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Surface tension of pure heavy *n*-alkanes: a corresponding states approach

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Abstract

The surface tension of heavy *n*-alkanes is a poorly studied subject. Few data exist and the predictive methods used for their estimation are rather complex or show considerable errors for the higher members of the series.

In this work, the corresponding states theory is used to predict the surface tension of the series of the *n*-alkanes. Two approaches have been followed: the first is a second-order perturbation model based on a Taylor series expansion of the surface tension using the Pitzer acentric factor; the second approach uses shape factors to account for the non-conformalities. Comparisons of the two models with experimental data and other available predictive methods are presented. © 2001 Published by Elsevier Science B.V.

Keywords: Surface tension; Model; Extended corresponding states theory; *n*-alkanes; Shape factors

1. Introduction

Many engineering applications in the chemical process industry, such as the mass-transfer operations like distillation, extraction, absorption and adsorption, require surface tension data.

The petroleum industry is especially interested in the surface tension of the series of the *n*-alkanes [1]. To improve production and increase oil yields, it is not unusual in the extraction of crudes to add surfactants to modify the interfacial properties between crude oil and the geological reservoir. This occurs because in the petroleum rocks the flow is mainly dominated by the interfacial tension of the crude.

Although, there are enough experimental surface tension data for some of the lighter *n*-alkanes, there are few for other elements of the series, particularly for the heavier ones, and the available data only cover a narrow range of temperature. In fact, surface tension data are lacking at low temperatures and the near critical region.

Good estimation methods are thus required to evaluate surface tension. *Parachor* [2], *Gradient theory* [3] and *corresponding states* methods [1,4,5] are most frequently used. Of the latter, *corresponding states*

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are the simpler, requiring only detailed knowledge of the reference fluid (or fluids) and of a small number of well defined pure component properties. The coupling between the strong theoretical basis behind *corresponding states principle* and the accuracy of the empirical equations used to describe the reference fluid justify the effort in developing such models.

2. Corresponding states principle

The basic concept of corresponding states principle is to apply dimensional analysis to the configurational portion of the statistical mechanical partition function. The end result of this analysis is the expression of residual thermodynamic properties in terms of dimensionless groups.

The original, two-parameter corresponding states principle leads to an equation of state which expresses the residual compressibility factor in terms of a universal function of two parameters, usually the dimensionless temperature and molar volume. Experimental evidence has shown that the two-parameter corresponding states is only obeyed by the noble gases and nearly spherical molecules such as methane, nitrogen and oxygen. In order to extend the corresponding states theory to a larger spectrum of fluids, additional characterization parameters have been introduced to account for the non-conformalities between fluids. Two main approaches have been applied in this parameterization: the first introduces additional characterization parameters and then performs a multi-parameter Taylor's series expansion of the property of interest about the parameters; the second approach is to extend the simple two-parameter corresponding states principle at its molecular origin. This is accomplished by making the intermolecular potential parameters functions of the additional characterization parameters and the thermodynamic state, e.g. the temperature. The net result is a corresponding states model which has the same mathematical form as the simple two-parameter model, but the definitions of the dimensionless volume and temperature are more complex. The aim of this paper is to explore both of these corresponding states approaches in order to apply them to surface tension calculations.

2.1. Taylor series expansion in Pitzer acentric factor

The estimation of surface tension applying a Taylor series expansion in Pitzer acentric factor has already been proposed [1,5]. The series is truncated beyond the first derivative, giving a linear function

$$\gamma_{rj} = \gamma_{r1} + \frac{\omega_j - \omega_1}{\omega_2 - \omega_1} (\gamma_{r2} - \gamma_{r1}) \quad (1)$$

where γ represents the surface tension, j stands for the target fluid and the subscripts 1 and 2 refer to two reference fluid properties.

