



ELSEVIER

Journal of Hazardous Materials B88 (2001) 53–62

**Journal of
Hazardous
Materials**

www.elsevier.com/locate/jhazmat

Vapor–liquid activity coefficients for methanol and ethanol from heat of solution data: application to steam–methane reforming

R.G. Kunz*, W.F. Baade

Air Products and Chemicals, Inc., Allentown, PA 18195-1501, USA

Received 30 November 2000; accepted 17 March 2001

Abstract

This paper presents equations and curves to calculate vapor–liquid phase equilibria for methanol and ethanol in dilute aqueous solution as a function of temperature, using activity coefficients at infinite dilution. These thermodynamic functions were originally derived to assess the distribution of by-product contaminants in the process condensate and the steam-system deaerator of a hydrogen plant [Paper ENV-00-171 presented at the NPRA 2000 Environmental Conference, San Antonio, TX, 10–12 September 2000], but have general applicability to other systems as well. The functions and calculation method described here are a necessary piece of an overall prediction technique to estimate atmospheric emissions from the deaerator-vent when the process condensate is recycled as boiler feed water (BFW) make-up.

Having such an estimation technique is of particular significance at this time because deaerator-vent emissions are already coming under regulatory scrutiny in California [Emissions from Hydrogen Plant Process Vents, Adopted 21 January 2000] followed closely elsewhere in the US, and eventually worldwide. The overall technique will enable a permit applicant to estimate environmental emissions to comply with upcoming regulations, and a regulatory agency to evaluate those estimates. It may also be useful to process engineers as a tool to estimate contaminant concentrations and flow rates in internal process streams such as the steam-generating system. Metallurgists and corrosion engineers might be able to use the results for materials selection. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Vapor–liquid phase equilibria; Deaerator-vent; Steam–methane reforming

* Corresponding author. Tel.: +1-610-395-5114.

E-mail address: kunzrg@aol.com (R.G. Kunz).

1. Introduction

Now that many major sources of industrial emissions to the atmosphere have been addressed, some miscellaneous emission points of a lesser nature are coming to light as greater scrutiny is focused on petrochemical manufacturing processes [2,3]. One such emission from a steam–methane reformer (SMR) plant producing hydrogen is the vent from the steam-system deaerator vessel when process condensate is recycled for reuse as boiler feed water (BFW) make-up. Atmospheric contaminants in units of parts per million by volume (ppmv) are formed in the gas-phase reaction product during hydrogen production, enter the liquid-phase process condensate, and are released to the environment along with the vented steam.

In developing a method to predict the methanol and ethanol components in the vented steam, it became necessary to estimate the vapor–liquid equilibrium (VLE) of methanol and ethanol in dilute aqueous solution, both in the condensation step and in the steam-stripping step of the deaerator. For this situation, the vapor–liquid distribution ratio for the contaminants is most appropriately calculated from Henry's law. Because no satisfactory expression for the Henry's law constant (H) for methanol and ethanol was found to be readily available over the temperature range of interest, it was decided to obtain H from the product of vapor pressure and the VLE activity coefficient at infinite dilution. The activity coefficient function was, in turn, computed from heat of solution data at infinite dilution and compared with point values of activity coefficients summarized in the literature.

Following a very brief description of the SMR hydrogen manufacturing process and the origin of the methanol and ethanol by-products, the remainder of this paper explores the derivation of their activity coefficient functions and compares them with the reported data. These functions have proven useful in estimating process condensate composition and atmospheric emissions from the deaerator-vent. Those results are discussed elsewhere [1].

2. H₂ process description

The SMR process reacts natural gas, refinery fuel gas, or other hydrocarbons with an excess of steam (H₂O) to produce a mixture of hydrogen (H₂) and carbon monoxide (CO), generically known as synthesis gas (syngas). Excess steam must be added to the hydrocarbon feedstock to prevent coke formation. Major process steps consist of sulfur removal to protect process catalysts, reforming, water-gas shift (WGS), and H₂ product purification. A more complete description, including flow diagrams, is given in our previous presentation [1].

The SMR equilibrium reaction, shown below for methane (CH₄), occurs in catalyst-packed tubes at high temperature and pressure in a radiant furnace:



The WGS reaction



also occurs to some extent in the reformer tubes. To maximize hydrogen production, the WGS reaction can be continued by supplying additional steam to one or more shift-converter vessels downstream of the furnace. These vessels are known as the high-temperature shift (HTS) and low-temperature shift (LTS), respectively. They contain catalysts which are different from reformer catalyst and different from each other.

