TEMPERATURE DEPENDENCE OF HEATS OF VAPORIZATION, SATURATED VAPOUR PRESSURES AND COHESIVE ENERGIES OF SECONDARY AMINES*

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Dedicated to Professor E. Hála on the occasion of his 60th birthday.

The temperature dependence of heats of vaporization of methylisopropylamine, ethylisopropylamine, propylisopropylamine, diisopropylamine, butylisopropylamine, ethylbutylamine and dibutylamine has been measured. Further, the dependence of saturated vapour pressures on temperature has been measured for methylisopropylamine, ethylisopropylamine, propylisopropylamine, butylisopropylamine, diisopropylamine and ethylbutylamine. The densities of the liquid phase at 25°C have been determined for methylisopropylamine, ethylisopropylamine, propylisopropylamine, butylisopropylamine and ethylbutylamine. The cohesive energies at several temperatures have been computed from the experimental data for all the substances of the set.

This work is a continuation of our more extensive study on the temperature dependence of heat of vaporization of industrially important organic substances[1-5]. In our foregoing paper[6], the data on heats of vaporization of some mostly primary aliphatic amines were reported; this work deals with a group of secondary aliphatic amines. The temperature dependence of their saturated vapour pressures and heats of vaporization has been measured; for some substances, in addition, the densities of the liquid phase have been measured owing to the absence of literature data.

EXPERIMENTAL
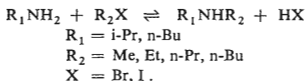
To synthetize the amines two procedures have been employed:

a) Reductive amination of ketones:

$$CH_3COCH_3 + i\text{-}C_3H_7NH_2 + H_2 \rightleftharpoons i\text{-}C_3H_7NHi\text{-}C_3H_7 + H_2O \, .$$
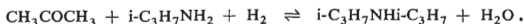
The reaction takes place at higher temperatures (130°C) and pressures (5 MPa) in a selective way on a modified Pd-carrier catalyst and has been used to prepare diisopropylamine.

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b) Alkylation of primary amines with alkyl halides:

$$R_1NH_2 + R_2X \rightleftharpoons R_1NHR_2 + HX$$
$$R_1 = \text{i-Pr, n-Bu}$$
$$R_2 = \text{Me, Et, n-Pr, n-Bu}$$
$$X = \text{Br, I}.$$

The urgent requirements of purity of substances prepared have made us modify the usually used procedures of the alkylation reactions of amines. The choice of reacting pairs has been carried out with regard to the subsequent separation of reaction mixture by rectification. For the same reason the use of solvents has been entirely eliminated (alcohols form azeotropic mixtures with water and amines). The classical batch way of preparation has been replaced by a procedure which reduces the formation of higher alkylated amines whose separation by rectification from the secondary amines is in many cases uneasy. The reaction has been carried out in such a way that the amine has been added continuously to the vigorously stirred alkyl halide at temperatures $10-15°C$ below its boiling point, at such a velocity that its concentration in the reaction mixture may be as low as possible. In this manner it has been ensured that the formation of alkylamine salt has taken place after the alkylation of the amine and the liberation of hydrogen halide. The alkylamine salt is indifferent to further alkylation.

The separation of reaction mixtures by direct rectification has not been possible owing to the formation of a number of azeotropic mixtures. At first the mixture has been acidified with sulphuric acid (pH 2) and the unreacted alkyl halides (or acetone in synthesis of diisopropylamine) have been distilled off. The amines in the residual fraction have been liberated with alkali and after a mechanical separation of water and thorough drying of the organic layer (with Na_2SO_4 and Na), the mixture of amines has been separated by twofold rectification on an $1·5$ m packed column. The impurity content has been determined by means of gas chromatography on three columns separating according to different conditions.

The final content of impurities (excepting H_2O) has been as follows: methylisopropylamine $0·11$, ethylisopropylamine $0·06$, propylisopropylamine $0·06$, diisopropylamine $0·002$, butylisopropylamine $0·10$, ethylbutylamine $0·08$ and dibutylamine $0·03$ mass %.

