

The dissolution of propan-1-ol and dilution of 10 wt.% propan-1-ol solution in water as calibration and test reactions in solution calorimetry

Gerd Olofsson*, Dennis Berling, Natalia Markova, Mary Molund

Thermochemistry, Center for Chemistry and Chemical Engineering, Lund University, P.O. Box 124, S-221 00 Lund, Sweden

Received 5 August 1999; accepted 27 August 1999

Abstract

The enthalpy of solution of propan-1-ol in water is a convenient and reliable calibration and test reaction in titration microcalorimetry. The solution enthalpy varies significantly with concentration; hence, it is usually necessary to make extrapolations to infinitely dilute solution to determine $\Delta_{\text{sol}}H_{\text{m}}^{\infty}$ in order to derive a value suitable for comparison. We outline the thermodynamic formalism for the titration solution experiments and indicate an extrapolation procedure. An experimental example is given. Since less energetic test reactions are often desirable, the dilution of 10 wt.% propan-1-ol solution in water has been suggested as such a reaction. Thus, we have made dilution measurements in order to explore the accuracy of the reported enthalpy value and found that the uncertainty is, at present, at least a couple of percent. Some experimental considerations when performing titration microcalorimetric experiments are discussed. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Titration microcalorimetry; Calibration and test reactions; Solution enthalpy of propan-1-ol; Dilution enthalpy of propan-1-ol solutions; Thermodynamic formalism

1. Introduction

Titration calorimeters are usually calibrated electrically, but it is important to have available convenient chemical processes of the same type as those under study to check the function of the calorimeter in combination with the sample delivery system. Briggner and Wadsö [1] have suggested the use of the enthalpy of solution of *n*-propanol in water as a calibration and test reaction in titration microcalorimetry. The enthalpy of solution at infinite dilution,

$\Delta_{\text{sol}}H^{\infty}$, between 15 and 75°C is well known. However, the dissolution enthalpy varies significantly with concentration even at fairly high dilution, so it is usually necessary to extrapolate to infinitely dilute solution. In the experiments, incremental enthalpies of solution are measured which can be considered close approximations of the partial molar enthalpy changes in case the concentration change in each step is small. In this paper, we indicate the thermodynamic formalism for the titration solution experiments, suggest an extrapolation procedure to determine $\Delta_{\text{sol}}H^{\infty}$ and discuss some experimental considerations.

Often, the studied process gives much smaller heat effects than the solution of pure propanol; hence, it is

* Corresponding author. Fax: +46-46-222-4533.
E-mail address: gerd.olofsson@termk.lu.se (G. Olofsson).

of interest to have less energetic test reactions. Briggner and Wadsö [1] suggested the dilution in water of 10 wt.% aqueous propanol solution as such a test process. The dilution in water at 25°C gives <2% of the enthalpy change for the dissolution of the same amount of pure propanol.

2. Experimental

2.1. Material

High quality propan-1-ol is readily available from commercial sources. We have used the 'HiPerSolv' for HPLC quality from BDH, with a minimum assay of 99.8% according to the manufacturer, without further treatment. This sample gave the same value for $\Delta_{\text{sol}}H^\infty$ (within 0.1% uncertainty) as the dried and redistilled samples used in earlier studies at our laboratory [1,2]. Commercial samples with a stated purity >99.8% should be possible to use directly. Users should be aware that propan-1-ol is fairly hygroscopic, so the water content may need to be checked using, for instance, a Karl Fisher coulometer. If the sample is suspected to contain water it can be dried by letting it stand for a couple of hours with dust-free 4-Å molecular sieves. Propan-1-ol has a molar mass of 60.097, the normal boiling point is 97.20°C and the vapour pressure at 25.00°C is 20.85 mm Hg (27.8 mbar). The density is 0.80375 g cm⁻³ at 20.00°C and 0.79975 g cm⁻³ at 25.00°C [3]. The density of 10.00 wt.% propanol solution is 0.9840 g cm⁻³ at 20.00°C and 0.9821 g cm⁻³ at 25.00°C [4,5]. Densities of solutions of other compositions can be found in these same references.

