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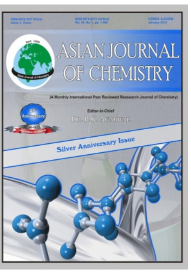

Prediction of Transport Properties of R142b Using A New Intermolecular Potential

Xiao-Po Wang*, Bo Song, Fu-Xin Yang and Zhi-Gang Liu

Key Laboratory of Thermo-Fluid Science and Engineering, Ministry of Education, Xi'an Jiaotong University, Xi'an 710049, P.R. China

*Corresponding author: Fax: +86 29 82668789; Tel: +86 29 82663708; E-mail: wangxp@mail.xjtu.edu.cn

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An iterative inversion scheme was used to determine the pair interaction potential of refrigerant R142b from a new correlation of collision integrals. According to the Chapman-Enskog theory and the Wang Chang-Uhlenbeck-de Boer scheme, transport properties of pure R142b were predicted by the new potential from 273.15 to 973.15 K at low-density, including viscosity, thermal conductivity, self-diffusion coefficient and thermal diffusion factor. The accuracy of the calculated values is estimated to be 1.5 % for viscosity, 5.0 % for thermal conductivity and 7.5 % for self-diffusion coefficient.

Key Words: Inversion method, Potential energy surface, Transport property, Refrigerant R142b.

INTRODUCTION

The transport properties of fluids, such as viscosity and self-diffusion coefficient, are important in many fields. It may not be possible to measure transport coefficients for all of the fluids, so they need to be supplemented by theoretical calculations, especially under high temperature conditions or in the low temperature region. From the statistical mechanics point of view, there are quantitative relationships between transport properties and potential energy functions[1,2]. With the help of well-established formulas derived from the kinetic theory of fluids, the predictions of transport properties will be straight forward if accurate intermolecular potentials are already known. Therefore, an inversion method has been developed in 1970s[3], which can extract the potential of a specific fluid from experimental data without any assumptions about it.

Based on the correlations of reduced collision integrals[4-6], the inversion scheme was modified and applied by researchers to generate interaction potentials for different kinds of simple gases[7-13], including monoatomic gases, diatomic gases and polyatomic gases. Recently, Papari and his co-workers have extended this method to determine the effective potentials of refrigerants[14-17], which are composed of multi-dimensional molecules with the larger size and lower symmetry. The invert potentials are good enough to predict transport properties within the experimental uncertainties.

In previous work, transport coefficients of CO_2-O_2 mixtures have been reported[18]. Present study is concerned with obtaining accurate transport properties of polar refrigerants by employing the inversion technique. The isotropic pair potential of refrigerant R142b was determined from a new corresponding-states correlation. From the new invert potential, four important transport properties of pure R142b were calculated using the Chapman-Enskog and the Wang Chang-Uhlenbeck-de Boer version of kinetic theory. The viscosity η, thermal conductivity λ, self-diffusion coefficient D and thermal diffusion factor α_0 were predicted in low-density regions as a function of temperature in the range 273.15-973.15 K.

COMPUTATIONAL METHOD

Transport properties: The collision integrals $\Omega^{(l,s)}$ are central to the classical mechanical description of transport properties of the dilute gas. For a pure gas at temperature 'T' with molecular mass 'm', the expressions of transport properties at low-density are[4],

$$\eta = \frac{5}{16}(\pi m k T)^{1/2}\frac{f_\eta}{\Omega^{(2,2)}} \tag{1}$$

$$\lambda = \frac{75}{64}\left(\frac{\pi k^3 T}{m}\right)^{1/2}\frac{f_\lambda}{\Omega^{(2,2)}} \tag{2}$$

$$D = \frac{3}{8}\left(\frac{\pi k^3 T^3}{m}\right)^{1/2}\frac{f_D}{P\Omega^{((1,1)}} \tag{3}$$

$$\alpha_0 = \frac{15}{2}\frac{(6C^* - 5)(2A^* + 5)}{A^*(16A^* - 12B^* + 55)}(1 + \kappa_0) \tag{4}$$

