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Estimation of Hansen Solubility Parameters with an Entropy-Based Solubility-Parameter-Translated SRK Equation of State

Masaki Ota [1,2,*], Naishu Yang [1], Hiroyuki Komatsu [3], Hiroshi Inomata [4] and Richard Lee Smith [2]

[1] Department of Chemical Engineering, Graduate School of Engineering, Tohoku University, Aramaki Aza Aoba, 6-6-07-715, Aoba-ku, Sendai 980-8579, Japan; yang.naishu.s2@dc.tohoku.ac.jp
[2] Graduate School of Environmental Studies, Tohoku University, Aramaki Aza Aoba, 468-1, Aoba-ku, Sendai 980-8572, Japan; richard.smith.c6@tohoku.ac.jp
[3] Department of Advanced Materials Science and Technology, Graduate School of Science and Technology, Niigata University, 8050, Ikarashi 2-no-cho, Nishi-ku, Niigata 950-2181, Japan; h-komatsu@eng.niigata-u.ac.jp
[4] New Industry Creation Hatchery Center, Tohoku University, 6-6-11-403, Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan; hiroshi.inomata.b1@tohoku.ac.jp
* Correspondence: otam@tohoku.ac.jp; Tel.: +81-(0)22-795-7282

Abstract

The equation of state (EoS) is very helpful for the prediction of both high-pressure phase diagrams and fundamental properties. However, the general cubic EoS has low prediction accuracy for compressed and saturated liquid densities and the pure component critical density, especially for highly polar substances like water and alcohol. Therefore, an entropy-based solubility-parameter-translated Soave–Redlich–Kwong equation of state (*e*SPT-SRK EoS) was developed that incorporates two correction parameters that can be linearly correlated with the critical compressibility factor. The correlated values gave an average relative deviation (ARD) value of 7.9% at the critical density for a database of 28 widely used chemical compounds. Estimation of liquid densities at standard temperature and pressure conditions (298.2 K and 101.3 kPa) gave an average ARD value of 6.1% compared with the original SRK EoS value of 16.6%. The *e*SPT-SRK EoS was applied to calculate thermodynamic properties (entropy, fugacity, cohesive energy density) and was found to be reliable for estimating entropy-based Hansen-type solubility parameters (*e*HSPs). The *e*SPT-SRK EoS was compared with a corrected form of the entropy-based solubility-parameter-translated Peng–Robinson EoS (*e*SPT-PR EoS), and both functional forms were found to give reliable *e*HSP values. Therefore, the formulation methodology can be applied to other cubic equations of state for specialized fluid mixtures.

Keywords: critical molar volume; liquid density; equation of state; critical compressibility factor; Soave–Redlich–Kwong (SRK) EoS; entropy-based solubility parameter (*e*SP); volume translated

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1. Introduction

The Soave–Redlich–Kwong (SRK) equation of state (SRK EoS) [1] and the Peng–Robinson EoS (PR EoS) [2] are widely used by scientists and engineers to predict high-pressure phase diagrams for manufacturing products. Property prediction is based on the pure substance acentric factor and critical properties, not only for pure substances but also for multicomponent mixtures. The SRK EoS has wide applicability for the simulation of both processes, operating at both subcritical and supercritical conditions [3–6], and is commonly used in the petroleum industry [7,8].

However, both SRK EoS and PR EoS have low prediction accuracy for liquid densities and densities in the critical region, especially for highly polar substances like water and alcohol. Therefore, volume-translated cubic EoS forms have been proposed [9–12] to improve volumetric representation.

Recently, an entropy-based solubility parameter (*e*SP)-translated form of EoS has been proposed that is applicable at arbitrary temperature and pressure conditions and denoted as the entropy-based solubility-parameter-translated PR EoS (*e*SPT-PR EoS) [13]. From this form, although the predictive accuracy of both pure-substance liquids and critical densities could be improved, the fugacity and entropy had issues in their calculation using departure functions due to ideal gas representation. From this point of view, a new technique was necessary to address these issues.

Initially, the SRK EoS was modified by adding an *e*SP translation correction to fugacity and entropy expressions, and this modification is denoted as the *e*SPT-SRK EoS. In the *e*SPT-SRK EoS, new constants, *C*, *D*, *E* and *F*, were added to the EoS, and the resulting *C* and *D* values were generalized with fundamental properties of chemical species. The other universal constants (*E* and *F*) were determined with selected data. Finally, entropy-based Hansen-type solubility parameters (*e*HSP) were calculated according to the functional form of the *e*SPT-SRK EoS. Furthermore, we corrected the *e*SPT-PR EoS through comparison with the developed *e*SPT-SRK EoS.

2. Materials and Methods

As in a previous study [13], we selected 27 substances generally used in the chemical industry. Carbon dioxide was added to the list of substances because it is widely used and is in a gaseous state in ambient temperature and pressure conditions. Thus, a total of 28 substances were used in EoS development. Critical properties and acentric factors are listed in Table 1. The Hildebrand solubility parameter (SP) is generally evaluated in ambient conditions [14] and is defined by Equation (1):

$$\text{HildebrandSP(SP)} \cong \sqrt{\frac{\Delta_{\text{VP}}U}{v_{\text{Liquid}}}} = \sqrt{\frac{\Delta_{\text{vp}}H - P(v_{\text{G}} - v_{\text{L}})}{v_{\text{L}}}} \quad (1)$$

Table 1. Fundamental properties of 28 selected chemicals.

No.	Substance	M [1] [g/mol]	T_C [2] [K]	P_C [3] [MPa]	ρ_C [4] [kg/m^3]	ω [5] [-]	ρ_L at SATP [kg/m^3]	Hildebrand SP at SATP [MPa$^{0.5}$]	*e*SP at SATP [(Pa/K)$^{0.5}$]
1	Water	18.015	647.1	22.064	321.98	0.345	997.0	48.0	2780
2	Ethylene Glycol	62.068	719	8.2	331.91	0.521	1110.1	34.5	1997
3	*N*-Methyl-2-pyrrolidone	99.131	721.6	4.52	319.78	0.373	1026.1	30.3	1754
4	Methanol	32.042	512.5	8.084	273.86	0.566	789.6	29.5	1710
5	Ethanol	46.068	514	6.137	274.21	0.644	785.9	26.4	1530
6	Dimethyl Sulfide	62.134	503.04	5.53	309.12	0.194	842.6	26.3	1525
7	1-Propanol	60.095	536.8	5.169	274.41	0.621	799.5	24.6	1422
8	*N*,*N*-Dimethylformamide	73.094	649.6	4.42	279.00	0.318	944.5	24.0	1388
9	1-Butanol	74.122	563.1	4.414	271.51	0.588	804.0	23.3	1349
10	2-Butanol	74.122	535.9	4.188	274.53	0.581	802.3	22.6	1311
11	Pyridine	79.1	619.95	5.63	311.42	0.239	978.0	21.8	1263
12	Cyclopentanone	84.116	624.5	4.6	326.03	0.288	944.2	21.1	1222
13	Acetophenone	120.149	709.6	4.01	311.27	0.383	1023.5	20.9	1210
14	Dichloromethane	84.933	510	6.08	459.10	0.199	1318.2	20.4	1180
15	Dimethyl Carbonate	90.078	548	4.5	358.88	0.385	1063.2	20.3	1176
16	Cyclohexanone	98.143	653	4	315.57	0.299	942.7	20.1	1167
17	Acetone	58.079	508.1	4.7	272.67	0.307	785.6	19.8	1145

Table 1. *Cont.*

No.	Substance	M [1] [g/mol]	T_C [2] [K]	P_C [3] [MPa]	ρ_C [4] [kg/m^3]	ω [5] [-]	ρ_L at SATP [kg/m^3]	Hildebrand SP at SATP [MPa$^{0.5}$]	*e*SP at SATP [(Pa/K)$^{0.5}$]
18	Tetrahydrofuran	72.106	540.15	5.19	321.90	0.225	880.0	19.1	1108
19	Benzene	78.112	562.05	4.895	305.13	0.21	873.0	18.8	1089
20	Toluene	92.138	591.75	4.108	291.58	0.264	863.9	18.3	1060
21	1-Decanol	158.281	688	2.308	245.40	0.607	821.0	17.8	1032
22	Trans-Decahydronaphthalene	138.25	687	3.2	288.02	0.299	866.7	17.0	987.0
23	Cyclohexane	84.159	553.8	4.08	273.24	0.208	773.1	16.7	967.1
24	Tetradecane	198.388	693	1.57	221.17	0.643	759.3	15.9	920.9
25	1-Decene	140.266	616.6	2.223	240.18	0.48	738.2	15.9	918.1
26	Decane	142.282	617.7	2.11	230.60	0.492	726.6	15.5	899.9
27	Hexane	86.175	507.6	3.025	232.28	0.301	656.0	15.0	868.0
28	Carbon Dioxide	44.01	304.21	7.383	464.57	0.224	-	-	18.54 [6]

[1] M: Molar mass, [2] T_c: Critical temperature, [3] P_c: Critical pressure, [4] ρ_c: Critical density, [5] ω: Acentric factor, [6] The calculation used the *e*SPT-SRK EoS. SATP: standard atmospheric temperature and pressure (298.2 K and 101.3 kPa).

