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Study of the Liquid–Vapor Critical Temperatures for Methyladamantanes and Their Mixtures with Cyclohexane

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Abstract—The liquid–vapor critical temperatures of individual 1,3-dimethyl- and 1,3,5-trimethyladamantanes and their binary mixtures with cyclohexane were determined over the entire range of composition by means of the ampule method. It was found that an excess of the critical temperatures over calculated values reached 20 K for both mixtures studied. The predictive capabilities of several calculation methods are discussed.

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Development of optimal technologies for separation of complex hydrocarbon mixtures of different classes suggests detailed testing of models and combination rules used for the prediction of basic properties of individual components and their solutions. The effectiveness of a selected model is determined to a considerable extent by the correctness of the prediction of one of the critical properties, namely, the critical temperature (T_c), which forms the basis for the calculation of a large number of parameters in terms of the law of corresponding states [1, 2]

An analysis of experimental data on T_c for individual cycloalkanes and their mixtures [1–7] showed that the array of experimental data has to be substantially complemented by information about entities of fundamental importance from practical and theoretical standpoints. Of these entities, cage compounds occupy a special place. The specifics of their molecular structure are obvious and have been well documented in the literature [8–10]. The question is what is the significance of such specifics in the formation of properties of materials with the cage structure of their molecules.

In this work, we consider methyladamantanes (MA) with bridgehead substituents, which have become relatively available to date. These compounds are used as intermediates for the synthesis of a variety of medicines and other industrially important chemicals with unique properties, as well as in the search for new biologically active substances [8].

The theoretical interest stirred by these compounds is due to the fact that the substituent-bearing bridgehead carbon atom in adamantane is unique and seems to match neither a quaternary carbon atom in substituted cyclohexane nor a quaternary carbon atom of aliphatic compounds. If this is indeed the case, the existing methods for the prediction of the critical properties of organic compounds should be corrected in a corresponding manner. This refinement is impossible unless reliable experimental data are available.

In this work, we determined the critical (liquid–vapor) temperatures for 1,3-dimethyladamantane (1,3-DMA), 1,3,5-trimethyladamantane (1,3,5-TMA), cyclohexane (CH), and CH–1,3-DMA and CH–1,3,5-TMA mixtures.

EXPERIMENTAL

Commercial cyclohexane (reagent grade for chromatography, 99.96%(GLC)) and the in-house synthesized chemicals 1,3-dimethyladamantane and 1,3,5-trimethyladamantane were used.

1,3-DMA (or 1,3,5-TMA) was synthesized in two successive steps, the exhaustive hydrogenation of acenaphthene (or fluorene) to afford a mixture of perhydroacenaphthene (or perhydrofluorene) stereoisomers and the liquid-phase isomerization of the stereoisomers on aluminum chloride [8, 11, 12].

To obtain the mixture of isomeric perhydroacenaphthenes (perhydrofluorenes), commercial acenaphthene (fluorene) with a content of the title compound of at least 98% was used. Before hydrogenation, acenaphthene (or fluorene) (100 g) was dissolved in hexane (500 ml), the solution was placed in an autoclave, and Raney nickel (10 g) prepared as described in [13] was added. The autoclave was sealed and purged three times with hydrogen. The hydrogenation was carried out at a temperature of 423 K and a hydrogen pressure of 1.5 MPa with stirring for 6 (or 10 h). The conversion of acenaphthene or fluorene exceeded 99.5 (or 99%) according to GLC data. After completion of hydrogenation, the catalyst was filtered off, cyclohexane was removed by distillation, and a mixture of perhydroacenaphthene (or perhydrofluorene) stereoisomers was obtained with a practically quantitative yield.

The mixture of perhydroacenaphthene (or perhydrofluorene) stereoisomers was isomerized at 343 K in the presence of $AlCl_3$ (20 wt %) for 50 (or 70 h) in a thermostatically controlled flask equipped with a stirrer, a reflux condenser, and a thermometer. On completion of the reaction, the isomerizate containing about 90% 1,3-DMA (or 85% 1,3,5-TMA) was separated from the catalyst complex and treated with a mixture of ice and 15% HCl to remove the residual catalyst. The organic layer was separated and washed with a sodium carbonate solution and water.

1,3-DMA and 1,3,5-TMA (purity > 99.9% according to GLC) were obtained by distillation of a preliminarily dried isomerizates on a laboratory fractionating column (20 theoretical plates) at atmospheric pressure.

