DETERMINATION OF HEATS OF VAPORIZATION AND SOME OTHER THERMODYNAMIC QUANTITIES FOR FOUR ALKYLCYCLOPARAFFINS*

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Heats of vaporization and some other related thermodynamic quantities were determined for the four alkylcycloparaffins: ethylcyclopentane, n-butylcyclopentane, ethylcyclohexane and tert-butylcyclohexane. The temperature dependence of heats of vaporization was measured and employed for calculating standard heats of vaporization, internal and cohesive energies of vaporization, entropies of vaporization, and differences between heat capacities of liquids and vapours at constant pressure and along the saturation line of vapours.

This work represents a further continuation in the series "Enthalpy data on liquids" published in this journal. Here we concentrated our attention on alkylcycloparaffins with straight and branched substituents. Only few reliable calorimetric data are available in the literature for these substances. For the experimental determination and calculations we employed methods described earlier[1-5] and therefore they will be mentioned in this work only briefly.

EXPERIMENTAL

Preparation and purity of substances. All the four substances were of a high purity grade, namely gas chromatography standards. They were kept over Nalsit A4 molecular sieves. The purity was verified mass-spectrographically and no other substances were identified.

Measurements. The temperature dependence of heats of vaporization was measured on an isothermal vaporization calorimeter, which was described in detail earlier[6]. The measurements were performed in the temperature range 40—95°C with a step of 10—15°C. The experimental error was estimated from an analysis of the accuracy of input quantities and individual corrections; it was lower than 0·2%.

RESULTS

Results of our measurements of heats of vaporization ΔH_v were correlated by a relation proposed in our laboratory[2]; its form is

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$$\Delta H_v = K(1 - T_r)^{\alpha} e^{-\beta T_r}, \qquad (1)$$

where K, α, β are constants, T_r is reduced temperature. An advantage of this relation in comparison with the Thiesen equation[7] recommended in the literature is in the fact that it can express with a better accuracy not only the temperature dependence of ΔH_v, but also the temperature dependences of the standard heat of vaporization ΔH_v^0, internal energy of vaporization ΔU_v and cohesive energy ΔU_c in a wider temperature range than the Thiesen relation even if only two correlation constants are used ($\alpha = \beta$). Experimental values and results of the correlations are given in Table I. Values of K and α are correlation constants in relation (*1*), T_c is the critical temperature in K, δ is the standard correlation deviation in kJ/mol, T_{NBP} is the normal boiling point in K.

Further we report values of two heats of vaporization most frequently employed in the literature, namely $\Delta H_{v,NBP}$ – heat of vaporization at the normal boiling temperature and $\Delta H_{v,25}$ – heat of vaporization at 25°. Both values were obtained using the correlation form (*1*). Necessary values of physical quantities were taken from the literature: T_c (ref.[8,9]), P_c (ref.[8,9]) and T_{NBP} (ref.[8,10]). Values of the critical quantities of n-butylcyclopentane were estimated: T_c according to Lydersen[11] and P_c according to Forman and Thodos[12,13]. The choice of methods was affected by the knowledge of input data and recommendations from the literature[8].

TABLE I

Experimental heats of vaporization (kJ/mol) and results of the correlation

°C	Ethylcyclopentane	n-Butylcyclo-pentane	Ethylcyclohexane	tert-butylcyclo-hexane
40	35·60		39·75	
55	34·75	43·76	38·87	45·02
70	33·91	42·68	37·90	44·02
85	33·01	41·60	37·00	43·03
95	32·50	40·85	36·33	42·37
K	51·1567	66·4008	57·8648	65·8810
α	0·2693	0·3268	0·3035	0·3208
T_c	569·50	622·59	609·00	659·00
δ	0·020	0·008	0·023	0·009
T_{NBP}	376·62	429·75	404·95	444·70
$\Delta H_{v,NBP}$	31·98	36·13	33·93	37·00
$\Delta H_{v,25}$	36·39	45·89	40·67	46·97

Standard heats of vaporization ΔH_v^0, internal energies of vaporization ΔU_v, cohesive energies ΔU_c and entropies of vaporization ΔS_v were calculated from values of heats of vaporization employing data on saturated vapour pressures, densities of the liquid phase and state behaviour of the vapour phase. The relation to the heat of vaporization is given by the equations:

$$\Delta H_v^0 = \Delta H_v + \Delta H^* \qquad (2)$$

TABLE II

Temperature dependence of standard heats of vaporization, internal energies of vaporization, cohesion energies (in kJ/mol) and entropies of vaporization (in J/(mol K)) as expressed by Eq. (7)

Quantity	K'	β	δ^a
	Ethylcyclopentane, 40—95°C		
ΔH_v^0	49·2911	0·2403	0·022
ΔU_v	51·2716	0·3269	0·005
ΔU_c	49·8135	0·3043	0·021
ΔS_v	308·271	0·7433	0·362
	n-butylcyclopentane, 55—95°C		
ΔH_v^0	65·3082	0·3130	0·011
ΔU_v	67·2241	0·3867	0·001
ΔU_c	66·3434	0·3757	0·008
ΔS_v	407·511	0·8760	0·291
	Ethylcyclohexane, 40—95°C		
ΔH_v^0	56·5731	0·2846	0·016
ΔU_v	58·4061	0·3656	0·002
ΔU_c	57·3853	0·3508	0·014
ΔS_v	359·957	0·8458	0·368
	Tert-butylcyclohexane, 55—95°C		
ΔH_v^0	65·1010	0·3102	0·008
ΔU_v	66·6663	0·3833	0·000
ΔU_c	66·0417	0·3749	0·006
ΔS_v	413·197	0·9294	0·280

