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Determination of enthalpic pairwise interaction parameters using a titration calorimeter: urea, monoethylurea and hexamethylenetetramine in aqueous solutions at 298 K

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Abstract

A rapid and convenient method is described for estimating enthalpic pairwise interaction parameters h_{jj} for solute j in aqueous solution using a titration calorimeter. Good agreement is obtained with published estimates for h_{jj} in the cases of urea, monoethylurea and hexamethylenetetramine.

INTRODUCTION

A powerful thermodynamic description of the properties of dilute aqueous solutions containing neutral solutes is based [1–5] on a formulation for the excess Gibbs energies G^E of a solution containing 1 kg of solvent and m_j moles of solute:

$$G^E = g_{ij}(m_j/m^0)^2 + g_{jjj}(m_j/m^0)^2 + \ldots \quad (1)$$

where g_{ij} and g_{jjj} are pairwise and triplet solute–solute interaction parameters respectively and $m^0 = 1\ \text{mol kg}^{-1}$. The term m^0 tidies up the units such that G^E, g_{jj} and g_{jjj} are expressed in J kg^{-1} where kg refers to the mass of solvent. Appropriate differentiation of eqn. (1) yields the corresponding equations for excess volumes and excess enthalpies. In the latter case, a direct link is formed with the apparent molar enthalpies of solute j. For a given aqueous solution in 1 kg of solvent the enthalpy $H(\text{aq})$ is given by eqn. (2) where M_1 is the molar mass of water and $H_1^*(\text{l})$ is the molar enthalpy of pure liquid water at the same temperature and pressure

$$H(\text{aq}) = (1/M_1)H_1^*(\text{l}) + m_j\phi(H_j) \quad (2)$$

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where $\phi(H_j)$ is the apparent molar enthalpy of solute j in the solution. In effect, we have loaded all the non-ideal properties of the solution onto the $\phi(H_j)$ quantity. For the corresponding ideal solution

$$H(\text{aq; id}) = (1/M_1)H_1^* (\text{l}) + m_j\phi^\infty(H_j) \quad (3)$$

where

$$\lim_{m_j \to 0} \phi(H_j) = \phi^\infty(H_j)$$

Then

$$H^E = H(\text{aq}) - H(\text{aq; id}) = m_j[\phi(H_j) - \phi^\infty(H_j)] = m_j\phi(L_j) \quad (4)$$

By definition $\phi(L_j)$ is the relative apparent molar enthalpy of solute j (expressed in J mol^{-1}) in solution. The Gibbs–Helmholtz equation in conjunction with eqns (1) and (4) yields

$$m_j\phi(L_j) = h_{ij}(m_j/m^0)^2 + h_{jj}(m_j/m^0)^3 \quad (5)$$

The pairwise enthalpic parameter h_{ij} (expressed in J kg^{-1}) is an important quantity for dilute aqueous solutions because its sign and magnitude are determined by interactions between Gurney hydration cospheres [6] around solute molecules. Current debates about the nature of interactions in aqueous solutions, particularly hydrophobic interactions [7, 8], highlight the importance of these parameters in building models for aqueous solutions. Hence a rapid and convenient method for their determination would have merit.

We show how this need can be satisfied by a titration microcalorimeter (Microcal) which was originally designed to probe the thermodynamics of binding of substrates to enzymes [9]. A consequence of the design of this calorimeter is that only small amounts of materials are required. We confirm the reliability of the method using a comparison between parameters measured using this calorimeter and those previously reported in the literature for urea [1, 10], monoethylurea (MEU) [11] and hexamethylenetetramine (HMT) [12]. These three solutes were chosen because they span the range where, in conventional terms [5], urea is a water structure breaker and HMT is a hydrophobic structure former.

EXPERIMENTAL

Calorimeter

The heart of the Omega titration calorimeter (Microcal, Northampton, MA, USA) is an inert alloy (Hastelloy) sample cell, volume 1.4115 cm^3, held within an evacuated (adiabatic) jacket. The temperatures of the sample cell, a similar reference cell (also inside the jacket) and the jacket itself are continuously monitored and controlled.