2.2. Equipment

We have used, for our titration microcalorimetric measurements, twin heat-conduction calorimeters with 3 or 20 ml insertion vessels. The calorimeter with the smaller vessel was the 2277 TAM Thermal Activity Monitor system (Thermometric AB, Järfälla, Sweden). The properties of the microcalorimeters are discussed in Ref. [6], where they are identified as calorimeters A and E. The samples were injected through thin stainless-steel capillary tubes with 0.15 mm inner diameter, permanently fixed to the

gas-tight Hamilton syringes. The tubes reached directly into the calorimetric vessel and ended a few mm below the water surface. The injection capillary should not be wider than 0.15 mm in order to avoid significant diffusion effects [7]. The syringes were positioned in computer-controlled syringe drive units. The injection volumes were between 2 and 15 µl and the injection rate varied between 0.2 and 5 µl min⁻¹. The temperature of the syringes should be measured to within 0.1°C and preferably controlled as the temperature of the syringe determines the amount of sample injected. In a temperature interval of a couple of degrees around 25°C, the change of density with temperature of propan-1-ol is 8×10⁻⁴ g cm⁻³, that is 0.1% per degree. When performing measurements at temperatures above or below the temperature at which the syringe is kept (usually room temperature) the injection rate should be moderate to allow the injected liquid to equilibrate to the temperature in the calorimeter.

The volume of water in the calorimetric vessel was 2.7 and 19 cm³ in the experiments of dissolving propanol and 2.7 cm³ in the dilution of 10% propanol solution. Turbine stirrers made of high-grade stainless steel or Kel F were used with a stirring speed of at least 100 rpm. [8]. It is important that the stirrer induces a vertical movement in the liquid. Horizontal stirring resulting in liquid layers is easily achieved, particularly in the cylindrically shaped 3-ml vessel of the TAM microcalorimeter, but this does not give a homogenous solution. We have found it valuable to perform bench experiments using transparent plastic vessels to check the stirring efficiency. The flow pattern in the solution can then be examined by injecting coloured solutions. Experiments were made using both the fast titration method with 5 or 6 min interval between each injection and applying a dynamic correction [6,9] and the equilibrium procedure with 60 min between each injection. Blank experiments of water in water were made to check the performance of the system, whether it is an open system or not. The calorimetric vessels were calibrated by the use of electrical insertion heaters as described in Ref. [1].

We have also made batch reaction-solution experiments of dilution of 10 wt.% propanol solution using the 2225 SolCal Precision Solution Calorimeter (Thermometric AB, Järfälla, Sweden). It is a semi-adiabatic calorimeter, consisting of a 100-cm³ thin-walled glass

vessel fitted with a temperature sensing thermistor and an electrical heater. During measurements, the calorimeter unit is put into a stainless-steel container permanently mounted in the TAM high-precision thermostatted water bath. The propanol solution was placed in cylindrical glass ampoules (1 cm³ volume) that had thin end walls and narrow necks that were sealed under low flame and detached. The amount of solution was determined from the difference in weight between the sealed ampoule plus neck and the ampoule prior to filling. In the calorimetric experiments the ampoules were mounted in the combined stirrer and ampoule holder and broken over a sapphire tip in 105.0 cm³ of water. Electrical calibrations were made prior to the breaking of ampoules. Experiments of breaking ampoules filled with water in water gave an exothermic heat effect of (-0.0401 ± 0.0022) J ($n = 3$). The dilution experiments were corrected for this small effect. The temperature changes in the calorimetric experiments were evaluated using Dickinson's extrapolation method.

All calorimetric results refer to 25.00°C.

3. Thermodynamic description

Titration calorimetric experiments on the solution of propan-1-ol in water consist of consecutive additions of small amounts of propanol to the calorimetric vessel initially containing water. In the following the solute propanol is denoted B and the solvent A. Let us first consider a hypothetical experiment where a truly infinitesimal amount of solute is added to the calorimetric cell, that is, the amount injected is so small that the composition of the mixture does not change. Because enthalpy is a state function, we can analyse the experiment in terms of total enthalpy of the system before, and after, the injection. Before the injection the enthalpy content H^i of the system is:

$$H^i = n_A \bar{H}_A(x) + n_B \bar{H}_B(x) + dn_B H_B^* \quad (1)$$

where $\bar{H}_A(x)$ and $\bar{H}_B(x)$ indicate the partial molar enthalpies of solvent and solute at composition x . The term $dn_B H_B^*$ indicates the enthalpy content of the pure solute to be injected. After the injection the enthalpy content H^f has changed to:

$$H^f = n_A \bar{H}_A(x) + n_B \bar{H}_B(x) + dn_B \bar{H}_B(x) \quad (2)$$

For a truly differential addition of solute, the enthalpy change between the initial and the final state is:

$$dH = dn_B (\bar{H}_B(x) - H_B^*) \quad (3)$$

Expressed per mole of added B, this gives the partial molar enthalpy of solution:

$$\Delta_{\text{sol}} \bar{H}_B = (\bar{H}_B(x) - H_B^*) \quad (4)$$

The enthalpy change or heat measured during the injection is:

$$dQ = dn_B \Delta_{\text{sol}} \bar{H}_B \quad (5)$$

In a real experiment, a finite amount of solute has to be administered and the change in composition of the calorimetric liquid must be taken into account. The initial enthalpy content (Eq. (1)) must then be changed to:

$$H^i = n_A \bar{H}_A(x_i) + n_B \bar{H}_B(x_i) + \partial n_B H_B^* \quad (6)$$

where ' x_i ' is the composition in the calorimetric cell before the injection and ∂n_B represents a finite amount of solute. After the injection we have:

$$H^f = n_A \bar{H}_A(x_f) + n_B \bar{H}_B(x_f) + \partial n_B \bar{H}_B(x_f) \quad (7)$$

The difference in enthalpy is:

$$dH = n_A d\bar{H}_A + n_B d\bar{H}_B + \partial n_B (\bar{H}_B(x_i) + d\bar{H}_B - H_B^*) \quad (8)$$

where $d\bar{H}_A$ and $d\bar{H}_B$ denote the infinitesimal changes in the partial molar enthalpies due to the altered composition of the sample mixture. By applying the Gibbs–Duhem equation on the components present in the calorimetric vessel ($n_A d\bar{H}_A = -n_B d\bar{H}_B$), Eq. (8) is further simplified. The measured enthalpy change expressed per mole of added B is given by:

$$\Delta_{\text{sol}} \bar{H}(\text{exp}) = (\bar{H}_B(x_i) + d\bar{H}_B - H_B^*) \quad (9)$$

Due to the usually very small amount of solute injected during a single experiment, the quantity measured is very close to the true differential enthalpy of solution (Eq. (4)). We can simplify Eq. (9) by assuming that $\bar{H}_B(x_i) + d\bar{H}_B \approx \bar{H}_B(\bar{x})$, where $\bar{H}_B(\bar{x})$ is the partial molar enthalpy of B at the mean concentration \bar{x} . The measured differential enthalpy of solution can then be expressed as:

$$\Delta_{\text{sol}} \bar{H}(\text{exp}) = (\bar{H}_B(\bar{x}) - H_B^*) \quad (10)$$

It can be noted that if pure A is injected into the sample mixture, relation (10) is equally valid for the solvent.

The apparent molar enthalpy $H_{B,\phi}$ of a solute B in a solvent A is defined by the relation:

$$n_B H_{B,\phi} = H - n_A H_A^* \quad (11)$$

where H indicates the enthalpy content of the system. The (integral) solution enthalpy $\Delta_{\text{sol}}H_m$ can be expressed as

$$\Delta_{\text{sol}}H_m = H_{B,\phi} - H_B^* \quad (12)$$

which in the extreme of infinitely dilute solution can be written as:

$$\Delta_{\text{sol}}H_m^\infty = H_{B,\phi}^\infty - H_B^*$$

The variation of the apparent molar enthalpy $H_{B,\phi}$ (or the integral enthalpy of solution $\Delta_{\text{sol}}H_m$) with composition (in molality) is often expressed in terms of enthalpy interaction coefficients:

$$H_{B,\phi} = H_B^\infty + h_{xx}m_B + h_{xxx}m_B^2 + \dots \quad (13)$$

Values of h_{xx} and h_{xxx} for propanol in water at 15, 25 and 40°C are reported in Ref. [2].

