VISCOSITY AND SECOND VIRIAL COEFFICIENT OF CCl_4 AND CCl_4–CH_4 MIXTURE

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Abstract. Potential parameters of an isotropic $(n-6)$ potential with temperature depended equilibrium distance r_m^{eff} and potential well depth ε^{eff} are justified by a simultaneous reproducing of the measured second virial coefficient B and viscosity η of the pure CCl_4 and interaction second virial coefficient B_{12} of the mixture CCl_4–CH_4. The potential parameters of the ground state and the enlargement of the first excited level were justified by a minimization of the squared sum of deviations between the experiment and the model calculations. The temperature dependency of the equilibrium distance does not depend on the experimental data and was defined by means of the vibrational partition function.

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1. Introduction

Second virial coefficient B and viscosity η of the CCl_4 are scarcely measured and the temperature range of the experimental second virial coefficient data is relatively narrow. The available recommended values of $B(T)$ [1, 2] and viscosity $\eta(T)$ [3, 4] present approximations and extrapolations of the corresponding experiments by means of the (12-6) Lennard-Jones potential. Different pairs of parameters r_m-ε of the (12-6) potential have been derived from the measured η [5] or B [6] data. The drawback of this approach is that it cannot be used to calculate simultaneously $B(T)$ and $\eta(T)$. The problem was solved using the rationalized VESM model [7] to restore the isotropic temperature-depending potential of binary CCl_4–CCl_4 and CCl_4–CH_4 interactions.

2. Brief Description of the Theoretical Background

A detailed description of the model is given elsewhere [7-9]. We used an $(n-6)$ Lennard-Jones model with temperature dependent equilibrium distance r_m^{eff} and po-

tential well depth ε^{eff}.

$$r_{mls}^{\text{eff}}(T) = r_m(T = 0) + \delta_{ls}^{\text{eff}}(T), \qquad \varepsilon_{ls}^{\text{eff}} = \varepsilon_{ls}\left(\frac{r_m}{r_{mls}^{\text{eff}}}\right)^6 \tag{1}$$

$$\delta_{ls}^{\text{eff}}(T) = \left\langle \sum_{k,l} \delta\left[C_k x_k(T) + C_l x_l(T)\right] \right\rangle \tag{2}$$

where $x_k(T)$ is the relative population of the k-th vibrationally excited state at given temperature T $\left(\sum_k x_k(T) = 1\right)$ and C_k for the harmonic oscillator [10] are known constants equal to the enlargement of the excited level k normalized to the enlargement of the first level δ. Subscripts l and s note interactions between "like" ($l = s$) and "unlike" ($l \neq s$) molecules. The temperature dependence of the equilibrium distance is attributed to the change in x_k with the temperature.

The parameters r_m, and ε (corresponding to the potential parameters defined at $T = 0$ K), the repulsive parameter n and the enlargement of the first excited states δ were determined by the minimization of the sum of squared relative deviations between experimental and calculated B and η normalized to the experimental error a_{exp}.

3. Results and Discussion

All available data for B, η and interaction second virial coefficient B_{12} are presented in Table 1. Altogether 41 experimental points from 6 experiments were considered as primary data and formed the set for restoring potential parameters. We put into the procedure 19 experimental points of B [6, 11, 12] as well as 18 of η [13–15]. Four values of the CCl₄–CH₄ interaction second virial coefficient B_{12} [16] were also taken into account. The secondary data of B [1, 2] and of η [3, 4] were used as a set for evaluation.

Table 1. Experimental data of pure CCl₄ and CCl₄–CH₄ mixture

Authors	Substance	Property	M	Temperature range (K)	Experimental error (%)	Symbol
Lambert et al. (1949)	CCl₄	B	10	319–351	4	+
Francis and McGlashan (1955)	CCl₄	B	5	316–343	4	○
Pérez Masiá et al. (1964)	CCl₄	B	4	354–419	4	□
Dymond and Smith (1980)	CCl₄	B^*	4	320–420	4	△
Lucas (1987)	CCl₄	η	3	398–573	2–4	◇
Braune and Linke (1930)	CCl₄	η	9	296–760	3	○
Titani (1933)	CCl₄	η	6	401–588	3	+
Lapidus et al. (1968)	CCl₄	η^*	10	273–573	3	△
Vargaftîc (1975)	CCl₄	η^*	7	273–873	3	□
Gupta and King (1972)	CCl₄–CH₄	B_{12}	4	273–348	10	●

