

Combined Helmholtz Energy, Extended Corresponding States and Local Composition Model for Fluid Mixtures¹

J. F. Estela-Uribe^{2,4}, A. De Mendoza², J. P. M Trusler³

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² Facultad de Ingeniería, Universidad Javeriana – Cali.
Calle 18 118-250, Cali, Colombia.

³ Department of Chemical Engineering and Chemical Technology, Imperial College London, South Kensington Campus, London SW7 2AZ, United Kingdom.

⁴ Corresponding author: Tel.: +57-2-3218390; Fax: +57-2-552823; e-mail:
jfe@puj.edu.co

Abstract.

We present a thermodynamic model of mixtures in which the Helmholtz energy is computed from an extended corresponding states (ECS) method with a correction term. The ECS model is based upon the van der Waals one-fluid theory with pure-component shape factors represented as functions of reduced temperature and density. The correction term is given by a local composition model with a coordination number taken from lattice gas theory. Densities and speeds of sound of binary mixtures were calculated with deviations within ± 0.20 per cent, while deviations in bubble pressures were within ± 2 per cent on average.

Keywords: Binary mixtures, Helmholtz energy, corresponding states, densities, speeds of sound, vapour pressures.

1. Introduction

Extended corresponding states (ECS) models have been widely used for the prediction of mixture properties as they are both accurate and easily applicable to multicomponent systems. Examples of accurate ECS models are those for liquefied natural gas [1], for refrigerants [2] and for the ternary system (N₂+Ar+O₂) and air [3]. More recently, Estela-Uribe and Trusler [4] reported an ECS model for natural gas systems with which densities and speeds of sound of natural gas systems can be calculated with accuracy matching that of the standard models AGA8-DC92 [5] and MGREG-88 [6].

Recent mixture models have been based upon expressing the residual Helmholtz energy of the mixture as the sum of ideal-mixture and excess contributions [7,8]. The ideal-mixture term was calculated from reference equations of state for the pure components while the excess term was expressed as a multi-parameter empirical function of temperature, density and composition [7,8].

In the present work we also express residual Helmholtz energy of the mixture as a sum of two contributions. However, the leading contribution is calculated from a one-fluid ECS model while the correction term is calculated from a local-composition model. The rationale behind this approach is that a one-fluid ECS mixture model [4] is expected to provide a better initial approximation than an ideal-mixture term and so the correction term should be correspondingly smaller.

2. Theory

For a mixture, the corresponding states condition may be expressed as [9]:

$$Z_x(T, \rho) = Z_0(T/f_x, h_x \rho), \quad (1)$$

$$\Phi_x^{\text{res}}(T, \rho) = \Phi_0^{\text{res}}(T/f_x, h_x \rho). \quad (2)$$

Here, the scaling parameters f_x and h_x are given by the following one-fluid mixing rules:

$$h_x = \sum_i \sum_j x_i x_j h_{ij}, \quad (3)$$

$$f_x h_x = \sum_i \sum_j x_i x_j f_{ij} h_{ij}. \quad (4)$$

The unlike scaling parameters f_{ij} and h_{ij} are given by

$$f_{ij} = \xi_{ij} (f_{ii} f_{jj})^{1/2}, \quad (5)$$

$$h_{ij} = \eta_{ij} [\frac{1}{8} (h_{ii}^{1/3} + h_{jj}^{1/3})^3], \quad (6)$$

where f_{ii} and h_{ii} are given by

$$f_{ii} = (T^c/T_0^c) \theta_{ii}(T_r, \rho_r), \quad (7)$$

$$h_{ii} = (\rho_0^c/\rho^c) \varphi_{ii}(T_r, \rho_r), \quad (8)$$

and θ_{ii} and φ_{ii} are pure-component shape factors. In this work, the binary interaction parameters ξ_{ij} and η_{ij} are taken to be independent of temperature and density.

