

Prediction of thermophysical properties of alternative refrigerants by computational chemistry

Oliver Milocco, Maurizio Fermeglia*, Sabrina Prici

*Department of Chemical, Environmental and Raw Materials Engineering—DICAMP,
University of Trieste, Piazzale Europa 1, I-34127 Trieste, Italy*

Abstract

This paper presents two alternative procedures based on quantum/conductor-like screening model (COSMO) calculations and on molecular mechanics/dynamics simulations, respectively for estimating the PHSCT equation of state (EOS) parameters and to predict vapor–liquid equilibria (VLE) behavior for pure, alternative refrigerants, as well as for their binary mixtures. The quality of the predictions achieved with both method proposed, in conjunction with the confined computational time aspects involved, can be considered satisfactory, so that these strategies can be judged as promising routes toward an on-line coupling between molecular and process simulation. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Equation of state; Alternative refrigerants; Vapor–liquid equilibria; COSMO calculations; Density functional theory; Molecular dynamics

1. Introduction

The year 2000 has ratified the banning of ozone-damaging substances such as fully chlorinated hydrocarbons used as working fluids in existing refrigeration units. As a consequence, this action has uncovered new horizons for research activity in the field, looking for new alternatives. It is well known that only a few existing pure fluids can ensure performances equal or at least comparable to those of the banned substances; therefore, the main search for substitute refrigerants will be devoted to mixtures. Azeotropic mixtures, used so far as alternatives to pure components, do not possess the required flexibility to exhibit thermophysical properties at least close to those of banned substances. For this reason, zeotropic mixtures are now considered as alternative refrigerant fluids but, for these mixtures, the availability of a predictive tool for the calculation of phase equilibria is of paramount importance in the selection of the correct process fluids. However, the number of potentially useful mixtures is huge, and it would be extremely uneconomical, if not even inconceivable, to evaluate experimentally the thermodynamic properties of all possible alternatives.

* Corresponding author. Tel.: +39-40-6763438; fax: +39-40-569823.
E-mail address: mauf@dicamp.univ.trieste.it (M. Fermeglia).

In previous papers [1–4], we have shown how, from computer experiments, it is possible to extract the characteristic parameters of some equation of state (EOS), thus, reducing the experimental efforts necessary to characterize the vapor–liquid equilibria (VLE) behavior of pure components and, particularly, of mixtures.

In this work, we propose two alternative procedures to derive the PHSCCT EOS parameters A^* , V^* and E^* characteristic of the reformulation of the original EOS by Fermeglia et al. [5,6] for a series of 10 alternative refrigerants, and the corresponding binary interaction parameter k_{ij} in the case of 9 relative binary mixtures by computational chemistry. The first method is based on the description of the solvation phenomena at a molecular level using the conductor-like screening model for real solvents (COSMO-RS) [7]. The second procedure is the natural extension of a method proposed in our previous works, and is essentially based on molecular mechanics/dynamics experiments [1,3].

The two methods presented in this paper can be schematically summarized as follows:

Method 1: DMol³/COSMO-RS calculations can be used to predict the activity coefficients (and, hence, directly VLE), and to obtain the PHSCCT EOS parameters A^* and V^* for each pure component; the third PHSCCT EOS parameter E^* for the pure components can be found by fitting one single relevant experimental vapor pressure value. Finally, the binary interaction parameters k_{ij} of the EOS can be obtained from the activity coefficients found for each binary mixture.

Method 2: In this case, A^* and V^* can be calculated using MM/QM techniques [1]. E^* can be found by MD simulations in the gas state. The parameters k_{ij} are in this case found by performing NPT simulations of equimolar mixtures of each binary in the gas state. However, in this work, A^* and V^* were set equal to those obtained by method 1.

