

DETERMINATION OF THE POTENTIAL ENERGY SURFACES OF REFRIGERANT MIXTURES AND THEIR GAS TRANSPORT COEFFICIENTS

by

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In this work, the inversion scheme was used to determine the potential energy surfaces of five polar refrigerant mixtures. The systems studied here are R123-R134a, R123-R142b, R123-R152a, R142b-R134a, and R142b-R152a. The low density transport coefficients of the refrigerant mixtures were calculated from the new invert potentials by the classical kinetic theory. The viscosity coefficient, binary diffusion coefficient, and thermal diffusion factor were computed for the temperature range from 313.15-973.15 K. The agreement with the NIST viscosity data demonstrates that the present calculated values are accurate enough to supplement experimental data over an extended temperature range. Correlations of the transport properties were also provided for the refrigerant mixtures at equimolar ratios.

Key words: *potential energy surface, inversion method, transport coefficient, polar refrigerant mixture*

Introduction

The knowledge of transport coefficients is important in many fields of fundamental science and engineering. It is not practically possible to measure the transport properties for all fluids, especially under extreme temperature conditions. Therefore, theoretical predictions have been utilized to supplement experimental data where measurements are difficult. From the statistical mechanics point of view, the macroscopic properties of fluids are determined by interactions between molecules. The evaluations of transport coefficients will be straightforward if the interaction potentials are already known. Basically, there are three major ways to obtain the potential energy surface: theoretical calculations, experimental measurements, and methods combining both approaches. The *ab initio* method can determine the potential energy without the application of experimental data. However, the extensive quantum-mechanical computations have limited its extension to larger molecules with more electrons [1].

On the other hand, since there are quantitative relationships between them, the information of intermolecular potentials can also be extracted from measurements on transport properties. The common way is to perform a cut-and-try procedure [2]. Potential

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parameters, like the hard sphere diameter, are varied until the smallest discrepancy is achieved between experimental data and the calculated values. In this approach, the optimal potential from one property, say diffusion coefficient, may fail to produce another property, say viscosity coefficient, with the desired accuracy. This shortcoming has resulted in a search for more effective solutions. Among these efforts, a semi-empirical inversion scheme was first proposed in 1970s [3]. It employs transport property data to obtain the interaction potential without knowing its function form and parameters in advance. Later, the inversion method was further improved by including some new correlations of reduced collision integrals [4-6], and has recently been applied to a wide variety of diatomic and polyatomic gases [7-13].

In previous work, we have studied the interaction potentials of two polyatomic gas mixtures containing CO₂ [14, 15] and one refrigerant R142b [16] by the inversion technique. Refrigerant mixtures are considerably involved in refrigeration, air-conditioning, and heat pump units [17]. In addition, they are used in many industrial processes as good blowing agents [18]. Hence, there are great demands for the transport properties of refrigerant mixtures in different temperature conditions. This work is concerned with five practically important refrigerant mixtures: R123-R134a, R123-R142b, R123-R152a, R142b-R134a, and R142b-R152a. The novelty of the present investigation is to extend the inversion scheme to polar refrigerant mixtures. The effective and isotropic potentials of the refrigerant mixtures were determined from a corresponding-states correlation of collision integrals [19]. The new invert potentials were utilized to calculate the low density transport properties of refrigerant mixtures by the classical kinetic theory. The viscosity coefficient, binary diffusion coefficient, and thermal diffusion factor were computed over a wide temperature range from 313.15-973.15 K.

