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Solvent activity meter based on a high sensitivity heat-flow microcalorimeter

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Abstract

A calorimetric solvent activity meter has been developed which allows fast and accurate measurements of the solvent activity as a function of solute concentration. By the use of the Gibbs–Duhem equation, the activity of the solute can be determined. The principle of operation is to measure the heat flow associated with the isothermal evaporation of solvent using a flow of dry nitrogen gas. The calorimeter consists of a precise thermostatic bath with a twin heat-conduction calorimetric unit. Special care has been taken to build the gas-handling system. The solvent activity is determined from the measured difference in thermal power for the evaporation from a solution and from the pure solvent. The solute concentration is changed by the stepwise addition of known amounts of concentrated solution to the calorimetric cell. The instrument has the potential of being both sensitive and precise and allows measurements to be made faster and more conveniently than by using the presently available methods. © 1997 Elsevier Science B.V.

Keywords: Activity measurements; Calorimetric solvent activity meter; Calorimetric vapour pressure meter; Solvent activity; Vapour pressure

1. Introduction

This paper examines the possibility of expanding the usefulness of calorimetry to include measurements of solvent activity. We present a method which uses a high-precision isothermal heat-flow calorimeter and which is suitable for solvent activity measurements on solutions containing a single volatile component. The method proposed has the potential of being rapid while still maintaining good accuracy and precision and, because of the computerised control systems used in the microcalorimeter, the procedures are straightforward and simple. At present, the performance of the gas-handling system is not optimised but the simplicity of the method allows those with an access to an isothermal heat-conduction calorimeter to readily improve our results. It would appear that the current, commercially available calorimetric instrumentation will, without too much effort, readily allow an increase in the accuracy attained in the present work by at least one order of magnitude. This note therefore serves the purpose of introducing the general principle of using a sensitive calorimeter to determine solvent activity.

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2. Measuring principle

The solvent activity measurements are carried out using a gas-flow system connected to an isothermal heat conduction calorimeter. A continuous flow of pure nitrogen gas is used to maintain a constant evaporation of solvent from the solution; moreover, because of the isothermal conditions which prevail in the calorimeter, the evaporation process is associated with a simultaneous heat flow from the surroundings. The heat-flow rate is directly proportional to the evaporation rate through the enthalpy of vaporization of the solvent. The evaporation rate is determined by the gas-flow rate and the vapour pressure of the solution. Thus, if a steady flow of carrier gas is maintained, the calorimetric signal will vary with the vapour pressure of the solution and the activity of the solvent can be determined from the decrease in the calorimetric signal for the solution relative to that of the pure solvent.

If the initially pure carrier gas is assumed to become fully saturated by solvent vapour during the evaporation process, the heat-flow rate $\mathrm{d}q/\mathrm{d}t$ needed to maintain isothermal conditions can be expressed according to:

$$\frac{\mathrm{d}q}{\mathrm{d}t} = \Delta_{\mathrm{vap}}H_{\mathrm{i}}J_{\mathrm{g}}\frac{p_{\mathrm{i}}}{p_{\mathrm{g}}} \tag{1}$$

where p_{i} is the vapour pressure of the solvent and p_{g} the partial pressure of the carrier gas. The molar flow rate of carrier gas is denoted as J_{g} and $\Delta_{\mathrm{vap}}H_{\mathrm{i}}$ as the enthalpy of vaporization of the solvent. The variation of $\Delta_{\mathrm{vap}}H_{\mathrm{i}}$ with composition can be calculated if the relative enthalpy of the solvent is known in the actual composition range. For the aqueous sodium chloride solutions used in this work $\Delta_{\mathrm{vap}}H_{\mathrm{i}}$ does not change significantly with composition [1]. The aim of the arrangements of the gas-flow system is to keep J_{g} constant, thus making the heat-flow rate directly proportional to the ratio between the solvent vapour pressure and the partial pressure of the carrier gas:

$$\frac{\mathrm{d}q}{\mathrm{d}t} \propto \frac{p_{\mathrm{i}}}{p_{\mathrm{g}}} \tag{2}$$

The vapour pressure of the solvent is evaluated as the quotient between the heat-flow rate associated with a test solution and the heat-flow rate using a reference solution with a well-known solvent activity.

$$\frac{\mathrm{d}q/\mathrm{d}t(\mathrm{sol})}{\mathrm{d}q/\mathrm{d}t(\mathrm{ref})} \equiv \frac{p_{\mathrm{i}}/(p_{\mathrm{tot}} - p_{\mathrm{i}})}{p_{\mathrm{i,ref}}/(p_{\mathrm{tot}} - p_{\mathrm{i,ref}})} = Q \tag{3}$$

