

1998

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M. Grigante
Universita di Padova

G. Scalabrin
Universita di Padova

S. Bobbo
Istituto per la Tecnica del Freddo

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Grigante, M.; Scalabrin, G.; and Bobbo, S., "Liquid Density of Alkanes and Halogenated Alkanes Mixtures in a Corresponding States Format" (1998). *International Refrigeration and Air Conditioning Conference*. Paper 428.
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LIQUID DENSITY OF ALKANES AND HALOGENATED ALKANES MIXTURES IN A CORRESPONDING STATES FORMAT

M. Grigante, G. Scalabrin

Istituto di Fisica Tecnica, Università di Padova, via Venezia 1 - I-35131 Padova, Italy

S. Bobbo

Istituto per la Tecnica del Freddo, C.N.R., corso Stati Uniti 4 - I-35127 Padova, Italy

ABSTRACT

The Corresponding States (CS) density models for mixture proposed here, one for saturated and one for compressed liquid, are analytically similar to the pure fluid liquid density exposed in the former paper, but now with critical constants and δ_m replacing ω_m , as from the mixing rules.

The mixing rules present two adjustable interaction coefficients for each binary pair, but they are set to unity making the two models completely *predictive*: both in fact do not preliminarily require any density data for the mixture of interest. To improve the prediction accuracy a *correlative* mode is here proposed in which the δ_m parameter is substituted with a $\delta_m(x)$ function which parameters are regressed from saturated liquid data, when available, for the binary mixture of interest.

The two models are validated with mixtures experimental data for the families of alkanes and hydrofluoroalkanes (HFC) and the prediction accuracy obtained is significantly better with respect to the existing predictive liquid density models for mixtures. The result is particularly useful for the studies about the new generation refrigerants applications.

INTRODUCTION

The prediction of thermodynamic properties of pure fluids and mixtures through accurate models is essential for the study and design of refrigeration components and systems. The need for these models is greatly increased in the last times particularly for alkanes and halogenated alkanes mixtures due to their interest as new generation refrigerants.

In the present work a three parameters CS model is proposed for the saturated and compressed liquid density prediction of alkanes and HFC mixtures. For both these two families of fluids a conformality has been formerly ascertained by the Authors, as it is required in a CS domain modelling.

DENSITY MODEL

Mixture Models

The density of a saturated liquid mixture is represented through a model which structure is similar to that used for the pure fluids [1]:

$$\log \rho_{r,sl}(T_r, \delta) = \log \rho_{r,sl}^{(c1)}(T_r) + \frac{\delta_m}{\delta_r} \left[\log \rho_{r,sl}^{(c2)}(T_r) - \log \rho_{r,sl}^{(c1)}(T_r) \right] \quad (1)$$

In this equation with c1 and c2 are indicated the mixture components and their reduced saturated liquid densities $\rho_{r,sl}$ are obtained from the pure fluid model formerly proposed in [1]. In eq. (1) δ and δ_r are both obtained from the definition of δ , already utilized in the same pure fluids density models:

$$\delta = -\log_{10} \left[\frac{(\rho_r^S)_i}{(\rho_r^S)_j} \right]_{T_r=0.8} \quad (2)$$

with δ_r assuming the same value as for the pure fluid model, while for δ_m a suitable mixing rule has to be introduced which combines the δ_i values of the pure components as function of composition.

For a compressed liquid mixture the proposed model is similarly :

$$\log \rho_{r,l}(T_r, P_r, \delta) = \log \rho_{r,l}^{(c1)}(T_r, P_r) + \frac{\delta_m}{\delta_r} \left[\log \rho_{r,l}^{(c2)}(T_r, P_r) - \log \rho_{r,l}^{(c1)}(T_r, P_r) \right] \quad (3)$$

The same considerations are here retained for δ_m and δ_r as for the former eq. (1). In this case too the reduced compressed liquid densities $\rho_{r,l}$ for c1 and c2 are obtained from the pure fluid model [1]. In this way from the saturated liquid and compressed liquid dedicated equations of only two reference fluids of a conformal family the liquid density of any mixture of the family can be predicted.

Mixing Rules

Similarly to the *one-fluid-model* technique utilized to extend a pure fluid EoS to a mixture, the density models for pure fluids presented formerly can be extended to mixtures utilizing a *one-fluid-model* with the same mixing rules proposed for the mixture thermodynamic behaviour representation. The classical method, common to the corresponding states techniques, of modifying the critical properties of the pure fluids through suitable mixing rules and introducing these pseudo critical properties of the mixture into the pure fluid model, is here utilized for the pseudo critical temperature and pressure, making them dependent from composition.

