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Calculation of Second Virial Coefficients and Gaseous Viscosities of the Refrigerants HFC-32 (CH_2F_2), HFC-23 (CHF_3), and HCFC-22 ($CHClF_2$)

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The second virial coefficients of refrigerants HFC-32 (CH_2F_2), HFC-23 (CHF_3), and HCFC-22 ($CHClF_2$) have been correlated on the basis of site–site model potential and have been compared with experimental results. The molecular interactions consisted of repulsion–dispersion and electrostatic parts. From the site–site potentials adjusted to the experimental second virial coefficients, spherically averaged potentials have been determined and a subsequent calculation of gaseous viscosity has been carried out. Agreement between measured and calculated values of second virial coefficients and gaseous viscosity is satisfactory. Calculated values of second virial coefficients and gaseous viscosity beyond available experimental data, therefore, can be assumed as a reliable extrapolation to lower and higher temperatures.

KEY WORDS: alternative refrigerants; collision integrals; second virial coefficient; spherically averaged potential; viscosity.

1. INTRODUCTION

Difluoromethane (HFC-32; CH_2F_2), trifluoromethane (HFC-23; CHF_3), and chlorodifluoromethane (HCFC-22; $CHClF_2$) are halogenated derivatives of methane (CH_4) with strong dipole moments. Among them, in particular, HCFC-22 is being dominantly applied to conventional air-conditioning

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and heat-pumping equipment. HFC-32 and HFC-23 are promising alternatives to substitute HCFC-22, because they do not contain chlorine atoms, so their ozone depletion potential is zero. The global warming potential of HFC-32 may become smaller than that of HCFC-22, because the atmospheric life time for this refrigerant is shorter than HCFC-22, due to more hydrogen atoms in the HFC-32 molecule.

Presently, most of the experimental thermodynamic-property data are available [1]. In cases where only a limited set of experimental data is known, it would be highly desirable to have a theoretical scheme to predict other property values. The present paper focuses on this problem. First, we correlated the second virial coefficients on the basis of site–site potential. The repulsion–dispersion interactions were described by a distance-buffered potential: Buf 14-7(δ, γ). Minimum-energy separations and well depths of the Buf 14-7(δ, γ) potential were taken from the AMBER molecular mechanics force field [2]. The electrostatic interactions were approximated by a Coulombic potential. Charges were obtained by means of neutrality, the dipole-moment value, the degree of ionicity and the strength of the bonds between the central C atom and other atoms in the molecule. The interaction sites were considered at the atom nucleii and molecules were assumed as mechanically rigid bodies.

From the site–site potentials adjusted to the experimental second virial coefficients, spherically averaged potentials, their well depth, and their collision diameters as a function of temperature were determined. Subsequent evaluation of reduced collision integrals and gaseous viscosity was carried out.

2. THE SECOND VIRIAL COEFFICIENT

For the sake of comparison, the measured values of second virial coefficients [3] are shown in a reduced plot of B/v_c against T/T_c (Fig. 1); v_c is the critical molar volume and T_c is the critical temperature. One can observe that the curves for HFC-32, HFC-23, and HCFC-22 are rather steep (the steepest one is for the HFC-32), whereas the curve for methane as a reference fluid is flatter. The reduced virial coefficients for HFC-32 are more negative; those for HCFC-22 are more positive.

The second virial coefficient of a nonlinear molecule is given by Watts and McGee [4] as follows:

$$B(T) = -\frac{N_A}{16\pi^2} \int_0^{\infty} r^2\, dr \int_0^{\pi} \sin\theta\, d\theta \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta_2\, d\theta_2 \times \int_0^{2\pi} d\phi_2 \int_0^{2\pi} \{\exp[-\beta U(1,2)] - 1\}\, d\chi_2 \tag{1}$$

