a}{\mathrm{d}y_1} = a + 2y_2(a_{11}y_1 + a_{12}(y_2 - y_1) - a_{22}y_2).$$

The optimal value of the interaction parameter k_{12}^{opt} minimizes the objective function $\Phi(k_{12})$

$$\Phi(k_{12}) = \sum_{i=1}^{N}\left(\frac{y_{1,i}^{\mathrm{exp}} - y_{1,i}^{\mathrm{calc}}}{y_{1,i}^{\mathrm{exp}}}\right)^2 \tag{13}$$

where T_i, P_i, $y_{1,i}^{\mathrm{exp}}$ (i = 1, 2, ..., N) are experimental points and $y_{1,i}^{\mathrm{calc}}$ is calculated from (*5*) for the given values of temperature T_i, pressure P_i and k_{12}. The mean quadratic percentage standard deviation σ(%)

$$\sigma(\%) = 100\sqrt{\Phi(k_{12}^{\mathrm{opt}})/(N-1)} \tag{14}$$

is used as a measure of goodness of fit.

Derivation of the explicit formula: Dependence of the fugacity of water in the gaseous phase on temperature and pressure is described by the general relation[38]

$$f_1^{\text{gas}}(T,P,y_1) = y_1 P \exp\left(\frac{1}{RT}\int_0^P (\bar{v}_1 - \frac{RT}{P})\,\mathrm{d}P\right) \quad \bar{v}_1 = v^{\text{gas}} + y_2\left(\frac{\partial v^{\text{gas}}}{\partial y_1}\right)_{T,P} . \qquad (15)$$

The volume explicit (Berlin) form of the virial EOS containing the second virial coefficient B

$$v^{\text{gas}} = \frac{RT}{P} + B(T,y_1) \quad B = B_{11}y_1^2 + 2B_{12}y_1y_2 + B_{22}y_2^2 \qquad (16)$$

is used to describe the state behavior of the gaseous phase. Combining (*15*), (*16*) and the equilibrium condition

$$f_1^{\text{gas}}(T,P,y_1) = f_1^{0,\text{liq}}(T,P) \qquad (17)$$

we obtain

$$y_1 = \frac{f^{0,\text{liq}}(T,P)}{P}\exp\left(\frac{B_{11}y_1(1+y_2) + y_2^2(2B_{12} - B_{22})}{RT}P\right). \qquad (18)$$

The value of y_1 (water content) is less than 0.01 at temperatures from 273 to 293 K and pressures from 0.5 to 10 MPa (the pressure in gas pipelines is usually significantly higher than 0.5 MPa and less than 10 MPa). So, the assumption $\bar{v}_1 \approx \bar{v}_1^\infty$ can be used. Therefore, the final explicit analytical formula has the following form

$$y_1 = \frac{f^{0,\text{liq}}(T,P)}{P}\exp\left(\frac{2B_{12} - B_{22}}{RT}P\right) \qquad (19)$$

where $f^{0,\text{liq}}$ is given in (*8*). The virial coefficient B_{22} depends only on temperature, but the cross virial coefficient B_{12} depends on the interaction parameter l_{12}

$$B_{12} = (1 - l_{12})\beta_{12} \qquad (20)$$

where β_{12} depends only on temperature. There are many possibilities in choosing β_{12}, but the geometric or arithmetic mean of B_{11} and B_{22} is often used. Relations between the harmonic, geometric, arithmetic and quadratic mean

$$\xi_1 < 2 / \left(\frac{1}{\xi_1} + \frac{1}{\xi_2} \right) < \sqrt{\xi_1 \xi_2} < \frac{\xi_1 + \xi_2}{2} < \sqrt{\frac{\xi_1^2 + \xi_2^2}{2}} < \xi_2 \qquad (21)$$

hold for an arbitrary pair of two different positive numbers ξ_1, ξ_2, $\xi_1 < \xi_2$. In our case, the values of $-B_{11}$ and $-B_{22}$ are always positive. Table III contains data from Rigby and Prausnitz[16] where the B_{12} values were determined from experimental values of water content in compressed methane. It is evident that B_{12} values are very close to the virial coefficients of methane B_{22}. Obviously, the harmonic mean is a significantly better choice than the geometric one. For example (see Table III), the geometric mean of two virial coefficients –1170 and –43.25 is –225, and the harmonic mean is –83. Therefore, the harmonic mean of B_{11} and B_{22}

$$\beta_{12} = 2 / \left(\frac{1}{B_{11}} + \frac{1}{B_{22}} \right) \qquad (22)$$

was used in relation (*20*).

