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THERMODYNAMIC STUDY OF ORGANIC COMPOUNDS IN OCTAN-1-OL. 3. ENTHALPY EFFECTS CONNECTED WITH THE PARTITIONING OF SOME BIFUNCTIONAL COMPOUNDS BETWEEN WATER AND OCTAN-1-OL *

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ABSTRACT

The values of the enthalpy changes for the transfer of some open-chain and cyclic bifunctional organic compounds (diethers, diamines, aminoethers) from gas state to dilute solution in octan-1-ol have been obtained by the enthalpies of vaporisation of the pure solutes and the limiting enthalpies of solution in octanol. These data have been combined with the known values of the enthalpy of solvation in water, and the values of enthalpy of the transfer process from pure water to pure octan-1-ol have also been calculated.

From an analysis of these data, it emerges that: the enthalpies of solvation in water and in octan-1-ol are linearly related and distinctive values were obtained for the slopes of the two straight lines which connect bifunctional open-chain and cyclic compounds; the enthalpies of transfer from water to octanol are always endothermic and linearly related to the intrinsic volumes of the solutes, irrespective of whether they have an open-chain or a cyclic structure.

The enthalpy changes for the transfer from gas to aqueous or alcoholic solution, or for the transfer from water to octan-1-ol, have been related to the molecular structure of the solutes.

INTRODUCTION

To gain a better understanding of the partitioning of organic solutes between water and octan-1-ol, we are carrying out a thermodynamic study on the functions of solvation, $\Delta_{\text{solv}} X^{\ominus}(j)$ $(X \equiv G,\ H,\ S)$, in water $(j = \text{w})$ and in octanol $(j = \text{oct})$, of compounds differing in the type and number of

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their functional groups. These quantities will be used to obtain values of the standard thermodynamic functions for the ideal transfer of organic compounds from pure water to pure octanol. Knowledge of these functions is of interest because they permit an initial rough evaluation of the thermodynamic quantities associated with the partitioning, and provide an insight into the reasons which govern it. It has, in fact, been shown that the thermodynamic functions of solvation and the molecular structures of the solutes can be simply yet effectively correlated [1].

In previous papers [2–4], we have reported and discussed the free energy and enthalpy values associated with the processes of transfer of monofunctional compounds from the gas state and dilute aqueous solution to octan-1-ol. Here we report the enthalpies for these processes for some bifunctional compounds, namely diethers, aminoethers and diamines.

EXPERIMENTAL

Materials

The compounds examined (1,2-dimethoxyethane, 1,4-dioxane, 2-methoxyethanamine, 3-methoxypropanamine, morpholine, 4-methylmorpholine, 1-methyl-piperazine and 1,2-diaminoethane) were all of the purest ($>99\%$ purity) commercially available grade. All compounds were fractionally distilled under nitrogen at atmospheric pressure after prolonged reflux over metallic sodium or potassium hydroxide pellets. The purity of the fractions collected at constant boiling point was checked by GLC and was, in all cases, better than 99.8%. 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 enthalpies of solution of the pure substances were measured by an isoperibol calorimeter at 298 K. Details of the apparatus and the measurement procedure are reported in ref. 2. For each compound at least 15 measurements were carried out in the concentration range 0.000 3–0.02 mole fraction. A linear dependence on the solute concentration was observed for all the compounds examined. The uncertainty on the limiting enthalpies of solution did not exceed 0.10 kJ mol^{-1}.

RESULTS AND DISCUSSION

Table 1 lists the limiting values of the enthalpy of solution in octan-1-ol, $\Delta_{\mathrm{soln}}H^{\ominus}(\mathrm{oct})$, and the values of the enthalpy of solvation in water, $\Delta_{\mathrm{solv}}H^{\ominus}(\mathrm{w})$, and in octanol, $\Delta_{\mathrm{solv}}H^{\ominus}(\mathrm{oct})$. The same table also shows the enthalpy changes, $\Delta_{\mathrm{trf}}H^{\ominus}(\mathrm{w{-}oct})$, associated with the transfer from pure water to pure octan-1-ol as evaluated by

$$\Delta_{\mathrm{trf}}H^{\ominus}(\mathrm{w{-}oct}) = \Delta_{\mathrm{solv}}H^{\ominus}(\mathrm{oct}) - \Delta_{\mathrm{solv}}H^{\ominus}(\mathrm{w}) \qquad (1)$$

