

Tests proved that new zeotropic CFC-free mixtures also are fully satisfactory replacements for partial refrigerant losses of up to at least 25% in older systems still containing CFC refrigerants. It is possible to remove the remaining refrigerant, repair the leak, replace the captured refrigerant, and add sufficient CFC-free 'top-off' charge to continue satisfactory operation.

### Summary

A brief history of Auto-Refrigerating Cascade systems has been presented. Moderate sized (less than 14 kW power input) ARC systems have been successfully converted from the use of CFC components to completely CFC-free refrigerant mixtures with successful operation. New zeotropic mixtures have over-all ODP levels below 0.02 with nearly identical Carnot efficiencies, as well as requiring no hardware or lubricant changes. Present efforts have reduced the ODP by a ratio of 20 to 30 times compared to pre-conversion mixes. Additional efforts show promise of obtaining an ODP of less than 0.01 and eventually down to zero when more acceptable zero ODP substances become available.

### References

- 1 ASHRAE Handbook Refrigeration, Cryogenics (1994) 27.9-37.10
- 2 Bosnjakovic, F. *Technische Thermodynamik*, Part II, Theodor Steinkopff, Dresden (1960) (German); *Technical Thermodynamics*, Holt, Rinehart & Winston, New York (1965) (English)
- 3 Perry's Chemical Engineering Handbook, Distillation, 6th edition, McGraw-Hill, New York (1984) 13.1-13.97
- 4 Kruse, H. The advantages of non-azeotropic refrigerant mixtures for heat pump applications *Int. J. Refrig.* (1981) 4(3) 119-125
- 5 Hesse, U., Arnemann, H. Carbon dioxide-hydrocarbon mixtures as alternative fluids in refrigeration systems, *IIR Conference*, Hanover (May 1994)
- 6 Hesse U., Spauschus, H. O. Selection of R502 and R22 alternatives for different applications, *19th Int. Congress on Refrigeration*, The Hague (Aug. 1995)
- 7 Fuderer, A. German patent 1,426,956 (1969)
- 8 Longworth, R.C. U.S. patent 5,337,572 to APD Cryogenics (1994)
- 9 Podbielniak, W. J. U.S. patent 2,041,725 (1936)
- 10 Kleemenko, A. P. One-flow cascade cycle, *IIR Int. Congress of Refrigeration*, Copenhagen (1959)
- 11 Smith, H., Kennedy, P. *Ultra-Low Temperature Mechanical Refrigeration Systems for High-Vacuum Traps and Baffles*, Univ. of Calif. Lawrence Radiation Laboratory, Berkeley, CA, U.S.A.-AEC Contract No. W-7405-eng-48 (1959)
- 12 Fuderer, A. U.S. patent 3,203,194 to Farbwerke Hoechst (1965)
- 13 Missimer, D. J. U.S. patent 3,768,273 to Gulf & Western Industries (1973)
- 14 Gray, R. A. U.S. patent 4,482,465 to Phillips Petroleum Company (1984)
- 15 Bivens, D. B. U.S. patent 4,810,403 to E.I. DuPont de Nemours and Company (1989)
- 16 Stevenson, R. U.S. patent 5,360,566 to Intermagnetics General Corp. (1994)
- 17 ASHRAE Standard, ANSI/ASHRAE 34-1992, Number Designation and Safety Classification of Refrigerants (1992)

## An improved extended corresponding states method for estimation of viscosity of pure refrigerants and mixtures\*

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The extended corresponding states method for calculating the viscosity of pure refrigerants and mixtures is investigated. The accuracy of pure fluid viscosity values is significantly improved by introducing a third shape factor evaluated using available pure fluid viscosity data. A modification to the method of Huber and Ely (*Fluid Phase Equilibria*, 1992, **80**, 45–46) is proposed for estimation of the viscosity of mixtures; this modification eliminates the possibility of discontinuities at the critical point, ensures that the pure component viscosity is provided in the limit of a component mole fraction approaching 1, and improves the overall accuracy of the method. The method has been applied to 12 pure refrigerants including three hydrocarbons and mixtures. The average absolute deviations between the calculated and experimental viscosity values are within 4% for all of the pure fluids and most of the mixtures investigated. Published by Elsevier Science Ltd and IIR

(Keywords: refrigerant; mixture; viscosity; calculation; design; corresponding state)

## Méthode des états correspondants améliorée pour estimer la viscosité de frigorigènes simples et en mélanges

*On étudie l'amélioration de la méthode des états correspondants pour calculer la viscosité de frigorigènes simples et de mélanges. On améliore significativement la précision des valeurs pour des corps purs en introduisant un troisième facteur évalué au moyen de données disponibles. On propose une modification de la méthode de Huber et Ely (*Fluid Phase Equilibria*, 1992, **80**, 45–46), pour estimer la viscosité de mélanges; cette modification élimine le risque de discontinuités au point critique, garantit que la viscosité des composants simples est obtenue pour une fraction moléculaire proche de 1, et améliore la précision globale de la méthode. On applique cette méthode à 12 frigorigènes purs comprenant trois hydrocarbures et à des mélanges. Les déviations absolues moyennes entre valeurs calculées et expérimentales restent inférieures à 4% pour tous les fluides simples et la plupart des mélanges étudiés. Published by Elsevier Science Ltd and IIR*

(Mots clés: frigorigène; mélange; viscosité; calcul; conception; état correspondant)

This paper describes a modification to the extended corresponding states viscosity method of Huber and Ely.<sup>1</sup> This new method provides improved accuracy by taking advantage of high accuracy thermodynamic property models and available pure component viscosity data.

The recent availability of reliable experimental data and improved correlating techniques has allowed high-accuracy equations of state to be formulated for the thermodynamic properties of pure refrigerants, e.g. Younglove and McLinden,<sup>2</sup> Tillner-Roth and Baehr,<sup>3</sup> and refrigerant mixtures, e.g. Tillner-Roth.<sup>4</sup> These highly accurate thermodynamic property models are explicit in temperature and density and provide a single representation for the entire thermodynamic surface including the subcooled, saturated, superheated, and supercritical regimes. Unfortunately,