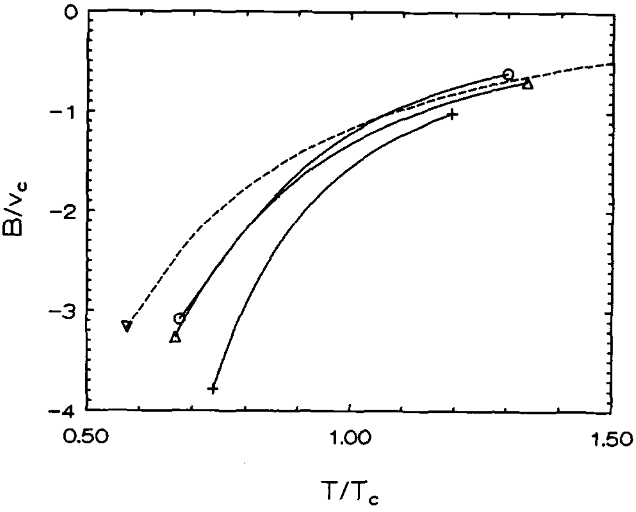

Fig. 1. The reduced second virial coefficient B/v_c against reduced temperature T/T_c; HFC-32 (+——+), HFC-23 (△——△), HCFC-22 (○——○), and methane as reference fluid (▽——▽).

where $\vec{r}$ is the vector joining the center of masses of molecule 1 and molecule 2, $r = |\vec{r}|$, (θ, ϕ) are the orientational angles of $\vec{r}$, $(\theta_2, \phi_2, \chi_2)$ are the Euler angles of molecule 2, and N_A is the Avogadro number. The orientation of molecule 1 is kept fixed at some arbitrary value. $\beta = 1/k_B T$, T is the temperature, and k_B is the Boltzmann constant. This six-dimensional integral is easily calculated with the aid of a nonproduct algorithm [5].

The molecules are represented by interaction sites located at the positions of atom nucleii and they are assumed to be mechanically rigid bodies. Molecular geometries [3] are listed in Table I.

The molecular interaction is pairwise additive, with a pair potential between molecules taken as the sum of site–site interactions. The site–site interactions consist of the repulsion–dispersion part described by the Buf 14-7(δ, γ) potential [6] and the electrostatic part is approximated by the Coulombic potential. The intermolecular pair potential $U(1, 2)$ can thus be written

$$U(1,2) = \sum_{i=1}^{5} \sum_{j=1}^{5} \varepsilon_{ij} \left[\frac{(1+\delta) R_{ij}}{r_{ij} + \delta R_{ij}} \right]^7 \left[\frac{(1+\gamma) R_{ij}^7}{r_{ij}^7 + \gamma R_{ij}^7} - 2 \right] + \sum_{i=1}^{5} \sum_{j=1}^{5} \frac{q_i q_j e^2}{4\pi\epsilon_0 r_{ij}} \qquad (2)$$

where r_{ij} is the distance between the sites of atom i on molecule 1 and atom j on molecule 2, ε_{ij} is the well depth, R_{ij} is the minimum-energy separation,

Table I. Molecular Geometries, Final Adjustment of the Buffering Constants δ of the Buf 14-7(δ, γ) Potential, and Dipole-Moment Value μ with Corresponding Charges q for HFC-32, HFC-23, and HCFC-22

	Geometry		Atom	q
				$\delta = 0.175$ $\mu = 7.588 \times 10^{-30}$ C · m
HFC-32 (CH_2F_2)	C–H	0.1093 nm		
	C–F	0.1357 nm	C	0.66
	H–C–H	112.5°	F	−0.31
	F–C–F	108.3°	H	−0.02
	H–C–F	108.7°		
				$\delta = 0.27$ $\mu = 4.956 \times 10^{-30}$ C · m
HFC-23 (CHF_3)	C–H	0.1098 nm		
	C–F	0.1332 nm	C	0.74
	F–C–F	108.8°	F	−0.24
	H–C–F	110.1°	H	−0.02
				$\delta = 0.155$ $\mu = 6.394 \times 10^{-30}$ C · m
HCFC-22 ($CHClF_2$)	C–H	0.109 nm		
	C–F	0.135 nm	C	0.66
	C–Cl	0.174 nm	F	−0.29
	F–C–F	107.0°	H	−0.02
	Cl–C–H	107.0°	Cl	−0.06
	Cl–C–F	110.5°		

