

## HEATS OF VAPORIZATION OF ALKYL ESTERS OF FORMIC, ACETIC AND PROPIONIC ACIDS\*

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Heats of vaporization of ethyl, propyl, butyl esters of formic acid, methyl, ethyl, propyl and butyl esters of acetic acid and methyl, ethyl and propyl esters of propionic acid were measured. These measurements reassume and complete data known from the literature. From the combination of values of heats of vaporization, the cohesive and vaporization internal energies of the set investigated were computed in the dependence on temperature.

In our previous papers<sup>1,2</sup>, the values of heats of vaporization of alkyl esters of formic, acetic and propionic acids had been given as a beginning of a more detailed measurement of heats of vaporization of alkyl esters of aliphatic monocarboxylic acids. The design of a new type of calorimeter<sup>3</sup> had made it possible to extend the temperature range for heats of vaporization determination and so perform measurements unrealizable with the original vaporization calorimeter. This work reassumes and completes our foregoing measurements. Along with the selected literature data, it provides the compiled set of data on heats of vaporization of the chosen series of esters. The formation of such representative sets pursues above all the aim to obtain as reliable as possible data on a property investigated even by excluding the values whose determination has been accompanied by a systematic error. This set of data has become a basis for computing the cohesive and vaporization internal energies which, together with the data on heat of vaporization, characterize the description of phase vapor-liquid equilibrium.

### EXPERIMENTAL

*Preparation and purity of substances.* The substances used in this work have been prepared in the same way as the syntheses, purification and drying described in previous papers<sup>1,2</sup>. As well the values of determined physical properties, *i.e.* normal boiling point, refractive index and density, have been in good agreement with the data given in the literature. The content of impurities has been proved by a mass spectrometer analysis not to be higher than 0.05% for all the esters.

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The measurement of heats of vaporization of esters has been carried out in the same calorimeter whose design and experimental procedure when determining heats of vaporization had been described formerly<sup>3</sup>. It is a vaporization isothermal calorimeter which makes it possible to measure in the temperature range of 25–100°C at saturated vapour pressures of 1–200 kPa. The apparatus works on the principle of total evaporation of liquid and is equipped with a removable evaporation vessel. This arrangement enables to determine the mass of evaporated substance by differential weighing of the vessel before the experiment and after it. The error of the heats of vaporization measured is lower than 0.2%.

## RESULTS

The measured values of heats of vaporization of the esters along with the references of original and taken over data are given in Table I. The compiled set has been made up from the values reported in this work and from selected values for the following substances and temperatures: From the work by Cihlár and coworkers<sup>1</sup>, the data have been taken on  $\Delta H_v$  of ethyl formate (for the temperatures of 30.85, 40.30, 54.55°C) and of propyl formate (52.70, 57.50, 57.70, 70.50, 77.75, 81.50, 90.25°C). From the data measured by Svoboda and coworkers<sup>2</sup>, the values of  $\Delta H_v$  have been used for methyl acetate (30.85, 40.30, 54.55, 57.50°C), ethyl acetate (52.70, 57.50, 70.50, 77.70, 90.25°C), propyl acetate (62.95, 70.50, 77.70, 90.25°C), methyl propionate (52.70, 57.50, 70.50, 81.45, 90.25°C) and ethyl propionate (62.95, 70.50, 77.70, 90.25°C). From the measurement by Mathews<sup>4</sup>, the data have been taken on  $\Delta H_v$  for methyl acetate at the temperature of 56.34°C and for methyl propionate at 79.00°C; from the work by Connet and coworkers<sup>5</sup>, the data for methyl acetate

TABLE I

Measured Heats of Vaporization (kJ/mol) and Literature Sources for the Set of Selected Esters at Different Temperatures