In Equation (1), $\Delta_{VP}U$ is the cohesive energy and v_L is the molar volume of the liquid. Typically, the Hildebrand SP is calculated in SATP conditions (298.2 K and 101.3 kPa), where $\Delta_{vp}H$ is the enthalpy of vaporization and v_G is the molar volume of gas.

The *e*SP [15,16] defined in Equation (2) is used not only for vapor and liquid phases but also for homogeneous supercritical fluid phases. The *e*SP is defined as:

$$e\mathrm{SP} \equiv \sqrt{(\partial P/\partial T)_v} = \sqrt{(\partial s/\partial v)_T} \quad (2)$$

In Equation (2), s is the molar entropy, and a Maxwell relationship is used to determine its volumetric dependence.

At the critical point (cp), the thermodynamic relationship is given as follows [17]:

$$\sqrt{\left.\frac{dP}{dT}\right|_{\mathrm{cp}}} = \sqrt{\left.\left(\frac{\partial P}{\partial T}\right)_v\right|_{\mathrm{cp}}} \equiv e\mathrm{SP}_{\mathrm{cp}} \quad (3)$$

In the calculation of $\left.\frac{dP}{dT}\right|_{\mathrm{cp}}$, the end point of saturated vapor pressure curve that is differentiated with respect to temperature is shown in Equation (4), as shown in ref. [18]:

$$\sqrt{\left.\frac{dP}{dT}\right|_{\mathrm{cp}}} = \sqrt{P_c\left(-\frac{B^*}{{T_c}^2} + \frac{C^*}{T_c} + D^*\, E^*\, {T_c}^{E^*-1}\right)} \quad (4)$$

In Equation (3), the $\left.\left(\frac{\partial P}{\partial T}\right)_v\right|_{\mathrm{cp}}$ was calculated for each equation of state. In Equation (5), average relative deviation (ARD) was defined as follows:

$$\mathrm{ARD}\left(e\mathrm{SP}_{\mathrm{cp}}\right)\ [\%] = \frac{100}{n}\sum_{i=1}^{n}\left|\frac{\sqrt{\left.\frac{dP}{dT}\right|_{\mathrm{cp}}} - \sqrt{\left.\left(\frac{\partial P}{\partial T}\right)_v\right|_{\mathrm{cp}}}}{\sqrt{\left.\frac{dP}{dT}\right|_{\mathrm{cp}}}}\right| \quad (5)$$

In Table 2, the thermodynamic relationship shown in Equation (3) was assessed for the 28 substances selected in this work. The ARD ($e\mathrm{SP}_{\mathrm{cp}}$) values were 39.3% for the original SRK EoS [1], 4.3% for the original PR EoS [2] and 1.9% for the original *e*SPT-PR EoS [13], respectively. Due to the high ARD ($e\mathrm{SP}_{\mathrm{cp}}$) value for the original SRK EoS compared with the other EoSs, function forms were examined for improvement.

Table 2. ARD (eSP$_{cp}$) values in 28 selected chemicals.

	Original SRK EoS	Original PR EoS	Original eSPT-PR EoS
ARD [%]	39.3	4.3	1.9

By applying the concepts of both SRK EoS and eSPT-PR EoS, a relationship denoted as the eSPT-SRK EoS was parameterized as follows:

$$P = \frac{RT}{v - Eb} - CT\left(\frac{1}{v - Eb} - \frac{1}{v + Fb}\right) - \frac{a_c\,\alpha(T) + D}{v(v + Fb)} \tag{6}$$

In Equation (6), C, D, E and F were newly introduced, where it should be noted that the original SRK EoS has $C = D = 0$ and $E = F = 1$.

One can obtain the fugacity coefficient φ from the departure function (Equation (7)) by substitution of Equation (6):

$$\ln\varphi = \ln\frac{f}{p} = \frac{1}{RT}\int_V^\infty \left(\frac{p}{n} - \frac{RT}{V}\right)dV + (z - 1) - \ln z \tag{7}$$

where f and z are fugacity and compressibility factors, respectively. The resulting expression for the fugacity coefficient φ can be expressed as follows:

$$\ln\varphi = \ln\frac{v}{v - Eb} + \frac{C}{R}\ln\frac{v - Eb}{v + Fb} - \frac{(a_c\alpha(T) + D)}{FbRT}\ln\frac{v + Fb}{v} + (z - 1) - \ln z \tag{8}$$

Entropy can be calculated from the departure function (Equation (9)):

$$s(T,P) - s_{\mathrm{IG}}(T,P) = R\ln z + \int_{T,v=\infty}^{T,v}\left[\left(\frac{\partial P}{\partial T}\right)_v - \frac{R}{v}\right]dv \tag{9}$$

where IG is ideal gas state at constant T, respectively, and $\left(\frac{\partial P}{\partial T}\right)_v$ can be calculated by substituting in Equation (6) as follows:

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v - Eb} - C\left(\frac{1}{v - Eb} - \frac{1}{v + Fb}\right) - \frac{a_c\left(\frac{\partial\alpha(T)}{\partial T}\right)_v}{v(v + Fb)} \tag{10}$$

The resulting entropy difference for gas or liquid phase can be expressed as follows:

$$s_G(T,P) - s_{\mathrm{IG}}(T,P) = R\ln z_G + R\ln\frac{v_G - Eb}{v_G} + C\ln\frac{v_G + Fb}{v_G - Eb} - \frac{a_c}{Fb}\left(\frac{\partial\alpha(T)}{\partial T}\right)_{v_G}\ln\frac{v_G}{v_G + Fb} \tag{11}$$

$$s_L(T,P) - s_{\mathrm{IG}}(T,P) = R\ln z_L + R\ln\frac{v_L - Eb}{v_L} + C\ln\frac{v_L + Fb}{v_L - Eb} - \frac{a_c}{Fb}\left(\frac{\partial\alpha(T)}{\partial T}\right)_{v_L}\ln\frac{v_L}{v_L + Fb} \tag{12}$$

Thus, both fugacity and entropy can be readily calculated with the eSPT-SRK EoS, which resolves the limitations of the previously proposed eSPT-PR formulation near the ideal gas state. The corrected form of the eSPT-PR EoS is given in Appendix A.

For eSPT-SRK EoS parameters a_c and b in Equation (6), a constant C was introduced as follows:

$$a_c = a_0\frac{R^2(1 - C/R)^2\,T_C^2}{P_C} \tag{13}$$

$$b = b_0 \frac{R(1 - C/R)\, T_C}{P_C} \tag{14}$$

The $\alpha(T)$ function of original SRK EoS was adopted and is described by Equation (15):

$$\alpha(T) = \left\{1 + \left(K_{C1} + K_{C2}\omega + K_{C3}\omega^2\right)\left(1 - T_r^{0.5}\right)\right\}^2 \tag{15}$$

In Equation (15), T_r is the reduced temperature (=T/T_C). For *e*SPT-SRK EoS, pure parameters a_0 in Equation (13), b_0 in Equation (14) and K_{C1}, K_{C2}, K_{C3} in Equation (15) were redetermined by fitting to experimental data for the compounds in the database.