Although, the formalism is the same, the literature displays a variety of ways to reduce the surface tension: Rice and Teja [5] used the critical volume and critical temperature, while Zuo and Stenby [1] used the critical pressure and critical temperature.

$$\gamma_r = \gamma \frac{V_c^{2/3}}{T_c} \quad (2)$$

$$\gamma_r = \ln \left(\frac{\gamma}{P_c^{2/3} T_c^{1/3}} + 1 \right) \quad (3)$$

Other authors [6] propose a linear form with the critical pressure and critical temperature

$$\gamma_r = \frac{\gamma}{P_c^{2/3} T_c^{1/3}} \quad (4)$$

In all cases, good agreement with experimental data was obtained in the range of fluids covered by the two selected reference fluids. However, considerable deviations can be found if an extrapolation of Eq. (1) is attempted, or if the reference fluids are not very far apart in the family sequence (Fig. 1).

In order to account for these deviations, the Taylor series expansion of the reduced surface tension is carried out to the second-order term, thus yielding the following equation:

$$\gamma_r = \gamma_{r1} + D_1(\omega_j - \omega_1) + D_2(\omega_j - \omega_1)(\omega_j - \omega_2) \quad (5)$$

where

$$D_1 = \frac{\gamma_{r2} - \gamma_{r1}}{\omega_2 - \omega_1}, \quad D_2 = \frac{((\gamma_{r3} - \gamma_{r2})/(\omega_3 - \omega_1)) - ((\gamma_{r2} - \gamma_{r1})/(\omega_2 - \omega_1))}{\omega_3 - \omega_2} \quad (6)$$

Note that a third reference fluid has to be introduced.

2.2. Extended corresponding states theory

In the extended corresponding states theory, the surface tension of the target fluid is calculated from a single reference fluid using the following equation:

$$\gamma_j = \frac{f_j}{h_j^{2/3}} \gamma_0 \left(\frac{T_{rj}}{\theta} \right) \quad (7)$$

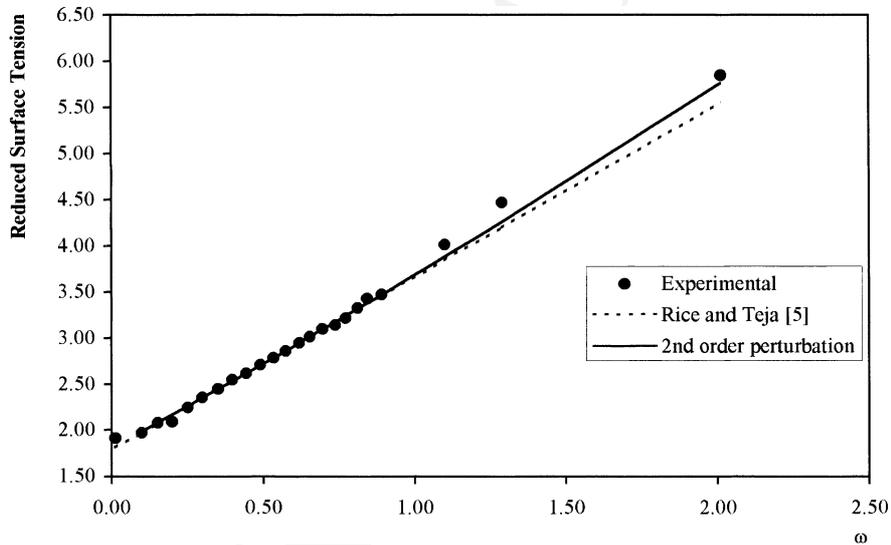


Fig. 1. Reduced surface tension for *n*-alkanes (Eq. (2)) as a function of acentric factor at $T_r = 0.49$.

where h_j and f_j are the equivalent substance reducing ratios and θ and ϕ the shape factors. The relationship between these quantities is given by

$$V = V_0 h_j = V_0 \frac{V_{jc}}{V_{0c}} \phi, \quad T = T_0 f_j = T_0 \frac{T_{rj}}{T_{0c}} \theta \quad (8)$$

The shape factors are weak functions of the reduced temperature, and in principle, of the reduced density. They are evaluated by solving simultaneously any two equations relating the thermophysical property of the target and the reference fluid. Normally, the compressibility factor and the Helmholtz energy are used. Several review papers have been published focusing on this approach and the most extensive are those of Leland and Chappellear [7], Rowlinson and Watson [8] and Mentzer et al. [9].