* secondary data

In the minimization procedure we used for justification of the parameters only primary data. Our best solution achieved with the defined temperature dependence [7] of the equilibrium distance is: $n = 19.4$, $r_m = 5.528 \times 10^{-10}$ m, $\varepsilon = 742.3$ K and $\delta = 0.0032 \times 10^{-10}$ m. The repulsive parameter $n_{12} = 38.5$ for CCl_4–CH_4 mixture was defined as a fifth parameter in the procedure of the minimization. The interaction second virial coefficient B_{12} was calculated using the scheme described in details in [17]. The experimental data [16] were reproduced with rms of $0.9a_{exp}$.
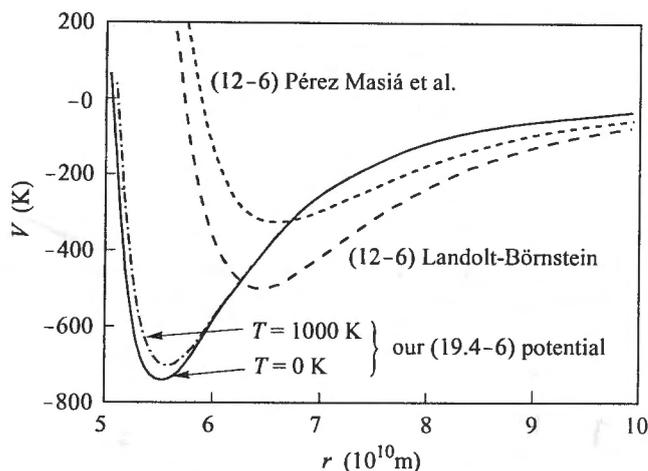
Fig. 1. A comparison between CCl_4–CCl_4 potential proposed by different authors

Table 2. A comparison between CCl_4–CCl_4 potentials proposed by different authors

Authors	Property	n	ε (K)	$10^{10}r_m$ (m)	C_6 (a.u.)	rms
Landolt-Börnstein (1955)	η	12.0	327.0	6.60	3898	10.31
Pérez Masiá et al. (1964)	B	12.0	497.0	6.44	5113	3.64
Our solution	B and η	19.4	742.3	5.528	2212	0.81

C_6 is the dispersion constant in atomic units

We compared the relative deviations between experimental and calculated using different intermolecular potentials B and η. In Fig. 1 we present our potential at 0 and 1000 K and the (12–6) potentials derived from the second virial coefficient [6] and from the viscosity [5]. Corresponding parameters (shown in Table 2) were used to calculate deviations of all considered data of B (Fig. 2a and η (Fig. 2b). It is obvious that the best simultaneous fit can be obtained only with our (19.4–6) potential. Each one of the other two available potentials approximates well only the properties of the type used in the procedure of restoring (B or η). The sum of the squared deviations F calculated for 62 (primary and secondary data) in both cases is larger ($F = 820a_{exp}$ with potential of [6] and $F = 6592a_{exp}$ — with that of [5] compared to $F = 41a_{exp}$ obtained with our potential).
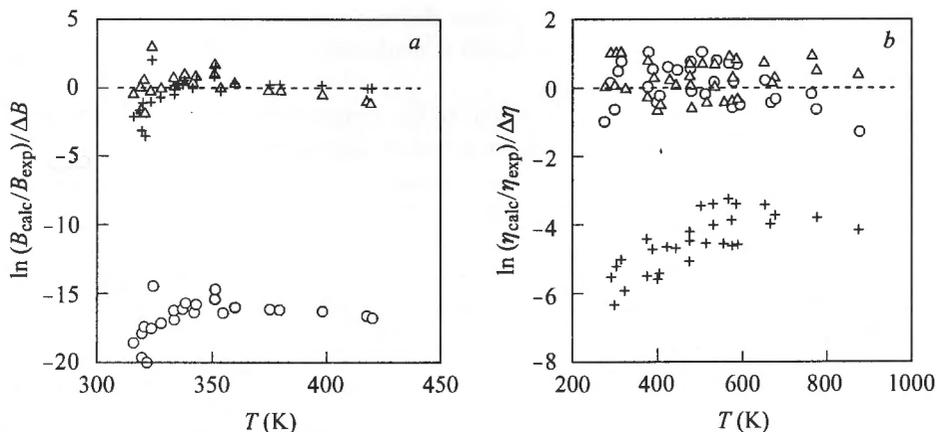
Fig. 2. The deviations between experimental data (zero line) and calculations performed using our potential ($\triangle$), Pérez Masiá et al. ($+$) or Landolt-Börnstein ($\bigcirc$)