Immediately before the measurements the substances have been dried by boiling with CaH_2 $(2-3$ hours) and then distilled. The content of water has been then determined by titrating with the Fischer reagent and has been in all cases lower than $0·02$ mass %. The substances have been stored in the presence of molecular sieves Potasit A3 and placed in a dry box with a CO_2 trap and protected from light.

To measure the temperature dependence of heat of vaporization the isothermal adiabatic calorimeter has been used whose detailed description together with the measuring procedure were reported formerly[7]. The chemical reactivity of amines has necessitated some constructional changes[6] of the evaporation vessel as well as other parts of the calorimeter which come into contact with the amine vapours. The calorimeter in this arrangement has made it possible to measure heats of vaporization in the temperature range of $25\rightarrow85°C$ in the saturated vapour pressure range of $1-200$ kPa. The error of measurement is estimated[6], with regard to the strong hygroscopicity and reactivity of the group of substances measured, at $0·15\%$ at temperatures below normal boiling point, in the vicinity of normal boiling point and above it then the error in the determination of heat of vaporization does not exceed $0·25\%$.

To measure the temperature dependence of saturated vapour pressures we have used the standard equipment[8] whose fundamental part is a Swietoslawski dynamic ebulliometer. The temperature has been measured with an accuracy of $\pm0·01°C$ by means of mercury normals, the pressure in the apparatus has been maintained at a constant value with fluctuations ±30 Pa.

RESULTS

The values of molar volume (or density) of the liquid phase at the temperature of experiment must be known when determining experimentally heat of vaporization and when calculating cohesive energies. Experimental data have been found only for diisopropylamine and dibutylamine[9]. The density of the remaining substances of the set at 25°C has been established in the Sprengel–Oswald pycnometer. To extrapolate density to higher temperatures and to interpolate the literature data the procedure based on the Rackett equation[10] has been used:

$$\frac{M}{d^1} = V^1 = \frac{RT_c}{P_c} z_c^{[1+(1-T_r)^{0.28751}]} . \qquad (1)$$

Values d^1 and V^1 denote the density and molar volume of the liquid phase, respectively, M is the relative molecular mass, the symbols T_c, P_c denote the critical temperature

TABLE I

Saturated Vapour Pressures of Secondary Amines

Pressure kPa	Temperature, °C/deviation in pressure, Pa					
	methyliso-propylamine	ethyliso-propylamine	propyliso-propylamine	butyliso-propylamine	diisopropyl-amine	ethylbutyl-amine
7·843				52·32/33		40·25/−60
9·210				55·76/9		43·61/21
10·426				58·50/−7		46·10/10
11·876			38·62/−31	61·43/−36	26·92/−15	48·85/31
13·159			40·92/7	63·87/−18	29·17/23	51·07/51
15·372			44·41/23	67·66/19		54·48/55
18·252			48·36/22	71·80/−56		58·32/8
21·892		29·87/−1	52·69/16	76·40/−109	40·62/−12	
25·265		33·13/6	56·20/−9	80·27/−41	44·08/−5	66·18/43
30·864	19·99/14	37·80/−15	61·34/14	85·83/53	49·07/−9	71·13/−148
37·544	24·52/37	42·58/15	66·54/−18	91·44/113	54·19/32	76·34/−227
45·356	28·99/−63	47·31/−35	71·76/−79	97·07/190	59·27/−18	81·64/−272
56·449	34·48/−9	53·08/46	78·14/−64	103·80/182	65·44/−51	88·53/476
69·487	39·93/70	58·74/25	84·55/72		71·64/39	
86·046	45·73/−1	64·80/−42	91·38/27		78·36/261	101·83/81
98·219			95·80/32			
98·925					82·70/−230	
99·032				122·45/−410		
99·218		69·02/8				

and pressure. The critical compressibility factor z_c has been in this work replaced by an adjustable parameter calculated from the following experimental data at 25°C: methylisopropylamine 0·69866, ethylisopropylamine 0·71220, propylisopropylamine 0·72357, butylisopropylamine 0·73724, ethylbutylamine 0·73911 g/cm³. In case of diisopropylamine and dibutylamine the literature data[9] at 20°C have been used for calculating their densities. The error due to extrapolation by 80°C does not exceed 0·4% when using the given way of calculation.