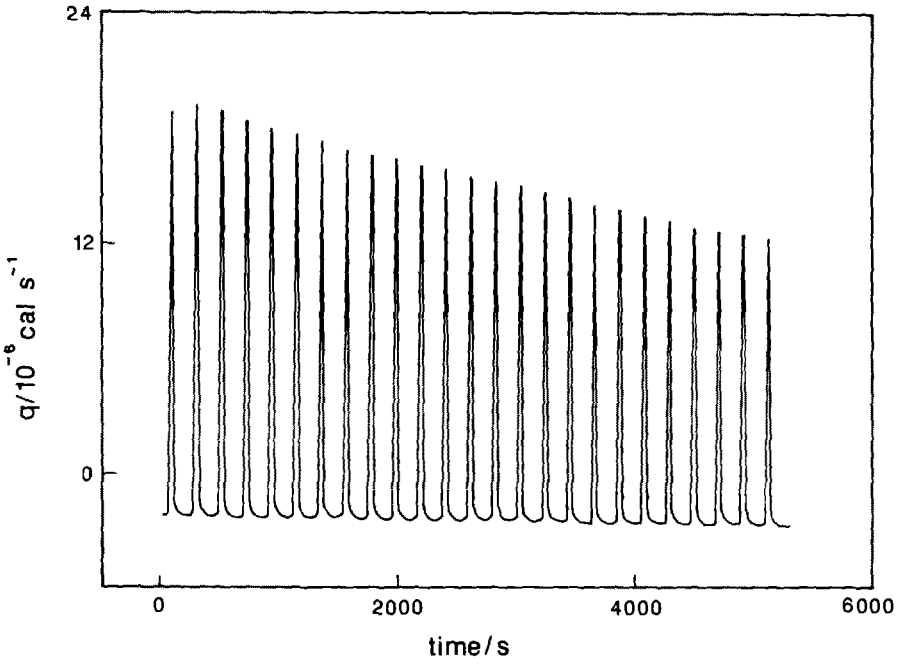

Fig. 1. Rate of heating in rebalancing temperatures of sample and reference cells following a series of injections as a function of time for urea(aq; 0.828 mol kg^{-1}); here the injection process is endothermic.

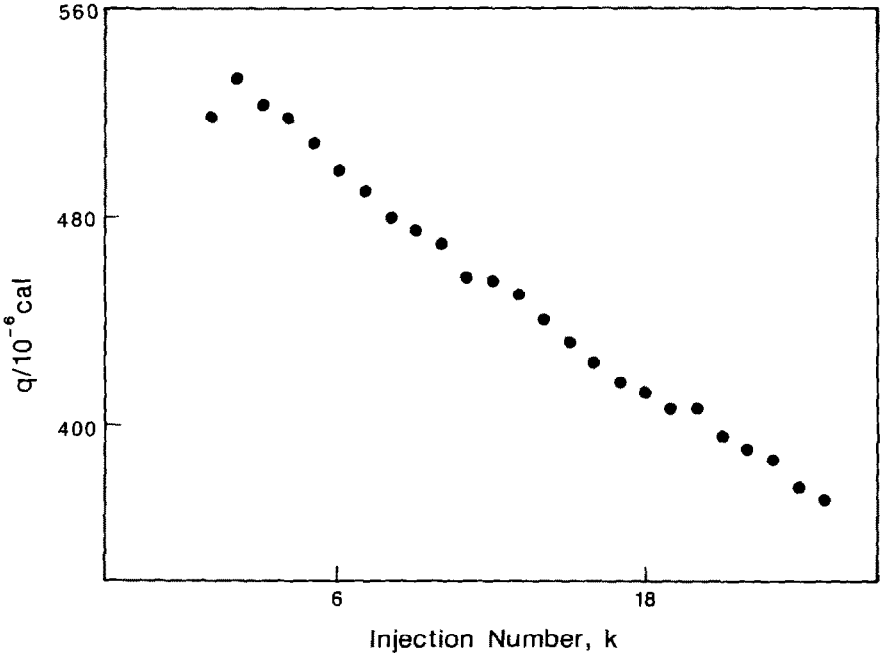

Fig. 2. Integrated heat pulses as a function of injection number for urea(aq; 0.828 mol kg^{-1}).