In order to apply this theory to evaluate surface tension, Murad [4] calculate shape factors by the simultaneous solution of the reduced compressibility factors and the reduced surface tensions. The values of these shape factors were then fitted to functions of the temperature and density, using the formulae proposed by Leach et al. [10].

This procedure has the disadvantage of yielding shape factors that are not the same of those obtained by solving the compressibility factor and the Helmholtz energy. Since, theoretically, these shape factors should be the same, recalculation of these shape factors showed that this difference is essentially due to the lack of accuracy of the reference fluid data available at the time. Another weak point of the model proposed by Murad is the fixed reference fluid, methane, which does not allow an accurate mapping for heavy n -alkanes.

Following Cullick and Ely [11], Marrucho and Ely [12] proposed a new predictive method for the determination of the shape factors along the saturation boundary. Using the Frost–Kalkwarf–Thodos equation [13] to describe the saturation pressure and the Rackett equation [13] for the saturated liquid density, the expressions for the shape factors are

$$\theta = \frac{1 - C_{r0} + 2(1 - T_{rj})^{2/7} \ln(Z_{cj}/Z_{c0}) - \Delta B_r + \Delta C_r \ln T_{rj} + B_{rj}/T_{rj}}{1 - C_{r0} + B_{r0}/T_{rj}} \quad (9)$$

$$\phi = \frac{(Z_{cj})^{(1-T_{rj})^{2/7}}}{(Z_{c0})^{(1-T_{rj}/\theta)^{2/7}}} \quad (10)$$

where

$$B_r = -6.207612 - 15.37641\omega - 0.574946 \times 10^{-\omega} \quad (11)$$

$$C_r = \frac{8}{3} + \frac{9B_r}{5 \ln 10} \quad (12)$$

$$\Delta B_r = B_{rj} - B_{r0} \quad (13)$$

$$\Delta C_r = C_{rj} - C_{r0} \quad (14)$$

This is a predictive approach if vapor pressure and liquid density data are available, but Z_c and the exponent in the Rackett equation can be treated as adjustable parameters, and B_r and C_r can be found by a correlation scheme.

3. Results

Although, a considerable amount of data exists, special care has been taken regarding selection since the values very often differ considerably from author to author [14–24]. The data reported by Jasper and coworkers [18,20,21] and by Grigoryev et al. [19] were used preferentially. The latter article covers all the liquid region of *n*-alkanes between C_5 and C_8 . Eq. (15) was used to correlate the experimental surface tension values of the reference fluids for both methods, thus yielding two parameters per each fluid

$$\gamma = A(1 - T_r)^B \quad (15)$$

The reduction of the surface tension values obtained with this equation was attempted Eqs. (2)–(4). Despite that the critical volume usually has a considerable error, the results showed that Eq. (2) was the best choice.

The experimental values of the critical properties and acentric factor were used when available [25–29]. Otherwise, correlations for critical temperature [26], critical volume [27], critical pressure [28] and acentric factor [29] were used.

For the Taylor series expansion, a system of three reference fluids is needed. This selection is not an easy task since discrepancies may lead to erroneous results. For the purpose of this work *n*-hexane, *n*-undecane and *n*-pentadecane were chosen as references because there are enough accurate experimental data and they described the entire series of *n*-alkanes well.

