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An Improved ISM Equation of State for Polar Fluids

M.H. Mousazadeh*

Department of Chemistry, Amirkabir University of Technology, 15875-4413, Tehran, Iran
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We developed an equation of state (EOS) proposed by Ihm, Song, and Mason (ISM) for polar fluids. The model consists of four parameters, namely, the second virial coefficient, an effective van der Waals co-volume, a scaling factor, and the reduced dipole moment. The second virial coefficient is calculated from a correlation that uses the heat of vaporization, and the liquid density at the normal boiling point. The reduced dipole moment is calculated from experimental dipole moments data and other parameters were obtained by regressing against saturated liquid density data. In this work, we generalized this equation to calculate the saturated liquid density of *n-alkanol*, water, and ammonia. The calculated results are also compared with SAFT equation of state and show that the saturated liquid density can be predicted within about 1.2%.

Keywords: Equation of state, Statistical mechanics, Heat of vaporization, Polar fluids, Reduced dipole moment

INTRODUCTION

Liquids have been studied theoretically using statistical mechanics. Modern perturbation theories of liquids have been developed over the past 30 years [1-3]. It is based on the knowledge of the structure of dense fluid is determined primarily by the repulsive forces so that fluids of spherical or non-spherical hard bodies can serve as useful reference systems. The influence of the attractive forces and the softness of repulsions can be treated by the statistical-mechanical perturbation theory. The statistical-mechanical theory has been presented to derive a new analytical equation of state (EOS) of fluids by Song and Mason [4]. Three integrations arose in their formulations; one to find the second virial coefficient, one to find a scaling factor, and one to find an effective van der Waals co-volume. All the parameters can be calculated if the intermolecular forces are known. Recent work on this model for fluids has yielded accurate results for both pure and binary molecular liquids [5-9]. Knowledge of the second virial coefficient as a function of temperature enables one to predict the entire

equation of state [5].

The purpose of this paper is to develop a reliable equation of state suitable for polar fluids. To this end, a method is outlined for obtaining the equation of state parameters (α , b) of the experimental vapor-liquid equilibrium data and a substance-dependent parameter (ΔH_{vap} , ρ , μ). We report, here, the results of correlating the pure compound saturated liquid densities of *n-alkanol*, water, ammonia. The modified ISM (MISM) EOS is also compared with the statistical associating fluid theory (SAFT) equations of state.

THEORY

In a series of articles, Ihm, Song, Mason, (ISM) and Colleagues [4,5,10,11] have derived a simple analytic equation of state for nonpolar fluids:

$$\frac{p}{\rho RT} = 1 + p_{\text{att}} + p_{\text{rep}} \quad (1)$$

where,

*Corresponding author. E-mail: mousazadeh@aut.ac.ir

$$p_{att} = -\frac{(\alpha - B_2)\rho}{1 + 0.22\lambda b\rho} \quad (2)$$

$$p_{rep} = \frac{\alpha\rho}{1 - \lambda b\rho} \quad (3)$$

$$B_2 = 2\pi \int_0^\infty (1 - e^{-\beta u}) r^2 dr \quad (4)$$

$$\alpha(T) = 2\pi \int_0^\infty [1 - e^{-u_0(r)/kT}] r^2 dr \quad (5)$$

$$b(T) \equiv \frac{2}{3} \pi \sigma^3 = \alpha + T \frac{d\alpha}{dT} = 2\pi \int_0^{r_m} [1 - (1 + \frac{u_0}{kT}) e^{-u_0/kT}] r^2 dr \quad (6)$$

B_2 is the second virial coefficient, that depends on the intermolecular potential, u . $\alpha(T)$ and $b(T)$ are two parameters dependent to the molecular repulsive part (u_0). T is the temperature, ρ is the density, kT is the thermal energy, and $\lambda = 0.55$. The product λb is analogous to the van der Waals excluded volume.

$U_o(r)$ is the repulsive part of $u(r)$,

$$u_o(r) = \begin{cases} u(r) + \varepsilon & r < r_m \\ r > r_m \end{cases}$$

where ε is the depth of the potential well and r_m is its minimum position; this is the Weeks-Chandler-Andersen decomposition of $u(r)$ [2].