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**Nomenclature**

$a_i$	Coefficients to Equation (13) provided in Table 1	$\Delta\eta$	Residual viscosity = $\eta - \eta^*$
A	Helmholtz free energy	$\epsilon/k$	Empirical factor appearing in Equations (13) and (15)
AAD	Absolute average deviation between calculated and experimental values	$\eta$	Viscosity
$b_i$	Coefficients to Equation (15) provided in Table 1	$\phi_j$	Density related shape factor for substance $j$
$B_\eta$	Second viscosity virial coefficient defined in Equation (15)	$\theta_j$	Temperature related shape factor for substance $j$
$c_i$	Coefficients to reference fluid viscosity correlation [Equation (14)] provided in Table 1	$\rho$	Density
$E$	Temperature function defined in Equation (16)	$\sigma$	Hard-sphere diameter
$f$	Equivalent substance reducing ratio for temperature	$\Omega$	Collision integral; given in Equation (13) for R134a
$F_\eta$	Factor defined in Equations (11) and (30) for pure fluids and mixtures, respectively.	$\psi_j$	Viscosity related shape factor for substance $j$
$g$	Equivalent mass	<i>Subscripts</i>	
$h$	Equivalent substance reducing ratio for density	$c$	At critical point
$K$	Constant appearing in Equation (6)	$ij$	Mixed average value for substances $i$ and $j$
$M$	Molar mass	$j$	Pertaining to substance $j$
$P$	Absolute pressure	$o$	Pertaining to the reference fluid
$T$	Absolute temperature	$r$	Reduced property (property divided by critical value)
$Z$	Compressibility factor defined by Equation (20)	$x$	Pertaining to the mixture
$\Delta a$	Reduced residual Helmholtz free energy defined by Equation (19)	<i>Superscripts</i>	
		*	Dilute gas value
		$^o$	Conformal property used to evaluate viscosity of reference fluid
		K.T.	Property determined from kinetic theory

transport property models are not as well-developed as those for thermodynamic properties. Reliable experimental data for transport properties over the temperature and density ranges of interest are often not available, particularly for mixtures. Complete surface correlations for viscosity and thermal conductivity are available for only a few pure refrigerants of current interest. At this time, the extended corresponding states (ECS) models, e.g. Hanley,<sup>5</sup> Ely and Hanley,<sup>6</sup> Teja and Rice,<sup>7</sup> Ely,<sup>8</sup> Huber and Ely,<sup>1</sup> provide the best methods for estimating the transport properties of pure refrigerants and refrigerant mixtures when detailed experimental data are lacking.

**Extended corresponding states model for viscosity**

A general form for viscosity of a dilute gas is provided by kinetic theory as described in Reid *et al.*<sup>9</sup> The gas is assumed to consist of non-interacting rigid particles of diameter  $\sigma$ . An expression for the momentum flux between two layers in relative motion yields the

following expression for viscosity

$$\eta^{\text{K.T.}} = C \frac{T^{1/2} M^{1/2}}{\sigma^2} \quad (1)$$

where  $T$  is absolute temperature,  $M$  is molecular mass and  $C$  is a constant.

The superscript K.T. in Equation (1) indicates that the viscosity is based on kinetic theory. This viscosity model is applicable only to low-density gaseous states for which intermolecular distances are large and molecular interaction effects are negligible.

The corresponding states approach attempts to express viscosity in a reduced form for which it will have a similar value for different fluids at the same reduced conditions. Critical point properties provide reference values to reduce the thermodynamic properties. In an analogous manner, a reduced viscosity  $\eta_r$  can be defined as

$$\eta_r = \frac{\eta}{\eta_c^{\text{K.T.}}} \quad (2)$$

where  $\eta_c^{\text{K.T.}}$  is the viscosity determined from Equation (1) evaluated at the critical temperature. Critical

region theory<sup>10</sup> indicates that the viscosity of a pure fluid approaches infinity at the critical point. The critical viscosity in Equation (2) thus has no physical meaning in itself, but it is used to arrive at a theoretically based reducing parameter. If the molecular diameter  $\sigma$  is taken as the cube root of the critical molecular volume (critical specific volume divided by Avogadro's number  $N_A$ ) the reduced viscosity can be represented as

$$\eta_r = \frac{\eta}{CN_A^{2/3} T_c^{1/2} M^{1/2} \rho_c^{2/3}} = f(T_r) \quad (3)$$

Corresponding states theory indicates that the reduced viscosity at a given reduced temperature and density should be the same for all fluids. Applying Equation (3) to both a reference fluid and a fluid of interest allows the viscosity to be expressed as

$$\eta_j(T) = \eta_o(T^o) \left[ \frac{M_j}{M_o} \right]^{1/2} \left[ \frac{T_{c,j}}{T_{c,o}} \right]^{1/2} \left[ \frac{\rho_{c,j}}{\rho_{c,o}} \right]^{2/3} \quad (4)$$

where subscript  $j$  indicates a pure fluid for which viscosity is to be determined and subscript  $o$  indicates the reference fluid for which a complete viscosity surface is known. The viscosity  $\eta_o$  of the reference fluid is evaluated at a so-called 'conformal' temperature  $T^o$  equal to  $T$  ( $T_{c,o}/T_{c,j}$ ) so that it represents the same reduced state for both fluids.

The kinetic theory approach is appropriate for conditions of very low density in which the fluid molecules are far apart and thus have little interaction. However, as density increases, molecular interactions become increasingly important, necessitating a correction which, for a pure fluid, can be represented as

$$\eta(T, \rho) = \eta^*(T) + \Delta\eta(T, \rho) \quad (5)$$

where  $\eta^*$  is the Chapman-Enskog<sup>11</sup> dilute gas contribution given by

$$\eta^* = \frac{KT^{1/2}M^{1/2}}{\sigma^2\Omega} \quad (6)$$

$\Omega$  is a collision integral which accounts for intermolecular force interactions and  $K$  is a constant. The molecular diameter appearing in Equation (6) is a parameter related to the intermolecular interaction potential. The Chapman-Enskog dilute gas model provides excellent results for low density refrigerant vapors as shown by Kim and Sonntag<sup>12</sup>.

The residual viscosity  $\Delta\eta$  depends on both temperature and density. This term is needed for liquids and dense vapors, and it is the focus of this paper. Assuming that the residual viscosity term obeys corresponding states arguments, then

$$\Delta\eta_j(T, \rho) = \Delta\eta_o(T(T_{c,o}/T_{c,j}), \rho(\rho_{c,o}/\rho_{c,j})) \times \left[ \frac{M_j}{M_o} \right]^{1/2} \left[ \frac{T_{c,j}}{T_{c,o}} \right]^{1/2} \left[ \frac{\rho_{c,j}}{\rho_{c,o}} \right]^{2/3} \quad (7)$$

A number of authors including Hanley<sup>5</sup>, Ely and Hanley<sup>6</sup>, Hwang and Whiting<sup>13</sup>, Monnery *et al.*<sup>14</sup>,

and Huber and Ely<sup>1</sup> refine this approach by introducing equivalent substance reducing ratios,  $f_j$  and  $h_j$ , which replace the critical temperature and density ratios in Equation (7). The equivalent substance reducing ratios (or, simply, "reducing ratios") are defined by

$$f_j = \frac{T_{c,j} \theta_j}{T_{c,o}} \quad (8)$$

$$h_j = \frac{\rho_{c,o}}{\rho_{c,j}} \phi_j \quad (9)$$

where  $\theta_j$  and  $\phi_j$  are shape factors which are, in general, functions of temperature and density.

