

RESEARCH NOTE

Improved results for the potential parameters of methyl and methylene obtained from second virial coefficients of n-alkanes

By ANTONIO LÓPEZ RODRÍGUEZ†, CARLOS VEGA, JUAN J. FREIRE‡
and SANTIAGO LAGO

Departamento de Química Física, Facultad de Ciencias Químicas,
Universidad Complutense, 28040 Madrid, Spain

(Received 28 June 1993; accepted 27 July 1993)

Second virial coefficients of n-alkanes have been evaluated using the rotational isomeric state model. Methyl and methylene groups have been modelled as Lennard-Jones (12-6) sites differing in size and in energy well depth. The parameters have been chosen to reproduce experimental values of second virial coefficients of a number of n-alkanes in a broad range of temperatures. The new proposed parameters improve the description of the experimental data with respect to our previous work (López Rodríguez, A., Vega, C., Freire, J. J., and Lago, S., 1991, *Molec. Phys.*, **73**, 691). Moreover, differences in the fitted size and well depth of the methyl and methylene groups appear now as physically reasonable.

In previous work [1–3], we have described a Monte Carlo method for obtaining binary properties of n-alkanes with a rotational isomeric state model in which the methyl and methylene groups are considered as Lennard-Jones (12-6) interaction sites (LJ). Recent interest in this or similar models [4–6] has induced us to revise our results in an effort to resolve the remaining inconsistencies in the reproduction of experimental data for second virial coefficients $B_2(T)$. Thus we have attempted a more systematic way to fit our numerical results to the existing experimental values. With this aim, we have established a new fitting criterion. According to this criterion, the fits should provide similar relative differences (though with opposite signs) between the numerical and experimental values at the lowest and highest temperatures for which the data have been obtained. Simultaneously, we have detected a mistake in our code that affects the calculation of the z coordinate in a terminal site of one of the interaction chains. This error may slightly affect the numerical fitting parameters. Consequently, we have decided to make a complete recalculation of the second virial coefficients, perform new fits, and compare the final results with those of [1] and [3]. (Our calculations for viscosity coefficients in the dilute gas phase [2], based on the same model, are not affected by this revision.)

In the light of the new results, we have verified that the conclusions described in [1] (where we modelled the methyl and methylene groups as identical sites) can still

† Present address: Centro de Investigación REPSOL Petroleo S.A., c/Embajadores 183, 28045 Madrid, Spain.

‡ Author to whom correspondence should be addressed.

Table 1. Corrected values of $(\epsilon/k)/\text{K}$ obtained from fits of the theoretical results for $B(T)$ to experimental data or empirical predictions for n-alkanes at several temperatures (with $\sigma = 3.923 \text{ \AA}$).

n	ϵ/k
4	74
5	67.5
6	65.5
7	62.5
8	60.5
16	53.5

Table 2. Fitted potential parameters of methyl and methylene groups ϵ_1/k and ϵ_2/k (in K) obtained with the fixed values of σ_1 and σ_2 and the procedures described in [3].

Set	$\sigma_1/\text{\AA}$	$\sigma_3/\text{\AA}$	$(\epsilon_1/k) \text{ K}$	$(\epsilon_2/k) \text{ K}$	$(\epsilon_3/k) \text{ K}$	ϵ_1/ϵ_3
I	3.70	3.70	116	81.2	56.8	2.04
II	3.923	3.923	104	71.9	49.7	2.09
III	3.983	3.863	102	72.3	51.3	1.99
IV	4.123	3.723	96	73.8	56.7	1.69
V	4.323	3.523	92	77.0	65.5	1.43

Table 3. Averaged relative deviation $\Delta(\%)$ between the calculated and experimental values of $B(T)$ for n-alkanes. Calculations performed: Δ^a , with the parameter set of table 1; Δ^b , with parameter set I of table 2; Δ^c , with parameter set II of table 2; and Δ^d , with parameter set IV of table 2.

n	$\Delta^a(\%)$	$\Delta^b(\%)$	$\Delta^c(\%)$	$\Delta^d(\%)$
4	7.8	7.3	7.9	7.5
5	5.5	7.5	8.4	6.9
6	5.3	5.4	6.1	4.6
7	4.2	4.4	5.4	4.4
8	3.1	3.4	4.3	3.8
Average	5.2	5.6	6.4	6.0

be considered valid, though precise best fits for the site-site LJ parameter ϵ yield values slightly different from those previously reported (see table 1).