Substance	25°C	40°C	55°C	70°C	85°C
Ethyl formate	ref. <sup>1</sup>	ref. <sup>1</sup>	ref. <sup>1</sup>	28.80	
Propyl formate	37.49	36.52	ref. <sup>1</sup>	ref. <sup>1</sup>	ref. <sup>1</sup>
Butyl formate	41.25	40.05	38.97		36.79
Methyl acetate	32.30	ref. <sup>2,4,5</sup>	ref. <sup>2,4,5</sup>	29.50	
Ethyl acetate	35.62	34.60	ref. <sup>2,5</sup>	ref. <sup>2,5</sup>	31.41
Propyl acetate	39.83	38.59	ref. <sup>2,5</sup>	ref. <sup>2,5</sup>	35.30
Butyl acetate		42.96	41.72	40.58	39.44
Methyl propionate	35.85	34.93	ref. <sup>2,4</sup>	ref. <sup>2,4</sup>	ref. <sup>2,4</sup>
Ethyl propionate	39.25	38.22	ref. <sup>2</sup>	ref. <sup>2</sup>	ref. <sup>2</sup>
Propyl propionate		42.14	41.11	39.98	38.83

(22.35, 38.75°C), ethyl acetate (47.41, 65.47, 77.17°C) and propyl acetate (62.25, 80.11, 101.75°C). The data given by Wadsö<sup>6</sup> and those by Geiseler and coworkers<sup>7</sup> have not been included because of considerable deviations from those of the other authors. The compiled set of data on the temperature dependence of heat of vaporization has been correlated for each ester by the Thiesen relation

$$\Delta H_v = K(1 - T/T_k)^\alpha, \quad (1)$$

where  $K$  and  $\alpha$  are the correlation constants in Eq. (1) and  $T_k$  is the critical temperature. Table II gives summary of calculated constants of the Thiesen relation, the  $T_k$  value used and the standard deviations of correlations  $\sigma$ . Further, the values of heat of vaporization at normal boiling point ( $\Delta H_{v,NBP}$ ) and the temperature range in which the data have been treated are given. The values of  $T_k$  for majority of esters have been taken over from the paper by Kudchadker and coworkers<sup>8</sup>,  $T_k$  for butyl formate has been estimated according to Forman and Thodos<sup>9</sup>.

The normal boiling points of most esters have been calculated from the Antoine equation using the constants given in the literature<sup>10</sup>; for butyl acetate they have been taken from the work<sup>11</sup>.

#### Calculation of Vaporization Internal and Cohesive Energies

The vaporization internal ( $\Delta U_v$ ) and cohesive energies ( $\Delta U_c$ ) are quantities which characterize the reversible phase transition of the liquid-vapour type and which can be defined in terms of the following schemes:

$$\Delta U_v = U(g, T, P^0) - U(l, T, P^0), \quad (2)$$

where the symbols  $g(l)$  denote the gas (liquid) phase and  $P^0$  the saturated vapour pressure;

$$\Delta U_c = U(g, T, P \rightarrow 0) - U(l, T, P^0) = \Delta U_v + \int_{P^0}^0 (\partial U / \partial P)_T^\# dP. \quad (3)$$

The last term in Eq. (3) is a correction for the non-ideal behaviour of the gas phase.

The most natural way of calculation of vaporization internal and cohesive energies is based on the data on heat of vaporization. Both energies are simple functions of heat of vaporization, viz.

$$\Delta U_v = \Delta H_v - P^0 \Delta V = \Delta H_v - P^0(V^g - V^l) \quad (4)$$

and

$$\Delta U_c = \Delta H_v + P^0 V^l - RT + \int_{P^0}^0 [V - T(\partial V / \partial T)_P]^\# dP. \quad (5)$$

TABLE II  
Summary of Constants  $K$  and  $\alpha$  of the Thiesen Relation for  $\Delta H_v$