A syringe holding an aqueous solution is mounted directly above the sample cell. An electric motor is arranged to inject small volumes (typically 10^{-2} cm^3) of this solution into the sample cell in a series of controlled pulses. In the experiments reported here the reference cell contained water. At the start of each experiment, the sample cell also contained water. Therefore, gradually, during the process of making k injections from the syringe, the composition of the sample cell changed. The output from the calorimeter control system comprised the rate of heating required to rebalance the temperatures of sample and reference cells as a function of time following each pulse, see Fig. 1. The ORIGIN software used these data to produce a plot recording heat $q(k)$ as a function of injection number k (Fig. 2).

Analysis of data

Key parts of the sample cell and injector are shown diagrammatically in Fig. 3 which highlights a complexity not discussed so far. Each injection of volume V^i of solution produces an overflow of an equal volume of solution out of the sample cell. Figure 3 also shows how (a) the syringe injects fresh solution near the bottom of the sample cell, and (b) part of the old mixed solution overflows from this cell. In developing the analysis outlined below we treat the processes of injection and overflow as separate stages.

In the overflow stage, a volume V^i of solution is lost from the sample cell leaving volume $(V^R - V^i)$ of solution. A volume V^i of solution was then added from the syringe. The two solutions mix completely to form a final solution volume V^R. Two further assumptions were made.

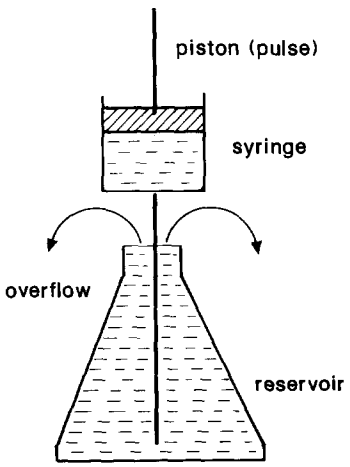

Fig. 3. Diagrammatic representation of injection and overflow accompanying a pulse of fresh solution into the reservoir.

In practice the calorimeter was so sensitive that the solutions in the injector and sample cell could differ only slightly in composition. Hence, we assumed that the excess volumes of mixing of the two solutions are zero for each injection. A further assumption follows therefrom. We assume that the densities of the solutions in the sample cell and injector are the same. For example, in the series of experiments reported below we assumed that the densities of the three solutions, urea(aq), MEU(aq) and HMT(aq) equal that of water at the same temperature and pressure.

At the outset of a given experiment, the sample cell volume V^R contained water. Each injection forces into the sample cell a volume V^i of a solution, molality m_j^i of solute j.

Syringe

The solution in the syringe has molality m_j^i. A volume V^i of solution having molality m_j^i (and concentration c_j^i) was injected into the sample cell. Then, in volume V^i there are $V^i c_j^i$ moles of solute j. If the solution in the injector is dilute, then $n_j^i = V^i m_j^i \rho_1^*$ (l), where ρ_1^* (l) is the density of the solvent. The number of moles of solvent injected into the sample cell is n_1^i. Hence, for each injection we increase the enthalpy of the sample cell by $H[V^i]$, where

$$H[V^i] = n_1^i H_1^*(l) + n_j^i \phi^i(H_j; m_j^i) \tag{6}$$

At the start of the experiment, we designated the system as in the zero state. The number of moles of water in the sample cell is n_1^{RZ}, the volume is V^R and enthalpy H^{RZ}, where

$$H^{RZ}(V^R) = n_1^{RZ} H_1^*(l) \tag{7}$$

Because volume V^i of solution is about to be injected into the sample cell, volume V^i must overflow from the sample cell. This volume contains n_1^{A1} moles of water where $n_1^{A1} = \rho_1^* V^i / M_1$. Thus the enthalpy of liquid lost from the sample cell by the first overflow is given by

$$H(\text{overflow A1}) = n_1^{A1} H_1^*(l) \tag{8}$$

Having lost this solvent, the enthalpy of the liquid in the sample cell is given by

$$H^R(n_1^{RZ} \text{ moles of water}; V^R) - H^{A1}(n_1^{A1} \text{ moles of water}; V^i) = n_1^{RZ} H_1^*(l) - n_1^{A1} H_1^*(l) \tag{9}$$

