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Thermophysical Property Formulations for R32/R134a Mixtures*

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Abstract

This paper deals with the thermophysical properties of R32/R134a mixtures. A computer code has been developed based on widely acceptable correlations for property predictions. The fundamental problem of the vapor-liquid equilibrium relationship is solved by using related activity and fugacity coefficients. All results are in good agreement with available experimental and computational data.

Key words: R32/R134a mixtures, phase-equilibrium, thermophysical properties

1. Introduction

During the last years particular attention has been concentrated in the field of environment friendly refrigerants. R22 has been used in a variety of applications, but there are concerns that it contributes to an increased ozone depletion. As a result of this point of view, several substances and mixtures are being evaluated as alternatives to R22. The mixtures R32/R134a in compositions 20/80%, 30/70%, 40/60% by mass, are potential replacements.

It is well known that, in order to account for heat and mass transfer processes, accurate thermophysical properties of the working fluids involved are needed. A significant part of this work is the prediction of the vapor-liquid equilibrium relationship. The calculations are based on UNIFAC method (Reid et al. 1988) wherein activity coefficients in mixtures are related to interactions between structural groups. The fugacity coefficients for the vapor phase of the binary system are provided by using the virial form of equation of state. Extensive comparisons have been made with available experimental and computational data without significant differences (Nagel and Bier 1995-1996, NIST 1996). The results are shown schematically in a P-T- compositions diagram which represents equilibrium states of saturated vapor and saturated liquid for the mixture. Analytical relations and diagrams are also given for the quantities: liquid density, thermal conductivity for gas mixtures and liquids and surface tension.

It is hoped that results from this attempt may be used in a variety of applications, as replacement refrigerants will be needed for new or existing equipment.

2. Phase-Equilibrium Relationship

A mathematical approach, based on thermodynamics, is provided which forms the basis for prediction equilibrium states of saturated vapor and saturated liquid for a binary system. For such a system, the PT relation for saturated liquid is clearly different from that for saturated vapor of the same composition. This is in contrast with the behavior of a pure material, for which the bubble line and the dew line coincide. The thermodynamic criterion for phase equilibrium is expressed by means of fugacity coefficient φ_i for vapors and the activity coefficient γ_i for liquids. The relevant correlation is (Smith and Van Ness 1975) :

$$y_i P \hat{\varphi}_i = \gamma_i x_i P_i^{sat} \varphi_i^{sat} \quad i=1, 2 \qquad (1)$$

x_i is the mole fraction of component i in liquid phase, y_i is the mole fraction of component i in vapor phase, P_i^{sat} / φ_i^{sat} are the saturated vapor pressure/fugacity of pure i and P the system's pressure.

The two term virial equation of state is chosen as applicable to the vapor phase; so the quantity $\hat{\varphi}_i$ of a component i in a binary mixture like the R32/R134a, is calculated as a function of temperature T and pressure P by (Smith and Van Ness 1975):

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$$\hat{\varphi}_i = \exp\frac{P}{RT}\left[B_i + (1-y_i)^2\delta\right]$$

$$\delta = 2B_{12} - B_1 - B_2 \qquad (2)$$

For each of the refrigerants the second virial coefficient is expressed as (Smith and Van Ness 1975)

$$: B\frac{P_c}{RT} = B^{(0)} + \omega B^{(1)} \qquad (3)$$

where $B^{(0)}$ and $B^{(1)}$ are:

$$B^{(0)} = 0.083 - \frac{0.422}{T_r^{1.6}}$$

$$B^{(1)} = 0.139 - \frac{0.172}{T_r^{4.2}} \qquad (4)$$

$$T_r = T/T_c$$

The acentric factor ω is derived from (Perry and Green 1984) :

$$\omega = \frac{-\ln P_c - 5.92714 + 6.09648\theta^{-1} + 1.28862\ln\theta - 0.169347\theta^6}{15.2518 - 15.6875\theta^{-1} - 13.472\ln\theta + 0.43577\theta^6} \qquad (5)$$

with P_c in atm and $\theta = T_b/T_c$. The critical values according to ASHRAE (1993) are presented in Table I.