δ and $\gamma = 0.12$ are the buffering constants, q_i and q_j are the charges on atoms i and j, e is the electron charge, and ϵ_0 is the vacuum permittivity. Combination rules used for repulsion–dispersion interactions between unlike atoms are Lorentz–Berthelot mixing rules. The well depths ε and the minimum-energy separations R for all atoms of interest [2] are listed in Table II.

The Buf 14-7(δ, γ) potential terms with the buffering constants δ and γ are combined to produce the repulsive part of the potential, while the δ-buffered term and the constant -2 describe the dispersion interaction. The buffered terms keep the potential being finite as $r_{ij} \to 0$. The use of the exponent 7 allows the dispersion term to reproduce the power-series expansion accurately (r_{ij}^{-6}, r_{ij}^{-8}, and r_{ij}^{-10}) for a distance up to several times that

Table II. AMBER Molecular Mechanics Force Field Well Depths ε and Minimum-Energy Separations R [2]

Atom–atom interaction	ε/k_B (K)	R (nm)
C	55.05	0.382
F	30.70	0.350
Cl	100.64	0.450
H	7.55	0.242 for CHF_3 and $CHClF_2$ 0.258 for CH_2F_2

for R_{ij}. A positive value for δ serves to dampen the dispersion term at a smaller r_{ij}. The shape parameter δ primarily controls the magnitude of the dispersion power-series expansion and influences only very slightly the distance and the magnitude of the potential minimum. These facts suggest that δ may be taken as an adjustable parameter for calculating of second virial coefficients.

To assign effective charges on the atoms in the molecules, a scheme which makes use of the charge neutrality, dipole-moment value, degree of ionicity, and strength of the bonds between the central C atoms and the other atoms in the molecules was applied [7]. Only the dipole-moment value must be specified to calculate the atomic charges according to this scheme. Charge neutrality requires

$$q_C + \sum n_j q_j = 0 \tag{3a}$$

where q_C is the charge on the carbon, q_j are the charges on atoms besides C, and n_j are the number of atoms of type j. The dipole moment μ is expressed as

$$\mu = q_C z_C + \sum n_j z_j q_j \tag{3b}$$

where z_j is the distance along the direction of the dipole moment from the center of charge of the molecule. If we introduce the bond strength ε_j and the degree of ionicity α_j of the jth bond, then we can form $J-1$ (J is the number of species besides C in the molecule) equations of the type

$$\alpha_i \varepsilon_i q_j l_i = \alpha_j \varepsilon_j q_i l_j \tag{3c}$$

where l_j is the length of the jth bond. This provides $J+1$ equations for the $J+1$ charges.

Trial and error adjustment of the buffering constant δ of Buf 14-7(δ, γ) potential and the dipole-moment value μ with the subsequent calculation of the second virial coefficients was carried out for the refrigerants HFC-32, HFC-23, and HCFC-22. Other potential parameters were not changed and the charges were calculated by means of Eqs. (3a)–(3c). It was found that changes in the adjustable parameters influenced the second virial coefficients in the following manner: an increase in δ reflects a similar increase in the absolute value of $B(T)$ at all temperatures, and a larger μ makes the $B(T)$ curve steeper. If the dipole-moment value μ increases, then δ decreases, and vice versa. The final adjustment of δ and μ (with corresponding charges) which gave the best agreement between calculated and experimental second virial coefficients is presented in Table I.

