TEMPERATURE DEPENDENCE OF HEATS OF VAPORIZATION, SATURATED VAPOUR PRESSURES AND COHESIVE ENERGIES FOR A GROUP OF AMINES*

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Received June 23th, 1978

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

The temperature dependences of heats of vaporization of propylamine, isopropylamine, butylamine, isobutylamine, sec-butylamine, cyclohexylamine, diethylamine and triethylamine and saturated vapour pressures of butylamine, isobutylamine, sec-butylamine and triethylamine were measured. The cohesive energies of amines studied in dependence on temperature were calculated from the experimental values.

This work is a part of a long-term study of the temperature dependence of heats of vaporization of important organic substances. In previous parts of this series, we published data on heats of vaporization of some alcohols[1], esters[2,3], bromides[4] and hydrocarbons[5]. Reassuming those measurements, we have paid our attention to the study of amines. Even though we treat technologically important substances only a small number of experimental data is known which would enable their thermodynamic description. Our aim has been to measure the temperature dependence of heat of vaporization and of saturated vapour pressures for several more significant amines. By combining the calorimetric and vapour pressure data, the values of cohesive energies have been determined as the basic quantities characterizing the liquid state. The measurements have been carried out for a group of industrially important amines; five primary aliphatic amines (propylamine, isopropylamine, butylamine, isobutylamine, sec-butylamine), cyclohexylamine, diethylamine and triethylamine have been treated.

EXPERIMENTAL

Preparation and purity of substances. The amines used have been commercial products of different origin: propylamine, sec-butylamine, isobutylamine and cyclohexylamine (Fluka A. G.,

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* Part XVI in the series Enthalpy Data of Liquids; Part XV: This Journal *44*, 2869 (1979).

Switzerland); diethyl- and triethylamine (Apolda-Chemie, GDR); isopropylamine (MCHZ Ostrava, Czechoslovakia); butylamine (Koch-Light, England). The amines have been purified by threefold rectification with sodium on a packed column 1·5 m long. The ratio of volumes of the initial amine and purified product has been 12 : 4. The impurity content has been determined by gas chromatography on three columns separating according to different view-points (the stationary phase: 10 mass% phenyldiethanolamine, Tetramin-W, Apiezon-L always on Chromaton N-AW-HMDS). Isopropylamine has been converted into sulphate before the rectification and separated from isopropyl alcohol and acetone which have formed the main impurities in the technical product. After converting the sulphate back to amine and dehydrating, isopropylamine has been purified by rectification as the other amines. The final contents of impurities (except water) in mass per cent have been as follows: propylamine <0·01, butylamine <0·03, isopropylamine <0·05, sec-butylamine <0·1, isobutylamine <0·1, diethylamine <0·005, triethylamine <0·005, cyclohexylamine <0·05%.

With respect to the strong hygroscopicity (especially of primary amines) a thorough drying has been carried out immediately before measurements. The substances have been freed from water by boiling with CaH_2 (2—3 hours) and then distilled. The water content has then been determined by titrating with the Fischer reagent and has been lower than 0·02 mass% in all cases.

The substances have been stored in bottles with molecular sieves Potasit A3. With respect to the hygroscopicity and reactivity of aliphatic amines with carbon dioxide, the reagent bottles have been placed in a dry box with a CO_2 trap and protected from light.

Experimental procedure of the determination of heat of vaporization and the design of the calorimeter, in which the measurements have been carried out, were described thoroughly[6] in detail. The adiabatic isothermal calorimeter has been used which makes it possible to measure in the temperature range of 25—100°C at a saturated vapour pressure of 1—200 kPa. The apparatus operates on the principle of total evaporation of liquid and is equipped with a removable evaporation vessel. This enables to determine the amount of evaporated liquid before experiments by weighing the vessel prior to its filling and after it. Amines are substances rather aggressive which already at ambient temperatures react strongly with brass which is the construction material of main parts of the calorimeter centre. Therefore two new brass vessels have been constructed for the measurement and their inner surface together with the inside silver built-in parts have been electroplated by the layer of about 30 μm of gold. In the same manner, some parts of the calorimeter head which come into intensive contact with amine vapours have been protected, too. The filling of vessels has been carried out in a dry box. With regard to the strong hygroscopicity and reactivity of amines, we assume that the error of measurement will be rather higher in comparison with the inaccuracy determined by analysis in paper[6]. At temperatures below normal boiling point, we assume the error of 0·15%, about the temperature of normal boiling point and above it 0·25%.