In view of the high-pressure region, the volume explicit form of the virial EOS containing the third virial coefficient[38] C

TABLE III
Virial coefficients of water (1) and methane (2)

T, K	$-B_{11}$	$-B_{22}$	$-B_{12}$	C_{222}	$C_{222}-B_{22}^2$
273	1700[a]	53.37±0.15	–	2660±50	–190
283	1450[a]	48.91±0.15	–	2565±50	170
293	1250±50	44.82±0.15	–	2480±50	470
298	1170±50	43.25±0.15	63±6	2440±50	570
323	825±15	34.31±0.15	46±5	2250±50	1070
348	590±10	27.5±0.3	37±4	2100±100	1340
373	454±5	21.3±0.3	30±3	2000±100	1550

[a] Extrapolated value. $[B] = cm^3/mol$, $[C] = cm^6/mol^2$.

$$v^{\mathrm{gas}} = \frac{RT}{P} + B + (C - B^2)\frac{P}{RT} \qquad B = B_{11}y_1^2 + 2B_{12}y_1y_2 + B_{22}y_2^2 \qquad (23)$$

$$C = C_{111}y_1^3 + 3C_{112}y_1^2y_2 + 3C_{122}y_1y_2^2 + C_{222}y_2^3$$

was at first chosen to describe the gaseous state behavior. Combining (*15*) and (*23*) the formula for the partial molar volume of water in an infinite dilute solution is

$$\bar{v}_1^{\infty} = \frac{RT}{P} + 2B_{12} - B_{22} + \frac{P}{RT}(3C_{122} - 2C_{222} - 4B_{22}B_{12} + 3B_{22}^2)\,. \qquad (24)$$

Different types of weighted harmonic means were used for the estimation of the cross virial coefficient C_{122}. Values for the third virial coefficient of methane C_{222} were taken from literature[39]. Absolute values of C_{111} are very high[40] in the considered temperature interval 273–288 K, and thus the estimated value C_{122} is close to the value C_{222}. The influence of the term $(C - B^2)P/RT$ in (*23*) on the calculated value of water content was surprisingly very small and neglectable even for pressures close to 10 MPa. The implication

$$B_{12} \approx B_{22} \text{ and } C_{122} \approx C_{222} \Rightarrow 3C_{122} - 2C_{222} - 4B_{22}B_{12} + 3B_{22}^2 \approx C_{222} - B_{22}^2 \qquad (25)$$

explains this result. The last column in Table III contains values $C_{222} - B_{22}^2$ at different temperatures. The convex behavior of the isothermal methane z–P curve becomes concave and vice versa in the temperature interval 273–283 K. Therefore, the absolute values of $C_{222} - B_{22}^2$ are very low in this temperature region. Hence, the simple EOS (*16*) can be used up to a pressure of 10 MPa.

Up to now we focused on the liquid–gas region (see Fig. 1). Use of both methods (*5*) and (*19*) in the ice–gas region is simple. If $T < 273$ K, then it is necessary to replace superscript "liq" in relations (*8*) and (*19*) by superscript "solid", where $v^{0,\mathrm{solid}}$ is molar volume of ice. Symbol P^{sat} is the vapor pressure above liquid water (if $T > 273$ K) or above ice (if $T < 273$ K).

CALCULATION AND DISCUSSION

Results of the first method are given in Table IV. The different set of data+ were separately used for the determination of the interaction parameter k_{12}, its confidence interval (the level of significance is 95%) and the standard deviation σ(%) defined in the relation (*14*). The temperature dependence of the interaction parameter was assumed in the form

$$k_{12} = k_{12,0} + k_{12,1}\left(\frac{T}{273.15} - 1\right). \qquad (26)$$

The value $k_{12,1}$ was set to zero for all of the data sets, as any non-zero value of $k_{12,1}$ did not make a statistical significant decrease in the objective function (*13*). In agreement with Folas et al.[24] we conclude that Culbertson's data[15] are greatly scattered. We performed a statistical analysis of our results. Based on the temperature intervals given in Table II and results given in Table IV, most pairs of experimental data sets are surprisingly not mutually consistent. The relatively great disagreements exist also between new data sets. A comparison of the three "newest" authors is presented in Table V. It is difficult to compare experimental points from various authors because

TABLE IV
Interaction parametr k_{12} and standard deviation σ(%) for different set of experimental data

