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DESIGN AND APPLICATION OF A LIQUID-FLOW ADSORPTION MICRO CALORIMETER BASED ON THE CALVET-TYPE DAK 1–1 MICROCALORIMETER (USSR)

J. Seidel

RESEARCH INSTITUTE OF MINERAL PROCESSING, ACADEMY OF SCIENCES OF THE GDR,
STR. DES FRIEDENS 40, FREIBERG 9200, G.D.R.

The construction and the properties of a liquid-flow adsorption microcalorimeter are described. The calorimeter is based on the commercially available Calvet-type DAK 1-1 microcalorimeter (USSR), which has been equipped with a flow system consisting of a pump, several sets of heat exchangers and an adsorption cell. The minimum detectable heat effect is 1 μW up to a flow rate of 30 cm^3/h.

Results on the application of the calorimeter to adsorption and desorption processes of nonionic (Triton X–100) and anionic (styrene phosphonic acid) surfactant solutions in water at an α–Al_2O_3 surface are presented and discussed.

The adsorption of surfactants from solution is of great industrial and scientific interest, but our knowledge on this complex phenomenon is often only empirical. In particular, more experimental data relating to the thermodynamics and mechanism of adsorption from solution are needed.

Recently, remarkable progress has been made in the application of adsorption calorimetry to this problem [1–2]. With special regard to reagent adsorption in mineral dressing processes such as flotation or fine grinding, a liquid-flow adsorption microcalorimeter was designed to investigate the influence of several parameters on the adsorption process and to collect data in addition to adsorption isotherm data for thermodynamic modelling.

Description of the calorimeter

The measurement of enthalpies of adsorption or displacement is technologically interesting systems with small specific surface areas and small surfactant concentrations requires highly sensitive microcalorimeters with low baseline drift. Therefore, the liquid-flow microcalorimeter was designed on the basis of the commercially available Calvet-type DAK 1-1 microcalorimeter (USSR). For this calorimeter, a flow system consisting of a precision peristaltic pump, several sets of heat exhangers and an adsorption cell with a calibration heater was constructed. A scheme of the whole system is

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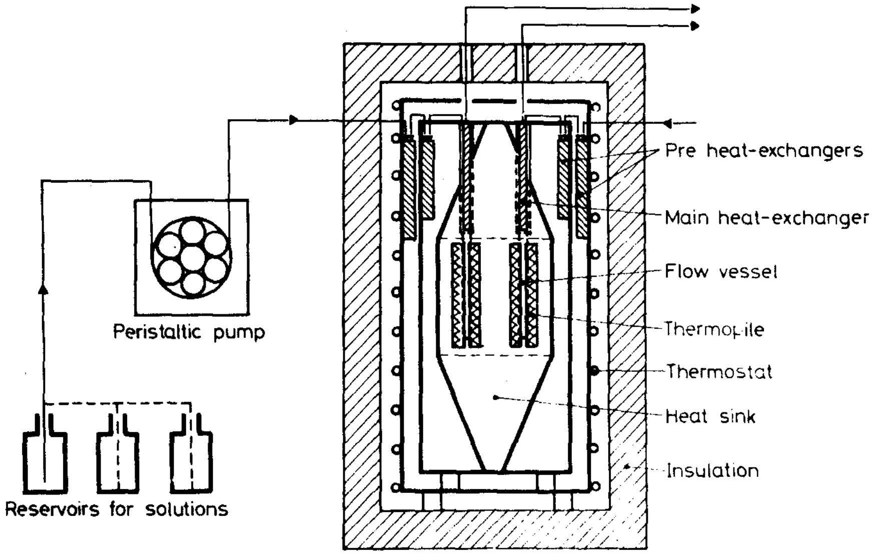

Fig. 1 Scheme of the flow adsorption microcalorimeter (DAK 1-1)