The transfer from water to octanol is always endothermic, as was found for the monofunctional compounds [4], and generally increases with the molecular dimensions (see Fig. 1). Plotting the values of $\Delta_{\mathrm{solv}}H^{\ominus}(\mathrm{oct})$ against $\Delta_{\mathrm{solv}}H^{\ominus}(\mathrm{w})$ produces straight lines corresponding to families of compounds with similar structural features [4]. Figure 2a shows two such lines: the first for open-chain bifunctional compounds and the second for cyclic hexatomic solutes. The slope of the first line is steeper. Both slopes are different from those characterising the $\Delta_{\mathrm{solv}}H^{\ominus}(\mathrm{oct})$ versus $\Delta_{\mathrm{solv}}H^{\ominus}(\mathrm{w})$ plot for monofunctional compounds [4]. The slopes change from $\cong 0.6$ to $\cong 1$ to $\cong 1.8$ for bifunctional cyclic, monofunctional and bifunctional open-chain compounds, respectively.

In the bifunctional compounds, different interactions are obviously operative according to the nature of the two functional centres, their reciprocal distance, as well as the type of molecular frame (open-chain or cyclic) in

TABLE 1

Enthalpies of solution in octan-1-ol, $\Delta_{\mathrm{soln}}H^{\ominus}(\mathrm{oct})$, of solvation in octan-1-ol, $\Delta_{\mathrm{solv}}H^{\ominus}(\mathrm{oct})$, and in water, $\Delta_{\mathrm{solv}}H^{\ominus}(\mathrm{w})$, and of transfer from water to octan-1-ol, $\Delta_{\mathrm{trf}}H^{\ominus}(\mathrm{w{-}oct})$, for bifunctional compounds at 298.15 K [a]

Compounds	$\Delta_{\mathrm{soln}}H^{\ominus}$ (oct) [b]	$-\Delta_{\mathrm{solv}}H^{\ominus}$ (oct) [c]	$-\Delta_{\mathrm{solv}}H^{\ominus}$ (w) [d]	$\Delta_{\mathrm{trf}}H^{\ominus}$ (w–oct) [e]
1,2-Dimethoxyethane	5.73	30.67	59.34	28.67
1,4-Dioxane	9.32	29.05	47.97	18.92
2-Methoxyethanamine	−4.33	42.66	63.51	20.85
3-Methoxypropanamine	−5.43	49.45	72.30	22.85
Morpholine	−2.53	47.01	69.45	22.44
4-Methylmorpholine	0.90	43.58	68.66	25.08
1-Methylpiperazine	−12.22	58.03	90.42	32.39
1,2-Diaminoethane	−14.75	60.44	76.10	15.66

[a] All quantities in kJ mol^{-1}.

[b] This work.

[c] Calculated from: $\Delta_{\mathrm{solv}}H^{\ominus}(\mathrm{oct}) = \Delta_{\mathrm{soln}}H^{\ominus}(\mathrm{oct}) - \Delta_{\mathrm{vap}}H^{\ominus}$; the enthalpies of vaporisation are taken from ref. 5.

[d] Ref. 1a.

[e] Calculated from eqn. (1) by us.

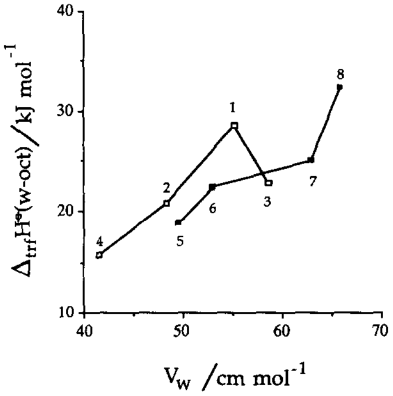


Fig. 1. Enthalpy of transfer from water to octan-1-ol, $\Delta_{trf}H^{\ominus}$(w–oct), vs. the intrinsic molar volume, V_W. Compounds: □, open-chain; ■, cyclic saturated hexatomic. 1, 1,2-dimethoxyethane; 2, 2-methoxyethanamine; 3, 3-methoxypropanamine; 4, 1,2-diaminoethane; 5, 1,4-dioxane; 6, morpholine; 7, 4-methylmorpholine; 8, 1-methylpiperazine. The $\Delta_{trf}H^{\ominus}$(w–oct) values are taken from Table 1; the V_W values, estimated as the van der Waals volume, were calculated according to ref. 6.