in which k is the Boltzmann constant (1.380658×10^{-23} J K^{-1}) and P the pressure of one atmosphere (101.3 kPa). The exact calculations require higher-order approximations of the kinetic theory. Therefore, f_η and f_λ up to the fifth-order approximations[19] were adopted, whereas f_D and κ_0 represent the second-order corrections to the corresponding property[4]. The quantities A^*-F^* can be estimated by the ratios of collision integrals[4],

$$A^* = \frac{\Omega^{(2,2)}}{\Omega^{(1,1)}} \tag{5}$$

$$B^* = \frac{[5\Omega^{(1,2)} - 4\Omega^{(1,3)}]}{\Omega^{(1,1)}} \tag{6}$$

$$C^* = \frac{\Omega^{(1,2)}}{\Omega^{(1,1)}} \tag{7}$$

$$E^* = \frac{\Omega^{(2,3)}}{\Omega^{(2,2)}} \tag{8}$$

$$F^* = \frac{\Omega^{(3,3)}}{\Omega^{(1,1)}} \tag{9}$$

In the Wang Chang-Uhlenbeck-de Boer theory (WCUB), the contributions of internal degrees of freedom can not be neglected when evaluating λ of polyatomic gases. Hence, the dilute gas thermal conductivity is derived as the sum of two components[20],

$$\lambda_{WCUB} = \lambda + \lambda_{int} \tag{10}$$

where λ denotes the value obtained directly from eqn. 8, whereas the second term λ_{int} corresponds to internal modes of energy transfer,

$$\lambda_{int} = \frac{f_{int}\eta}{m}\left(C_p - \frac{5}{2}R\right) \tag{11}$$

in which C_p is the molar heat capacity at constant pressure and R the Universal gas constant (8.314 J mol^{-1} K^{-1}). A modified version of f_{int} has been used and follows from,

$$f_{int} = \frac{1.3\Omega^{(2,2)}}{\Omega^{(1,1)}} \tag{12}$$

Inversion method: According to the Champan-Enskog solution of the Boltzmann transport equation, the collision integrals $\Omega^{(1,s)}$, which governed by potential energy functions of gases, can be defined as follow[2],

$$\Omega^{(1,s)}(T) = [(s+1)!(kT)^{s+2}]^{-1}\int_0^x Q^{(t)}(E)e^{-E/kt}E^{s+1}dE \tag{13}$$

where E is the relative kinetic energy and the energy-dependent cross sections $Q^{(l)}$ would be obtained by,

$$Q^{(t)}(E) = 2\pi\left[1 - \frac{1+(-1)^t}{2(1+1)}\right]^{-1}\int_0^x (1-\cos^l\theta)bdb \tag{14}$$

in which b represents the impact factor. The scattering angle θ depend on the collisions between molecules and can be written as,

$$\theta(E,b) = \pi - 2b\int_0^x \frac{dr/r^2}{\sqrt{1-b^2/r^2 - V(r)/E}} \tag{15}$$

where r is the separation between two molecules and V(r) the intermolecular potential energy. The distance r_0, showing the closest approach of molecules, can be estimated by the expression,

$$\frac{1-b^2}{r_0^2} - \frac{V(r_0)}{E} = 0 \tag{16}$$

In the inversion procedure, initially, we adopted an arbitrary potential model, like Lennard-Jones 12-6. Information about intermolecular forces, *i.e.*, the potential energy surface, can be evaluated by[3],

$$V^* = \frac{V(r)}{(\varepsilon/\kappa)} = G(T^*)T^* \tag{17}$$

$$r^* = \frac{r}{\sigma} = (\Omega^{*(2,2)}(T^*))^{1/2} \tag{18}$$

where ε/k is the well depth, σ the hard-sphere diameter and $G(T^*)$ the inversion variables. The reduced term $\Omega^{*(1,s)} = \Omega^{(1,s)}/\pi\sigma^2$ and $T^* = T/(\varepsilon/k)$. The correlation of $O^{*(2,2)}$, proposed by Najafi *et al.*[21], were used in the calculations. Then, from eqns. 13-18, the inversion process is repeated until converge. In principle, after two or three iterations, the results are close to the true values and the new potential V(r) can be determined.