The calculated and measured second virial coefficients for HFC-32, HFC-23, and HCFC-22, together with standard (SD) and maximum (d.max.) deviations, are listed in Table III. Experimental values of $B(T)$ were taken from Hozumi et al. [8] for HFC-32, according to Ref. 3 for

Table III. Experimental and Calculated Values of Second Virial Coefficients $B(T)$ ($cm^3 \cdot mol^{-1}$) of HFC-32, HFC-23, and HCFC-22

HFC-32 (CH_2F_2)			HFC-23 (CHF_3)			HCFC-22 ($CHClF_2$)		
T (K)	B^{exp}	B^{cal}	T (K)	B^{exp}	B^{cal}	T (K)	B^{exp}	B^{cal}
200.0		−1026.7	180.0		−556.3	220.0		−763.9
221.5		−728.6	191.0	−479.5[b]	−482.7	240.0		−603.0
240.0		−567.0	220.0	−350.3[b]	−349.0	273.2	−439.6[b]	−432.5
273.2	−389.8[a]	−387.5	240.0	−288.4[b]	−287.7	298.0	−360.7[b]	−348.8
300.0	−292.7[a]	−298.2	273.2	−215.5[b]	−216.5	303.2	−345.8[b]	−334.3
325.0	−232.9[a]	−239.3	299.0	−175.9[b]	−177.4	323.2	−293.8[b]	−285.8
351.3	−189.0[a]	−193.5	325.0	−145.7[b]	−147.1	333.4	−270.7[b]	−264.8
375.0	−160.1[a]	−161.8	350.0	−123.4[b]	−123.9	348.2	−240.9[b]	−238.0
400.0	−136.9[a]	−135.1	375.0	−105.7[b]	−105.0	373.0	−199.8[b]	−200.4
420.0	−122.2[a]	−117.6	400.0	−91.6[b]	−89.3	424.5	−141.2[b]	−143.0
450.0		−95.9	450.0		−64.8	474.9	−105.1[b]	−103.8
500.0		−68.8	500.0		−46.5	500.0		−88.4
600.0		−33.9	600.0		−21.4	600.0		−43.9
700.0		−13.0	700.0		−5.0	700.0		−15.6
SD (%)	2.1			0.7			2.0	
SD	4.7			1.1			7.2	
d.max. (%)	−3.8			−1.7			−4.0	

[a] From Ref. 8.

[b] From Ref. 3.

HFC-23 and for HCFC-22. The uncertainty claimed in the measured data by Hozumi et al. [8] is up to 1%, and that in the experimental data reported in Ref. 3 is between 2 and 5%.

3. THE SPHERICALLY AVERAGED POTENTIAL

A definition of the spherically averaged potential follows from a comparison of the second virial coefficient of monatomic gases [9]:

$$B(T) = -2\pi N_A \int_0^\infty \{\exp[-\beta U(1,2)] - 1\}\, r^2\, dr \tag{4a}$$

with a Monte Carlo algorithm [10] for the integration of Eq. (1),

$$B(T) = -2\pi N_A \int_0^\infty \langle \exp[-\beta U(1,2)] - 1 \rangle\, r^2\, dr \tag{4b}$$

The spherically averaged potential $U_{sa}(r)$ can then be expressed as

$$U_{sa}(r) = -\beta \ln \langle \exp[-\beta U(1,2)] \rangle \tag{5}$$

where $\langle \exp[-\beta U(1,2)] \rangle$ is the value of the function between brackets averaged over all the relative orientations at a fixed separations r;