To express the dependence of saturated vapour pressures on temperature we have used the Antoine equation

$$\log P^0 = A - B/(C + t),\qquad(2)$$

where P^0 is the saturated vapour pressure in kPa at a temperature t (°C), A, B, C are constants. Table I contains for each substance and temperature of measurement also the difference between the values of vapour pressures calculated from the Antoine equation and the experimental values.

The constants of correlation relation together with the standard deviation of correlation δ, the temperature range in which the measurement of saturated vapour pressures has been carried out and the calculated normal boiling point are given in Table II. For the sake of completeness, the data for dibutylamine, which have been taken over from the literature[11], are given in the table, too.

TABLE II
Constants of the Antoine Equation for Secondary Amines

Substance	A	B	C	δ, kPa	Temp. range °C	t_{NBP}, °C
Methylisopropyl-amine	5·963 416	1 042·344	213·000	0·059	20 — 46	50·37
Ethylisopropyl-amine	6·204 094	1 220·628	221·090	0·032	30 — 69	69·65
Propylisopropyl-amine	5·587 278	1 009·819	185·100	0·045	39 — 96	96·85
Butylisopropyl-amine	5·800 924	1 192·907	190·900	0·157	52 — 122	123·42
Diisopropylamine	5·698 125	1 038·183	197·600	0·126	27 — 83	83·57[b]
Ethylbutylamine	5·160 447	812·2 294	150·000	0·198	40 — 102	107·46
Dibutylamine[a]	6·362 891	1 601·606	207·780	0·007	13 — 98	159·80[c]

[a] Data reported in ref.[11] have been used for correlation; [b] in ref.[14] t_{NBP} 83·00°C is given; [c] in refs[9,14] t_{NBP} 159·0 and 159·6°C are given.

TABLE III
Heats of Vaporization of Secondary Amines

Temperature °C	Heat of vaporization, kJ/mol/deviation, %						
	methyliso-propylamine	ethyliso-propylamine	propyliso-propylamine	butyliso-propylamine	diiso-propylamine	ethyl-butylamine	dibutylamine
25	30·69/0·03	33·12/0·06	37·25/0·11	42·07/0·12	34·58/−0·20	40·18/0·15	—
40	29·52/−0·07	32·10/0·03	36·18/−0·11	40·91/−0·12	33·68/0·18	39·05/−0·08	—
55	—	30·99/−0·13	35·18/−0·06	39·86/−0·03	32·57/0·03	37·95/−0·16	
70	27·11/0·04	28·78/0·07	34·12/−0·03	38·72/−0·05	31·49/0·16	36·87/−0·05	46·02/0·00
85			33·03/0·06	37·60/0·08	30·21/−0·20	35·77/0·14	44·75/0·00
K	47·405	47·900	52·052	58·394	50·011	55·931	68·008
α	0·4652	0·4179	0·4138	0·4371	0·4336	0·4219	0·4553
$T_c{}^a$	490·67[Lyd]	507·95[Lyd]	536·61[Lyd]	563·60[Lyd]	522·15[15]	547·11[Lyd]	595·76[9]
$\Delta H_{v,\text{NBP}}{}^b$	28·72	29·95	32·08[ext]	34·33[ext]	30·39	33·88[ext]	37·76[ext]

[a] Symbol Lyd denotes estimates by the Lydersen method; [b] Values $\Delta H_{v,\text{NBP}}$ marked by ext lie outside the measured range of temperature and have been obtained by extrapolation using Eq. (3).

The temperature dependence of heat of vaporization has been expressed by the Thiesen relation

$$\Delta H_v = K(1 - T/T_c)^\alpha, \tag{3}$$

where T is the temperature of measurement in K, T_c is the critical temperature, K and α are constants.

In Table III, the experimental values of heat of vaporization and the per cent deviation between the experimental value and the value calculated from the correlation equation (3) are given for each substance and temperature of measurement. The constants of the correlation relation and the used value of critical temperature are also given for each substance. For five substances of the set it has been necessary to estimate the data on critical temperature by the Lydersen method because of the lack of experimental data in the literature. The symbol $\Delta H_{v,NBP}$ in Table III denotes the heat of vaporization at normal boiling point. For the lack of published data, the comparison of our measured values of heat of vaporization with direct experimental ones of other authors can be carried out only for diisopropylamine. Wadsö[12] gives the values of $34 \cdot 51 \pm 0 \cdot 08$ kJ/mol at a temperature of 25°C, which is in good agreement with our measurement.