2. Computer simulation methodology

Molecular modeling, dynamics simulations and quantum calculations were performed on a Silicon Graphics Origin 200 using the commercial software Cerius² (Version 4.2) from Molecular Simulation Inc. (for both MM/QM and MD simulations) and in-house developed computer programs (stand-alone and add-on to the commercial package). Accurate molecular models of each refrigerant were obtained via MM using the COMPASS98 force field (FF) which is the first ab initio FF that has been parameterized and validated using condensed-phase properties in addition to various ab initio and empirical data for molecules in isolation [8]. The details of this procedure are given elsewhere [1,3].

The gas-phase reference energies for all the structures of the data sets were obtained from non-local DFT VWN-BP gas-phase optimization applying the DNP basis (Version 4.0.0) of DMol³ as implemented in the Quantum 1 platform of Cerius², and a real space cut-off = 5.50 Å. All structures were then re-optimized in a continuum conductor (i.e. with DMol³/COSMO and $f(\epsilon) = 1$, using a number of segments = 92). The values of the area and volume of the dielectric cavity in which the solute molecule is embedded can be extracted directly from the corresponding COSMO files. Finally, the phase equilibrium properties of each binary mixture considered, necessary for the determination of the EOS parameters according to the procedure reported above, were obtained again from the COSMO files generated by DFT calculations using the new software COSMOtherm from COSMOlogic (Version C1.0, Leverkusen, Germany).

For the calculations of the PHSCCT EOS pure component parameter E^* by method 2—path (b), 256 total molecules were confined in a cubic box with periodic boundary conditions, and NPT MD simulations

were run at $T = 800$ K, under the same conditions reported in details in [1,3]. To obtain the value of the binary interaction parameter k_{ij} , the same simulation conditions were applied on the corresponding equimolecular binary mixtures [4,9].

3. Results and discussion

3.1. Method 1—direct VLE prediction for pure components

On average, the application of these calculations to the direct prediction of VLE for pure components yields acceptable results: the average root mean square deviation (RMSD) between prediction and experiment on the entire data set of 10 compounds is about 10%. The worst prediction is obtained for R290 (propane), for which RMSD is about 35%, but this is an expected result, due to the intrinsic incapacity of COSMO-RS to describe poorly polarizable molecules such as alkanes. A graphical example of the direct VLE prediction for pure components obtained from the application of quantum-mechanical calculations by DMol³/COSMO-RS is reported in Fig. 1.

3.2. Comparison between methods 1 and 2 for pure components

The results for the VLE prediction obtained using the PHSCT EOS parameter values estimated by the two procedures described above as methods 1 and 2, and reported in Table 1, are compared in Table 2. Table 2 also reports the quality of the prediction achieved with the EOS parameters obtained from data fitting. From an inspection of these tables we can conclude that the two sets of E^* values obtained from the two methods are not very different, and that both methods give reasonable and comparable results. In particular, the method based on MD simulation yields better predictions, especially if we consider that no recourse to experimental information was made to calculate the EOS parameters. Accordingly, method 2 can be considered as a “pure prediction” method. The better prediction achieved with the E^* value obtained by method 2 can be easily justified considering the high sensitivity of the PHSCT EOS to the value of the energetic parameter.

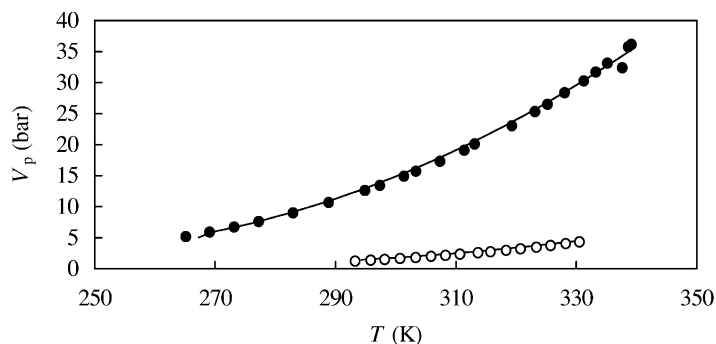


Fig. 1. Comparison between vapor pressure values predicted with COSMO-RS based calculations (solid lines) and experimental (symbols) for R125 (filled circles) and R32 (open circles).

