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THERMODYNAMIC STUDY OF ORGANIC COMPOUNDS IN OCTAN-1-OL.

2. Enthalpy changes in the transfer of primary, secondary, and tertiary amines from gas and the dilute aqueous state.

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SUMMARY

Values of the enthalpy changes for the transfer of some aliphatic primary, secondary, and tertiary amines from gas state to dilute solutions in octan-1-ol have been obtained as a difference between the enthalpies of solution, determined by calorimetry, and the enthalpies of vaporization of the pure liquid amines.

A comparison is made between these data and the corresponding enthalpies of hydration; the values of the enthalpies of partitioning of the amines between pure water and pure octan-1-ol phases have been also calculated.

Lastly, some observations are made with respect to the relations between the molecular structure of the amines and their enthalpies of solvation in octanol, in water, and in their pure liquid state.

INTRODUCTION

As a part of a systematic study on the thermodynamics of solvation of organic compounds in octan-1-ol, we recently reported (ref. 1) data concerning the free energy, enthalpy, and entropy of transfer of some open-chain and cyclic alkanes, ethers, and ketones from gas state to dilute solution in octan-1-ol. The enthalpy data related to this process for primary, secondary, and tertiary aliphatic amines of symmetric type $R_{j+1}NH_{2-j}$ (j=0,1,2; R = ethyl, n-propyl, n-butyl, and n-pentyl radical) are considered in this paper.

To the best of our knowledge, investigation of amine solutions in octan-1-ol has so far been limited to determination of the values of the enthalpies of solution and solvation of triethylamine (ref. 2), and to the values of the molar excess enthalpy at 298.15 K for binary di-n-propylamine/octanol mixtures over the whole composition range (ref. 3). In addition, fourteen octan-1-ol/water partition coefficient values for primary, secondary, and tertiary amines have been collected by Leo, Hansch, and Elkins (ref. 4).

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EXPERIMENTAL PART

Materials

All amines were best-grade commercial products. Some (n-propylamine, n-butylamine, n-pentylamine, diethylamine, di-n-propylamine, and triethylamine) were dried over CaH_2. All compounds were fractionally distilled under nitrogen at atmospheric or reduced pressure. The used fractions were collected at constant boiling point and their purity, checked by glc, was always better than 99.8%. The water used in the experiments was first deionized and then distilled from alkaline $KMnO_4$. The solvent, octan-1-ol, was a Fluka product of purissimum grade (> 99.5%). It was refluxed over metallic sodium and then distilled under nitrogen at reduced pressure. The samples used showed a glc purity better than 99.9% and a water content < 0.01%, determined by Karl Fischer titration.

Apparatus

The calorimetric measurements of the heat of solution in pure and in water-saturated octan-1-ol were performed with an isoperibol calorimeter. Successive additions of solute were made to the cell containing ca. 100 cm^3 of solvent, with a programmable precision hand-pipette (Microlab-P, Hamilton AG). Further details of the apparatus and the measurement procedure are reported in ref. 1. About 20 experiments were usually carried out with the mole fraction of the amines, X_2, ranging from 0.001 to 0.03.

TABLE 1

Limiting enthalpies of solution, $\Delta_{soln}H°(oct)$, in octan-1-ol at 298.15 K.[a]

Solute	n.exp. pts.	X_2 range	$\Delta_{soln}H°(oct)$/ kJ mol^{-1}	b/ kJ mol^{-1}
n-propylamine	17	0.006-0.038	-8.75±0.07	13.5±1.7
n-butylamine	22	0.001-0.033	-9.42±0.08	17.2±1.7
pentylamine	22	0.003-0.033	-9.95±0.07	19.3±1.8
diethylamine	24	0.003-0.039	-11.38±0.07	22.3±1.4
di-n-propylamine	20	0.003-0.034	-10.78±0.08	22.5±2.0
di-n-butylamine	24	0.002-0.024	-10.62±0.05	29.0±1.7
triethylamine	20	0.002-0.027	-8.64±0.07	41.3±2.2
tri-n-propylamine	21	0.001-0.025	-3.24±0.08	24.7±2.4
tri-n-butylamine	19	0.001-0.021	-2.98±0.03	29.5±1.2
n-butylamine[b]	18	0.001-0.034	-11.92±0.04	28.6±1.4
di-n-propylamine[b]	26	0.001-0.021	-11.93±0.08	32.1±3.0
triethylamine[b]	25	0.001-0.026	-11.51±0.08	41.2±2.4

