ISSN 0965-5441, Petroleum Chemistry, 2007, Vol. 47, No. 6, pp. 434–441. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © I.A. Nesterov, A.G. Nazmutdinov, V.S. Sarkisova, T.N. Nesterova, N.N. Vodenkova, 2007, published in Neftekhimiya, 2007, Vol. 47, No. 6, pp. 466–473.

Determination of Critical Temperatures for Mixtures of Alkylbenzenes

I. A. Nesterov, A. G. Nazmutdinov, V. S. Sarkisova, T. N. Nesterova, and N. N. Vodenkova
Samara State Technical University, Samara, Russia
e-mail: kinterm@samgtu.ru

Received February 7, 2007

Abstract—The liquid–vapor critical temperatures of benzene mixtures with 1,3-di-*tert*-butylbenzene, 1,4-di-*tert*-butylbenzene, and 1,3,5-tri-*tert*-butylbenzene; a mixture of di-*tert*-butylbenzene isomers; and a toluene mixture with 3,5-di-*tert*-butyltoluene were determined over the entire range of composition by means of the ampoule method. It was found that the excess critical temperature of the mixtures is related to the critical volumes of the substances. The capabilities of several calculation methods for predicting the critical temperature of mixtures were analyzed on the basis of published data and the obtained results. The Lee–Kesler rules of mixtures were refined by introducing binary interaction parameters.

DOI: 10.1134/S0965544107060114

The critical temperature (T_c) is not only a quantity of independent value in the establishment of the relation of the properties of substances to their molecular structure; it is also the key property of modern prediction methods based on the law of corresponding states [1, 2]. Since new information for the database of experimental critical temperatures is gathered very slowly, special attention is given to improvement in methods for the prediction of critical temperatures. In order to verify the workability of calculation methods and to modernize them, it is necessary to have experimental data on the critical temperatures of the most informative mixtures. It is binary mixtures of this kind that were the objects of study in the present work. These mixtures are formed by benzene with 1,3-di-*tert*-butylbenzene (1,3-diTBB), 1,4-di-*tert*-butylbenzene (1,4-diTBB), and 1,3,5-tri-*tert*-butylbenzene (1,3,5-triTBB); by diTBB isomers; and by toluene with 3,5-di-*tert*-butyltoluene (3,5-diTBT). That is, we considered alkylbenzenes with strongly different extents of hindering of the aromatic ring by alkyl substituents. The critical temperatures of these mixtures were determined for the first time and over the entire range of their composition.

EXPERIMENTAL

Used in the experiments were benzene, toluene, and ethylbenzene samples of the reagent grade for chromatography, with a purity of 99.9% (GLC) and in-house synthesized *tert*-butylbenzenes (TBB) and *tert*-butyltoluenes (TBT), namely, 1,3-di-*tert*-butylbenzene, 1,4-di-*tert*-butylbenzene, 1,3,5-tri-*tert*-butylbenzene, and 3,5-di-*tert*-butyltoluene.

1,4-Di-*tert*-butylbenzene was prepared via the alkylation of benzene with isobutylene in the presence of 87% H_2SO_4 (10–15 vol %). The reaction was carried out in a thermostated flask equipped with a stirrer, a reflux condenser, and a thermometer with a continuous isobutylene supply to the reaction mixture emulsified by vigorous stirring. The synthesis temperature did not exceed 40°C. The yield of 1,4-diTBB was 80–85 mol % on a converted benzene basis. The reaction mixture also contained 10–15% TBB and an insignificant amount of benzene and isobutylene oligomers. After completion of the synthesis, the reaction mixture was allowed to settle and the organic layer was separated by decantation and was cooled to a temperature of 10°C. Precipitated 1,4-diTBB crystals were filtered off, washed with water to neutral reaction, and recrystallized from ethanol (90–99 vol %). Pure 1,4-diTBB was isolated via vacuum distillation.

1,3-Di-*tert*-butylbenzene and 1,3,5-tri-*tert*-butylbenzene (or 3,5-di-*tert*-butyltoluene) were prepared via the alkylation of benzene (or toluene) with 1.5–2-fold excess of *tert*-butyl chloride synthesized according to a known procedure [3] from *tert*-butanol and concentrated HCl. The alkylation was carried out in the presence of 10–15 (5–7) wt % $AlCl_3$ at a temperature of 0°C in a thermostated flask with stirring for 10–20 (5–7) h.

After completion of the reaction, the alkylate containing 1–3 wt % TBB, 8–11 % 1,3-diTBB (10–20% 3-TBT), 7–10% 1,4-diTBB (7–12% 4-TBT), 70–80% 1,3,5-triTBB (55–70% 3,5-diTBT), impurities, and trace amounts of the substrate was separated from the catalyst complex and treated with a mixture of ice and 15% HCl for decomposition of the dissolved residual catalyst. The organic layer was separated, washed with a sodium bicarbonate solution and water, and dried over

Na_2SO_4 or $CaCl_2$. The alkylate was fractionated by sharp rectification under vacuum on a laboratory fractionating column.