The combined hydrogen production reaction can be written as follows:



3. By-products from side reactions

In addition to the desired reforming and shift reactions, a number of side reactions occur, with concentrations measured in units of parts per million by volume (vppm) in the syngas. The resulting process contaminants include, among others [1] ammonia synthesized in the reformer by reaction of hydrogen with the nitrogen (N_2) originating from the feedstock, and methanol and ethanol (the subjects of this paper) formed in the shift converters when using copper-promoted shift catalysts [4–6]. No appreciable methanol is found in SMR plants without shift conversion.

Ten to one hundred times more methanol is made in the LTS than in the HTS because of the more favorable conditions of the LTS [5–7] and the higher copper concentrations in LTS catalyst formulations, although the development of low-methanol LTS catalysts has been subsequently reported [8].

The overall reaction for methanol formation is [9–14]



Ethanol occurs presumably by condensation of methanol and splitting out of water [15].



4. Hydrogen plant process condensate

When the intermediate syngas product is cooled prior to hydrogen purification, excess moisture above saturation condenses along with water-soluble process contaminants such as methanol and ethanol. Each of the major syngas components — hydrogen, carbon monoxide, methane, and nitrogen — exhibits limited solubility in the condensate because of an unfavorable (high) Henry's law constant at the temperature of condensation. With the pressure-swing-adsorption (PSA) option for hydrogen product separation, condensation temperature may vary from 80 to 100°F (300 to 311K).

Although dilute, process condensate makes up a complex aqueous solution. Even in the simplest case, it consists of dissolved gases and molecular and ionic species dissolved in water; its pH is roughly in the range of 4–6, governed by ionic equilibria involving carbon dioxide, ammonia, and traces of organic acids and bases.

At typical HTS exit temperatures, methanol formation is controlled by equilibrium [5,6,16] and is more or less independent of catalyst type. This results in methanol

concentrations on the order of 100–300 parts per million by weight (wppm or mg/l), as measured in the process condensate following HTS alone [5,16]. Ethanol (C₂H₅OH) also occurs at 5–10% of the methanol concentration in the HTS.

In the LTS, methanol formation is favored by equilibrium, but limited by kinetics [5,6,16] including the activity of the catalyst. In one study [7], methanol concentrations decreasing with catalyst age extrapolate back to the range of 1000–10,000 wppm for fresh catalyst, depending on temperature.

5. The deaerator-vent

Process condensate is typically recycled to the steam-generation system where it joins a stream of pretreated make-up water upstream of the deaerator to become boiler feed water (BFW). This is one of the final stages of water conditioning prior to steam production. A typical operating condition for a hydrogen-plant deaerator vessel is 230°F (383K), corresponding to a saturated-steam pressure of approximately 6 psig (~143 kPa, absolute).

In the deaerator vessel, the feed water make-up is stripped with steam to remove dissolved oxygen, carbon dioxide, and other dissolved gases detrimental to boiler operation. When raw process condensate is reused as make-up to the steam generating system, methanol, ethanol, and other dissolved atmospheric contaminants are also stripped in the deaerator. These are emitted to atmosphere from the deaerator-vent, along with the intended treatment targets, oxygen and carbon dioxide.

6. Phase equilibria — Henry's law

Volatile species like methanol and ethanol will tend to distribute themselves between a liquid and a gaseous phase. This applies both to the interchange between the syngas and condensate and to the steam-stripping of condensate in the deaerator. Because the concentrations of contaminant species are relatively low in a large excess of solvent (liquid water), the appropriate vapor–liquid equilibrium expression is Henry's law¹

$$p = Hx \quad (6)$$

where p is the partial pressure of a given component (units of pressure); H the Henry's law constant (pressure/mole fraction); and x the mole fraction of constituent in solution (dimensionless).

¹ As calculated for typical compositions [18–21] the synthesis-gas reaction milieu is a nearly ideal gas at the high temperatures and moderate pressures being considered. The water-vapor constituent at its own vapor pressure is also close to ideal. Concentrations of contaminants in the process condensate are dilute. Therefore, in the ensuing thermodynamic relationships, pressures, rather than fugacities, and liquid concentrations, rather than activities, are being employed. In estimating properties of the condensate, it is assumed that different components condense independently; that is, each forms its own binary system with water, and nonaqueous component-to-component interactions are not important. These assumptions become better with increasingly dilute solutions. It is further assumed that the various thermodynamic constants used in the estimation are independent of pressure and of the concentration of their own or other species.