which they are inserted. The large number of variables makes it difficult to determine the relative weights of these effects. However, the cyclic compounds examined here enable the effects of interaction between two hydrophilic centres in the 1,4-positions of a hexatomic saturated ring to be examined. Table 2 lists the effects of the substitution of a methylene group in the 4-position with O, NH or NCH_3 group, when the 1-position is occupied by a CH_2, O, NH or NCH_3 group.

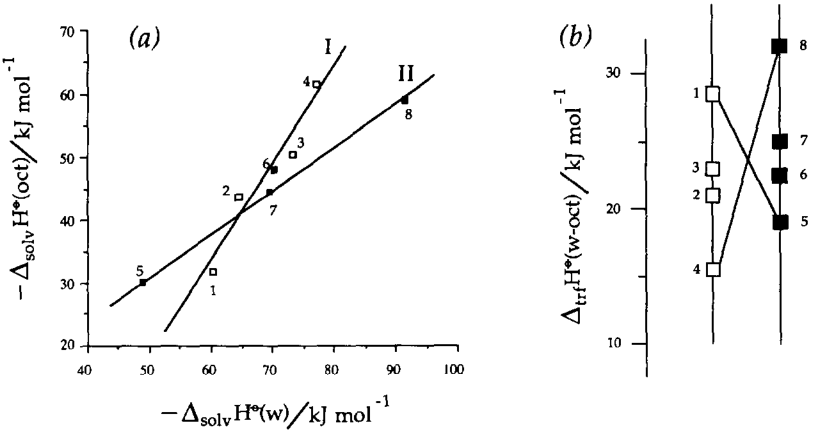
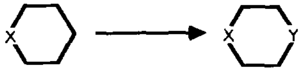


Fig. 2. a, Enthalpy of solvation in octan-1-ol, $\Delta_{solv}H^{\ominus}$(oct), vs. enthalpy of solvation in water, $\Delta_{solv}H^{\ominus}$(w); b, enthalpy of transfer from water to octan-1-ol, $\Delta_{trf}H^{\ominus}$(w–oct). Symbols as in Fig. 1; data taken from Table 1.

TABLE 2

Changes in the enthalpy of solvation in octan-1-ol and water caused by the introduction of a Y group in a hexatomic saturated ring according to



X	Y	$\delta\,\Delta_{\mathrm{solv}}H^{\ominus}(\mathrm{oct})$ [a]	$\delta\,\Delta_{\mathrm{solv}}H^{\ominus}(\mathrm{w})$ [a]
CH_2	O	0.89	−15.68
O	O	1.61	0.91
NH	O	1.98	−4.04
N–CH_3	O	−0.34	−2.89
CH_2	NH	−17.44	−32.21
O	NH	−16.35	−20.57
NH	NH	–	−24.96
N–CH_3	NH	−14.79	−24.65
CH_2	N–CH_3	−11.69	−32.57
O	N–CH_3	−12.92	−19.78
NH	N–CH_3	−9.04	−25.01
N–CH_3	N–CH_3	–	−24.94

[a] The values of $\delta\,\Delta_{\mathrm{solv}}H^{\ominus}(j) = \Delta_{\mathrm{solv}}H^{\ominus}(j)(\mathrm{X},\mathrm{Y}) - \Delta_{\mathrm{solv}}H^{\ominus}(j)(\mathrm{X})$ (j = oct, w) are in kJ mol^{-1}. The $\Delta_{\mathrm{solv}}H^{\ominus}(\mathrm{oct})(\mathrm{X})$ values are taken from ref. 2 (X ≡ CH_2) or are our unpublished results (X ≡ O, NH, N–CH_3); the $\Delta_{\mathrm{solv}}H^{\ominus}(\mathrm{w})$ values of mono- and bifunctional compounds are taken from ref. 1a.

When water is the solvent, large and very different values are observed in the enthalpic effects caused by the substitution of a CH_2 group in cyclohexane with a polar centre generating monofunctional compounds such as tetrahydropyran, piperidine or 1-methylpiperidine. In contrast, very reduced effects are observed when the CH_2 group in the 4-position of these monofunctional compounds is replaced by another hydrophilic centre.

