THE SECOND VIRIAL COEFFICIENTS OF n-ALKANES AND THEIR MIXTURES FROM THE KIHARA CONVEX CORE INTERMOLECULAR PAIR POTENTIAL

Jan PAVLÍČEK[a], Karel AIM[a] and Tomáš BOUBLÍK[b]

[a] *Institute of Chemical Process Fundamentals,*
Academy of Sciences of the Czech Republic, 165 02 Prague 6-Suchdol, The Czech Republic
[b] *Department of Physical and Macromolecular Chemistry,*
Charles University, 128 40 Prague 2, The Czech Republic

Received April 19, 1993
Accepted June 15, 1993

Dedicated to Professor Otto Wichterle on the occasion of his 80th birthday.

The second virial coefficients for a series of C_2 to C_8 n-alkanes and the second virial cross coefficients for their binary mixtures were calculated as a function of temperature from the exact expressions derived for the Kihara rod-like molecules. The three parameters of the Kihara pair potential, ε/k, σ and l for the individual compounds were either used as determined from vapour–liquid equilibrium and saturated liquid density data in a previous study or with ε/k adjusted to the second virial coefficient data. The results are accurate almost within experimental uncertainty estimates of the data. In the case of mixtures the second virial cross coefficients were calculated from a similar expression in which only the ε_{12}/k parameter was adjusted whereas $\sigma_{12} = (\sigma_1 + \sigma_2)/2$ and l_1 and l_2 of pure compounds were employed. It appears that the correction factor to the geometric mean combining rule for ε_{12}/k is always less than and close to unity. Comparison with the values obtained from the Tsonopoulos generalized correlation reveals fair agreement between the characteristic binary k_{12} parameters from the two methods.

The second virial coefficient, $B(T)$, is of practical interest as a basic thermodynamic quantity which makes it possible to determine the state behaviour of gases and their mixtures at normal and moderately elevated pressures. From the theoretical point of view, $B(T)$ can be directly determined from exact expression on the basis of known intermolecular pair potential, see e.g. ref.[1].

In our recent work[2] we have successfully applied the perturbation theory of the Kihara convex molecule fluid to describe the vapour–liquid equilibrium coexistence region of pure n-alkanes ranging from ethane to hexadecane. The parameters of the Kihara pair potential[3] evaluated from the vapour pressure and saturated liquid density data (for the reduced temperatures, $T_r = T/T_c$, from the range 0.6 to 0.85) were found to obey simple dependencies on the number of carbon atoms in the n-alkane molecule.

In this paper we employ the exact expressions for $B(T)$ of the Kihara molecules to calculate the second virial coefficients of n-alkanes and the second virial cross coefficients for their seventeen binary mixtures. In the first step we use the values of all three Kihara potential parameters as obtained in ref.[2]. In the second step we retain two of the three formerly[2] determined parameters, namely σ and l, and by using a parameter estimation procedure we adjust the ε/k parameter to obtain the best fit of the experimental second virial coefficient data. To calculate the cross-terms we make use of the parameters l_i and l_j and of the simple combining rules $\sigma_{ij} = (\sigma_i + \sigma_j)/2$, and (as a first estimate) $\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$. To get a better fit, we introduce the correction factor $(1 - k_{ij})$ to the geometric mean rule for ε_{ij}. The results so obtained are then compared with the corresponding values calculated from the commonly used generalized correlation for the second virial coefficients and cross coefficients.

THEORETICAL

The Kihara convex core intermolecular potential has the following form,

$$u^{K}(s) = 4\varepsilon\left[\left(\frac{\sigma}{s}\right)^{12} - \left(\frac{\sigma}{s}\right)^{6}\right] = \varepsilon\left[\left(\frac{\sigma_0}{s}\right)^{12} - 2\left(\frac{\sigma_0}{s}\right)^{6}\right], \qquad (1)$$

where s is the shortest surface-to-surface distance of the hard cores, ε is the depth of the potential well, σ_0 is the distance of the potential minimum and σ is the distance where the potential is equal to zero. If V, S and R are the geometric functionals of the hard core (i.e. the volume, surface and the $1/4\pi$-multiple of the mean curvature integral), then the second virial coefficient is given by relation[3]

$$B = N_A\left[\frac{2\pi}{3}\sigma_0^3 F_3(T^*) + 4\pi R\,\sigma_0^2 F_2(T^*) + (S + 4\pi R^2)\,\sigma_0 F_1(T^*) + (V + RS)\right], \qquad (2)$$

where N_A is the Avogadro number and T^* the reduced temperature, $T^* = kT/\varepsilon$, where k is the Boltzmann constant. For the functions $F_m(T^*)$ it holds

$$F_m(T^*) = \int_0^\infty \{1 - \exp[-(\xi^{-12} - 2\xi^{-6})/T^*]\}\,\mathrm{d}(\xi^m) =$$

$$= -\frac{m}{12}\sum_{i=0}^{\infty}\frac{2^i}{i\,!}\,\Gamma\left(\frac{6i - m}{12}\right)T^{*-(6i+m)/12}. \qquad (3)$$

In the case of the virial cross coefficient $B_{ij}(T)$ for unlike molecules i and j the intermolecular potential has characteristic parameters ε_{ij}, σ_{ij}, σ_{0ij} and we have to consider different cores with geometric functionals R_i, S_i, V_i and R_j, S_j, V_j, respectively. The relation for $B_{ij}(T)$ is somewhat more complicated, namely

$$\begin{aligned} B_{ij} &= (N_A/2)\,[(4\pi/3)\,\sigma_{0ij}^3 F_3(T_{ij}^*) + 4\pi(R_i + R_j)\,\sigma_{0ij}^2 F_2(T_{ij}^*) + \\ &+ (S_i + S_j + 8\pi R_i R_j)\,\sigma_{0ij} F_1(T_{ij}^*) + (V_i + V_j + R_i S_j + R_j S_i)]\,. \end{aligned} \tag{4}$$

The functions F_m may be expressed in the form of expansions in powers of T^*; these expansions can further be written in the form of simple Padé approximants in terms of the square root of the reduced temperature[4]. The latter form was adopted in this work.