In a local-composition model, one defines the local mole fraction x_{ji} of species j around a molecule of species i as follows:

$$x_{ji} = \frac{N_{ji}}{N_{ci}}. \quad (9)$$

Here, N_{ji} is the number of molecules of species j clustered around a molecule of species i and N_{ci} is the coordination number of species i . From statistical mechanics and Monte Carlo simulations, Sandler [10] demonstrated that local composition effects should be more important at low densities. In particular, in the zero-density limit the radial distribution function is $\lim_{\rho \rightarrow 0} g_{ji}(r) = \exp(-u_{ji}(r)/k_B T)$ and for mixtures of square-well molecules of approximately the same size, it can be shown that:

$$\lim_{\rho \rightarrow 0} \frac{x_{ji}}{x_{ii}} = \frac{x_j}{x_i} \exp[(\varepsilon_{ji} - \varepsilon_{ii})/k_B T] \quad (10)$$

Although equation (10) holds only in the zero-density limit, it is nonetheless in good agreement with the simulation results of [10] and the theoretical observation of Weeks *et al.* [11] that the low-density structure of the fluid is largely determined by attraction forces. As the density increases and the fluid structure becomes dominated by repulsive forces, the local compositional ordering is expected to decrease. In fact, simulation results [10] show that the ratio x_{ji}/x_{ii} tends to the bulk ratio x_j/x_i as the density increases.

In the present work, we represent the reduced residual Helmholtz energy of the mixture as

$$\Phi_x^{\text{res}}(T, \rho) = \Phi_{\text{ECS}}^{\text{res}}(T, \rho) + \sum_i \sum_j x_i x_{ji} d_{ij} \rho / T. \quad (11)$$

Equation (11) complies with the necessary boundary condition of $\lim_{\rho \rightarrow 0} \Phi_x^{\text{res}} = 0$ because $\lim_{\rho \rightarrow 0} \Phi_{\text{ECS}}^{\text{res}} = 0$. Also, this model leads to mixture second virial coefficients that are quadratic in composition. For the term $\Phi_{\text{ECS}}^{\text{res}}$ we have used the same ECS model of [4] with CH₄ as the reference fluid and the reference equation of state given in [12]. The shape factors are calculated with the following correlations presented in [13]:

$$\theta(\tau, \delta) = 1 + (\omega - \omega_0) (A_1(\tau) + A_2(\tau) \exp(-\delta^2) + \Psi_\theta(\tau, \delta)), \quad (12)$$

$$\varphi(\tau, \delta) = (Z_0^c/Z^c) \left\{ 1 + (\omega - \omega_0) (A_3(\tau) + A_4(\tau) \exp(-\delta^2) + \Psi_\varphi(\tau, \delta)) \right\}. \quad (13)$$

The temperature- and density-dependent functions are given by:

$$A_i(\tau) = a_{i,1} - a_{i,2} \ln \tau. \quad (14)$$

$$\Psi_\theta(\tau, \delta) = b_1 \delta \exp(-b_2 \Delta^2), \quad (15)$$

$$\Psi_\varphi(\tau, \delta) = c_1 \delta \exp(-c_2 \Delta^2), \quad (16)$$

$$\Delta(\tau, \delta) = (\delta - 1)^2 + (\tau^{-1} - 1)^2. \quad (17)$$

Turning to the local composition (LC) model, for binary mixtures we start with the local balances of species:

$$x_{21} + x_{11} = 1, \quad (18)$$

$$x_{12} + x_{22} = 1. \quad (19)$$

The condition of the invariance of the combinatory counting of species [14] is:

$$x_1 x_{21} N_{c1} = x_2 x_{12} N_{c2}. \quad (20)$$

where N_{c1} and N_{c2} are, respectively, the coordination numbers of species 1 and 2. Equation (10) holds only in the limit of zero-density but may be extended approximately to finite densities as suggested by Sandler and collaborators [15]:

$$\frac{x_{ji}}{x_{ii}} = \frac{x_j}{x_i} \exp[\alpha_i(\varepsilon_{ji} - \varepsilon_{ii})/k_B T]. \quad (21)$$

Here, $\alpha_i = (\rho_{\max} - \rho_i)/\rho_{\max}$, where $\rho_i = x_i \rho$ and $\rho_{\max} \sigma_i^3 = \sqrt{2}$ [15]. However, in the present work, we used the value $\rho_{\max} = 18 \text{ mol}\cdot\text{dm}^{-3}$ for all components. With this density dependence it is clear that the LC model of equation (21) leads to non-random mixing when $\rho \rightarrow 0$, whereas random mixing arises as $\rho \rightarrow \rho_{\max}$.