Literature	k_{12}	σ, %	Literature	k_{12}	σ, %
Olds[13]	0.470±0.0075	1.9	Yarym-Agaev[19]	0.452±0.035	4.9
Gillespie[14]	0.520±0.031	3.0	Yokoyama[20]	0.500±0.060	3.5
Culberson[15]	0.520±0.051	11.9	Althaus[21]	0.544±0.0061	1.0
Rigby[16]	0.510±0.0088	0.8	Chapoy[23]	0.504±0.0068	4.1
Sharma[17]	0.470±0.031	5.6	Folas[24]	0.692±0.046	4.2
Kosyakov[18]	0.630±0.076	4.6	Refs[16+21]	$k_{12,0} = 0.552$ $k_{12,1} = -0.170$	1.1

+ Water content measured by Yokoyama et al.[20] at $T = 298.15$ K and $P = 8$ MPa was not included into the fit. It was probably an outlier. Water content measured by Folas et al.[24] at $T = 293.15$ K and $P = 18$ MPa was also not considered.

each author has a different set of (T, P) points. If pressure P_2 is close to pressure P_1 then the Taylor series

$$y_1(T,P_2) = y_1^{\exp}(T,P_1) + \left(\frac{\mathrm{d}y_1}{\mathrm{d}P}\right)_{T,P=P_1} (P_2 - P_1) \qquad (27)$$

is used for the determination of the "experimental" point at pressure P_2. The numerical formula

$$\left(\frac{\mathrm{d}y_1}{\mathrm{d}P}\right)_{T,P=P_1} \approx \frac{y_1^{\mathrm{calc}}(T,P_1+h) - y_1^{\mathrm{calc}}(T,P_1-h)}{2h} \qquad h = 0.001P_1 \qquad (28)$$

is used for the calculation of the first derivative in relation (*27*). The last column in Table V contains the maximum percentage deviation between two authors. We have found only one pair of data (Rigby[16] and Althaus[21]) where the union data in one input file does not lead to a significant increase of the standard deviation σ(%). The union of temperature intervals of both sets of data is the temperature interval 273–373 K which is the object of our attention. Including both data sets into one data file and minimizing the objective function (*13*), the values of

TABLE V
Water content $y_1 \times 10^3$ measured in the gas phase of the water–methane system. Comparison of three experimental data sets

T, K	P, MPa	Althaus[21]	Chapoy[23]	Folas[24]	%[a]
273	1.5	0.426	–	0.4157	2.5
283	1.5	0.851	–	0.8530	2.3
283	4	0.357	–	0.3139	13.7
283	6	0.251	0.292	0.2402	14.0
288	6	0.350	0.381[b]	–	8.9
288	10	0.244	0.273	–	11.8
293	4	0.665	–	0.5935	12.0
293	6	0.470	0.464[c]	0.4281	9.8
293	10	0.332	0.322[d]	0.2544	30.5

[a] The percentage deviation. [b] Calculated from experimental pressure 6.023 MPa. [c] Calculated from experimental pressure 5.77 MPa. [d] Calculated from experimental pressure 9.52 MPa.

$$k_{12,0} = 0.552 \quad k_{12,1} = -0.170 \tag{29}$$

and σ(%) = 1.1 were obtained (see the last row in Table IV).

The temperature dependence of the interaction parameter l_{12} in the explicit formula (*19*) was chosen analogically as in relation (*26*) in the form

$$l_{12} = l_{12,0} + l_{12,1}\left(\frac{T}{273.15} - 1\right). \tag{30}$$

TABLE VI
Comparison of experimental[21] and calculated values of water content. The explicit formula (*19*) with parameters (*31*) is used

T, K	P, MPa	$y_1^{\mathrm{exp}} \times 10^3$	$y_1^{\mathrm{calc}} \times 10^3$	%
273.15	0.5	1.23	1.24	–0.7
273.15	1.5	0.426	0.428	–0.5
278.15	0.5	1.75	1.77	–1.1
278.15	1.5	0.616	0.611	0.7
278.15	4	0.250	0.251	–0.3
283.15	1.5	0.851	0.860	–1.1
283.15	4	0.357	0.353	1.2
283.15	6	0.251	0.252	–0.6
288.15	1.5	1.18	1.19	–1.2
288.15	4	0.485	0.489	–0.9
288.15	6	0.350	0.350	–0.0
288.15	8	0.284	0.282	0.8
288.15	10	0.244	0.242	0.8
293.15	4	0.665	0.670	–0.7
293.15	6	0.470	0.479	–1.8
293.15	8	0.386	0.385	0.3
293.15	10	0.332	0.330	0.5

Results for Althaus[21] data are given in Table VI. A standard deviation of σ(%) = 0.89 is obtained when parameters[+]

$$l_{12,0} = 0.431 \quad l_{12,1} = -1.020 \qquad (31)$$

are used. The statistical difference between the zero and non-zero values of parameter $l_{12,1}$ is small. A standard deviation of σ(%) = 1.1 is obtained when parameters $l_{12,0} = 0.373$ and $l_{12,1} = 0$ are used.