The objective function for data fitting was chosen to be dimensionless as follows:

$$\text{O.F.} = \sum \left[\left\{ \frac{\left(\rho_{L,\text{Calc}}^{\text{SATP}} - \rho_{L,\text{Exp}}^{\text{SATP}}\right)}{\rho_{L,\text{Exp}}^{\text{SATP}}} \right\}^2 + \left\{ \frac{\left(\rho_{C,\text{Calc}} - \rho_{C,\text{Exp}}\right)}{\rho_{C,\text{Exp}}} \right\}^2 + \left\{ \frac{\sqrt{\frac{dP}{dT}\big|_{cp}} - \sqrt{\left(\frac{\partial P}{\partial T}\right)_v\big|_{cp}}}{\sqrt{\frac{dP}{dT}\big|_{cp}}} \right\}^2 + \left\{ \frac{\sqrt{\frac{dP_{vp}}{dT}\big|_{SAT}(\text{Eq.}(17))} - \sqrt{\frac{dP_{vp}}{dT}\big|_{SAT}(\text{Eq.}(18))}}{\sqrt{\frac{dP_{vp}}{dT}\big|_{SAT}(\text{Eq.}(17))}} \right\}^2 \right] \tag{16}$$

where $\left.\frac{dP_{vp}}{dT}\right|_{SAT}$ is the $\frac{dP_{vp}}{dT}$ value at standard temperature (T_0 = 298.2 K), evaluated with Equation (17) or Equation (18). Equation (18) is the Clapeyron equation, and the $\sqrt{\frac{dP_{vp}}{dT}}$ value can be calculated with the *e*SPT-SRK EoS as follows:

$$\sqrt{\left.\frac{dP_{vp}}{dT}\right|_{SAT}} = \sqrt{P_{vp}\left(-\frac{B^*}{{T_0}^2} + \frac{C^*}{T_0} + D^*\, E^*\, {T_0}^{E^*-1}\right)} \tag{17}$$

$$\sqrt{\frac{dP_{vp}}{dT}} = \sqrt{\frac{\Delta_{vp}s}{\Delta_{vp}v}} = \sqrt{\frac{s_G - s_L}{v_G - v_L}} \tag{18}$$

In Equation (16), the applied weight in each term was unity, and the initial parameter values were set to be those of the original SRK EoS.

Average relative deviation (ARD) of the calculated properties was defined as follows:

$$ARD\left(\rho_L^{\text{SATP}}\right) = \frac{100}{n}\sum_{i=1}^{n}\left|\frac{\rho_{L,\text{Calc}}^{\text{SATP}} - \rho_{L,\text{Exp}}^{\text{SATP}}}{\rho_{L,\text{Exp}}^{\text{SATP}}}\right| \tag{19}$$

$$ARD(\rho_c) = \frac{100}{n}\sum_{i=1}^{n}\left|\frac{\rho_{c,\text{Calc}} - \rho_{c,\text{Exp}}}{\rho_{c,\text{Exp}}}\right| \tag{20}$$

3. Results and Discussion

Substance dependence C and D parameters in Equation (6) were correlated against the critical compressibility factor (z_c), as shown in Equations (21) and (22):

$$C = C_1 z_c + C_0 \tag{21}$$

$$D = D_1 z_c + D_0 \tag{22}$$

The five pure parameters (a_0 in Equation (13), b_0 in Equation (14) and K_{C1}, K_{C2}, K_{C3} in Equation (15)) and constant C_0, C_1, D_0 and D_1 in Equations (21) and (22) were determined by fitting the properties of the 28 selected chemicals (Table 1) and the objective function given by Equation (16) using a least-squares method. Namely, a total 11 parameters including E and F in Equation (6) were fit simultaneously. The resulting parameters are listed in Table 3, and detailed results are given in Table 4.

Table 3. Pure parameters in original SRK EoS and *e*SPT-SRK EoS given by Equation (6).

	a_0	b_0	K_{C1}	K_{C2}	K_{C3}
Original SRK EoS [1]	0.42748	0.08664	0.48	1.574	−0.176
*e*SPT-SRK EoS (This work)	0.47029	0.16585	0.39841	2.09757	−1.2685
	C_1	C_0	D_1	D_0	E	F
Original SRK EoS [1]	0	0	0	0	1	1
*e*SPT-SRK EoS (This work)	4.7231×10^{-5}	0.015878	−0.075541	0.018651	0.41785	1.00782

Table 4. ARDs calculated with *e*SPT-SRK EoS from experimental data values.

No.	Substance	Group	*ARD* (ρ_L^{SATP}) [%]		*ARD* (ρ_C) [%]	
1	Water	Water	8.0	(2.4) [1]	12.9	(1.4) [1]
2	Ethylene Glycol	Alcohol	1.2	(2.7) [1]	6.3	(2.2) [1]
3	*N*-Methyl-2-pyrrolidone	Cyclic compound	7.1	(0.9) [1]	13.8	(1.5) [1]
4	Methanol	Alcohol	9.9	(6.5) [1]	16.2	(1.2) [1]
5	Ethanol	Alcohol	1.0	(7.5) [1]	10.9	(1.8) [1]
6	Dimethyl Sulfide	Sulfur compound	7.7	(4.6) [1]	3.9	(2.4) [1]
7	1-Propanol	Alcohol	4.1	(6.5) [1]	7.3	(2.1) [1]
8	*N*,*N*-Dimethylformamide	Nitrogen compound	21.5	(6.1) [1]	20.2	(0.9) [1]
9	1-Butanol	Alcohol	5.5	(5.6) [1]	6.0	(2.2) [1]
10	2-Butanol	Alcohol	3.6	(5.7) [1]	7.1	(2.1) [1]
11	Pyridine	Aromatic	6.9	(2.5) [1]	0.1	(2.6) [1]
12	Cyclopentanone	Ketone	3.6	(8.0) [1]	15.4	(1.4) [1]
13	Acetophenone	Ketone	1.6	(2.5) [1]	4.1	(2.3) [1]
14	Dichloromethane	Halide	2.9	(0.1) [1]	4.2	(2.4) [1]
15	Dimethyl Carbonate	Carbonate	1.0	(2.8) [1]	9.0	(1.9) [1]
16	Cyclohexanone	Ketone	5.0	(5.8) [1]	15.3	(1.4) [1]
17	Acetone	Ketone	6.7	(2.2) [1]	12.4	(1.6) [1]
18	Tetrahydrofuran	Cyclic ether	8.9	(7.9) [1]	5.7	(2.2) [1]
19	Benzene	Aromatic	9.2	(4.0) [1]	2.7	(2.4) [1]
20	Toluene	Aromatic	6.6	(2.8) [1]	3.8	(2.3) [1]
21	1-Decanol	Alcohol	0.3	(2.8) [1]	4.6	(2.2) [1]
22	Trans-Decahydronaphthalene	Cyclic compound	12.1	(4.9) [1]	1.8	(2.4) [1]
23	Cyclohexane	Cyclic compound	11.7	(4.5) [1]	1.1	(2.5) [1]
24	Tetradecane	Alkane	8.5	(4.6) [1]	10.2	(1.8) [1]
25	1-Decene	Alkene	2.2	(2.9) [1]	7.1	(2.1) [1]
26	Decane	Alkane	0.1	(0.6) [1]	7.0	(2.1) [1]
27	Hexane	Alkane	6.6	(3.3) [1]	3.2	(2.4) [1]
28	Carbon Dioxide	Inorganic Carbon	-	-	8.5	(2.6) [1]
-	-	Average	6.1	(4.0) [1]	7.9	(2.0) [1]

[1] Values obtained with the original *e*SPT-PR EoS (predictive form) [13] (in parentheses).

The *e*SPT-SRK EoS compared favorably with the original *e*SPT-PR EoS (Table 4). In Table 5, four pure substances (*n*-hexane, CO_2, methanol and water) were predicted with the *e*SPT-SRK EoS given by Equation (6) in several (T, P) conditions and compared with the pc-SAFT EoS [19]. For water, the pc-SAFT EoS was fit to an intermediate isotherm of NIST data (523.15 K) and then applied to calculate densities in the other stated conditions.