The proposed model, Eq. (5), was tested for 320 surface tension values for the *n*-alkanes and resulted in an average absolute deviation (AAD) of 1.14% (Table 1 and Figs. 2 and 3). In Figs. 1 and 2, comparisons of this model with the one proposed by Rice and Teja [5] and Zuo and Stenby [1] are presented. It

Table 1
Evaluation of the second-order perturbation model for surface tension

Substance	AAD (%)	No. of points	Temperature range, T , (K)
Ethane	0.96	23	129.2–273.50
Propane	2.94	22	202.15–312.6
<i>n</i> -butane	4.60	20	238.0–318.5
<i>n</i> -pentane	1.47	18	144.8–407.25
<i>n</i> -heptane	0.53	26	183.21–459.18
<i>n</i> -octane	1.53	20	218.51–501.27
<i>n</i> -nonane	0.31	13	273.15–393.15
<i>n</i> -decane	0.33	13	273.15–393.15
<i>n</i> -dodecane	0.22	13	273.15–393.15
<i>n</i> -tridecane	0.23	13	273.15–393.15
<i>n</i> -tetradecane	0.20	12	283.15–393.15
<i>n</i> -hexadecane	0.98	11	293.15–393.15
<i>n</i> -heptadecane	0.76	10	303.15–393.15
<i>n</i> -octadecane	0.21	10	303.15–393.15
<i>n</i> -nonadecane	1.24	11	293.15–393.15
<i>n</i> -eicosane	0.19	11	293.15–393.15
<i>n</i> -hexacosane	2.73	11	343.15–453.15
<i>n</i> -dotriacontane	2.26	11	346.35–422.45
<i>n</i> -hexacontane	5.48	7	383.15–453.15

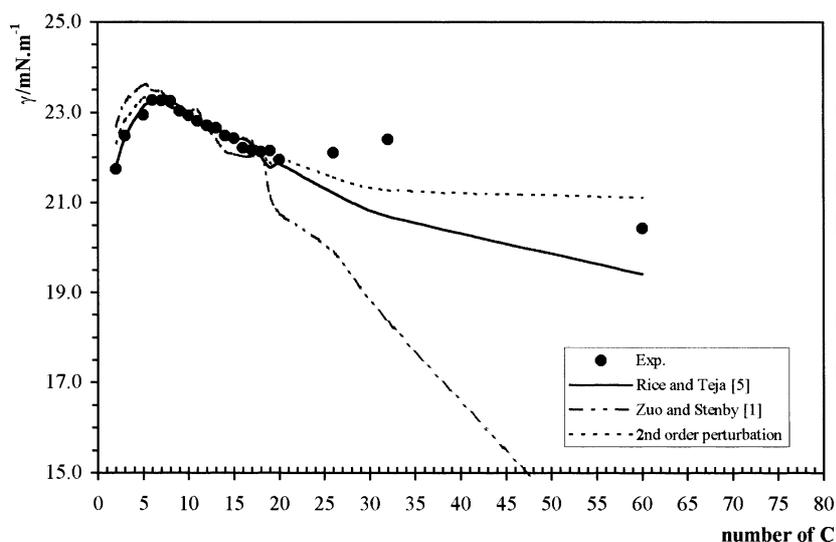


Fig. 2. Surface tension of n -alkanes at $T_r = 0.49$. Experimental data and predictive methods based on the Taylor series expansion.

can clearly be seen that the new model improves the surface tension calculation especially for heavy n -alkanes.

The surface tension values calculated using the shape factors from Eqs. (9) and (10), for several n -alkanes, C_2 – C_{20} , C_{26} and C_{32} are compared with experimental results in Table 2 and Fig. 4. An average absolute deviation of 3.7% was obtained. The selected reference fluids were n -pentane for the range

