REFRIGERATION CYCLE DESIGN FOR REFRIGERANT MIXTURES BY MOLECULAR SIMULATION

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Dedicated to Professor Ivo Nezbeda on the occasion of his 65th birthday.

We describe a molecular simulation methodology to calculate the properties of a vapor-compression refrigeration cycle and its Coefficient of Performance, in the case when the refrigerant is a mixture. The methodology requires only a molecular force-field model for each refrigerant pure component and, for improved accuracy, an expression for the vapor pressure of each pure component as a function of temperature. Both may be constructed by means of theoretical approaches in combination with minimal amounts of experimental data, and the latter may also be estimated by empirical formulae with reasonable accuracy. The approach involves a combination of several available molecular-level computer simulation techniques for the individual processes of the cycle. This work extends our earlier study to cases when the refrigerant is a pure fluid. The mixture refrigerant simulations entail the calculation of bubble- and dew-point curves for the refrigerant mixtures, and we propose a new approach for dew-point calculations via molecular simulation. We compare results for a test case with those obtained from the Equation-of-State model used in the standard REFPROP software and with experimental data for a commercially available refrigerant mixture of R32 (CH_2F_2) and R143a (CH_2FCF_3).

Keywords: Refrigerants; Molecular simulations; Vapor–liquid equilibrium; Dew point; Refrigeration cycle; Thermodynamics.

The design of refrigeration systems is typically performed using calculations based on thermodynamic models for the working fluid, such as those incorporated within the REFPROP software package[1]. The models are typically

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based on fitting experimental data to empirical multiparameter expressions. Their accuracy depends on the availability of sufficient experimental data, which are typically expensive and time-consuming to obtain. They are generally less accurate in the case of mixtures, due to the requirement for empirically-based intercomponent combining rules for the model parameters. The design of refrigeration systems involving newly proposed working fluids for which experimental data are unavailable, especially in the case of mixtures, for which a design parameter is the mixture composition, may be particularly problematic.

We describe a molecular simulation methodology that may be used to calculate the properties of a Vapor-Compression Refrigeration Cycle (VCRC) and its Coefficient of Performance (COP) that requires a minimal amount of experimental data. The methodology requires a molecular force-field model for each refrigerant pure component and expressions for the vapor pressure of each pure component as a function of temperature. Both may be constructed by means of theoretical approaches in combination with minimal amounts of experimental data, and the latter may often be estimated by empirical formulae with reasonable accuracy. The latter requirement is not strictly necessary, but improves the accuracy of the approach proposed here. Our approach involves a combination of several available computer simulation techniques for the individual processes of the cycle. The basic methodology was recently proposed and tested for pure-fluid refrigerants[2], and is herein extended to the case of mixtures; it incorporates the Reaction Gibbs Ensemble Monte Carlo (RGEMC) method[3], an accurate methodology for the simulation of the vapor–liquid equilibrium properties of mixtures, that requires only the standard combining rules for the inter-component parameters of the force fields. In order to demonstrate the approach, we compare the results with those obtained from REFPROP and from experiment for a VCRC involving the commercially available binary refrigerant R32/R134a.

THEORY

The Vapor-Compression Refrigeration Cycle

The VCRC may be conveniently illustrated using a pressure–enthalpy (P–h) diagram (Fig. 1). In this diagram, three of the four processes appear as straight lines, and the heat transfers in the condenser (at P_{high}) and the evaporator (at P_{low}) are equal to the lengths of the corresponding horizontal lines.

The thermodynamic efficiency of a VCRC is measured by its COP, defined by:

$$\mathrm{COP} = \frac{Q_{\mathrm{low}}}{W_{\mathrm{C}}} \tag{1}$$

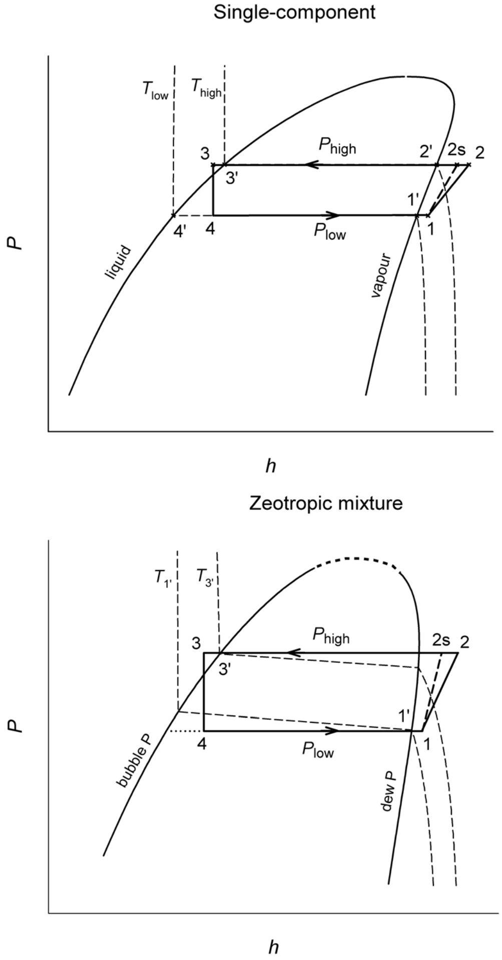

FIG. 1
The *P*–*h* diagram and VCRC diagrams for a pure refrigerant working fluid (left) and for a zeotropic mixture (right). The numbers indicate the state points of cycle, and primes indicate points on the vapor–liquid saturation curve of the refrigerant: the 1–2 process is compression, 2–3 is condensation, 3–4 is expansion, and 4–1 is evaporation (1′–1 is the superheating of vapor and 3′–3 subcooling of liquid). The points 2s, connected to points 1 by dashed lines, denote an ideal isentropic compression

where Q_{low} is the heat absorbed during the evaporation per mole of working fluid, and W_C is the work done by the compressor per mole of working fluid. These can be determined from the enthalpies at the state points in Fig. 1, yielding:

$$\mathrm{COP} = \frac{h_1 - h_4}{h_2 - h_1} . \tag{2}$$

Molecular Simulation of a VCRC for a Binary Refrigerant Mixture

We have previously described[2] our methodology for predicting the properties of a VCRC in the case of pure-fluid refrigerants. This entails a combination of RGEMC phase equilibrium calculations[3], constant pressure–constant temperature (*NPT*) Monte Carlo simulations[4], and isentropic simulations[5]. The approach must be modified in the case of mixtures. In Fig. 1, for a pure fluid the vapor–liquid equilibrium isotherms are horizontal, whereas in the case of a mixture they are at a negative angular displacement. The fundamental difference in the P–h diagrams is that for a pure fluid the vapor–liquid equilibrium and dew-point/bubble-point curves coincide, whereas for a mixture the vapor–liquid equilibria are described by surfaces in P–T–composition space, and only the dew-point and bubble-point curves are relevant.

To simulate a VCRC for a refrigerant mixture, we take as specified the evaporation and condensation temperatures (T_{low} and T_{high}), the superheating and subcooling temperature increments (ΔT_{sh} and ΔT_{sc}), and the compressor adiabatic efficiency (ω). The simulation involves the following calculations:

1. Obtain the dew point (1′) at $T_{1'} = T_{low}$ (see discussion of methodology below) to obtain P_{low} and $h_{1'}$.
2. Perform an *NPT* Monte Carlo simulation (*1*) at P_{low} and $T_1 = T_{1'} + \Delta T_{sh}$ to determine h_1, μ_1, and the molar entropy s_1.
3. Obtain the bubble point (3′) at $T_{3'} = T_{high}$ by means of a pseudo-GEMC simulation method[6], obtaining P_{high} and $h_{3'}$.
4. Perform an *NPT* simulation (*3*) at P_{high} and $T_3 = T_{3'} - \Delta T_{sc}$ to determine h_3.
5. Perform an isentropic simulation at P_1, $S_{2s} = S_1$ to obtain T_2 and h_{2s}.
6. Calculate h_2 from the compressor's adiabatic efficiency, $h_2 = h_1 + \dfrac{h_{2s} - h_1}{\omega}$
7. Calculate the COP from Eq. (*2*).

Bubble points were calculated by the method of Ungerer et al.[6] The analogous approach does not converge for dew points, which were calculated by two different methods. The first is the Gibbs–Duhem integration (GDI) method for a binary mixture developed by Kofke[7] and later extended to the calculation of dew and bubble points of multicomponent mixtures by Escobedo[8].

In the second method, we calculated dew points by solving the nonlinear equation

$$y_i(T,P) = y_i^* \tag{3}$$

where y_i^* is the specified mole fraction of the vapor. We solved the above equation for P at a specified T using the Newton–Raphson method:

$$P_{n+1} = P_n - \frac{y_{i,n} - y_i^*}{\left(\frac{\partial y_i}{\partial P}\right)_{\sigma,n}} \tag{4}$$

where n denotes the iteration number. This requires calculation of a sequence of RGEMC simulations at different pressures and calculation of the derivatives $(\partial y_i/\partial P)_\sigma$ along the vapor–liquid coexistence curve.

