

IMMERSION HEAT STUDY OF MODIFIED QUARTZ SURFACES

by

JIM JIH-LIN WANG

A thesis submitted in partial fulfillment
of the requirement for the degree of
MASTER OF SCIENCE

UNIVERSITY OF TEXAS AT EL PASO

1972

Approved by

James W. Whalen.

John Brient

Michael Eastman

Samuel S. Seely

UMI Number: EP00866

UMI[®]

UMI Microform EP00866

Copyright 2003 by ProQuest Information and Learning Company.

All rights reserved. This microform edition is protected against
unauthorized copying under Title 17, United States Code.

ProQuest Information and Learning Company
300 North Zeeb Road
P.O. Box 1346
Ann Arbor, MI 48106-1346

ACKNOWLEDGEMENT

The author wishes to express deep gratitude to Dr. James W. Whalen for his valuable advice and supervision during this investigation. He expresses gratitude to his thesis committee members, Dr. S. J. Brient and Dr. M. P. Eastman, for their critical suggestions. Thanks to his wife Julie for typing this thesis.

The author is also grateful to the Petroleum Research Foundation for financial assistance.

TABLE OF CONTENTS

	PAGE
INTRODUCTION	1
EXPERIMENTAL	10
A. CALORIMETER	10
B. SAMPLES	10
C. IMMERSION FLUIDS	12
D. SURFACE AREA	13
E. SAMPLE HANDLING	16
DISCUSSION	24
REFERENCES	36
VITA	38

INTRODUCTION

The phenomenon of the evolution of heat on wetting (i.e. construction of a solid-liquid interface by immersion of solid surface into a bulk liquid) has been known since the report by Pouillet¹ in 1822. However, this phenomenon did not receive much attention until the early 1930s. The lack of properly identified surfaces (outgassing techniques) and difficulties in the construction of sensitive calorimeters hampered experimental progress. Also until the advent of a method for estimating specific surface area, the heat effect could not be put on a sound basis, i.e. energy evolved per unit area of wetted solid. Following Boyd and Harkins², the Harkins³ and Bartell⁴ groups made significant contributions to the practical thermodynamics of interfacial systems and to measurement techniques. Nevertheless, the influence of immersional calorimetry in surface chemistry did not become important, due to difficulties in the construction and manipulation of the sensitive and complex calorimeters, until advances in other aspects of surface chemistry emphasized problems which could only be investigated by heat of immersion measurements. Under this impetus several highly sensitive calorimeters^{5,6,7}, using thermistors or thermopiles as temperature sensing elements were developed.

Among the many immersional studies which can be related to useful application, it is possible,

1. To obtain fundamental information concerning interactions of surfaces with adsorbate molecules, particularly where other techniques are not suitable⁷.
2. To rate the polarity of solid surfaces from their heats of immersion in simple organic liquids having different dipole moments⁸.
3. To measure the site energy distribution⁹.
4. To study the nature and extent of adsorption from solution¹⁰.
5. To resolve of thermodynamic parameters related to the fluid-solid contact angle and its temperature derivative¹¹.

Several of the above immersional heat approaches require immersion of a solid having a film presorbed from the vapor phase of the immersion liquid, i.e. immersion of a partially complete solid-vapor interface. General forms of such experimently observed curves (heat-of-immersion isotherms) are shown in Figure 1 where the heat of immersion in ergs/cm² of solid surface ($h_i^p(s)$) is plotted against the fraction of saturation vapor pressure (P/P^0 , referred to as relative pressure) under which the solid was equilibrated prior to immersion. The vapor phase pressure characterizes the adsorbed film through the adsorption isotherm¹².

Curve (a) in Figure 1 is typical of a homogeneous, moderately high energy surface, i.e. a surface exhibiting high interaction energy with vapor or liquid phase molecules. Curve (b) is the most common type of heat of immersion isotherm. It reflects a heterogeneous high energy surface, e.g. silica