In terms of the reducing ratios, Equation (7) can be rewritten as

$$\Delta\eta_j(T, \rho) = \Delta\eta_o(T/f_j, \rho h_j) F_\eta \quad (10)$$

where

$$F_\eta = f_j^{1/2} h_j^{-2/3} \left[ \frac{M_j}{M_o} \right]^{1/2} \quad (11)$$

### The reference fluid

In the extended corresponding states approach, the properties of a pure fluid or mixture are inferred from those of a reference fluid for which the properties are well known over a large range of conditions. The methodology presented here for estimating viscosity is not tied to a particular reference fluid. However, R134a has been selected as the reference fluid because both its thermodynamic and transport properties have been well-studied and because it is chemically similar to the refrigerants of current interest. The thermodynamic properties are provided by the modified Benedict-Webb-Rubin formulation of Huber and McLinden<sup>15</sup>. A correlation for the viscosity of R134a is given by Krauss *et al.*<sup>16</sup>. However, due to the data available to them at that time, their correlation is valid only for temperatures between 290 and 430 K, a range which does not encompass the range of interest for refrigerants. Consequently, the R134a viscosity correlation recently developed by Laesecke<sup>17</sup> has been adopted for the reference fluid. The Laesecke viscosity correlation for R134a is given by

$$\eta = \eta^* + \Delta\eta \quad (12)$$

The low density  $\eta^*$  term is given by Equation (6) with  $K = 0.021357$  for viscosity in  $\mu$  Pa/s,  $M = 102.03184$  g/mol,  $\sigma = 0.50647$  nm.  $\Omega$  is approximated by Wilhelm and Vogel<sup>18</sup> as

$$\ln(\Omega) = \sum_{i=0}^4 a_i \left( \ln \left( \frac{T}{\epsilon/k} \right) \right)^i \quad (13)$$

where  $\epsilon/k$  is an empirical factor related to the molecular interaction potential and determined by Wilhelm and Vogel<sup>18</sup> to be 288.82 K for R134a. The  $a_i$

**Table 1** Coefficients used in Equations (13)–(16) for viscosity of R134a in  $\mu\text{Pa/s}$ **Tableau 1** Coefficients utilisés dans les équations (13)–(16) pour la viscosité du R134a en  $\mu\text{Pa/s}$ 

$i$	$a_i$	$b_i$	$c_i$
0	2.218816E-01	-1.7999496E+00	
1	-5.079322E-01	4.6692621E+01	-0.331249E-01
2	1.285776E-01	-5.3460794E+02	-0.468509E-03
3	-8.328165E-02	3.3604074E+03	0.156983E+00
4	-2.713173E-02	-1.3019164E+04	3.073830E+00
5		3.3414230E+04	-0.306398E+00
6		-5.8711743E+04	0.215221E+00
7		7.1426686E+04	
8		-5.9834012E+04	
9		3.3652741E+04	
10		-1.2027350E+04	
11		2.4348205E+03	
12		-2.0807957E+02	

coefficients appearing in Equation (13) are provided in *Table 1*.

The residual viscosity term in units of  $\mu\text{Pa/s}$  is represented by

$$\Delta\eta = (c_1 + B_\eta\eta^*)\rho_r + c_2\rho_r^2 + \frac{c_5 + c_6\rho_r}{c_4E - \rho_r} - \frac{c_5}{c_4E} \quad (14)$$

where  $\rho_r$  is the reduced density.

$$B_\eta = 602.2137\rho_c\sigma^3 \sum_{i=0}^{12} b_i \left( \sqrt{\frac{T}{\epsilon/k}} \right)^i \quad (15)$$

is the second viscosity virial coefficient as given by Vogel<sup>19</sup> based on the theory of Rainwater and Friend<sup>20</sup>.

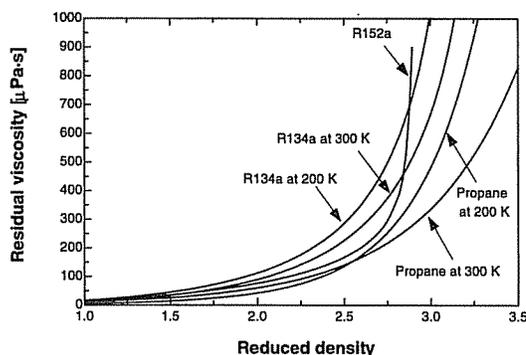
The temperature dependence associated with the close-packed density  $c_4$  is

$$E = 1 + c_3 \frac{T}{T_c} \quad (16)$$

$T_c = 374.18$  K is the critical temperature and  $\rho_c = 4.9788$  mol/l is the critical density. The  $b_i$  and  $c_i$  coefficients appearing in Equations (14)–(16) are provided in *Table 1*. The Laesecke<sup>17</sup> correlation is based on data for temperatures in the range 200–440 K and up to a maximum density of 1550 kg/m<sup>3</sup> which it represents with an average error of 1.69% and a maximum error of 5.5%. The form of Equation (14) should extrapolate reliably for temperatures between 170 and 460 K.

### Pure fluid viscosity

Huber and Ely<sup>1</sup> provide empirical equations for the shape factors  $\theta_j$  and  $\phi_j$  of many refrigerants in terms of reduced temperature, acentric factor, and critical compressibility. In theory, the shape factors should depend upon density as well. However, their shape factor equations were derived from data along the saturation boundary, so density and temperature are not independent. Hwang and Whiting<sup>13</sup> demonstrate

**Figure 1** Residual viscosity of R134a, R152a, and propane as a function of reduced density**Figure 1** Viscosité résiduelle des R134a, R152a et propane en fonction de la densité réduite

that the extended corresponding states model of Ely and Hanley<sup>6</sup> does not provide accurate results for polar fluids. They state that the 'the effect of the density shape factor ( $\phi_j$ ) on viscosity is not as significant as the effect of the temperature (energy) shape factor ( $\theta_j$ )', contrary to our observations for refrigerants. They propose modifications that affect the temperature-dependent shape factor but retain the density shape factor [Equation (9)] in its original form. Monnery *et al.*<sup>14</sup> also provide shape factor relations which are independent of density. Neglect of the density dependence is cause for concern because the residual viscosity term is a strong function of density, but only a weak function of temperature, as seen in *Figure 1*. In fact, the residual viscosity terms in the recent viscosity correlations for R134a<sup>16</sup> and R152a<sup>21</sup> are entirely functions of density with no temperature dependence. The Laesecke R134a correlation given in the previous section and the propane correlation of Younglove and Ely<sup>22</sup> do include temperature dependence but it is less pronounced than the density dependence.