The *tert*-butylbenzenes used had the following purity according to GLC data: 1,3-diTBB, 98.3% (1,4-diTBB as the only impurity); 1,4-diTBB, 99.9%; 1,3,5-triTBB, 99.7%; and 3,5-diTBT, 99.8 wt %.

The critical temperatures were determined by means of the ampoule method, monitoring the disappearance of the meniscus upon heating and its appearance upon cooling [4]. The schematic of the setup and the experimental procedure were reported in the previous paper [4]. *tert*-Butylbenzenes are unstable under the conditions of long-term exposure to high temperatures, unlike the methyladamantanes studied earlier [4], which possess T_c values close to those of TBB. Therefore, because of the considerable thermal degradation of the *tert*-butyl substituents, it was necessary to exercise a special approach, the maximum allowable reduction in the time of the experiment.

The quality of most test mixtures was monitored gas-chromatographically both before and after the experiment. The results of monitoring of the composition of the test compounds before and after the measurements of T_c, the values of the critical temperatures, and the measurement time are presented in Table 1.

The analysis was carried out on a Kristall-2000M work station operated by means of the version 2.2 Chromatec-Analytic software and equipped with a flame-ionization detector and a quartz capillary column (30 × 0.00025 m) with the bonded OV-101 liquid phase and a split ratio of 1 : 40. The carrier-gas (helium) flow rate was 2 ml/min. The evaporator temperature was 350°C, the detector temperature was 300°C, and the column oven temperature was programmed from 30 to 150°C K at a heating rate of 5°C/min.

RESULTS AND DISCUSSION

Table 1 lists the experimental values of the critical temperatures with their standard deviations ($p = 0.05$); the coefficients ($\mathbf{A}_{1-3}$ for the Redlich–Kister equation [5] calculated for the test mixtures; the binary interaction parameters for the three mixing rules that we have selected: the quadratic form of Kay's rule [1, 4], Lee–Kesler rule [1] with the binary interaction parameters that we introduced, and the Higashi rule [6, 7]; and the mean absolute deviations in T_c estimated by these methods.

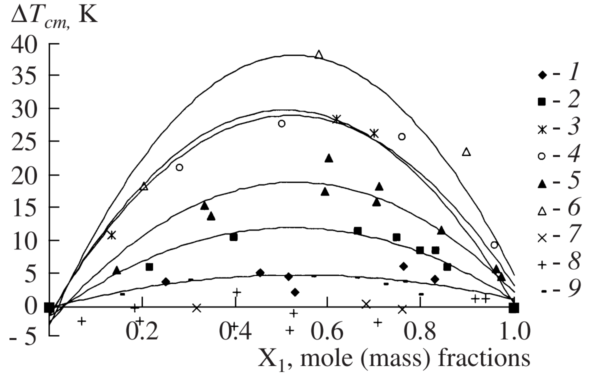

Fig. 1. Excess critical temperatures of the (*1*) benzene–ethylbenzene, (*2, 9*) benzene–isopropylbenzene, (*3*) benzene–1,3-di-*tert*-butylbenzene, (*4*) benzene–1,4-di-*tert*-butylbenzene, (*5*) toluene–3,5-di*tert*-butyltoluene, (*6*) benzene–1,3,5-tri-*tert*-butylbenzene, and (*7*) 1,3-di-*tert*-butylbenzene–1,4-di-*tert*-butylbenzene mixtures against the composition expressed in mole fractions, and the (*8*) toluene–3,5-di*tert*-butyltoluene and (*9*) benzene–isopropylbenzene mixtures with the composition expressed in mass fractions.

A dramatic decrease in the level of critical temperatures on passing from mole to mass fractions indicates that the critical temperatures of mixtures (T_{cm}) are related to the critical volumes (V_c) of individual substances. Figure 1 depicts the dependence of the excess critical temperatures on the mass fractions of the components only for the benzene–isopropylbenzene and toluene–3,5-diTBT systems characterized by the highest values of ΔT_{cm}. The maximal values of ΔT_{cm} for these mixtures are 4.7 and 3.4 K, respectively. For all other alkylbenzene mixtures examined, the values of ΔT_{cm} are much lower, not exceeding 2 K at maximum.

We complemented the existing database of Kay binary interaction parameters [1] with some structures that have been absent from it.

The Lee–Kesler mixing rules

$$T_{cm} = \frac{1}{8V_{cm}}\sum_i\sum_j y_i y_j (V_{ci}^{1/3} + V_{cj}^{1/3})^3 (T_{ci}T_{cj})^{1/2}$$

are recommended in [1] for normal liquids and are extensively used for predicting most intermolecular interaction-dependent properties with the use of methods based on the law of corresponding states. We attempted to apply the mixing rule in the original version [1]; however, the results turned out to be worse that in the case of application of Kay's rule and the Higashi method. To increase the efficiency of this widely used method, we complement the above equation with the parameters of binary interactions

$$T_{cm} = \frac{1}{8V_{cm}}\sum_i\sum_j k_{ij} y_i y_j (V_{ci}^{1/3} + V_{cj}^{1/3})^3 (T_{ci}T_{cj})^{1/2},$$

where $k_{ii} = k_{jj} = 1$, and k_{ij} are determined via the least-square treatment of experimental data.