TABLE I. Critical and Characteristic Constants

	R32	R134a
Critical Temperature T_c (K)	351.56	374.18
Critical Pressure P_c (kPa)	5858	4056
Boiling Point T_b (K)	221.48	247.08
Critical Volume V_c (m^3/mol)	123.8076	198.9585

The interaction coefficient B_{12} may be calculated by using Eqs. (3) and (4) with the following combination rules (Smith and Van Ness 1975)

$$Z_c = P_c\frac{V_c}{RT}\ ,\ T_{c12} = (T_{c1}T_{c2})^{1/2}$$

$$Z_{c12} = \frac{Z_{c1} + Z_{c2}}{2}\ ,\ \omega_{12} = \frac{\omega_1 + \omega_2}{2} \qquad (6)$$

$$V_{c12} = \left[\frac{(V_{c1})^{1/3} + (V_{c2})^{1/3}}{2}\right]^3\ ,\ P_{c12} = \frac{Z_{c12}RT_{c12}}{V_{c12}}$$

The fugacity coefficient φ_i^{sat} of pure i, as a saturated vapor, is (Smith and Van Ness 1975):

$$\varphi_i^{sat} = \exp\left(\frac{B_i P_i^{sat}}{RT}\right) \qquad (7)$$

The activity coefficients γ_i are expressed by (Reid et al. 1988), based on UNIFAC method:

$$\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R$$

$$\ln\gamma_i^C = \ln\frac{\Phi_i}{x_i} + \frac{z}{2}q_i\ln\frac{\Theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i}\sum_j^2 x_j l_j$$

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1)\ ,\ z = 10$$

$$\Theta_i = \frac{q_i x_i}{\sum_1^2 q_j x_j}\ ,\ \Phi_i = \frac{r_i x_i}{\sum_1^2 r_j x_j} \qquad (8)$$

In UNIFAC method the activity coefficients are related to interactions between structural groups. For our system there is only one main group ($\ln\gamma_i^R = 0$). The parameters r_i, q_i are respectively measures of molecular van der Waals volumes and molecular surface areas. For the substances R32 and R134a these parameters (r_i,q_i)are given below (Reid et al. 1988):

TABLE II. Parameters r_i,q_i

	r_i,	q_i
R32	1.4655	1.544
R134a	2.4769	2.464

Figure 1 illustrates the dependence of bubble line and dew line on temperature for mixtures R32/R134a in compositions 20/80%, 30/70%, 40/60% by mass. In the same diagram the vapor pressure curves of R32, R134a and R22 have also been plotted. An extensive compilation of data from various sources (ASHRAE 1993, Hozumi et al. 1995, ICI 1995, Nagel and Bier 1995-1996, NIST 1996, Zhang et al. 1995) has been carried out in order for us to have complete comparisons with our results. In all cases there are no significant deviations.

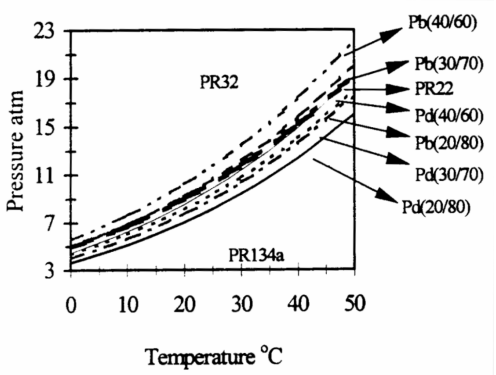

Figure 1. Vapor-liquid equilibrium relationship. Pb: bubble line, Pd: dew line, P: vapor pressure of pure substance.

3. Liquid Density

The saturated liquid density of our binary mixture can be calculated from (Perry and Green 1984):

$$\rho_L = \frac{1}{V_L} = \sum_1^2 x_i \frac{1}{\rho_{Li}^{sat}} \text{ where}$$

$$\rho_{Li}^{sat} = \frac{P_{ci}}{RT_{ci}Z_{ci}^{[1+(1-T_{ri})^{2/7}]}} \quad (9)$$

where, i=1 forR32 and 2 for R134a, P_{ci} in atm.

Figure 2 presents density values for the mixtures under consideration, the components R32, R134a and the conventional refrigerant R22. For all fluids the proposed density values almost coincide with the corresponding ones in ASHRAE (1993), ICI (1995) and NIST (1996).

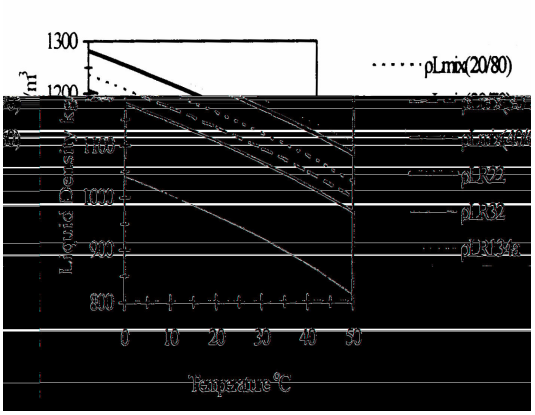

Figure 2. Saturated liquid density as a function of temperature.