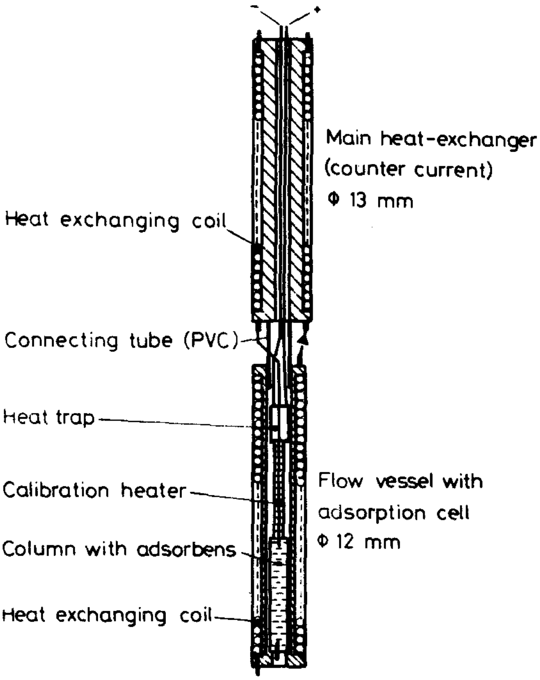

Fig. 2 Flow adsorption vessel for the microcalorimeter DAK 1-1

shown in Fig. 1. Some more details of the flow vessel are presented in Fig. 2. The heat exchangers consist of polyethylene or stainless steel tubing (1.1 mm i.d.) wound between an inner brass body and an outer aluminium cylinder. The real adsorption cell has a volume of approx. 0.5 cm^3 and contains the solid adsorbent housed between two 20 μm stainless steel sieves. The position of the calibration heater (manganin wire) minimizes the systematic errors during electrical calibration.

To test the efficiency of the heat-exchanging system, some calibration and blank experiments were carried out with an empty adsorption cell at different flow rates of water. The results of these experiments are summarized in Figs 3 and 4, showing that the heat exchangers work satisfactorily. A heat effect sensitivity value of 1 μW up to a flow rate of 30 cm^3/h was evaluated from the stability of the voltagers *vs.* time curve. The time constant of the flow calorimeter was approx 250 s.

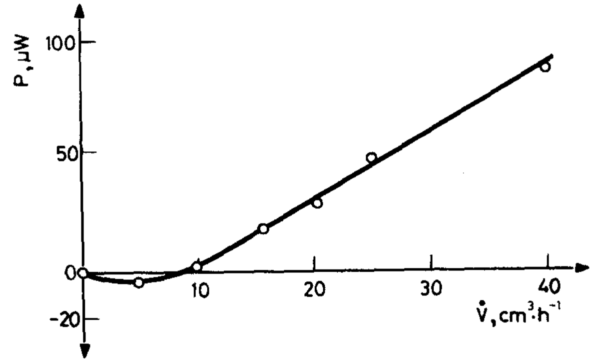

Fig. 3 Zero effect as a function of flow rate (empty cell)

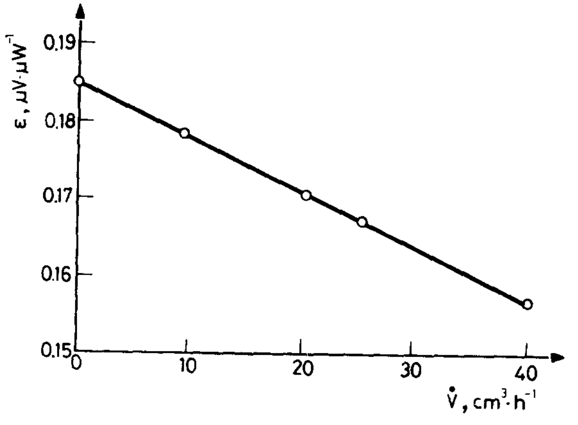

Fig. 4 Calibration constant (ϵ) as a function of flow rate

Application examples

In Figs 5 and 6 some results of adsorption and desorption of a nonionic alkylphenol-oxyethylenic surfactant (Triton X-100) and the anionic styrene phosphonic acid at the α-Al_2O_3 (0_{BET}= 4.0 m^2/g, particle size: 80–90 μm) surface are presented. In both cases, the measured heat effects are very small,