Residual viscosity is strongly dependent upon reduced density, particularly at high densities. Given this strong dependence, we propose two improvements for estimating pure fluid viscosity. The first is to determine 'exact' values of the shape factors (or equivalently, the reducing ratios  $f_j$  and  $h_j$ ) as originally recommended by Ely and Hanley<sup>6</sup> and Ely<sup>8</sup>. Exact reducing ratios make use of high-accuracy equations of state for the fluid of interest and the reference fluid. They are determined by applying the conformal relations

$$\Delta a_j(T, \rho) = \Delta a_o(T/f_j, \rho h_j) \quad \text{and} \quad (17)$$

$$Z_j(T, \rho) = Z_o(T/f_j, \rho h_j) \quad (18)$$

where  $\Delta a$  is the reduced residual Helmholtz free energy

$$\Delta a(T, \rho) = \frac{A(T, \rho) - A^*(T, \rho)}{RT} \quad (19)$$

and  $Z$  is the compressibility factor

$$Z = P/(RT\rho) \quad (20)$$

In Equation (19),  $A$  is the Helmholtz free energy and  $A^*$  is the Helmholtz free energy that would result if the fluid behaved according to the ideal gas law at this temperature and density.

The determination of the reducing ratios by Equations (17) and (18) is straightforward, in principle, but somewhat complicated in practice. An iterative procedure is required to simultaneously determine both  $f_j$  and  $h_j$ . Complications arise at both low and high densities. At low densities, ideal gas behavior is approached and the conformal relations, Equations (17) and (18), tend toward singularity. As density increases, the conformal equations become strong functions of  $f_j$  and  $h_j$  which can confound a traditional two-dimensional secant method of iteration. A solution scheme that was found to work consistently and requires a modest amount of calculation effort is as follows. A one-dimensional parabolic interpolation scheme called Brent's method<sup>23</sup> is applied to determine the value of  $h_j$  that minimizes the difference between the left and right sides of Equation (18). For each trial value of  $h_j$ , a value of  $f_j$  is determined by numerically solving Equation (17).

This approach is illustrated in Figure 2 in which residual viscosities based on experimental data for three fluids are plotted versus reduced density. The residual viscosities were determined by subtracting the dilute gas contribution given by Equation (6) from the reported experimental values. Also shown in Figure 2 are the residual viscosities calculated using the ECS method. These values were determined using Equation (10) with the viscosity for reference fluid R134a evaluated using the correlation in the previous section at conformal conditions, that is, at temperature  $T/f_j$  and density  $\rho h_j$ . The conformal conditions were determined by finding for each data point, the values of  $f_j$  and  $h_j$  which satisfy Equations (17) and (18). The thermodynamic properties of R134a were determined using the correlation of Huber and McLinden<sup>15</sup>. The equations of state and sources of the saturated and compressed liquid viscosity data for the three fluids in Figure 2 are indicated in Table 2.

Figure 2 shows that the residual viscosity predicted using extended corresponding states shows the correct trend, but does not exactly match the experimental data even when 'exact' values of the substance reducing ratios are employed. There is no apparent trend. The viscosity is overestimated for R32 and R152a, but slightly underestimated for R11. Similar behavior is seen for other refrigerants and for other reference fluids.

The ECS method can be improved if any experimental viscosity data are available. Monnery *et al.*<sup>14</sup> suggest that the shape factors (reducing ratios) should be determined from experimental viscosity data rather than from thermodynamic information. In

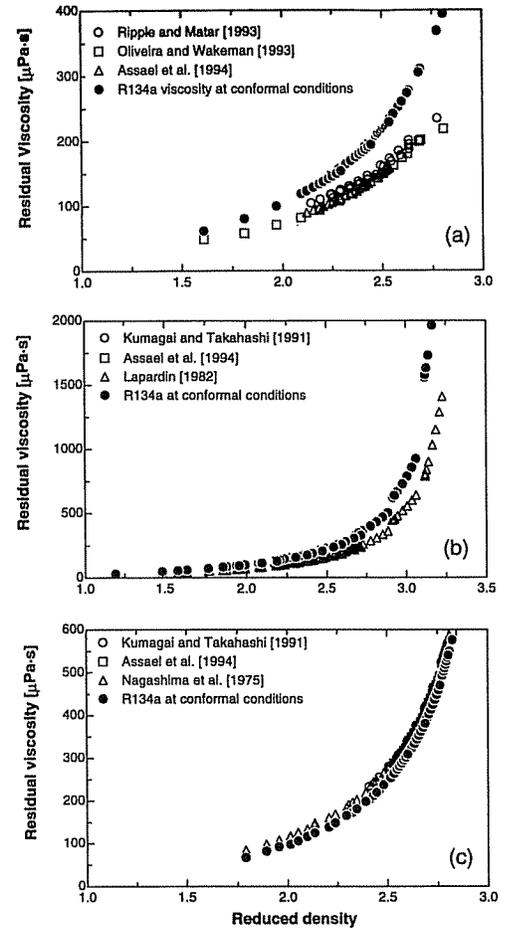


Figure 2 Residual viscosity versus reduced density for R134a evaluated at conformal conditions and for: (a) R32, (b) R152a, and (c) R11 based on experimental data

Figure 2 Viscosité résiduelle en fonction de la densité réduite pour le R134a évaluée aux conditions de base et pour: (a) R32, (b) R152a et (c) R11, sur la base des données expérimentales

their approach, they assume that the density of the fluid of interest is also known and thereby eliminate the  $\phi_j$  shape factor from further consideration. They then provide correlations for  $\theta_j$  as a function of reduced temperature based on the experimental viscosity and density data. A limitation of this approach is that their residual viscosity is only a function of temperature with no density dependence. As seen in Figures 1 and 2, however, residual viscosity is a strong function of density. For this reason, it does not seem prudent to eliminate the density dependence from the shape factor correlations.

The second modification to the Huber and Ely<sup>1</sup> method we propose is to use experimental viscosity data to improve the estimate of the conformal density. A simple way to introduce this improvement is by defining a third shape factor  $\psi_j$ , such that

$$\psi_j = \frac{\rho^0}{\rho h_j} \quad (21)$$

**Table 2** Equations for  $\psi_j$  and associated errors based on reference fluid R134aTableau 2 Equations donnant  $\psi_j$  et les erreurs associées pour le frigorigène de référence R134a

Fluid	$\psi_j$	No. of points	Error $_{\psi=1}$ %	Error $_{\psi}$ %	Eqn of state Ref.	Viscosity data source Ref.
R11	$\psi_j = 1.171 - 0.0592\rho_r$	92	8.9	1.3	24	25, 26, 27
R12	$\psi_j = 1.087 - 0.0379\rho_r$	32	7.0	2.3	28	27
R113	$\psi_j = 1.212 - 0.0569\rho_r$	9	31.3	0.2	28	25
R22	$\psi_j = 1.106 - 0.0491\rho_r$	95	14.6	2.1	29	25, 30, 31
R32	$\psi_j = 0.898 + 0.0099\rho_r$	75	40.4	3.3	32	33, 34, 27
R123	$\psi_j = 1.155 - 0.0513\rho_r$	30	12.3	3.1	2	25, 35
R125	$\psi_j = 1.110 - 0.0332\rho_r$	45	13.3	1.7	32	36, 33
R143a	$\psi_j = 1.134 - 0.0801\rho_r$	6	15.6	1.7	37	25
R152a	$\psi_j = 0.807 + 0.0496\rho_r$	105	45.3	3.9	38	25, 27, 39
Propane	$\psi_j = 0.800 + 0.0345\rho_r$	23	112.8	3.6	22	22
Isobutane	$\psi_j = 0.798 + 0.0476\rho_r$	25	65.8	3.9	22	22
n-Butane	$\psi_j = 0.801 + 0.0375\rho_r$	29	167.7	2.7	22	22

