# Thermodynamic Aspects of the Partitioning of Organic Compounds between Water and Octan-1-ol; Towards a Rationalization of the Energetics of the Partitioning

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The enthalpy values for the partitioning of monofunctional organic compounds between water and octan-1-ol are related to the way the functional group is inserted into the hydrocarbon frame, rather than its chemical nature.

The standard thermodynamic functions of partitioning of organic molecules between water and octan-1-ol, *i.e.* $\Delta_{\text{trf}}X^{\circ}$(w–oct),† which are supposed to be totally immiscible, may be calculated by equation (1), where $\Delta_{\text{solv}}X^{\circ}$(oct) and $\Delta_{\text{solv}}X^{\circ}$(w) represent the changes of the thermodynamic quantity $X$ in the solvation process, *i.e.*, the transfer of the solute molecule from standard gas state to standard state solution in octan-1-ol and in water, respectively.[1,2]

$$\Delta_{\text{trf}}X^{\circ}(\text{w–oct}) = \Delta_{\text{solv}}X^{\circ}(\text{oct}) - \Delta_{\text{solv}}X^{\circ}(\text{w}) \qquad (1)$$

Here, we show the interesting features exhibited by the values of the enthalpy changes, $\Delta_{\text{trf}}H^{\circ}$(w–oct), associated with the transfer of monofunctional organic solutes from pure water to pure octan-1-ol, which were evaluated by combining through equation (1) the enthalpies of solvation in octan-1-ol, $\Delta_{\text{solv}}H^{\circ}$(oct), and in water, $\Delta_{\text{solv}}H^{\circ}$(w).

Figure 1a shows that a family of straight lines which are almost parallel, is obtained when the $\Delta_{\text{solv}}H^{\circ}$(oct) values are plotted against the $\Delta_{\text{solv}}H^{\circ}$(w) values. Each of these straight lines is typical of compounds which may be described in terms of a well distinguished general feature. Line **I**, assembles the n-alkanes and cycloalkanes. Line **II** includes the various monofunctional saturated compounds of general formula RY, where R is an open-chain or a cyclic hydrocarbon frame and Y is a polar group, *e.g.*, O in ketones and cyclic ethers, $NH_2$ in primary aliphatic amines, NH in cyclic secondary amines. Line **III** collects compounds of $R^1R^2Y$ type, where $R^1$ and $R^2$ are alkyl radicals and Y a functional group, *e.g.*, O in aliphatic ethers and NH in secondary aliphatic amines. Finally, as a separate point, **IV** shows the value of the only compound of structure $R^1R^2R^3Y$ (Y = N in tertiary aliphatic amines) for which we have data at the moment.

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† w = water; oct = octan-1-ol.

