

HEATS OF VAPORIZATION OF ALKYL ACETATES AND PROPIONATES*

V.SVOBODA, F.VESELÝ, R.HOLUB and J.PICK

*Department of Physical Chemistry,
Prague Institute of Chemical Technology, 166 28 Prague 6*

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Heats of vaporization of methyl, ethyl, and propyl acetates and methyl and ethyl propionates were measured at various temperatures. The data were correlated with good results by a two-constant equation. The values of heats of vaporization were then used for calculating cohesion energies of the individual esters.

In a previous communication¹ we reported values of heats of vaporization of alkyl formates as the first step of more detailed measurements of heats of vaporization of alkyl esters of aliphatic monobasic acids. This work collects data from our experimental investigation of heats of vaporization of alkyl acetates and propionates.

EXPERIMENTAL

Preparation and Purity of Substances

Commercial ethyl acetate, methyl propionate, and ethyl propionate, A. R. grade, were employed. Methyl acetate and propyl acetate were prepared by esterification of acetic acid by the corresponding alcohol in the presence of sulphuric acid and the ester layer was separated after salting-out with potassium carbonate. All esters were further dried with anhydrous CaCl_2 and subsequently rectified on a 1.5 m-long column packed with stainless spirals. Middle fractions, whose physicochemical constants were in agreement with literature data, were used for the measurements. Measured and literature data are compared in Table I.

Calorimeter

For the measurements we employed an apparatus of our own design whose detailed description has been given in a previous communication². To simplify manipulation and to increase reproducibility some construction changes in the apparatus were performed. These changes together with the working procedure have been described elsewhere¹.

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RESULTS

The heat of vaporization H_v (cal g^{-1}) has been calculated in all cases from the relation $H_v = (W - q_1 - q_2)/m$, where m is mass of evaporated liquid in g, W total amount of heat in calories delivered to the calorimeter ($W = 0.239 UI \tau_1$), q_1 and q_2 are corrections. The first correction determines the heating input compensating heat leak from the vessel and the second one is an enthalpy correction for the increase of the vapour space of the evaporating vessel. A more detailed description of determination of these corrections has been given in the previous work¹. Results of the measurements are collected in Table II. The fourth column of this table contains our experimental values corrected for the increase of the vapour space, the fifth column gives the difference between corrected experimental data and values calculated from the equation

$$H_v = A(1 - T_r)^B, \quad (1)$$

TABLE I
Physicochemical Constants of Pure Substances

Substances	Property	This work	Ref. ^{3,4}
Methyl acetate	$t_{\text{NBP}}, ^\circ\text{C}$	57.15	57.1—57.3
	n_{D}^{20}	1.3617	1.3619
	d_4^{25}	0.9273	0.92730—40
Ethyl acetate	$t_{\text{NBP}}, ^\circ\text{C}$	77.15	77.10—77.18
	n_{D}^{20}	1.3723	1.37239
	d_4^{25}	0.8945	0.89446—0.89468
Propyl acetate	$t_{\text{NBP}}, ^\circ\text{C}$	101.55	101.55—101.6
	n_{D}^{20}	1.3841	1.38406
	d_4^{25}	0.8831	0.88303
Methyl propionate	$t_{\text{NBP}}, ^\circ\text{C}$	79.7	79.65—79.70
	n_{D}^{20}	1.3773	1.3775
	d_4^{20}	0.9151	0.9151
Ethyl propionate	$t_{\text{NBP}}, ^\circ\text{C}$	99.1	99.0—99.2
	n_{D}^{20}	1.3838	1.38394
	d_4^{30}	0.8790	0.87903

in which T_r is the reduced absolute temperature, A and B are constants whose values are in the first column of this table under the name of the ester. Molar volumes of liquids necessary for the calculation of the correction were taken from literature³ except for butyl formate, where this value was estimated from the molar volume of the liquid phase at 20°C (ref.⁴) according to the Watson relation⁵. Molar volumes of vapour were estimated by the method proposed by Pitzer⁶.