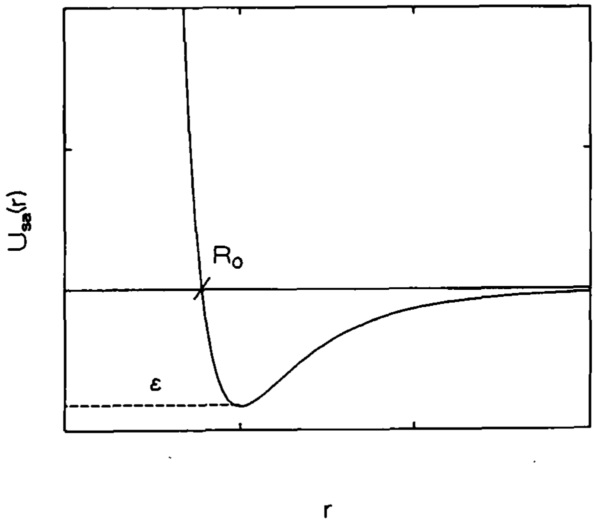

Fig. 2. Schematic drawing of the spherically averaged potential; R_0 is its collision diameter and ε is its well depth.

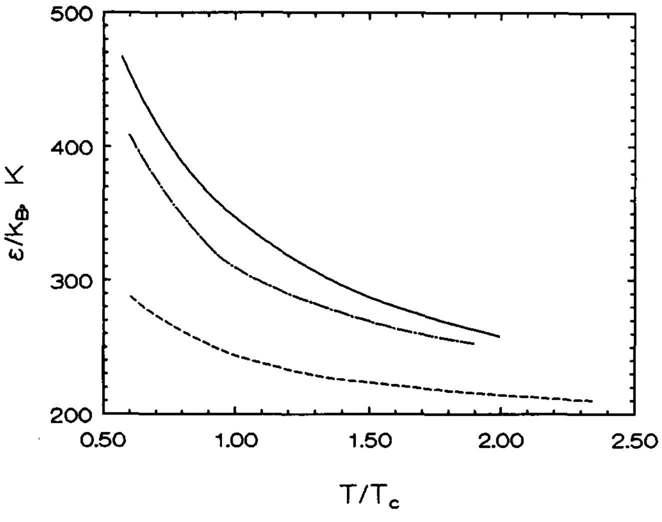

Fig. 3. Well depth of the spherically averaged potential ε/k_B against the reduced temperature T/T_c: HFC-32 (——), HFC-23, (– – –), and HCFC-22 (–·–·–).

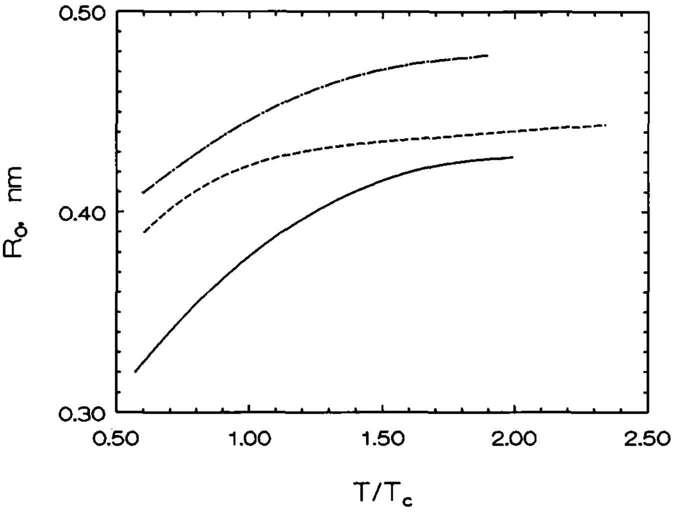

Fig. 4. Collision diameter of the spherically averaged potential R_0 against the reduced temperature T/T_c: HFC-32 (——), HFC-23, (– – –), and HCFC-22 (–·–·–).

$\langle \exp[-\beta U(1,2)] \rangle$ was calculated as the average over 1.5×10^6 random mutual orientations of molecules 1 and 2 at fixed separation r. A schematic drawing of the spherically averaged potential is shown in Fig. 2.