The explicit formula (*19*) with parameters (*31*) and equilibrium conditions (*5*) with parameters (*29*) were used for water content prediction in the gaseous phase in equilibrium with ice. Results are given in Table VII. The third column contains data published by Althaus[21]. Both calculation methods gave almost the same results (differences were always less than 0.3%), the percentage differences between experimental and calculated points are given in the fourth column. A comparison with the experimental data reveals a strong correlation, which is promising, especially considering that deviations between experimental data of different authors are about 10% (see note *a* in Table VII).

TABLE VII
Experimental[21] and calculated water contents in the ice–gas region. The explicit formula (*19*) with parameters (*31*) is used

T, K	*P*, MPa	$y_1^{\text{exp}} \times 10^3$	$y_1^{\text{calc}} \times 10^3$	%
253.15	0.5	0.213	0.209	1.9
258.15	0.5	0.307	0.335	–9.1
258.15	1.5	0.111	0.116	–4.5
263.15	0.5	0.523	0.527	–0.8
263.15	1.5	0.185[a]	0.182	1.6
268.15	0.5	0.829	0.817	1.5
268.15	1.5	0.280	0.283	–1.1

[a] The value measured by Folas et al.[23] was 0.2031.

[+] The symbol k_{12} in relations (*13*) and (*14*) is replaced by the symbol l_{12}.

INPUT DATA

Critical values and acentric factors of water and methane were taken from Section A in Poling et al.[41]. Parameters of the Wagner equation to describe the temperature dependence of vapor pressure of water ($T > 273$ K) were also taken from Section D in Poling et al.[41]. The Setzmann and Wagner equation[42,43] for vapor pressure of water was used at the temperature range 253–273 K.

Temperature dependencies of virial coefficients

$$
\begin{aligned}
B_{11} &= -4324.3 + \frac{0.3419 \times 10^{7}}{T} - \frac{0.738 \times 10^{9}}{T^{2}} \quad [\mathrm{cm^3/mol}] \\
B_{22} &= 67 - \frac{32890}{T} \quad [\mathrm{cm^3/mol}] \\
C_{222} &= 189 + \frac{712800}{T} \quad [\mathrm{cm^6/mol^2}]
\end{aligned}
\tag{32}
$$

were determined from data by Dymond and Smith[44], Cholinski et al.[45] and Kleinrahm et al.[39] in the temperature interval 273–373 K. (Relations (*32*) and (*33*) were also used (see Table VII) at temperatures below 273 K.) Parameters describing the temperature dependence of the molar volume of liquid water (influence of pressure is neglected)

$$
v^{0,\mathrm{liq}} = 18.0214 + 0.3085 \times 10^{-2}\,\xi + 0.6128 \times 10^{-4}\,\xi^{2} \quad [\mathrm{cm^3/mol}] \tag{33}
$$

$$
\xi = T - 283.15
$$

were calculated from data given by Vargaftik[46]. The temperature dependence of the molar volume of ice was calculated from the equation

$$
v^{0,\mathrm{solid}} = 19.651 - 2.95 \times 10^{-3}\,\xi \quad [\mathrm{cm^3/mol}] \tag{34}
$$

$$
\xi = 273.15 - T\,.
$$

CONCLUSIONS

Two methods to calculate the water content of water (1)–methane (2) system in the liquid–gas and ice–gas regions were proposed and tested in this work. Both of them are based on the assumption that the influence of methane solubility in liquid water on the calculated water contents can be neglected (i.e., only pure water is considered in the liquid phase). Usage of the first method described by relations (*5*), (*10*), (*11*) and (*26*) with parameters (*29*) allows for the accurate calculation of the water content in the gaseous phase of water–methane system in the ice–gas and liquid–gas regions up to 380 K. Application of the explicit formula described by relations (*19*), (*20*) and (*22*) with parameters (*31*) is limited up to a pressure of 10 MPa.