For the determination of the parameters ε_{ij} and σ_{ij} of unlike interactions we used the following simple combining rules,

$$\sigma_{ij} = (\sigma_i + \sigma_j)/2\,, \tag{5}$$

$$\varepsilon_{ij} = (1 - k_{ij})\sqrt{\varepsilon_i\,\varepsilon_j}\,. \tag{6}$$

For comparisons with a generalized second virial coefficient correlation we employed the formulation due to Tsonopoulos, see e.g. ref.[5]. Basically, the correlation is an expansion (with universal coefficients) in powers in inverse reduced temperature, $T_r = T/T_c$, where T_c is the critical temperature. In the case of mixtures, a correction factor with a characteristic binary parameter (here denoted as q_{ij}) enters in a combining rule for the pseudocritical temperature of a mixture,

$$T_{cij} = (1 - q_{ij})\sqrt{T_{ci}\,T_{cj}}\,. \tag{7}$$

For details on the generalized correlation we refer the reader to the literature[5].

RESULTS AND DISCUSSION

The relations of the preceding section were used to calculate the second virial coefficients of pure n-alkanes from ethane to octane and the second virial cross coefficients of their seventeen mixtures. The Kihara intermolecular potential was employed in the same form as in our recent work[2], i.e. the core was a hard rod of length l. Parameters σ and l were always taken as evaluated from the vapour–liquid equilibrium (VLE) calculations on pure n-alkanes (i.e. from the vapour pressure and saturated density data) whereas ε was alternatively adjusted by using the recommended experimental values of the virial coefficients of pure n-alkanes[5,6]. To this end the relative deviations $(B_{\text{Kihara}} - B_{\text{exp}})/B_{\text{exp}}$ were minimized. The resulting values of ε_{vir} are slightly higher than the values obtained from VLE calculations, ε_{VLE}, but the difference is in all cases lower than 4% as it can be seen in Table I. The differences between the calculated and experimental values of the second virial coefficients of pure n-alkanes are usually within the experimental uncertainty and never exceed double the value as it can be seen in Tables II through VIII. (It is also seen that for the pure n-alkane second virial coefficients the generalized Tsonopoulos correlation performs very well; the input acentric factors were taken from ref.[7] and the critical properties from ref.[8].)

The found values of the potential parameters were used to calculate the second virial cross coefficients for seventeen mixtures for which the experimental data are available

TABLE I
Parameters of the Kihara potential; σ, l, $\varepsilon_{\text{VLE}}/k$ taken from ref.[2]; $\varepsilon_{\text{vir}}/k$ adjusted to experimental data on virial coefficients

n-Alkane	σ Å	l Å	$\varepsilon_{\text{VLE}}/k$ K	$\varepsilon_{\text{vir}}/k$ K
Ethane	3.5073	1.8448	305.49	313.37
Propane	3.6713	2.8954	399.51	406.18
Butane	3.8123	3.7659	483.11	498.65
Pentane	3.9411	4.5827	556.91	567.74
Hexane	4.0180	5.5910	628.42	634.84
Heptane	4.0971	6.4498	690.10	704.65
Octane	4.1756	7.3204	747.30	763.22

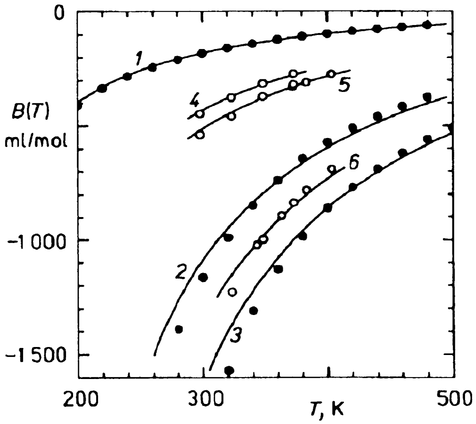

FIG. 1
The second virial coefficients of ethane, pentane, hexane and the cross coefficients of their binary mixtures. ● Recommended experimental data of pure compounds, ○ experimental data of mixtures; —— results calculated by using ε_{vir}: *1* ethane, *2* pentane, *3* hexane, *4* ethane + pentane, *5* ethane + hexane, *6* pentane + hexane

in ref.[7]. The coefficients were calculated both by using the simple geometric mean rule for ε_{ij}, i.e. for the binary parameter k_{ij} defined in Eq. (*6*) equal to zero, and by using the k_{ij} values fitted to the experimental data on the second virial cross coefficients. The estimated values of k_{ij} are usually greater than zero, but no trends can be detected. The reason for such behaviour can be the fact that the ε parameters of pure n-alkanes were obtained on the basis of data from different ranges of temperatures (in all cases wider) than those for mixture data. Therefore in further study we considered new values for the ε parameters of pure n-alkanes for the same or similar temperature interval as that covered by the data on mixtures. It was found that the values of ε slightly depend on the underlying temperature interval. They become lower if the center of the interval is shifted to the higher temperatures and also if the center of the interval is fixed and the interval is more narrow. If these values of parameters are used to calculate the second virial cross coefficients, the evaluated binary parameters k_{ij} are also slightly changed.