Model and methods

Inversion method

In the classical kinetic theory of gases, the collision integrals $\Omega^{(l,s)}$, containing the information on transport coefficients, can be expressed as a function of the temperature, T [20]:

$$\Omega^{(l,s)}(T) = \left[(s+1)! (kT)^{s+2} \right]^{-1} \int_0^{\infty} Q^{(l)}(E) e^{-E/kT} E^{s+1} dE \quad (1)$$

in which l and s are the weighting factors for molecular collisions. The cross-sections $Q^{(l)}$ are determined over wide ranges of the collision energy, E :

$$Q^{(l)}(E) = 2\pi \left[1 - \frac{1+(-1)^l}{2(1+l)} \right]^{-1} \int_0^{\infty} (1 - \cos^l \theta) b db \quad (2)$$

where b is the impact parameter. The scattering angle, θ , depends upon the two-body collisions between molecules and are defined:

$$\theta(E, b) = \pi - 2b \int_{r_0}^{\infty} \frac{dr}{r^2 \sqrt{1 - \frac{b^2}{r^2} - \frac{V(r)}{E}}} \quad (3)$$

in which $V(r)$ is the potential energy surface and r – the separation between molecules. The distance r_0 represents the closest approach of the colliding molecules and can be solved from the condition:

$$1 - \frac{b^2}{r_0^2} - \frac{V(r_0)}{E} = 0 \quad (4)$$

In the inversion scheme, an arbitrary potential model, such as the Lennard-Jones 12-6, can be used as the initial function form to evaluate the interaction potential by [21]:

$$V^* = \frac{V(r)}{\frac{\varepsilon}{k}} = G(T^*)T^* \quad (5)$$

$$r^* = \frac{r}{\sigma} = [\Omega^{*(2,2)}(T^*)]^{1/2} \quad (6)$$

where ε/k is the well depth of the potential, σ – the zero location of the potential, and $G(T^*)$ – the inversion parameters. A superscript * denotes that the collision integrals are scaled by σ :

$$\Omega^{*(l,s)} = \frac{\Omega^{(l,s)}}{\pi\sigma^2} \quad (7)$$

in which the reduced temperature $T^* = T/(\varepsilon/k)$. The correlations for $\Omega^{*(2,2)}(T^*)$ are usually available in the literature. The inversion procedure is repeated through eqs. (1)-(7) until convergence. After two or three iterations, the final results are very close to the true values and we can determine the new potential energy surface. The basic steps of the inversion technique are given briefly in fig. 1.

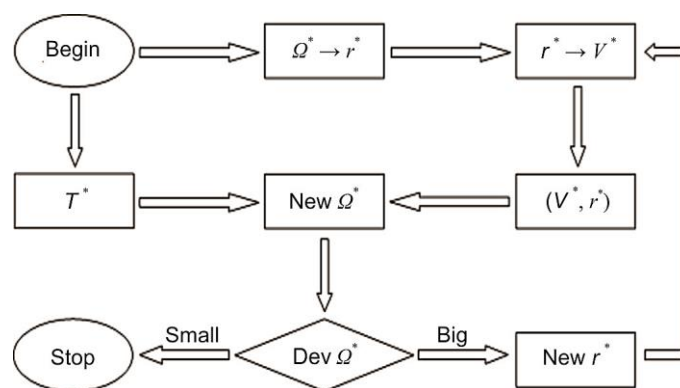


Figure 1. Flow diagram of the inversion scheme

Transport coefficient

For a binary mixture of gases 1 and 2, the transport coefficients are evaluated according to [4]:

$$\eta_{\text{mix}} = \frac{1 + Z_{\eta}}{X_{\eta} + Y_{\eta}} \quad (8)$$

$$D_{12} = \frac{3}{8} \sqrt{\frac{\pi k^3 T^3 (m_1 + m_2)}{2m_1 m_2}} \frac{1 + \Delta}{P\Omega_{12}^{(1,1)}(T_{12})} \quad (9)$$

$$\alpha_T = (6C_{12}^* - 5) \frac{x_1 S_1 - x_2 S_2}{x_1^2 Q_1 + x_1 x_2 Q_{12} + x_2^2 Q_2} (1 + \kappa_2) \quad (10)$$