The Higashi binary interaction parameters, being surprisingly simple:

$$T_{cm} = \theta_1 T_{c1} + \theta_1 T_{c2} + 2\theta_1\theta_2\Delta_T,$$

$$\text{where } \theta_i = \frac{x_i V_{ci}^{2/3}}{\sum_{i=1}^{2} x_j V_{cj}^{2/3}}, \quad i = 1, 2,$$

Table 1. Results of investigation of the critical temperatures of alkylbenzene mixtures

Composition X_1/X_2, wt %		Experiment time, min[c]	T_{cm} exp, K	T_{cm} exp – T_{cm} calc[d]		
before experiment[a]	after experiment[b]			**I**	**II**	**III**
Benzene–ethylbenzene (A_1 = 15.567, A_2 = 6.9172, A_3 = 33.055, $/\Delta T_{cm,\ \mathrm{av}}/$ = 0.7)						
Binary interaction parameters				**1.016**	**1.009**	**2.700**
0.0/99.9			617.55	0.0	0.0	0.0
19.70/80.30	–	596	607.3 ± 0.3	0.0	0.3	1.2
38.04/61.96	–	522	597.2 ± 0.2	0.2	0.2	2.3
43.88/56.12	–	326	593.5 ± 0.1	–0.3	–0.3	–2.7
45.23/54.77	–	50	590.3	–2.6	–2.7	–0.3
70.45/29.55	–	441	581.2 ± 0.3	2.6	2.3	0.2
78.16/21.84	–	221	575.7 ± 0.2	1.5	1.2	0.3
99.9/0.0			562.05	0.0	0.0	0.0
Mean absolute error, $/\Delta T_{cm,\ \mathrm{av}}/$, K				0.9	0.9	0.9
Benzene–isopropylbenzene [8] (A_1 = 49.014, A_2 = 16.374, A_3 = –8.4171, $/\Delta T_{cm,\ \mathrm{av}}/$ = 0.3)						
Binary interaction parameters				**1.042**	**1.027**	**11.99**
0.0/	–	–	631.0	0.0	0.0	0.0
21.73/	–	–	622.4	–2.2	–0.9	–0.7
39.89/	–	–	614.4	–1.1	–0.1	0.1
66.66/	–	–	596.8	0.6	0.2	0.2
74.96/	–	–	590.0	1.3	0.5	0.4
79.94/	–	–	584.7	0.8	–0.1	–0.2
83.28/	–	–	582.3	1.7	0.8	0.7
85.73/	–	–	578.0	–0.1	–0.9	–1.0
1.0/	–	–	562.05	0.0	0.0	0.0
Mean absolute error, $/\Delta T_{cm,\ \mathrm{av}}/$, K				0.9	0.4	0.4
Benzene–1,3-di-*tert*-butylbenzene (A_1 = 114.26, A_2 = 27.690, A_3 = 2.6223, $/\Delta T_{cm,\ \mathrm{av}}/$ = 0.0)						
Binary interaction parameters				**1.096**	**1.048**	**16.85**
0.0/98.3			687.6	0.0	0.0	0.0
5.92/94.08	6.41/84.29	345	681.9 ± 0.3	–2.8	1.2	1.3
40.02/59.98	49.49/48.65	215	638.4 ± 0.3	0.3	0.2	0.3
48.79/51.21	52.63/46.36	224	626.3 ± 0.1	1.2	–0.6	–0.6
99.9/0.0			562.05	0.0	0.0	0.0
Mean absolute error, $/\Delta T_{cm,\ \mathrm{av}}/$, K				0.9	0.4	0.5
Benzene–1,4-di-*tert*-butylbenzene (A_1 = 109.09, A_2 = 36.852, A_3 = 66.507, $/\Delta T_{cm,\ \mathrm{av}}/$ = 0.5)						
Binary interaction parameters				**1.093**	**1.048**	**15.40**
0.0/99.9			702.9	0.0	0.0	0.0
13.89/86.11	14.69/67.91	254	684.3 ± 0.2	–2.8	1.0	1.1
29.25/70.75	28.48/65.60	417	660.1 ± 1.3	–1.6	–1.0	–1.0
56.73/43.27	58.05/41.62	304	621.4 ± 0.3	4.3	–0.3	–0.4
90.50/9.50	91.34/8.60	359	577.3 ± 0.2	4.8	2.5	2.4
99.9/0.0			562.05	0.0	0.0	0.0
Mean absolute error, $/\Delta T_{cm,\ \mathrm{av}}/$, K				2.3	0.8	0.8
Benzene–1,3,5-tri-*tert*-butylbenzene (A_1 = 141.88, A_2 = 89.374, A_3 = 70.146, $/\Delta T_{cm,\ \mathrm{av}}/$ = 0.0)						
Binary interaction parameters				**1.122**	**1.065**	**24.28**
0.0/99.7			700.5	0.0	0.0	0.0
7.51/92.49	8.47/64.11	570	690.7 ± 0.4	–6.7	–0.5	–0.2
30.51/69.49	32.09/63.87	639	658.6 ± 0.2	0.9	–0.9	–0.9
73.38/26.62	73.38/26.62	316	600.1 ± 0.6	9.5	1.8	1.4
99.9/0.0			562.35	0.0	0.0	0.0
Mean absolute error, $/\Delta T_{cm,\ \mathrm{av}}/$, K				3.4	0.6	0.5

Table 1. (Contd.)