In the titration calorimetric experiments, however, we measure differential enthalpies of solution (cf. Eq. (10)), and we need to express the composition dependence in terms of the apparent partial molar enthalpy $\bar{H}_{B,\phi}$. The relation between the integral and partial apparent molar enthalpies is:

$$\bar{H}_{B,\phi} = H_{B,\phi} + m_B \left(\frac{\partial H_{B,\phi}}{\partial m_B} \right) \quad (14)$$

This gives the following relationship for the composition dependence in terms of interaction coefficients:

$$\bar{H}_{B,\phi} = H_B^\infty + 2h_{xx}m_B + 3h_{xxx}m_B^2 \quad (15)$$

In order to derive the value for the enthalpy of solution at infinite dilution $\Delta_{\text{sol}}H_m^\infty$, the experimental values of $\Delta_{\text{sol}}H_{\text{obs}}$ are plotted against the mean molality in the injections. For dissolution of propan-1-ol in water h_{xx} is $(558 \pm 9) \text{ J kg mol}^{-2}$ [2,10], so we should expect a straight line with a slope of about $1100 \text{ J kg mol}^{-2}$ at 25°C at molalities, say below 0.25 mol kg^{-1} . The measurements by Franks, et al. [10] cover a higher molality range than those by Hallén, et al. [2] and, therefore, we believe that their value for the third interaction coefficient $h_{xxx} = (158 \pm 8) \text{ J mol}^{-1} (\text{mol kg}^{-1})^{-2}$ is more reliable.

The titration experiments of dilution of 10 wt.% propan-1-ol solution can be described in the same way, but by taking into account the fact that a mixture of propan-1-ol and water is injected.

4. Results and discussion

The enthalpy of solution of propan-1-ol in water has been measured over an extensive temperature range and reliable values of $\Delta_{\text{sol}}H_m^\infty$ are available between 5 and 75°C [1]. The value is $-10.16 \pm 0.02 \text{ kJ mol}^{-1}$ at 25.00°C, and values at other temperatures t (in °C) can be calculated from the following relation:

$$\Delta_{\text{sol}}H_m^\infty = -15.880 + 0.2450t - 6.474 \times 10^{-4}t^2 \quad (16)$$

A typical set of results in the form of a plot of observed enthalpy changes, ΔH_{obs} , against mean molality in the injection steps is shown in Fig. 1. The titration series consisted of 20 consecutive injections of $16.64 \mu\text{l}$ of propanol, starting with 18.46 g of water in the calorimetric vessel. A linear least-squares fit of the results gave $\Delta_{\text{sol}}H_m^\infty = -(10.164 \pm 0.007) \text{ kJ mol}^{-1}$ and a slope of $(1436 \pm 38) \text{ J kg mol}^{-2}$. The uncertainties are expressed as twice the standard deviation. It is our experience that the value for the slope can

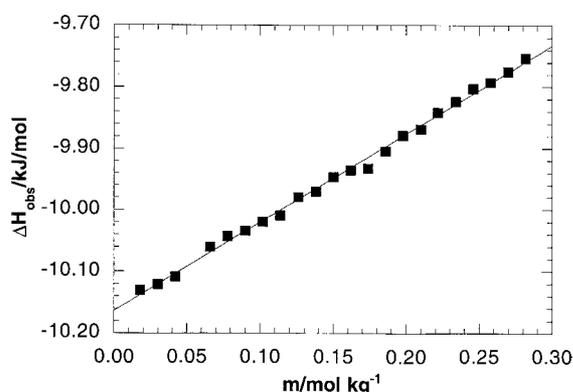


Fig. 1. Observed enthalpy changes ΔH_{obs} for consecutive additions of $16.64 \mu\text{l}$ of propan-1-ol at 25°C plotted against the mean molality of each injection step. The calorimeter vessel contained 18.64 g water at the beginning and the time between each injection was 60 min.

vary significantly from the expected value of $1116 \text{ J kg mol}^{-2}$ (see Eq. (15)), but still the value of $\Delta_{\text{sol}}H_{\text{m}}^{\infty}$ will be as expected.