Any comparison of our experimental values is difficult. Direct experimental data are known only for methyl acetate at its normal boiling point⁷ (97.0 cal g⁻¹), which

TABLE II
Heats of Vaporization (cal g⁻¹) of Acetates and Propionates

Constants	$t, ^\circ\text{C}$	H_v^{exp}	H_v^{corr}	$H_v^{\text{corr}} - H_v^{\text{calc}}$
Methyl acetate				
	30.85	104.10	103.98	-0.06
$A = 156.87$	40.30	102.10	101.93	0.09
$B = 0.448$	54.55	98.66	98.38	-0.03
$T_k = 506.85$	57.50	98.00	97.69	0.01
Ethyl acetate				
	52.70	91.70	91.56	0.09
$A = 135.74$	57.50	90.66	90.49	-0.08
$B = 0.405$	70.50	88.23	87.96	-0.08
$T_k = 523.2$	77.70	86.95	86.61	0.02
	90.25	84.50	84.02	0.04
Propyl acetate				
	62.95	86.50	86.36	-0.03
$A = 128.99$	70.50	85.20	85.08	-0.00
$B = 0.424$	77.70	84.00	83.84	0.04
$T_k = 549.3$	90.25	81.75	81.50	-0.01
Methyl propionate				
	52.70	92.80	92.67	0.12
	57.50	91.79	91.63	-0.05
$A = 135.70$	70.50	89.33	89.09	-0.14
$B = 0.402$	81.45	87.35	87.01	-0.08
$T_k = 530.5$	90.25	85.90	85.46	0.15
Ethyl propionate				
	62.95	85.75	85.65	-0.01
$A = 128.85$	70.50	84.40	84.27	-0.06
$B = 0.427$	77.70	83.30	83.13	0.09
$T_k = 546.0$	90.25	80.95	80.69	-0.02

agrees rather well with our results. Our data for the other esters may be compared partially with those obtained by Polák⁸ by calculation from saturated vapour pressures at temperatures of the normal boiling point. Deviations between these calculations (methyl acetate 98.8 cal g⁻¹, ethyl acetate 87.7 cal g⁻¹, propyl acetate 77.8 cal g⁻¹, methyl propionate 88.97 cal g⁻¹, ethyl propionate 80.60 cal g⁻¹) and our data are relatively large (1.5–2.2%). This deviation exceeds considerably differences in experimental values of the heat of vaporization of benzene (0.2%), whose heat of vaporization may be up to now considered as most reliable. Taking into account the considerable uncertainty in determination of state behaviour of the individual esters, which has not been so far measured with sufficient accuracy, experimental values of heat of vaporization may be considered as more reliable.

Calculation of Cohesion Energy of Esters

In view of increasing importance of cohesion energy as a characteristic of intermolecular forces, it seemed use our experimental values of heat of vaporization for its calculation.

Cohesion energy is defined as a change in the internal energy of a system due to isothermal evaporation of one mol of liquid at the corresponding vapour pressure into the gaseous state at the same temperature and zero pressure. The total value of ΔU_c may be divided into two terms according to the relation

$$\Delta U_c = \Delta U_c^{(1)} + \Delta U_c^{(2)}, \quad (2)$$

in which $\Delta U_c^{(1)}$ represents the change in the internal energy during evaporation of one mol of liquid at the given temperature and vapour pressure, whereas term $\Delta U_c^{(2)}$, in absolute value much smaller, is the change in the internal energy of vapour during isothermal expansion to zero pressure. The first term in Eq. (2) may be further replaced by the relation

$$\Delta U_c^{(1)} = H_v - P^0 \Delta V, \quad (3)$$

and the second one by

$$\Delta U_c^{(2)} = \int_0^{P^0} [T(\partial v_g / \partial T)_P + P(\partial v_g / \partial P)_T] dP. \quad (4)$$

If the deviation of the state behaviour of vapour from the ideal behaviour is in the region of low pressures expressed by the second virial coefficient, we obtain

$$\Delta U_c = \Delta U_{c,id} + K, \quad (5)$$

where

$$K = P^0(v_1 - B + TB'), \quad B' = dB/dT.$$

To be able to determine the dependence of the total error in the calculated cohesion energy on errors in its individual terms in more detail, we can rearrange Eq. (5) into the dimensionless form

$$\Delta U_c/RT = (H_v/RT) - 1 + K', \quad (6)$$

with

$$K' \equiv K/RT = 1 - \Delta z + (P^0 B'/R). \quad (7)$$

Considering that the value of term H_v/RT is equal approximately to 10 in a sufficiently wide vicinity of the normal boiling point temperature (Pictet-*Trouton* rule), the value of Δz , which equals approximately unity, may be determined with an accuracy by an order lower. As long as the heat of vaporization is calculated from data on vapour pressures, the resulting error of such heats does not usually drop below 1–2% (ref.^{8,9}). In this case it is therefore sufficient to determine the value of Δz . ($\Delta z \approx z_g$) from relation (7) with a 10–20% error, which may be achieved by usual estimation methods or directly by approximating $\Delta z = 1$. Only if we employ experimental heats of vaporization, whose error is 0.1–0.2% (ref.¹⁰), we must proceed with term Δz more carefully as in this case its error cannot exceed 1–2%.