The mixture model is once more represented by the equations (1) and (3), but now with the critical constants turned into the mixture pseudocritical constants obtained from the following mixing rules[2,3]:

$$\delta_m (T_{cm} / P_{cm})^{2/3} = \sum_i \sum_j x_i x_j \delta_{ij} (T_{cij} / P_{cij})^{2/3} \quad (4)$$

$$T_{cm} / P_{cm} = \sum_i \sum_j x_i x_j T_{cij} / P_{cij} \quad (5)$$

$$T_{cm}^2 / P_{cm} = \sum_i \sum_j x_i x_j T_{cij}^2 / P_{cij} \quad (6)$$

$$T_{cij} = \varepsilon_{ij} (T_{ci} T_{cj})^{1/2} \quad (7)$$

$$P_{cij} = 8T_{cij} / \left\{ \eta_{ij} \left[(T_{ci} / P_{ci})^{1/3} + (T_{cj} / P_{cj})^{1/3} \right]^3 \right\} \quad (8)$$

$$\delta_{ij} = (\delta_i + \delta_j) / 2 \quad (9)$$

The proposed mixing rules present the two adjustable interaction coefficients ε_{ij} and η_{ij} for each binary pair, which have to be regressed over some sets of density data for the mixture of interest. In this case the mixing rule is *correlative*. Setting those coefficients to 1 makes the mixing rule completely *predictive*. In the present work only the *predictive* mode was utilized for the mixing rule.

It was furthermore observed that the prediction accuracy of the models, both for saturated and compressed liquid mixtures, is much more sensible to δ_m than to any one of the two pseudocritical parameters P_{cm} and T_{cm} . In case of a *correlative* mode for the mixing rule the following procedure is then proposed. The two eqs. (4) and (9), through which the δ_m value is obtained, are omitted and a local δ_m value is generated for each saturated liquid density point of an experimental data set for the mixture of interest. The locally generated δ_m values are then correlated only as function of their composition dependence, obtaining the mixture *ij* specific function for $\delta_m(x)$:

$$[\delta_m = \delta_m(x)]_{ij} \quad (10)$$

For the mixtures studied a suitable analytic form of this function was found to be:

$$[\delta_m]_{ij} = a + bx + cx^2 + dx^3 \quad (11)$$

In Table X the equation coefficients are reported for three mixtures together with the references from which the data utilized for the coefficients regression were obtained.

Table X: Equation (11) coefficients and data sources for three mixtures.

	R22-R142b	R22-R152a	R32-R134a
a	-3.87506481	+0.05767926	+0.04490487
b	-0.58329812	-0.04837927	+0.00019852
c	+0.23641053	+0.03517521	+0.03862046
d	-	-0.02702388	-
Ref.	[4]	[5]	[6]

It is evident that the predictive mode is typical of a mixture for which no saturated liquid density data are available, while the correlative mode may be assumed in the opposite condition.

MODELS VALIDATION

Saturated Liquid

A model validation is here proposed for saturated liquid densities of alkanes and HFC mixtures and against the conventional model of Hankinson, Brobst and Thomson (HBT) [7].

In Figures from 1 to 3 three binary systems of alkanes are considered with results always favourable for the present model. The data are plotted as function of composition and no evident variation of the error deviation with composition is noticed. Moving from nonpolar to the polar systems, composed of halogenated alkanes, the error deviation of the proposed model slightly decreases, but it is still better than that obtained from the HBT model. If the tuning function $\delta_m(x)$ is furthermore utilized the model performance improves reaching results similar to those of the predictive model for alkanes. In fact the tuning function in the present work is only used for the halogenated refrigerants. The prediction error deviations for the systems R22/R142b, R22/152a and R32/134a are shown in Figures from 4 to 6. It is evident the effectiveness of the mixing rule modification through the tuning function $\delta_m(x)$.

Compressed Liquid

In Figs. from 7 to 8 the compressed liquid density model is tested for alkanes mixtures. Here also the HBT model is assumed for comparison. The two alkanes mixtures ethane/propane and propane/n-butane are examined with results similar to those verified formerly [1] for the same pure components: no effect of accuracy decrease is observed, neither as function of composition nor as function of pressure.

In Figs. from 9 to 12 the validation is presented for the halogenated refrigerant mixtures. Fig. 9 indicates that the model in predictive mode reaches good results with respect to the HBT mixture model, practically without taking account of the pressure effect. Very satisfactory results are obtained with the introduction of the same tuning function $\delta_m(x)$ previously introduced for saturated liquid conditions. This is evident from Figs. 10 and 11 for the mixtures R22/R142b and R32/R134a.

The Fig. 12 presents a case where the $\delta_m(x)$ function cannot be obtained, because saturated liquid density data were not found. Also the HBT model fails for this system due to the erroneous prediction of the pseudocritical properties; in fact the data are quite close to the mixture critical locus, where the HBT mixing rules become unreliable. However the proposed model in predictive mode give very interesting results.