Composition X_1/X_2, wt %		Experiment time, min[c]	T_{cm} exp, K	T_{cm} exp – T_{cm} calc[d]		
before experiment[a]	after experiment[b]			**I**	**II**	**III**
1,3-Di-*tert*-butylbenzene–1,4-di-*tert*-butylbenzene (A_1 = 5.2463, A_2 = 3.6386, A_3 = –34.204, $/\Delta T_{cm,\ \mathrm{av}}/$ = 0.0)						
Binary interaction parameters				**1.000**	**1.000**	**–0.004**
0.0/99.9	–		702.9	0.0	0.0	0.0
31.87/68.13	–	170	697.9 ± 0.4	–0.1	–0.1	–0.1
68.23/31.77	–	385	692.9 ± 0.5	0.4	0.4	0.4
75.95/24.05	–	299	690.9 ± 1.0	–0.4	–0.4	–0.4
98.3/0.0	–		687.6	0.0	0.0	0.0
Mean absolute error, $/\Delta T_{cm,\ \mathrm{av}}/$, K				0.2	0.2	0.2
Toluene–3,5-di-*tert*-butyltoluene (A_1 = 75.140, A_2 = 31.836, A_3 = –3.4323, $/\Delta T_{cm,\ \mathrm{av}}/$ = 1.3)						
Binary interaction parameters				**1.060**	**1.029**	**9.865**
0.0/99.8	–		695.5	0.0	0.0	0.0
7.07/92.93	7.22/69.29	242	686.2 ± 1.0	–3.9	–1.8	–1.7
18.41/81.59	–	516	676.4 ± 0.6	–1.7	0.6	0.6
19.40/80.60	–	149	673.3 ± 0.5	–3.7	–1.5	–1.4
39.72/60.28	40.21/55.83	326	651.6 ± 0.4	–1.0	–1.4	–1.5
40.44/59.56	40.57/57.34	220	655.9 ± 0.6	4.2	3.6	3.6
51.90/48.10	–	277	638.4 ± 0.8	0.0	–1.8	–1.9
52.56/47.44	–	360	640.2 ± 0.6	2.5	0.7	0.6
70.88/29.12	71.06/28.49	134	619.8 ± 1.9	1.6	–0.8	–0.9
91.57/8.43	91.82/8.03	296	601.9 ± 0.5	3.1	2.0	1.9
93.88/6.12	–	413	599.5 ± 0.3	2.6	1.8	1.8
99.9/0.0	–		591.75	0.0	0.0	0.0
Mean absolute error, $/\Delta T_{cm,\ \mathrm{av}}/$, K				2.0	1.3	1.3
Mean absolute error of the entire sample				1.50	0.67	0.66

[a] The composition was determined gravimetrically.

[b] The composition was determined chromatographically. The total concentration of unidentified components is x = 100 – X_1 – X_2, %.

[c] The residence time in the region of critical and near-critical temperatures.

[d] The prediction results for critical temperatures of mixtures with the use of (**I**) the quadratic form of Kay's rule [1], (**II**) the Lee–Kesler mixing rules [1] with the binary interaction parameters that we introduced, and (**III**) the Higashi mixing rules [6, 7].

proved to be effective for compounds from different classes, including polar substances [6, 7, 9, 10].

The binary interaction parameters for all methods and all of the test systems are given in Table 1 as having been determined from experimental data. The critical properties of individual compounds used for optimization are presented in Table 2.

An analysis of the results (Table 1) shows that the use of the binary interaction parameters of all of the types in question is effective for the systems of alkylbenzenes having different molecular structures up to the complete hindrance of the aromatic ring by alkyl substituents, the mean absolute error in all cases is comparable to the error of approximation of experimental data with the Redlich–Kister equation. In this case, the Lee–Kesler and Higashi methods, which suggest the direct relation of T_{cm} to the critical volumes of the compounds, ensure the best prediction; the mean absolute error over the entire sample (Table 1) is 0.67 and 0.66, respectively, versus 1.50 according to Kay's method.

Note that the data for the benzene–1,3,5-triTBB, benzene–1,4-diTBB and toluene–3,5-diTBT systems have a greater error in the case of application of Kay's rule. This deviation may be due to the large values of the corresponding critical volumes of the compounds.