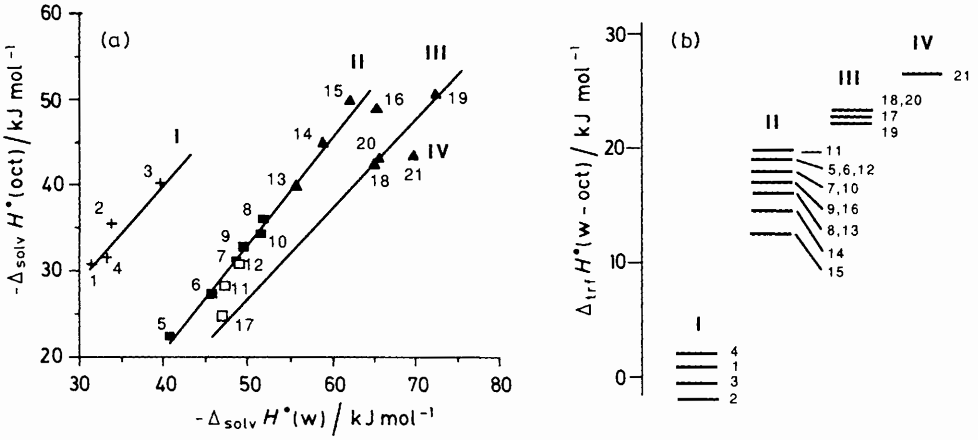

**Figure 1.** (a) Enthalpy of solvation in octan-1-ol, $\Delta_{solv}H^\circ$(oct), *vs.* enthalpy of solvation in water, $\Delta_{solv}H^\circ$(w). (b) Enthalpy of transfer from water to octan-1-ol, $\Delta_{trf}H^\circ$(w–oct) [= $\Delta_{solv}H^\circ$(oct) − $\Delta_{solv}H^\circ$(w)]. Compounds: (+) hydrocarbons; (■) ketones; (□) ethers; (▲) amines. Line **I**: 1, n-hexane; 2, n-heptane; 3, n-octane; 4, cyclohexane. Line **II**: 5, propanone; 6; butan-2-one; 7, pentan-2-one; 8, hexan-2-one; 9, pentan-3-one; 10, cyclopentanone; 11, tetrahydrofuran; 12, tetrahydropyran 13, n-propylamine; 14, n-butylamine; 15, n-pentylamine; 16, piperidine. Line **III**: 17, diethyl ether; 18, diethylamine; 19, di-n-propylamine; 20, *N*-methylpiperidine. Line **IV**: 21, triethylamine. $\Delta_{solv}H^\circ$(w) data are taken from ref. 3; $\Delta_{solv}H^\circ$(oct) values are from refs. 1 and 2, except for compounds 2, 3, 6, 7, 8, 12 (unpublished results).

Corresponding to the four lines, all lying in the plane $\Delta_{solv}H^\circ$(oct) *vs.* $\Delta_{solv}H^\circ$(w), are four distinctive groupings of enthalpies of partitioning, $\Delta_{trf}H^\circ$(w–oct) (Figure 1b). For compounds on the first line, the $\Delta_{trf}H^\circ$(w–oct) values range from −1.6 to +1.6 kJ $mol^{-1}$, for compounds on the second line the $\Delta_{trf}H^\circ$(w–oct) values are in the range 12—19 kJ $mol^{-1}$, on the third line 21.5—22.6 kJ $mol^{-1}$, whereas for compound **IV** a value of $\Delta_{trf}H^\circ$(w–oct) of about 26 kJ $mol^{-1}$ is found.

The linearity of the functions $\Delta_{solv}H^\circ$(oct) *vs.* $\Delta_{solv}H^\circ$(w) arises from the linearity of the thermodynamic functions of solvation of monofunctional compounds in water[3] and in organic solvents[4] when plotted against quantities related to the sizes of molecules (*i.e.*; the number of carbon atoms, the partial molar volumes, the intrinsic volumes, *etc.*).

The values found for $\Delta_{trf}H^\circ$(w–oct) are the result of many effects often compensating each other. *I.e.*, the energetics of alkanes in octan-1-ol are governed by hydrocarbon–hydrocarbon interactions, while the energetics of alkanes in water are related to the organization of the water molecules near to non-polar surfaces (hydrophobic hydration). Both these interactions produce negative enthalpy effects, which increase as the volumes of the dissolved alkanes increase. The energetics for the transfer from gas to solution for the compounds in line **II** are determined by hydrocarbon–solvent interactions and also the Y · · · solvent interactions. The latter are strongly dependent on the nature of both the solvent and the Y group. For these reasons, on line **II** ketones and cyclic ethers are found at smaller $\Delta_{solv}H^\circ$(oct) values, while primary aliphatic amines are found at larger values. Although the Y · · · $H_2O$ interactions in water and the Y · · · OH interactions in octan-1-ol produce negative enthalpy effects, which vary when Y is changed, the differences between the enthalpy effects of the Y · · · $H_2O$ and Y · · · OH interactions are much less dependent on Y. For this reason, a crowding of values for $\Delta_{trf}H^\circ$(w–oct) is observed for the category of solutes described by the formula RY. The statements made for compounds on line II may be repeated for the compounds of the third, and probably the fourth group.

It is noteworthy that as a result of the different effect of varying the number of alkyl groups bonded to Y on the Y · · · solvent interactions, depending on whether the solvent is water or octan-1-ol, the $\Delta_{trf}H^\circ$(w–oct) values may be almost zero for alkanes, but very large for compounds which are extensively substituted around the Y group *e.g.*, the tertiary amines. Probably this fact is related to the accessibility of water to the hydrophilic centre of the solute molecule, even when the latter is strongly buried by the hydrocarbon chains, and in contrast, to the inaccessibility of the OH group of octan-1-ol to the Y centre. As a result of this mechanism, the partitioning of organic solutes between octan-1-ol and water is almost independent of temperature for hydrocarbon compounds, whereas it changes significantly with temperature for compounds very rich of hydrocarbon moieties, but having a 'hidden' functional group. By increasing the temperature, the partitioning of alkanes remains unchanged, whereas compounds of the $R^1R^2R^3Y$ type are transferred from aqueous to alcoholic solution.

The effect is not 'all or nothing' but is displayed progressively according to the possibility of assembling the organic compounds in distinguished groups with regard to the $\Delta_{trf}H^\circ$(w–oct) function.

We think that this rationalization of the temperature effect in the distribution of solutes between water and octan-1-ol is interesting. Of course, in order to obtain a more complete picture, other thermodynamic properties need to be studied, *e.g.*, the free energy function of transfer. The effect of the mutual solubility of the solvents, and the effect of increasing the concentration of the solutes, should also be investigated.

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