TABLE II

Comparison of experimental and calculated second virial coefficients for ethane; B_{exp} recommended experimental data[5], B_{VLE}, B_{vir}, B_{cor} values calculated by using ε_{VLE}, ε_{vir}, and from the generalized correlation, respectively; Δ estimated experimental error, $\delta = B_{cal} - B_{exp}$, $\Sigma = \Sigma\delta^2$

T K	B_{exp}	Δ	B_{VLE}	δ ml/mol	B_{vir}	δ	B_{cor}	δ
200.	-410.0	±10.	-377.7	32.3	-396.7	13.3	-433.6	-23.6
210.	-370.0	±5.	-343.9	26.1	-361.1	8.9	-388.6	-18.6
220.	-336.0	±5.	-314.6	21.4	-330.3	5.7	-351.2	-15.2
240.	-283.0	±3.	-266.3	16.7	-279.6	3.4	-292.2	-9.2
260.	-243.0	±2.	-228.1	14.9	-239.7	3.3	-247.5	-4.5
280.	-210.0	±2.	-197.2	12.8	-207.4	2.6	-212.4	-2.4
300.	-182.0	±2.	-171.8	10.2	-180.8	1.2	-184.0	-2.0
320.	-159.0	±2.	-150.4	8.6	-158.6	0.4	-160.6	-1.6
340.	-140.0	±2.	-132.3	7.7	-139.7	0.3	-141.0	-1.0
360.	-122.0	±2.	-116.7	5.3	-123.5	-1.5	-124.3	-2.3
380.	-108.0	±1.	-103.1	4.9	-109.4	-1.4	-109.9	-1.9
400.	-96.0	±1.	-91.2	4.8	-97.0	-1.0	-97.4	-1.4
420.	-85.0	±1.	-80.7	4.3	-86.1	-1.1	-86.5	-1.5
440.	-75.5	±1.	-71.4	4.1	-76.4	-0.9	-76.8	-1.3
460.	-67.0	±1.	-63.1	3.9	-67.8	-0.8	-68.1	-1.1
480.	-59.0	±1.	-55.6	3.4	-60.0	-1.0	-60.4	-1.4
Σ				3 219.		326.8		1 266.9

All the results on binary systems are summarized in Tables IX through XXV. For three pure n-alkanes and their binaries the good agreement with experimental data is also documented in Fig. 1. The binary parameter k_{ij} is always small and greater than zero for most of the systems investigated. It also seems that k_{ij} increases with increasing difference in number of C-atoms of the mixture components. As a matter of fact, for systems of components with small difference in chain length, the binary parameters are virtually zero. (As already stated above, the binary parameters were estimated by using an objective function based on relative deviations in the virial coefficients whereas the absolute deviations and their squares are given in the tables as the goodness-of-fit indicators. Tables XVIII and XIX for the butane–pentane and butane–hexane systems, respectively, document that the sums of squares of absolute deviations are in fact lower for $k_{12} = 0$ and that the resulting nonzero values only slightly improve the objective function actually used.) The comparison of the k_{ij} parameters with the q_{ij} parameters of the Tsonopoulos correlation reveals that the two parameters usually take on very similar values. This is, however, not very surprising in view of the fact that there is a

TABLE III

Comparison of experimental and calculated second virial coefficients for propane; B_{exp} recommended experimental data[5], B_{VLE}, B_{vir}, B_{cor} values calculated by using ε_{VLE}, ε_{vir}, and from the generalized correlation, respectively; Δ estimated experimental error, $\delta = B_{cal} - B_{exp}$, $\Sigma = \Sigma\delta^2$

T	B_{exp}	Δ	B_{VLE}	δ	B_{vir}	δ	B_{cor}	δ
K				ml/mol				
240.	-630.0	±20.	-576.3	53.7	-595.8	34.2	-648.1	-18.1
250.	-574.0	±20.	-531.0	43.0	-548.9	25.1	-587.3	-13.3
260.	-525.0	±20.	-491.0	34.0	-507.4	17.6	-535.9	-10.9
280.	-446.0	±20.	-423.6	22.4	-437.8	8.2	-453.2	-7.2
300.	-384.0	±15.	-369.2	14.8	-381.6	2.4	-389.4	-5.4
320.	-335.0	±10.	-324.3	10.7	-335.3	-0.3	-338.6	-3.6
340.	-294.0	±10.	-286.7	7.3	-296.6	-2.6	-297.1	-3.1
360.	-260.0	±10.	-254.7	5.3	-263.6	-3.6	-262.6	-2.6
380.	-232.0	±10.	-227.2	4.8	-235.3	-3.3	-233.4	-1.4
400.	-207.0	±10.	-203.2	3.8	-210.7	-3.7	-208.4	-1.4
420.	-186.0	±10.	-182.3	3.7	-189.2	-3.2	-186.7	-0.7
440.	-167.0	±10.	-163.8	3.2	-170.2	-3.2	-167.7	-0.7
460.	-150.0	±5.	-147.3	2.7	-153.3	-3.3	-151.0	-1.0
480.	-136.0	±5.	-132.6	3.4	-138.2	-2.2	-136.2	-0.2
Σ				6 899.		2 261.		739.1

proportional relation linking the critical temperature with the energetic parameter of the intermolecular pair potential.