where η_{mix} is the viscosity coefficient, D_{12} – the binary diffusion coefficient, α_T – the thermal diffusion factor, k – the Boltzmann constant, $1.380658 \cdot 10^{-23}$ [J/K], m – the molecular mass, P – the pressure of one atmosphere, 101.3 kPa, and x – the mole fraction. The subscript ij represents the quantities from the interaction potential between molecules i and j and Δ is the second-order correction to the binary diffusion coefficient. For the thermal diffusion factor, the factor κ_2 is negligible in the calculations due to its small magnitude. The quantities X_η , Y_η , and Z_η can be evaluated by:

$$X_\eta = \frac{x_1^2}{\eta_1} + \frac{2x_1 x_2}{\eta_{12}} + \frac{x_2^2}{\eta_2} \quad (11)$$

$$Y_\eta = \frac{3}{5} A_{12}^* \left[\frac{x_1^2}{\eta_1} \left(\frac{m_1}{m_2} \right) + \frac{2x_1 x_2}{\eta_{12}} \frac{(m_1 + m_2)^2}{4m_1 m_2} \left(\frac{\eta_{12}^2}{\eta_1 \eta_2} \right) + \frac{x_2^2}{\eta_2} \left(\frac{m_2}{m_1} \right) \right] \quad (12)$$

$$Z_\eta = \frac{3}{5} A_{12}^* \left\{ x_1^2 \left(\frac{m_1}{m_2} \right) + 2x_1 x_2 \left[\frac{(m_1 + m_2)^2}{4m_1 m_2} \left(\frac{\eta_{12} + \eta_{12}}{\eta_1 \eta_2} \right) - 1 \right] + x_2^2 \left(\frac{m_2}{m_1} \right) \right\} \quad (13)$$

In addition, S and Q have the form:

$$S_1 = \frac{m_1}{m_2} \sqrt{\frac{2m_2}{m_1 + m_2}} \frac{\Omega_{11}^{(2,2)}}{\Omega_{12}^{(1,1)}} \left(\frac{\sigma_{11}}{\sigma_{12}} \right)^2 - \frac{4m_1 m_2 A_{12}^*}{(m_1 + m_2)^2} + \frac{15m_2 (m_1 - m_2)}{2(m_1 + m_2)^2} \quad (14)$$

$$Q_1 = \frac{2}{m_2 (m_1 + m_2)} \left(\frac{2m_2}{m_1 + m_2} \right)^{1/2} \frac{\Omega_{11}^{(2,2)}}{\Omega_{12}^{(1,1)}} \left(\frac{\sigma_{11}}{\sigma_{12}} \right)^2 \left[\left(\frac{5}{2} - \frac{6}{5} B_{12}^* \right) m_1^2 + 3m_2^2 + \frac{8}{5} m_1 m_2 A_{12}^* \right] \quad (15)$$

$$Q_{12} = 15 \left(\frac{m_1 - m_2}{m_1 + m_2} \right)^2 \left(\frac{5}{2} - \frac{6}{5} B_{12}^* \right) + \frac{4m_1 m_2 A_{12}^*}{(m_1 + m_2)^2} \left(11 - \frac{12}{5} B_{12}^* \right) + \frac{8(m_1 + m_2)}{5(m_1 m_2)^{1/2}} \left[\frac{\sigma_{11}^2 \Omega_{11}^{(2,2)}}{\sigma_{12}^2 \Omega_{12}^{(1,1)}} \right] \left[\frac{\sigma_{22}^2 \Omega_{22}^{(2,2)}}{\sigma_{12}^2 \Omega_{12}^{(1,1)}} \right] \quad (16)$$