However, no satisfactory H as a function of temperature over the range of interest could be found for either methanol or ethanol. Instead, it was decided to obtain values of H indirectly from pure component vapor pressure (P_{vap}) and an activity coefficient at infinite dilution in water (γ^∞) [17]. Vapor pressures for methanol, ethanol, and water are readily available, but activity coefficients at infinite dilution must be derived from other properties.

From vapor–liquid equilibrium theory (low pressure ideal-gas phase, but not ideal-liquid behavior)

$$K = \frac{y}{x} = \frac{(\gamma^\infty P_{\text{vap}})}{P_T} \quad (7)$$

where K is the distribution coefficient, i.e. the ratio of methanol or ethanol (mole fraction) in the gaseous phase (y) divided by the mole fraction of methanol or ethanol in the liquid phase (x); γ^∞ the liquid-phase activity coefficient at infinite dilution (ppm by weight, wppm, or mg/l levels of methanol or ethanol); and P_T the total pressure.

Since

$$y = \frac{p}{P_T} \quad (8)$$

and $p = Hx$ by Eq. (6)

$$H = \gamma^\infty P_{\text{vap}} \quad (9)$$

Therefore

$$K = \frac{H}{P_T} \quad (10)$$

The activity coefficient for the water solvent becomes 1.0 at infinite dilution of the solute species, and the water mole fraction approaches 1.0. Hence, the Henry's law constant for water reduces to its vapor pressure.

7. Activity coefficients at infinite dilution

Activity coefficients can be calculated from heat of mixing data at various temperatures [22,23]. The integrated form is

$$\gamma_1^\infty \text{ at } T = \frac{1}{R \ln(10)} \int_{1/T_0}^{1/T} L_1 d(1/T) + I \quad (11)$$

where L_1 is the heat of mixing of the solute at infinite dilution, and I the activity coefficient at infinite dilution (γ_1^∞) at the reference temperature (T_0).

Data quoted in a standard reference was used [23], supplemented as necessary by additional sources [24–29]. The tabulated or estimated values for heats of solution at infinite dilution (Figs. 1 and 2) were regressed against temperature to obtain the constants of best fit for methanol and ethanol. The integration constant (I) needed in Eq. (11) above was chosen to force agreement of γ^∞ for methanol or ethanol between its temperature function and a

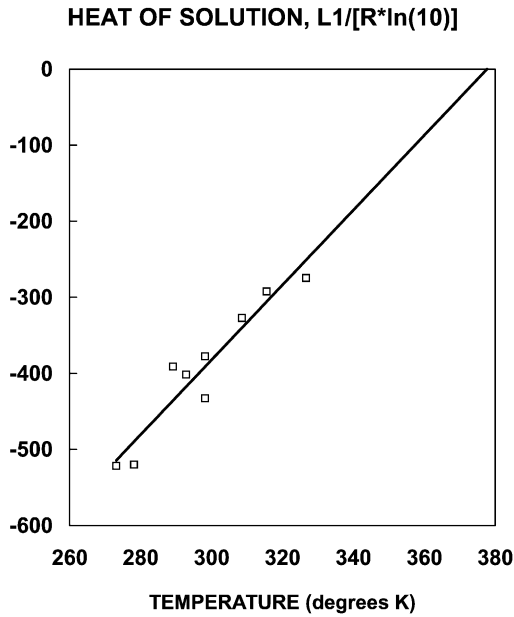


Fig. 1. Heat of solution at infinite dilution for methanol in water (data from literature sources).

