A Microcalorimetric Study of Powder Surface Energetics

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INTRODUCTION

The surface energetics of a powder plays an important role in the ease of preparation, stability and dissolution of pharmaceutical products. Existing techniques for assessing surface energetics of powders (i.e. liquid penetration and contact angles) suffer from practical and theoretical limitations as well as being somewhat subjective.

The objective of this study was to evaluate the data obtained by microcalorimetric techniques from which ∆H and other kinetic parameters of adsorption can be determined. Results were supplemented by data obtained by vacuum microbalance methods.

EXPERIMENTAL

Measurements of the enthalpy of adsorption (∆H) were undertaken using an LKB 10700 microcalorimeter. A specially constructed calorimeter cell was connected to a vacuum pump and water reservoir. A series of powders was placed in the cell, outgassed and weighed quickly to allow minimal adsorption from the atmosphere. The powders were then assayed under repeated adsorption/desorption experiments in the microcalorimeter. It is important to note that 2277 Thermal Activity Monitor, TAM, the successor to the LKB 10700 has now been used in such studies.

RESULTS
Enthalpy of adsorption

This was calculated by subtraction of the heat flow produced by control experiments and corrected for moles of water adsorbed.

Gibb's function and entropy of adsorption

The standard state is assumed to be the number of moles of water adsorbed [b] per gram of powder at saturated vapour pressure [p] of water. The equilibrium constant is thus defined as:

$k_{ad} = [b]/[p]$

The Gibb's function is obtained by: $\Delta G = -RT \ln k_{ad}$

The entropy of adsorption can then be obtained from:

$\Delta G = \Delta H - T \Delta S$

The thermodynamic parameters are shown in Table 1.

Kinetics of Adsorption

The experiments conducted in this study can be regarded as batch experiments, the excess heat output decay function can thus be compared to the decay from an electrical

calibration peak. The logarithm of the difference in area under the heat flow curve compared to the calibration curve plotted against time, can give an indication of the kinetics of the reaction; the gradient being equal to the apparent first-order rate constant.

DISCUSSION

Previous studies have shown that the use of contact angles for the determination of ΔG and subsequent calculations of ΔS for wetting processes are not suitable. Microcalorimetric techniques coupled with data from the vacuum microbalance have shown it is possible to obtain direct measurements of ΔH for the adsorption process, and ΔG from a single adsorption isotherm. The combination of methods therefore allows the study of small changes in powder surface energetics which affect the adsorption process.

Values of ΔG were the same for each powder because the same amount of water was adsorbed (Table 1). However, ΔH values were found to differ significantly between each of the powders. Liquid penetration data showed the ranking of powders in terms of hydrophobicity to be different to results from microcalorimetric techniques. Furthermore, microcalorimetric data revealed that wetting of the more hydrophobic powders was enthalpically favoured and this was associated with a large unfavourable entropy term. Thus, previous predictions on the wetting process using enthalpy data derived from classical methods of analysis may not be completely accurate.

Powder	Quantity of Adsorbed Water (mg/10,000 mg)	ΔH_{cal} (kJ - mol^{-1})	ΔG (kJ - mol^{-1})	ΔS_{cal} (J - mol^{-1}, mol^{-1})	ΔH_{iso} (kJ - mol^{-1})	ΔS_{iso} (J - mol^{-1}, mol^{-1})
Amylobarbitone	0.080	-25.5	+38.4	-214.4	-66.8	-353.0
Pentobarbitone	0.080	-12.7	+38.4	-171.5	-67.5	-355.4
Phenobarbitone	0.074	-8.1	+38.6	-156.7	-65.2	-348.3
Butobarbitone	0.080	-4.5	+38.4	-144.0	-61.4	-334.9

Table 1. The thermodynamic functions of adsorption at 25°C

CONCLUSION

The combination of microcalorimetric and vacuum microbalance techniques allows the possibility of calculating the thermodynamic parameters associated with the wetting process and in addition, gives insight into the mechanism of wetting.

REFERENCES

1. G. Buckton and A.E. Beezer. *International Journal of Pharmaceutics* 41:139-145 **(1988)**

NOTE

Application Note written by M. Shafiq, Thermo-Metric AB.