Following the first injection the volume of solution in the cell is again V^R where the amount of water is $n_1^{RZ} - n_1^{A1} + n_1^i$ and the amount of solute is n_j^i. The enthalpy of the solution now in the sample cell is given by

$$H^R(I1) = (n_1^{RZ} - n_1^{A1} + n_1^i) H_1^*(l) + n_j^i \phi^i(H_j) \tag{10}$$

Therefore the change in enthalpy accompanying injection I1, $\Delta H(\mathrm{I1})$, is given by H (solution now in sample cell) minus H (solution which was in sample cell after overflow 1) minus H (injection)

$$\Delta H(\mathrm{I1}) = (n_1^{\mathrm{RZ}} - n_1^{\mathrm{A1}} + n_1^{\mathrm{i}}) + H_1^*(\mathrm{l}) + n_j^{\mathrm{i}}\phi(H_j; \mathrm{I1}) - [(n_1^{\mathrm{RZ}} - n_1^{\mathrm{A1}})H_1^*(\mathrm{l})] - [n_j^{\mathrm{i}}H_1^*(\mathrm{l}) + n_j^{\mathrm{i}}\phi^{\mathrm{i}}(H_j)] \quad (11)$$

or

$$\Delta H(\mathrm{I1}) = n_j^{\mathrm{i}}[\phi(H_j; \mathrm{I1}) - \phi^{\mathrm{i}}(H_j)] \quad (12)$$

Hence

$$\Delta H(\mathrm{I1}) = n_j^{\mathrm{i}}[\phi(L_j; \mathrm{I1}) - \phi^{\mathrm{i}}(L_j)] \quad (13)$$

No solute was lost because prior to the injection, the sample cell contained just water. The solution now in the sample cell has enthalpy $H(\mathrm{l})$, where

$$H(\mathrm{I1}) = (n_1^{\mathrm{RZ}} - n_1^{\mathrm{A1}} + n_1^{\mathrm{i}})H_1^*(\mathrm{l}) + n_j^{\mathrm{i}}\phi^{\mathrm{i}}(H_j) \quad (14)$$

At this stage, volume V^{i} of fresh solution is about to be injected into the sample cell. Therefore, we need to eject volume V^{i} of the solution from the sample cell. This volume contains (a) $(V^{\mathrm{i}}/V^{\mathrm{R}})(n_1^{\mathrm{RZ}} - n_1^{\mathrm{A1}} + n_1^{\mathrm{i}})$ or, by definition, n^{A2} moles of solvent, and (b) $(V^{\mathrm{i}}/V^{\mathrm{R}})n_j^{\mathrm{i}}$ or, by definition, n^{A2} moles of solute. Then, in the sample cell afterflow A2, we have $(n_1^{\mathrm{RZ}} - n_1^{\mathrm{A1}} - n_1^{\mathrm{A2}} + n_1^{\mathrm{i}})$ moles of solvent and $(n_j^{\mathrm{i}} - n_j^{\mathrm{A2}})$ moles of solute. The enthalpy of the solution in the sample cell is given by

$$H^{\mathrm{R}}(\mathrm{I1 \text{ less overflow } 2}) = (n_1^{\mathrm{RZ}} - n_1^{\mathrm{A1}} - n_1^{\mathrm{A2}} + n_1^{\mathrm{i}})H_1^*(\mathrm{l}) + (n_j^{\mathrm{i}} - n_j^{\mathrm{A2}})\phi(H_j; \mathrm{I1}) \quad (15)$$