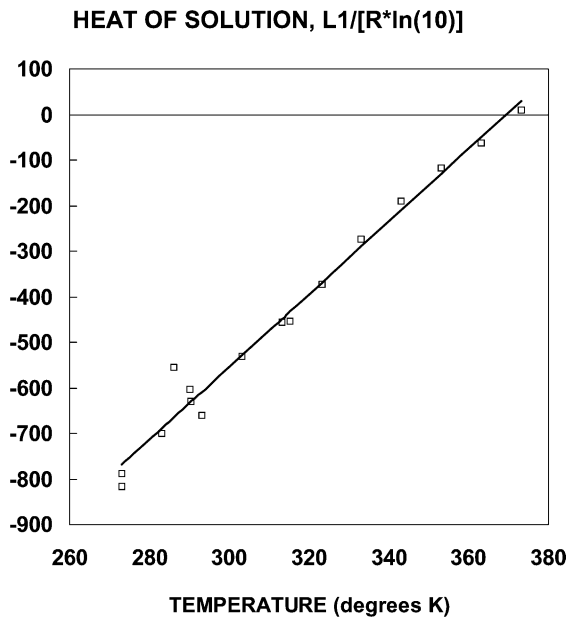


Fig. 2. Heat of solution at infinite dilution for ethanol in water (data from literature sources).

representative experimental point for each from the DECHEMA tabulations [30–32]. The dataset(s) considered to have the highest probability of producing the most accurate value of γ^∞ was/were arbitrarily selected to fix each compound's integration constant.

This methodology finally produces the following equations for $\ln \gamma^\infty$:

$$\begin{aligned} \text{Methanol : } \ln \gamma^\infty = \ln(10) & \left[-1854.74 \left(\frac{1}{T(^{\circ}K)} - \frac{1}{373.15} \right) \right. \\ & \left. - 4.921365(\ln(T(^{\circ}K)) - \ln(373.15)) \right] + \ln(2.395) \end{aligned} \quad (12)$$

$$\begin{aligned} \text{Ethanol : } \ln \gamma^\infty = \ln(10) & \left[-2947.73 \left(\frac{1}{T(^{\circ}K)} - \frac{1}{393.15} \right) \right. \\ & \left. - 7.978363(\ln(T(^{\circ}K)) - \ln(393.15)) \right] + \ln(6.23) \end{aligned} \quad (13)$$

which have *not* been simplified in order to show the origin of the constants.

The resulting curves for $\ln \gamma^\infty$ versus temperature are shown in Figs. 3 and 4, along with point values of $\ln \gamma^\infty$ derived from low-pressure vapor–liquid equilibrium data as reported by DECHEMA [30–32]. Despite considerable scatter in the data, the curves appear to provide a reasonable approximation of the point values, especially for the constant-temperature

NATURAL LOGARITHM OF GAMMA INFINITY

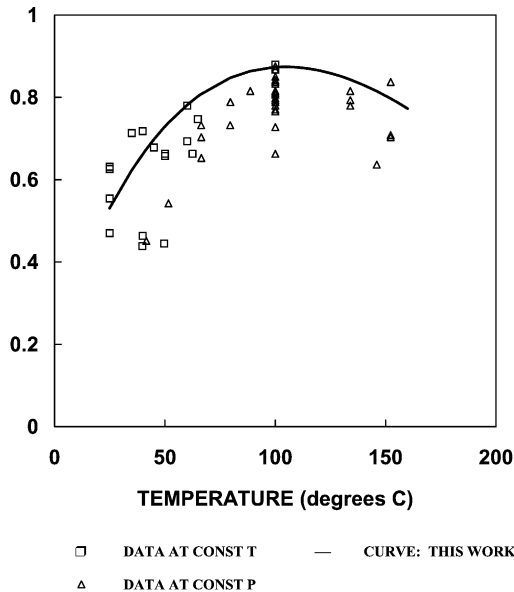


Fig. 3. Temperature variation of activity coefficient for methanol in water (VLE data from literature sources).

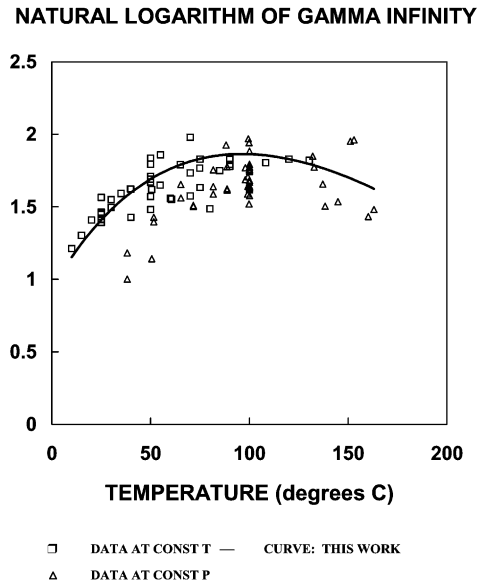


Fig. 4. Temperature variation of activity coefficient for ethanol in water (VLE data from literature sources).

data. Each curve passes through a maximum point, which corresponds to the location where the corresponding heat-of-solution relationship passes through zero. Because of the scatter of the $\ln \gamma^\infty$ data, the proper functional form for curve-fitting γ^∞ or $\ln \gamma^\infty$ directly to temperature is not obvious, necessitating the indirect approach described.