Substance	$K$ , kJ/mol	$\alpha$	$T_k$ , K	$\sigma$ , kJ/mol	$t_{\text{NBP}}$ , °C	$\Delta H_v$ , NBP kJ/mol	Temperature interval, °C
Ethyl formate	46.749	0.4314	508.4	0.060	54.30	29.94	31—70
Propyl formate	52.370	0.4136	538.0	0.018	80.85	33.60	25—90
Butyl formate	57.558	0.4470	565.2	0.094	105.60	35.06	25—85
Methyl acetate	45.028	0.3747	506.8	0.034	56.90	303.3	22—70
Ethyl acetate	50.172	0.4070	523.2	0.031	77.15	31.97	25—90
Propyl acetate	56.051	0.4398	549.4	0.073	101.60	33.86	25—90
Butyl acetate	61.567	0.4632	579.0	0.088	126.10	35.81	40—85
Methyl propionate	49.729	0.3965	530.6	0.030	79.76	32.23	25—90
Ethyl propionate	54.774	0.4220	546.0	0.024	99.10	33.79	25—90
Propyl propionate	59.445	0.4404	578.0	0.020	122.4	35.77	40—85

When calculating these quantities we can assume, for usual types of substances, that within the range from ambient temperatures to the temperatures close to normal boiling point, the  $P$ - $V$ - $T$  behaviour of the gas phase can be expressed in terms of the volume-explicit virial equation of state restrained to the second virial coefficient.

Then we can rearrange the relations for calculating the vaporization internal and cohesive energies to the forms

$$\Delta U_v = \Delta H_v + P^0 V^1 - RT - BP^0 \quad (6)$$

and

$$\Delta U_c = \Delta H_v + P^0 V^1 - RT - P^0 [B - T(dB/dT)], \quad (7)$$

where  $B$  denotes the second virial coefficient. Eqs (6) and (7) have been used in this work.

When calculating the vaporization internal and cohesive energies, the effect of  $P$ - $V$ - $T$  behaviour of the gas phase increases with increasing temperature. This can also influence negatively the accuracy of calculated quantities. Therefore we must pay proper attention to the description of the volumetric behaviour of the gas phase. Providing that the direct experimental values of the second virial coefficient are not known it is necessary to find a suitable relation which would enable us to estimate these values with sufficient accuracy.

The literature data on the second virial coefficient for the set of esters considered are known only for higher temperature<sup>12</sup>. The extrapolation of these data down to the temperature of 25°C, for which the  $\Delta H_v$  values are known, would be uncertain. It would appear especially unfavourably when calculating the temperature derivative. Therefore they have been used only for selecting a suitable relation to estimate the second virial coefficient. Good agreement between the literature and calculated  $B$  values, especially with regard to the temperature derivative, has been proved when using the relation proposed by Vetere<sup>13</sup>:

$$B = (B^{(0)} + \omega B^{(1)} + \omega_p B^{(2)}) RT_k / P_k, \quad (8)$$

where  $B^{(0)}$  and  $B^{(1)}$  are terms of the relation recommended by Pitzer and Curl<sup>14</sup>, the term  $\omega_p B^{(2)}$  involves the effect of polar substances,  $\omega$  is the Pitzer acentric factor,  $R$  is the gas constant and  $P_k$  the critical pressure. The constant  $\omega_p$  is defined by

$$\omega_p = T_{\text{NBP}}^{1.72} / M - 263.$$

In the cases when the constant  $\omega_p$  is negative, it is set to be zero and the Vetere relation reduces to the Pitzer-Curl one. The acentric factor  $\omega$  has been calculated by means of the Antoine constants<sup>10,11</sup> which have also been used for calculating the saturated vapour pressures in Eq. (6) and (7).

TABLE III  
Summary of Constants  $A_1$  to  $A_3$  of Relations for Vaporization Internal and Cohesive Energies