In conclusion the present paper we have shown that the values of the parameters of the Kihara pair potential obtained on the basis of the vapor pressure and saturated liquid density data can be used to determine the second virial coefficients and second virial cross coefficients of n-alkanes and their mixtures with fair accuracy. The agreement with experimental data is improved when the ε/k parameter is adjusted to experimental second virial coefficient data. This can be expected since the original ε/k, σ and l are the parameters of the effective pair potential (for the liquid phase) whereas the actual pair potential is to be considered for the rarefied gas. It is obvious that by adjusting two (or even all the three) parameters a still better agreement with experimental data could be obtained.

The calculations on mixtures show that the characteristic binary parameters entering the combining rules for the ε_{ij} parameter of the Kihara potential and the pseudocritical temperature T_{cij} in the generalized method have similar values when adjusted to experimental data on the second virial cross coefficients; at the same time these parameters increase with the difference in chainlength of the mixture constituents.

TABLE IV
Comparison of experimental and calculated second virial coefficients for butane; B_{exp} recommended experimental data[5,6], B_{VLE}, B_{vir}, B_{cor} values calculated by using ε_{VLE}, ε_{vir}, and from the generalized correlation, respectively; Δ estimated experimental error, $\delta = B_{cal} - B_{exp}$, $\Sigma = \Sigma\delta^2$

T K	B_{exp}	Δ	B_{VLE}	δ ml/mol	B_{vir}	δ	B_{cor}	δ
250.	-1 170.0	±30.	-957.1	212.9	-1 024.5	145.5	-1 146.8	23.2
260.	-1 050.0	±30.	-880.7	169.3	-941.8	108.2	-1 026.2	23.8
270.	-925.0	±50.	-813.8	136.2	-869.5	55.5	-926.6	-1.6
280.	-845.0	±40.	-754.6	107.4	-805.8	39.2	-842.9	2.1
290.	-780.0	±30.	-701.9	86.1	-749.3	30.7	-771.6	8.4
300.	-722.0	±20.	-654.8	67.2	-698.7	23.3	-710.0	12.0
320.	-620.0	±20.	-574.0	46.0	-612.2	7.8	-609.1	10.9
340.	-535.0	±20.	-507.2	27.8	-541.0	-6.0	-529.5	5.5
360.	-472.0	±20.	-451.1	20.9	-481.4	-9.4	-465.2	6.8
380.	-417.0	±20.	-403.3	13.7	-430.7	-13.7	-412.0	5.0
400.	-370.0	±20.	-362.2	7.8	-387.2	-17.2	-367.2	2.8
420.	-332.0	±15.	-326.5	5.5	-349.3	-17.3	-329.0	3.0
440.	-299.0	±15.	-295.1	3.9	-316.2	-17.2	-296.1	2.9
460.	-270.0	±10.	-267.4	2.6	-286.9	-16.9	-267.4	2.6
480.	-243.0	±10.	-242.7	0.3	-260.9	-17.9	-242.1	0.9
Σ				108 700.		40 830.		1 582.5

TABLE V

Comparison of experimental and calculated second virial coefficients for pentane; B_{exp} recommended experimental data[5,6], B_{VLE}, B_{vir}, B_{cor} values calculated by using ε_{VLE}, ε_{vir}, and from the generalized correlation, respectively; Δ estimated experimental error, $\delta = B_{cal} - B_{exp}$, $\Sigma = \Sigma\delta^2$

T K	B_{exp}	Δ	B_{VLE}	δ ml/mol	B_{vir}	δ	B_{cor}	δ
280.	−1 390.0	±100.	−1 211.2	178.8	−1 263.5	126.5	−1 473.7	−83.7
290.	−1 270.0	±70.	−1 122.2	147.8	−1 170.0	100.0	−1 328.1	−58.1
300.	−1 165.0	±60.	−1 043.4	121.6	−1 087.3	77.7	−1 206.0	−41.0
310.	−1 170.0	±50.	−973.1	96.9	−1 013.7	56.3	−1 102.1	−32.1
320.	−990.0	±30.	−910.0	80.0	−947.7	42.3	−1 012.7	−22.7
340.	−850.0	±20.	−801.5	48.5	−834.4	15.6	−866.7	−16.7
360.	−740.0	±20.	−711.5	28.5	−740.6	−0.6	−752.4	−12.4
380.	−645.0	±20.	−635.8	9.2	−661.8	−16.8	−660.4	−15.4
400.	−575.0	±15.	−571.2	3.8	−594.7	−19.7	−584.7	−9.7
420.	−510.0	±15.	−515.4	−5.4	−536.8	−26.8	−521.3	−11.3
440.	−460.0	±15.	−466.8	−6.8	−486.4	−26.4	−467.4	−7.4
460.	−415.0	±15.	−424.1	−9.1	−442.2	−27.2	−421.1	−6.1
480.	−375.0	±15.	−386.3	−11.3	−403.1	−28.1	−380.8	−5.8
Σ				87 940.		40 830.		14 630.