If a large volume of water is used, so that the final concentration is below 1.0 g dm^{-3} ($0.017 \text{ mol kg}^{-1}$), the observed $\Delta_{\text{sol}}H_{\text{m}}$ will differ by less than 0.02 kJ mol^{-1} from $\Delta_{\text{sol}}H_{\text{m}}^{\infty}$ and the concentration dependence can be ignored.

We find the solution of propanol in water to be a convenient and reliable test reaction that gives values accurate to better than 0.3%. It has the disadvantage that the heat effect may be much larger than that from the processes to be studied because an injection volume of $2 \mu\text{l}$, which is the lower limit [7], will give 0.27 J . Briggner and Wadsö [1] suggested the dilution of 10 wt.% propan-1-ol as a test reaction giving a much lower heat effect. They reported results from measurements of dilution of $2 \mu\text{l}$ propanol solution in 0.9 g of water at 25°C . This is rather limited conditions and, in order to see if the reported values for the interaction coefficients h_{xx} and h_{xxx} give reliable values for the dilution enthalpies of propanol solutions, we have made batch reaction-solution experiments using the 2225 SolCal precision solution calorimeter. Two solutions containing 9.998 and 9.999 wt.% propan-1-ol, respectively, were prepared by weighing. The amount of solution in the ampoules varied between 0.82 and 0.97 g. Seven experiments on the two propanol solutions gave $\Delta_{\text{dil}}H_{\text{m}} = (-1.620 \pm 0.012) \text{ J mol}^{-1}$ (the uncertainty expressed as twice the standard deviation of the mean). The molality of the sample solution was $1.849 \text{ mol kg}^{-1}$ and the propanol content in the vessel after dilution was $0.013\text{--}0.015 \text{ mol kg}^{-1}$. The experimental value corrected for dilution to infinitely dilute solution is $\Delta_{\text{dil}}H_{\text{m}}^{\infty} = (-1.628 \pm 0.012) \text{ kJ mol}^{-1}$. Using the values for h_{xx} and h_{xxx} given above, we calculate $\Delta_{\text{dil}}H_{\text{m}}^{\infty} = (-1.572 \pm 0.044) \text{ kJ mol}^{-1}$. The difference between the experimental and calculated values is equal to the sum of the uncertainty limits and, thus, not significant.

As a result of their measurements, Briggner and Wadsö [1] reported that the enthalpy of dilution of 1 mg aqueous 10.000 wt.% propan-1-ol is $(2.570 \pm 0.015) \text{ mJ}$, provided that the final propanol content is below 1.4 mg per ml of water. This corresponds to $\Delta_{\text{dil}}H_{\text{m}} = (-1.544 \pm 0.009) \text{ kJ mol}^{-1}$. However, the variation of $\Delta_{\text{dil}}H_{\text{m}}$ with the final concentration is

small, but not insignificant, amounting to 26 J mol^{-1} at a propanol content of 1.4 mg cm^{-3} ($0.023 \text{ mol kg}^{-1}$). In view of this, the given uncertainty limit appears too narrow. Assuming the reported value to refer to the mean concentration in the given range, the value at infinite dilution $\Delta_{\text{dil}}H_{\text{m}}^{\infty} = (-1.557 \pm 0.020) \text{ kJ mol}^{-1}$ which is fully consistent with the calculated value. However, considering the narrower uncertainty limits of the experimental values, it is significantly lower than the batch calorimetric value. We made three titration calorimetric series of dilution of 10.00 wt.% propanol solution; starting with 2.74 g of water in the calorimetric vessel and these gave $\Delta_{\text{dil}}H_{\text{m}} = (-1.591 \pm 0.010) \text{ kJ mol}^{-1}$. The uncertainty limits are expressed as twice the standard deviation of the weighted mean. Each series consisted of between five and seven injections of 4.992 or $2.496 \mu\text{l}$ and the final concentration of propanol was $<0.015 \text{ mol kg}^{-1}$. The scatter in the individual values masked the effect of increasing propanol concentration amounting to 17 J mol^{-1} at the upper limit. This latter value is between the batch calorimetric value and the value reported by Briggner and Wadsö [1]. It is clear that further studies are needed in order to reduce the uncertainty in the value for the dilution enthalpy of 10 wt.% propanol solution which, at present, is at least a couple of percent. In general, enthalpies of dilution of aqueous propanol solutions with initial and final molalities below 2 mol kg^{-1} can be calculated using the values of the $h_{\text{xx}} = 558 \pm 9 \text{ J kg mol}^{-2}$ and $h_{\text{xxx}} = (158 \pm 8) \text{ mol}^{-1} (\text{mol kg}^{-1})^{-2}$. However, the uncertainty in the derived values will be larger than the reproducibility of measurements attainable using modern microcalorimeters. It is highly desirable to improve the accuracy of the interaction coefficients so that they can be used to calculate values of dilution enthalpies between varying propanol concentrations and make possible the choice of the magnitude of the heat effect of the test reaction.