From equations (18), (20) and equation (21) for a binary mixture we get:

$$x_{12} = \frac{x_1 N_{c1} \exp[\alpha_1(\varepsilon_{21} - \varepsilon_{11})/k_B T]}{N_{c2} (x_1 + x_2 \exp[\alpha_1(\varepsilon_{21} - \varepsilon_{11})/k_B T])}. \quad (22)$$

and from equations (19), (20) and (21) we get the relationship between the coordination numbers as:

$$\frac{N_{c1}}{N_{c2}} = \frac{\exp[\alpha_2(\varepsilon_{12} - \varepsilon_{22})/k_B T]}{\exp[\alpha_1(\varepsilon_{21} - \varepsilon_{11})/k_B T]} \cdot \frac{(x_1 + x_2 \exp[\alpha_1(\varepsilon_{21} - \varepsilon_{11})/k_B T])}{(x_2 + x_1 \exp[\alpha_2(\varepsilon_{12} - \varepsilon_{22})/k_B T])}. \quad (23)$$

For the coordination number we adapted the model proposed by Lee *et al.* [16]:

$$N_{c1} = \frac{Z_M \rho_1 \sigma_1^3 \exp[\alpha_1(\varepsilon_{21} - \varepsilon_{11})/k_B T]}{\sqrt{2 + \rho_1 \sigma_1^3 (\exp[\alpha_1(\varepsilon_{21} - \varepsilon_{11})/k_B T] - 1)}}. \quad (24)$$

where Z_M is the maximum lattice-site coordination number for molecules of species 1, for which we used the value $Z_M = 19$, and ρ_1 is a number density. In equations (22) to (24) ε_{ii} and σ_i are square-well energy and distance parameters. In section 3 we indicate the procedure used to obtain ε_{ii} and σ_i ; the unlike interaction parameters ε_{ij} were obtained with the combining rule $\varepsilon_{ij} = \varepsilon_{ji} = (\varepsilon_{ii} \varepsilon_{jj})^{1/2}$.

3. Results

In table 1 we report the values of the coefficients of the shape factor correlations of equations (14) to (16), which we optimised as indicated in [4]. In table 1 the coefficients

d_{ii} correspond to like interactions generated by the LC mixing rule of equation (11) so that the mixture model of equation (11) applies also to the pure-component limit. In table 2 we present the square-well energy and distance parameters obtained by fitting to experimental second virial coefficients of CH₄ [17], C₂H₆ [18], C₃H₈ [19], N₂ [20] and CO₂ [21]. In table 3 we present the values of the three binary interaction parameters fitted to the densities of the binary systems as indicated in table 3.

All derived thermodynamic properties were obtained through appropriate manipulations of equation (11). In tables 4, 5 and 6 we present deviations in calculated densities, speeds of sound and bubble pressures for binary mixtures.

The results reported in tables 4 to 6 are in good agreement with those of the generalised model for mixtures of [7]. For the intervals 270 ≤ T/K ≤ 330 K and p/MPa ≤ 12 the overall AAD in densities is 0.045, and for the intervals 250 ≤ T/K ≤ 350 K and p/MPa ≤ 30, deviations are, in general, within ±0.10 per cent. In the vicinity of the critical region, deviations in density may reach ±5 per cent. On the other hand, the AAD's in bubble pressures is within ±2 per cent for systems whose critical temperatures differ by less than 120 K, whereas for systems with critical temperatures more than 120 K apart, the AAD's are within 10 per cent. Finally, the overall average deviation in calculated vapour-phase mole fractions is 10⁻².