Table 5. Prediction of properties for four pure chemical compounds with *e*SPT-SRK EoS given by Equation (6) in several (T, P) conditions. For water, the pc-SAFT EoS [19] was fit to an intermediate isotherm (523.15 K) for parameter determination.

n-Hexane	*e*SPT-SRK EoS *ARD* (ρ_L) [%]	*e*SPT-SRK EoS *ARD* (ρ_G) [%]	Original *e*SPT-PR EoS *ARD* (ρ_L) [%]	Original *e*SPT-PR EoS *ARD* (ρ_G) [%]	pc-SAFT EoS *ARD* (ρ_L) [%]	pc-SAFT EoS *ARD* (ρ_G) [%]
(T_r = 0.8, P_r = 0.8)	1.2	-	1.8	-	2.2	-
(T_r = 1.15, P_r = 1.2)	-	3.8	-	23.9	-	2.6
CO_2	*e*SPT-SRK EoS *ARD* (ρ_L) [%]	*e*SPT-SRK EoS *ARD* (ρ_G) [%]	Original *e*SPT-PR EoS *ARD* (ρ_L) [%]	Original *e*SPT-PR EoS *ARD* (ρ_G) [%]	pc-SAFT EoS *ARD* (ρ_L) [%]	pc-SAFT EoS *ARD* (ρ_G) [%]
(T_r = 0.8, P_r = 0.8)	4.0	-	1.1		6.0	-
(T_r = 1.2, P_r = 1.2)	-	2.9	-	19.0	-	5.1
Methanol	*e*SPT-SRK EoS *ARD* (ρ_L) [%]	*e*SPT-SRK EoS *ARD* (ρ_G) [%]	Original *e*SPT-PR EoS *ARD* (ρ_L) [%]	Original *e*SPT-PR EoS *ARD* (ρ_G) [%]	pc-SAFT EoS *ARD* (ρ_L) [%]	pc-SAFT EoS *ARD* (ρ_G) [%]
(T_r = 0.8, P_r = 0.8)	16.3	-	3.5	-	0.53	-
(T_r = 1.2, P_r = 1.2)	-	2.3	-	43.7	-	1.7
Water	*e*SPT-SRK EoS *ARD* (ρ_L) [%]	*e*SPT-SRK EoS *ARD* (ρ_G) [%]	Original *e*SPT-PR EoS *ARD* (ρ_L) [%]	Original *e*SPT-PR EoS *ARD* (ρ_G) [%]	pc-SAFT EoS * *ARD* (ρ_L) [%]	pc-SAFT EoS * *ARD* (ρ_G) [%]
(T_r = 0.8, P_r = 0.8)	18.3	-	3.9	-	0.09	-
(T_r = 1.2, P_r = 1.2)	-	2.9	-	42.3	-	1.5

* m_i 1.59364, σ [Å] 2.46841, ε_i/kT [K] 235.681, k_{AB} 0.071007, ε_{AB}/kT [K] 3387.68.

In the calculation of ARD [%], values from the NIST chemistry webbook [20] were used for reference as follows:

$$ARD(\rho_G) = \frac{100}{n}\sum_{i=1}^{n}\left|\frac{\rho_{G,\mathrm{Calc}} - \rho_{G,\mathrm{NIST}}}{\rho_{G,\mathrm{NIST}}}\right| \quad (23)$$

$$ARD(\rho_L) = \frac{100}{n}\sum_{i=1}^{n}\left|\frac{\rho_{L,\mathrm{Calc}} - \rho_{L,\mathrm{NIST}}}{\rho_{L,\mathrm{NIST}}}\right| \quad (24)$$

The ARDs of liquid densities of the *e*SPT-SRK EoS (Table 5) were comparable with those of both the *e*SPT-PR EoS and pc-SAFT EoS for two non-polar substances (*n*-hexane, CO_2), but deviations were higher than those of pc-SAFT EoS for two polar substances (methanol, water). On the other hand, the ARDs of gas densities were much lower for the *e*SPT-SRK EoS than the *e*SPT-PR EoS (Table 5). The pc-SAFT EoS is neither a cubic equation nor a fixed-degree polynomial and incorporates statistical–mechanical integral terms that enable an accurate description of substance properties in the critical region. All cubic EoSs have a cubic critical isotherm and a quadratic coexistence curve [17] unlike that of the pc-SAFT EoS. Nevertheless, the generalized form of the *e*SPT-SRK EoS developed in this work improved gaseous density representation compared with the *e*SPT-PR EoS (Table 5).

Figure 1 shows assessment of the thermodynamic relationship, Equation (3), for the 28-substance database. The *e*SPT-SRK EoS compared well with the original *e*SPT-PR EoS, although the deviations for the *e*SPT-SRK EoS were slightly higher than those of the original *e*SPT-PR EoS. However, modifications in the *e*SPT-SRK EoS improved its reliability compared with the original SRK EoS.

The entropy-based Hansen-type solubility parameter was used with the *e*SPT-SRK EoS, Equation (6), and differentiated with temperature to give:

$$eSP^2 = (\partial P/\partial T)_v = \frac{R}{v - Eb} - C\left(\frac{1}{v - Eb} - \frac{1}{v + Fb}\right) - \frac{a_c\left(\frac{\partial \alpha(T)}{\partial T}\right)_v}{v(v + Fb)} \quad (25)$$

In the *e*SPT-SRK EoS, polar and hydrogen bond terms were defined by the following equations:

$$eHSP\,|_{Polar,EoS}{}^2 = \frac{C}{v + Fb} \quad (26)$$

$$eHSP\,|_{Hydrogenbond,EoS}{}^2 = -\frac{a_c\left(\frac{\partial \alpha(T)}{\partial T}\right)_v}{v(v + Fb)} \quad (27)$$

where subscript EoS is the calculation with the *e*SPT-SRK EoS in this case.

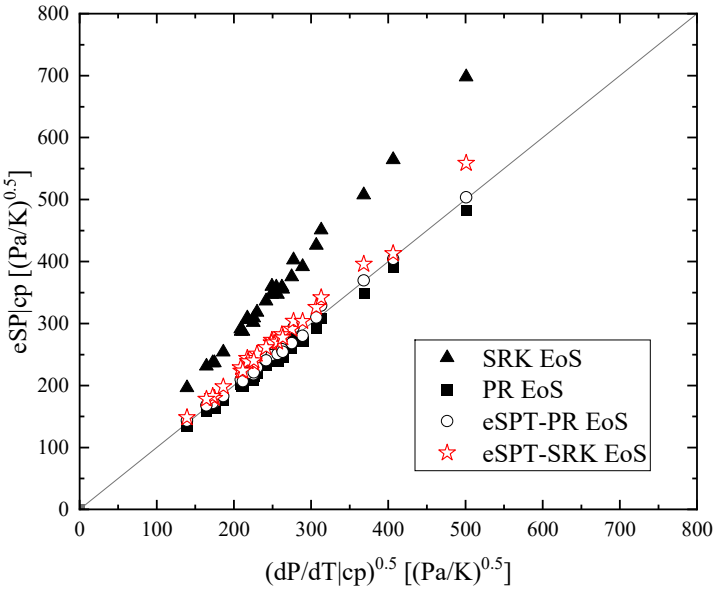


Figure 1. Thermodynamic relationship, Equation (3), assessed for four different equation-of-state formulations using the 28-substance database (Table 1).