(*a*) — second virial coefficients, (*b*) — viscosity

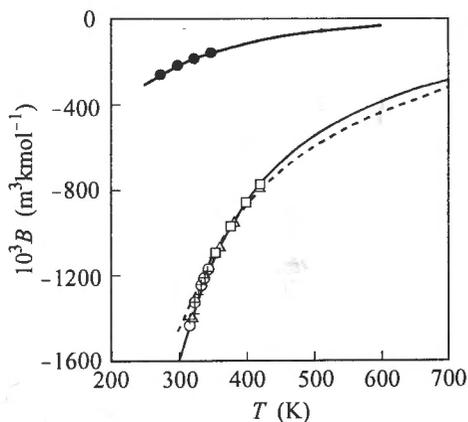**Fig. 3.** Second virial coefficient of pure CCl₄ and CCl₄–CH₄ (Gupta and King [16]) Experimental data are shown by symbols from Table 1, our calculations — by full lines and extrapolation of Gloushko — by dashed line
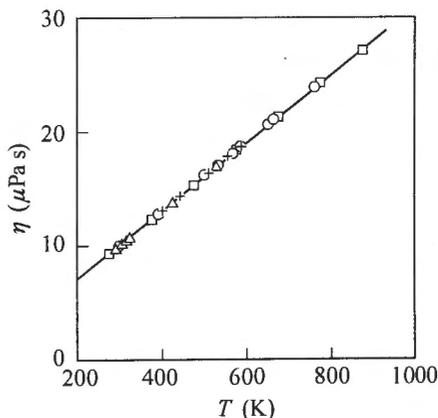
Fig. 4. Viscosity of pure CCl₄ Experimental data are shown by symbols from Table 1, our calculations — by full line

The temperature dependences $B(T)$ and $\eta(T)$ calculated with our potential are plotted in Figs 3 and 4 correspondingly. We present there the primary and secondary data (shown by symbols from Table 1) and the obtained with the same potential parameters curve (full line). When the minimization procedure was repeated including reference data for B [2] and for η [3, 4] the potential parameters were changed unessentially. The difference between our calculations and those received with the use of the polynomial dependence recommended in the temperature range $T = 300$ to 1000 K [1] (short dash

line in Fig. 3 is of about 10-15 %. We believe that recommended by us $B(T)$ [18] for $T = 200$ to 1000 K is more reliable because it is made using the results of simultaneous approximation of B and η.

The calculated B_{mix} and η_{mix} as functions of the temperature and the mole fractions of the mixture CCl_4-CH_4 constitutions are given in Figs 5a and 5b.
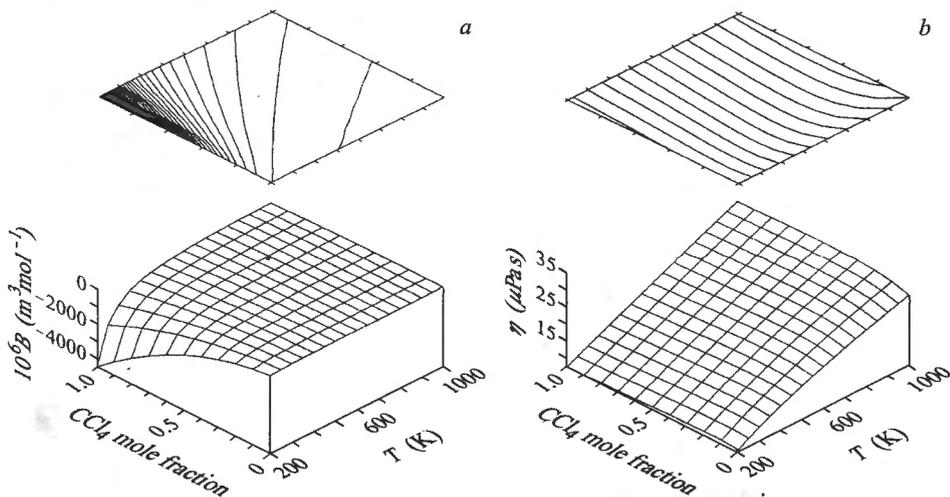

Fig. 5. The thermophysical properties of CCl_4-CH_4 mixtures as functions of the temperature T and the mole fractions of CCl_4 (x)

$$(a) - B_{mix}(T, x), (b) - \eta_{mix}(T, x)$$

Acknowledgements

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