A second sample of solution is now injected into the solution in the sample cell (volume $V^{\mathrm{R}} - V^{\mathrm{i}}$). So the sample cell now contains (a) $(n_1^{\mathrm{RZ}} - n_1^{\mathrm{A1}} - n_1^{\mathrm{A2}} + 2n_1^{\mathrm{i}})$ moles of solvent, and (b) $(2n_j^{\mathrm{i}} - n_j^{\mathrm{A2}})$ moles of solute. Hence the new enthalpy of the solution in the sample cell after injection I2 is given by

$$H^{\mathrm{R}}(\mathrm{I2}) = (n_1^{\mathrm{RZ}} - n_1^{\mathrm{A1}} - n_1^{\mathrm{A2}} + 2n_1^{\mathrm{i}})H_1^*(\mathrm{l}) + (2n_j^{\mathrm{i}} - n_j^{\mathrm{A2}})\phi(H_j; \mathrm{I2}) \quad (16)$$

Hence the change in enthalpy on injection I2 is given by

$$\Delta H(\mathrm{I2}) = (n_1^{\mathrm{RZ}} - n_1^{\mathrm{A1}} - n_1^{\mathrm{A2}} + 2n_1^{\mathrm{i}})H_1^*(\mathrm{l}) + [2n_j^{\mathrm{i}} - n_j^{\mathrm{A2}}]\phi(H_j; \mathrm{I2}) - (n_1^{\mathrm{RZ}} - n_1^{\mathrm{A1}} - n_1^{\mathrm{A2}} + n_1^{\mathrm{i}})H_1^*(\mathrm{l}) - (n_j^{\mathrm{i}} - n_j^{\mathrm{A2}})\phi(H_j; \mathrm{I1}) - [n_1^{\mathrm{i}}H_1^*(\mathrm{l}) + n_j^{\mathrm{i}}\phi^{\mathrm{j}}(H_j)] \quad (17)$$

or

$$\Delta H(\mathrm{I2}) = (2n_j^{\mathrm{i}} - n_j^{\mathrm{A2}})[\phi(H_j; \mathrm{I2})] - [(n_j^{\mathrm{i}} - n_j^{\mathrm{A2}})\phi(H_j; \mathrm{I1})] - n_j^{\mathrm{i}}\phi^{\mathrm{i}}(H_j) \quad (18)$$

or

$$\Delta H(\mathrm{I2}) = (2n_j^{\mathrm{i}} - n_j^{\mathrm{A2}})[\phi(L_j; \mathrm{I2})] - [(n_j^{\mathrm{i}} - n_j^{\mathrm{A2}})\phi(L_j; \mathrm{I1})] - n_j^{\mathrm{i}}\phi^{\mathrm{i}}(L_j) \quad (19)$$

The change in enthalpy is recorded by heat $q(\mathrm{I2})$. If we follow through the sequence, overflow, injection, overflow, . . . , we obtain a general form of the equation for the change of enthalpy $\Delta H(\mathrm{I}k)$ and heat $q(k)$ accompanying injection k. Hence, for the kth injection

$$\begin{aligned}\Delta H(k) &= q(k) \\ &= \left[kn_j^{\mathrm{i}} - \sum (w = 1; w = k) n_j^{\mathrm{A}k}\right]\phi(H_j; \mathrm{I}k) \\ &\quad - \left[(k-1)n_j^{\mathrm{i}} - \sum (w = 1; w = k) n_j^{\mathrm{A}k}\right]\phi(H_j; I(k-1)) \\ &\quad - n_j^{\mathrm{i}}\phi^{\mathrm{i}}(H_j) \end{aligned} \quad (20)$$