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[a] X_2, $\Delta_{soln}H°(oct)$, and b refer to eqn. (1).

[b] Measurements carried out using water-saturated octan-1-ol as solvent (mole fraction of water = 0.28, ref. 5).

RESULTS AND DISCUSSION

The experimental heat of solution, $\Delta_{soln}H(oct)$, showed always a linear dependence on mole fraction of solute according to the equation:

$$\Delta_{soln}H(oct) = \Delta_{soln}H^{\circ}(oct) + bX_2 \qquad (1)$$

The values of $\Delta_{soln}H^{\circ}(oct)$, the limiting enthalpy of solution in octan-1-ol, and the slope b, obtained by a simple least-squares method, are reported in Table 1. The uncertainity on $\Delta_{soln}H^{\circ}(oct)$ did not exceed 0.10 kJ mol^{-1}. The only corresponding reference in the literature comparable with ours regards triethylamine. A very good agreement exists with the value of $\Delta_{soln}H^{\circ}(oct)$ = -8.70 kJ mol^{-1} reported by Stephenson and Fuchs (ref. 2).

Table 2 lists the enthalpies of solvation in octan-1-ol, $\Delta_{solv}H^{\circ}(oct)$, the enthalpies of hydration, $\Delta_{solv}H^{\circ}(w)$, and the enthalpies of solvation of the amine in itself, - $\Delta_{vap}H^{\circ}$.

TABLE 2

Enthalpies of vaporization, $\Delta_{vap}H^{\circ}$, of solvation in octan-1-ol, $\Delta_{solv}H^{\circ}(oct)$, and of hydration, $\Delta_{solv}H^{\circ}(w)$, at 298.15 K.[a]

Solute	$\Delta_{vap}H^{\circ}$	$\Delta_{solv}H^{\circ}(oct)$[b]	$\Delta_{solv}H^{\circ}(w)$[c]
n-propylamine	31.34[d]	-40.09	-55.75
n-butylamine	35.69[e]	-45.11	-59.04
n-pentylamine	40.08[e]	-50.03	-62.12
diethylamine	31.14[e]	-42.52	-65.12
di-n-propylamine	40.04[e]	-50.82	-72.30
di-n-butylamine	49.45[e]	-60.07	-75.99
triethylamine	34.94[e]	-43.58	-69.68
tri-n-propylamine	46.11[e]	-49.35	=
tri-n-butylamine	61.04[f]	-64.02	=

[a] All data are in kJ mol^{-1}.
[b] $\Delta_{solv}H^{\circ}(oct) = \Delta_{soln}H^{\circ}(oct) - \Delta_{vap}H^{\circ}$.
[c] Taken from ref. 6.
[d] Ref. 7.
[e] Ref. 8.
[f] Estimated by method of Ducros (ref. 9).

For a better discussion of these data, a frame of the enthalpy values of solvation in octanol and in water is given in Fig. 1 for the amines and other compounds. The enthalpy changes, $\Delta_{trf}H^{\circ}(w\text{-}oct)$, associated with the transfer from pure water to pure octan-1-ol are also reported as evaluated by :

$$\Delta_{trf}H^{\circ}(w\text{-}oct) = \Delta_{solv}H^{\circ}(oct) - \Delta_{solv}H^{\circ}(w) \qquad (2)$$