4. Thermal Conductivity for Gases and Liquids at Saturation State

The thermal conductivity of the R32/R134a gas mixtures can be determined from the relation (Perry and Green 1984):

$$\lambda_{Gmix} = \sum_1^2 \frac{y_i\lambda_i}{\sum_j y_j A_{ij}}, \quad A_{ij} = \frac{\left[1+\left(\frac{g_i}{g_j}\right)^{\frac{1}{2}}\left(\frac{MB_i}{MB_j}\right)^{\frac{1}{4}}\right]^2}{\left[8\left(1+\frac{MB_i}{MB_j}\right)\right]^{\frac{1}{2}}}$$

$$A_{11} = A_{22} = 1$$

$$\frac{g_i}{g_j} = \left(\frac{\Gamma_j}{\Gamma_i}\right)\left[\frac{\exp(0.0464T_{ri}) - \exp(-0.2412T_{ri})}{\exp(0.0464T_{rj}) - \exp(-0.2412T_{rj})}\right] \quad (10)$$

For the components we propose (Perry and Green 1984):

$$\lambda_{Gi} = 10^{-6}(14.52T_{ri} - 5.14)^{\frac{2}{3}}\frac{C_{Pi}^o}{\Gamma_i},$$

$$\Gamma_i = T_{ci}^{\frac{1}{6}} MB_i^{\frac{1}{2}} P_{ci}^{-\frac{2}{3}} \quad (11)$$

with the ideal gas heat capacity C_p^o calculated by (Perry and Green 1984) :

$$C_{pi}^o = a + bT + cT^2 + dT^3 \quad (12)$$

The constants a, b, c, d are given in Table III.

TABLE III. Constants a, b, c, d

	a	$b\times10^2$	$c\times10^4$	$d\times10^8$
R32	3.2709	2.8267	–0.1409	0.2528
R134a	–0.4724	9.2507	–0.7448	2.0509

For the liquid mixtures we have (Perry and Green 1984):

$$\lambda_{L,mix} = s_1^2\lambda_{L,1} + s_2^2\lambda_{L,2} + 2s_1s_2\lambda_{L,12}$$

$$\lambda_{L,12} = 2\left(\lambda_{L,1}^{-1} + \lambda_{L,2}^{-1}\right)^{-1}$$

$$s_1 = \frac{x_1V_1}{x_1V_1 + x_2V_2}$$

$$s_2 = 1 - s_1$$

$$V_2 = V_{R134a} = \frac{1}{\rho_{L,R134a}}$$

$$V_1 = V_{R32} = \frac{1}{\rho_{L,R32}} \quad (13)$$

The thermal conductivity of the liquid components is derived by (Perry and Green 1984):

$$\lambda_{L,1} = \lambda_{L,R32} = 3.51*10^{-4}\left(\frac{2T_b - T}{2T_b - 273}\right) \quad (14)$$

$$\lambda_{L,2} = \lambda_{L,R134a} = \left(\frac{2.64*10^{-3}}{MB^{1/2}}\right)\left[\frac{3+20(1-T_r)^{2/3}}{3+20(1-T_{br})^{2/3}}\right] \quad (15)$$

$$T_{br} = \frac{T_b}{T_c}, \quad T_b \text{ the boiling point}$$

The choice of the above equations has been made after extensive comparisons which have shown very small deviations from ASHRAE (1993), ICI data (ICI 1995) and Stegou-Sagia (1996) regarding the components, while our predictions for the mixtures have been tested with the NIST REFPROP database (NIST 1996). *Figures 3, 4* show our results.

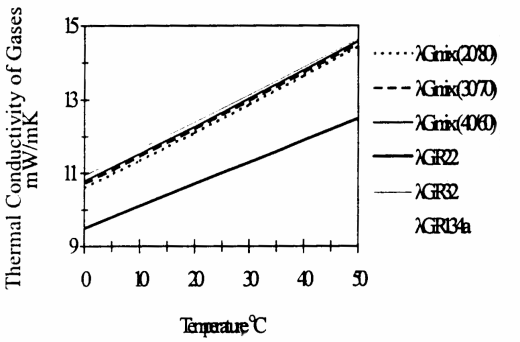

Figure 3. Variation of saturated gas thermal conductivity with temperature.

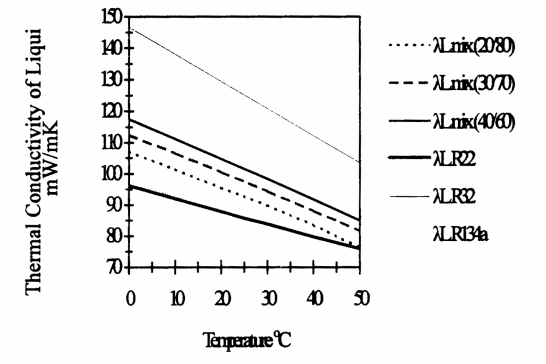

Figure 4. Saturated liquid thermal conductivity for various temperatures.