The first term is the product of the apparent molar enthalpy of solute in the solution in the sample cell after the kth injection multiplied by the amount of solute in the sample cell after the kth injection less that lost in k overflows. The second term is the product of the apparent molar enthalpy of solution in the sample cell before the kth injection multiplied by the amount of solute in the sample cell after $(k-1)$ injections less the amount of solute lost in k overflows. The final term is the product of the number of moles of solute in each sample injected into the solution multiplied by the apparent molar enthalpy of solute in the injected solution. Equation (20) can be rearranged in terms of an equation for $\Delta H(k)$ and $q(k)$ in terms of apparent molar enthalpies of the solute j

$$\begin{aligned}\Delta H(k) &= q(k) \\ &= [kn_j^{\mathrm{i}}[\phi(L_j; \mathrm{I}k) - \phi(L_j; \mathrm{I}(k-1))]] \\ &\quad - \sum (w = 1; w = k)\{n_j^{\mathrm{A}w}[\phi(L_j; \mathrm{I}k) - \phi(L_j; \mathrm{I}(k-1))] \\ &\quad + n_j^{\mathrm{i}}[\phi(L_j; \mathrm{I}(k-1)) - \phi^{\mathrm{i}}(L_j)]\} \end{aligned} \quad (21)$$

At this stage we make two important assumptions: (1) $\phi(L_j; \mathrm{I}k) = \phi(L_j; \mathrm{I}(k-1))$, and (2) $\phi(L_j; \mathrm{I}(k-1))$ is approximately zero. This assumption (1) is based on the idea that the solutions in the sample cell before and after an injection differ only very slightly in composition. Their molalities and, therefore, their associated $\phi(L_j)$ values are almost the same. Assumption (2) implies that the solutions in the sample cell prior to an injection are extremely dilute. Hence for these solutions, $\phi(H_j) - \phi(H_j)^{\infty} = \phi(L_j) =$ zero. Hence

$$\Delta H(k) = q(k) = n_j\phi^{\mathrm{i}}(L_j) \quad (22)$$

Then, for example, if $\phi(L_j)$ is positive, the dilution process is exothermic. If the above assumptions are valid, the $q(k)$ should be independent of k, because n_j and $\phi^i(L_j)$ are constants. In practice, $q(k)$ depends on k, the difference between $q(k)$ and $q(k=1)$ increasing with increase in k. In other words, assumptions (1) and (2) become less acceptable with increase in injection number. We observed, however, that over the first series of injections, $q(k)$ was close to a linear function of k (see below). Hence, we used this dependence to determine q in the limit that k is zero. So we explored the idea of plotting $q(k)$ against k and hence calculated using a linear least-squares procedure, limit $(k \rightarrow \text{zero})$ $q(k) = -n_j^i \phi(L_j; m_j^i)$. Typically, in the study reported here, this analysis was based on 24 injections over the range $2 \leq k \leq 25$. In nearly all cases the data point at $k = 1$ showed the most marked deviation from a straight line dependence of $q(k)$ on k, a feature which we linked to an experimental artefact rather than having any thermodynamic significance. In other words, the data point at $q(k = 1)$ was ignored.

RESULTS

In the experiments reported here, the temperatures of the solutions were at or near 298 K. The calculated h_{jj} parameters are based on the assumption that the corresponding pairwise isobaric heat capacity parameters c_{pjj} are zero.

Urea(aq)

The raw data comprise a plot showing a rate of heating for a series of injections at regular time intervals. Figure 1 shows the pattern produced by injecting at regular time intervals an aqueous solution of urea, where $m(\text{urea}) = 0.828\ \text{mol kg}^{-1}$. The areas under the pulses are integrated to yield the dependence of $q(k)$ and, hence, of the enthalpy of injection

TABLE 1

Determination of pairwise enthalpic parameters for urea(aq) at 298 K

m(urea) (mol kg^{-1})	$q(k=0)$ (10^{-6} cal)	$-h_{jj}$ (J kg^{-1})
0.579	200	310
0.579	215	333
0.671	314	291
0.671	344	319
0.669	366	342
0.726	397	314
0.727	477	377
0.828	523	319
0.828	540	329