The formulas for S_2 and Q_2 can be gained from S_1 and Q_1 by exchange of subscripts. The quantities $A^* - C^*$, which characterize the interactions between like and unlike pairs, are defined as the ratios of different collision integrals:

$$A^* = \frac{\Omega^{(2,2)}}{\Omega^{(1,1)}} \quad (17)$$

$$B^* = \frac{5\Omega^{(1,2)} - 4\Omega^{(1,3)}}{\Omega^{(1,1)}} \quad (18)$$

$$C^* = \frac{\Omega^{(1,2)}}{\Omega^{(1,1)}} \quad (19)$$

Results and discussion

The inversion scheme was utilized to determine the potential energy surfaces of five refrigerant mixtures: R123-R134a, R123-R142b, R123-R152a, R142b-R134a, and R142b-R152a. Najafi *et al.* [19] developed an accurate collision integral correlation with only

two adjustable parameters. The wide-ranging equation of Najafi *et al.* [19] was adopted in the inversion procedure to improve the quality of interaction potential. The details of the new potentials were provided in a tabulated form in the supplementary material. The transport coefficients of the refrigerant mixtures were calculated from the new invert potentials by the kinetic theory of gases. The viscosity coefficient, binary diffusion coefficient, and thermal diffusion factor were predicted at low density for the temperature range from 313.15-973.15 K.

A comprehensive survey was undertaken for the transport property data of the refrigerant mixtures. Since no direct measurements are available in the literature, the comparisons with experimental data were not included for the considered refrigerant mixtures. As a result, we employed the viscosity data recommended by NIST [22] to check the quality of the present calculated values. In fig. 2, the calculated values of R123-R134a are in excellent agreement with the data by NIST within $\pm 0.18\%$ from 313-473 K. The theoretical results of R142b-R134a in this work are (0.10–0.81)% higher than those by NIST from 313-423 K. For the refrigerant mixtures R142b-R152a, the calculated values of this work show deviations of $\pm(0.01\text{--}0.69)\%$ at temperatures from 313-473 K.

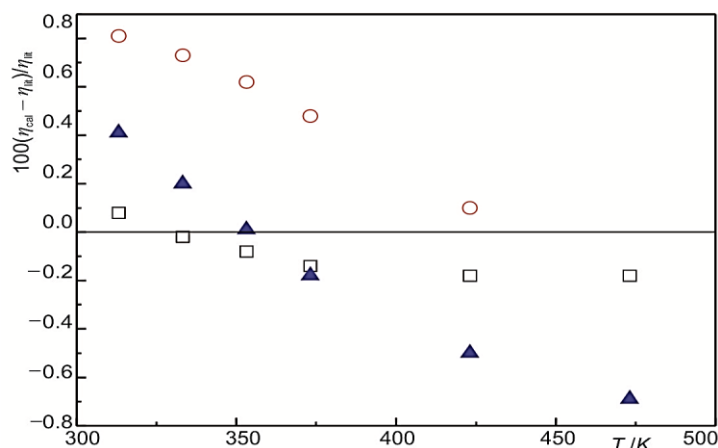


Figure 2. Relative deviations of the viscosity coefficient calculated in this work; η_{cal} from the data recommended by NIST [22], η_{lit} for the refrigerant mixtures at equimolar concentrations. Sources: \square R123-R134a, \circ R142b-R134a, and \blacktriangle R142b-R152a

The transport coefficients computed from the invert potentials were correlated as a function of temperature for the refrigerants mixtures at equimolar ratios. We used the non-linear least-squares technique to fit the calculated values to the following equations:

$$\ln \frac{\eta_{\text{mix}}}{\eta_0} = a_\eta \ln \frac{T}{T_0} + \frac{b_\eta}{T} + \frac{c_\eta}{T^2} + d_\eta \quad (20)$$

$$\ln \frac{D_{12}}{D_0} = a_D \ln \frac{T}{T_0} + \frac{b_D}{T} + c_D \quad (21)$$

$$\alpha_T = a_\alpha + b_\alpha T + c_\alpha T^2 + d_\alpha T^3 + e_\alpha T^4 \quad (22)$$

where $\eta_0 = 1 \mu\text{Pa}\cdot\text{s}$, $T_0 = 1 \text{ K}$, and $D_0 = 1 \cdot 10^{-4} \text{ m}^2/\text{s}$. The coefficients of eqs. (20)-(22) were given in tabs. 1-3 over the temperature range from 313.15-973.15 K.