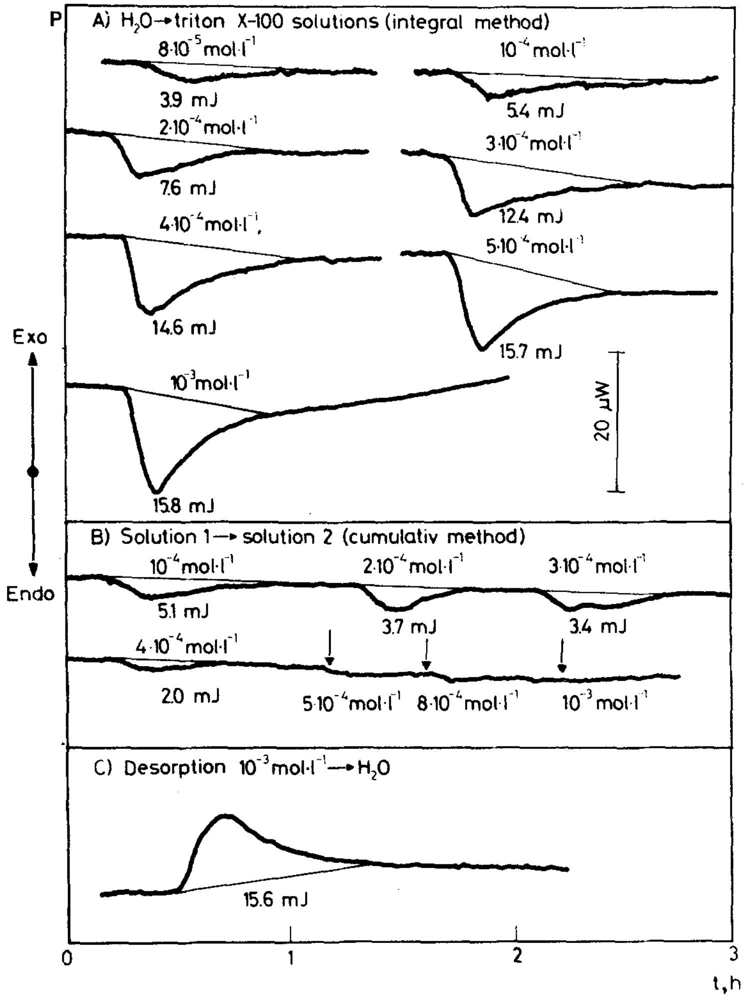

Fig. 5 Calorimetric recordings of Triton X–100 adsorption and desorption at α–Al_2O_3 (mass of adsorbent: 0.537g flow rate: 20 cm^3/h, *T*: 298.1 K)
Effects are due to *A* adsorption on fresh samples from solutions of different concentrations (integral method), *B* successive adsorption on one sample from solutions of progressively increasing concentration (cumulative method), *C* desorption by water after maximal load.