To obtain $(\partial y_i/\partial P)_\sigma$, we first use the Gibbs–Duhem equations for each phase in a multicomponent mixture of m components:

$$\mathrm{d}P^{\mathrm{V}} = -u^{\mathrm{V}}\,\mathrm{d}\beta^{\mathrm{V}} + \sum_{j=1}^{m} \rho_j^{\mathrm{V}}\,\mathrm{d}\nu_j^{\mathrm{V}} \tag{5}$$

$$\mathrm{d}P^{\mathrm{L}} = -u^{\mathrm{L}}\,\mathrm{d}\beta^{\mathrm{L}} + \sum_{j=1}^{m} \rho_j^{\mathrm{L}}\,\mathrm{d}\nu_j^{\mathrm{L}} \tag{6}$$

where V and L denote vapor and liquid, respectively, $\rho_i = N_i/V$, N_i is the number of particles of species i, $\beta = 1/(k_{\mathrm{B}}T)$, k_{B} is Boltzmann constant, $p = \beta P$, $u = U/V$, $\nu_j = \beta\mu_j$, and μ_j is the chemical potential of component j. Finally, we express the total differentials of the vapor compositions y_i in terms of the independent variables β and $\{\nu_j\}$:

$$\mathrm{d}y_i = \left(\frac{\partial y_i}{\partial \beta}\right)_{\{\nu_k\}}^{\mathrm{V}} \mathrm{d}\beta^{\mathrm{V}} + \sum_{j=1}^{m} \left(\frac{\partial y_i}{\partial \nu_j}\right)_{\beta,\nu_{k,k\neq j}}^{\mathrm{V}} \mathrm{d}\nu_j^{\mathrm{V}}\ ; \quad i = 1, 2, \ldots, m. \tag{7}$$

In general, the working equations to be solved depend on the input data. In the case of a dew-point pressure calculation, the temperature and the composition of the vapor phase are specified. Setting $d\beta^V = d\beta^L = 0$, $dp^V = dp^L$, $d\nu_i^V = d\nu_i^L$, and using the covariances[8,10]:

$$\left(\frac{\partial y_i}{\partial \nu_j}\right)_V \equiv \gamma(y_i, N_j^V) = \langle y_i, N_j^V \rangle - \langle y_i \rangle \langle N_j^V \rangle \tag{8}$$

we obtain, for a binary mixture:

$$\left(\frac{\partial y_1}{\partial p}\right)_\sigma = \frac{\gamma(y_1, N_1^V) N_1^V (\rho_2^V - \rho_2^L) + \gamma(y_1^V, N_2^V)(\rho_1^L - \rho_1^V)}{k_B T(\rho_2^V \rho_1^L - \rho_1^V \rho_2^L)} \tag{9}$$

where the density, number of particles and covariances for component i are calculated for the liquid (L) and vapor (V) phases independently by GEMC at the given T and chemical potentials μ_i, $i = 1, 2$.

Molecular Model

To validate our approach, we illustrate the methodology for the refrigerant mixture of R32 (CH_2F_2) and R134a (CH_2FCF_3). Several force-field models are available for the pure components[9,11]. We used the force fields of Stoll et al.[11], in which the components are modeled by dipolar two-center Lennard–Jones (2CLJD) potentials with two interaction centers a distance L apart, and a point dipole D in the center of the molecule. The force-field parameters were obtained by fitting to experimental vapor–liquid equilibria. We used the standard Lorentz–Berthelot rules in our implementation of the RGEMC method[3].

RESULTS AND DISCUSSION

We first tested the ability of our molecular model to capture the phase equilibrium behavior of the binary mixture of R32 and R134a over its entire composition range. Figure 2 shows vapour–liquid equilibrium (VLE) P–x–y curves at two temperatures, in comparison with sets of experimental data from two research groups[12,13]. Our results were obtained by performing NPT RGEMC simulations[3] incorporating pure-fluid vapour pressures obtained from REFPROP[1]. Both the REFPROP and the simulation results appear to give reasonable agreement with the experimental results.