To complete the calculation of H , necessary vapor pressures can be obtained from the Antoine equation

$$\log_{10}(P_{\text{vap}} \text{ (mmHg)}) = A - \frac{B}{[t \text{ (}^\circ\text{C)} + C]} \quad (14)$$

with constants from a standard reference, e.g., [33]. Calculation of K from Eq. (10) requires the total pressure (P_T) as well.

8. Summary and conclusions

Methanol and ethanol are produced as unwanted by-products of the water-gas-shift (WGS) reaction in the steam–methane reforming (SMR) process when using a copper-containing shift catalyst. Methanol and ethanol are among the soluble constituents that wind up in the process condensate. These and other atmospheric contaminants are released to atmosphere in the stripping steam from the deaerator of the boiler feed water (BFW) treatment system when the process condensate is recycled as BFW make-up. This paper has presented equations and curves useful in computing the phase equilibria for methanol and ethanol both in the condensate and in the steam-system deaerator. Despite the scatter

of experimental data for activity-coefficients at infinite dilution, the temperature functions derived here provide a reasonable approximation of the experimental values. These functions were developed as part of an overall technique to estimate atmospheric emissions from the deaerator-vent, one of the miscellaneous sources now coming under greater regulatory scrutiny.

Acknowledgements

The authors wish to thank their many colleagues whose work has contributed in any way to this paper, and are especially grateful to Ms. Justine McFarland for preparing the manuscript for publication.

References

- [1] R.G. Kunz, W.F. Baade, Predict Methanol and Ammonia in Hydrogen-Plant Process Condensate, Paper ENV-00-171 presented at the NPRA 2000 Environmental Conference, San Antonio, TX, 10–12 September 2000.
- [2] California Air Resources Board Rule #1189, Emissions from Hydrogen Plant Process Vents, Adopted 21 January 2000.
- [3] H.J. Taback, R.C. Russell, Methanol Emissions from Hydrogen Plants, Status Report Prepared for American Petroleum Institute, Hal Taback Company, Walnut, CA, November 1997.
- [4] J.H. Carstensen, J.B. Hansen, P.S. Pedersen, New high-temperature shift catalysts solve the Fischer–Tropsch problem, ammonia plant safety (and related facilities), *AIChE Tech. Manual* 30 (1990) 139–151.
- [5] J.H. Carstensen, J. Bøggild-Hansen, P.S. Pedersen, Methanol by-product formation over HTS and LTS catalysts, ammonia plant safety (and related facilities), *AIChE Tech. Manual* 31 (1991) 113–120.
- [6] R.W. Hartye, Effect of low steam on water gas shift operation, ammonia plant safety (and related facilities), *AIChE Tech. Manual* 26 (1986) 107–114.
- [7] H. Roos, H. Wanjek, M. Sprague, New developments in LTS catalysts, ammonia plant safety (and related facilities), *AIChE Tech. Manual* 30 (1990) 187–199.
- [8] J.H. Carstensen, B.S. Hammershøi, Reducing methanol by-product formation over the LTS converter, ammonia plant safety (and related facilities), *AIChE Tech. Manual* 39 (1999) 171–178.
- [9] T.S. Askgaard, J.K. Nørskov, C.V. Ovesen, P. Stoltze, A kinetic model of methanol synthesis, *J. Catal.* 156 (1995) 229–242.
- [10] J. Skrzypek, M. Lachowska, H. Moroz, Kinetics of methanol synthesis over commercial copper/zinc oxide/alumina catalysts, *Chem. Eng. Sci.* 46 (11) (1991) 2809–2813.
- [11] M.S. Wainwright, D.L. Trimm, Methanol synthesis and water-gas shift reactions on Raney copper catalysts, *Catal. Today* 23 (1995) 29–42.
- [12] K.M. Vanden Bussche, G.F. Froment, A steady-state kinetic model for methanol synthesis and the water gas shift reaction on a commercial Cu/ZnO/Al₂O₃ catalyst, *J. Catal.* 161 (1996) 1–10.
- [13] R.A. Koepfel, A. Baiker, Ch. Schild, A. Wokaun, Effect of preparation variables on catalytic behaviour of copper/zirconia catalysts for the synthesis of methanol from carbon dioxide, *Stud. Surf. Sci. Catal.* 63 (1991) 59–68.
- [14] D.F. Smith, L.L. Hirst, Reactions that occur on a methanol catalyst, *Ind. Eng. Chem.* 22 (10) (1930) 1037–1040.
- [15] K. Frolich, D.S. Cryder, Catalysts for the formation of alcohols from carbon monoxide and hydrogen, *Ind. Eng. Chem.* 22 (10) (1930) 1051–1057.
- [16] J. Madsen, Process condensate purification in ammonia plants, ammonia plant safety (and related facilities), *AIChE Tech. Manual* 31 (1991) 227–240.