The relationships between $eHSP|_{Polar,EOS}$ and $eHSP|_{Polar,Original}$, corresponding to the same contribution of δ_{Polar} in δ_{Total}, between $eSP|_{Hydrogenbond,EoS}$ and $\delta_{Hydrogenbond,Original}$, corresponding to the same contribution of $\delta_{Hydrogenbond}$ in the δ_{Total}, were examined (Figures 2 and 3). In Figure 2, the $eHSP|_{Polar,Original}$ showed quadratic correlation with $eSP|_{Polar,EoS}$ in HSP (R^2 = 0.4789), although some deviations were observed. In Figure 3, $eHSP|_{Hydrogenbond,Original}$ was strongly correlated with $eHSP|_{Hydrogenbond,EoS}$ (R^2 = 0.9395). These results support the development of the *e*HSP concept, as summarized by the following predictive forms.

$$eSP^2 = (eHSP\,|_{Total}{}^2 =)eHSP\,|_{Dispersion}{}^2 + eHSP\,|_{Polar}{}^2 + eHSP\,|_{Hydrogenbond}{}^2 \quad (28)$$

From the positive correlations observed in both Figures 2 and 3, the following relationships result in:

$$eHSP|_{Polar} = -3.2114\,(eHSP\,|_{Polar,EoS})^2 + 126.30\;eHSP|_{Polar,EoS} - 490.37 \quad (29)$$

$$eHSP|_{Hydrogenbond} = 2.3754 \times eHSP|_{Hydrogenbond,EoS} - 949.62 \quad (30)$$

$$e\text{HSP}|_{\text{Dispersion,EoS}} = \sqrt{e\text{HSP}|_{\text{Total,EoS}}{}^2 - e\text{HSP}|_{\text{Polar,EoS}}{}^2 - e\text{HSP}|_{\text{Hydrogenbond,EoS}}{}^2} \quad (31)$$

Table 6 shows the *e*HSP values for the 28 selected chemicals. If polar contribution showed negative values, the value was set to zero. In Table 5, the prediction with the *e*SPT-SRK EoS was well correlated with the original HSP data [21]. Figure 4 shows the relationship between the predicted *e*HSP and original HSP at 298.2 K and 101.3 kPa. Each term denoted as "Dispersion", "Polar", or "Hydrogen bond" showed linearity between predicted *e*HSPs and the original HSP. Thus, the method for calculating *e*HSP with the *e*SPT-SRK EoS can be considered to be internally consistent and reliable. The present prediction method with the *e*SPT-SRK EoS is applicable to the calculation of HSP values under arbitrary conditions of temperature, pressure, or mixture composition. Results with the corrected form of the *e*SPT-PR EoS gave similar results as those for the *e*SPT-SRK EoS.

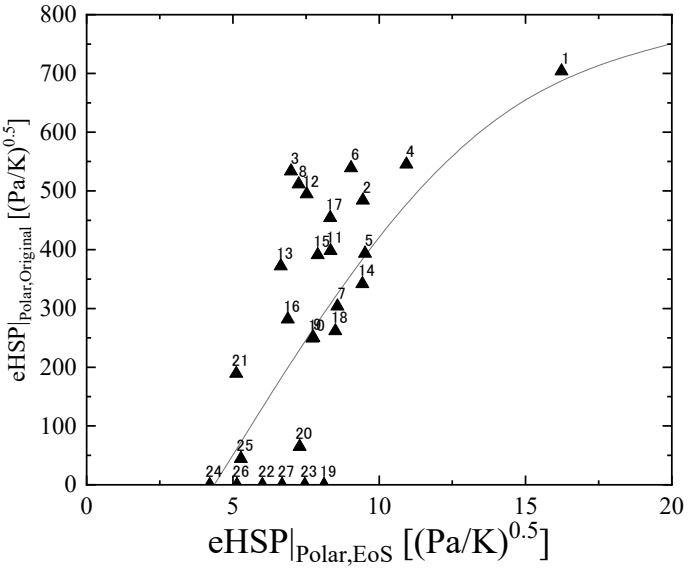


Figure 2. Relationship in Equation (29) between $e\text{HSP}|_{\text{Polar,EOS}}{}^{-1}$ and $e\text{HSP}|_{\text{Polar,Original}}$. Symbols are the calculated data and line is interpolation.

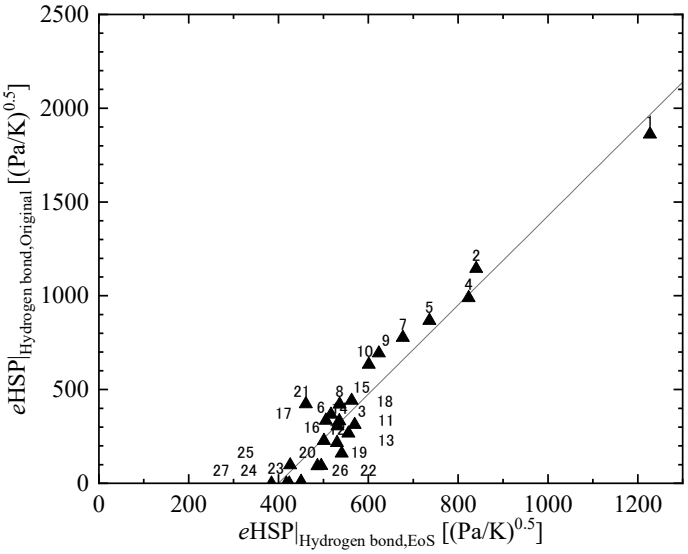
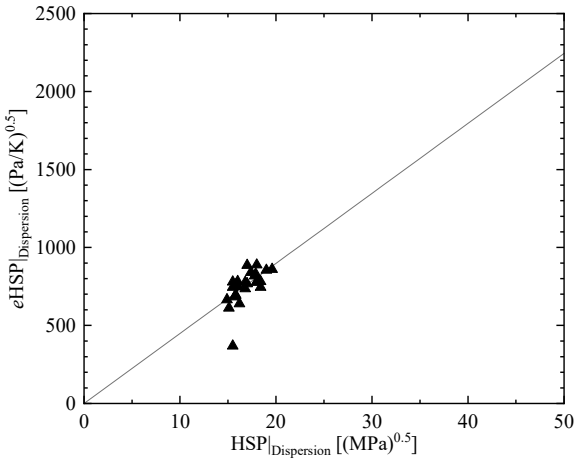


Figure 3. Relationship in Equation (30) between $e\text{HSP}|_{\text{Hydrogenbond,EoS}}$ and $e\text{HSP}_{\text{Hydrogenbond,Original}}$. Symbols are the calculated data and line is linear interpolation.

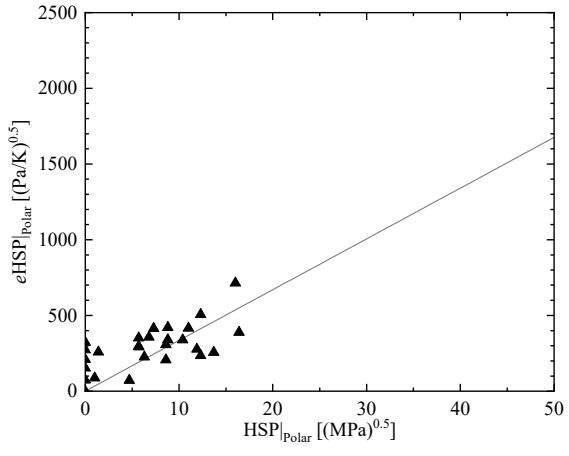
Table 6. Entropy-based Hansen solubility parameter (*e*HSP) of 28 selected chemicals (Table 1).