Table 1
Estimated PHSCT EOS parameters (for explanations, see text)

Refrigerant	A^* (10^{-9} cm ² /mol)	V^* (cm ³ /mol)	E^* method 1 (bar dm ³ /mol)	E^* method 2 (bar dm ³ /mol)
R32	4.42	29.7	33.18	33.50
R125	9.26	41.8	61.10	61.13
R245	7.82	46.9	56.65	56.49
R290	4.72	27.0	41.10	40.40
CF ₃ SCF ₃	8.39	48.9	51.19	51.00
E218	9.62	55.9	53.21	52.98
RE170	5.38	17.8	76.43	75.40
R236ea	8.21	32.3	85.04	85.56
R236fa	8.05	31.7	82.01	82.60
R134	6.37	39.6	43.69	43.70

3.3. Comparison between methods 1 and 2 for mixtures

The application of COSMO-based calculations to the direct prediction of the VLE of the nine binary mixtures at all temperature considered shows that, on average, the RMSD between real and virtual experiment is about 5%. Nonetheless, to gain such quality of prediction by using COSMOtherm, the knowledge of the experimental vapor pressure for pure components is necessary. Fig. 2 shows, as an example, the graphical comparison between experimental and virtual data for the binary mixture R125–R236ea at three different temperatures.

The comparison of the results on VLE prediction for a selection of mixtures considered obtained with the PHSCT EOS parameters evaluated by methods 1 and 2, and reported in Table 3, are shown in Table 4. Once again, the inspection of this table allows us to conclude that both methods can be used to predict with an acceptable degree of accuracy the VLE behavior of binary mixtures, with the only remarkable exception of the systems containing R290 (i.e. propane).

Table 2
Comparison of the VLE prediction with PHSCT EOS parameters obtained by data fitting (second column), method 1 (third column) and method 2 (fourth column)

Refrigerant	RMSD V_p	RMSD V_p method 1	RMSD V_p method 2
R32	0.095	5.9	3.2
R125	0.42	0.64	0.5
R245	0.21	2.7	1.7
R290	2.4	17	9.2
CF ₃ SCF ₃	0.40	3.7	2.6
E218	0.79	3.2	2.5
RE170	1.5	18	9.7
R236ea	0.29	6.6	4.5
R236fa	0.029	7.5	5.2
R134	0.046	1.8	1.2

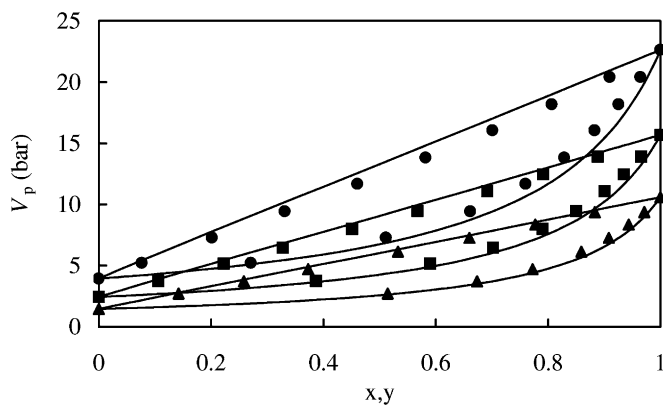


Fig. 2. Comparison between experimental (symbols) and COSMO-RS predicted VLE (solid lines) for the binary mixture R125–R236ea at different temperatures: $T = 288$ K (triangles), $T = 303.2$ K (squares) and $T = 318$ K (circles).