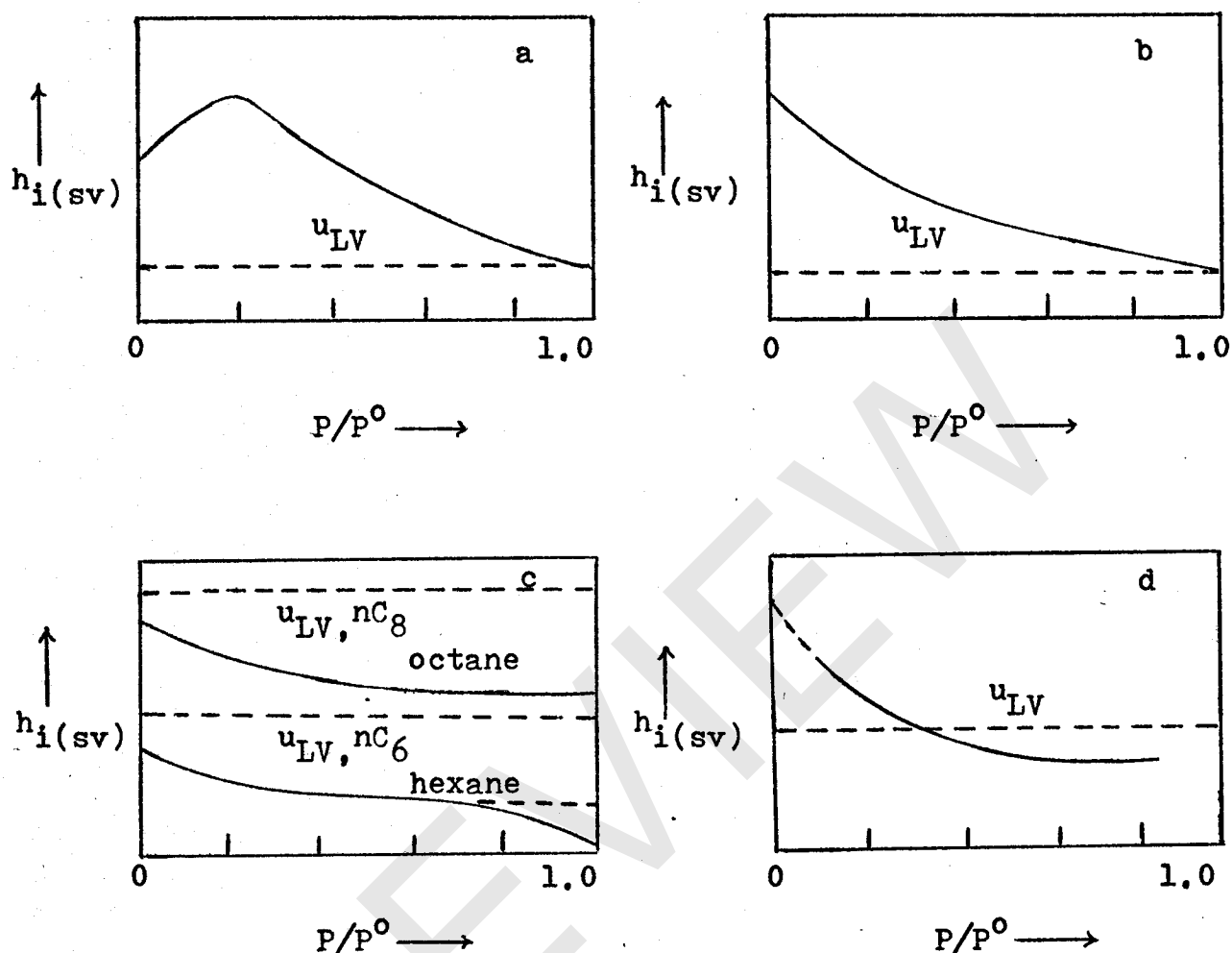


Figure 1

 P/P^0 vs. $h_i(sv)$ Immersion liquid surface energy (u_{LV})---

immersed into water. The exact form, in particular the immersion heat of the clean solid ($h_{i(s)}$), depends on the nature of the surface heterogeneity and on specific interaction between the solid surface and the immersional liquid. Curve (c) is a homogeneous low energy surface, such as Teflon 6, immersed into hexane or octane¹¹, i.e. a non-wetting

(finite contact angle) system.

When the relative pressure for the presorbed film approaches saturation pressure for high energy surfaces (cure a and b) the immersion heat should decline to surface energy of the liquid (u_{LV})^{7,13}. For low energy surfaces, heats of immersion are generally below u_{LV} and usually decrease sharply as P approaches P^{oll} . If a significant amount of a generally low energy surface consists of high energy heterogeneities, the heat curve may start above the liquid surface energy declining below that value as P approaches P^0 (Figure 1-d).

As with all equilibrium processes involving molecular systems, it is most appropriate to discuss free energy and relationships based on free energy rather than energy. Surface free energy terms (G) may be defined for all interfacial phases, i.e. G_{sv} denotes surface free energy of the solid-vapor interface and G_s the surface free energy of clean solid when it is under vacuum. The free energy change on adsorption (π) may be written

$$(G_{sv} - G_s) = -\pi \quad (1)$$

Surface free energy terms, G , for all interfaces are completely equivalent to interfacial tension γ (dynes/cm = dyne-cm/cm² = ergs/cm²), i.e. $G_{sv} = \gamma_{sv}$, $G_s = \gamma_s$, $G_{SL} = \gamma_{SL}$, and γ terms are conventionally used in discussion of free interfacial energies.

The molecule density in the interfacial region, whether the subject interface is solid-liquid or solid-vapor, defined

as $\Gamma = N_A/\Sigma$, denoting molecules (N_A) adsorbed on the total solid surface area (Σ), is expressed by the Gibbs Equation¹⁴,

$$\Gamma = -(a/RT) (d\gamma/da)$$

or

$$d\gamma = -RT \Gamma (da/a) = -RT \Gamma d \ln a .$$

For an ideal gas, the activity (a) can be replaced by the pressure,

$$d\gamma = -RT \Gamma d \ln P ,$$

and on integration,

$$-\int d\gamma = \pi = RT \int_{p=0}^{p=p} \Gamma d \ln P . \quad (2)$$

The value of π associated with integration over the entire range of accessible equilibrium pressures is designated as π^0 ,

$$\pi^0 = RT \int_{p=0}^{p=p^0} \Gamma d \ln P . \quad (3)$$

Such superscript notation will, in this discussion, always designate a term applicable at saturation pressure. Standard thermodynamic relationships relating changes in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) provide:

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

$$(\partial G / \partial T)_p = -\Delta S$$

and permit expression of relationships between enthalpy change (ΔH_{ad}), free energy change (π) and entropy change $(\partial \pi / \partial T)_p$ associated with the adsorption process

$$\Delta H_{ad} = \pi - T (d\pi/dT)_p \quad (5)$$

where ΔH_{ad} is defined as

$$\Delta H_{ad} = H_{sv}^p - H_s , \quad (6)$$