For this reason, it is necessary to consider the correlation of the binary interaction parameters with the crit-

Table 2. Critical properties of hydrocarbons used for analysis of experimental data

Compound	T_c, K	V_c, cm^3/mol	Compound	T_c, K	V_c, cm^3/mol
Benzene	562.05 [2]	256 [2]	1,3-diTBB	687.6 [11]	672^e
Toluene	591.75 [2]	316 [2]	1,4-diTBB	702.9 [11]	672^e
Ethylbenzene	617.15 [2]	374 [2]	1,3,5-triTBB	700.5 [11]	877^e
Isopropylbenzene	631.0 [2]	434.7 [2]	3,5-diTBT	695.5 [11]	726^e
Cyclohexane	553.5 [2]	296.88 [2]	1,3-Dimethyladamantane	706.7 [4]	571.45 [2]
Methane	190.56 [2]	98.6 [2]	1,3,5-Trimethyladamantane	701.9 [4]	611^e
Ethane	305.32 [2]	145.5 [2]	2-Methylpentane	497.50 [2]	366.7 [2]
Propane	369.83 [2]	200.0 [2]	2,2-Dimethylpropane	433.75 [2]	303.2 [2]
n-Pentane	469.70 [2]	311.0 [2]	2-Methylhexane	530.10 [2]	421.0 [2]
n-Hexane	507.60 [2]	368.0 [2]	2-Methylheptane	559.60 [2]	488.2 [2]
n-Decane	617.70 [2]	624.0 [2]	2-Methyloctane	587.00 [2]	529.0 [2]

^{e} Calculated according to the Lydersen method [1].

ical volumes of the compounds involved in the interaction. This approach was practiced by Kay [1] and turned out to be successful for the relevant group of compounds. Of a broad set of combinations of binary-mixture components, Kay distinguished two groups of substances related by independent equations. Moreover, all organic compounds were approximated by the same universal equation.

The models that we selected for study and complemented with published data (Table 3) for alkane mixtures [5, 12, 13] make it possible to partly explain the cause of this unity. From Fig. 2a, it follows that the Kay binary interaction parameters for the mixtures of tertiary alkylbenzenes with benzene or toluene form an individual series that diverges from the alkane–alkane series, for which data are well consistent with the general correlation given in [1] for organic substances. Thus, the general correlation equations for binary interaction parameters should be used with a great care, better, after their experimental verification. It is likely that such correlations will be more rigorous for compounds from the same class belonging to normal liquids or compounds that are close in nature and their intermolecular interaction energy monotonically varies with a change in the size of molecules in the molecular volumes of substances.

The result of analysis of the dependence for the Lee–Kesler binary interaction parameters (Fig. 2b) leads to the same conclusion: alkanes and *tert*-alkylbenzenes form independent series. As regards the Higashi parameters (Fig. 2c), such a conclusion is not obvious. It cannot be ruled out that the groups of compounds under consideration obey a general law, especially, in the view that the cyclohexane–1,3-dimethyladamantane and cyclohexane–1,3,5-trimethyladamantane systems studied earlier [4] (Fig. 2c) fit well the general correlation. We suppose that, to resolve this problem, it is necessary to complement the array of experimental data with information on mixtures of alkanes for which $0.5 > V_{ci}/V_{cj} > 2$.

Although works on the perfection of experimental methods for determining the critical temperatures of substances that have low thermal stability continue [14–16], not everything is directly measurable. In some cases, an indirect approach appears to be fruitful. Let us give an example.

There are two values of the critical temperature for 1,4-diTBB: Steele [17] obtained a value of 708 K by means of the DSC technique, and we determined it by the ampule method to be 702.9 K [11]. The discrepancy of 5 K is beyond the limits of the error of the methods. The temperature level used, however, did not rule out the partial degradation and consolidation of molecules. The experimental data for the benzene–1,4-diTBB system can serve as a source of additional information in this case. At a 1,4-diTBB concentration up to 70 wt % (50 mol %) in this system, the critical temperature of the mixture is 40 K or more below the T_c of 1,4-diTBB, a fact that is very important in the case of high-temperature experiments.

We treated the experimental results for the benzene–1,4-diTBB system by means of the Lee–Kesler and Higashi methods, as the most accurate of those considered in this work, over the range 562.1–660.6 K (Table 1). Using the binary interaction parameters calculated by the equations for alkylbenzenes (Figs. 2b, 2c) as $L_{ij} = 1.045$ and $\Delta T = 16.05$, we obtained values of 703.5 and 701.2 K, respectively for the T_c of

Table 3. Results of analysis of published experimental data on the critical temperatures of hydrocarbon mixtures