No.	Substance	$eHSP\|_{Dispersion}$ $[(Pa/K)^{0.5}]$		$eHSP\|_{Polar}$ $[(Pa/K)^{0.5}]$		$eHSP\|_{Hydrogenbond}$ $[(Pa/K)^{0.5}]$	
1	Water	685.8	(368.3) [1]	708.0	(713.6) [2]	1871.7	(1965.0) [3]
2	Ethylene Glycol	793.4	(885.8) [1]	513.4	(415.9) [2]	1213.5	(1046.7) [3]
3	*N*-Methyl-2-pyrrolidone	790.2	(888.6) [1]	540.0	(235.4) [2]	316.1	(403.5) [3]
4	Methanol	718.8	(612.3) [1]	585.5	(506.5) [2]	1061.5	(1006.5) [3]
5	Ethanol	772.5	(691.5) [1]	430.2	(420.9) [2]	948.5	(798.9) [3]
6	Dimethyl Sulfide	567.6	(745.6) [1]	505.9	(388.7) [2]	314.7	(251.3) [3]
7	1-Propanol	776.4	(749.7) [1]	330.0	(356.3) [2]	844.3	(658.3) [3]
8	*N*,*N*-Dimethylformamide	644.1	(841.0) [1]	507.2	(256.4) [2]	418.3	(324.3) [3]
9	1-Butanol	757.7	(782.5) [1]	269.9	(295.9) [2]	748.2	(531.6) [3]
10	2-Butanol	743.0	(760.0) [1]	268.1	(293.2) [2]	681.9	(478.5) [3]
11	Pyridine	823.3	(854.8) [1]	381.3	(339.7) [2]	255.7	(370.3) [3]
12	Cyclopentanone	728.9	(829.2) [1]	484.6	(278.1) [2]	211.8	(310.1) [3]
13	Acetophenone	860.5	(860.5) [1]	377.6	(206.2) [2]	162.4	(334.5) [3]
14	Dichloromethane	749.1	(767.2) [1]	321.7	(414.6) [2]	312.8	(321.9) [3]
15	Dimethyl Carbonate	715.9	(779.3) [1]	397.2	(307.2) [2]	448.0	(387.4) [3]
16	Cyclohexanone	782.8	(818.8) [1]	277.0	(226.3) [2]	224.3	(240.8) [3]
17	Acetone	668.5	(745.7) [1]	448.6	(338.6) [2]	301.9	(312.6) [3]
18	Tetrahydrofuran	734.4	(777.6) [1]	249.2	(351.6) [2]	349.7	(278.0) [3]
19	Benzene	819.6	(781.7) [1]	0.0	(323.2) [2]	89.1	(226.8) [3]
20	Toluene	807.9	(781.2) [1]	62.8	(258.9) [2]	89.8	(206.2) [3]
21	1-Decanol	698.4	(751.5) [1]	205.1	(71.9) [2]	458.3	(145.3) [3]
22	Trans-Decahydronaphthalene	779.3	(777.6) [1]	0.0	(152.6) [2]	0.0	(116.7) [3]
23	Cyclohexane	746.7	(735.8) [1]	0.0	(272.9) [2]	8.9	(119.5) [3]
24	Tetradecane	729.3	(639.8) [1]	0.0	(0.0) [2]	0.0	(0.0) [3]
25	1-Decene	732.9	(695.9) [1]	46.4	(86.7) [2]	102.0	(62.2) [3]
26	Decane	729.7	(684.0) [1]	0.0	(73.7) [2]	0.0	(42.6) [3]
27	Hexane	684.4	(665.7) [1]	0.0	(210.2) [2]	0.0	(57.0) [3]
28	Carbon Dioxide	-	(-) [1]	-	(-) [2]	-	(-) [3]

[1] Prediction with Equation (31), [2] Prediction with Equation (29) and [3] Prediction with Equation (30) (in parentheses).

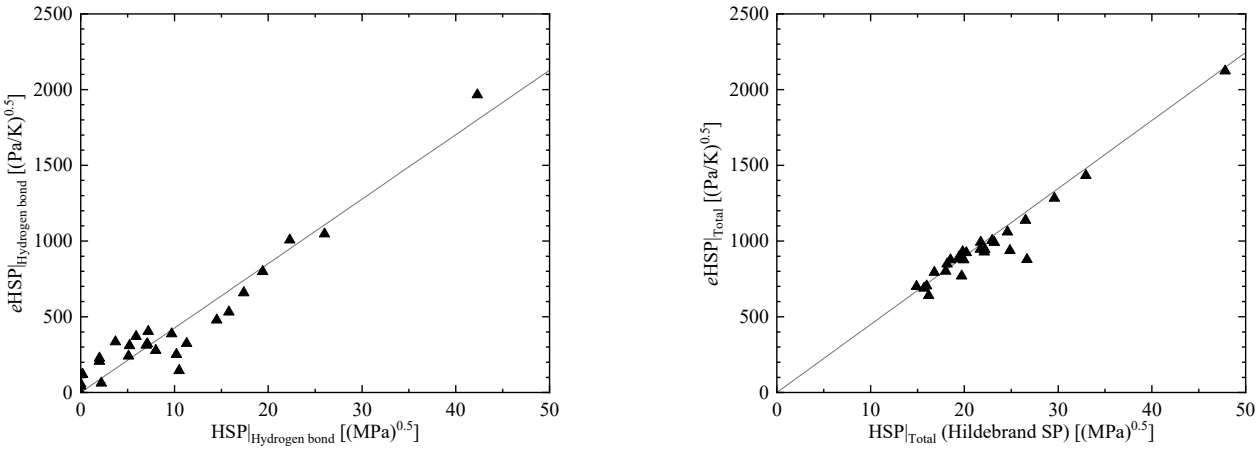


(**a**)



(**b**)

Figure 4. *Cont.*



(**c**) (**d**)

Figure 4. Relationship between the predicted *e*HSP and original HSP. (**a**) $e\text{HSP}|_{\text{Dispersion}}$ vs. $\text{HSP}|_{\text{Dispersion}}$ (R^2 = 0.989), (**b**) $e\text{HSP}|_{\text{Polar}}$ vs. $\text{HSP}|_{\text{Polar}}$ (R^2 = 0.794), (**c**) $e\text{HSP}|_{\text{Hydrogenbond}}$ vs. $\text{HSP}|_{\text{Hydrogenbond}}$ (R^2 = 0.959), (**d**) $e\text{HSP}|_{\text{Total}}$ vs. $\text{HSP}|_{\text{Total}}$ (Hildebrand SP) (R^2 = 0.995). Symbols are the calculated data and line is linear interpolation.

4. Conclusions

A translation type of correction (*e*SP) was applied to develop an alternate form of the popular Soave–Redlich–Kwong equation. The resulting *e*SPT-SRK EoS showed good correlation results for both liquid and critical densities. Thermodynamic expressions of the *e*SPT-SRK EoS and the corrected *e*SPT-PR EoS are simple and have closed forms. In the *e*SPT-SRK EoS, the additional constants *C* and *D* correlate with the compressibility factor $Z_{C,}$ which gives a convenient predictive form. The *e*HSP values obtained from either the *e*SPT-SRK or *e*SPT-PR EoS can be used to predict solubility parameters for extractions and separations under conditions far from atmospheric pressure and ambient temperature.

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Data Availability Statement: The data that support the findings of this study are available from the corresponding author [M.O.] upon reasonable request.

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Conflicts of Interest: The authors declare no conflicts of interest.

Nomenclature

a_0	Energetic parameter in Equation (13) [-]
b_0	Volumetric parameter in Equation (14) [-]
C	New parameter in Equations (6), (13) and (14) [J K^{-1} mol^{-1}]
C_0	New parameter in Equation (21) [J K^{-1} mol^{-1}]
C_1	New parameter in Equation (21) [J K^{-1} mol^{-1}]
D_0	New parameter in Equation (21) [Pa m^3 mol^{-1}]
D_1	New parameter in Equation (21) [Pa m^3 mol^{-1}]
D	New parameter in Equation (6) [Pa m^3 mol^{-1}]
E	New parameter in Equation (6) [-]
F	New parameter in Equation (6) [-]
F	Fugacity [Pa]
H	Enthalpy [J/mol]
N	Moles [mol]
P	Pressure [Pa]
R	Gas constant [J K^{-1} mol^{-1}]
s	Molar entropy [J K^{-1} mol^{-1}]
T	Temperature [K]
U	Internal energy [J/mol]
v	Molar volume [m^3 mol^{-1}]
z	Compressibility factor (=Pv/RT) [-]
ϕ	Fugacity coefficient [-]
ρ	Density [kg m^{-3}]
ω	Acentric factor [-]
Subscripts	
c	Critical point
G	Gas phase
IG	Ideal gas state
L	Liquid Phase
vp	Vaporization

Appendix A

The original *e*SPT-PR EoS was parameterized as follows:

$$P = \frac{RT}{v-b} - CT\left(\frac{1}{v-b}\right) - \frac{a_c\,\alpha(T)}{\left(v+b-\sqrt{2}b\right)\left(v+b+\sqrt{2}b\right)} \tag{A1}$$

The equation denoted as the corrected *e*SPT-PR EoS was parameterized as follows:

$$P = \frac{RT}{v-Eb} - CT\left(\frac{1}{v-Eb} - \frac{1}{v+Fb+\sqrt{2}Fb}\right) - \frac{a_c\,\alpha(T)+D}{\left(v+Fb-\sqrt{2}Fb\right)\left(v+Fb+\sqrt{2}Fb\right)} \tag{A2}$$

In Equation (A2), D, E and F were newly introduced into the corrected *e*SPT-PR EoS, though the original PR EoS has $C = D = 0$ and $E = F = 1$.