Most pairs of experimental data sets are not mutually consistent and, combining two data sets, the standard deviation (*13*) significantly increases. We conclude that Althaus data[21] and Rigby and Prausnitz data[16] are the best. Most of the data is measured at temperatures higher than 300 K, and there is lack of experimental data in the temperature interval 273–288 K. This range is important from a practical point of view, as there is a possibility of hydrate formation from the liquid water phase during natural gas transport.

SYMBOLS

a, b	parameters in EOS
B	second virial coefficient
C	third virial coefficient
f or f^{0}	general denotation for fugacity or fugacity of pure compound
$f_1^{0,\mathrm{liq}}$ or $f_1^{0,\mathrm{gas}}$	fugacity of pure liquid or gaseous water
k_{12}^{opt}	optimal value of the interaction parameter k_{12}
l_{12}	interaction parameter
n_i	number of moles of the i-th component
N	number of experimental points
P_{c}	critical pressure
P^{sat}	saturated vapor pressure of water
R	universal gas constant
T_{c}	critical temperature
v	molar volume
$\bar{v}_1$	partial molar volume of the first component (water)
$\bar{v}_1^{\infty}$	partial molar volume of water in the infinite dilute solution, $\bar{v}_1^{\infty} = \lim\limits_{x_1 \to 0} \bar{v}_1$
V	total volume, $V = nv$
x	molar fraction in liquid phase
y	molar fraction in gaseous phase
z	compressibility factor

P. Voňka thanks Prof. J. Lovland for very useful discussions in the time of the author's stay at NTNU Trondheim. This work was supported by the Ministry of Education, Youth and Sports of the Czech Republic (Grant No. 6046137307).

REFERENCES

1. Kabadi V. N., Danner R. P.: *Ind. Eng. Chem. Process Des. Dev.* **1985**, *24*, 537.
2. Michel S., Hooper H. H., Prausnitz J. M.: *Fluid Phase Equilib.* **1989**, *45*, 173.
3. Meistr V.: *Ph.D. Thesis*. Institute of Chemical Technology, Prague, Prague 2008.
4. Nasrifar K., Moshfeghian M., Rasmussen P.: *Fluid Phase Equilib.* **2002**, *193*, 261.
5. Tsonopoulos C., Wilson G. M.: *AIChE J.* **1983**, *29*, 990.
6. Economou I. G., Tsonopoulos C.: *Chem. Eng. Sci.* **1997**, *52*, 511.
7. Economou I. G., Heidman J. L., Tsonopoulos C., Wilson G. M.: *AIChE J.* **1997**, *43*, 535.
8. Heidman J. L., Tsonopoulos C., Brady C. J., Wilson G. M.: *AIChE J.* **1985**, *31*, 376.
9. Kontogeorgis G. M., Voutsas E. C., Yakoumis I. V., Tassios D. P.: *Ind. Eng. Chem. Res.* **1996**, *35*, 4310.
10. Kontogeorgis G. M., Yakoumis I. V., Meijer H., Hendriks E. M., Moorwood T.: *Fluid Phase Equilib.* **1999**, *158–160*, 201.
11. Eubank T. B., Scheloske J. J., Joffrion L. L.: *Fluid Phase Equilib.* **1986**, *30*, 255.
12. Munck J., Skjold-Jorgensen S., Rasmussen P.: *Chem. Eng. Sci.* **1988**, *43*, 2661.
13. Olds R. H., Sage B. H., Lacey W. N.: *Ind. Eng. Chem.* **1942**, *34*, 1223.
14. Gillespie P. C., Wilson G. M.: *GPA Research Report RR-48*. University of Tulsa, Tulsa 1948.
15. Culberson O. L., McKetta J. J.: *Trans. AIME* **1951**, *192*, 297.
16. Rigby M., Prausnitz J. M.: *J. Phys. Chem.* **1968**, *72*, 330.
17. Sharma S. S.: *Ph.D. Thesis*. University of Oklahoma, Oklahoma City 1969.
18. Kosyakov N. E., Ivchenko B. I., Krishtopa P. P.: *Vopr. Khim. Khim. Tekhnol.* **1982**, *68*, 33.
19. Yarym-Agaev N. L., Sinyavskaya R. P., Koliushko I. I., Levinton L. Ya: *Zh. Prikl. Khim.* **1985**, *58*, 165.
20. Yokoyama C., Wakana S., Kaminishi G., Takahashi S.: *J. Chem. Eng. Data* **1988**, *33*, 274.
21. Althaus K.: *Measurement and Calculation of the Water Contents of Hydrocarbon-Containing Gas Mixtures*. Fortschritt-Berichte VDI, Reihe 3, No. 590, p. 175. VDI Verlag, Düsseldorf 1999.
22. Chapoy A., Coquelet C., Richon D.: *Fluid Phase Equilib.* **2003**, *214*, 101.
23. Chapoy A., Coquelet C., Richon D.: *Fluid Phase Equilib.* **2005**, *230*, 210. (Corrigendum to ref.[22].)
24. Folas G. K., Froyna E. W., Lovland J., Kontogeorgis G. M., Solbraa E.: *Fluid Phase Equilib.* **2007**, *252*, 162.
25. Avila S., Blanco S. T., Velasco I., Rauzy E., Otin S.: *Phys. Chem. Liq.* **2002**, *40*, 661.
26. Peng D. Y., Robinson D. B.: *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59.
27. Trebble M. A., Bishnoi P. R.: *Fluid Phase Equilib.* **1987**, *35*, 1.
28. Daridon J. L., Lagourette B., Saint-Guirons H., Xans P.: *Fluid Phase Equilib.* **1993**, *91*, 31.
29. Renon H., Prausnitz J. M.: *AIChE J.* **1968**, *14*, 135.
30. ISO 18453: *Natural Gas, Correlation Between Water Content and Dew Point*. International Organization for Standardization, Geneva 2004.
31. Soave G.: *Chem. Eng. Sci.* **1972**, *27*, 1197.

