Use of Titration Calorimetry to Determine Excess Enthalpy of Binary Mixtures

Introduction
Excess enthalpy of mixtures, $\Delta H^E$, are usually determined by measuring the power released or absorbed when both components flow and mix in the mixing chamber. A number of experiments at different flow ratios of the two components to properly cover the mole fraction range to be investigated are carried out. This method offers these advantages: 1) it provides direct measurements of $\Delta H^E$; 2) it requires a fairly short time for carrying out a single measure; 3) no vapor space is in the mixing cell, so uncertainties due to vapor-liquid equilibration are avoided. Nevertheless, this technique is difficult to apply when the two components, though being thermodynamically mixable, mix slowly either because of difference in their density or because their viscosity is high, or the system is near a critical solution temperature. Also when measurements only at the two limits of the mole fraction range can be carried out, either because of a miscibility gap or because the availability of the chemicals is not enough to explore the whole mole fraction interval, the method is inadequate due to the small values of the power of mixing to be measured.

In this note we propose and test a calorimetric technique and a procedure which allow to obtain $\Delta H^E$ for mixtures which are affected by one or more of the above mentioned difficulties. The method, described in detail in a recent paper of ours [1], is based on the determination of the partial molar enthalpy $\overline{\Delta H}_i$ of each component by adding a small quantity of it to mixtures of known composition. $\overline{\Delta H}_i$ values are then treated with a least square routine to obtain the parameters of the model adopted to describe $\overline{\Delta H}_i$ and $\Delta H^E$. This method is in principle the same as those proposed in the past by others [2-5], but their calorimetric apparatuses present some disadvantages with respect to ours.

To test the method thoroughly, we have chosen mixtures having different features: perfluorohexane + hexane, because of its very slow mixing; water + 1,4-dioxane, which shows a S-shaped $\Delta H^E$ curve; ethanol + cyclohexane, a strongly asymmetric mixture; tetrachloromethane + benzene, to check the accuracy of predicting $\Delta H^E$ in the central region of composition by extrapolating from data obtained only in the mole fraction ranges 0-0.1 and 0.9-1. In all cases, the $\Delta H^E$ results have been found thermodynamically consistent and in excellent agreement with the literature data obtained from direct measurements.

Instrument configuration
The calorimeter is composed of the Thermal Activity Monitor Mod. 2277 (TAM) and of two Microcalorimetric Units with stainless steel ampoules of 20 and 4 cm³ capacity respectively. The cells are equipped with a stirrer and allow the insertion through a hole of a capillary tube connected to the dispensing unit.

References
This unit is composed of a Lund Syringe Pump Mod. 6120 and a number of Hamilton gas-tight syringes of capacity ranging from 100.0 to 1000 µl. The apparatus allows to make accurate injections starting from a minimum of 1 µl, and to measure accurate heat effects as low as 0.1 J. By an interfaced computer, calibrations, injections, acquisition of the signal and calculations of the heat involved in each addition are automatically carried out.

**Procedure and data treatment**

The ampoule is filled with a weighed amount of one component or of a stock mixture of them in such a quantity as to leave no more than 1 cm³ of vapour space for the ampoule of 20 cm³ capacity, or in general no more than 5% of the ampoule capacity. After the thermostating of the dispensing unit and the thermal and vapour-liquid equilibration (VLE) of the ampoule are reached, a series of programmed injections of the stock mixture of them is carried out and the heat effect involved in each addition is measured. The quantity of the mixture is calculated from the gas law using literature values of the the vapour pressures and activity coefficients. The calorimetric technique here described has proved capable to: 1) successfully replace the flow-mix technique for measuring $H^E$ of mixtures; 2) obtain, in addition to $H^E$, precise enthalpies of solution at infinite dilution; 3) overcome the difficulties often encountered in the mix-flow calorimetry: slowness of the mixing process, presence of a mixing gap in the central mole fraction range, and availability of only small sample quantities. On the other hand, the main drawback of the present technique is the presence of the vapour space, s0 that this technique can safely be applied when the volatility of the compounds is low and the VLE data of the mixture are available.

In the conditions chosen for carrying out the experiments, 3000 µW full scale sensitivity, and injections varying from 1 to 200 µl, $Q$ ranged from 0.15 to 2 J, with a reproducibility and precision of reading better than 1%. This result is compatible with the accuracy of the dispensing equipment, which by calibration with water was found around 0.5%. These features are in agreement with the values of the standard deviation of $Q$, which for our four systems ranges from 0.01 to 0.02 J.