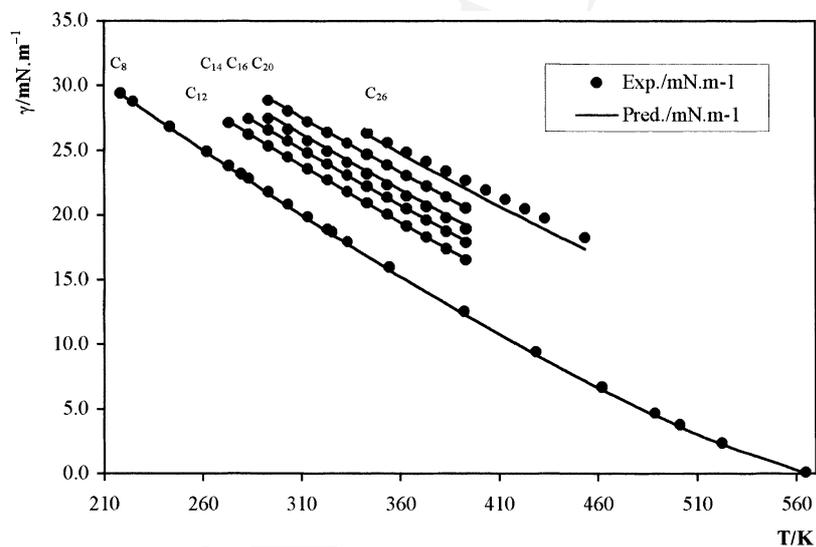


Fig. 3. Comparison of experimental and predicted surface tension for n -alkanes-second-order perturbation model.

Table 2
Evaluation of the new predictive ECST model for surface tension

Substance	AAD (%)	No. of points	Temperature range, T , (K)
Ethane	5.9	23	129.2–273.50
Propane	6.7	22	202.15–312.6
<i>n</i> -butane	9.0	20	238.0–318.5
<i>n</i> -hexane	1.7	21	175.12–447.13
<i>n</i> -heptane	3.5	26	183.21–459.18
<i>n</i> -octane	3.8	20	218.51–501.27
<i>n</i> -nonane	0.6	13	273.15–393.15
<i>n</i> -undecane	0.5	13	273.15–393.15
<i>n</i> -dodecane	2.6	13	273.15–393.15
<i>n</i> -tridecane	1.5	13	273.15–393.15
<i>n</i> -tetradecane	0.3	12	283.15–393.15
<i>n</i> -hexadecane	1.7	11	293.15–393.15
<i>n</i> -heptadecane	1.4	10	303.15–393.15
<i>n</i> -octadecane	1.0	10	303.15–393.15
<i>n</i> -nonadecane	1.7	11	293.15–393.15
<i>n</i> -eicosane	5.7	11	293.15–393.15
<i>n</i> -hexacosane	6.6	11	343.15–453.15
<i>n</i> -dotriacontane	13.0	11	346.35–422.45

C_2 – C_7 , *n*-decane for C_8 – C_{12} and C_{15} for those *n*-alkanes with >12 carbon atoms. Surface tension for *n*-hexacontane was not predicted due to the lack of a suitable reference fluid. Some deviations were found for the first elements of the series, but it should be kept in mind that experimental data for some fluids, like propane and *n*-butane, presents scatter.

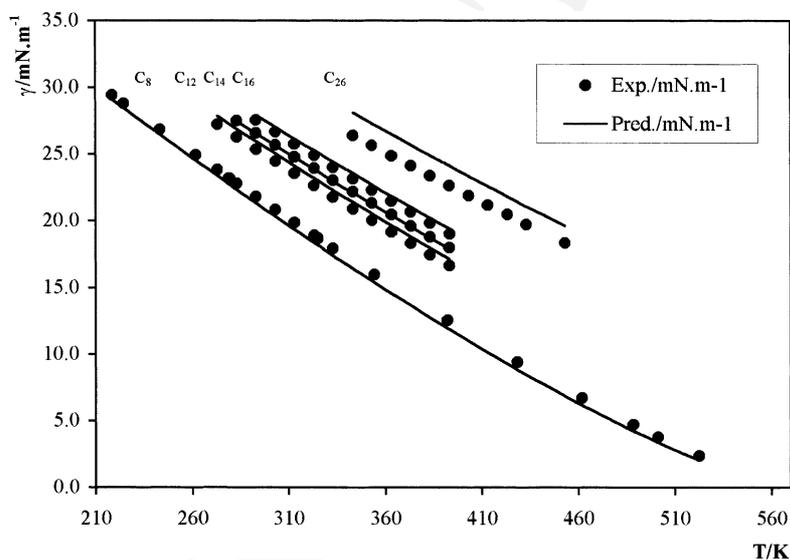


Fig. 4. Comparison of experimental and predicted surface tension for *n*-alkanes-ECST model.