The extended equation of state needs an additional property to describe the behavior of fluid properties for polar fluids; the dipole moment of the pure fluids. Based on the recent studies, it is possible to include dipolar forces in the repulsive term of EOS [12]. It is also possible to map the dipole interaction onto the general coefficients of the equation of state [13]. In this case an additional parameter is included. The development of ISM equation for a dipolar fluid requires the extension of Eq. (3) by c parameter,

$$p_{rep} = \frac{\alpha\rho}{(1 - \lambda b\rho)(1 - cb\rho)} \quad (7)$$

where c is the reduced dipole moment. The theory of intermolecular forces [14] depends on the ratio of electrostatic to van der Waals energies which can be estimated in a dimensionless fashion by $c = 4300\mu^2/k_B T_c V_c$,

where μ is dipole moment in Debye, T_c is critical temperature in K, V_c is critical molar volume, and k_B is the Boltzmann constant in J/K. We employed the experimental dipole moments data [14] for calculation of the reduced dipole moments (c). Based on the results, a and b are rather insensitive to details of the potential function [4], so they can be expressed in terms of the universal functions of the reduced temperature according to the corresponding states correlation scheme. The temperature dependence of a and b challenges their use as simply adjustable parameters. The model parameters α and b are regressed from the saturated liquid density data and their values are obtained by minimizing the objective function F which measures the sum of squares of the relative deviation between experimental and calculated saturated liquid density ρ :

$$F = \sum_{i=1}^N \left(\frac{\rho_i^{calc} - \rho_i^{exp}}{\rho_i^{exp}} \right)^2, \quad (8)$$

where N represents the number of data points used in the regression.

When intermolecular potential and the experimental B_2 values are not available, there are several correlation schemes, usually based on the corresponding-states principle, by which second virial coefficients can be calculated [14-17]. More conveniently, the parameter $B_2(T)$ can be calculated directly from the following equation [17]:

$$\rho_{bp} B_2 = 0.10 - 0.054(\Delta H_{vap}/RT)^2 - 0.00028(\Delta H_{vap}/RT)^4 \quad (9)$$

where ΔH_{vap} , and ρ_{bp} , are the heat of vaporization and the liquid density at the normal boiling point, respectively. The correlation embraces the temperature range $T_{nb} < T < T_c$.

RESULTS AND DISCUSSION

We have extended the ISM equation of state [5] for polar fluids. We have taken the p - v - T data, the heat of vaporization, and the density at the normal boiling point from the tabulations of Vargafik [18,19] to calculate the saturated liquid density of polar fluids. The results are also compared with those obtained using the SAFT equation of

Table 1. Parameters Used in the Calculations of Polar Fluids

Substances *	$\Delta H/R$ (K)	ρ (mol m ⁻³)	T_c (K)	V_c (m ³ mol ⁻¹)	μ (D)	$\alpha \cdot 10^5$ (m ³ mol ⁻¹)	$b \cdot 10^5$ (m ³ mol ⁻¹)
Methanol	4332	23330	512.6	0.118	1.7	7.1	6.5
Ethanol	4686	15930	513.9	0.167	1.7	13.6	9.5
1-Propanol	5007	12205	536.8	0.219	1.7	22.4	12.2
1-Butanol	5206	9756	563.1	0.275	1.8	28.2	15.2
1-Pentanol	5345	8087	588.2	0.326	1.7	35.1	18.1
1-Hexanol	5480	6881	611.4	0.381	1.8	42.0	21.0
1-Heptanol	5772	5976	631.9	0.435	1.7	52.1	24.1
1-Octanol	5750	5235	652.5	0.490	2.0	57.0	26.9
1-Nonanol	5820	4714	668.9	0.544	1.7	64.3	29.1
1-Decanol	5900	4173	684.4	0.600	1.8	74.8	32.3
3-Methyl-1-butanol	5300	8166	579.4	0.325	1.8	32.4	18.1
1,1-Difluoroethane	2747	15310	386	0.181	2.3	5.7	9.6
H ₂ O	4891	53202	647.1	0.056	1.8	1.9	3.0
NH ₃	2808	40034	405.4	0.073	1.8	1.6	3.6

* ΔH_{vap} and ρ in the calculation of B_2 are in the boiling point for polar fluids.

state [20]. This model was used to predict the saturated liquid density of one-component fluids representing a diverse range of molecular size and polarity. The analysis covered a temperature between $T_{\text{nb}} < T < T_c$. B_2 can be performed using Eq. (9). The equation of state parameters are calculated by regressing against saturated liquid density data for polar compounds. The results are summarised in Table 1.