In Fig.s 1 and 2, the experimental values $\overline{H}_{ij,exp} = (Q - Q_{vle})/n_{j,d}$ of enthalpies, which are an average over the mole fraction interval in between the starting and the end of the corresponding injections, $n_{j,d}$, are compared with the values calculated as explained above for two of the four systems studied. The comparison with literature of the $H^E$ curves for the other two systems can be seen in Fig.s 3,4. The agreement between experimental and calculated $\overline{H}_{ij}$ shows that the whole procedure is not biased by systematic errors, and the agreement with literature $H^E$ curves provides validation of the method.

**Conclusions**

The calorimetric technique here described is based on the following points:

1. Successfully replace the flow-mix technique for measuring $H^E$ of mixtures.
2. Obtain, in addition to $H^E$, precise enthalpies of solution at infinite dilution.
3. Overcome the difficulties often encountered in the mix-flow calorimetry: slowness of the mixing process, presence of a mixing gap in the central mole fraction range, and availability of only small sample quantities.

In all cases, the main drawback of the present technique is the presence of the vapour space, so that this technique can safely be applied when the volatility of the compounds is low and the VLE data of the mixture are available.

**Results and Discussion**

In the conditions chosen for carrying out the experiments, 3000 µW full scale sensitivity, and injections varying from 1 to 200 µl, $Q$ ranged from 0.15 to 2 J, with a reproducibility and precision of reading better than 1%. This result is compatible with the accuracy of the dispensing equipment, which by calibration with water was found around 0.5%. These features are in agreement with the values of the standard deviation of $Q$, which for our four systems ranges from 0.01 to 0.02 J. In Fig.s 1 and 2, the experimental values $\overline{H}_{ij,exp} = (Q - Q_{vle})/n_{j,d}$ of enthalpies, which are an average over the mole fraction interval in between the starting and the end of the corresponding injections, $n_{j,d}$, are compared with the values calculated as explained above for two of the four systems studied. The comparison with literature of the $H^E$ curves for the other two systems can be seen in Fig.s 3,4. The agreement between experimental and calculated $\overline{H}_{ij}$ shows that the whole procedure is not biased by systematic errors, and the agreement with literature $H^E$ curves provides validation of the method.
Fig. 1. Plot of the partial molar enthalpies $\overline{H}_j$ of the components vs $x_i$ of the mixture ethanol(1) + cyclohexane(2) at 298.15K. (O) experimental; (---) calculated by fitting $Q$.

Fig. 2. Partial molar enthalpies $\overline{H}_j$ of the components and excess enthalpies $H^E$ vs $x_1$ for perfluorohexane(1) + hexane(2) (a slowly mixing system) at 298.15K. (O) experimental; (---) calculated by fitting $Q$.

Fig. 3. Comparison with literature of the $\overline{H}^E$ curve of dioxane(1)+water(2) at 298.15K: (---), this work; (---), (---), (---), different literature data from Ref. [6].

Fig. 4. Comparison with literature of the upper part (central mole fraction range, extrapolated) of the $H^E$ curve for tetrachloromethane(1) + benzene (2) at 298.15K: (---), this work (only measurements at $x_1<0.1$ and $x_1>0.9$ were carried out); (---), Ref [4]; (---), Ref [6].
This unit is composed of a Lund Syringe Pump Mod. 6120 and a number of Hamilton gas-tight syringes of capacity ranging from 100.0 to 1000 µl. The apparatus allows to make accurate injections starting from a minimum of 1 µl, and to measure accurate heat effects as low as 0.1 J. By an interfaced computer, calibrations, injections, acquisition of the signal and calculations of the heat involved in each addition are automatically carried out.