TABLE VI

Comparison of experimental and calculated second virial coefficients for hexane; B_{exp} recommended experimental data[5,6], B_{VLE}, B_{vir}, B_{cor} values calculated by using ε_{VLE}, ε_{vir}, and from the generalized correlation, respectively; Δ estimated experimental error, $\delta = B_{cal} - B_{exp}$, $\Sigma = \Sigma\delta^2$

T K	B_{exp}	Δ	B_{VLE}	δ ml/mol	B_{vir}	δ	B_{cor}	δ
320.	−1 570.0	±100.	−1 366.1	203.9	−1 397.3	172.7	−1 579.5	−9.5
340.	−1 310.0	±70.	−1 196.2	113.8	−1 222.9	87.1	−1 328.8	−18.8
360.	−1 130.0	±50.	−1 057.3	72.7	−1 080.7	49.3	−1 138.6	−8.6
380.	−985.0	±50.	−941.8	43.2	−962.5	22.5	−989.4	−4.4
400.	−860.0	±40.	−844.3	15.7	−862.8	−2.8	−869.2	−9.2
420.	−770.0	±30.	−760.9	9.1	−777.6	−7.6	−770.4	−0.4
440.	−690.0	±30.	−688.8	1.2	−704.0	−14.0	−687.6	2.4
460.	−620.0	±25.	−625.8	−5.8	−639.7	−19.7	−617.3	2.7
480.	−560.0	±20.	−570.4	−10.4	−583.2	−23.2	−556.9	3.1
500.	−510.0	±20.	−521.2	−11.2	−533.1	−23.1	−504.4	5.6
520.	−460.0	±20.	−477.3	−17.3	−488.4	−28.4	−458.3	1.7
Σ				62 570.		42 890.		678.6

TABLE VII
Comparison of experimental and calculated second virial coefficients for heptane; B_{exp} recommended experimental data[5], B_{VLE}, B_{vir}, B_{cor} values calculated by using ε_{VLE}, ε_{vir}, and from the generalized correlation, respectively; Δ estimated experimental error, $\delta = B_{cal} - B_{exp}$, $\Sigma = \Sigma\delta^2$

T K	B_{exp}	Δ	B_{VLE}	δ ml/mol	B_{vir}	δ	B_{cor}	δ
350.	-1 800.0	±80.	-1 564.3	235.7	-1 639.5	160.5	-1 800.8	-0.8
360.	-1 665.0	±60.	-1 468.9	196.1	-1 538.8	126.2	-1 657.6	7.4
380.	-1 425.0	±50.	-1 303.7	121.3	-1 364.9	60.1	-1 422.1	2.9
400.	-1 230.0	±50.	-1 165.6	64.4	-1 219.8	10.2	-1 236.6	-6.6
420.	-1 080.0	±50.	-1 048.5	31.5	-1 097.0	-17.0	-1 086.9	-6.9
440.	-955.0	±50.	-947.9	7.1	-991.8	-36.8	-963.6	-8.6
460.	-850.0	±40.	-860.7	-10.7	-900.6	-50.6	-860.3	-10.3
480.	-760.0	±40.	-784.3	-24.3	-821.0	-61.0	-772.6	-12.6
Σ				114 600.		53 320.		493.2

TABLE VIII
Comparison of experimental and calculated second virial coefficients for octane; B_{exp} recommended experimental data[5], B_{VLE}, B_{vir}, B_{cor} values calculated by using ε_{VLE}, ε_{vir}, and from the generalized correlation, respectively; Δ estimated experimental error, $\delta = B_{cal} - B_{exp}$, $\Sigma = \Sigma\delta^2$

T K	B_{exp}	Δ	B_{VLE}	δ ml/mol	B_{vir}	δ	B_{cor}	δ
380.	-1 990.0	±140.	-1 754.0	236.0	-1 840.2	149.8	-1 971.9	18.1
400.	-1 710.0	±100.	-1 562.9	147.1	-1 638.5	71.5	-1 698.2	11.8
420.	-1 490.0	±100.	-1 402.3	87.7	-1 469.4	20.6	-1 481.1	8.9
440.	-1 310.0	±100.	-1 265.4	44.6	-1 325.6	-15.6	-1 304.8	5.2
460.	-1 155.0	±80.	-1 147.5	7.5	-1 202.0	-47.0	-1 158.9	-3.9
480.	-1 025.0	±80.	-1 044.8	-19.8	-1 094.5	-69.5	-1 036.4	-11.4
Σ				87 440.		35 270.		718.6

TABLE IX
Comparison of experimental and calculated second virial cross coefficients for system ethane(1)–propane(2). B_{exp} experimental data[7]; B_0, B_k values calculated by using $k_{12} = 0$ and k_{12} adjusted, respectively; B_{cor} values calculated from the generalized correlation with q_{12} adjusted; $\delta = B_{cal} - B_{exp}$, $\Sigma = \Sigma\delta^2$; $\varepsilon_1/k = 313.27$ K; $\varepsilon_2/k = 405.66$ K; $k_{12} = -0.0024$; $q_{12} = -0.0009$

T K	B_{exp}	B_0	δ	B_k ml/mol	δ	B_{cor}	δ
288.72	-282.4	-283.2	-0.8	-284.5	-2.1	-290.7	-8.3
298.15	-274.0	-265.7	8.3	-267.0	7.0	-271.7	2.3
323.15	-230.0	-226.0	4.0	-227.1	2.9	-229.1	0.9
348.15	-193.0	-193.8	-0.8	-194.8	-1.8	-195.4	-2.4
373.15	-165.0	-167.2	-2.2	-168.1	-3.1	-167.9	-2.9
Σ			91.2		75.1		89.8

TABLE X
Comparison of experimental and calculated second virial cross coefficients for system ethane(1)–butane(2). Symbols have the same meaning as in Table IX. $\varepsilon_1/k = 313.27$ K; $\varepsilon_2/k = 500.79$ K; $k_{12} = 0.0144$; $q_{12} = 0.0028$