In this way, one can obtain the fugacity coefficient φ from the departure function (Equation (A3)) by substitution of Equation (A2):

$$\ln\varphi = \ln\frac{f}{p} = \frac{1}{RT}\int_V^\infty \left(\frac{p}{n} - \frac{RT}{V}\right)dV + (z-1) - \ln z \tag{A3}$$

where f and z are fugacity and compressibility factors, respectively. The resulting expression for the fugacity coefficient φ can be expressed as follows:

$$\ln \varphi = RT\ln \frac{v}{v-Eb} - CT\ln \frac{v+Fb+\sqrt{2}Fb}{v-Eb} - \frac{(a_c\alpha(T)+D)}{2\sqrt{2}Fb}\ln \frac{v+Fb-\sqrt{2}Fb}{v+Fb+\sqrt{2}Fb} \quad \text{(A4)}$$

Entropy can be calculated from the departure function (Equation (A5)):

$$s(T,P) - s_{\mathrm{IG}}(T,P) = R\ln z + \int_{T,v=\infty}^{T,v}\left[\left(\frac{\partial P}{\partial T}\right)_v - \frac{R}{v}\right]dv \quad \text{(A5)}$$

where G and IG are gas state and ideal gas state at constant T, respectively, and $\left(\frac{\partial P}{\partial T}\right)_{v_G}$ can be calculated by substituting in Equation (A2) as follows:

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v-Eb} - C\left(\frac{1}{v-Eb} - \frac{1}{v+Fb+\sqrt{2}Fb}\right) - \frac{a_c\left(\frac{\partial \alpha(T)}{\partial T}\right)_v}{\left(v+Fb-\sqrt{2}Fb\right)\left(v+Fb+\sqrt{2}Fb\right)} \quad \text{(A6)}$$

The resulting entropy difference for gas or liquid phase can be expressed as follows:

$$s_G(T,P) - s_{\mathrm{IG}}(T,P) = R\ln z_G + R\ln \frac{v_G-Eb}{v_G} + C\ln \frac{v_G+Fb+\sqrt{2}Fb}{v_G-Eb} - \frac{a_c}{2\sqrt{2}Fb}\left(\frac{\partial \alpha(T)}{\partial T}\right)_{v_G}\ln \frac{v_G+Fb-\sqrt{2}Fb}{v_G+Fb+\sqrt{2}Fb} \quad \text{(A7)}$$

$$s_L(T,P) - s_{\mathrm{IG}}(T,P) = R\ln z_L + R\ln \frac{v_L-Eb}{v_L} + C\ln \frac{v_L+Fb+\sqrt{2}Fb}{v_L-Eb} - \frac{a_c}{2\sqrt{2}Fb}\left(\frac{\partial \alpha(T)}{\partial T}\right)_{v_L}\ln \frac{v_L+Fb-\sqrt{2}Fb}{v_L+Fb+\sqrt{2}Fb} \quad \text{(A8)}$$

For the corrected *e*SPT-PR EoS parameters a_c and b in Equation (A2), a constant C was introduced as in the *e*SPT-PR EoS as follows:

$$a_c = a_0\frac{R^2(1-C/R)^2\,T_C^2}{P_C} \quad \text{(A9)}$$

$$b = b_0\frac{R(1-C/R)\,T_C}{P_C} \quad \text{(A10)}$$

The $a(T)$ function of original PR EoS was adopted and is described by Equation (A11):

$$\alpha(T) = 1 + \left(K_{C1} + K_{C2}\omega + K_{C3}\omega^2\right)\left(1 - T_r^{0.5}\right) \quad \text{(A11)}$$

Substance dependence C and D parameters in Equation (A2) were correlated against the critical compressibility factor (z_c), as shown in Equations (A12) and (A13), respectively:

$$C = C_1 z_c + C_0 \quad \text{(A12)}$$

$$D = D_1 z_c + D_0 \quad \text{(A13)}$$

The five pure parameters (a_0 in Equation (A9), b_0 in Equation (A10) and K_{C1}, K_{C2}, K_{C3} in Equation (A11)) and constant C_0, C_1, D_0 and D_1 in Equations (A12) and (A13) in the corrected *e*SPT-PR EoS were determined by the properties of the selected 28 chemicals (Table A1) using the objective function in Equation (17) by a least-squares method. Namely, a total of 11 parameters including E and F in Equation (A2) were simultaneously fitted. The resulting parameters are listed in Table A1, and detailed results are given in Table A2.

For comparison of the entropy-based Hansen-type solubility parameter with the corrected *e*SPT-PR EoS, Equation (A2) was differentiated with temperature to give:

$$e\mathrm{SP}^2 = (\partial P/\partial T)_v = \frac{R}{v-Eb} - C\left(\frac{1}{v-Eb} - \frac{1}{v+Fb+\sqrt{2}Fb}\right) - \frac{a_c\left(\frac{\partial \alpha(T)}{\partial T}\right)_v}{\left(v+Fb-\sqrt{2}Fb\right)\left(v+Fb+\sqrt{2}Fb\right)} \quad \text{(A14)}$$

In the *e*SPT-PR EoS, polar and hydrogen bond terms were defined by the following equations:

$$e\mathrm{HSP}\,|_{\mathrm{Polar,EoS}}{}^2 = -C\left(\frac{1}{v-Eb} - \frac{1}{v+Fb+\sqrt{2}Fb}\right) \quad \text{(A15)}$$

$$e\mathrm{HSP}\,|_{\mathrm{Hydrogenbond,EoS}}{}^2 = -\frac{a_c\left(\frac{\partial \alpha(T)}{\partial T}\right)_v}{\left(v+Fb-\sqrt{2}Fb\right)\left(v+Fb+\sqrt{2}Fb\right)} \quad \text{(A16)}$$

where subscript EoS is the calculation with the corrected *e*SPT-PR EoS.

We summarized that an *e*HSP concept was developed, as shown in the following predictive forms.

$$e\mathrm{SP}^2 = (e\mathrm{HSP}\,|_{\mathrm{Total}}{}^2 =)e\mathrm{HSP}\,|_{\mathrm{Dispersion}}{}^2 + e\mathrm{HSP}\,|_{\mathrm{Polar}}{}^2 + e\mathrm{HSP}\,|_{\mathrm{Hydrogenbond}}{}^2 \quad \text{(A17)}$$

We found the next relationships:

$$e\mathrm{HSP}|_{\mathrm{Polar}} = -\frac{337101}{e\mathrm{HSP}|_{\mathrm{Polar,EoS}}} + 1356.6 \qquad \left(R^2 = 0.6414\right) \quad \text{(A18)}$$

$$e\mathrm{HSP}|_{\mathrm{Hydrogenbond}} = 2.2949 \times e\mathrm{HSP}|_{\mathrm{Hydrogenbond,EoS}} - 1035.8 \qquad \left(R^2 = 0.9495\right) \quad \text{(A19)}$$

$$e\mathrm{HSP}|_{\mathrm{Dispersion,EoS}} = \sqrt{e\mathrm{HSP}\,|_{\mathrm{Total,EoS}}{}^2 - e\mathrm{HSP}\,|_{\mathrm{Polar,EoS}}{}^2 - e\mathrm{HSP}\,|_{\mathrm{Hydrogenbond,EoS}}{}^2} \quad \text{(A20)}$$

Table A1. Pure parameters in original PR EoS, original *e*SPT-PR EoS in Equation (A1) and corrected form of *e*SPT-PR EoS Equation (A2).

	a_0	b_0	K_{C1}	K_{C2}	K_{C3}
Original PR EoS Equation (A2)	0.42748	0.08664	0.48	1.574	−0.176
Original *e*SPT-PR EoS Equation (A1)	0.51119	0.09079	0.34687	1.93487	−0.25698
(Corrected form) *e*SPT-PR EoS Equation (A2) (This work)	0.38053	0.068472	0.17755	1.76389	−0.10468
	C_1	C_0	D_1	D_0	E	F
Original PR EoS Equation (A2)	0	0	0	0	1	1
Original *e*SPT-PR EoS Equation (A1)	−27.6704	8.73306	-	-	-	-
(Corrected form) *e*SPT-PR EoS Equation (A2) (This work)	−0.11957	−1.28693	−0.055156	0.0150935	0.90092	1.12988

Table A2. ARDs calculated with the corrected *e*SPT-PR EoS from experimental data values.