However, when different well-depths for the methyl-methyl, and methylene-methylene interactions, ϵ_1 and ϵ_3 , are considered, following the procedures described in [3], we find further differences which deserve a more detailed description. Thus, in table 2 we present different sets of LJ parameters, which correspond to the best fits of ϵ_1 and ϵ_3 , and several choices for the LJ length parameters σ_1 and σ_3 (the same choices selected in reference [3]). The results in this table exhibit interesting variations with respect to those contained in the equivalent table 8 of [3]. In particular, set IV in table 2 contains values of the parameters compatible with the range of differences in ϵ and σ that one can expect for the methyl and methylene groups according to atom-atom potentials [4, 7]. In table 3 we present the average relative deviations between the calculated and experimental data for the different sets of

Table 4. Simulation results for $B(T)$ ($\text{cm}^3 \text{mol}^{-1}$) obtained with set IV of table 2 for different n-alkanes at different temperatures, compared with experimental data from [8].

n	T/K	$B(T)_{\text{exp}}/\text{cm}^3 \text{mol}^{-1}$	$B(T)/\text{cm}^3 \text{mol}^{-1}$
4	250	-1170 ± 30	-1060
	280	-862 ± 20	-828
	340	-535 ± 20	-552
	400	-370 ± 20	-395
	560	-164 ± 10	-187
6	320	-1640 ± 60	-1519
	360	-1180 ± 40	-1139
	400	-900 ± 30	-888
	500	-510 ± 20	-527
	600	-318 ± 15	-342
8	380	-1990 ± 140	-1960
	440	-1310 ± 100	-1339
	520	-834 ± 40	-881
	580	-638 ± 40	-674

parameters. Since these deviations are similar in all the cases and can be considered as reasonably low (about 5%), we can propose now set IV in table 2 as a realistic choice of parameters which can simultaneously describe the experimental data or empirical predictions for the second virial coefficients of n-alkanes, from n-butane to n-hexadecane, in the range of temperatures of about 300 K for which these data are available. As a final illustration, we include in table 4 a comparison between our numerical results obtained with set IV and experimental data.

This work has been supported by Grants PB92-0227 and PB91-0364 of the DGICYT. Correspondence with J. Nagy (Department of Chemistry, Queen's University, Ontario, Canada) led to detection of the code mistake reported in the text.

References

- [1] LÓPEZ RODRÍGUEZ, A., and FREIRE, J. J., 1988, *Molec. Phys.*, **63**, 591.
- [2] FREIRE, J. J., and LÓPEZ RODRÍGUEZ, A., 1988, *Molec. Phys.*, **63**, 601.
- [3] LÓPEZ RODRÍGUEZ, A., VEGA, C., FREIRE, J. J., and LAGO, S., 1991, *Molec. Phys.*, **73**, 691.
- [4] PADILLA, P., and TOXVAERD, S., 1992, *Molec. Phys.*, **75**, 1143.
- [5] YETHIRAJ, A., CURRO, J. G., SCHWEIZER, K. S., and MCCOY, J. D., 1993, *J. chem. Phys.*, **98**, 1635.
- [6] NAGY, J., Private communication.
- [7] JORGENSEN, W. L., MADURA, J. D., and SWENSON, C. J., 1984, *J. Am. chem. Soc.*, **106**, 6638.
- [8] DYMOND, J. H., CHOLINSKI, J. A., SZAFRANSKI, A., and WYRZYKOWSKA-STANKIEWICZ, D., 1986, *Fluid Phase Equilibria*, **27**, 1.