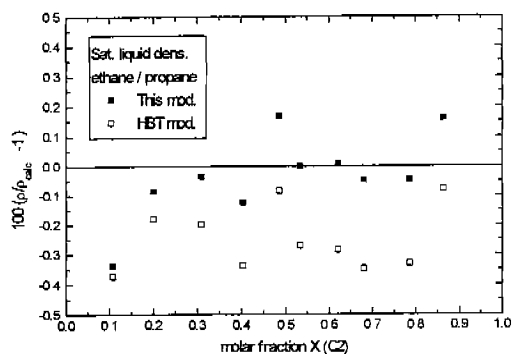


Fig. 1. Saturated liquid density percent deviation of mixture ethane/propane for the proposed and the HBT models; data from [8].

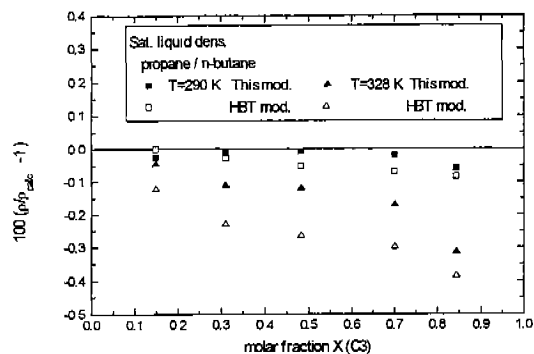


Fig. 2. Saturated liquid density percent deviation of mixture propane/n-butane for the proposed and the HBT models; data from [8].

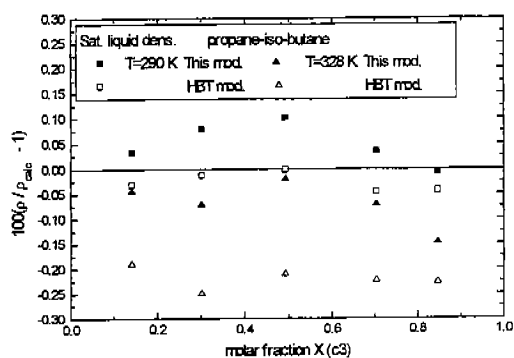


Fig. 3. Saturated liquid density percent deviation of mixture propane/iso-butane for the proposed and the HBT models; data from [8].

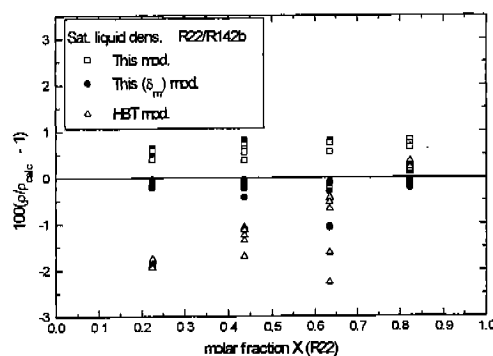


Fig. 4. Saturated liquid density percent deviation of mixture R22/R142b for the proposed model, without and with the tuning function $\delta_m(x)$, and for the HBT model; data from [4].

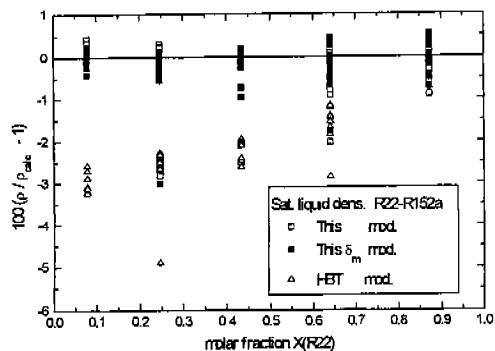


Fig. 5. Saturated liquid density percent deviation of mixture R22/R152a for the proposed model, without and with the tuning function $\delta_m(x)$, and the HBT model; data from [5].

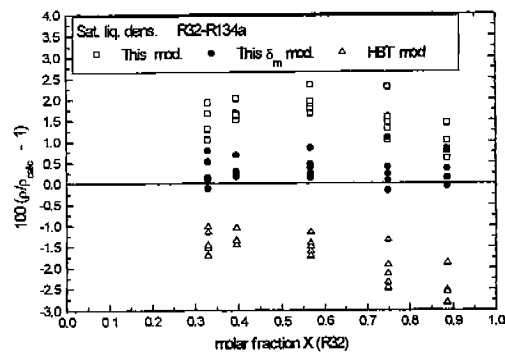


Fig. 6. Saturated liquid density percent deviation of mixture R32/R134a for the proposed model, without and with the tuning function $\delta_m(x)$, and the HBT model; data from [6].