The well depth ε and the collision diameter R_0 of the spherically averaged potential as a function of reduced temperature T/T_c are shown for all substances in Figs. 3 and 4. One can see that the largest ε is for HFC-32 and the smallest is for HFC-23. The ratio among $\varepsilon^{\text{HFC-32}}$, $\varepsilon^{\text{HFC-23}}$, and $\varepsilon^{\text{HCFC-22}}$ is 1.0:0.7:0.9 at $T/T_c = 1$. The collision diameter of the spherically averaged potential R_0 has the largest value for HCFC-22 and the smallest for HFC-32. The ratio among $R_0^{\text{HFC-32}}$, $R_0^{\text{HFC-23}}$, and $R_0^{\text{HCFC-22}}$ is 1.0:1.1:1.2 at $T/T_c = 1$.

The spherically averaged potentials thus obtained, their ε and R_0 were then used as input for a numerical evaluation of the reduced collision integrals $\Omega^{(l,s)*}$ [11], which are needed for calculation of the gaseous viscosity. Figure 5 shows a comparison between the universal collision integral Ω_η^* (solid line) defined as [12]

$$\Omega_\eta^*(T^*) = \frac{\Omega^{(2,2)*}}{1 + (3/49)[4(\Omega^{2,3)*}/\Omega^{(2,2)*}) - (7/2)]^2} \tag{6}$$

and its calculated values for HFC-32, HFC-23, and HCFC-22. The functional $\Omega_\eta^*(T^*)$, which is universal for the interactions among monatomic gases, is also universal for the interactions between several quite complicated nonpolar molecules and some weakly polar molecules [12]. In our

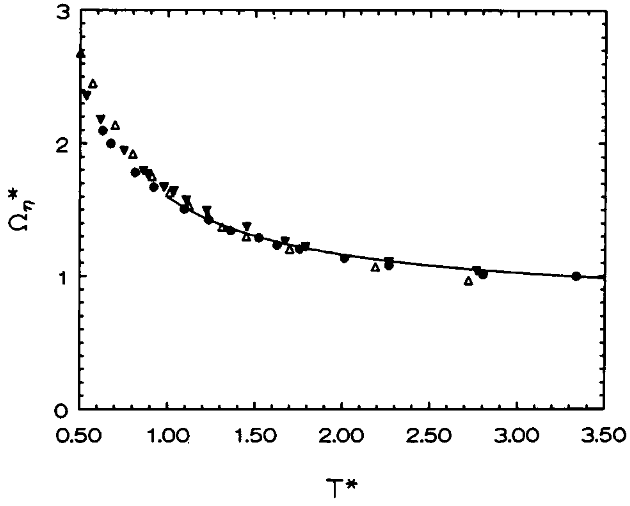

Fig. 5. Comparison of universal collision integral Ω_η^* (——) with model calculation: HFC-32 (△), HFC-23 (●), and HCFC-22 (▼).

case, the agreement between the universal correlation of $\Omega_\eta^*(T^*)$ and the calculated values of $\Omega_\eta^*(T^*)$ for weakly polar HFC-23; (CHF_3) and HCFC-22; ($CHClF_2$) is very good. The agreement is unsatisfactory for HFC-32; (CH_2F_2) due to the strong polar characteristics of its molecule. Polar characteristics of molecules can be described by the reduced dipole moment [13] $\mu^* = (\mu^2/4\pi\epsilon_0 \varepsilon R_0^3)^{1/2}$. The reduced dipole moment μ^* at $T/T_c = 1$ is 1.42 for HFC-32, 0.93 for HFC-23, and 0.98 for HCFC-22.

4. THE GASEOUS VISCOSITY

The viscosity η of a monatomic gas is given in terms of the collision integrals by the equation [12] (with η in Pa · s, R_0 in Å, and T in K)

$$\eta \cdot 10^7 = \frac{26.693\sqrt{MT}}{R_0^2 \Omega^{(2,2)*}} \left\{ 1 + \frac{3}{49} \left[4 \frac{\Omega^{(2,3)*}}{\Omega^{(2,2)*}} - \frac{7}{2} \right]^2 \right\} \tag{7}$$

where M ($g \cdot mol^{-1}$) is the relative molecular mass.