5. Conclusions

The enthalpy of solution of *n*-propanol in water is a convenient and reliable calibration and test reaction in titration microcalorimetry at temperatures between 15 and 75°C . However, it is usually necessary to determine $\Delta_{\text{sol}}H_{\text{m}}^{\infty}$ by extrapolation to infinitely dilute

solution in order to derive a value suitable for comparison.

The dissolution of pure propanol in water is a fairly exothermic process, and often it is desirable to have less energetic test reactions. The dilution of aqueous propanol solutions offers such a possibility. The enthalpy of dilution $\Delta_{\text{dil}}H$ of aqueous propanol solution with molality below 2 mol kg^{-1} can be described by enthalpic interaction coefficients. Values of $\Delta_{\text{dil}}H_{\text{m}}$ can be calculated using the values $h_{\text{xx}} = (558 \pm 9) \text{ J kg mol}^{-1}$ [2,10] and $h_{\text{xxx}} = (158 \pm 8) \text{ J mol}^{-1} (\text{mol kg}^{-1})^{-2}$ [10]. For instance, the dilution of 10 wt.% solution to infinite dilution will give $\Delta_{\text{dil}}H_{\text{m}}^{\infty} = (-1572 \pm 44) \text{ J mol}^{-1}$. However, the uncertainty in the calculated value is larger than the reproducibility achieved when using modern microcalorimeters which, for this process, may be of the order of 10 J mol^{-1} . Therefore, it is desirable to improve the accuracy of the interaction coefficients so that reliable values of $\Delta_{\text{dil}}H$ can be calculated. This would make it possible to design test reactions with a preselected enthalpy change.

References

- [1] L.-E. Briggner, I. Wadsö, J. Biochem. Biophys. Methods 22 (1991) 101–118.
- [2] D. Hallén, S.-O. Nilsson, W. Rothschild, I. Wadsö, J. Chem. Thermodyn. 18 (1986) 429–442.
- [3] J.A. Riddick, W.B. Bunger, Organic Solvents, Techniques of Chemistry, vol. II, 3rd Edition, Wiley–Interscience, New York, 1970.
- [4] K. Schäfer (Ed.), Landolt–Börnstein: Numerical Data and Functional Relationships in Science and Technology, New Series, Group IV, vol. 1, Part b, Densities of Binary Aqueous Systems and Heat Capacities of Liquid Systems, Springer, Berlin, 1977.
- [5] C. Dethlefsen, P.G. Sørensen, A. Hvidt, Solution Chem. 13 (1984) 191–194.
- [6] P. Bäckman, M. Bastos, D. Hallén, P. Lönnbro, I. Wadsö, J. Biochem. Biophys. Methods 28 (1994) 85–100.
- [7] S.-O. Nilsson, I. Wadsö, J. Chem. Thermodyn. 16 (1984) 317–330.
- [8] M. Görman Nordmark, J. Laynez, A. Schön, J. Suurkuusk, I. Wadsö, J. Biochem. Biophys. Methods 10 (1984) 187–202.
- [9] M. Bastos, S. Hägg, P. Lönnbro, I. Wadsö, J. Biochem. Biophys. Methods 23 (1991) 255–258.
- [10] F. Franks, M. Pedley, D. Reid, J. Chem. Soc., Faraday Trans. 1 72 (1976) 359–367.