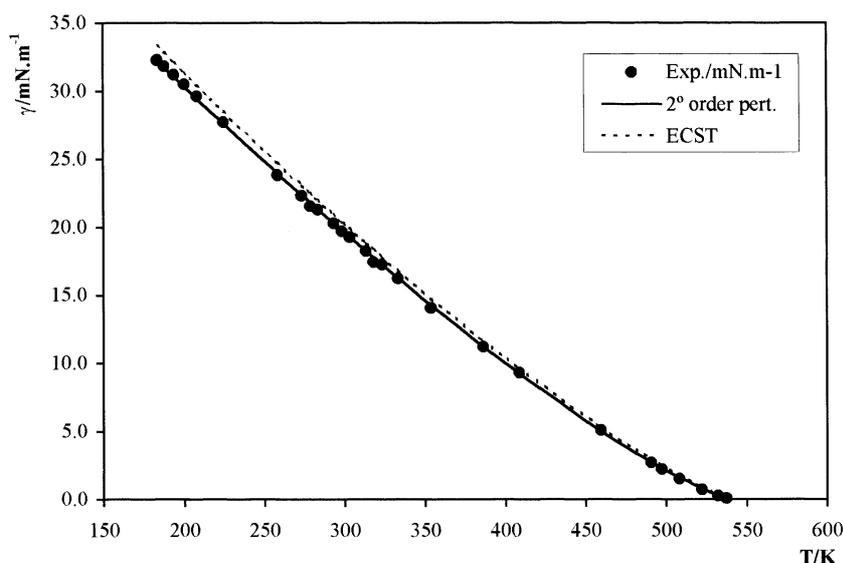


Fig. 5. Graphical presentation of experimental and predicted values of surface tension of *n*-heptane using the new predictions.

When using this approach, special care should also be presented in the choice of the reference fluid. The ideal reference fluid should be structurally similar to the target fluid and have a broad temperature range of surface tension experimental values.

The two proposed models, the Taylor series expansion and the shape factor models, are compared with each other for *n*-heptane in Fig. 5. It can be observed that the Taylor series expansion yields better predictions than the shape factors model. This fact is mainly due to the larger number of reference fluids used in the first model. Nevertheless, both these models are more accurate than the equivalent models proposed so far.

4. Summary and conclusions

Two new corresponding states predictive models were proposed for the determination of the surface tension of a large number of pure *n*-alkanes, within a large temperature range. The Pitzer acentric factor Taylor series expansion was extended to include a third reference fluid and a group of reference fluids was proposed for the determination of the surface tension with an average absolute error of 1.14%.

The extended corresponding states theory was also suggested for the determination of surface tension, this time with the possibility of selecting an adequate reference fluid and given a minimum amount of information: critical temperature, critical volume, critical compressibility factor and acentric factor of the reference and the target fluid as well as some surface tension data of the reference fluid. Although, this last approach has shown notable deviation, it is much simpler to use and involves less information. In order to improve its accuracy this model will be further studied.

List of symbols

- A* correlated parameter for Eq. (15)
- B* calculated parameter for Eq. (9) using Eq. (11)

C	calculated parameter for Eq. (9) using Eq. (12)
D	reference fluid dependent parameters for Eq. (5)
f	equivalent substance reducing ratio for temperature
h	equivalent substance reducing ratio for volume
P	pressure
R	gas constant
T	absolute temperature
V	volume
Z	compressibility factor
Z_{ra}	Rackett compressibility factor

Greek letters

ϕ	volume shape factor
γ	surface tension (mN m^{-1})
λ_i	characterization parameters for extending the simple two-parameter CST
θ	energy shape factor
ω	Pitzer acentric factor