Table 2 summarises the average absolute deviation (AAD) in the saturated liquid density obtained from the comparison of theory with experiment, *i.e.*;

$$AAD \% = \frac{1}{N} \sum_{i=1}^N \left| \frac{\rho_{i,\text{exp}t} - \rho_{i,\text{calc}}}{\rho_{i,\text{exp}t}} \right| * 100 \quad (10)$$

According to these tables the ISM and SAFT equations of

state show that the AAD% of saturated liquid density can be predicted for polar compounds within about 0.91% and 1.30, respectively. The variation of the EOS parameters with carbon number for *n-alcohol* is depicted on Fig. 1. A linear correlation is observed between the EOS parameters and the number of carbons. The linearity of parameters with carbon number allows extrapolating the EOS parameters for heavier hydrocarbons [21].

For an estimate, α and b have been regressed as a simple linear function of carbon number n for the alcohols,

$$\alpha = -8.67\text{e-}7 + 7.37\text{e-}5n \quad (r = 0.9986) \quad (11)$$

$$b = 3.75\text{e-}5 + 2.86\text{e-}5n \quad (r = 0.9997) \quad (12)$$

Table 2. The Average Absolute Deviation (AAD) between Experimental Saturated Liquid Density Data and the Results Obtained Using ISM and SAFT Equations of State for Polar Fluids

Substances	ΔT (K)	AAD	
		This work	SAFT
Methanol	273-487	1.39	0.88
Ethanol	302-483	0.97	0.83
1-Propanol	293-493	0.97	1.20
1-Butanol	313-493	0.54	1.00
1-Pentanol	333-513	0.42	1.10
1-Hexanol	343-573	0.95	1.22
1-Heptanol	353-573	0.53	0.96
1-Octanol	373-593	1.12	1.00
1-Nonanol	383-613	0.82	0.47
1-Decanol	393-633	0.87	0.57
3-Methyl-1-butanol	380-550	0.4	-
H ₂ O	283-613	1.91	3.20
NH ₃	200-380	0.96	3.20
1,1-Difluoroethane	223-368	0.94	-
Overall		0.91	1.30

where, r , is the linear correlation coefficient.

To verify the precision of the equations of state for small polyatomic polar molecules, the saturated liquid density was calculated for 1,1-difluoroethane, 3-methyl-1-butanol, ammonia and water. The discrepancy between experiment and theory using the MISM equation of state is <1.50% for these fluids (Table 3).

We have selected a number of polar fluids to check the predictive power of the present equation of state at high temperature and pressure. The results are shown as the average absolute deviation of compressed liquid densities in Table 4, compared with experimental data [18,19] for

a wide range temperature and pressure with a good accuracy. It seems that the capability of the ISM EoS is strongly dependent on the T and P conditions. The AAD diverged from 1.2 to 4.4%; 1.2% for n-pentane and elsewhere AAD is 4.3% for H₂O. This is due to parameter estimations in the saturation region.

The residual enthalpy can be calculated from:

$$H^R = -RT^2 \int_0^p \left(\frac{\partial Z}{\partial T} \right)_p \frac{d\rho}{\rho} + RT(Z-1) \quad (13)$$