T K	B_{exp}	B_0	δ	B_k ml/mol	δ	B_{cor}	δ
288.72	-371.3	-384.8	-13.5	-373.9	-2.6	-387.0	-15.7
298.15	-362.0	-361.1	0.9	-350.8	11.2	-360.9	1.1
304.50	-332.0	-346.2	-14.2	-336.4	-4.4	-344.8	-12.8
323.15	-307.0	-307.4	-0.4	-298.5	8.5	-303.3	3.7
348.15	-258.0	-264.2	-6.2	-256.4	1.6	-258.2	-0.2
363.20	-233.0	-242.1	-9.1	-234.8	-1.8	-235.5	-2.5
373.15	-215.0	-228.7	-13.7	-221.8	-6.8	-222.0	-7.0
Σ			696.2		275.3		489.1

TABLE XI
Comparison of experimental and calculated second virial cross coefficients for system ethane(1)–pentane(2). Symbols have the same meaning as in Table IX. ε_1/k = 312.92 K; ε_2/k = 574.59 K; k_{12} = 0.0161; q_{12} = 0.0141

T K	B_{exp}	B_0	δ	B_k ml/mol	δ	B_{cor}	δ
298.15	-448.0	-452.0	-4.0	-437.5	10.5	-448.3	-0.3
323.15	-377.0	-384.6	-7.6	-372.2	4.8	-374.7	2.3
348.15	-315.0	-330.7	-15.7	-319.8	-4.8	-317.8	-2.8
373.15	-272.0	-286.6	-14.6	-277.0	-5.0	-272.5	-0.5
Σ			531.2		180.6		13.6

TABLE XII
Comparison of experimental and calculated second virial cross coefficients for system ethane(1)–hexane(2). Symbols have the same meaning as in Table IX. ε_1/k = 312.73 K; ε_2/k = 649.15 K; k_{12} = 0.0289; q_{12} = 0.0269

T K	B_{exp}	B_0	δ	B_k ml/mol	δ	B_{cor}	δ
298.15	-540.0	-552.0	-12.0	-520.3	19.7	-536.0	4.0
323.15	-458.0	-469.0	-11.0	-441.9	16.1	-445.9	12.1
348.15	-373.0	-403.0	-30.0	-379.4	-6.4	-377.0	-4.0
372.20	-330.0	-351.0	-21.0	-330.2	-0.2	-324.3	5.7
373.15	-319.0	-349.2	-30.2	-328.4	-9.4	-322.5	-3.5
383.20	-310.0	-330.3	-20.3	-310.5	-0.5	-303.6	6.4
403.20	-274.0	-296.5	-22.5	-278.4	-4.4	-270.4	3.6
Σ			3 435.		796.8		275.5

TABLE XIII
Comparison of experimental and calculated second virial cross coefficients for system ethane(1)–octane(2). Symbols have the same meaning as in Table IX. ε_1/k = 311.85 K; ε_2/k = 772.87 K; k_{12} = 0.0500; q_{12} = 0.0620

T K	B_{exp}	B_0	δ	B_k ml/mol	δ	B_{cor}	δ
403.20	-354.0	-392.6	-38.6	-351.6	2.4	-339.1	14.9
413.20	-331.0	-372.6	-41.6	-333.2	-2.2	-319.9	11.1
Σ			3 220.		10.9		346.6

TABLE XIV

Comparison of experimental and calculated second virial cross coefficients for system propane(1)–pentane(2). Symbols have the same meaning as in Table IX. $\varepsilon_1/\boldsymbol{k}$ = 404.89 K; $\varepsilon_2/\boldsymbol{k}$ = 574.59 K; k_{12} = 0.0053; q_{12} = 0.0069

T K	B_{exp}	B_0	δ	B_k ml/mol	δ	B_{cor}	δ
298.15	-671.0	-656.0	15.0	-648.8	22.2	-671.6	-0.6
323.15	-558.0	-556.7	1.3	-550.7	7.3	-555.6	2.4
348.15	-466.0	-478.3	-12.3	-473.1	-7.1	-468.6	-2.6
373.15	-399.0	-414.8	-15.8	-410.2	-11.2	-400.7	-1.7
Σ			628.2		720.6		15.4

TABLE XV

Comparison of experimental and calculated second virial cross coefficients for system propane(1)–hexane(2). Symbols have the same meaning as in Table IX. $\varepsilon_1/\boldsymbol{k}$ = 404.51 K; $\varepsilon_2/\boldsymbol{k}$ = 649.15 K; k_{12} = 0.0137; q_{12} = 0.0147

T K	B_{exp}	B_0	δ	B_k ml/mol	δ	B_{cor}	δ
298.15	-822.0	-802.7	19.3	-780.0	42.0	-816.6	5.4
323.15	-682.0	-679.5	2.5	-660.4	21.6	-670.8	11.2
344.20	-574.0	-596.7	-22.7	-579.9	-5.9	-578.0	-4.0
348.15	-562.0	-582.8	-20.8	-566.4	-4.4	-562.8	-0.8
363.20	-519.0	-534.0	-15.1	-519.0	-0.0	-510.3	8.7
373.15	-478.0	-505.0	-27.0	-490.7	-12.7	-479.6	-1.6
396.90	-418.0	-444.0	-26.0	-431.3	-13.3	-416.3	1.7
Σ			2 957.		2 624.		252.0