Table 1. Coefficients of eq. (20)

Mixtures	a_η	b_η , [K]	c_η , [K ²]	d_η
R123-R134a	0.53642	-207.566	11458.23	-0.06594
R123-R142b	0.56331	-185.578	9196.939	-0.32004
R123-R152a	0.52713	-240.261	15635.32	-0.00716
R142b-R134a	0.61554	-150.941	6062.092	-0.65507
R142b-R152a	0.54841	-234.841	15707.35	-0.16482

Table 2. Coefficients of eq. (21)

Mixtures	a_D	b_D , [K]	c_D
R123-R134a	1.65866	-94.3433	-12.6569
R123-R142b	1.68013	-86.0805	-12.8502
R123-R152a	1.68845	-93.8832	-12.6543
R142b-R134a	1.69649	-87.6513	-12.6965
R142b-R152a	1.67442	-100.318	-12.3743

Table 3. Coefficients of eq. (22)

Mixtures	a_α	b_α , [K ⁻¹]	c_α , [K ⁻²]	d_α , [K ⁻³]	e_α , [K ⁻⁴]
R123-R134a	-0.05154	2.83832E-4	-2.52553E-9	-2.52346E-10	1.3215E-13
R123-R142b	-0.06221	3.66729E-4	-2.59787E-7	1.37337E-11	3.85742E-14
R123-R152a	-0.05062	1.63929E-4	6.72669E-7	-1.02613E-9	4.18202E-13
R142b-R134a	0.00363	-1.91636E-5	7.99311E-9	7.52171E-12	-5.45372E-15
R142b-R152a	-0.01987	2.02127E-5	5.41721E-7	-7.22584E-10	2.81678E-13

Conclusions

In this work, the isotropic potentials of five polar refrigerant mixtures were determined by the inversion method from a collision integral correlation of Najafi *et al.* [19]. The systems considered here are R123-R134a, R123-R142b, R123-R152a, R142b-R134a, and R142b-R152a. The new invert potentials were used to calculate the transport coefficients of the refrigerants mixtures by the classical kinetic theory of dilute gases. The viscosity coefficient, binary diffusion coefficient, and thermal diffusion factor were computed for the temperature range of 313.15-973.15 K. The NIST data over a limited temperature range was compared with the present calculated values to assess the quality of this work. The mean absolute deviations are 0.11% for R123-R134a, 0.55% for R142b-R134a, and 0.33% for R142b-R152a. The maximum deviations are 0.18% for R123-R134a, 0.81% for R142b-R134a, and 0.69% for R142b-R152a. The good agreement shows that the transport property values of this work are accurate enough to supplement experimental data for refrigerant mixtures. The calculated values at equimolar concentrations were also correlated as a function of temperature to satisfy the needs of different areas.

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Nomenclature

A, B, C, E – ratios of collision integrals
 D_{12} – binary diffusion coefficient ($\cdot 10^{-4}$), [m^2s^{-1}]
 G – inversion parameter
 k – Boltzmann constant, [JK^{-1}]
 m – mass of molecule, [kg]
 P – pressure, [MPa]
 $Q^{(l)}$ – cross-section, [m^2]
 r – molecule separation, [m]
 T – temperature, [K]
 V – potential energy, [J]
 x – mole fraction

Greek symbols

α_T – thermal diffusion factor
 Δ, κ_2 – second-order correction factor

ε – well depth, [J]
 η – viscosity, [$\mu\text{Pa}\cdot\text{s}$]
 θ – scattering angle, [rad]
 σ – hard sphere diameter, [m]
 $\Omega^{(l,s)}$ – collision integral, [Jm^2]

Superscripts

* – reduced

Subscripts

mix – mixture
1 – gas with heavier molecular mass
2 – gas with light molecular mass
12 – interaction

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