Now let us turn to term $P^0 B'/R$ and find out the relation between magnitudes of terms $P^0 B'/R$ and $1 - \Delta z$. The value of $1 - \Delta z$ reaches in the examined range of temperatures values between 0.01 and 0.05. The term $P^0 B'/R$ may be for our purposes estimated from the generalized Redlich-Kwong equation, which yields¹¹

$$B = 0.0867(1 - 4.93/T_r^{1.5}) RT_k/P_k \quad (8)$$

and, consequently,

$$P^0 B'/R = 0.64 P_r^0 / T_r^{2.5}, \quad (9)$$

Table III contains values of $P^0 B'/R$ calculated for the range of temperatures and pressures of our experiments. It is obvious that the value of $P^0 B'/R$ exceeds that of the

TABLE III
Dependence of the Term $P^0 B'/R$ on Temperature and Pressure

T_r	P_r					
	0.005	0.01	0.02	0.03	0.04	
0.5	0.018	0.036	0.072	0.110	0.144	
0.6	0.012	0.023	0.043	0.069	0.092	
0.7	0.008	0.016	0.031	0.047	0.062	

TABLE IV
Cohesion Energies of Formates, Acetates, and Propionates

Constants	$t, ^\circ\text{C}$	ΔU_c^* cal mol ⁻¹	v_1 cm ³ mol ⁻¹	K_1 cal mol ⁻¹	K_2 cal mol ⁻¹	ΔU_c cal mol ⁻¹	Deviation cal mol ⁻¹
$A = 5.1147 \cdot 10^6$ $B = 1.625$	20.10	6 269.8	61.6	47.8	45.6	6 317.6	1.79
	31.57	6 060.2	62.7	71.5	63.6	6 131.8	- 4.99
	39.98	5 915.0	63.6	93.9	79.8	6 008.9	3.22
$A = 1.4463 \cdot 10^7$ $B = 1.735$	30.65	6 946.4	81.5	40.8	43.2	6 987.2	4.39
	39.98	6 756.8	82.6	56.5	56.3	6 813.3	- 7.65
	54.16	6 484.9	84.5	88.8	81.8	6 573.7	3.28
$A = 1.2015 \cdot 10^7$ $B = 1.585$	52.39	7 895.8	101.5	46.9	45.2	7 942.8	9.74
	57.08	7 794.0	102.2	55.2	51.7	7 849.2	- 1.75
	69.98	7 531.4	104.1	84.1	73.4	7 615.5	- 10.73
	77.18	7 392.0	105.2	104.7	88.4	7 496.6	- 3.76
	80.89	7 310.6	105.7	116.7	97.0	7 427.3	- 8.92
89.68	7 140.7	107.2	149.4	119.8	7 290.1	15.51	
$A = 5.7896 \cdot 10^7$ $B = 1.835$	72.18	8 570.1	121.8	-	49.0	8 619.1	- 5.29
	80.89	8 405.7	123.1	-	62.2	8 467.9	9.63
	89.68	8 209.5	124.4	-	78.3	8 287.8	- 4.33
$A = 1.2698 \cdot 10^7$ $B = 1.705$	30.65	7 099.0	80.5	41.0	39.5	7 140.0	- 3.16
	39.98	6 928.6	81.6	57.6	52.1	6 986.2	3.44
	54.16	6 637.5	83.4	92.3	76.9	6 729.7	- 2.21
57.08	6 580.5	83.8	101.0	83.0	6 681.6	2.01	