No.	Substance	Group	*ARD* (ρ_L^{SATP}) [%]	*ARD* (ρ_C) [%]
1	Water	Water	7.2 (2.4) [1]	0.1 (1.4) [1]
2	Ethylene Glycol	Alcohol	0.7 (2.7) [1]	1.0 (2.2) [1]

Table A2. *Cont.*

No.	Substance	Group	*ARD* (ρ_L^{SATP}) [%]		*ARD* (ρ_C) [%]	
3	*N*-Methyl-2-pyrrolidone	Cyclic Compound	6.9	(0.9) [1]	9.8	(1.5) [1]
4	Methanol	Alcohol	6.6	(6.5) [1]	6.3	(1.2) [1]
5	Ethanol	Alcohol	3.0	(7.5) [1]	2.8	(1.8) [1]
6	Dimethyl Sulfide	Sulfur compound	10.9	(4.6) [1]	1.6	(2.4) [1]
7	1-Propanol	Alcohol	7.6	(6.5) [1]	1.1	(2.1) [1]
8	*N*,*N*-Dimethylformamide	Nitrogen compound	20.9	(6.1) [1]	15.2	(0.9) [1]
9	1-Butanol	Alcohol	8.3	(5.6) [1]	1.2	(2.2) [1]
10	2-Butanol	Alcohol	6.8	(5.7) [1]	1.9	(2.1) [1]
11	Pyridine	Aromatic	7.9	(2.5) [1]	1.6	(2.6) [1]
12	Cyclopentanone	Ketone	2.6	(8.0) [1]	10.0	(1.4) [1]
13	Acetophenone	Ketone	1.8	(2.5) [1]	1.4	(2.3) [1]
14	Dichloromethane	Halide	5.7	(0.1) [1]	1.8	(2.4) [1]
15	Dimethyl Carbonate	Carbonate	1.2	(2.8) [1]	3.3	(1.9) [1]
16	Cyclohexanone	Ketone	4.4	(5.8) [1]	10.9	(1.4) [1]
17	Acetone	Ketone	4.0	(2.2) [1]	5.3	(1.6) [1]
18	Tetrahydrofuran	Aromatic	11.2	(7.9) [1]	0.1	(2.2) [1]
19	Benzene	Aromatic	11.1	(4.0) [1]	1.1	(2.4) [1]
20	Toluene	Aromatic	8.0	(2.8) [1]	0.2	(2.3) [1]
21	1-Decanol	Alcohol	0.7	(2.8) [1]	2.9	(2.2) [1]
22	Trans-Decahydronaphthalene	Aromatic	12.4	(4.9) [1]	0.2	(2.4) [1]
23	Cyclohexane	Cyclic Compound	13.8	(4.5) [1]	1.5	(2.5) [1]
24	Tetradecane	Alkane	7.5	(4.6) [1]	9.5	(1.8) [1]
25	1-Decene	Alkene	7.2	(2.9) [1]	4.9	(2.1) [1]
26	Decane	Alkane	0.7	(0.6) [1]	4.9	(2.1) [1]
27	Hexane	Alkane	6.9	(3.3) [1]	0.2	(2.4) [1]
28	Carbon Dioxide	Inorganic Carbon	-	-	0.2	(2.6) [1]
-	-	Average	6.9	(4.0) [1]	3.6	(2.0) [1]

[1] Values obtained with the original *e*SPT-PR EoS (predictive form) [13] (in parentheses).

References

1. Soave, G. Equilibrium constants from a modified Redlich–Kwong equation of state. *Chem. Eng. Sci.* **1972**, *27*, 1197–1203. [CrossRef]
2. Peng, D.-Y.; Robinson, D.B. A new two-constant equation of state. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59–64. [CrossRef]
3. Heidemann, R.A.; Khalil, A.M. The calculation of critical points. *AIChE J.* **1980**, *26*, 769–779. [CrossRef]
4. Maeta, Y.; Ota, M.; Sato, Y.; Smith, R.L.; Inomata, H. Measurements of vapor–liquid equilibrium in both binary carbon dioxide–ethanol and ternary carbon dioxide–ethanol–water systems with a newly developed flow-type apparatus. *Fluid Phase Equilibria* **2015**, *405*, 96–100. [CrossRef]
5. Huron, M.; Vidal, J. New mixing rules in simple equations of state for representing vapour-liquid equilibria of strongly non-ideal mixtures. *Fluid Phase Equilibria* **1979**, *3*, 255–271. [CrossRef]
6. Michelsen, M.L. A modified Huron-Vidal mixing rule for cubic equations of state. *Fluid Phase Equilibria* **1990**, *60*, 213–219. [CrossRef]
7. Holderbaum, T.; Gmehling, J. PSRK: A Group Contribution Equation of State Based on UNIFAC. *Fluid Phase Equilibria* **1991**, *70*, 251–265. [CrossRef]
8. Ota, M.; Morohashi, K.; Abe, Y.; Watanabe, M.; Smith, R.L.; Inomata, H. Replacement of CH_4 in the hydrate by use of liquid CO_2. *Energy Conv. Manag.* **2005**, *46*, 1680–1691. [CrossRef]
9. Péneloux, A.; Rauzy, E.; Fréze, R. A consistent correction for Redlich-Kwong-Soave volumes. *Fluid Phase Equilibria* **1982**, *8*, 7–23. [CrossRef]
10. Ahlers, J.; Gmehling, J. Development of an universal group contribution equation of state: I. Prediction of liquid densities for pure compounds with a volume translated Peng-Robinson equation of state. *Fluid Phase Equilibria* **2001**, *191*, 177–188. [CrossRef]
11. Tsai, J.-C.; Chen, Y.-P. Application of a volume-translated Peng-Robinson equation of state on vapor-liquid equilibrium calculations. *Fluid Phase Equilibria* **1998**, *145*, 193–215. [CrossRef]
12. Schmid, B.; Gmehling, J. Present status of the group contribution equation of state VTPR and typical applications for process development. *Fluid Phase Equilibria* **2016**, *425*, 443–450. [CrossRef]

13. Ota, M.; Yang, N.; Komatsu, H.; Inomata, H.; Smith, R.L. Entropy-based solubility parameter-translated Peng-Robinson equation of state (eSPT-PR EoS). *Liquids* **2025**, *5*, 21. [CrossRef]
14. Hildebrand, J.H.; Scott, R.L. *The Solubility of Nonelectrolytes*, 3rd ed.; Reinhold Pub. Corporation: New York, NY, USA, 1950.
15. Ota, M.; Hashimoto, Y.; Sato, M.; Sato, Y.; Smith, R.L.; Inomata, H. Solubility of flavone, 6-methoxyflavone and anthracene in supercritical CO_2 with/without a co-solvent of ethanol correlated by using a newly proposed entropy-based solubility parameter. *Fluid Phase Equilibria* **2016**, *425*, 65–71. [CrossRef]
16. Ota, M.; Sugahara, S.; Sato, Y.; Smith, R.L.; Inomata, H. Vapor-liquid distribution coefficients of hops extract in high pressure CO_2 and ethanol mixtures and data correlation with entropy-based solubility parameters. *Fluid Phase Equilibria* **2017**, *434*, 44–48. [CrossRef]
17. Levelt Sengers, J.M.H. From Van der Waals' equation to the scaling laws. *Physica* **1974**, *73*, 73–106. [CrossRef]
18. Elliott, J.R.; Diky, V.; Knotts, T.A., IV; Wilding, W.V. *The Properties of Gases and Liquids*, 6th ed.; Mc Graw Hill: NY, USA, 2023; pp. 687–747.
19. Gross, J.; Sadowski, G. Perturbed-Chain SAFT: An Equation of State Based on a Perturbation Theory for Chain Molecules. *Ind. Eng. Chem. Res.* **2001**, *40*, 1244–1260. [CrossRef]
20. NIST Chemistry Webbook. Available online: https://webbook.nist.gov/chemistry/fluid (accessed on 25 June 2026).
21. Hansen, C.M. *Hansen Solubility Parameters: A User's Handbook*, 2nd ed.; CRC Press: Boca Raton, FL, USA, 2007.

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