The enthalpy is related to the ideal gas at the same

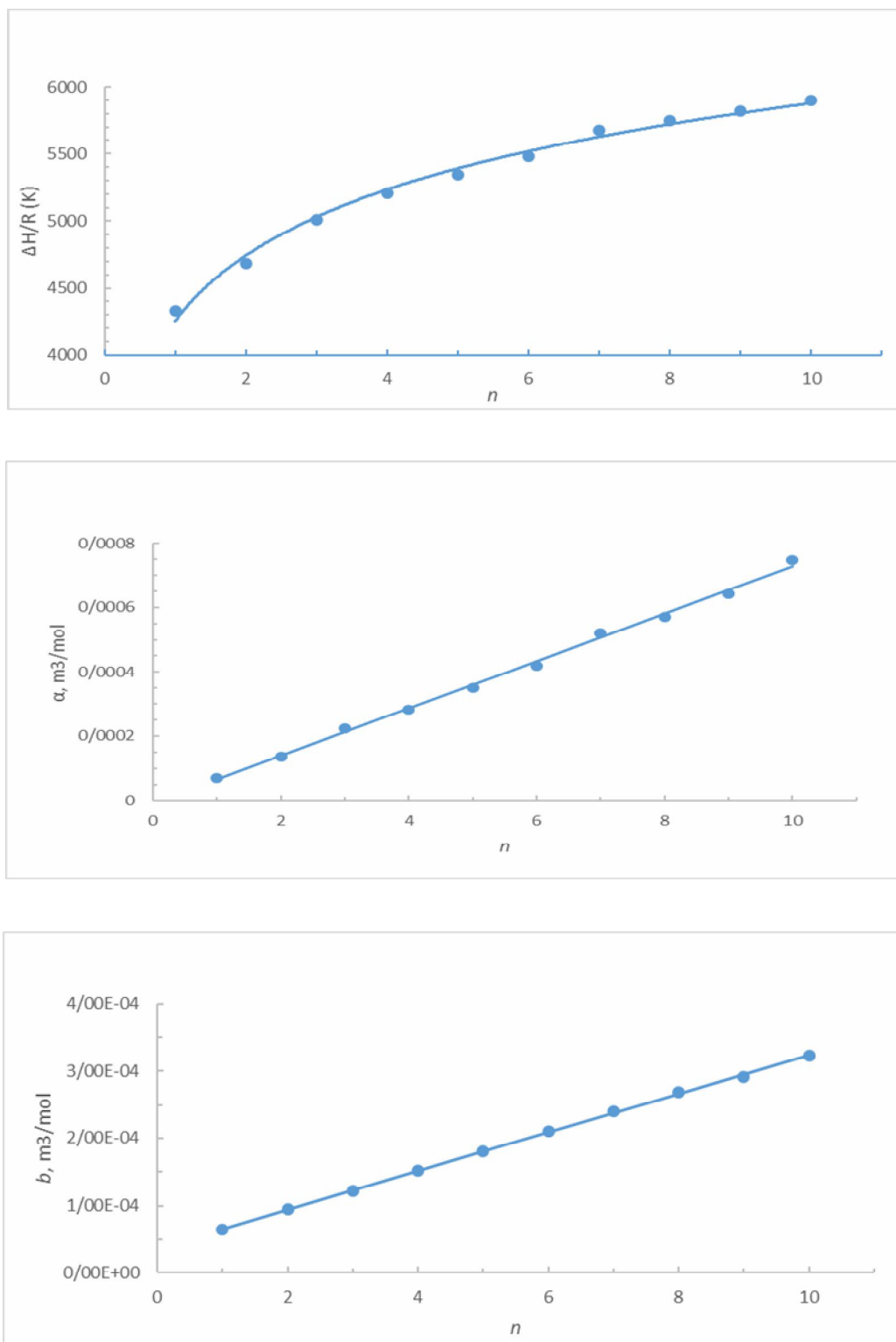


Fig. 1. Correlation of EOS parameters ($\Delta H/R$, α , b) for n-alkanols with carbon number (n).

Table 3. Ability of the Proposed Method in Correlating Saturated Liquid Density of Pure Compounds with Applying Eqs. (11) and (12)

Substance	ΔT	AAD
	(K)	This work
3-Methyl-1-butanol	380-550	0.9
1,1-Difluoroethane	223-368	1.2
H ₂ O	283-613	2.2
NH ₃	200-380	1.13
Overall		1.41

Table 4. AAD Results for Correlating the Compressed Liquid Densities of Pure Compounds

Substance	ΔT	ΔP	AAD
	(K)	(bar)	This work
Methanol	183-498	1-500	3.2
H ₂ O	373-648	1-10000	4.3
NH ₃	200-750	1-4000	4.1
Methane	100-1000	1-1000	4.1
n-Pentane	293-393	10-200	1.2
n-Decane	313-393	20-200	2.2
n-Eicosane	373-573	0-5000	4.2
CO ₂	273-1800	35-600	3.0