4. Conclusions

Given the objectives defined for this work, the results we report are satisfactory. The ECS model was determinant for the accuracy of the mixture model. However, in the highly accurate ECS model presented in [4], temperature- and density-dependent binary interaction parameters were used, whereas in this work ξ_{ij} and η_{ij} are simple constants. The introduction of the one-parameter local-composition correction enabled the model to remain accurate over wide intervals of temperature and pressure but with significantly fewer adjustable parameters. Finally, the calculations of properties other than density were truly predictive as the model was fitted only to density data.

5. List of symbols

a	Coefficient in temperature-dependent term of shape-factor correlations;
A	Helmholtz free energy; temperature-dependent term in shape-factor correlations.
b, c	Coefficients of critical-enhancement functions in shape-factor correlations.
d	binary interaction parameter in correction term to residual Helmholtz energy.
f, h	Equivalent substance reducing ratios (scaling parameters)
k_B	Boltzmann constant.
M	Molecular weight.
n	Amount of substance.
N_c	Species coordination number.
R	Universal gas constant ($R = 8.31451 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$).
T	Temperature.
x	Mole fraction.
Z	Compression factor.
Z_M	Maximum lattice-site coordination number.

Greek letters

α	Density function in local composition model.
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δ	Reduced density, ρ/ρ^c .
Δ	Distance function.
ε	Energy parameter of model intermolecular potential.
Φ	Dimensionless residual Helmholtz free energy, A^{res}/nRT .
η, ξ	Binary interaction parameters in ECS mixing rules.
θ, φ	Shape factors.
ρ	Amount-of-substance density, n/V
σ	Distance parameter of model intermolecular potential.
τ	Inverse reduced temperature, T^c/T .
ω	Acentric factor.
Ψ	Critical enhancement function.

Superscripts.

c	Critical property.
res	Residual property.

Subscripts.

0	Reference-fluid property.
i,j	Component indices.
r	Reduced property.
x	Mixture property.

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Table 1. Coefficients of shape factor correlations.

Coefficient	C ₂ H ₆	C ₃ H ₈	N ₂	CO ₂
$a_{1,1}$	0.0566294	0.0570434	-0.147682	0.0774824
$a_{1,2}$	-1.04897	-0.913233	-1.269604	-1.147428
$a_{2,1}$	-0.091546	-0.086215	-0.082961	-0.072398
$a_{2,2}$	0.1597312	0.1915019	0.2031349	0.1963194
$a_{3,1}$	0.0277851	0.0137768	0.0165218	0.0048711
$a_{3,2}$	0.1615031	0.2802471	0.3726316	0.5866264
$a_{4,1}$	0.0334163	0.0097308	0.4050661	-0.061117
$a_{4,2}$	0.5127836	0.3981214	0.6000147	0.544246
b_1	0.2616417	0.2069084	0.0248678	0.2119026
b_2	-0.882718	-0.651406	-0.304907	-0.797052
c_1	-0.163237	-0.123163	-0.005592	-0.084548
c_2	0.071371	0.1211579	15.291975	0.1332814
ω	0.0898413	0.154642	0.0373094	0.180955
d_{ii}	-0.002716	-0.001208	0.0014333	0.0

Table 2. Square-well potential parameters.

Fluid	ε / k_B (K)	σ (nm)
CH ₄	124.14	0.3406
C ₂ H ₆	231.43	0.4040
C ₃ H ₈	309.24	0.4532
N ₂	83.63	0.3322
CO ₂	340.25	0.3317

Table 3. Binary interaction parameters.