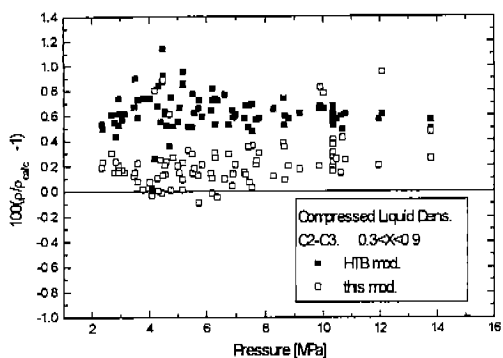


Fig. 7. Compressed liquid density percent deviation of mixture ethane/propane for the proposed model and the HBT model; data from [9].

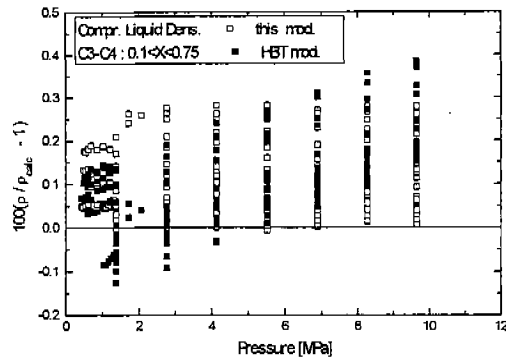


Fig. 8. Compressed liquid density percent deviation of mixture propane/n-butane for the proposed model and the HBT model; data from [10].

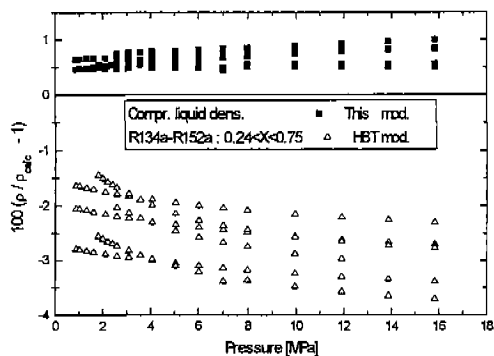


Fig. 9. Compressed liquid density percent deviation of mixture R134a/R152a for the proposed model and the HBT model; data from [11].

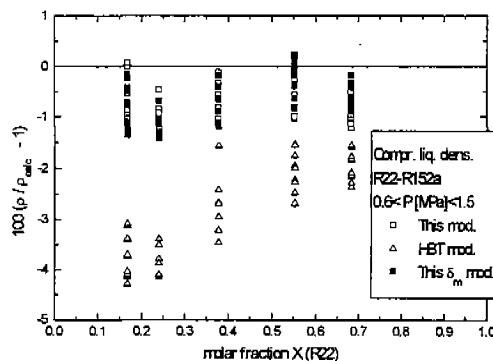


Fig. 10. Compressed liquid density percent deviation of mixture R22/R152a for the proposed model, without and with the tuning function $\delta_m(x)$, and the HBT model; data from [12].

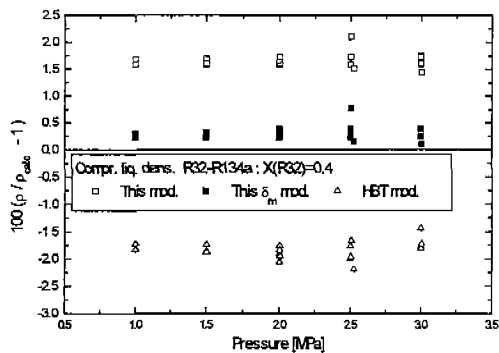


Fig. 11. Compressed liquid density percent deviation of mixture R32/R134a for the proposed model, without and with the tuning function $\delta_m(x)$, and the HBT model; data from [6].

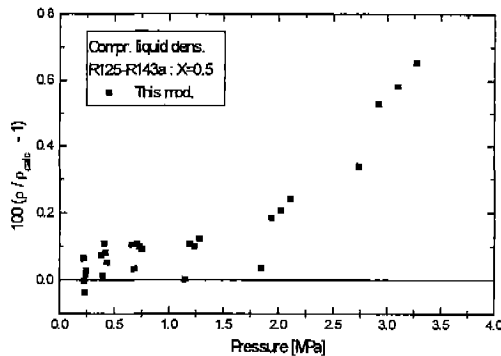


Fig. 12. Compressed liquid density percent deviation of mixture R125/R143a for the proposed model; data from [13].

CONCLUSIONS

The proposed model demonstrates to perform effectively in predictive mode for alkanes and particularly in correlative mode for halogenated alkanes. The introduction of the tuning function into the mixing rules allows to reach an accuracy level comparable with those of the pure fluids density models formerly exposed. The model is quite simple and is particularly suitable to be used also for new refrigerant mixtures coming out. The kind of experimental data needed for the tuning function are easily available and their required amount, sufficient for a positive result of the model, can be quite limited.

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