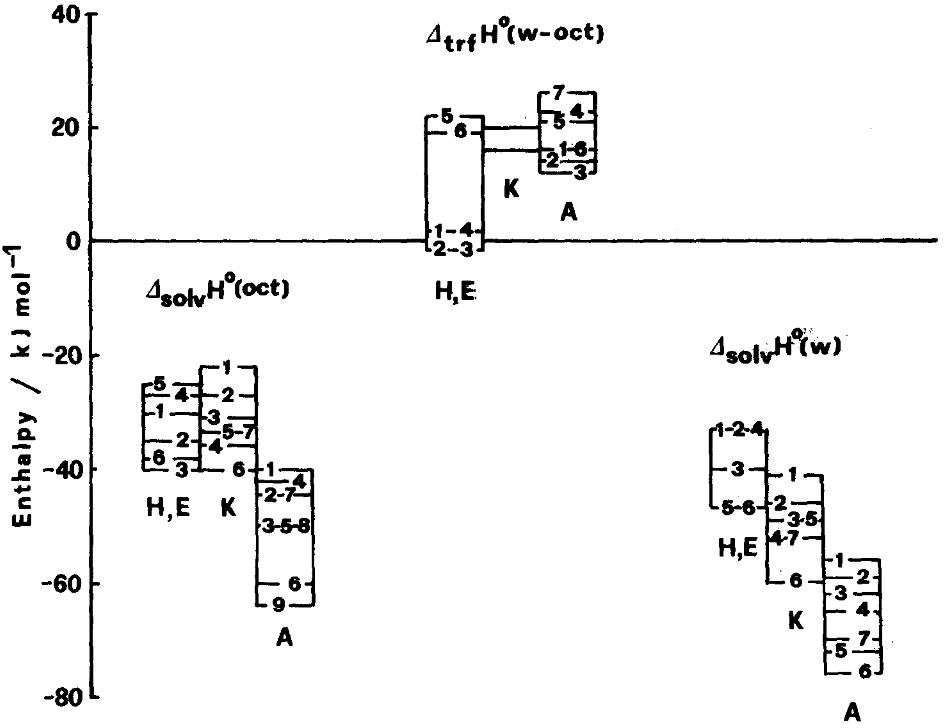

Fig. 1. Enthalpies of solvation in octan-1-ol, $\Delta_{\mathrm{solv}}H^\circ(\mathrm{oct})$, in water, $\Delta_{\mathrm{solv}}H^\circ(\mathrm{w})$, and of transfer from water to octanol, $\Delta_{\mathrm{trf}}H^\circ(\mathrm{w\text{-}oct})$ (eqn. (2)). H,E: hydrocarbons and ethers (1, n-hexane; 2, n-heptane; 3, n-octane; 4, cyclohexane; 5, ethyl ether; 6, THF); K: ketones (1, propanone; 2, butan-2-one; 3, pentan-2-one; 4, hexan-2-one; 5, pentan-3-one; 6, heptan-4-one; 7, cyclopentanone); A: amines (1, n-propylamine; 2, n-butylamine; 3, n-pentylamine; 4, diethylamine; 5, di-n-propylamine; 6, di-n-butylamine; 7, triethylamine; 8, tri-n-propylamine; 9, tri-n-butylamine). $\Delta_{\mathrm{solv}}H^\circ(\mathrm{oct})$ data of amines are taken from this work; the others from ref. 1 (H,E: compds. no. 1,4,5,6; K: compds. no. 1,5,7) and from ref. 10 (H,E: compds. no. 2,3; K: compds. no. 2,3,4,6). $\Delta_{\mathrm{solv}}H^\circ(\mathrm{w})$ values are taken from ref. 6.