Substance	$A_1$ , kJ/mol	$A_2$	$A_3$	$\sigma$ , kJ/mol	$A'_1$ , kJ/mol	$A'_2$	$A'_3$	$\sigma$ , kJ/mol
Ethyl formate	47.41	0.0905	0.4868	0.002	49.74	0.4132	0.3111	0.002
Propyl formate	53.57	0.1262	0.4388	0.003	56.86	0.4782	0.2688	0.003
Butyl formate	58.35	0.0753	0.4947	0.002	60.31	0.2980	0.3809	0.004
Methyl acetate	45.47	0.0949	0.4108	0.002	54.35	0.4602	0.2230	0.004
Ethyl acetate	51.08	0.1091	0.4391	0.004	54.35	0.4602	0.2731	0.003
Propyl acetate	57.05	0.0914	0.4808	0.003	58.39	0.2749	0.4011	0.003
Butyl acetate	62.26	0.0521	0.5209	0.002	63.46	0.2010	0.4408	0.003
Methyl propionate	50.46	0.1012	0.4310	0.003	53.58	0.4490	0.2644	0.004
Ethyl propionate	55.70	0.0950	0.4599	0.003	58.57	0.3870	0.3199	0.004
Propyl propionate	59.72	0.0457	0.4958	0.001	62.74	0.3192	0.3678	0.003

The values of critical temperatures and pressures needed for the calculations have been taken from the literature sources used for correlating the  $\Delta H_v$  data. The values of  $P_k$  for butyl acetate<sup>13</sup>, butyl formate and propyl propionate<sup>9</sup> have been obtained from other sources.

The values of molar volumes of the liquid phase in their dependence on temperature have been obtained by calculating from the modified Rackett equation<sup>15</sup>:

$$V^l = (RT_k/P_k) z_{RA}^{[1+(1-T_r)^{2/7}]}, \quad (9)$$

where  $V^l$  is the molar volume of the liquid phase,  $T_r$  is the reduced temperature and  $z_{RA}$  the constant determined from experimental data. For seven esters, the relation has been used to express  $z_{RA}$

$$z_{RA} = P_k V_{RA} / RT_k,$$

where  $V_{RA}$  is a parameter determined by Spencer and Adler<sup>16</sup> for individual substances from the temperature dependence of densities using Eq. (9). For the remaining three substances (butyl formate, butyl acetate and propyl propionate),  $z_{RA}$  has been determined from a known value of density at one temperature, in our case at the temperature of 35°C. For this purpose, the densities have been determined by the pycnometric method for the three esters and two temperatures 25°C and 35°C: propyl formate ( $\rho_{25} = 0.87704$ ,  $\rho_{35} = 0.86878$ ), butyl formate ( $\rho_{25} = 0.88536$ ,  $\rho_{35} = 0.87696$ ) and butyl acetate ( $\rho_{25} = 0.87758$ ,  $\rho_{35} = 0.87009$ ). The numerical values of densities are given in  $\text{g/cm}^3$ .

For analytical expression of the temperature dependence of cohesive and vaporization internal energies, the empirical relation has been proposed in the form

$$\Delta U_v = A_1 e^{-A_2 T_r} (1 - T_r)^{A_3} \quad (10)$$

and

$$\Delta U_c = A'_1 e^{-A'_2 T_r} (1 - T_r)^{A'_3}. \quad (11)$$

The symbols  $A_1(A'_1)$ ,  $A_2(A'_2)$  and  $A_3(A'_3)$  denote the correlation constants in Eqs (10) and (11). The results of the correlations are given in Table III. The values of standard deviations prove the convenience of the analytical form for the temperature dependence of  $\Delta U_v$  and  $\Delta U_c$ .

#### Error Estimation

To estimate the error in the cohesive and vaporization internal energies computation we start from the assumption that  $\Delta H_v$  is determined with an accuracy of 0.2%. The error connected with the determination of the last term on the right-hand side

of Eq. (7) and that connected with the determination of  $\Delta H_v$ , take part in the highest degree in the error of calculation of cohesive energy. The error of the term  $P^0V^1$  is negligible, the value of  $RT$  can be considered as accurate. We assume that the inaccuracy of the determination of the term with second virial coefficient does not exceed the value of 15%, and for the term with the temperature derivative of the second virial coefficient the value of 25%. Both terms take the value of about  $-0.45$  kJ/mol in the vicinity of normal boiling point. Consequently the error in the calculation of cohesive energy increases at most by  $0.2-0.3\%$  compared with that in  $\Delta H_v$ , and when calculating the vaporization internal energy, at most by  $0.1\%$ . This error substantially diminishes with decreasing temperature.

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