TABLE XVI
Comparison of experimental and calculated second virial cross coefficients for system propane(1)–heptane(2). Symbols have the same meaning as in Table IX. ε_1/k = 403.44 K; ε_2/k = 717.44 K; k_{12} = 0.0321; q_{12} = 0.0475

T K	B_{exp}	B_0	δ	B_k ml/mol	δ	B_{cor}	δ
338.60	-646.0	-700.6	-54.6	-655.1	-9.1	-661.4	-15.4
348.50	-606.0	-660.2	-54.2	-617.4	-11.4	-617.5	-11.5
354.90	-584.0	-636.0	-52.0	-594.7	-10.7	-591.4	-7.4
363.50	-564.0	-605.4	-41.4	-566.1	-2.1	-558.9	5.1
365.50	-542.0	-598.6	-56.6	-559.7	-17.7	-551.7	-9.7
373.20	-526.0	-573.5	-47.5	-536.1	-10.1	-525.3	0.7
383.20	-537.0	-543.0	-6.0	-507.6	29.4	-493.8	43.2
383.50	-505.0	-542.2	-37.2	-506.7	-1.7	-492.9	12.1
393.40	-470.0	-514.3	-44.3	-480.6	-10.6	-464.3	5.7
403.20	-490.0	-488.7	1.3	-456.5	33.5	-438.3	51.7
403.30	-461.0	-488.4	-27.4	-456.3	4.7	-438.1	22.9
413.20	-448.0	-464.3	-16.3	-433.6	14.4	-413.9	34.1
414.20	-422.0	-462.0	-40.0	-431.4	-9.4	-411.5	10.5
Σ			21 810.		3 170.		7 061.

TABLE XVII
Comparison of experimental and calculated second virial cross coefficients for system propane(1)–octane(2). Symbols have the same meaning as in Table IX. ε_1/k = 403.31 K; ε_2/k = 785.27 K; k_{12} = 0.0895; q_{12} = 0.0818

T K	B_{exp}	B_0	δ	B_k ml/mol	δ	B_{cor}	δ
353.20	-596.0	-782.7	-186.7	-643.2	-47.2	-638.4	-42.4
362.60	-574.0	-740.8	-166.8	-608.7	-34.7	-599.4	-25.4
363.00	-531.0	-739.1	-208.1	-607.3	-76.3	-597.9	-66.9
367.60	-602.0	-719.9	-117.9	-591.4	10.6	-580.2	21.8
373.00	-605.0	-698.3	-93.3	-573.4	31.6	-560.3	44.7
377.40	-561.0	-681.3	-120.3	-559.3	1.7	-544.9	16.1
382.90	-557.0	-661.0	-104.0	-542.4	14.6	-526.5	30.5
393.60	-509.0	-623.8	-114.8	-511.4	-2.4	-493.1	15.9
403.20	-541.0	-592.9	-51.9	-485.6	55.4	-465.7	75.3
404.00	-468.0	-590.5	-122.5	-483.6	-15.6	-463.5	4.5
410.20	-512.0	-571.8	-59.8	-467.9	44.1	-447.0	65.0
413.20	-508.0	-563.0	-55.0	-460.5	47.5	-439.3	68.7
413.80	-457.0	-561.3	-104.3	-459.1	-2.1	-437.7	19.3
Σ			202 200.		18 090.		16 892.

TABLE XVIII

Comparison of experimental and calculated second virial cross coefficients for system butane(1)–pentane(2). Symbols have the same meaning as in Table IX. ε_1/k = 497.58 K; ε_2/k = 574.59 K; k_{12} = 0.0006; q_{12} = 0.0018

T	B_{exp}	B_0	δ	B_k	δ	B_{cor}	δ
K				ml/mol			
298.15	-928.0	-891.5	36.5	-890.3	37.7	-931.3	-3.3
323.15	-764.0	-753.8	10.2	-752.8	11.2	-760.3	3.7
348.15	-635.0	-646.3	-11.3	-645.5	-10.5	-635.6	-0.6
373.15	-540.0	-560.2	-20.2	-559.5	-19.5	-540.6	-0.6
Σ			1 971.		2 033.		25.4

TABLE XIX

Comparison of experimental and calculated second virial cross coefficients for system butane(1)–hexane(2). Symbols have the same meaning as in Table IX. ε_1/k = 495.82 K; ε_2/k = 649.15 K; k_{12} = 0.0124; q_{12} = 0.0132

T	B_{exp}	B_0	δ	B_k	δ	B_{cor}	δ
K				ml/mol			
298.15	-1 111.0	-1 091.5	19.5	-1 062.6	48.4	-1 128.7	-17.7
323.15	-943.0	-919.3	23.7	-895.5	47.5	-913.4	29.6
348.15	-775.0	-786.2	-11.2	-766.0	9.0	-758.9	16.1
363.20	-694.0	-719.8	-25.8	-701.3	-7.3	-685.2	8.8
373.15	-650.0	-680.4	-30.4	-662.9	-12.9	-642.5	7.5
373.20	-651.0	-680.2	-29.2	-662.7	-11.7	-642.3	8.7
383.60	-610.0	-642.3	-32.3	-625.8	-15.8	-601.9	8.1
393.20	-579.0	-610.0	-31.0	-594.2	-15.2	-567.9	11.1
Σ			5 505.		5 523.		1 843.3

TABLE XX

Comparison of experimental and calculated second virial cross coefficients for system butane(1)–octane(2). Symbols have the same meaning as in Table IX. ε_1/k = 487.43 K; ε_2/k = 772.87 K; k_{12} = 0.0218; q_{12} = 0.0111