The liquid–vapor critical temperatures were determined by the ampule method from the temperatures of meniscus disappearance upon heating and appearance upon cooling [14]. The schematic of the setup is depicted in Fig. 1.

The experimental procedure was as follows. An individual compound or mixture to be tested was placed in a Pyrex ampule with an inner diameter of 4 mm and a length of 75 mm. The filling of the ampule corresponded to the meniscus disappearance and appearance in the middle third of the ampule. The sample in the ampule was cooled to 255 K to prevent the loss of the substance during sealing. This is especially important in the study of mixtures, because the mixture composition was determined from the mass ratio of the components, and the nonequivalent carry over of compounds during the sealing of ampoules would inevitably change the mixture composition. The cooled ampule was sealed. The mass before and after sealing was controlled by weighing on a VRL-200 balance. The difference in mass did not exceed 0.4 mg.

Ampule *1* with a sample was inserted in cylindrical thermometric cell *2* made from heat-resistant glass (Pyrex) covered with an aluminum foil except an observation slit. To heat the sample, air thermostat *3* of the thermal conductivity detector for a Tsvet-100 gas chromatograph was used, which allowed the precritical temperature to be attained at a high rate and the temperature to be maintained accurate within 0.2 K. To prevent a temperature gradient in the detector thermostat, the thermostat was equipped with powerful fan *4*. The temperature was regulated with electronic device *5*. In the region of the critical state, heating and cooling were carried out at a rate of ≤ 0.5 K/minute.

To observe the behavior of the sample, incandescent lamp *6* was mounted in the thermostat; the lamp was separated from the temperature control zone by double screen *7* made from mica and dull quartz to mitigate the effect of thermal radiation on the sample. The processes in the ampule were monitored through observation slit *8* in the thermostat body; the slit was shielded by an organic glass to protect in the event of breaking of the ampule and to decrease heat losses.

The temperature was measured with chromel–copel thermocouple thermometer (TCT) *9*, whose hot junction was placed in the thermometric cell near the ampoule and the cool junction was placed in Dewar flask *10* at 273.15 K. The TCT thermal electromotive force was measured by the compensation method with P 4833 dc potentiometer *11* with a precision class of 0.05. The thermocouple was calibrated with respect to the melting points of reference substances, the measurement error was ≤ 0.5 K.

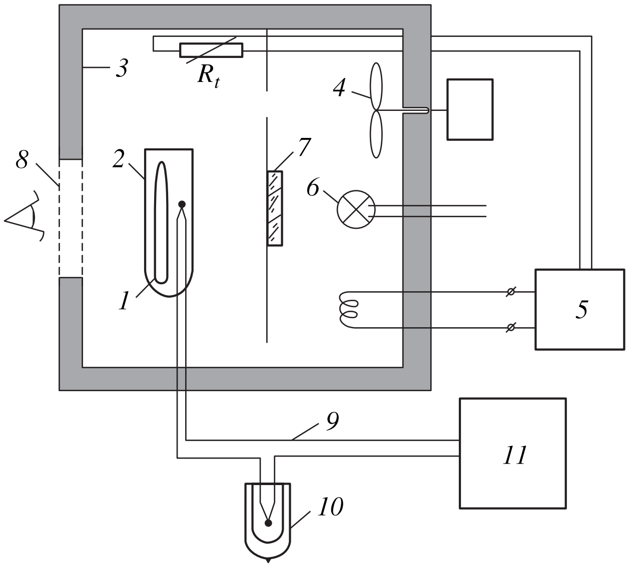

Fig. 1. Schematic of the setup for the measurement of critical temperatures: (*1*) ampule, (*2*) thermometric cell, (*3*) thermostat, (*4*) fan, (*5*) temperature control unit, (*6*) incandescent lamp, (*7*) screen, (*8*) observation slit, (*9*) thermocouple, (*10*) Dewar flask, and (*11*) potentiometer; R_i is a resistant thermometer.

The critical temperatures of the mixtures were measured over the entire range of composition. The quality of the samples was controlled gas chromatographically before and after the experiment. The data presented in Table 1 indicate that the test compounds and mixtures behaved as thermally stable. The mixture composition in the ampule practically did not change after the measurement of the critical temperature despite the long-term residence in the high-temperature zone. The highest degree of decomposition did not exceed 0.3, 1.3, and 1.4 wt % for cyclohexane, 1,3-DMA, and 1,3,5-TMA, respectively.