The heat-flow rates for the test and reference solutions are denoted as $\mathrm{d}q/\mathrm{d}t(sol)$ and $\mathrm{d}q/\mathrm{d}t(\mathrm{ref})$, respectively. The solvent vapour pressure of the reference solution and the total pressure in the calorimeter are denoted as $p_{\mathrm{i,ref}}$ and p_{tot}, respectively. The partial pressure of the carrier gas is equal to the total pressure minus the actual solvent vapour pressure. Thus, at a constant p_{tot} the value of p_{g} will decrease with increasing p_{i}. The solvent vapour pressure in solutions of varying composition can be evaluated directly using Eq. (3). By noting that the vapour pressure of the solvent is equal to the solvent activity, a_{i}, multiplied by the vapour pressure of pure solvent, p_{i}^{*}, Eq. (3) can be written as,

$$a_{\mathrm{i}} = \frac{a_{\mathrm{i,ref}}Q\,p_{\mathrm{tot}}}{p_{\mathrm{tot}} - a_{\mathrm{i,ref}}\,p_{\mathrm{i}}^{*}\,(1 - Q)} \tag{4}$$

where Q denotes the result of Eq. (3) and $a_{\mathrm{i,ref}}$ the solvent activity of the reference solution. In the present study, we have used pure water as the reference solution.

3. Description of the apparatus

A schematic diagram of the instrumental assembly is shown in Fig. 1. The twin calorimeter is of the same design as calorimeter E in reference [2] but mounted with medium-sized thermocouple plates to give a sensitivity of $\approx 0.33\ \mathrm{VW}^{-1}$. It was mounted in a high-precision thermostated water bath. (An equivalent calorimetric system is available from Thermometric AB, Järfälla, Sweden.) The calorimeter vessel is made of high-grade stainless steel and has a volume of $20\ \mathrm{cm}^3$. In order to improve the resistance to corrosion when using aqueous solutions containing chloride ions, the interior of the cell was coated with Teflon. In the pneumatic system, pure nitrogen gas at a relatively high pressure, 1.5 MPa, flows from the supply gas cylinder via two pressure regulators (A) connected in series, through a flow restriction (B). The two serially connected regulators (model 8601 by Brooks Instrument, Veenerdaal, the Netherlands, followed by model 8311 by Porter Instrument, Hatfield,

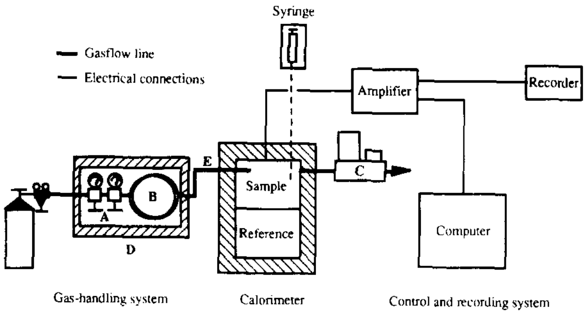

Fig. 1. Calorimetric solvent activity meter. The gas-handling system consists of the following major components: (A) – two pressure regulators connected in series; (B) – flow restricting capillary tube; (C) – back pressure regulator; (D) – air thermostat and (E) – valve.

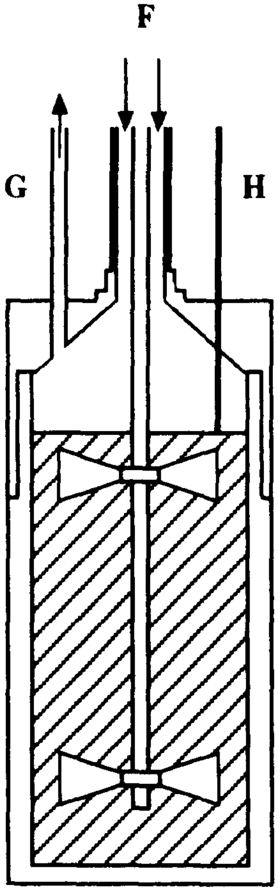

Fig. 2. The calorimetric cell with F for inlet of the pure carrier gas, G for outlet of the gas and vapour mixture and tube H used for guidance of syringe capillary.

PA, USA) act as a two-stage regulator, creating a stable pressure, 0.4 MPA, at the inlet of the flow restriction. The flow resistor consists of a 10 m long capillary tube with an inner diameter of 0.1 mm of fused silica. The outlet pressure is equal to the pressure in the calorimetric vessel and is controlled by an electronic back pressure regulator (C), (model 5067 A by Brooks Instrument, Veenerdaal, the Netherlands). Using this arrangement, continuous monitoring of p_{tot} was not necessary. Further, by controlling both the inlet and the outlet pressure of the capillary and by positioning all pneumatic components inside an air thermostatic bath (D), a steady flow of gas (J_g) is created. The flow rate of the carrier gas can be changed by adjusting the inlet pressure of the capillary tube. The pneumatic system can be readily disengaged from the calorimeter using a valve at point (E). The gas enters the calorimetric cell where it is mixed with solvent vapour. A simplified picture of the lower section of the cell with the sample compartment is shown in Fig. 2. The carrier gas is introduced through the shaft of the cell (F) and the evaporation takes place at the liquid/gas interface. Temperature gradients at the phase boundary and in the liquid are inhibited by stirring. The mixture of carrier gas and solvent vapour leaves through the stainless steel tube (G). A second tube (H) is used to guide the thin capillary tube fastened to a gas-tight Hamilton syringe used for the administration of stock solution. We found that it was necessary to keep the volume of the liquid constant during a measurement series so that tube (H) is also used for removing the surplus solution formed after injecting a volume of stock solution.