Table 5. Average Absolute Deviation (AAD) of the Thermodynamic Properties Calculated from the Literature Data at Vapor Region Using ISM EOS for Polar Fluids

Fluid	ΔT	ΔP	^a N	C _p	C _v	Entropy	Enthalpy	Density
	(K)	(bar)						
CH ₃ OH	515-620	0-50	10	4.20	5.76	4.12	3.03	1.71
H ₂ O	300-1200	0-50	10	1.25	3.11	2.41	2.91	0.94
NH ₃	450-700	0-50	20	2.91	1.62	1.98	1.61	0.79

^aNumber of points.

temperature and pressure. The enthalpy can be found by adding the residual enthalpy to enthalpy of the ideal gas, which can be calculated via the following equation:

$$H^{ig}(T) = H^{ig}(T_0) + \int_{T_0}^T C_p^{ig} dT \quad (14)$$

where C_p^{ig} stands for ideal gas heat capacity at constant pressure, and subscript zero refers to the reference state. The AAD of the enthalpy of ammonia, methanol, and water are given in Table 5. As it is obvious, the maximum deviation for the calculated enthalpy from the literature data [19,22] at vapor is less than 3.10%.

The residual entropy is obtained through the following equation and an equation of state:

$$S^R = -R \int_0^{\rho} \left\{ T \left(\frac{\partial Z}{\partial T} \right)_\rho + Z - 1 \right\} \frac{d\rho}{\rho} \quad (15)$$

where S^R is the residual entropy. The entropy S can be calculated by adding the residual entropy to the entropy of the ideal gas:

$$S = S_0 \int_{T_0}^T C_p^{ig} dT / T - R \ln(P/P_0) + S^R \quad (16)$$

where P_0 is the reference pressure.

Table 5 represents AAD of the entropy for ammonia, methanol, and water over a temperature range of 300-1200 K and a pressure range of 0-50 bar using ISM EOS for the polar fluids. In the vapor phase, the deviations are about 4.20%.

The estimation of heat capacities is of industrial interest. The heat capacity at constant volume and constant pressure are defined by:

$$C_V(T, \rho) = (C_p^{ig} - R) - \int_0^{\rho} \left[\partial^2 P / \partial T^2 \right]_\rho T / \rho^2 d\rho$$

$$C_p(T, \rho) = C_V(T, \rho) - \left[(\partial P / \partial T)_\rho^2 (\partial \rho / \partial P)_T (T / \rho^2) \right]$$

As shown in Table 5, the deviation in vapor is of the order of 3.5%.

CONCLUSIONS

The ISM equation of state [5] has been modified for the polar components. The EOS predicts the saturated liquid density for pure polar components as in the SAFT EOS. This fact shows that the modifications in the repulsive term cause a considerable improvement in the equation of state. Knowing just a substance-dependent parameter is sufficient to determine the equation of state of polar fluids. The values of μ along with other parameters used in the equation of state are listed in Table 1. The values of μ for all the polar compounds are nearly close to each other, indicating the structural complexities of all the polar compounds governing the thermos-physical properties show similarities and thus group laws of corresponding states are applicable. The thermodynamic functions of 3 selected associated fluids having a variety of structures and polarities were calculated using this modified ISM EOS over a wide PVT range. We conclude from the foregoing collective calculations by modified ISM EOS that this EOS is accurate in vapor/gas.

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REFERENCES

- [1] Wei, Y. S.; Sadus, R. J., Equations of state for the calculation of fluid + phase. *Equilibria. Am. Inst. Chem. Eng. J.* **2000**, *46*, 169-196. DOI: 10.1002/aic.690460119.
- [2] Barker, J. A.; Henderson D., Perturbation theory and equation of state for fluids. II. A successful theory of liquids. *J. Chem. Phys.* **1967**, *47*, 4714-4721. DOI: 10.1063/1.1701689.
- [3] Carnahan, N. F.; Starling, K. E., Equation of state for nonattracting rigid spheres. *J. Chem. Phys.* **1969**, *51*, 635-639. DOI: 10.1063/1.1672048.
- [4] Song, Y.; Mason, E. A., Statistical + mechanical theory of a new analytical equation of state. *J. Chem. Phys.* **1989**, *91*, 7840-7855. DOI: 10.1063/1.457252.
- [5] Ihm, G.; Song, Y.; Mason, E. A. A new strong principle of corresponding states for nonpolar fluids.