System	ξ_{ij}	η_{ij}	a_{ij}
CH ₄ + C ₂ H ₆	0.100859·10 ¹	0.101188·10 ¹	-0.347479·10 ⁻⁴
CH ₄ + C ₃ H ₈	0.100151·10 ¹	0.102527·10 ¹	0.763988·10 ⁻⁵
CH ₄ + N ₂	0.970173·10 ⁰	0.102022·10 ¹	-0.204659·10 ⁻³
CH ₄ + CO ₂	0.974014·10 ⁰	0.103609·10 ¹	0.166908·10 ⁻⁴
N ₂ + C ₂ H ₆	0.111100·10 ¹	0.104858·10 ¹	0.485732·10 ¹
N ₂ + C ₃ H ₈	0.100516·10 ¹	0.111586·10 ¹	0.238149·10 ¹
N ₂ + CO ₂	0.115994·10 ¹	0.977918·10 ⁰	0.178841·10 ¹
CO ₂ + C ₂ H ₆	0.916494·10 ⁰	0.980847·10 ⁰	0.792091·10 ⁻⁵

Table 4. Percentage absolute average deviations in calculated densities of binary mixtures.

System	References	No. points	Temp. range (K)	Max. Press. (MPa)	Comp. range, x_1	AAD
(CH ₄ + C ₂ H ₆)	22,23,24,25,26, 27,28,29,30,31	1509	91-343	36	0.19-0.96	0.11
(CH ₄ + C ₃ H ₈)	22,25,28,29,32	453	91-330	65	0.3-0.97	0.16
(CH ₄ + N ₂)	22,25,28,30,33, 34,35,36,37,38, 39,40,41,42,43	2136	82-673	507	0.10-0.98	0.12
(CH ₄ + CO ₂)	22,41,42,44,45, 46,47	709	250-673	60	0.02-0.90	0.17
(N ₂ + C ₂ H ₆)	22,25,48,49,50	929	105-478	62	0.05-0.75	0.19
(N ₂ + C ₃ H ₈)	22,25	159	100-330	12	0.02-0.95	0.03
(N ₂ + CO ₂)	22,42,44,45, 51,52,53,54	1071	209-473	100	0.02-0.90	0.30
(CO ₂ + C ₂ H ₆)	22,42,55,56,57, 58	932	245-478	69	0.10-0.99	0.11
Overall		7898	82-673	507	0.02-0.99	0.15

Table 5. Percentage absolute average deviations in calculated speeds of sound of binary mixtures.

System	References	No. points	Temp. range (K)	Max. Press. (MPa)	Comp. range, x_1	AAD
(CH ₄ + C ₂ H ₆)	59,60,61	550	200-375	20	0.34-0.95	0.21
(CH ₄ + C ₃ H ₈)	59,62	89	250-350	12	0.85-0.90	0.20
(CH ₄ + N ₂)	59,13,63	686	170-400	20	0.46-0.95	0.13
(CH ₄ + CO ₂)	59,13	324	200-450	17	0.70-0.95	0.13
(N ₂ + C ₂ H ₆)	63	102	250-400	20	0.30-0.70	0.28
(N ₂ + CO ₂)	59	65	250-350	10	0.50	0.21
Overall		1816	200-450	20	0.34-0.95	0.17

Table 6. Percentage average absolute deviations in calculated bubble-point vapour pressures of binary mixtures.

System	References	No. points	Temp. range (K)	Max. Press. (MPa)	Comp. range, x_1	AAD
(CH ₄ + C ₂ H ₆)	64,65,66,67,68	172	90-250	6.6	0.02-1.0	1.52
(CH ₄ + C ₃ H ₈)	68,69,70,71	133	111-344	9.0	0.02-1.0	3.27
(CH ₄ + N ₂)	68,72,73,74, 75,76,77,78	300	91-183	5.0	0.0-1.0	0.60
(CH ₄ + CO ₂)	79,64	29	209-271	8.5	0.01-0.64	5.83
(N ₂ + C ₂ H ₆)	80,81,73,82,64	36	111-290	13.5	0.01-0.99	5.20
(N ₂ + CO ₂)	83,84,85	44	220-298	16.7	0.0-0.48	7.31
(CO ₂ + C ₂ H ₆)	86,64,87, 88,89,90,91	343	207-298	6.6	0.02-0.99	2.15
Overall		1057	90-344	16.7	0.02-1.0	2.17