Calculation of Cohesive Energy

The cohesive energy is defined as a change of internal energy of system connected with the isothermal transfer of one mole of liquid at the saturated vapour pressure

TABLE IV
Values of Cohesive Energies of Secondary Amines

Substance	ΔU^*, kJ/mol				
	20°C	40°C	60°C	80°C	100°C
Methylisopropylamine	28·82	27·30	25·76	24·18	
Ethylisopropylamine	31·10	29·70	28·27	26·91	25·33
Propylisopropylamine	37·32	35·83	34·30	32·74	31·13
Butylisopropylamine	39·95	38·42	36·85	35·24	33·60
Diisopropylamine	31·31	28·86	26·28	23·85	21·91
Ethylbutylamine	38·06	36·57	35·06	33·50	31·91
Dibutylamine			44·16	42·39	

to the gaseous state at zero pressure. To calculate this quantity it is possible to employ the experimental data on heat of vaporization:

$$\Delta U^* = \Delta H_v + \int_{P=P^0}^{P=0} \left(V^g - T\left(\frac{\partial V^g}{\partial T}\right)_P \right) dP - RT + P^0 V^1 , \qquad (4)$$

where the symbols V^g and V^1 denote the volumes of the gas and the liquid phase respectively, P^0 is the saturated vapour pressure. On the assumption that the $P - V - T$ behaviour of real gas can be described by the volume-explicit form of the virial expansion on neglecting the third- and higher-order virial coefficients, it is possible to rearrange Eq. (4) into the form

$$\Delta U^* = \Delta H_v - RT - P^0[B - T(dB/dT) - V^1] . \qquad (5)$$

B is the second virial coefficient for whose calculating, owing to the absence of experimental data, the Vetere method[13] suitable for polar substances has been used:

$$BP_c/RT_c = f_1 + \omega f_2 + \omega' f_3 \qquad (6)$$
$$f_1 = 0{\cdot}1445 - 0{\cdot}330/T_r - 0{\cdot}1385/T_r^2 - 0{\cdot}0121/T_r^3$$
$$f_2 = 0{\cdot}073 + 0{\cdot}46/T_r - 0{\cdot}50/T_r^2 - 0{\cdot}097/T_r^3 - 0{\cdot}0073/T_r^8$$
$$f_3 = 0{\cdot}1042 - 0{\cdot}2717/T_r + 0{\cdot}2388/T_r^2 - 0{\cdot}0716/T_r^3 +$$
$$+ 1{\cdot}502 \cdot 10^{-4}/T_r^8$$
$$\omega = -\log(P_{0.7}^0/P_c) - 1$$
$$\omega' = T_{NBP}^{1.72}/M - 263 .$$

P_c, (T_c) denotes the critical pressure (temperature), the acentric factor ω, ω' and the functions f_1, f_2, f_3 are defined by respective equations, T_r denotes the reduced temperature and M is the relative molecular mass. The symbol $P_{0.7}^0$ denotes the saturated vapour pressure at a temperature $T = 0{\cdot}7T_c$. The Vetere method is an extension of the Pitzer–Curl estimation relationship and with regard to the way of adjusting the parameters of equations defining the functions f_1, f_2 it is to be assumed (as the experimental data on temperature dependence of molar heat capacities, i.e. on the second derivative of virial coefficient with respect to temperature were used) a satisfactory accuracy even for the determination of the derivative of second virial coefficient with respect to temperature. The molar volume of the liquid phase has been calculated in the above-mentioned way using Eq. (1).

On the basis of the analysis of errors in quantities occurring in Eq. (5) it has been found out[6] that the upper limit of uncertainty in the determination of cohesive

energy for the temperatures below normal boiling point does not exceed 0·25% and in the vicinity of boiling point and above it, the cohesive energy is subject to an error lower than 0·55%. The values of cohesive energy of the studied substances are summarized in Table IV.

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