The behaviour is completely different when the solvent is octan-1-ol. Noticeable differences are found on introduction of a polar group in a cyclohexane ring, according to the nature of the entering centre (O, NH, or NCH_3). Furthermore, very similar enthalpic values are observed when the CH_2 group of the monofunctional compounds is replaced by another Y centre. Figure 3 summarises these effects. Only mean values are reported for the process producing a bifunctional compound. The nature of the entering group must be taken into consideration, as is evident from the data reported in Table 2. It is nevertheless sufficient, though incorrect, to use the mean value to characterise the Y-substitution in the 4-position, when the 1-position is occupied by an X hydrophilic centre (X ≡ O, NH, or NCH_3). By comparing the values of $\delta\,\Delta_{\mathrm{solv}}H^{\ominus}(j)$ for this process with those of the first, it is evident that in octan-1-ol the 1,4-positioned groups interact with each other to a negligible extent. In water, on the other hand, the interaction

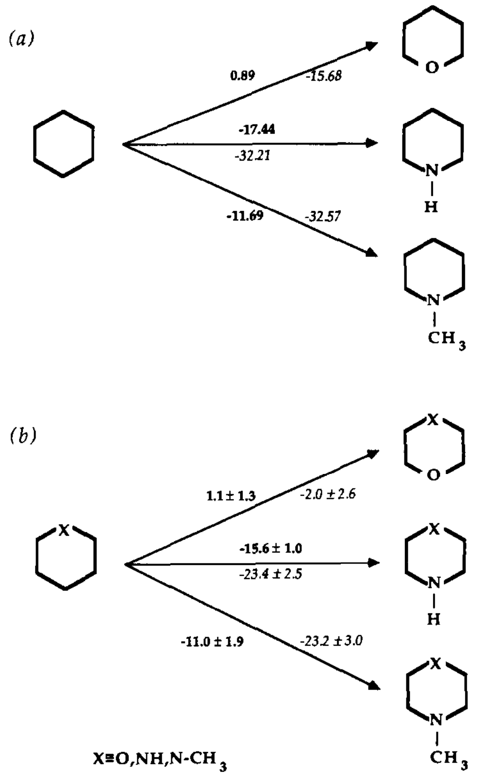


Fig. 3. Changes in the enthalpy of solvation in octan-1-ol (bold numerals) and water (italic numerals) for the process of introduction of an O, NH, or N–CH_3 centre in: (a) a cyclohexane ring; (b) a hexatomic monofunctional X-compound ($X \equiv O$, NH, or N-CH_3). Mean values (calculated from data of Table 2) are shown for process (b).

is such that the effect of solvation is almost completely compensated for when the Y-entering group is an ethereal oxygen. When an NH or NCH_3 group enters, the compensation is about a third of the value found in the formation of the monofunctional compound (Fig. 3). In practice, the effect of the interaction between the two groups is about 13 kJ mol^{-1} when the 1-position is occupied by an ethereal oxygen, and about 10 kJ mol^{-1} when the substituted group is NH or NCH_3.

The pattern exhibited by the open-chain compounds on the scale of the $\Delta_{trf}H^{\ominus}$(w–oct) values differs from that of the cyclic compounds. The value for 1,2-dimethoxyethane is at the top of the scale, whereas that for 1,2-diaminoethane is at the bottom (see Fig. 2b). For the cyclic compounds, the $\Delta_{trf}H^{\ominus}$(w–oct) value of 1-methylpiperazine is at the top of the scale, and that of 1,4-dioxane is at the bottom. The $\Delta_{solv}H^{\ominus}$(oct) values for diethereal open-chain and cyclic solutes are very similar, and this is also the case when two nitrogen centres are present in the molecular frame of the solute. However, the cause of the trend observed for the $\Delta_{trf}H^{\ominus}$(w–oct) values is the different interaction the two hydrophilic centres suffer in water, following their insertion in an open-chain or cyclic structure.

Consideration of the enthalpies of solvation in pure solvents is certainly helpful in identifying the causes of the energetics of the partitioning. The partitioning itself will be discussed when the free energies of solvation in octan-1-ol of the compounds examined are also available.

ACKNOWLEDGEMENT

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