Table IV. Experimental and Calculated Values of Gaseous Viscosity η(Pa · s) of HFC-32, HFC-23, and HCFC-22

HFC-32 (CH_2F_2)			HFC-23 (CHF_3)			HCFC-22 ($CHClF_2$)		
T (K)	$10^7 \eta^{exp}$	$10^7 \eta^{cal}$	T (K)	$10^7 \eta^{exp}$	$10^7 \eta^{cal}$	T (K)	$10^7 \eta^{exp}$	$10^7 \eta^{cal}$
200.0		87.3	180.0		93.8	220.0		95.1
221.5		99.2	191.0		100.1	240.0	104.0[b]	103.7
240.0		110.3	220.0	111.4[b]	112.5	273.2	118.5[c]	120.4
273.2		120.7	240.0	120.8[b]	124.0	298.0	129.0[c]	131.4
298.15	127.0[a]	132.2	273.2	136.5[b]	139.3	300.65	128.9[d]	132.8
323.15	136.7[a]	141.5	299.0	149.0[b]	152.4	328.15	142.2[d]	144.7
348.15	147.0[a]	151.4	325.0	161.7[b]	163.3	368.15	157.6[d]	161.1
373.15	156.7[a]	163.0	350.0	174.1[b]	177.1	418.15	179.2[d]	178.8
398.15	167.7[a]	172.7	375.0	186.5[b]	188.4	424.5	177.8[b]	180.8
423.15	178.8[a]	182.7	400.0	199.0[b]	201.3	473.15	200.9[d]	200.1
450.0		190.5	450.0	224.1[b]	226.8	474.9		200.8
500.0		208.4	500.0		247.2	500.0		211.7
600.0		246.9	600.0		284.6	600.0		247.7
700.0		280.7	700.0		318.3	700.0		279.5
SD (%)	3.2			1.8			1.7	
10^7 SD	5.0			2.7			2.4	
d.max. (%)	3.9			2.6			2.9	

[a] From Ref. 14.

[b] From Ref. 15.

[c] From Ref. 17.

[d] From Ref. 16.

The results of the calculation of the gaseous viscosity η^{cal} for HFC-32, HFC-23, and HCFC-22 together with the standard (SD) and maximum (d.max.) deviations and a comparison with experimental data are presented in Table IV. Experimental values of gaseous viscosity η^{exp} were taken from Takahashi et al. [14] for HFC-32, from Ref. 15 for HFC-23, and from Kestin and Wakeham [16] and Takahashi et al. [17] for HCFC-22. The uncertainty reported in these measured data is up to 2%.

5. CONCLUSION

The second virial coefficients of the refrigerants HFC-32; (CH_2F_2), HFC-23; (CHF_3) and HCFC-22; ($CHClF_2$) have been correlated on the basis of a site–site model potential and compared with the experimental results. The agreement between calculated and measured values of second virial coefficients is satisfactory. The standard deviation does not exceed 2%, while the maximum deviation is up to −4% in the worst case of HCFC-22.

From the site–site potentials adjusted to the experimental second virial coefficients, the spherically averaged potentials, their well depth, and their collision diameter as a function of temperature were determined. They were used as input for the numerical calculation of the reduced collision integrals. A comparison between the universal collision integral and its calculated values for HFC-32, HFC-23, and HCFC-22 revealed that the agreement was very good for the weakly polar refrigerants HFC-23 and HCFC-22, but the agreement was unsatisfactory for HFC-32 due to the strong polar characteristics of its molecule. The values of gaseous viscosity calculated by using reduced collision integrals are systematically higher than the experimental data by about 3%. The calculated values of second virial coefficients and gaseous viscosity at lower and higher temperatures, because of their very good agreement in the experimentally investigated region, can be assumed to be a reliable extrapolation to these temperatures.

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