The measurement of saturated vapour pressures has been carried out using a standard equipment[7] whose main part is a Swietoslawski dynamic ebulliometer. The temperature has been measured by means of mercury normals with an accuracy of ±0·01°C, the pressure in apparatus has been held at a constant value ±30 Pa.

RESULTS AND DISCUSSION

The saturated vapour pressures of butylamine, sec-butylamine, isobutylamine and triethylamine have been measured. Vapour pressure measurements have not been carried out for the remaining four amines; most accurate values for propylamine and isopropylamine give Osborn and Douslin[8], the data for cyclohexylamine were published by Novák and coworkers[9], ethylamines were studied by Bittrich and coworkers[10].

The measured saturated vapour pressures (kPa) for the four substances investigated are given in Table I. The experimental values have been correlated by the Antoine equation

$$\log P = A - B/(t + C)\,, \tag{1}$$

where t denotes temperature in °C and P pressure in kPa. Deviations of vapour pressures determined *via* Antoine equation from experimental ones are given for each substance and temperature. Table II contains then the values of constants of the Antoine equation for the individual substances, the temperature range within which they hold, the calculated value of normal boiling point and the standard deviation of the correlations. For the sake of lucidity, the constants of the Antoine equation for propylamine, isopropylamine, cyclohexylamine and diethylamine are listed in the

TABLE I

Results of Measurements of Saturated Vapour Pressures

Pressure kPa	Temperature, °C/deviation in pressure, Pa			
	butylamine	isobutylamine	sec-butylamine	triethylamine
11·876	23·94/−20	—	—	—
13·159	26·10/+26	—	—	32·64/− 53
15·372	29·30/+ 5	—	—	36·20/+ 46
18·252		24·24/+10	—	40·06/+ 21
21·892	—	28·16/−18	—	44·38/+ 49
25·265	40·25/− 5	—	26·71/+ 6	47·86/+ 27
30·864	44·98/+23	—	31·30/− 6	52·92/− 11
37·544	49·74/− 9	40·72/+17	—	58·10/− 73
45·356	54·53/−12	45·41/− 8	40·67/+ 7	63·40/− 46
56·449	60·29/−40	51·09/+13	46·32/+12	69·71/−257
69·487	66·05/+45	56·70/−10	51·91/−16	76·44/+354
86·046	72·15/−83	62·75/+30	57·96/+69	83·32/+150
97·925	—	—	—	87·63/−145
98·225	76·15/+79	—	—	—
98·459	—	66·68/−21	—	—
99·432	—	—	62·16/−24	—

table, too, as determined from the original experimental data on saturated vapour pressures[8-10] in the compilation by Boublík and coworkers[11]. The given values of standard deviations provide at the same time a comparison of the accuracy of measurements of individual authors.

The heats of vaporization in dependence on temperature have been measured for all eight amines in 15°C intervals from temperature 25°C (for cyclohexylamine 40°C) up to temperatures slightly above normal boiling point. The experimental values have been correlated by the Thiesen relation

$$\Delta H_v = K(1 - T/T_c)^\alpha , \qquad (2)$$

where K, α are the correlation constants and T_c denotes the critical temperature. Table III gives the measured data on heat of vaporization in dependence on temperature and the per cent deviations of the values calculated using the correlation equation (2) from the experimental values. For each substance, the correlation constants K and α, the used value of critical temperature T_c and the value of heat of vaporization at normal boiling point calculated from Eq. (2) are given. For cyclohexylamine and triethylamine, the critical temperatures have been estimated according to Lydersen[12] for the other substances, the experimental values published by Castello and Bowden[13] have been used. For five substances of the studied set of amines, the comparison coud be carried out with the experimental values obtained by Wadsö[14] at 25°C with an