5. Surface Tension

Surface tension for pure substances can be estimated from (Perry and Green 1984, Reid et al. 1988) :

$$\sigma_i = P_{c,i}^{\frac{2}{3}} T_{c,i}^{\frac{1}{3}} Q_i \left(1 - T_{r,i}\right)^{\frac{11}{9}}$$

$$Q_i = 0.1207 \left(1 + \frac{T_{br,i} \ln P_{c,i}}{1 - T_{br,i}}\right) - 0.281 \quad (16)$$

Significant part of our work is the comparison with widely accepted data for the refrigerants R32, R22, R134a encountered in ASHRAE (1993) with success (less than 2 %).

For the mixtures, in a first attempt, we propose the same formula with Eqs. (16) by using the following mixing rules (Perry and Green 1984):

$$T_{c,mix} = y_1 T_{c,1} + y_2 T_{c,2}$$

$$P_{c,mix} = R T_{c,mix} \frac{y_1 Z_{c,1} + y_2 Z_{c,2}}{y_1 V_{c,1} + y_2 V_{c,2}} \quad (17)$$

$$T_{br,mix} = \frac{T_{b,mix}}{T_{c,mix}} = \frac{y_1 T_{b,1} + y_2 T_{b,2}}{T_{c,mix}}$$

A detailed presentation of our results is given in *Figure 5*.

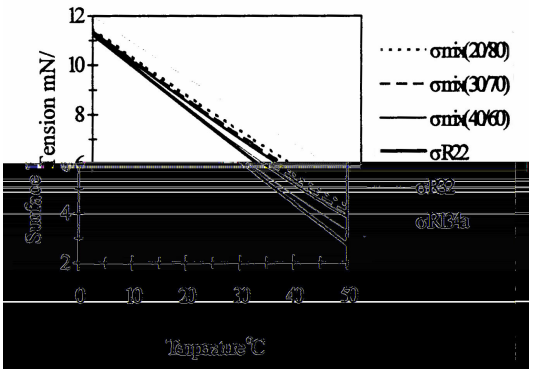

Figure 5. Surface tension as a function of temperature.

6. Conclusions

Thermophysical property equations of environmentally acceptable refrigerant mixtures R32/R134a as an alternative solution for R22 replacements are reported. Extensive correlational work , based on suitable numerical methods, formulation of equations (Nagel and Bier 1995-1996, Reid et al. 1988, Stegou-Sagia 1996, Stegou-Sagia and Katsanos 1996) and information concerning the thermodynamic and transport properties of refrigerants examined in this article (ASHRAE 1993, Hozumi et al. 1995, Huber and Ely 1992, ICI 1995, NIST 1996 and Zhang et al. 1995), lead to the *Figures 1 to 5*. All curves have been plotted by using the above listed equations and the relevant computer code prepared by the present authors. Comparisons with the various sources are illustrated in *Figure 6*. On the basis of the proposed equations, a number of important processes such as evaporation and condensation may be investigated with computational techniques.

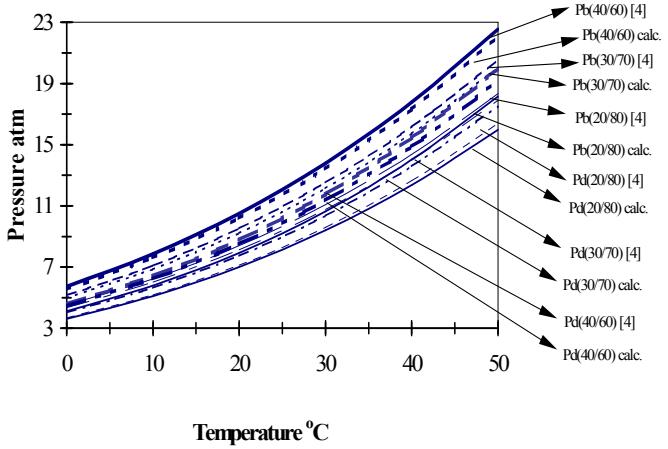

Figure 6. Vapor-liquid equilibrium relationship for R32/R134a mixtures in compositions 20/80, 30/70 and 40/60 % .Comparisons with NIST Database (1996)

Nomenclature

B	Second virial coefficient, cm^3/mol
C_p^0	Ideal gas heat capacity, cal/mol K
MB	Molecular weight
P	Pressure, atm
R	Constant of gases
T	Temperature, K
V	Molar volume, cm^3/mol
x	Mole fraction of liquid component i
y	Mole fraction of gas component i
γ	Activity coefficient
λ	Thermal conductivity, cal/(cm)(s)(K) in Eqs. (10), (11), (13), (14), (15)
ρ	Molar density
σ	Surface tension, dyn/cm Eq. (16)
φ_i	Fugacity coefficient of pure i
$\hat{\varphi}_i$	Fugacity coefficient of component i in mixture
ω	Acentric factor

Subscripts

b	At boiling point
c	At critical point
G	Gas
L	Liquid
R	Reduced: divided by critical value

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