RESULTS AND DISCUSSION

In order to generate the potential of refrigerant R142b, we employed a new and more accurate correlation function of $\Omega^{*(2,2)}(T^*)$ with two adjustable parameters[21]. The intermolecular potential of R142b was determined by using the iterative inversion procedure. The calculated values of $\Omega^{*(1,1)}$, $\Omega^{*(2,2)}$ and their ratios A^*-F^* are displayed in Table-1 over the reduced temperatures from 0.0 to 2.0. The new potential was used to predict transport properties of pure R142b in low-density regions from the kinetic theory of gases. The viscosity, self-diffusion coefficient and thermal diffusion factor are presented by eqns. 1, 3 and 4 at the temperature range between 273.15 and 973.15 K. In the case of thermal conductivity for polyatomic gases, it can be evaluated by eqn. 10 to correct its dependence on internal degrees of freedom.

To validate the quality of present calculations for transport properties, we compare the theoretically calculated values with available data from the literature (Figs. 1-3).

Viscosity: Among the viscosity data of pure R142b measured by an oscillating disk viscometer, those of Nabizadeh and Mayinger[22] agree well with the calculated values with average deviations of 0.76 %, whereas the data of Takahashi *et al.*[23] deviate by +(0.41 to 1.23) %. Haghighi *et al.*[17] calculated the viscosity of pure R142b from their invert potential. The differences between the data of Haghighi *et al.*[17] and the theoretical results of this work increase from -1.43 % at 290 K to -1.92 % at 350 K. Fig. 1 illustrates that most of experimentally based η data differ by no more than ± 1.5 % from the calculated values in the complete temperature range.

Thermal conductivity: As displayed in Fig. 2, the theoretically calculated values are compared with all the low-density experimental λ data, available in the literature at low and

TABLE-1
REDUCED COLLISION INTEGRALS AND THEIR RATIOS OF PURE R142b AS A FUNCTION OF REDUCED TEMPERATURE

log T^*	$\Omega^{*(1,1)}$	$\Omega^{*(2,2)}$	A^*	B^*	C^*	E^*	F^*
0.0	1.4151	1.5804	1.1169	1.2023	0.8443	0.8797	0.9171
0.1	1.2750	1.4202	1.1138	1.1775	0.8545	0.8888	0.9243
0.2	1.1579	1.2889	1.1131	1.1584	0.8667	0.9007	0.9346
0.3	1.0606	1.1828	1.1152	1.1451	0.8792	0.9126	0.9470
0.4	0.9797	1.0965	1.1193	1.1364	0.8907	0.9226	0.9601
0.5	0.9116	1.0249	1.1243	1.1305	0.9005	0.9303	0.9727
0.6	0.8535	0.9639	1.1293	1.1258	0.9086	0.9360	0.9840
0.7	0.8032	0.9105	1.1336	1.1218	0.9153	0.9402	0.9936
0.8	0.7590	0.8630	1.1371	1.1183	0.9207	0.9434	1.0013
0.9	0.7197	0.8201	1.1395	1.1152	0.9252	0.9458	1.0074
1.0	0.6844	0.7809	1.1411	1.1127	0.9289	0.9478	1.0118
1.1	0.6523	0.7449	1.1420	1.1106	0.9319	0.9494	1.0151
1.2	0.6228	0.7114	1.1423	1.1089	0.9343	0.9508	1.0174
1.3	0.5956	0.6803	1.1423	1.1074	0.9363	0.9521	1.0190
1.4	0.5703	0.6513	1.1421	1.1062	0.9379	0.9532	1.0203
1.5	0.5466	0.6242	1.1419	1.1051	0.9393	0.9543	1.0213
1.6	0.5244	0.5987	1.1417	1.1043	0.9404	0.9552	1.0222
1.7	0.5034	0.5747	1.1416	1.1036	0.9413	0.9559	1.0229
1.8	0.4835	0.5520	1.1416	1.1031	0.9420	0.9565	1.0236
1.9	0.4646	0.5304	1.1417	1.1027	0.9426	0.9570	1.0241
2.0	0.4466	0.5099	1.1417	1.1025	0.9430	0.9573	1.0245