The analysis was carried out on an automated Kristall-2000M gas chromatograph operated by means of the version 2.2 Chromatec-Analytic software and equipped with a flame-ionization detector and a quartz capillary column (50 × 0.00025 m) with the bonded OV-101 liquid phase. The evaporator temperature was 623 K; the column oven temperature was programmed from 423 to 473 K at a heating rate of 5°C/min, held at 473 K for 7 min, and then raised to 523 K at a rate of 15°C/min.

Table 1. Critical temperatures of 1,3-dimethyladamantane and 1,3,5-trimethyladamantane and methyladamantane–cyclohexane mixtures

Initial mixture composition, g[a]		CH/MA contents, wt %[b]		Experiment time, min[c]	T_{cm} exp, K	T_{cm} calc –T_{cm} exp[d], K		
CH	MA	before experiment	after experiment			I	II	III
Cyclohexane + 1,3-Dimethyladamantane								
–	+	0.0/99.9	0.0/98.6	460	706.7 ± 0.4	0.0	0.0	0.0
0.0094	0.3132	2.9/97.0	2.5/95.3	370	701.4 ± 0.3	–3.1	0.9	–1.4
0.0410	0.3180	11.4/88.5	11.1/87.7	360	685.9 ± 0.5	–9.6	2.6	–4.2
0.1034	0.2346	30.6/69.3	28.9/70.8	485	654.8 ± 0.1	–18.2	0.8	–9.1
0.1766	0.1427	55.3/44.7	53.9/45.8	500	619.2 ± 0.3	–19.6	–3.7	–11.3
0.3006	0.0409	88.0/12.0	87.3/12.6	200	568.3 ± 0.2	–3.1	1.6	–0.4
+	–	99.96/0.0	99.6/0.0	150	553.5 ± 0.5	0.0	0.0	0.0
Cyclohexane + 1,3,5-Trimethyladamantane								
–	+	0.0/99.9	0.0/98.5	420	701.9 ± 0.5	0.0	0.0	0.0
0.0516	0.2000	20.5/79.5	19.7/79.8	440	668.5 ± 0.6	–13.9	1.9	–9.6
0.1103	0.2265	32.7/67.3	31.7/67.9	485	648.8 ± 0.2	–18.4	0.9	–11.1
0.1428	0.0970	59.6/40.4	58.8/41.1	150	609.2 ± 0.1	–21.3	–2.0	–10.0
0.2209	0.0836	72.6/27.4	71.3/28.6	450	591.4 ± 0.2	–18.4	–2.4	–7.7
+	–	99.96/0.0	99.6/0.0	150	553.5 ± 0.5	0.0	0.0	0.0

[a] The composition was determined by the gravimetric method.

[b] The composition was determined chromatographically. The total concentration of unidentified components is $x = 100 - \mathrm{CH} - \mathrm{MA}$, %.

[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 linear form of Kay's rule [1], (II) the quadratic form of Kay's rule [1], and (III) the Leigh–Kesler mixing rules [1].

RESULTS AND DISCUSSION

The obtained experimental data are presented in Table 1 with an accuracy given by the standard deviation (at $p = 0.05$).

There is a wide variety of data on the critical temperature of cyclohexane. Our value agrees within the limits of error with the data reported in [15] (the average over 18 runs is 554 ± 1 K).

The T_c value obtained for 1,3-DMA in this work is 706.7 ± 0.4 K, which is practically the same as 708 K determined by Steele et al. [16] with the use of the DSC technique and exceeds by 2.7 K the critical temperature estimated by Varushchenko according to the Filippov method via the extrapolation of an experimental P–T curve to the critical point [17].

The critical temperature of 1,3,5-TMA was determined by a direct method for the first time in this work and was equal to 701.9 ± 0.5 K, which practically coincides with the estimates by the Filippov method (701 K) given in [17].

It is noteworthy that the experimental value of T_c for 1,3,5-TMA is below that for 1,3-DMA. This ratio is reflected well by the Filippov method, although the normal boiling points T_b of 1,3-DMA and 1,3,5-TMA are 476.53 and 483.31 K [17], respectively; i.e., they increase with an increase in the number of substituents on the adamantane nucleus.