Some facts emerge from Fig. 1:

a) The enthalpies of solvation in water are always larger in magnitude than those in octan-1-ol.

b) The enthalpies of solvation in octanol and in water of the amines are noticeably more negative than the $\Delta_{\mathrm{solv}}H^\circ(\mathrm{oct})$ and $\Delta_{\mathrm{solv}}H^\circ(\mathrm{w})$ values of alkanes, ethers, and ketones.

c) Except for n-heptane and n-octane, the $\Delta_{\mathrm{trf}}H^\circ(\mathrm{w\text{-}oct})$ values are always positive.

d) When the $\Delta_{trf}H°(w\text{-}oct)$ values are considered, only hydrocarbons (compds. 1-4) distinguish themselves sharply from the other classes of solutes, the amines being comparable with ethers and ketones.

As a consequence of points (c) and (d), an increase of temperature produces an enrichment of the alcoholic phase in compounds containing a polar group, while the temperature is almost without influence on the water/octanol partitioning of alkanes. This statement, however, must be accepted with some reserve owing to the reduced number of compounds examined to date. Furthermore, our $\Delta_{trf}H°(w\text{-}oct)$ values refer to pure solvents, while actual experiments of partitioning deal with mutually saturated octan-1-ol and water phases. A survey of the data (Table 1) brings out the effect of the water content of the alcoholic phase on the enthalpy of transfer of amines from water to octanol.

Solvation in different thermodynamic media is affected, among others, by the structural features of the solute molecule. In the case of amines, the number of hydrogen atoms bonded to nitrogen and the extension of the alkyl radicals are relevant. To provide an immediate picture of these features, the $\Delta_{solv}H°(oct)$, $\Delta_{solv}H°(w)$, and $\Delta_{vap}H°$ data vs. n_C*, the number of carbon atoms per single alkyl chain present in the $R_{j+1}NH_{2-j}$ amine (j = 0,1,2), are reported in Fig. 2. The figure shows that:

a) For primary amines, all the enthalpies of transfer from gas to condensed liquid state are linear functions of n_C*, the slopes changing from -3.1 kJ mol^{-1} for water to -4.4 kJ mol^{-1} for pure liquids, to -5.0 kJ mol^{-1} for octan-1-ol.

b) For the secondary amines, the linearity between the enthalpy of transfer and n_C* is preserved only for solvation in the pure liquid and in octanol, the slopes being now -9.2 and -8.8 kJ mol^{-1}, respectively. The $\Delta_{solv}H°(w)$ vs. n_C* plot of secondary amines, on the other hand, displays a slight concave downward slope.

c) For tertiary amines, the linearity vs. n_C* is lost and the $\Delta_{solv}H°(oct)$ curve is concave upwards.

d) Going from primary to secondary to tertiary amines, the $\Delta_{vap}H°$ and $\Delta_{solv}H°(w)$ values lie in very well distinguished ranges, whereas the $\Delta_{solv}H°(oct)$ curves for secondary and tertiary amines cross each other twice.

e) For all amines, the order $\Delta_{vap}H° < \Delta_{solv}H°(oct) < \Delta_{solv}H°(w)$ is always respected in magnitude.

It is not easy to explain such a complex trend of the enthalpies of transfer. The distinguishing features showed by the thermodynamic media receiving the gaseous molecule of amine partially justify the additive behaviour exhibited in some cases, but not in others.