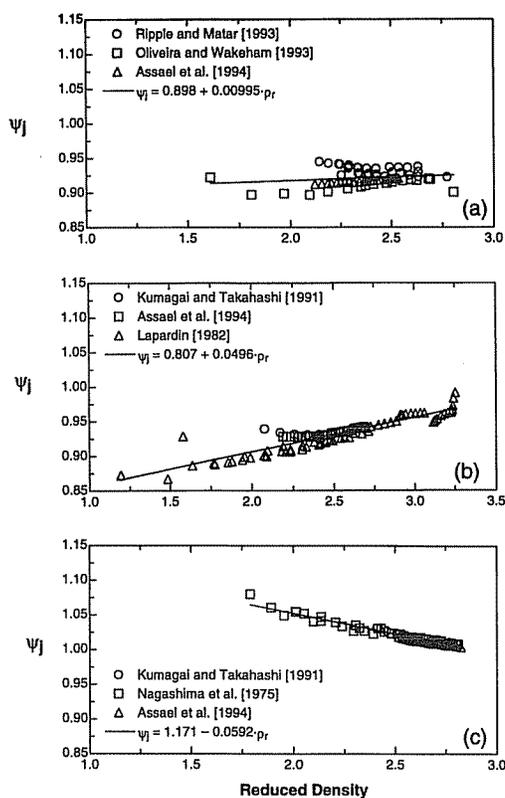
where  $\rho^o$  is the conformal density at which the reference fluid residual viscosity should be determined. Figure 3 shows the values of  $\psi_j$  which cause the residual viscosity estimated from extended corresponding states to exactly match the experimental data points (depicted in Figure 2) using R134a as the reference fluid. Exact reducing ratios determined from application of Equations (17) and (18) were used in the determination of these values of  $\psi_j$ . If extended corresponding states would apply perfectly for viscosity,  $\psi_j$  would be 1 for all fluids, independent of reduced density. However, as seen in the figures, the values of  $\psi_j$  differ from 1 and display some density dependence. The density dependence is well-represented by a linear equation. Unweighted least-squares fits were used to determine the linear functions superimposed on the data in Figure 3.

Linear equations for  $\psi_j$  as a function of reduced density (based on R134a as the reference fluid) are provided for a number of fluids in Table 2. Table 2 also shows average absolute deviations between calculated and experimental values for two cases:  $\psi_j = 1$ , the standard extended corresponding states method (Error $_{\psi=1}$ ), and  $\psi_j$  determined by the linear function of reduced density in Table 2 (Error $_{\psi}$ ). The average absolute deviation in percent is defined as

$$AAD = \frac{100}{n} \sum_{i=1}^n \frac{|\Delta\eta_{\text{calc},i} - \Delta\eta_{\text{exp},i}|}{\Delta\eta_{\text{exp},i}} \quad (22)$$

where  $n$  is the number of data points. The AAD values reported in Table 2 include experimental uncertainty and the differences in results reported by different investigators; these values would be smaller if experimental data from a single investigator were used. The distribution of errors is evident in Figure 4.

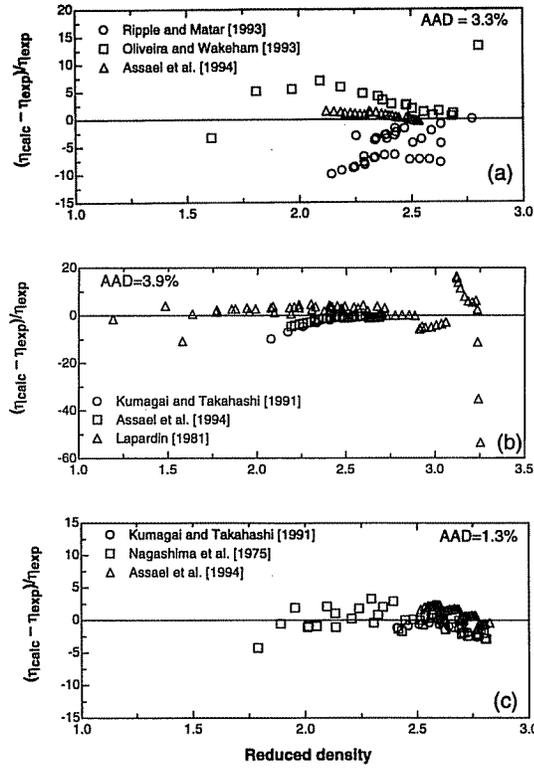
This simple change to the conformal density significantly improves the accuracy of the extended corresponding states estimate. The method can accommodate the available experimental data. If no data are available,  $\psi_j$  should be set to 1. One or more reliable experimental measurements of liquid viscosity can be used to provide a better value of  $\psi_j$ . If data are



**Figure 3** Values of the viscosity shape factor  $\psi_j$  based on experimental viscosity data. The line represents a linear least-squares fit of the points: (a) R32, (b) R152a and (c) R11

Figure 3 Valeurs du facteur additionnel  $\psi_j$  fondées sur les données expérimentales. Les droites des moindres carrés des points sont tracées pour: (a) R32, (b) R152a et (c) R11

available for only a limited range of reduced density,  $\psi_j$  should be fitted to a constant value. In principle, the method could be improved further by allowing  $\psi_j$  to be a function of temperature or a more complicated function of density. However, identification of a function that can be used over an extended range of conditions requires extensive viscosity data. If such



**Figure 4** Comparison of experimental residual viscosities with values calculated by the modified ECS method using the shape factor  $\psi_j$  relation in Table 2: (a) R32, (b) R152a, and (c) R11

Figure 4 Comparaisons des viscosités résiduelles expérimentales avec les valeurs calculées par la méthode ECS modifiée utilisant le facteur de forme  $\psi_j$  du tableau 2: (a) R32, (b) R152a et (c) R11

data were available, it would be preferable to develop a fluid-specific correlation.

#### Modification for the viscosity of mixtures

Huber and Ely<sup>1</sup> recommend that the viscosity of a refrigerant mixture be determined as

$$\eta(T, \rho, x) = \eta^*(T, x) + \Delta\eta_o(T/f_x, \rho h_x)F_\eta + \Delta\eta^*(\rho, x) \quad (23)$$

where

- $x$  is an array of component mole fractions
- $\eta^*(T, x)$  is the low density viscosity of the mixture determined from kinetic theory<sup>40</sup>
- $f_x$  and  $h_x$  are reducing ratios for the mixture
- $\Delta\eta_o$  is the residual viscosity for the reference fluid evaluated at conformal conditions appropriate for the mixture
- $\Delta\eta^*(\rho, x)$  is an Enskog hard sphere correction for effects of size and mass differences in a mixture as recommended by Ely<sup>41</sup>.