The potentialities of some methods for prediction of the critical temperature of MA are illustrated in Table 2. Taking into account the uncertainty in the choice of the parameter for the quaternary carbon atom in MA, we considered alternative approaches with the partial contribution of the cyclic and acyclic carbon in the original version of each method and with a value of this contribution adjusted to our experimental data.

All these methods employ normal boiling points as a reference parameter; thus, the reliability of the boiling-point data determines to a high degree the reliability of T_c estimates. Although precision measurements of T_b of 1,3-DMA and 1,3,5-TMA were made [13],

Table 2. Predicted critical temperatures of 1,3-dimethyladamantane and 1,3,5-trimethyladamantane

Method	T_c calc – T_c exp, K	
	1,3-DMA	1,3,5-TMA
Lydersen method with the cyclic (acyclic) component for the quaternary carbon atom in adamantane	–4.5 (–14.9)	9.5 (–6.0)
Lydersen method with a fitted cyclic component for the quaternary carbon atom in adamantane ($C_{4,Ad}$ = –0.005)	–7.5	5.0
Joback method with the cyclic (acyclic) component for the quaternary carbon atom in adamantane	–12.2 (–15.8)	–2.0 (–7.3)
Joback method with the adjusted cyclic component for the quaternary carbon atom in adamantane ($C_{4,Ad}$ = 0.0011)	–7.6	5.1
Wilson–Jasperson	–7.4	–5.6
Wilson–Jasperson method with addition of the group term for the quaternary carbon atom in adamantane ($C_{4,Ad}$ = –0.00671)	–0.9	0.4
Marrero–Pardillo method with taking into account the cyclic structure of the adamantane cage (all bonds are considered aliphatic)	–80.3 (–38.3)	139.8 (–33.1)

none of the aforementioned methods satisfactorily predicts the critical temperature of MA.

The Lydersen method [1] gives for 1,3-DMA and 1,3,5-TMA significant deviations in opposite directions (Table 2) when either the cyclic or the aliphatic component of the method is used for the substituent-bearing bridgehead atom of adamantane.

Retaining the basis of the Lydersen method, Joback introduced some corrections into the correlation equation and parameterized the additive components of the property [2]. Nevertheless, these changes did not improve the prediction for the compounds in question, except that the deviations turned out to have the same sign.

The two methods can be adjusted if a sufficient amount of reliable experimental data on T_c for compounds of the given class is available, with the number of fitting parameters directly depending on the amount of available information. Having T_c values for the two given compounds, we may try to adjust only one parameter of the calculation scheme. In our case, we decided upon the most specific substituent-bearing bridgehead atom of the adamantane skeleton. The value of the parameter after fitting and the calculation results are given in Table 2. One can see that neither method made the prediction any better; therefore, the parameters obtained cannot be recommended for calculations. It seems that it is necessary to fit the parameters of the scheme for all of the variety of adamantane cage atoms.

The Wilson–Jasperson method based on atom-connectivity information [2] is the only method that reflects the opposite signs of deviation in T_b and T_c for 1,3-DMA and 1,3,5-TMA despite considerable absolute values of the deviation itself.

We attempted to improve the predictive capabilities of the method by introducing the second-order component for the quaternary carbon atom of the adamantane cage. As a result, the prediction quality became better for both compounds under study (Table 2).

The Marrero–Pardillo method [2], which gives good estimates of T_c for alkanes, showed complete inadequacy in the prediction of T_c for methyladamanthanes. It is interesting that the quality of prediction slightly increases but still remains unacceptable when the cal-

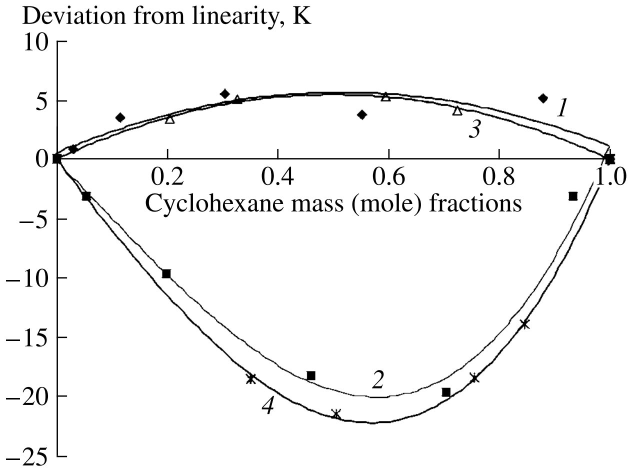

Fig. 2. Deviation of critical temperatures for mixtures from linearity. The cyclohexane–1,3-dimethyladamantane system: (*1*) mass fractions and (*2*) mole fractions. The cyclohexane–1,3,5-trimethyladamantane system: (*3*) mass fractions and (*4*) mole fractions.

culation is carried out with the use of aliphatic components only.