Subscripts

c	critical value
j	target or working fluid
l	liquid state
r	reduced property (dimensionless)
0	reference fluid

Superscripts

B	correlated parameter (exponent) in Eq. (15)
sat	saturation property

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References

- [1] Y. Zuo, E. Stenby, *Can. J. Chem. Eng.* 75 (1997) 1130–1137.
- [2] C.F. Wiens, D.L. Katz, *Ind. Eng. Chem.* 35 (1943) 239.
- [3] Y.X. Zuo, E.H. Stenby, *J. Coll. Int. Sci.* 182 (1996) 126–132.
- [4] S. Murad, *Chem. Eng. Commun.* 24 (1983) 353–358.
- [5] P. Rice, A. Teja, *J. Coll. Int. Sci.* 86 (1982) 158–163.
- [6] J.R. Brock, R.B. Bird, *A.I.Ch.E. J.* 1 (1955) 174–177.
- [7] T.W. Leland, P.S. Chapplear, *Ind. Eng. Chem.* 60 (7) (1968) 15–43.
- [8] J.S. Rowlinson, I.D. Watson, *Chem. Eng. Sci.* 24 (1969) 1565–1574.

- [9] R.A. Mentzer, K.L. Young, R.A. Greenkorn, K.C. Chao, *Sep. Sci. Technol.* 15 (9) (1980) 1613–1678.
- [10] J.W. Leach, P.S. Chappellear, T.W. Leland, *A.I.Ch.E. J.* 14 (4) (1968) 568–576.
- [11] A.S. Cullick, J.F. Ely, *J. Chem. Eng. Data* 27 (1982) 276–281.
- [12] I. Marrucho, J.F. Ely, *Fluid Phase Equil.* 150/151 (1998) 215–223.
- [13] R.C. Reid, J.A. Prausnitz, B.E. Poling, *The Properties of Gases and Liquids*, 4th Edition, McGraw-Hill, New York, NY, 1987.
- [14] D. Katz, W. Saltman, *Ind. Eng. Chem.* 31 (1939) 91–94.
- [15] A. Leadbetter, D. Taylor, B. Vincent, *Can. J. Chem.* 42 (1964) 2930–2932.
- [16] O. Mass, C. Wright, *J. Am. Chem. Soc.* 43 (1921) 1098–1110.
- [17] J. Calado, I. McLure, V. Soares, *Fluid Phase Equil.* 2 (1978) 199–213.
- [18] J. Jasper, E. Kring, *J. Phys. Chem.* 59 (1955) 1019–1021.
- [19] B. Grigoryev, B. Nemzer, D. Kurumov, J. Sengers, *Int. J. Therm.* 13 (1992) 453–464.
- [20] J. Jasper, *J. Phys. Chem. Ref. Data* 1 (1972) 841–984.
- [21] J. Jasper, E. Kerr, F. Gregorich, *J. Am. Chem. Soc.* 75 (1953) 5252–5254.
- [22] I. McLure, J. Sipowska, I. Pegg, *J. Chem. Therm.* 14 (1982) 733–741.
- [23] K. Hunten, O. Mass, *J. Am. Chem. Soc.* 51 (1929) 160.
- [24] S. Wu, Surface and interfacial tensions of polymers, oligomers, plasticizers, and organic pigments, in: J. Branrup, C. Immergut, E. Grulke (Eds.), *Polymer Handbook*, 4th Edition, Wiley/Interscience, New York, 1999.
- [25] D. Ambrose, C. Tsonopoulos, *J. Chem. Eng. Data* 40 (1995) 531–546.
- [26] C. Tsonopoulos, *A.I.Ch.E. J.* 33 (1987) 2080–2083.
- [27] J. Marano, G. Holder, *Ind. Eng. Chem. Res.* 36 (1997) 1895–1907.
- [28] K. Magoulas, D. Tassios, *Fluid Phase Equil.* 56 (1990) 119–140.
- [29] B. Han, D. Peng, *Can. J. Chem. Eng.* 71 (1993) 332–334.