

Flow Adsorption Calorimetry with Supercritical Fluids on Silica Gel

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The supercritical state has long held a fascination for chemists as a "fourth state of matter."^{1,2} Recently, it has been recognized that supercritical extractants are also of industrial value and play an important role in geochemical and extraterrestrial chemistry.^{3,4} Of particular significance is the use of supercritical carbon dioxide for tertiary oil recovery, coal extraction, and chromatography in all of which supercritical fluids interact with solid phases.⁵⁻⁸ In the course of a thermometric study of solid acids with basic solutions we became interested in determining heats of adsorption by flow calorimetry and extending this to elevated temperatures and pressures.

The apparatus shown in Figure 1 may be assembled, for the most part, from readily available components following recent accounts of high pressure, and high temperature flow calorimeters assembled for heats of mixing.⁹⁻¹¹

After preliminary calibration of the calorimeter under various batch conditions by heats of solution of KCl and BaCl₂ in water¹² and heats of immersion of silica gel in water¹³, and ΔH_{ads} of isopropylamine from an isopentane solution was determined on silica gel using again heats of immersion (batch mode) at ambient temperature (Table I) to establish standards of reference for the more difficult flow studies.

TABLE I

ΔH_{imm} (Batch Mode) of Silica Gel in Some Liquids at 26°C

Liquid	$\Delta H_{imm}/\text{cal g}^{-1}$	$T_c/^\circ\text{C}^a$	P_c/psi^a
(1) Isopentane	-4.83 ± 0.63	187.8	483.5
(2) 10% Isopropylamine	-21.66 ± 0.81	190.0 ^b	527.0 ^b
(3) Isopropylamine	-20.33 ± 0.30	209.7	700.0 ^c

$$(2) - (1) = \Delta H_{ads} = -16.83 \pm 1.02 \text{ cal g}^{-1}$$

$$\Delta H_{ads} \text{ (flow mode) at 30 PSI} = -17.97 \pm 0.27 \text{ cal g}^{-1}$$

- a. Ref. 16
- b. Ref. 17
- c. Ref. 18

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Table II presents ΔH_{ads} values of isopropylamine on the same sample of silica gel (Fisher grade 62) from an isopentane carrier stream over a range of temperatures and pressures from subcritical to supercritical. Results are given in terms of calories per gram of silica gel. Since this is a saturation experiment, the observed values at a given temperature and pressure should be (and are) independent of flow rate (7-30 ml/hr) or concentration (10-20%) of isopropylamine.

TABLE II

Heats of Adsorption, ΔH_{ads} of Isopropylamine on Silica Gel at Different Temperatures and Pressures by Flow Calorimetry

Temp. (°C)	P (PSI)	ΔH_{ads} (cal/g)
26	30	-17.97 +0.27
	1000	-17.44 +0.84
80	500	-15.79 +0.22
	1000	-15.34 +0.23
160	500	-12.52 +0.80
	1000	-9.86 +1.30
200	500	-11.52 +0.72
	1000	-13.61 +0.16
250	500	-4.30 +0.16
	1000	

The most obvious results from Table II are: a) The insignificant effect of pressure on ΔH_{ads} in the subcritical range. b) The decrease of ΔH_{ads} in response to increasing temperature at a given pressure. c) The significant increase in ΔH_{ads} with increase in pressure above the supercritical threshold at 200°C. These observations are consistent with the notion that isopropylamine, a strong base, is primarily chemisorbed on the silica gel surface by hydrogen-bonds.¹⁴ Increasing the temperature weakens this interaction. However, close to the critical temperature, a small increase in pressure results in a substantial increase in density causing an increase in the effective concentration of the base. Thus, an increase in pressure above the critical temperature manifests itself as an increase in the ΔH_{ads} . It remains to be seen how less strongly adsorbed materials will respond to crossing into the supercritical region.

A crucial component for extending flow calorimetry into the supercritical range is the use of a Setaram-80 heat flow calorimeter which may be operated in the flow mode at temperatures up to 300°C using the sample cell (5) in Figure 1. This was designed for adsorption thermochemistry so that a bed of adsorbent in cell (5) can be placed downstream from the switching valves in the pumps so that either of the fluid streams leaving the piston pumps (A and B) may be directed through the adsorbent bed. An important problem in flow calorimetry (even at ambient conditions) is to balance mass transfer and heat transfer.¹⁵ Unless the stream of fluid containing the adsorbate has been

brought to exactly the temperature of the adsorbent (in cell 5) the observed ΔH_{ads} will contain a contribution due to incomplete thermal equilibration of the streams. Figure 2 shows how this problem was solved by forcing the stream through a coil of 1/8" (OD) x 0.60" (ID) 316 stainless steel tubing positioned in the preheating chamber of the calorimeter.