X_1, mole fraction	T_{cm}, K	T_{cm} exp – T_{cm} calc^{f}, K			X_1, mole fraction	T_{cm}, K	T_{cm} exp – T_{cm} calc^{f}, K		
		I	**II**	**III**			**I**	**II**	**III**
Cyclohexane–1,3-dimethyladamantane [4] ($A_1 = 82.272$, $A_2 = 33.864$, $A_3 = -7.0476$, $/\Delta T_{cm,\,\mathrm{av}}/ = 0.6$)					**Cyclohexane–1,3,5-trimethyladamantane** [4] ($A_1 = 88.286$, $A_2 = 24.\ 212$, $A_3 = -27.630$, $/\Delta T_{cm,\,\mathrm{av}}/ = 0.1$)				
Binary interaction parameters		**1.064**	**1.033**	**7.964**	Binary interaction parameters		**1.075**	**1.039**	**11.03**
1.0000	553.5	0.0	0.0	0.0	0.0000	701.9	0.0	0.0	0.0
0.9349	568.3	–0.1	–1.5	–1.5	0.3534	668.5	–2.4	–0.1	–0.1
0.7073	619.3	4.2	2.3	2.2	0.5078	648.8	–1.2	–0.6	–0.6
0.4625	654.8	–1.1	–0.7	–0.8	0.7572	609.2	2.4	0.1	0.1
0.2010	685.5	–3.4	–1.7	–1.7	0.8485	591.4	3.3	0.8	0.8
0.0556	701.4	–1.0	–0.2	–0.3	1.0000	553.5	0.0	0.0	0.0
0.0000	706.7	0.0	0.0	0.0					
Mean absolute error		1.4	0.9	0.9	Mean absolute error		1.6	0.3	0.2
Methane–ethane [5] ($A_1 = 58.320$, $A_2 = 15.342$, $A_3 = -11.784$, $/\Delta T_{cm,\,\mathrm{av}}/ = 0.0$)					***n*-Pentane–*n*-hexane** [5] ($A_1 = 7.500$, $A_2 = 4.500$, $A_3 = 0.000$, $/\Delta T_{cm,\,\mathrm{av}}/ = 0.0$)				
Binary interaction parameters		**1.121**	**1.107**	**15.36**	Binary interaction parameters		**1.008**	**1.005**	**1.658**
0.0000	305.4	0.1	0.1	0.1	0.0000	507.7	0.1	0.1	0.1
0.2000	290.9	–1.1	–0.2	0.0	0.2000	500.8	–0.4	–0.4	–0.4
0.4000	272.8	–1.0	–0.5	–0.4	0.4000	494.0	–0.2	–0.2	–0.2
0.6000	251.3	0.4	0.0	–0.1	0.6000	486.9	0.2	0.2	0.2
0.8000	225.0	1.9	0.8	0.7	0.8000	478.9	0.4	0.4	0.4
1.0000	190.5	–0.1	–0.1	–0.1	1.0000	469.7	0.0	0.0	0.0
Mean absolute error		0.8	0.3	0.2	Mean absolute error		0.2	0.2	0.2
Ethane–propane [12] ($A_1 = 23.187$, $A_2 = 6.0368$, $A_3 = -2.6261$, $/\Delta T_{cm,\,\mathrm{av}}/ = 0.3$)					***n*-Pentane–*n*-decane** [5] ($A_1 = 118.12$, $A_2 = 59.375$, $A_3 = 0.0001$, $/\Delta T_{cm,\,\mathrm{av}}/ = 0.0$)				
Binary interaction parameters		**1.035**	**1.025**	**5.105**	Binary interaction parameters		**1.109**	**1.073**	**26.51**
0.0000	369.8	0.0	0.0	0.0	0.0000	617.7	0.0	0.0	0.0
0.1202	364.0	–0.6	–0.4	–0.4	0.2000	601.3	–5.7	–2.8	–2.5
0.2398	358.0	–0.7	–0.4	–0.4	0.4000	584.0	–2.8	–1.2	–1.0
0.3598	352.5	0.3	0.6	0.6	0.6000	560.1	2.9	1.2	1.0
0.4803	344.1	–0.8	–0.7	–0.7	0.8000	523.9	5.7	1.8	1.3
0.5807	337.9	–0.3	–0.4	–0.4	1.0000	469.7	0.0	0.0	0.0
0.6603	333.1	0.4	0.2	0.2	Mean absolute error		2.9	1.2	1.0
0.7389	327.5	0.7	0.4	0.4					
0.8205	321.4	1.0	0.7	0.6					
0.8997	314.1	0.1	–0.1	–0.1					
1.0000	305.3	0.0	0.0	0.0					
Mean absolute error		0.5	0.3	0.3					
Propane–2-methylpentane [5] ($A_1 = 72.207$, $A_2 = 16.121$, $A_3 = 0.55339$, $/\Delta T_{cm,\,\mathrm{av}}/ = 0.0$)					**2,2-Dimethylpropane–*n*-hexane** [5] ($A_1 = 16.309$, $A_2 = -5.0208$, $A_3 = 1.1393$, $/\Delta T_{cm,\,\mathrm{av}}/ = 0.0$)				
Binary interaction parameters		**1.083**	**1.051**	**10.72**	Binary interaction parameters		**1.017**	**1.013**	**3.419**
0.0000	497.7	0.2	0.2	0.2	0.0000	507.7	0.1	0.1	0.1
0.2000	482.0	–1.5	0.1	0.1	0.2000	496.0	0.5	0.7	0.7
0.4000	463.0	–0.8	0.2	0.2	0.4000	482.2	0.2	0.3	0.3
0.6000	439.0	0.8	0.0	0.0	0.6000	467.0	–0.2	–0.3	–0.3
0.8000	408.5	1.6	–0.3	–0.4	0.8000	450.7	–0.5	–0.6	–0.6
1.0000	369.8	0.0	0.0	0.0	1.0000	433.8	0.1	0.0	0.1
Mean absolute error		0.8	0.1	0.2	Mean absolute error		0.3	0.3	0.3

Table 3. (Contd.)