				Ethyl acetate				
		7 420.1	102.4	54.4	51.3	7 474.6	7.91	
		7 316.5	103.1	64.1	58.8	7 380.6	7.68	
		7 067.9	105.2	98.0	83.9	7 165.9	9.23	
	$A = 6.5768 \cdot 10^6$	6 940.9	106.4	122.1	101.2	7 062.9	2.94	
	$B = 1.465$	6 681.7	108.6	174.3	137.4	6 856.0	6.31	
				Propyl acetate				
		8 157.1	121.5	—	43.5	8 200.6	0.75	
		8 007.6	122.8	—	54.0	8 061.6	4.25	
	$A = 2.0014 \cdot 10^7$	7 866.7	124.0	—	65.9	7 932.6	3.11	
	$B = 1.625$	7 602.8	126.4	—	91.2	7 694.1	0.45	
				Methyl propionate				
		7 509.1	100.6	49.1	47.8	7 558.1	11.94	
		7 416.9	101.3	57.9	54.7	7 474.8	1.90	
		7 163.1	123.2	88.6	78.0	7 251.7	29.74	
	$A = 4.4791 \cdot 10^6$	6 953.7	105.7	123.0	103.0	7 077.0	31.13	
	$B = 1.385$	6 808.5	106.4	157.9	127.2	6 966.4	11.27	
				Ethyl propionate				
		8 080.5	121.4	—	46.2	8 126.7	1.27	
		7 924.9	122.8	—	57.3	7 982.1	5.88	
		7 794.1	124.0	—	69.8	7 864.0	9.96	
	$A = 1.8890 \cdot 10^7$	7 520.1	126.4	—	96.4	7 616.5	2.74	
	$B = 1.615$							

expression $1 - \Delta z$. This means that term $P^0 B'/R$ cannot be neglected in calculations. The outlined *a priori* analysis and tabulated results lead us to the conclusion that if the error in the heat of vaporization exceeds 1%, the use of any expression for cohesion energy which is more accurate than

$$\Delta U_c = H_v - RT, \quad (10)$$

is not justified at temperatures lower than that of the normal boiling point. This relation corresponds to the approximation $K = 0$. If correction K is not neglected, term $P^0 B'/R$ must be treated with appropriate care.

In view of the fact that our experiments yielded values of heats of vaporization at different temperatures, we tried to evaluate the temperature dependence of cohesion energies as well. There are several relations for this dependence in the literature¹²⁻¹⁴, of which we selected as the most suitable one the following two-constant equation

$$\Delta U_c = A/v_1^B \quad (11)$$

and investigated whether the constant B is for examined substances really constant within reasonable limits, which would confirm the validity of one of recommended one-constant relations.

Values of cohesion energies are in Table IV. Besides values of heats of vaporization from this and preceding work¹, we employed for the calculation literature data on second virial coefficients¹⁵, critical properties³, and constants in the Antoine equation¹⁶. Missing data were extrapolated or estimated: second virial coefficients of butyl formate and ethyl propionate by the Pitzer method⁶ and critical constants of butyl formate by the Lydersen method¹⁷. Constants in Eq. (11) are in the first column under the name of the ester, cohesion energies calculated from Eq. (5) for $K = 0$ are in the third column, molar volumes of liquids are in the fourth column, correction K calculated from published second virial coefficients is in the fifth column, correction K calculated from estimated virial coefficients in the sixth column, cohesion energy in the seventh column, and the last column contains differences between individual values of the cohesion energy and those calculated from Eq. (11). It is obvious from Table IV that Eq. (11) approximates well the temperature dependence of cohesion energy. Our investigation of possible independence of constant B in the homological series led to negative conclusion. By expanding the functional dependence into a Taylor series, assuming a fixed value for constant A and neglecting higher-order terms we namely obtain

$$A/v_1^{B+\Delta B} = A(1 - \Delta B \ln v_1)/v_1^B. \quad (12)$$

The percent deviation of the cohesion energy is then given by

$$\delta(\Delta U_c) = 100 \Delta B \ln v_1. \quad (13)$$

Taking into account that the order of the molar volume of liquid, v_1 , is $\sim 100 \text{ cm}^3 \cdot \text{mol}^{-1}$, relation (13) may be rewritten to read

$$\delta(\Delta U_c) \approx 500 \Delta B. \quad (14)$$

Obviously it follows from this relation that for $\delta(\Delta U_c) < 1\%$ to be valid, the error in the constant B in the considered temperature range and units should not go beyond the third position behind the decimal point, which is not satisfied. As it cannot be assumed that a minimization of constant A would compensate this error to a larger extent, the use of relation (11) with the generalized constant B for calculating cohesion energies of esters of aliphatic acids cannot be recommended.

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