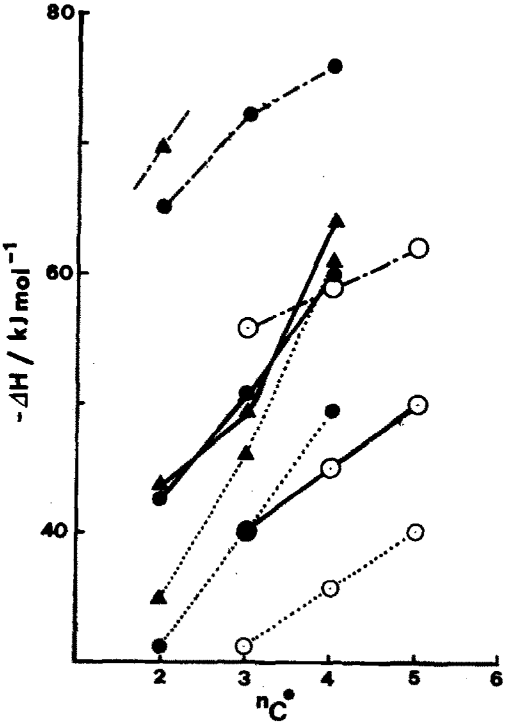

Fig. 2. Enthalpies of solvation in octan-1-ol, $\Delta_{solv}H°(oct)$ (——), in water, $\Delta_{solv}H°(w)$ (– – –), and in itself, $-\Delta_{vap}H°$ (··········), of $R_{j+1}NH_{2-j}$ (j=0,1,2) of aliphatic amines against the number n_C* of carbon atoms of the single R n-alkyl group: ○, primary amines; ●, secondary amines; ▲, tertiary amines. Source of data: Table 2.

As far as the pure liquids are concerned, the molecule of solute is surrounded by molecules of the same species. So, an increase of the total number of carbon atoms, $n_C = n_C*(j+1)$, produces a proportional increase in the hydrocarbon-hydrocarbon contacts. These do not seem to be particulary dependent on the number of alkyl groups bonded to the nitrogen atom. The slopes of the plot $\Delta_{vap}H°$ vs. n_C change in the order -4.4, -4.6, and -4.35 kJ mol^{-1} for primary, secondary, and tertiary amines, respectively. Comparison between isomer amines *with a different number of hydrogen atoms bonded to nitrogen enables a difference* of about 5 kJ mol^{-1} to be evaluated in the enthalpy of vaporization (see Table 3). This value may be bounded to the different $NH_{2-j}\cdots NH_{2-j}$ interactions which occour when j changes by a unity.

When the solvent is water, despite its complexity, a rather simple condition may be met for monofunctional molecules. Here two distinctive interactions are operative between water and the host molecule, i.e. water···hydrophilic center

TABLE 3
Comparison between enthalpies of solvation of isomeric amines in different thermodynamic media.[a]

Solute	$-\Delta_{vap}H^\circ$	$\Delta_{solv}H^\circ(oct)$	$\Delta_{solv}H^\circ(w)$	$\Delta_{solv}H^\circ(w)(NH_{2-j})$[b]
n-butylamine	-35.69	-45.11	-59.04	-33.21
diethylamine	-31.14	-42.52	-65.12	-39.46
	4.55	2.59	-6.08	-6.25
di-n-propylamine	-40.04	-50.82	-72.30	-39.46
triethylamine	-34.94	-43.58	-69.68	-38.92
	5.10	7.24	2.62	0.54

[a] All data in kJ mol^{-1}. Vap, vaporization; oct, solvation in octan-1-ol; w, solvation in water.

[b] $\Delta_{solv}H^\circ(w)(NH_{2-j})$ refers to the contribution of the NH_{2-j} group to the function $\Delta_{solv}H^\circ(w)$ (ref. 6).

and water hydrocarbon backbone interactions. The latter, for hydrophobic regions of the same nature, are proportional to the area exposed to the solvent. This produces a proportionality between the enthalpy of hydration and the number of carbon atoms of the alkyl chain. For large molecules, which are not able to expose to the solvent a surface strictly proportional to the total number of carbon atoms, it is logical to find a concave downward curvature. As far as the contribution of the nitrogen center to $\Delta_{solv}H^\circ(w)$ is concerned, by following the same comparison between isomer amines applied above for pure liquids, it is found that in the passage from primary to secondary amines $\Delta_{solv}H^\circ(w)$ changes by about -6.0 kJ mol^{-1}, but on going from secondary to tertiary amines the change in $\Delta_{solv}H^\circ(w)$ is about 2.6 kJ mol^{-1}. This emphasizes the very different enthalpic effects due to the interactions $NH_{2-j}\cdots H_2O$ when j changes by one unity. Owing to the different overall contribution of alkyl chains of the same length bonded to primary, secondary, and tertiary nitrogens, these estimates concerning the $NH_{2-j}\cdots H_2O$ interaction are very coarse, but close to the values found in a more detailed analysis (ref. 6) of group contributions to thermodynamic properties of organic compounds in the dilute aqueous solution: $\Delta_{solv}H^\circ(w)(NH) - \Delta_{solv}H^\circ(w)(NH_2) = -6.2$ kJ mol^{-1}; $\Delta_{solv}H^\circ(w)(N) - \Delta_{solv}H^\circ(w)(NH) = 0.54$ kJ mol^{-1} (see Table 3).