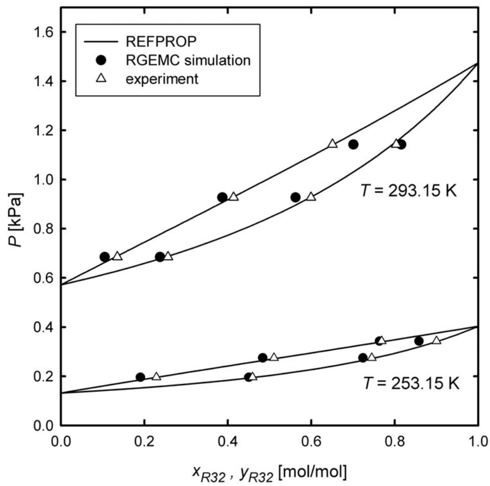

FIG. 2

Vapor–liquid equilibrium for the binary mixture of R32 and R134a at 2 different temperatures (vapor pressure as a function of mole fraction). Comparison of simulation results (●) with REFPROP[1] results (lines) and experimental results (Δ) at $T = 295.15$ K[12], and $T = 253.15$ K[13]. Error bars of the calculations lie within the data points

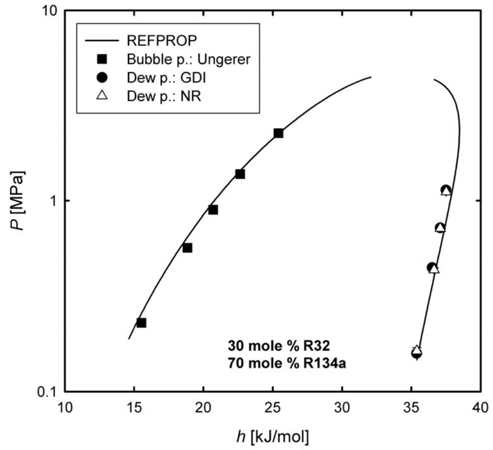

FIG. 3

Pressure–enthalpy diagram for the refrigerant R32/R134a at 30 mole % R32. Comparison of simulation results for bubble and dew points with REFPROP[1] calculations (lines). Bubble points are calculated by the method of Ungerer et al.[6] (■). Dew points are calculated by the GDI method of Escobedo[8] (●) and the Newton–Raphson method (NR) of Eq. (*4*) of this paper (Δ). Where not shown, error bars of the simulation results lie within the data points

In Fig. 3, we show calculations of the bubble- and dew-point data in the *P–h* diagram for a composition of 30 mole % R32. Simulation results are shown corresponding to several different temperatures. The results are compared with those from the REFPROP software[1]; the agreement is good.

Finally, in Fig. 4 we compare our calculations of the COP with those obtained from REFPROP[1,14] for a commercially available R32/R134a refrigerant corresponding to 30 mass % R32. The results correspond to a condenser outlet temperature T_{high} = 328.15 K, evaporator inlet temperature T_{low} = 278.15 K, subcooling is 5 K, superheating is zero, and the compressor is assumed to have an isentropic efficiency ω = 0.8. The agreement of the calculated and the experimental results is excellent.

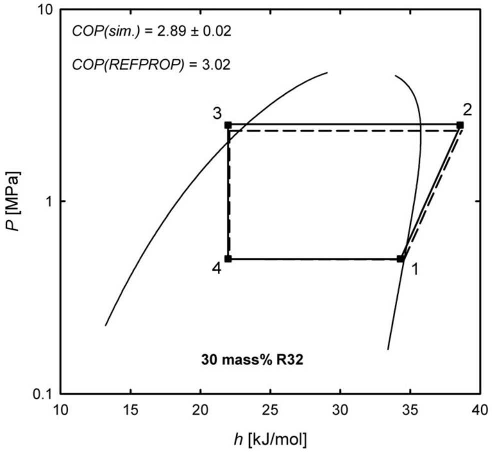

FIG. 4
VCRC pressure–enthalpy diagram for R32/R134a mixture of 30 mass % R32 from simulation (full line) and experiment (dashed line). The simulation error bars lie within the data points

CONCLUSIONS

We have demonstrated a new method for the direct molecular-level simulation of a vapor-compression refrigeration cycle for a refrigerant mixture. It requires only a molecular force-field model for each refrigerant pure component and expressions for the vapor pressure curves of the pure components. The former is readily constructed from a minimal set of experimental data, and the latter are available in the literature or may be estimated by empirical formulae. We have tested the approach for the refrigerant mixture R32/R134a, and obtained results in good agreement with experiment and with those calculated by the standard thermodynamic software package REFPROP. Our approach can be used for evaluation of the properties of a newly proposed refrigerant mixture without the requirement for mixture experimental data. We have also proposed a new simulation method for calculating dew-point pressures of mixtures by molecular simulation.

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