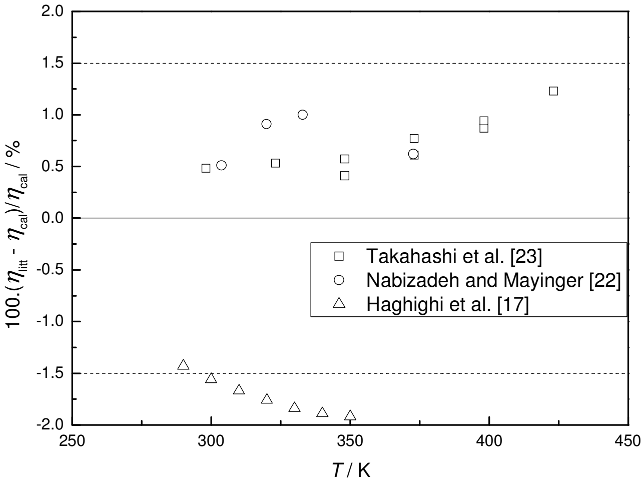

Fig. 1. Relative deviations of the literature viscosity coefficient, η_{litt}, from the values calculated in the present work, η_{cal}, for pure R142b

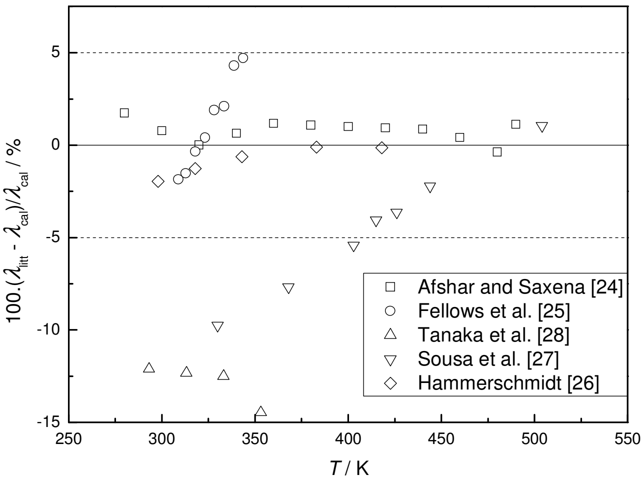

Fig. 2. Relative deviations of the literature thermal conductivity coefficient, λ_{litt}, from the values calculated in the present work, λ_{cal}, for pure R142b

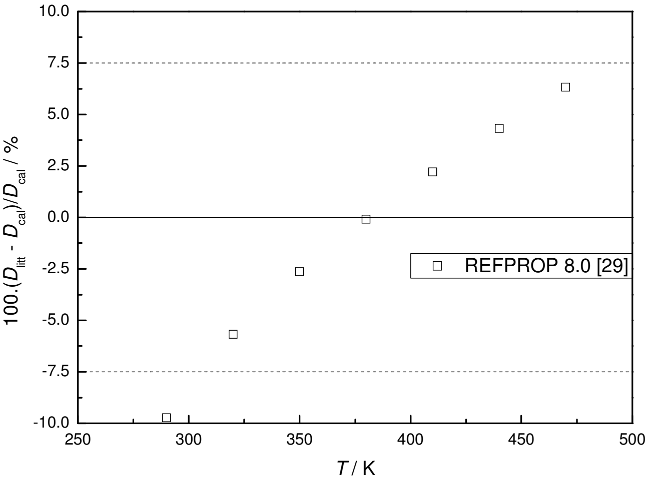

Fig. 3. Relative deviations of the literature self-diffusion coefficient, D_{litt}, from the values calculated in the present work, D_{cal}, for pure R142b