Huber and Ely<sup>1</sup> suggest that the equivalent substance reducing ratios  $f_x$  and  $h_x$  for the mixture be estimated

from the pure component values using the van der Waals one-fluid mixing rules

$$h_x = \sum_{i=1}^n \sum_{j=1}^n x_i x_j h_{ij} \quad (24)$$

$$f_x h_x = \sum_{i=1}^n \sum_{j=1}^n x_i x_j f_{ij} h_{ij} \quad (25)$$

where

$$f_{ij} = \sqrt{f_i f_j} \quad (26)$$

$$h_{ij} = \frac{(h_i^{1/3} + h_j^{1/3})^3}{8} \quad (27)$$

If an accurate formulation for the thermodynamic properties of the mixture is available, 'exact values' of  $f_x$  and  $h_x$  can alternatively be estimated by applying to the mixture the following conformal relations

$$\Delta a(T, \rho, x) = \Delta a_o(T/f_x, \rho h_x) \quad (28)$$

$$Z(T, \rho, x) = Z_o(T/f_x, \rho h_x) \quad (29)$$

The values of  $f_x$  and  $h_x$  are obtained from solving Equations (28) and (29) using the iterative scheme described above for Equations (17) and (18). The values thus obtained are quite similar to those determined from Equations (24) to (27) for the mixtures investigated in this paper.

The factor  $F_\eta$  for mixtures is defined by

$$F_\eta = f_x^{1/2} h_x^{-2/3} g_x^{1/2} \quad (30)$$

where  $g_x$  is an 'equivalent mass'. Several methods for determining  $g_x$  are provided by Huber and Ely<sup>1</sup>, the simplest being

$$g_x^{1/2} = \frac{\sum_{i=1}^n \sum_{j=1}^n x_i x_j f_{ij}^{1/2} h_{ij}^{4/3} M_{ij}^{1/2}}{f_x^{1/2} h_x^{4/3}} \quad (31)$$

where

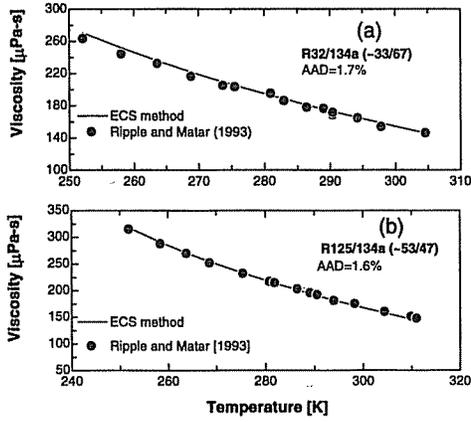
$$M_{ij} = \frac{2}{1/M_i + 1/M_j} \quad (32)$$

To improve the estimates of mixture viscosity in the liquid phase, Huber and Ely<sup>1</sup> suggest an alternative definition for  $g_x$  for densities greater than the critical density. In this case, the molecular mass of each mixture component  $M_j$  appearing in Equation (32) is replaced with an equivalent molecular mass calculated using pure component saturated liquid viscosity data, as follows:

$$M_j = g_j M_o \quad (33)$$

where

$$g_j^{1/2} = \frac{\Delta\eta_j^{\text{sat}}(T_j)}{\Delta\eta_o(T/f_j, \rho h_j)} f_j^{-1/2} h_j^{2/3} \quad (34)$$



**Figure 5** Experimental and calculated saturated liquid mixture viscosity values for (a) R32/134a and (b) R125/134a  
**Figure 5** Valeurs expérimentales et de la viscosité du mélange liquide à saturation calculées pour (a) R32/R134a et (b) R125/134a

Huber and Ely<sup>1</sup> also provide an empirical equation for  $g_j$  as a function of reduced temperature and a structural molecular factor based on group contributions which is to be used when saturated liquid viscosity data are not available.

We propose a minor modification to the method of Huber and Ely<sup>1</sup> which improves its overall accuracy, eliminates a possible discontinuity that can occur at the critical density, and allows it to correctly approach the pure component viscosity as the mole fraction of one of the mixture components approaches unity. The modification is to define the mass shape factor  $g_j$  in Equations (33) and (34) so that

$$g_j^{1/2} = \frac{\Delta\eta_j(T_j, \rho_j)}{\Delta\eta_o(T/f_j, \rho h_j)} f_j^{-1/2} h_j^{2/3} \quad (35)$$

The residual viscosity of pure fluid  $j$  appearing in the numerator of Equation (35) is evaluated at temperature  $T_j$  and density  $\rho_j$  deduced from the known mixture temperature  $T$  and density  $\rho$  as

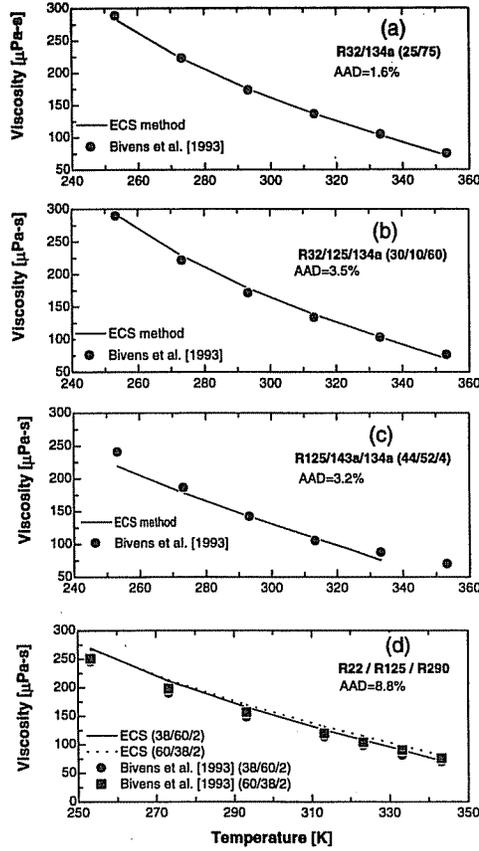
$$T_j = \frac{T f_j}{f_x} \quad (36)$$

$$\rho_j = \frac{\rho h_x}{h_j} \quad (37)$$

This residual viscosity is determined using either the pure fluid corresponding states method or a full surface viscosity correlation of experimental data if it is available. In the former case, the conformal density is determined using the  $\psi_j$  shape factor defined above so that the appropriate conformal temperature  $T^\circ$  and density  $\rho^\circ$  used to estimate the viscosity of fluid  $j$  in Equation (10) are

$$T^\circ = T_j / f_j \quad (38)$$

$$\rho^\circ = \rho_j h_j \psi_j \quad (39)$$



**Figure 6** Experimental and calculated saturated liquid mixture viscosity values for (a) R32/134a, (b) R32/125/134a, (c) R125/143a/134a and (d) R22/125/290

**Figure 6** Valeurs expérimentales et calculées de la viscosité du mélange liquide à saturation pour (a) R32/R134a et (b) R125/134a, (c) R125/143a/134a et (d) R22/125/290

Examination of the mixture viscosity Equations (23), (30)–(33) indicates that, in the limit as the mole fraction of one component approaches 1, defining  $g_j$  as indicated in Equation (35) results in the mixture viscosity correctly providing the pure component viscosity value, thereby eliminating an inconsistency between the different calculation methods.