TABLE 2

Enthalpic pairwise interaction parameters

	Solute		
	Urea	MEU	HMT
h_{ij} (J kg^{-1})	−326 ± 24	213 ± 3	1119 ± 57

(eqn. (22)) on injection number k. The dependence of $q(k)$ on k for urea(aq) is summarised in Fig. 2. This plot shows that $\phi(L_j)$ for urea(aq) decreases with increase in m(urea). Figure 2 shows that with increase in k the endothermicity of the injection process is diminished because the composition difference between the solution in the syringe and the sample cell is decreasing. In the limit ($k \rightarrow \infty$), the enthalpy of injection would be zero. A least-squares analysis of the dependence of $q(k)$ on k yielded $q(k=0)$ and hence, using eqn. (22), the pairwise enthalpic interaction parameter h_{jj} is obtained. The results of nine experiments are summarised in Table 1 for urea(aq) over the range $0.52 \leq m(\text{urea})(\text{mol kg}^{-1}) \leq 0.83$. A calculated h_{jj} showed no underlying dependence on m(urea) indicating that within the precision of the method, h_{jjj} is zero. The mean h_{jj} for urea(aq) and associated standard error is shown in Table 2.

Monoethylurea(aq)

In this case the dilution is exothermic indicating that $\phi(L_j)$ increases with increase in m(MEU). Nineteen independent measurements over the range $0.519 \leq m(\text{MEU})\ \text{mol kg}^{-1} \leq 1.705$ yielded the estimate for h_{jj} given in Table 2.

HMT(aq)

Injection of dilute solutions of HMT(aq) over the range $0.310 \leq m(\text{HMT})(\text{mol kg}^{-1}) \leq 0.531$ produced strong exothermic pulses. Analysis of the data from 23 independent experiments yielded a large positive pairwise enthalpic interaction parameter.

DISCUSSION

The calorimetric procedures described here probe deviations from ideal of a given aqueous solution. In broad terms, the relative apparent molar enthalpy of solute j, $\phi(L_j)$, may either increase or decrease with increase in molality m_j. Urea(aq) belongs to the latter class; see Fig. 4 and eqn. (5).

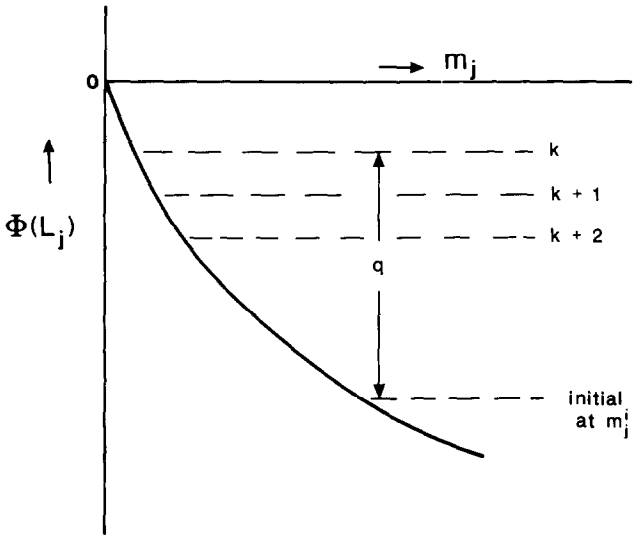

Fig. 4. Typical dependence of $\phi(L_j)$ for solute j (e.g. urea) on m_j indicating heat q absorbed (endothermic) at injection k and subsequent injections.

The operation of the titration calorimeter is indicated in Fig. 4. The change at injection k recorded by heat q measured the change $\phi(L_j;\text{sample cell};k)-\phi(L_j;\text{syringe})$. For this system, therefore, $q>0$ (see eqn. (22)) and the injection process (at constant pressure) is endothermic; $\Delta_{inj}H>\text{zero}$. With increase in injection number k, the magnitude of q decreases. We also calculated $q(k=0)$ in the limit $\phi(L_j;k)\rightarrow\text{zero}$, such that for this system $q(k=0)>0$ and $h_{jj}<0$; see eqn. (22).

For HMT(aq) and MEU(aq), the general pattern is shown in Fig. 5 where $\phi(L_j)$ increases with increase in m_j. Here the difference with the previous case is that $\phi(L_j;\text{sample cell};k)-\phi(L_j;\text{syringe})$ is negative, such that for injection k, q(i) is <0, and $\Delta_{inj}H$ is exothermic, i.e. eqn. (22). Hence with $q(k=0)<\text{zero}$, h_{jj} is positive; see Table 2.