32. Voňka P., Lovland J., Heimlid J. R.: *Water Content in n-Alkane + Water Gases*. Presented at *15th European Seminar on Applied Thermodynamics, Runcorn, Liverpool, June 12, 1996.*
33. Voňka P., Lovland J., Heimlid J. R. : *Equilibrium Water Content of Natural Gas Over Saturated NaCl Solutions*. Presented at *CHISA, Prague, August 25, 1996*.
34. Lovland J., Voňka P., Köckritz V., Walden S., Gautestad C.: *Water Content of Methane in Equilibrium with Saturated NaCl Solutions*. Presented at *First European Congress of Chemical Engineering, Firenze, May 4, 1997*.
35. Lovland J., Voňka P., Köckritz V., Walden S., Kadner K., Westby A.: *Water Content of Natural Gas in Equilibrium with Saturated Salt Solutions*. Presented at *Eighth International Conference on Properties and Phase Equilibria for Product and Process Design, Noordwijkerhout, April 26, 1998*.
36. Fichtner S., Voňka P., Lovland J.: *Water Content of Natural Gas Components*. Proc. *19th European Seminar on Applied Thermodynamics, p. 369, Santorini, September 6, 2002*.
37. Mohammadi A. H., Chapoy A., Tohodi B., Richon D.: *Ind. Eng. Chem. Res.* **2004**, *43*, 7137.
38. Prausnitz J. M., Lichtenthaler R. N., Azevedo E. G.: *Molecular Thermodynamics of Fluid-Phase Equilibria,* 3rd ed., pp. 34, 45, 128, 775–777. Prentice Hall, New Jersey 1999.
39. Kleinrahm R., Duschek W., Wagner W., Jaeschke M.: *J. Chem. Thermodyn.* **1988**, *20*, 621.
40. Kusalik P. G., Liden F., Svishchev I. M.: *J. Chem. Phys.* **1995**, *103*, 10169.
41. Poling B. E., Prausnitz J. M., O'Connel J. P.: *The Properties of Gases and Liquids*, 5th ed. McGraw–Hill, New York 2001.
42. Setzmann U., Wagner W.: *Int. J. Thermophys.* **1989**, *10*, 1103.
43. Wagner W., Saul A., Pruss A.: *J. Phys. Chem. Ref. Data* **1994**, *23*, 515.
44. Dymond J. H., Smith E. B.: *The Virial Coefficients of Pure Gases and Mixtures, A Critical Compilation*. Clarendon Press, Oxford 1980.
45. Cholinski J., Szafranski A., Stankiewicz D.: *Computer-Aided Second Virial Coefficient Data for Organic Individual Compounds and Binary Systems*. PWN – Polish Scientific Publishers, Warszawa 1986.
46. Vargaftik N. B.: *Tables on the Thermophysical Properties of Liquids and Gases*. John Wiley & Sons, New York 1975.