Viscosity data for mixtures of environmentally acceptable refrigerants are sparse, but two sources are available. *Figure 5* provides a comparison of the saturated liquid viscosity values for binary mixtures (R32/134a) and (R125/134a) calculated by the extended corresponding states methodology described here with the experimental data of Ripple and Matar<sup>33</sup>. Bivens *et al.*<sup>31</sup> report experimental saturated liquid mixture viscosity for (R32/134a) and for the ternary mixtures (R32/125/134a) and (R125/143a/134a), and for two compositions of (R22/125/290). A comparison of the extended corresponding states method with their data appears in *Figure 6*. The mixture compositions (in mass percentages) are reported on the figures along with the average absolute deviations (AAD) between the experimental and calculated viscosities.

## Conclusions

The extended corresponding states method provides good estimates of the viscosity of pure refrigerants and mixtures. However, the accuracy of the method for pure component viscosity can be improved significantly by defining a third shape factor whose value is determined from available experimental viscosity data. A simple modification to the method of Huber and Ely<sup>1</sup> for estimating the viscosity of mixtures which eliminates discontinuities at the critical density and approaches the pure component viscosity value as a component mole fraction approaches 1 is proposed. Absolute average deviations between the calculated and experimental values are generally less than 4% for both pure fluids and mixtures.

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## References

- Huber, M. L., Ely, J. F. Prediction of viscosity of refrigerants and refrigerant mixtures *Fluid Phase Equilibria* (1992) **80** 45–46
- Younglove, B. A., McLinden, M. O. An international standard equation of state for the thermodynamic properties of refrigerant 123 (2,2-dichloro-1,1,1-trifluoroethane) *J. Phys. Chem. Ref. Data* (1994) **23** 731–780
- Tillner-Roth, R., Baehr, H. D. An international standard formulation of the thermodynamic properties of 1,1,1,2-tetrafluoroethane (HFC-134a) covering temperatures from 170 to 455 K at pressures up to 70 MPa *J. Phys. Chem. Ref. Data* (1994) **23** 657–729
- Tillner-Roth, R. Die thermodynamischen Eigenschaften von R152a, R134a und ihren Gemischen – Messungen und Fundamentalgleichungen, Forschungsbericht Nr. 41, DKV, Deutscher Kälte- und Klimatechnischer Verein e. V., Stuttgart, (1993)
- Hanley, H. J. M. Prediction of the viscosity and thermal conductivity coefficients for mixtures *Cryogenics* (1976) **16** 643–651
- Ely, J. F., Hanley, H. J. M. Prediction of transport properties. 1. Viscosity of fluids and mixtures *Ind. Eng. Chem. Fundam.* (1981) **20** 323–332
- Teja, A. S., Rice, P. Generalized corresponding states method for the viscosities of liquid mixtures. *Ind. Eng. Chem. Fundam.* (1981) **20** 77–81
- Ely, J. F. A predictive exact shape factor extended corresponding states model for mixtures *Adv. Cryog. Eng.* (1990) **35** 1511–1520
- Reid, R. C., Prausnitz, J. M., Poling, B. E. *The Properties of Gases and Liquids*, 4th edition, McGraw-Hill, New York (1987)
- Luettnmer-Strathmann, J., Sengers, J. V., Olchowy, G. A. Non-asymptotic critical behavior of the transport properties of fluids *J. Chem. Phys.* (1995) **103** 7482–7501
- Chapman, S., Cowling, T. G. *The Mathematical Theory of Nonuniform Gases*, Cambridge University Press, New York (1970)
- Kim, Y., Sonntag, R. E. Estimation of transport properties of refrigerants *ASME Winter Annual Meeting*, Paper 94-WA/HT-7, Chicago, IL (1994)
- Hwang, M., Whiting, W. B. A corresponding states treatment for the viscosity of polar fluids *Ind. Eng. Chem. Res.* (1987) **26** 1758–1766
- Monnery, W. D., Mehrotra, A. K., Syrczek, W. Modified shape factors for improved viscosity predictions using corresponding states *Can. J. Chem. Eng.* (1991) **69** 1213–1219
- Huber, M. L., McLinden, M. O. Thermodynamic properties of R134a (1,1,1,2-tetrafluoroethane) *Int. Refrigeration Conf.*, West Lafayette, IN (1992)
- Krauss, R., Luettnmer-Strathmann, J., Sengers, J. V., Stephan, K. Transport properties of 1,1,1,2-tetrafluoroethane (R134a) *Int. J. Thermophys.* (1993) **14** 951–988
- Laesecke, A. Improved correlation of the viscosity of 1,1,1,2-tetrafluoroethane (R134a) *Int. J. Thermophys.*, (submitted)
- Wilhelm, J., Vogel, E. Gas phase viscosity of the alternative refrigerant R134a at low densities *4th Asian Thermophysical Properties Conf.*, Tokyo (1995)
- Vogel, E. The viscosity of gaseous propane and its initial density dependence *Int. J. Thermophys.* (1995) **16** 1335–1351
- Rainwater, J. C., Friend, D. G. Second viscosity and thermal-conductivity virial coefficients of gases: extension to low reduced temperatures *Phys. Rev. A* (1987) **36** 4062–4066
- Krauss, R., Weiss, V. C., Edison, T. A., Sengers, J. V., Stephan, K. Transport properties of 1-1-difluoroethane (R152a) *Int. J. Thermophys.* (1996) **17** 731–757
- Younglove, B. A., Ely, J. F. Thermophysical properties of fluids. II. Methane, ethane, propane, isobutane, and normal butane *J. Phys. Chem. Ref. Data* (1987) **16** 577–798
- Press, W. H., Flannery, B. P., Teukosky, S. A., Vetterling, W. T. *Numerical Recipes in Pascal*, Cambridge University Press, New York (1989)
- Jacobsen, R. T., Penoncello, S. G., Lemmon, E. W. A fundamental equation for trichlorofluoromethane (R-11) *Fluid Phase Equilibria* (1992) **80** 45–56
- Kumagai, A., Takahashi, S. Viscosity of saturated liquid fluorocarbon refrigerants from 273 to 353 K *Int. J. Thermophys.* (1991) **12** 105–117
- Nagashima, A., Harada, J., Tanashita, I. Experimental studies on the viscosity of Freon-refrigerant, 1st report: experimental method and measurement of R-11 (in Japanese) *Trans. Jap. Soc. Mech. Engrs* (1975) **41** 656–661
- Assael, M. J., Polimatidou, S. K., Vogel, E., Wakeham, W. A. Measurements of the viscosity of R11, R12, R141b, and R152a in the temperature range of 270–340 K at pressures up to 20 MPa *Int. J. Thermophys.* (1994) **15** 575–589
- Marx, V., Pruß, A., Wagner, W. Neue Zustandsgleichungen für R 12, R 22, R 11 und R 113. Beschreibung des thermodynamischen Zustandsverhaltens bei Temperaturen bis 525 K und Drücken bis 200 MPa. *VDI-Fortschritt-berichte, Reihe 19: Wärmetechnik/Kältetechnik, Nr. 57*, VDI Verlag, Düsseldorf (1992)
- Kamei, A., Beyerlein, S. W., Jacobsen, R. T. Application of nonlinear regression in the development of a wide range formulation for HCFC-22 *Int. J. Thermophys.* (1995) **16** 1155–1164