X_1, mole fraction	T_{cm}, K	T_{cm} exp – T_{cm} calc^f, K		
		I	**II**	**III**
2-Methylpentane–2-methylhexane [13] ($A_1 = 8.5645$, $A_2 = 0.78821$, $A_3 = 5.2895$, $/\Delta T_{cm,\text{ av}}/ = 0.1$)				
Binary interaction parameters		**1.009**	**1.007**	**3.180**
0.0000	530.43	0.3	0.1	0.3
0.1207	527.3	0.1	0.0	0.2
0.3326	521.3	0.0	0.0	0.0
0.5473	514.3	–0.3	0.1	–0.3
0.7210	508.7	0.2	0.0	0.2
0.9080	501.5	0.2	0.0	0.2
1.0000	497.75	0.3	0.1	0.3
Mean absolute error		0.2	0.2	0.2
2-Methylhexane–2-methylheptane [13] ($A_1 = 7.8774$, $A_2 = 2.5267$, $A_3 = 14.724$, $/\Delta T_{cm,\text{ av}}/ = 0.2$)				
Binary interaction parameters		**1.010**	**1.008**	**3.767**
0.0000	559.6	0.0	0.0	0.0
0.1301	557.3	0.4	0.4	0.4
0.3236	552.0	–0.3	–0.3	–0.3
0.5363	545.9	–0.5	–0.5	–0.5
0.7768	538.8	0.3	0.2	0.2
0.9074	534.8	1.1	1.0	1.0
1.0000	530.43	0.3	0.3	0.3
Mean absolute error		0.4	0.4	0.4
2-Methylhexane–2-methyloctane [13]				
Binary interaction parameters		**(1.0)**	**(1.0)**	**(5.5)**
0.0000	582.87	–4.1	–4.1	–4.1
0.1270	579.9	–2.0	–1.9	–1.9
0.3516	571.2	–0.2	–0.1	–0.1
0.5675	559.8	0.3	0.2	0.2
0.7519	548.6	0.7	0.5	0.5
0.9199	537	0.9	0.8	0.7
1.0000	530.43	0.3	0.3	0.3

X_1, mole fraction	T_{cm}, K	T_{cm} exp – T_{cm} calc^f, K		
		I	**II**	**III**
2-Methylpentane–2-methylheptane [13] ($A_1 = 18.899$, $A_2 = 9.4274$, $A_3 = 16.203$, $/\Delta T_{cm,\text{ av}}/ = 0.3$)				
Binary interaction parameters		**1.060**	**1.014**	**5.077**
0.0000	559.7	0.1	0.1	0.1
0.1375	554	0.4	0.6	0.6
0.3286	542.4	–1.6	–1.4	–1.4
0.5698	529.8	0.2	0.1	0.1
0.7547	517.7	0.9	0.7	0.6
0.9206	505.1	1.1	0.9	0.9
1.0000	497.75	0.3	0.3	0.3
Mean absolute error		0.7	0.6	0.6
2-Methylheptane–2-methyloctane [13]				
Binary interaction parameters		**(1.0)**	**(1.0)**	**(9.5)**
0.0000	582.87	–4.1	–4.1	–4.1
0.1384	577.4	–2.1	–1.5	–1.5
0.3938	560.9	–0.6	–0.2	–0.2
0.5976	543.7	0.4	0.1	0.1
0.7854	525.1	1.5	0.9	0.8
0.9272	507.3	0.5	0.1	0.1
1.0000	497.75	0.3	0.3	0.3
2-Methylpentane–2-methyloctane [13]				
Binary interaction parameters		**(1.0)**	**(1.0)**	**(0.54)**
0.0000	582.87	–4.1	–4.1	–4.1
0.1080	581.1	–3.2	–3.2	–3.2
0.3224	576.9	–1.8	–1.8	–1.8
0.5235	572.7	–0.6	–0.6	–0.6
0.7265	568.1	0.5	0.5	0.5
0.9075	562.9	0.6	0.5	0.5
1.0000	559.7	0.1	0.1	0.1

[f] The prediction results for critical temperatures of mixtures with the use of (**I**) the quadratic form of Kay's rule [1], (**II**) the Lee–Kesler mixing rules [1] with the binary interaction parameters that we introduced, and (**III**) the Higashi mixing rules [6, 7].

1.4-diTBB. The average value 702.4 K is consistent with the results of direct determination and, what is more important, complements the array of data on T_c of 1,4-diTBB.

The situation in the alkane group is close to the one discussed above. The values of T_c adopted for individual compounds in the literature agree well with the results of studies of the critical temperatures for almost all mixtures (Tables 2, 3). However, this is not the case for 2-methyloctane (2-MO) for which these are two known values, 587.00 [2] and 582.87 K [13]. In addition, there are experimental data [13] for 2-methyloctane mixtures. These data can be used for the estimation of the critical temperature of 2-methyloctane if the information region is limited to a temperature of 573 K. By means of calculating the binary interaction parameters via the equations given in Figs. 2b and 2c, we obtain the following set of T_c values for 2-MO, in K: 586.6 and 587.1, 587.1 and 588.5, and 587.2 and 587.1 with the use of the Lee–Kesler and Higashi methods as applied to the systems 2-methylpentane–2-MO, 2-methylhexane–2-MO, and 2-methylheptane–2-MO,