Finally, in the case of octan-1-ol, a local organization due to $OH\cdots OH$ and hydrocarbon···hydrocarbon interactions is present. When a molecule of primary amine is introduced, an interaction $OH\cdots OH$ is substituted by an interaction $NH_2\cdots OH$, while the hydrocarbon chain of the amine interacts with those of the solvent. The contribution of a CH_2 group to the property $\Delta_{solv}H°(oct)$ is greater than its contribution to the property $\Delta_{vap}H°$. This effect can be explained in terms of a stronger $NH_2\cdots OH$ bond in respect to $OH\cdots OH$, which promotes hydrocarbon···hydrocarbon interactions between the backbones of the solute and the solvent. In the case of secondary amines, the $NH\cdots OH$ interactions are still strong. This is clear from the fact that the differences $\Delta_{solv}H°(oct) - \Delta_{vap}H°$ are near to -10 kJ mol^{-1} for primary and secondary amines, with a very weak dependence on the length and number of alkyl groups. Instead, for tertiary amines the difference between $\Delta_{solv}H°(oct)$ and $\Delta_{vap}H°$ is near to -10 kJ mol^{-1} only in the case of triethylamine, but decreases strongly as n_C* increases. The differences between the values of $\Delta_{solv}H°(oct)$ of isomer amines (2.59 and 7.24 kJ mol^{-1}, see Table 3) may be interpreted in terms of $NH_{2-j}\cdots OH$ interactions in octan-1-ol, with decrease as j increases. The enthalpic effects connected with this type of interactions in octanol are moreover less than those due to the $NH_{2-j}\cdots H_2O$ interactions (see Table 2).

The loss of linearity between $\Delta_{solv}H°(oct)$ and n_C* for tertiary amines may be understood as a result of two opposite effects. In low molecular weight amines, the nitrogen center is not buried by hydrocarbon chains and acts noticeably in determining the value of $\Delta_{solv}H°(oct)$; for higher terms of the series, the molecule presents only its alkyl groups to the solvent and only the hydrocarbon···hydrocarbon interactions are to be considered. A slight difference is in effect found in the enthalpies of transfer from pure liquid amine to infinitely dilute solution in octanol for tripropylamine and tributylamine.

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REFERENCES

1 P.Berti, S.Cabani, G.Conti, and V.Mollica, J. Chem. Soc., Faraday Trans. 1, 82 (1986) 2547.
2 W.K.Stephenson and R.Fuchs, Can. J. Chem., 63 (1985) 2540.
3 F.Sarmiento, M.I.Paz-Andrade, J.Fernandez, R.Bravo, and M.Pintos, J. Chem. Eng. Data, 30 (1985) 321.
4 A.Leo, C.Hansch, and D.Elkins, Chem. Rev., 71 (1971) 525.
5 A.Apelblat, Ber. Bunsenges. Phys. Chem., 87 (1983) 2.
6 S.Cabani, P.Gianni, V.Mollica, and L.Lepori, J. Solution Chem., 10 (1981) 563.
7 J.D.Cox and G.Pilcher, Thermochemistry of organic and organometallic compounds, Accademic Press, London, 1970.
8 I.Wadso, Acta Chem. Scand., 23 (1969) 2061.
9 M.Ducros, J.F.Gruson, H.Sannier, and J.Velasco, Thermochim. Acta, 44 (1981) 131.
10 Unpublished results.