- [17] C. Yaws, H. Yang, X. Pan, Henry's law constants for 362 organic compounds in water, *Chem. Eng.* 98 (11) (1991) 179–185.
- [18] J.M. Smith, H.C. Van Ness, *Introduction to Chemical Engineering Thermodynamics*, 2nd Edition, McGraw-Hill, New York, 1959, pp. 85–117.
- [19] D.R. Stull, E.F. Westrum, Jr., G.C. Sinke, *The Chemical Thermodynamics of Organic Compounds*, Wiley, New York, 1969.
- [20] J.H. Dymond, E.B. Smith, *The Virial Coefficients of Pure Gases and Mixtures: A Critical Compilation*, Oxford University Press, New York, 1980.
- [21] J.M. Smith, H.C. Van Ness, M.M. Abbott, *Introduction to Chemical Engineering Thermodynamics*, 5th Edition, Problem 15.4, McGraw-Hill, New York, 1996, p. 604.
- [22] H.C. Carlson, A.P. Colburn, Vapor–liquid equilibria of nonideal solutions: utilization of theoretical methods to extend data, *Ind. Eng. Chem.* 34 (5) (1942) 581–589.
- [23] J.H. Perry (Ed.), *Chemical Engineers' Handbook*, 3rd Edition, McGraw-Hill, New York, 1950, pp. 528–530.
- [24] E.W. Washburn (Ed.), *International Critical Tables of Numerical Data: Physics, Chemistry, and Technology*, Vol. V, 1st Edition, 2nd Impression, McGraw-Hill, New York, 1929, pp. 115–117; 159–160.
- [25] S.I. Sandler, *Chemical and Engineering Thermodynamics*, Wiley, New York, 1989, pp. 251–262; 279–286.
- [26] C.A. Jones, E.M. Schoenborn, A.P. Colburn, Equilibrium still for miscible liquids: data on ethylene dichloride-toluene and ethanol–water, *Ind. Eng. Chem.* 35 (6) (1943) 666–672.
- [27] B.C.-Y. Lu, Heats of mixing and vapor–liquid equilibrium calculations, *Can. J. Chem. Eng.* 37 (5) (1959) 193–199.
- [28] J.J. Christensen, R.W. Hanks, R.M. Izatt, *Handbook of Heats of Mixing*, Wiley, New York, 1982, pp. 1437–1442.
- [29] J.J. Christensen, R.L. Rowley, R.M. Izatt, *Handbook of Heats of Mixing (Supplementary Volume)*, Wiley, New York, 1988, pp. 994–999.
- [30] J. Gmehling, U. Onken, Vapor–liquid Equilibrium Data Collection, Vol. I, Part 1, DECHEMA Chemistry Data Series, Verlag, Frankfurt, Germany, 1977, pp. 37–76; 150–196.
- [31] J. Gmehling, U. Onken, W. Arlt, Vapor–liquid Equilibrium Data Collection (Supplement 1), Vol. I, Part 1a, DECHEMA Chemistry Data Series, Schoen & Wetzel, Frankfurt, Germany, 1981, pp. 46–63; 116–157.
- [32] J. Gmehling, U. Onken, J.R. Rarey-Nies, Vapor–liquid Equilibrium Data Collection (Supplement 2), Vol. I, Part 1b, DECHEMA Chemistry Data Series, Schoen & Wetzel, Frankfurt, Germany, 1988, pp. 22–35; 83–114.
- [33] J.A. Dean (Ed.), *Lange's Handbook of Chemistry*, 11th Edition, McGraw-Hill, New York, 1973, pp. 10–45.