The estimate of h_{jj} for MEU(aq) is in reasonable agreement with that reported by Barone et al. [11], namely $+160\pm7\ \text{J kg}^{-1}$. These authors used a flow microcalorimeter which operated over a large range of molalities, $0.1947\leq m(\text{MEU})(\text{mol kg}^{-1})\leq 5.0$. Consequently, they were able to estimate both pairwise and triplet terms. Two estimates of h_{jj} are available for HMT(aq). Wood and coworkers [10, 12] report $872\pm 24\ \text{J kg}^{-1}$ whereas Quadrifoglio et al. [13] report $1142\ \text{J kg}^{-1}$. In any event there is clear agreement that h_{jj} increases dramatically on going from MEU to HMT. Hydrophobic interaction between two solutes usually means that, although $\Delta_rG^\circ<0$, in fact $\Delta_rH^\circ>0$, $T\Delta_rS^\circ>0$ and $|T\Delta_rS^\circ|>|\Delta_rH^\circ|$, i.e. endothermic association. In other words, separation of two hydrophobic solutes is exothermic. So, for example, dilution of

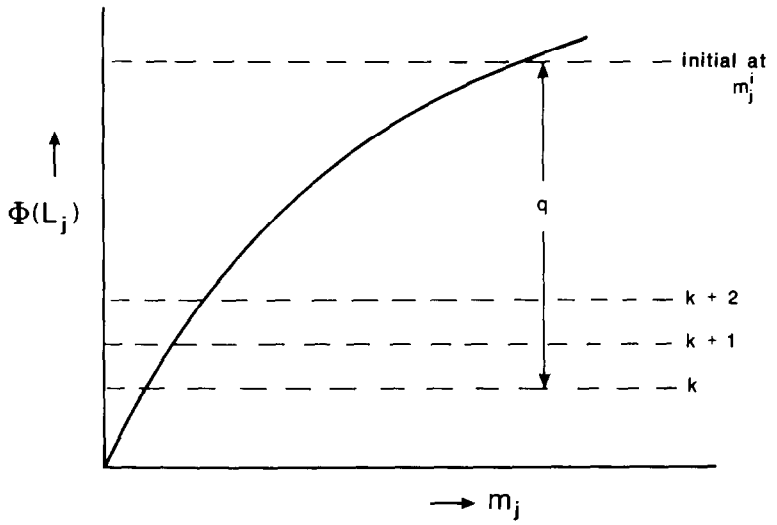

Fig. 5. Typical dependence of $\phi(L_j)$ for solute j (e.g. HMT) on m_j indicating heat liberated (exothermic) at injection k and subsequent injections.

HMT(aq) is exothermic. Because $\phi_j(L)$ increases with increase in m_j, dilution accompanying the titration moves down the $\phi_j(L)$ slope; see Fig. 4. Therefore, the trend for HMT and MEU is accounted for by the endothermicity of formation of hydrophobic bonds. The dilution process separates the hydration cospheres around the alkyl groups leading to an exothermic pulse.

In the case of urea, $\phi(L_j)$ decreases with increase in m_j, dilution accompanying the titration which moves up the slope of the $\phi(L_j)$ versus m(urea) plot; see Fig. 5. Two previous estimates of h_{jj} are available for this system. Cassel and Wood [10] report $-354\ J\ kg^{-1}$ whereas Franks et al. [1] report $-350\ J\ kg^{-1}$. The agreement with the estimate obtained here is reassuring although again we could not estimate the triplet term.

In summary, the trends in h_{ij} for urea(aq), MEU(aq) and HMT(aq) point to the important rôle of solute–solute interactions in aqueous solutions. This comment anticipates the next stage of the work reported here. The aim is to probe these interactions by titrating, say, HMT(aq) into an aqueous solution containing surfactants [14], enzyme [15] and vesicles.

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