- J. Chem. Phys.* **1991**, *94*, 3839-3851. DOI: 10.1063/1.460684.
- [6] Mousazadeh, M. H., A correlation of densities of liquid polar and nonpolar refrigerants from critical temperature. *Phys. Chem. Liq.* **2018** (Accepted). DOI: 10.1080/00319104.2018.1509968.
- [7] Kiani, M.; Papari, M. M.; Nowruzian, Z.; Moghadasi, J., Application of modified Tao-Mason equation of state to refrigerant mixtures. *Korean J. Chem. Eng.* **2015**, *32*, 1361-1373. DOI: 10.1007/s11814-014-0332-8.
- [8] Ghatee, M. H.; Boushehri, A., Equation of state for compressed liquids from surface tension. *Int. J. Thermophys.* **1996**, *17*, 945-957. DOI: 10.1007/BF01439197.
- [9] Mousazadeh, M. H.; Boushehri, A., A correlation of densities of liquid natural gas mixtures from Surface tension. *Fluid Phase Equilib.* **2000**, *168*, 125-134. DOI: 10.1016/S0378-3812(99)00328-3.
- [10] Song, Y.; Mason, E. A., Analytical equation of state for molecular fluids: Comparison with experimental data. *Phys. Rev. A.* **1990**, *42*, 4743-4748. DOI: 10.1103/PhysRevA.42.4743
- [11] McQuarri, D. A., *Statistical Mechanics*; Harper & Row, New York, 1976.
- [12] Bayan, P.; Prausnitz, J. M., Thermodynamic properties of polar fluids from a perturbed dipolar hard sphere equation of state. *Fluid Phase Equilib.* **1978**, *38*, 201-216. DOI: 10.1016/0378-3812(87)85001-X.
- [13] Yelash, L. V.; Kraska, T., A mapping equation of state: development for the dipolar hard sphere fluid. *Phys. Chem. Chem. Phys.* **2000**, *2*, 4734-4739. DOI: 10.1039/B005196I.
- [14] Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The Properties of Gases and Liquids*; The McGraw-Hill Companies, Inc. fifth edition, 2001.
- [15] Schreiber, D. R.; Pitzer, K. S., Equation of state in the acentric factor System. *Fluid Phase Equilib.* **1989**, *46*, 113-130. DOI: 10.1016/0378-3812(89)80032-9.
- [16] Vetere, A., An improved method to predict the second virial coefficients of pure compounds. *Fluid Phase Equilib.* **1999**, *64*, 49-60. DOI: 10.1016/0378-3812(91)90005-R.
- [17] Boushehri, A.; Mason, E. A., Equation of state for compressed liquid and their mixtures from the cohesive energy density. *Int. J. Thermophys.* **1993**, *14*, 685-697. DOI: 10.1007/BF00502102.
- [18] Vargaftik, N. B., *Handbook of Physical Properties of Liquids and Gases*; Hemisphere, Washington, DC, 1975.
- [19] Vargaftik, N. B.; Vinogradov, Y. K.; Yargin, V. S., *Handbook of Physical Properties of Liquids and Gases: Pure Substances and Mixtures*; 3rd Ed., Begell House, New York, 1996.
- [20] Huang, S. H.; Radosz, M., Equation of state for small, large, polydisperse, and associating molecules. *Ind. Eng. Chem. Res.* **1990**, *29*, 2284-2294. DOI: 10.1021/ie00107a014.
- [21] Peters, C. J.; Swaan De Arons, J.; Levelt Sengers, J. M. H.; Gallagher, J. S., Global phase behavior of mixtures of short and long n + alkanes. *AIChE J.* **1988**, *34*, 834-839. DOI: 10.1002/aic.690340513.
- [22] <http://webbook.nist.gov>.