Table 3

Estimated binary interaction parameters for mixtures (for explanations, see text)

Mixture	T (K)	k_{ij} method 1	k_{ij} method 2
R32–R134a	293	0.0013	0.033
	343	0.089	0.10
R32–R236ea	288	0.10	0.11
	303	0.11	0.12
	318	0.12	0.13
R32–R236fa	303	0.12	0.13
	323	0.12	0.14
R125–R134a	283	0.040	0.041
R125–R236ea	288	–0.027	–0.025
	303	–0.034	–0.031
	318	–0.038	–0.034
R125–R236fa	303	–0.036	–0.031
	323	–0.042	–0.036
R125–R245	298	0.021	0.021
	313	0.022	0.021
R290–R236fa	283	0.14	0.12
	303	0.13	0.11
	323	0.095	0.081
R290–R245	298	0.096	0.076

Table 4

Comparison of the VLE prediction with PHSCT EOS parameters obtained by method 1 (third and fourth columns) and method 2 (fifth and sixth columns)

Mixture	T (K)	RMSD V_p method 1	RMSD Y method 1	RMSD V_p method 2	RMSD Y method 2
R32–R134a	293	3.7	0.043	5.8	0.044
	343	7.8	0.055	8.8	0.057
R32–R236ea	288	2.3	0.011	4.4	0.029
	303	5.4	0.003	6.4	0.012
	318	7.9	0.009	9.2	0.010
R32–R236fa	303	5.6	0.003	6.7	0.014
	323	8.6	0.010	9.4	0.010
R125–R134a	283	0.82	0.014	0.80	0.014
R125–R236ea	288	0.66	0.009	1.6	0.020
	303	1.1	0.009	0.51	0.007
	318	2.7	0.015	1.6	0.005
R125–R236fa	303	1.3	0.009	0.52	0.009
	323	3.6	0.018	2.1	0.006
R125–R245	298	0.72	0.006	0.81	0.005
	313	1.3	0.010	1.1	0.007
R290–R236fa	283	1.7	0.011	8.8	0.03
	303	3.1	0.018	8.7	0.034
	323	7.5	0.047	12	0.051
R290–R245	298	5.0	0.016	13	0.029
	313	17	0.10	20	0.097

4. Conclusions

This paper reports the results obtained with two, alternative procedures for estimating EOS parameters from computer experiments. Both methods proposed give good results, are relatively inexpensive, absolutely general and can be applied in principle to any EOS, provided the parameters have a well defined physical meaning. With respect to the quantum-based calculations, the molecular mechanics/molecular dynamics method offers the following advantages: (a) it works well also for weakly polarizable molecules such as alkanes and (b) it does not require any experimental information. The overall quality of the results obtained, both in terms of VLE prediction capabilities and computational time aspects involved, allow us to conclude that a bridging between molecular and process simulation is now possible, also for mixture calculations, through the direct determination of the parameters of a physically based EOS model, and will be implemented in the next future, provided better EOS, improved intermolecular potentials and faster quantum-mechanical methods be available.

References

- [1] M. Fermeiglia, S. Pricl, *Fluid Phase Equilib.* 166 (1999) 21.
- [2] M. Fermeiglia, S. Pricl, *AIChE J.* 45 (1999) 2619.

- [3] F. Belloni, M. Fermeglia, S. Pricl, *Mol. Simulation* 25 (2000) 53.
- [4] M. Fermeglia, S. Pricl, A. Klamt, in: *Proceedings of the 1st International Conference Foundations of Molecular Modeling and Simulations*, Keystone Resort, CO, USA, 2000, p. A20.1.
- [5] M. Fermeglia, A. Bertucco, D. Patrizio, *Chem. Eng. Sci.* 52 (1997) 1517.
- [6] M. Fermeglia, A. Bertucco, S. Bruni, *Chem. Eng. Sci.* 53 (1998) 3117.
- [7] A. Klamt, G. Schüürmann, *J. Chem. Soc., Perkin Trans. 2* (1993) 799.
- [8] H.J. Sun, *J. Phys. Chem.* 102 (1998) 7338.
- [9] M. Fermeglia, S. Pricl, *AIChE J.* 47 (2001) 2371.