**Procedure and data treatment**

The ampoule is filled with a weighed amount of one component or of a stock mixture of them in such a quantity as to leave no more than 1 cm³ of vapour space for the ampoule of 20 cm³ capacity, or in general no more than 5% of the ampoule capacity. After the thermostating of the dispensing unit and the thermal and vapour-liquid equilibration (VLE) of the ampoule are reached, a series of programmed injections of the components (or even of mixtures of them) is carried out and the heat effect involved in each addition is measured. The vapour space in the ampoule, necessary to allow injections, makes the quantity \( Q \) a complex one: it depends not only on the \( H_j \) in liquid and vapour phases, but also on vaporization enthalpies, \( \Delta H^v \), and on the vapour pressures and activity coefficients of components which govern the VLE. This dependence can be expressed as follows:

\[
Q = \sum_{j,i} n_{j,i} H_{j,i,j} + \sum_{j} n_{j,i} (H_{j,i,j} - H_{j,i,f}) + Q_{\text{cal}} \tag{1}
\]

where \( H_{j,i,j} \) is the partial molar enthalpy of component \( j \) in the cell before the addition \((l=i)\), or after the addition but before the new VLE \((l=j)\), \( H_{j,i,f} \) is the partial molar enthalpy of component \( j \) in the dispensing unit, and \( n_{j,k} \) are the moles of component \( j \) in the ampoule \((k=c)\) or those added from the dispenser \((k=d)\). \( Q_{\text{cal}} \), the heat involved in the VLE occurring after the injection, can be calculated according to:

\[
Q_{\text{cal}} = \sum_{j} \left[ \Delta n_{j,i} \left( \Delta H^v_j - 2H_{j,i,f} - H_{j,i,j} \right) + \frac{1}{2} \left( n_{j,i} + n_{d,i} \right) \left( H_{j,i,f} - H_{j,i,j} \right) \right] \\
- n_{j,d} \left( H_{j,i,f} - H_{j,i,j} \right) \
\]

where \( n_{j,v} \) and \( \Delta n_{j,v} \) are the initial moles and the change of moles in the vapour phase due to the VLE after addition of component \( j \), respectively; subscripts indicate the final composition in both phases before \((f^*)\) or after \((f^*)\) equilibration. Vapour phase composition is calculated from the gas law using literature values of the the vapour pressures and activity coefficients. \( Q_{\text{cal}} \) calculated values were always less than 2% of \( Q \), except for perfluorohexane+hexane (maximum 8%).

By assuming a model equation the excess enthalpy, such as \( f.e. \) the Redlich-Kister equation, all values of the partial molar enthalpies in Eqs.1-2 can be calculated by differentiation using trial values of its parameters. The final values of the parameters (and hence the \( H^E \) and \( H^F \)) curves are determined by minimizing the objective function \( OF \) by a least-squares routine:

\[
OF = \sum (Q_{\text{exp}} - Q_{\text{calc}})^2 \tag{3}
\]

where \( Q_{\text{exp}} \) is the measured quantity and \( Q_{\text{calc}} \) is obtained through Eqs.(1,2).

**Results and Discussion**

In the conditions chosen for carrying out the experiments, 3000 µW full scale sensitivity, and injections varying from 1 to 200 µl, \( Q \) ranged from 0.15 to 2 J, with a reproducibility and precision of reading better than 1%. This result is compatible with the accuracy of the dispensing equipment, which by calibration with water was found around 0.5%. These features are in agreement with the values of the standard deviation of \( Q \), which for our four systems ranges from 0.01 to 0.02 J. In Fig.s 1 and 2, the experimental values \( H_{\text{exp}} = (Q - Q_{\text{cal}})/n_{j,d} \) enthalpies, \( H^E \), which are an average over the mole fraction interval in between the starting and the end of the corresponding injections, \( n_{j,d} \), are compared with the values calculated as explained above for two of the four systems studied. The comparison with literature of the \( H^E \) curves for the other two systems can be seen in Fig.s 3,4. The agreement between experimental and calculated \( H^E \) shows that the whole procedure is not biased by systematic errors, and the agreement with literature \( H^F \) curves provides validation of the method.

**Conclusions**

The calorimetric technique here described has proved capable to: 1) successfully replace the flow-mix technique for measuring \( H^F \) of mixtures; 2) obtain, in addition to \( H^E \), precise enthalpies of solution at infinite dilution; 3) overcome the difficulties often encountered in the mix-flow calorimetry: slowness of the mixing process, presence of a mixing gap in the central mole fraction range, and availability of only small sample quantities. On the other hand, the main drawback of the present technique is the presence of the vapour space, so that this technique can safely be applied when the volatility of the compounds is low and the VLE data of the mixture are available.
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