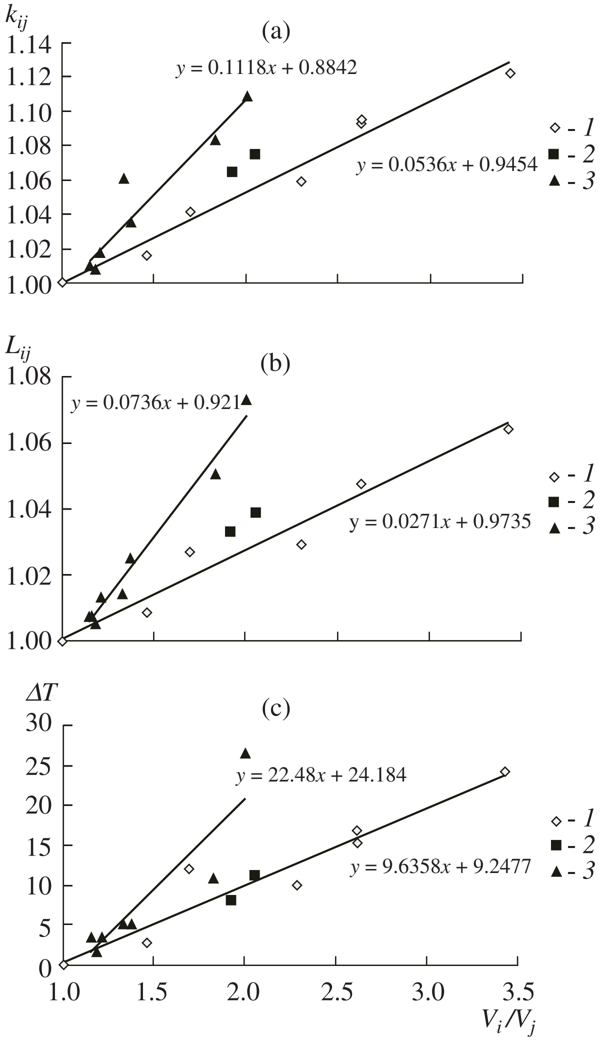

Fig. 2. Binary interaction parameters according to the (a) Kay, (b) Lee–Kesler, and (c) Higashi mixing rules for (*1*) alkylbenzenes, (*2*) methyladamantanes, and (*3*) alkanes.

respectively. The average value is 587.5 K, which is practically the same as that adopted in [2].

Thus, the results of the study on the critical temperatures of the mixtures not only are important as such but also can be a source of information for estimation of T_c of thermally unstable compounds.

ACKNOWLEDGMENTS

This work was supported by the Program "Development of the Scientific Potential of Higher School (2006–2008)," RNP.2.1.1.1198.

REFERENCES

1. R. C. Reid, J. M. Prausnitz, and T. K. Sherwood, *The Properties of Gases and Liquids* (McGraw-Hill, New York, 1977; Khimiya, Leningrad, 1982).
2. B. E. Poling, J. M. Prausnitz, and J. P. O'Connell, *The Properties of Gases and Liquids* (McGraw-Hill, New York, 2001).
3. C. Weygand and G. Hilgetag, *Organisch-chemische Experimentierkunst* (Johann Ambrosius Barth, Leipzig, 1964; Khimiya, Moscow, 1968).
4. A. G. Nazmutdinov, V. S. Sarkisova, N. N. Vodenkova, et al., Neftekhimiya **46**, 458 (2006) [Pet. Chem. **46**, 428 (2006)].
5. D. R. Lide and H. V. Kehiaian, in *CRC Handbook of Thermophysical and Thermochemical Data* (CRC, Boca Raton, 2000).
6. Y. Higashi, J. Chem. Eng. Data **42**, 1269 (1997).
7. Y. Uchida, M. Yasumoto, Y. Yamada, et al., J. Chem. Eng. Data **49**, 1615 (2004).
8. Guofu Wang, Zhangfeng Qin, Jianguo Li, et al., Ind. Eng. Chem. Res., **42**, 6531 (2003).
9. K. Otake, Y. Uchida, M. Yasumoto, et al., J. Chem. Eng. Data **49**, 1643 (2004).
10. M. Yasumoto, Y. Uchida, K. Ochi, et al., J. Chem. Eng. Data **50**, 596 (2005).
11. I. A. Nesterov, T. N. Nesterova, A. G. Nazmutdinov, et al., Zh. Fiz. Khim. **80**, 2032 (2006).
12. L. Freitas, G. Platt, and N. Henderson, Fluid Phase Equilib. **225**, 29 (2004).
13. J. A. Abara, D. W. Jennings, W. B. Kay, and A. S. Teja, J. Chem. Eng. Data **33**, 242 (1988).
14. E. D. Nikitin, A. P. Popov, and Y. G. Yatluk, J. Chem. Eng. Data **51**, 1335 (2006).
15. D. M. Von Niederhausern, G. M. Wilson, and N. F. Giles, J. Chem. Eng. Data **51**, 1986 (2006).
16. W. V. Steele, J. Chem. Thermodyn. **27**, 135 (1995).
17. W. V. Steele, R. D. Chirico, S. E. Knipmeyer, and A. Nguyen, J. Chem. Eng. Data **42**, 1021 (1997).