TABLE II

Constants of the Antoine Equation for Group of Amines[a]

Substance	A	B	C	δ kPa	Temperature range, °C	T_{NBP} °C
Propylamine[b]	6·05141	1 044·051	210·836	0·015	22—77	47·33
Isopropylamine[b]	6·01515	985·685	214·075	0·009	3—60	31·77
Butylamine	6·07009	1 157·810	207·800	0·048	23—76	77·07
Isobutylamine	6·07946	1 142·039	212·800	0·023	24—67	67·54
Sec-butylamine	6·01935	1 106·675	213·000	0·038	27—62	62,73
Cyclohexylamine[b]	5·81444	1 229·418	188·802	0·400	60—128	133·96
Diethylamine[b]	4·92649	583·297	144·145	0·271	31—62	55·55
Triethylamine	5·21914	834·442	170·800	0·167	30—88	88·87

[a] Constants of the Antoine equation hold for t in °C and P in kPa; [b] values of constants taken over from the literature[11].

TABLE III

Heats of Vaporization for Group of Amines

Temperature °C	Heat of vaporization, kJ/mol/deviation, %							
	propylamine	isopropylamine	butylamine	isobutylamine	sec-butylamine	cyclohexylamine	diethylamine	triethylamine
25	31·26/−0·03	28·36/0·00	35·74/−0·03	33·85/+0·03	32·70/+0·03		31·32/+0·06	34·81/+0·17
40	30·14/+0·07	27·19/0·00	34·67/+0·06	32·70/−0·09	31·64/+0·03	42·67/−0·02	30·20/−0·10	33·92/−0·06
55	28·92/−0·03		33·50/−0·06	31·60/+0·03	30·48/−0·13		29·08/−0·10	33·03/−0·18
70			32·36/0·00		29·39/+0·10	40·68/+0·02	27·96/+0·11	32·16/−0·12
85			31·17/+0·03			39·61/−0·03		31·33/+0·22
K	48·310	45·703	53·417	51·365	48·507	59·218	46·937	46·538
α	0·4749	0·4965	0·5300	0·5194	0·4483	0·4598	0·4417	0·3532
T_c	496·97	482·85	561·10	539·85	509·36	614·56	496·45	530·00
ΔH_{vNBP}	29·54	27·84	31·80	30·60	29·93	35·88	29·07	31·01

estimated error of 0·3%. The per cent deviations of the data by Wadsö from ours are as follows: butylamine (−0·1%), isobutylamine (−0·2%), sec-butylamine (−0·2%), diethylamine (−0·4%), triethylamine (+0·4%). Taking into account the error of measurement reported, the agreement can be considered very good.

The cohesive energy ΔU^* is defined as the change of internal energy when transferring one mole of liquid at a given temperature and respective saturated vapour pressure into the gaseous state at the same temperature and the zero pressure. For the calculation, it is convenient to exploit the experimental values of heat of vaporization which has the direct and simple relation to the cohesive energy:

$$\Delta U^* = \Delta H_v + \int_P^0 \left(V^g - T\left(\frac{\partial V^g}{\partial T}\right)_P \right) dP - RT + PV^l , \quad (3)$$

where V^l and V^g denote the molar volumes of the liquid and vapour phase, respectively. On using the volume-explicit form of virial expansion, we get for the cohesive energy:

$$\Delta U^* = \Delta H_v - RT - P(B - T(dB/dT)) + PV^l . \quad (4)$$

To determine the accuracy of ΔU^* it is necessary to find out what maximum error can arise from the conversion of heat of vaporization to cohesive energy owing to the second to fourth terms on the right-hand side of Eq. (*4*). The values of heat of vaporization for the studied set of substances are within the range of 27 – 36 kJ/mol. The sum of all the correction contributions on the right-hand side of Eq. (*4*) amounts to −(1·9 ÷ 2·5) kJ/mol. The absolute value of sum of these corrections decreases slightly with temperature because the difference between the enthalpy of the ideal and real vapour increases with temperature more rapidly than the value of the term RT. The last term in Eq. (*4*) is very small and influences the accuracy minimally. Considering that the essential part of the sum is formed by the RT contribution which is subject practically to no error, all uncertainty is introduced into the calculation by the term representing the difference of enthalpies of the real and ideal vapour. The maximum value of this contribution is −0·7 kJ/mol for the considered set of substances and corresponding temperature ranges. The mean values of B and dB/dT are −1 300 cm^3/mol and 10 cm^3 . mol^{-1} . K^{-1} and the error in these input terms is 10 and 20%. The overall uncertainty in the third term of Eq. (*4*) is then lower than 17% and the maximum error will be consequently 0·07 to 0·08 kJ . mol^{-1}; the error in the cohesive energy in comparison with that in the heat of vaporization may increase maximally by 0·2 to 0·3%.

For the substances studied except diethylamine and triethylamine, no experimental data are known on second virial coefficients. Their values have been estimated by means of the Vetere method[15] which makes it possible to calculate the second virial coefficients of polar substances:

$$BP_c/RT_c = f^1 + \omega f^2 + \omega' f^3 \,, \tag{5}$$

$$f^1 = 0{\cdot}1445 - 0{\cdot}330/T_r - 0{\cdot}1385/T_r^2 - 0{\cdot}0121/T_r^3$$

$$f^2 = 0{\cdot}073 + 0{\cdot}46/T_r - 0{\cdot}50/T_r^2 - 0{\cdot}097/T_r^3 - 0{\cdot}0073/T_r^8$$

$$f^3 = 0{\cdot}1042 - 0{\cdot}2717/T_r + 0{\cdot}2388/T_r^2 - 0{\cdot}0716/T_r^3 + 1{\cdot}502 \,.\, 10^{-4}/T_r^8$$

$$\omega' = T_{\mathrm{NBP}}^{1.72}/M - 263 \,,$$

where P_c denotes the critical pressure, ω the acentric factor, T_r stands for the reduced temperature and M is molecular mass. The expressions for f^1 and f^2 are quite identical with the Pitzer–Curl estimation relation[16]. The Vetere equation contains no adjustable parameter and so it is one of few up-to-date estimation methods enabling the calculation of the second virial coefficients of polar substances without knowing any data on P–V–T behaviour. The exploitation of this relation has been also convenient for our purposes because this method is in fact an extension of the Pitzer–Curl relation and consequently it has a chance to provide a realistic prediction of the temperature derivatives of second virial coefficients (Pitzer and Curl used the data on the pressure dependence of molar heat capacities of vapours as well to determine the numerical values of constants in the equations for f^1 and f^2).

TABLE IV

Values of Cohesive Energies for Group of Amines

Substance	ΔU^*, kJ/mol				
	20	40	60	80	100°C
Propylamine	29·50	28·05	26·56	—	—
Isopropylamine	26·65	25·17	—	—	—
Butylamine	33·77	32·29	30·82	29·35	—
Isobutylamine	31·90	30·41	28·91	—	—
Sec-butylamine	30·77	29·34	27·88	26·38	—
Cyclohexylamine	—	40·12	38·69	37·25	35·79
Diethylamine	29·40	27·98	26·54	25·03	—
Triethylamine	32·65	31·47	30·27	29·05	27·79

Molar volume of the liquid phase has been expressed by making use of the Rackett equation[17]:

$$V^{1}P_{c}/RT_{c} = z_{c}^{[1+(1-T_{r})^{0.28571}]} \, .$$

The quantity z_c have had in our modification the meaning of an adjustable parameter whose value has been established on the basis of knowledge of the density of corresponding substance at one temperature. These data have been found in the literature[18,19]. Table IV gives the values of cohesive energies as a function of temperature from 20°C to the temperatures around the normal boiling point.

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Translated by J. Linek.