- 30 **Diller, D. E., Aragon, A. S., Laesecke, A.** Measurements of the viscosities of saturated and compressed liquid chlorodifluoromethane (R22) *Int. J. Refrig.* (1993) **16** 19–22
- 31 **Bivens, D. B., Yokozeiki, A., Geller, V. Z., Paulaitis, M. E.** Transport properties and heat transfer of alternatives for R502 and R22, *R-22/R-502 Alternatives, ASHRAE/NIST Refrigerants Conf.*, Gaithersburg, MD (1993)
- 32 **Outcalt, S. L., McLinden, M. O.** Equations of state for the thermodynamic properties of R32 (difluoromethane) and R125(pentafluoroethane) *Int. J. Thermophys.* (1995) **16** 79–89
- 33 **Ripple, D., Matar, O.** Viscosity of the saturated liquid phase of six halogenated compounds and three mixtures *J. Chem. Eng. Data* (1993) **38** 560–564
- 34 **Oliveira, C. M. B. P., Wakeham, W. A.** The viscosity of R32 and R125 at saturation *Int. J. Thermophys.* (1993) **14** 1131–1143
- 35 **Diller, D. E., Aragon, A. S., Laesecke, A.** Measurements of the viscosities of saturated and compressed liquid 1,1,1,2-tetrafluoroethane (R134a), 2,2-dichloro-1,1,1-trifluoroethane (R123), and 1,1-dichloro-1-fluoroethane (R141b) *Fluid Phase Equilibria* (1993) **88** 251–262
- 36 **Diller, D. E., Peterson, S. M.** Measurements of the viscosities of saturated and compressed fluid 1-chloro-1,2,2,2-tetrafluoroethane (R124) and pentafluoroethane (R125) at temperatures between 120 and 420 K *Int. J. Thermophys.* (1993) **14** 55–63
- 37 **Outcalt, S. L., McLinden, M. O.** A modified Benedict–Webb–Rubin equation of state for the thermodynamic properties of R143a (1,1,1-trifluoroethane), Final report to Air-Conditioning and Refrigeration Technology Institute, Arlington, VA, report No. DOE/CE/23810-39, National Institute of Standards and Technology, Boulder, CO (1994)
- 38 **Outcalt, S. L., McLinden, M. O.** A modified Benedict–Webb–Rubin equation of state for the thermodynamic properties of R152a (1,1-difluoroethane) *J. Phys. Chem. Ref. Data* (1996) **25**
- 39 **Lapardin, N. I.** The viscosity of difluoroethane *Neft i Gaz (in Russian)* (1982) **25** 24–63
- 40 **Hirschfelder, J. O., Curtiss, C. F., Bird, R. B.** *Molecular Theory of Gases and Liquids*, Wiley, New York (1954)
- 41 **Ely, J. F.** An Enskog correction for size and mass difference effects in mixture viscosity prediction *J. Res. Natl. Bur. Stand. (U. S.)* (1981) **86** 597–604

## CYRANO: a computational model for the detailed design of plate-fin-and-tube heat exchangers using pure and mixed refrigerants

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A computational model for the detailed design of finned coils has been developed. This programme discretises heat exchangers into tube elements for which the governing equations are solved using local values of temperature, pressure, physical properties and heat transfer coefficients. Single-phase, condenser and evaporator cases can be automatically treated using water, R22, R134a, and refrigerant mixtures based on R32, R125, and R134a. The software can handle non-conventional coil circuits with different numbers of inlets and outlets, non-uniform air distribution at the coil inlet face, using smooth, wavy and louvered fins, and smooth and internally finned tubes. The programme has been validated on seven finned coils using pure fluids, with and without moisture condensation on the fins. Comparisons with tests show errors of less than 5% on the coil duty and of the order of 30% on the refrigerant pressure drop. A performance simulation of a coil using R22 and a ternary mixture is presented to validate the programme algorithms developed for mixtures. © 1997 Elsevier Science Ltd and IIR

(Keywords: heat transfer; heat exchanger; finned tube; battery; simulation; heat transfer coefficient; pressure loss, calculation)

## CYRANO: un modèle de calcul pour la conception détaillée d'échangeurs de chaleur à tubes et plaques-ailettes utilisant des frigorigènes purs et en mélange

*On a mis au point un modèle de calcul pour la conception détaillée de serpentins ailetés. Ce programme s'intéresse surtout aux éléments des tubes des échangeurs de chaleur pour lesquels les équations directrices sont résolues en utilisant des valeurs locales de température, pression, des propriétés physiques et des coefficients de transfert de chaleur. Les cas du fluide monophasique, du condenseur et de l'évaporateur peuvent être traités automatiquement en utilisant de l'eau, du R22, du R134a et des mélanges de frigorigènes à base de R32, de R125 et de R134a. Le logiciel peut traiter des circuits de serpentines non classiques avec plusieurs bouches d'aspiration et de refoulement, une distribution de l'air non uniforme à l'aspiration du serpentin, utilisant des ailettes lisses, ondulées et à persiennes, et des tubes lisses et à ailettes internes. Le programme a été validé avec 7 serpentins ailetés utilisant des fluides purs, avec et sans condensation sur les ailettes. Des comparaisons avec des essais montrent des erreurs inférieures à 5% pour le serpentin et ses possibilités, et de l'ordre de 30% pour la chute de pression du frigorigène. On présente une simulation de la performance d'un serpentin utilisant du R22 et un mélange ternaire, pour valider les algorithmes du programme mis au point pour les mélanges. © 1997 Elsevier Science Ltd and IIR*

(Mots clés: transfert de chaleur; échangeur de chaleur; tube aileté; batterie; simulation; coefficient d'échange thermique; perte de pression; calcul)

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