An analysis of the data listed in Table 2 leads to the conclusion that it is insufficient to detail these calculation methods, except the Wilson–Jasperson atomistic method, for the prediction of T_c of methyladamantanes with bridgehead substituents. A greater body of experimental information is needed for the adjustment of the methods.

The analysis of the experimental data on the mixtures showed that the critical temperature of a mixture $T_{\rm cm}$ nonlinearly depends on the molar composition for both test systems (Fig. 2), thus making the widespread simplest additive sum of mole components (known as Kay's rule [1, 2]) inapplicable to the prediction of the pseudocritical temperature of these mixtures

$$T_{\rm cm} = \sum_i y_i T_{cj}.$$

The highest calculation error for the systems under study is 3.2 rel % (–19.6 K).

The use of the quadratic form of Kay's rule taking into account the parameters of pair interactions k^*_{ij} seems more adequate:

$$T_{\rm cm} = \sum_i \sum_j y_i y_j T_{cij},$$

where

$$T_{cii} = T_{ci}; \quad T_{cij} = k^*_{ij}\frac{(T_{ci}+T_{cj})}{2}.$$

The k^*_{ij} values characterize pair interactions of the components. *i-j*. However, k^*_{ij} for each pair of compounds can be obtained only via back calculation from experimental data.

By the least-squares treatment of the results, we calculated the values of k^*_{ij} for the pairs of the compounds under study. The use of the quadratic form of Kay's rule makes it possible to reduce the error of prediction of the pseudocritical temperatures to 0.6 rel % (–3.7 K). The k^*_{ij} value was almost the same for the two systems: 2.12 and 2.14 for CH–1,3-DMA and CH–1,3,5-TMA, respectively. Therefore, we recommend a value of k^*_{ij} = 2.13 in the first approximation for use in the case of mixtures containing cyclohexane and methyladamantanes with bridgehead substituents.

Another widely used approach to the prediction of $T_{\rm cm}$, the Lee–Kesler mixing rule obtained via the modification of the Benedict–Webb–Rubin equation [1]

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

gives slightly better description than the linear form of Kay's rule. The error was 1.8 rel % (–11.3 K) with the use of the Lydersen method for critical volumes. We suppose that the error of $T_{\rm cm}$ calculation in terms of the Lee–Kesler model will be even smaller if necessary corrections are introduced into the method of prediction of the critical volumes of cage compounds. The finding that the plot of $T_{\rm cm}$ versus the mass fraction exhibits a weaker nonlinearity as compared with the plot against the mole fraction (see Fig. 2) confirms this suggestion. We also believe that the solution of problems related to the prediction of the critical volumes of cage compounds will make the discussion of the predictive capabilities of various methods and combination rules for hydrocarbon mixtures more sound.

CONCLUSIONS

The liquid–vapor critical temperatures for 1,3-dimethyl- and 1,3,5-trimethyladamantanes and their binary mixtures with cyclohexane over the entire range of composition were experimentally studied.

The predictive capabilities of the Lydersen, Joback, Wilson–Jasperson, and Marrero–Pardillo methods for the calculation of T_c were compared. It was shown that the original versions of the Lydersen and Joback methods inadequately describe the T_c of methyladamantanes and there is a lack of experimental data that are necessary for the adjustment of the methods. The original version of the bond-based Marrero–Pardillo method does not describe the T_c of methyladamantanes. To calculate their T_c, we recommend the Wilson–Jasperson method with the use of additional second-order component for the quaternary carbon atom of the adamantane cage.

To calculate $T_{\rm cm}$ for binary mixtures that contain alkyladamantanes, we recommend the quadratic form of Key's mixing rule with the use of the interaction parameters k^*_{ij}. For the cyclohexane–methyladamantane pair, the value k^*_{ij} = 2.13.

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