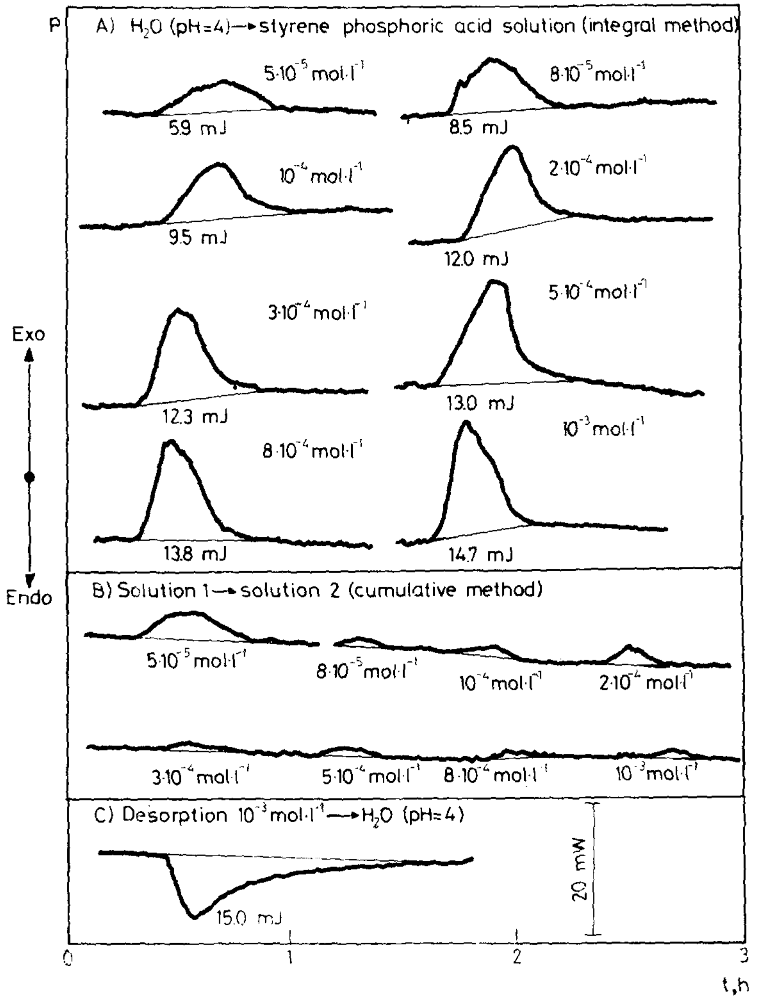

Fig. 6 Calorimetric recordings of styrene phosphonic acid adsorption and desorption at α–Al_2O_3 (mass of adsorbent: 0.618g, flow rate: 20.6 cm^3/h pH: 4,0, T: 298.1 K)
Effects are due to *A* adsorption on fresh samples from solutions of different concentrations (integral method), *B* successive adsorption on one sample from solutions of progressively increasing concentration (cumulative method), *C* desorption by water after maximal load.

demonstrating the high sensitivity and stability of the calorimeter. The accuracy of adsorption enthalpy measurements is mainly limited by baseline jumps which are caused by small differences in the solution viscosities. Heats of dilution could not be detected in the systems investigated.

The estimated heats of displacement for the two surfactant solutions have the same magnitude, but they are opposite in sign. The endothermal heat effects for Triton X–100 adsorption can be explained by the dominance of lateral interactions in the concentration range investigated [3]. The adsorption of styrene phoshonic acid can be characterized by an interaction of the phosphonic acid group with surface hydroxy groups of the α-Al_2O_3 [4], resulting in an exothermal heat effect. Analysis of the adsorption–desorption cycles showed that both adsorption processes are reversible.

References

1 J. Rouquerol, Pure and Appl. Chem., 57 (1985) 69.
2 R. Denoyel et al., in: Adsorption from Solution, R. H. Ottewill et al. (Ed.), Academic Press, London 1983, p. 225.
3 S. Partyka et al., Langmuir, 2 (1986) 101.
4 H. Braun and Ch. Cichos, in: VI. Internationale Tagung über Grenzflaechenaktive Stoffe, Akademie-Verlag, Berlin 1985, p. 505.

Zusammenfassung – Konstruktion und Eigenschaften eines Flüssigkeits-Strömungs-Adsorptions-Mikrokalorimeters werden beschrieben. Das Kalorimeter wurde weiterentwickelt aus dem Calvet-Mikrokalorimeter DAK 1-1 (USSR), das mit einem Strömungssystem aus einer Pumpe, verschiedenen Wärmeaustauschern und einer Adsorptionszelle ausgestattet wurde. Der kleinste nachweisbare Wärmeeffekt liegt bei 1 μW bis zu einer Durchflussgeschwindigkeit von 30 cm^3 h^{-1}. Mit dem Kalorimeter erhaltene Messergebnisse zur Adsorption und Desorption wässeriger Lösungen von nichtionischen (Triton X–100) und anionischen (Styrenphosphonsäuren) Tensiden an α–Al_2O_3 werden dargestellt und diskutiert.

РЕЗЮМЕ — Описана конструкция и характеристики жидкостного проточного адсорбционного микрокалориметра, основой которого является продажный микрокалориметр типа Кальвета ДАК 1-1 (СССР), соединенный с проточной системой, включающей насос, несколько комплектов теплообменников и адсорбционную ячейку. Величина минимально определяемого теплового эффекта составляет 1мкВ при скорости потока 30 $см^3$/час. Представлены и обсуждены результаты использования калориметра для изучения процессов адсорбции и десорбции водных растворов неионных (Тритон X—100) и анионных (стиров-фосфиновая кислота) поверхностно-аткивных веществ на поверхности α–Al_2O_3.