medium temperatures for pure R142b. The relative measurements by Afshar and Saxena performed[24] with the hot wire technique, deviate from the calculated values on average by ± 1.74 %, whereas the data of Fellows *et al.*[25] differ by -1.85 % at 308.93 K and by + 4.71 % at 343.65 K. Hammerschmidt[26] based their absolute measurements with a parallel-plate apparatus, resulting in negative differences of -0.11 % to -1.96 %. The experimental values between 330 and 504 K were gained by Sousa *et al.*[27] from the concentric-cylinder method, which are characterized by deviations of -9.76 % near to ambient temperature and down to +1.04 % with increasing temperature. The data of Tanaka *et al.*[28], also obtained by a concentric-cylinder instrument, deviate by more than -10 % from the calculated results. Fig. 2 makes obvious that 29 from 36 data points of λ measured in Refs.[24-28] agree within ± 5.0 % with that of theoretical values for the whole temperature range.

Self-diffusion coefficient: To the best of our knowledge, no experimental self-diffusion data have been reported for pure R142b in the literature. Hence, the recommended values of REFPROP 8.0[29] were used to check the quality of the calculated results. Fig. 3 reveals that the data of REFPROP 8.0 do not deviate by more than ± 7.5 % from the calculated values of this work, with the exception of one data point at 290 K.

Due to the lack of accurate data in the literature, a comparison of α_0 is not included for pure R142b. As a summary, the theoretically calculated values are estimated to be accurate within ± 1.5 % for viscosity, ± 5.0 % for thermal conductivity and ± 7.5 % for self-diffusion coefficient, which are not large with respect to the uncertainties of measurements. In principle, the differences for D are acceptable for its small values compared with viscosity and thermal conductivity at the same temperature. The predicted results are listed in Table-2, which contain the viscosity η, the thermal conductivity λ, the self-diffusion coefficient D and the thermal diffusion factor α_0 at temperatures from 273.15 to 973.15 K.

Conclusion

In this work, the isotropic pair potential of refrigerant R142b was determined from the inversion method by using a new correlation function of reduced collision integrals $\Omega^{*(2,2)}$. Based on the Chapman-Enskog version of kinetic theory,

TABLE-2
TRANSPORT PROPERTIES OF PURE R142b
AS A FUNCTION OF TEMPERATURE

T (K)	η (μPa s)	λ (mW m^{-1} K^{-1})	D (101.3 kPa) (10^{-4} m^2 s^{-1})	α_0
273.15	9.649	11.08	0.0289	0.0530
293.15	10.34	12.41	0.0332	0.0668
313.15	11.02	13.78	0.0377	0.0814
333.15	11.70	15.19	0.0426	0.0964
353.15	12.37	16.62	0.0477	0.1114
373.15	13.02	18.08	0.0530	0.1263
423.15	14.62	21.82	0.0675	0.1617
473.15	16.16	25.61	0.0834	0.1939
523.15	17.65	29.43	0.1008	0.2227
573.15	19.08	33.24	0.1196	0.2480
623.15	20.47	37.01	0.1396	0.2703
673.15	21.81	40.73	0.1609	0.2900
723.15	23.12	44.40	0.1835	0.3073
773.15	24.40	48.02	0.2073	0.3227
873.15	26.86	55.09	0.2583	0.3485
973.15	29.22	61.96	0.3139	0.3693

transport properties of pure R142b were predicted from the new invert potential at low-density, including viscosity, self-diffusion coefficient and thermal diffusion factor. In addition, the Wang Chang-Uhlenbeck-de Boer theory was employed to calculate dilute gas thermal conductivity to include the contributions of internal degrees of freedom. The theoretically calculated values are in reasonable agreements with the literature data for all considered transport properties at temperatures from 273.15 to 973.15 K. The inversion method is effective in evaluating transport coefficients of refrigerants to supplement the experimental data at high temperatures.

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