In each experiment, about 100-150 mg. of silica gel was used. After initial cleaning with methanol followed by hexane, the system was then purged with N_2 for about 10-15 min. before the assembled cell was put in line. The system was brought to the appropriate pressure by pumping an inert solvent (isopentane) at 75 ml/hr and adjusting the back pressure regulators. Once the appropriate pressure was obtained, the solvent flow rate was reduced to either 7 or 15 ml/hr and then the system was thermally equilibrated as demonstrated by a steady baseline on the recorder. Once a steady baseline was achieved, the reactive liquid in pump B was pressurized while still closed to the system to avoid a pressure drop and backflow when switching pumps. Simultaneously, pump A was turned off and pump B was opened to the system at the same flow rate as that of pump A. Heat evolved during the process of interaction of the isopropylamine with the silica gel was monitored by both digital and analog outputs, and was presented as an exothermic release of heat up to the point of surface saturation after which the system returned to its original baseline temperature in about 30 min.

ACKNOWLEDGEMENTS

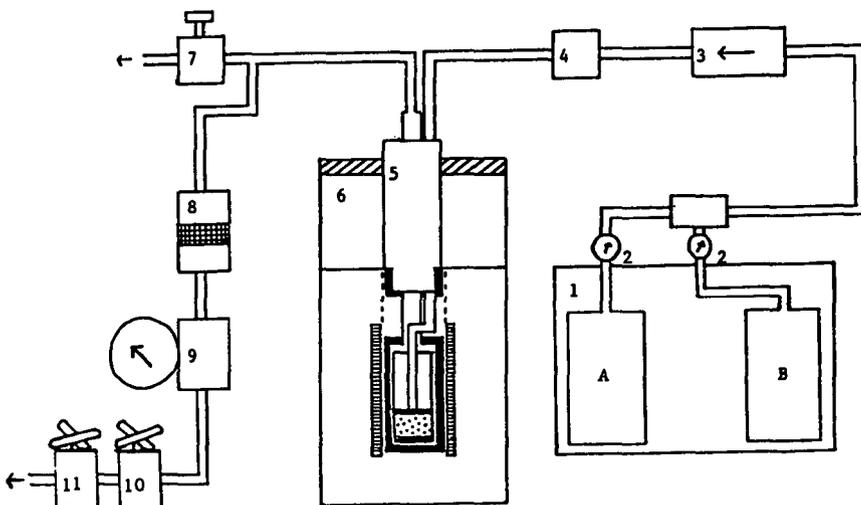
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12. Our ΔH_{soln} values for KCl and BaCl₂ of 4.25 ± 0.0.4 at 25°C and -6.85 ± 0.30 kcal mole⁻¹ at 75°C agree well with the literature values of 4.20 and -6.76 kcal mole⁻¹ respectively (Gunn, S. J. Phys. Chem. 1965, 69, 2902 and Criss, C. M.; Cobble, J. W. J. Amer. Chem. Soc. 1961, 83, 3223).
13. Our ΔH_{imm} value of -12.55 cal g⁻¹ for Silica gel in water agree with the range of values -11.95 to -13.14 cal g⁻¹ obtained at Bartlesville Laboratory (Noll, L. A. private communication) using different samples of silica gel (Fisher, grade 62).
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15. It is also important to reduce dead space in cell 5 by the use of a machined metal insert so that mixing of the flow stream is minimized following switching from pure solvent to the solution of base.
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17. Kay's approximation has been used to calculate pseudocritical constants for a mixture (Kay, W. B. Ind. Eng. Chem. 1936, 28, 1014 and Reid R. C.; Sherwood, T. K. "The properties of gases and liquids, their estimation and correlation" 1958. McGraw-Hill Book Co. Inc., New York).
18. P_c (isopropylamine) is an average value from estimates using Riedel's and Lydersen's methods reported in ref. 17.

Figure 1. Schematic of Adsorption Flow Calorimeter



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|--|---|
| 1. Perkin Elmer Model 601
Dual Piston Pumps | 7. Butech Pressure Systems High
Temperature Valve |
| 2. Perkin Elmer Bourden
Pressure Gauges | 8. Valco Filter |
| 3. High Pressure Equipment Co.
Check Valve | 9. Pilgrim Instruments Bourden
Pressure Gauge |
| 4. High Pressure Equipment Co.
Safety Valve | 10,11. Tescom Back Pressure Regulators,
Model 26-1724-24 |
| 5. High Pressure Cell | |
| 6. C-80 Setaram Calorimeter | |

Figure 2. Detail of Adsorption Cell (5 in Figure 1) Showing Preheater Coil

