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Implementation of PC-SAFT and SAFT + Cubic for modeling thermodynamic properties of haloalkanes. II. 7 Haloethanes and their mixtures

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ABSTRACT

This study compares PC-SAFT and SAFT + Cubic in predicting various thermodynamic properties of 7 haloethanes. The correct estimation of the pure compound critical points contributes to a superior over-all robustness and reliability of SAFT + Cubic. However SAFT + Cubic is less accurate in modeling vapor pressures and isobaric heat capacities away from the critical points. Nevertheless, while being imprecise in predicting C_P and C_V separately, SAFT + Cubic establishes a more successful mutual error cancellation of these properties, both for ratio and for arithmetic average. Hence, the inaccurate estimations of heat capacities have relatively small impact on predictions of sound velocities. Considering the fact that the heat capacities in engineering equipment are somewhere between constant-volume and constant-pressure conditions, SAFT + Cubic might in fact yield reasonable estimations of the actual data. However its strongest points in comparison to PC-SAFT are the predictions of sound velocities and phase equilibria.

Mise en œuvre d'équations PC-SAFT et SAFT + Cubic pour la modélisation des propriétés thermodynamiques des haloalcanes. II. 7 haloalcanes et leurs mélanges

Mots clés : fluide ; théorie ; statistiques ; frigorigènes ; density ; vitesse du son ; capacité thermique ; équilibres de phase

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1. Introduction

The current work continues a previous study (Polishuk et al., 2012) and it is devoted to investigation of performances of PC-SAFT (Gross and Sadowski, 2001) and SAFT + Cubic (Polishuk, 2011a, b) in modeling thermodynamic properties of 7 haloethanes, namely 1,1-Dichloro-2,2,2-trifluoroethane (R123), 1,2-Dichloro-1,2,2-trifluoroethane (R123a), Pentafluoroethane (R125), 1,1,1,2-Tetrafluoroethane (R134a), 1,1-Dichloro-1-fluoroethane (R141b), 1,1,1-Trifluoroethane (R143a), 1,1-Difluoroethane (R152a), and their mixtures.

Having lower ozone depletion potentials (ODP) and global warming potentials (GWP), haloethanes have replaced halomethanes in various industrial applications (McLinden, 1990; Downing, 1988; Stoecker, 1998). The practical importance of haloethanes and their mixtures has encouraged significant amount of experimental studies and derivation of precise empirical models interpolating their thermodynamic properties (see for example Poling et al., 2008; Younglove and McLinden, 1994; Lemmon and Jacobsen, 2005; Astina and Sato, 2004; Scalabrin et al., 2006, Lemmon and Jacobsen, 2000; Outcalt and McLinden, 1996; Lemmon and Jacobsen, 2004). Numerous studies have applied Cubic Equations of State and various versions of SAFT for modeling these compounds as well (see for example Feroiu and Geana, 2002; Feroiu and Geana, 2003; Feroiu et al., 2008, Feroiu and Geana, 2011; Swaminathan and Visco, 2005a; 2005b; Galindo, et al., 1998; McCabe et al., 1998; Vilaseca et al., 2010; Mejbri and Bellagi, 2005; Monsalvo, 2006).

Following the previous study (Polishuk et al., 2012), the current one aims at including the compounds under consideration in the parameter matrixes of PC-SAFT and SAFT + Cubic and at comparing accuracy of both models in wide *PVT* range. The thermodynamic properties, such as phase equilibria, densities, sound velocities, compressibility factors and heat capacities are considered as well.

1.1. Theory

Both equations and the aspects of their implementation for modeling data of haloalkanes have been discussed previously (Gross and Sadowski, 2001; Monsalvo, 2006; Polishuk, 2011a, b; Polishuk et al., 2012) in great details. For the non-associating compounds the SAFT + Cubic EoS is given as follows:

$$A^{res} = A^{hs} + A^{disp} + A^{chain} - \frac{a}{v+c} \tag{1}$$

where A is the Helmholtz free energy, v – molar volume, a and c – parameters of the cohesive correction term. The hard-sphere contribution is given as:

$$A^{HS} = RT\frac{m}{\zeta_0}\left(\frac{3\zeta_1\zeta_2}{1-\zeta_3} + \frac{\zeta_2^3}{\zeta_3(1-\zeta_3)^2} + \left(\frac{\zeta_2^3}{\zeta_2^3} - \zeta_0\right)\ln[1-\zeta_3]\right) \times \sqrt{\frac{d^3(\zeta_3-1)}{\zeta_3\sigma^3 - d^3}} \tag{2}$$

where

$$\zeta_k = \frac{\pi N_{av}}{6v}\sum_i x_i m_{ii} d_{ii}^k \tag{3}$$

N_{Av} is the Avogadro's number, m is the effective number of segments, d is effective Lennard-Jones segment diameter, σ is Lennard-Jones temperature-independent segment diameter and:

$$d_{ii} = \sigma_{ii}\left(\frac{1+0.2977\left(k/\varepsilon\right)_{ii}T}{1+0.33163\left(k/\varepsilon\right)_{ii}T+0.0010477\left(k/\varepsilon\right)_{ii}^2T^2}\right) \tag{4}$$

ε is the inter-segment interaction's dispersion energy and k is the Boltzmann's constant.

Table 1 – Pure compound adjustable parameters of PC-SAFT EoS.

Compound	m	ε/k (K)	σ (Å)
R123[a]	3.0694	211.260	3.4493
R123a	2.7230	226.570	3.6088
R125[b]	3.1030	156.891	3.1270
R134a[b]	3.4910	164.265	2.9350
R141b	2.5330	240.896	3.5951
R143a	2.6660	173.010	3.2114
R152a[b]	2.7180	192.117	3.1010
n-phenyloctane	4.8523	287.755	4.03554

a - From Mejbri and Bellagi (2005).
b - From Monsalvo (2006).

Table 2 – Pure compound parameters of SAFT + Cubic EoS.

	Adjustable parameters		Parameters obtained solving Equations (12) and (13)		
Compound	m	c (L/mol)	a (bar-mol/L)	σ (Å)	ε/k (K)
R123	2.10000	0.269643	18.1446	4.05362	356.877
R123a	2.05000	0.305384	19.8696	4.09541	361.884
R125	1.97000	0.202395	9.52248	3.75648	261.510
R134a	1.95000	0.206792	10.8886	3.68474	288.570
R141b	1.87000	0.285443	16.2472	4.09213	371.775
R143a	1.72000	0.223397	9.74905	3.78820	261.560
R152a	1.62000	0.219220	10.2330	3.74549	289.664
n-phenyloctane[a]	2.90000	0.471254	94.3900	5.01048	564.711

a - Critical volume displacement factor 1.1.