T	B_{exp}	B_0	δ	B_k	δ	B_{cor}	δ
K				ml/mol			
403.20	-735.0	-773.4	-38.4	-738.0	-3.0	-741.1	-6.1
410.50	-714.0	-744.5	-30.5	-710.4	3.6	-709.3	4.7
413.20	-700.0	-734.2	-34.2	-700.6	-0.6	-698.1	1.9
Σ			3 574.		22.3		63.3

TABLE XXI

Comparison of experimental and calculated second virial cross coefficients for system pentane(1)–hexane(2). Symbols have the same meaning as in Table IX. ε_1/k = 565.11 K; ε_2/k = 646.11 K; k_{12} = –0.0040; q_{12} = 0.0043

T	B_{exp}	B_0	δ	B_k	δ	B_{cor}	δ
K				ml/mol			
323.15	–1 229.0	–1 141.3	87.7	–1 151.3	77.7	–1 213.9	15.1
343.20	–1 023.0	–1 003.2	19.8	–1 011.8	11.2	–1 033.8	–10.8
348.15	–997.0	–973.1	23.9	–981.4	15.6	–996.1	0.9
363.20	–893.0	–889.7	3.3	–897.3	–4.3	–894.3	–1.3
373.15	–838.0	–840.4	–2.4	–847.5	–9.5	–835.9	2.1
383.20	–783.0	–794.6	–11.6	–801.4	–18.4	–782.9	0.1
403.20	–689.0	–713.9	–24.9	–720.0	–31.0	–691.8	–2.8
Σ			9 420.		7 813.		358.2

TABLE XXII

Comparison of experimental and calculated second virial cross coefficients for system pentane(1)–heptane(2). Symbols have the same meaning as in Table IX. ε_1/k = 557.78 K; ε_2/k = 708.29 K; k_{12} = 0.0023; q_{12} = 0.0046

T	B_{exp}	B_0	δ	B_k	δ	B_{cor}	δ
K				ml/mol			
393.20	–871.0	–870.6	0.4	–866.3	4.7	–874.4	–3.4
403.20	–823.0	–825.4	–2.4	–821.3	1.7	–821.2	1.8
413.20	–774.0	–783.6	–9.6	–779.7	–5.7	–772.8	1.2
Σ			97.5		57.0		16.2

TABLE XXIII

Comparison of experimental and calculated second virial cross coefficients for system pentane(1)–octane(2). Symbols have the same meaning as in Table IX. ε_1/k = 556.36 K; ε_2/k = 772.87 K; k_{12} = 0.0059; q_{12} = 0.0064

T	B_{exp}	B_0	δ	B_k	δ	B_{cor}	δ
K				ml/mol			
403.20	–953.0	–960.0	–7.0	–948.0	5.0	–953.2	–0.2
413.20	–895.0	–911.0	–16.0	–899.6	–4.6	–895.8	–0.8
Σ			305.0		46.0		0.7

TABLE XXIV
Comparison of experimental and calculated second virial cross coefficients for system hexane(1)–octane(2). Symbols have the same meaning as in Table IX. ε_1/k = 632.90 K; ε_2/k = 772.87 K; k_{12} = 0.0039; q_{12} = 0.0057

T K	B_{exp}	B_0	δ	B_k ml/mol	δ	B_{cor}	δ
403.20	–1 173.0	–1 179.1	–6.1	–1 169.2	3.8	–1 167.0	6.0
413.20	–1 105.0	–1 118.0	–13.0	–1 108.6	–3.6	–1 094.4	10.6
Σ			206.2		27.7		147.3

TABLE XXV
Comparison of experimental and calculated second virial cross coefficients for system heptane(1)–octane(2). Symbols have the same meaning as in Table IX. ε_1/k = 703.41 K; ε_2/k = 772.87 K; k_{12} = 0.0013; q_{12} = 0.0017

T K	B_{exp}	B_0	δ	B_k ml/mol	δ	B_{cor}	δ
403.20	–1 407.0	–1 405.3	1.7	–1 401.1	5.9	–1 409.8	–2.8
413.20	–1 322.0	–1 331.4	–9.4	–1 327.5	–5.5	–1 318.8	3.2
Σ			91.5		64.5		18.2

Partial financial support for this work was provided by the Grant Agency of the Academy of Sciences of the Czech Republic, Grant No. 47201.

REFERENCES

1. Mason E. A., Spurling T. H.: *The Virial Equation of State*. Pergamon, Oxford 1969.
2. Pavlíček J., Boublík T.: J. Phys. Chem. *96*, 2298 (1992).
3. Kihara T.: Adv. Chem. Phys. *5*, 47 (1963).
4. Boublík T., Vosmanský J.: Collect. Czech. Chem. Commun. *40*, 542 (1981).
5. Tsonopoulos C., Dymond J. H., Szafranski A.: Pure Appl. Chem. *61*, 1387 (1989).
6. Dymond J. H., Cholinski J. H., Szafranski A., Wyrzykowska-Stankiewicz D.: Fluid Phase Equilib. *27*, 1 (1986).
7. Cholinski J. H., Szafranski A., Wyrzykowska-Stankiewicz D.: *Computer-Aided Second Virial Coefficient Data for Organic Individual Compounds and Binary Mixtures*. Polish Sci. Publishers, Warsaw 1986.
8. Tsonopoulos C.: AIChE J. *33*, 2080 (1987).

Translated by the author (K. A.).