[a] Standard deviation in kJ/mol or J/(mol K) resp.

$$\Delta U_v = \Delta H_v - P^0(V^g - V^l), \tag{3}$$

$$\Delta U_c = \Delta H_v + \Delta H^* - RT + P^0 V^l, \tag{4}$$

$$\Delta S_v = \Delta H_v/T, \tag{5}$$

where ΔH^* denotes the difference between enthalpies of the ideal gas and the saturated vapour; P^0, V^g, V^l, R and T are the saturated vapour pressure, molar volumes of the gas (g) and liquid (l) phases, gas constant and temperature in K, resp. For the given pressure range and type of substances, the state behaviour of the vapour phase can be described by the pressure form of the virial equation of state truncated after the second virial coefficient B. Then it holds

$$\Delta H^* = P^0[T(\mathrm{d}B/\mathrm{d}T) - B]. \tag{6}$$

Second virial coefficients and their temperature derivatives were calculated from a relation proposed by Pitzer and Curl[14]. Data on the liquid phase volumes were estimated according to the Rackett equation[15]. Parameter z_c in this equation was determined from the known density of liquid at one temperature. Data on tert-butylcyclohexane[8] and the other substances were taken from the literature[16]. Necessary temperature dependences of saturated vapour pressures were calculated from the Antoine equation; numerical values of constants were taken from the literature[10,17]. The calculations were performed in temperature ranges identical with the measurements of heats of vaporization. The data were correlated by the two-constant relation (1)

$$X = K'[(1 - T_r)\exp(-T_r)]^{\beta'}, \tag{7}$$

where X denotes the correlated quantity (ΔH_v^0, ΔU_v, ΔU_c, ΔS_v); K' and β' are the correlation constants. The results are summarized in Table II. For all substances it contains constants in Eq. (7) for the calculation of quantities investigated, values of standard deviations δ in kJ/mol and temperature ranges for which the data are valid.

In the following calculations we employed the known temperature dependences of heats of vaporization for calculating other characteristic properties, namely the difference between heat capacities of the liquid and vapour phase along the saturation line, Δc_σ, and at constant pressure, Δc_p. The difference Δc_σ is defined as $\Delta c_\sigma = c_\sigma^g - c_\sigma^l$ and $\Delta c_p = c_p^l - c_p^{g0}$, where c_p^{g0} is the heat capacity of the vapour in the state of an ideal gas. These quantities are related to the heat of vaporization and its temperature derivative through the following relations:

$$\Delta c_\sigma = (\partial \Delta H_v/\partial T)_\sigma - \Delta H_v/T \tag{8}$$

and

$$\Delta c_p = -(\partial \Delta H_v/\partial T)_\sigma + (\Delta H_v/T)\,[1 - T\{(\partial V^g/\partial T)_p - (\partial V^1/\partial T)_p\}/(V^g - V^1)] - \\ - T\int_0^{P_0} (\partial^2 V^g/\partial T^2)_p \, dP\,. \qquad (9)$$

In the low-pressure limit, where the state behaviour of the vapour phase can be expressed by the pressure form of the virial equation of state limited to the second virial coefficient, Eq. (*9*) reads as

$$\Delta c_p = -(\partial \Delta H_v/\partial T)_\sigma + (\Delta H_v/T)\,[1 - T\{R/P^0 + dB/dT - (\partial V^1/\partial T)_p\}/ \\ (RT/P^0 + B - V^1)] - TP^0(d^2B/dT^2)\,. \qquad (10)$$

The calculations were performed for temperatures identical with those of experimental values of ΔH_v and they were correlated by the second-order polynomial

$$\Delta c_x = A + BT + CT^2\,, \qquad (11)$$

where Δc_x stands for Δc_σ and Δc_p, resp.; A, B, C are correlation constants. Results of these correlations are summarized in Table III. The first row of each substance in this table contains correlation constants in relation (*11*) for Δc_σ, the second row

TABLE III

The temperature dependence of heat capacity differences Δc_σ (upper row) and Δc_p (lower row) in J/mol K as expressed by Eq. (*11*)

Substance	$\Delta c_\sigma/\Delta c_p$			δ	Temperature range
	A	B	$-C \cdot 10^{-3}$		
Ethylcyclopentane	—474·388	1·49049	1·6334	0·016	40—95
	38·2185	0·09534	1·7170	0·015	
n-Butylcyclo-pentane	—590·469	1·77607	1·8318	0·017	55—95
	46·0430	0·14433	2·1879	0·001	
Ethylcyclohexane	—524·096	1·60330	1·6881	0·024	40—95
	36·2532	0·14699	2·3864	0·004	
Tert-butylcyclo-hexane	—580·200	1·72179	1·7419	0·018	55—95
	40·0862	0·14587	2·1896	0·002	

contains constants in the same relation for Δc_σ. Standard deviations and temperature ranges of validity of the data are reported for both quantities in the last two columns.

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