4. Experimental procedure

The calorimeter vessel has a total volume of 20 cm^3, but the volume of the liquid phase was kept at 18 cm^3. A typical experiment was initiated by charging the calorimeter vessel with a weighed amount of water slightly exceeding 18 cm^3. The surplus water was extracted using a syringe to which a thin capillary tube had been fastened, and then weighed. The stirring was started and the baseline recorded. The dry gas was then introduced and the pressure in the calorimeter was set using the back-pressure regulator to 150 kPa giving a volumetric gas-flow rate of ca. 0.9 $cm^3 min^{-1}$ as determined from volumetric measurements. The calorimetric signal from the evaporation process was recorded for at least two hours. The gas flow was then terminated and the pressure in the calorimeter was allowed to return to ambient pressure. From the difference between the evaporation signal and the baseline signal, the thermal power for the evaporation of pure solvent was measured. The experiment proceeded by injecting 0.75 cm^3 of pure water into the calorimetric cell, the exact amount determined by weighing. The surplus water was extracted, thus restoring the liquid surface to its original position. After recording the baseline, the gas flow was applied again. This procedure was repeated several times in order to fix the value of $dq/dt(\mathrm{ref})$. The experiment was continued by injecting 0.75 cm^3 of 6.062 mol kg^{-1} NaCl stock solution into the calorimeter vessel. (The stock solution was prepared from highly pure sodium chloride (Merk, Urtitersubtanz) that had been ground and dried at 110°C.) When the calorimeter signal returned to the baseline, the surplus solution was taken away and weighed. The heat-flow rate associated with the evaporation of solvent from the salt solution was then measured. Successive injections were made and the heat-flow rate of evaporation was measured after adjustment of the liquid volume for increasingly higher salt concentrations.

5. Result and discussion

Results from a typical series of experiments are summarised in Table 1. Heat-flow rates, dq/dt, registered for increasingly concentrated NaCl(aq) solutions of molality m are tabulated together with experimental values of water activity, $a(\mathrm{water})_{\mathrm{exp}}$, calculated using Eq. (4). Literature values of water activity are given in the last column [1]. As seen from the table, the deviations of the experimental from the reference values are relatively large. However, as we will show below, the limiting factor lies within the pneumatic system and the calorimeter measurements are capable of a much higher accuracy. The calorimeter was routinely calibrated using an electrical insertion heater and the baseline noise in the signal during these calibrations was better than ±0.1 μW. The calibration constant determined from the deflection of the signal for varying input of electrical power was reproducible to ±0.04% for powers varying between 200 and 1250 μW. Thus, systematic errors and random noise from the calorimetric system are not the origin of the discrepancies indicated in the table. Instead, the errors stem from the pneumatic system which was used. The repeatability of pressure regulator (C) used in these preliminary experiments do not allow the pressure of the carrier gas to be sufficiently controlled for optimal accuracy of the method. It is clear that further development of the gas-handling system will give an increased accuracy in the measurements. Another aspect which needs to be addressed is the fact that the carrier gas did not become fully saturated when passing through the calorimeter cell. The heat-flow rate was found to be ca. 94% of the heat-flow rate calculated using Eq. (1), thus indicating that the carrier gas did not become fully saturated. An efficiency value of less than unity indicates that additional parameters are influencing the heat-flow rate, e.g. the position of the liquid/gas interface in the cell. In spite of these limitations, the current experiments do show the feasibility of using a sensitivity calorimeter to monitor the evaporation of solvent, and thus to determine rapidly the solvent activity in solutions of non-volatile solutes. It is also possible, in principle, to apply the concept of the experiment to systems containing more than one volatile component, but the link between heat-flow rate and vaporization is less direct.

Table 1
Heat-flow rates and calculated values of water activity in NaCl(aq) solutions at 298.15 K

$m/(\mathrm{mol\ Kg^{-1}})$	$dq/dt/(\mu W)$	$a(\mathrm{water})_{\mathrm{exp}}$	$a(\mathrm{water})_{\mathrm{lit}}$ [a]
0.000	765.0 ± 0.6	—	1.000
0.206	762.5 ± 0.4	0.997	0.993
0.405	759.9 ± 0.3	0.993	0.987
0.610	751.6 ± 0.4	0.983	0.980
0.848	741.6 ± 0.5	0.970	0.972
1.079	733.1 ± 1.1	0.959	0.964
1.522	721.4 ± 0.6	0.945	0.949

[a] Literature values of water activity were taken from Ref. [1].

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