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Partial molar volume study of the complexes of calix[4]naphthalenes with [60]fullerene in different solvents

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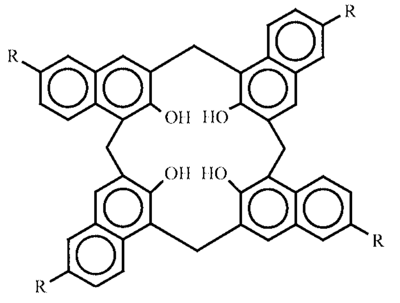
Calix[4]naphthalenes are a class of cavitands or container molecules that possess deeper cavities than those of analogous calix[4]arenes. Earlier studies of the complexation of [60]fullerene (C_{60}) with the C_4-symmetrical *endo*-calix[4]naphthalene (**1**) and its *tert*-butyl-substituted derivative (**2**) show that they form supramolecular 1 : 1 complexes with C_{60} in benzene, toluene or CS_2 solution with relatively high association equilibrium constants (K_{assoc}). Reported herein are densitometer-derived standard partial molar volume changes for the complexation, in these respective solvents, of C_{60} and the calix[4]naphthalenes **1** and **2**. In the case of the $C_{60}\subset$**2** complexes, the results are consistent with a solvophobic effect postulated previously. The results obtained for the $C_{60}\subset$**1** complexes however suggest that in addition to a solvophobic effect, other factors may be operating.

Introduction

Solution volume studies of the inclusion complex formed between [60]fullerene (C_{60}) and *p*-benzylcalix[5]arene were reported in 1997 by Isaacs *et al.*[1] These authors measured the changes in partial molar volumes ($\Delta_r\bar{V}$) upon complexation using high-precision densitometry. This technique was used earlier by Ruelle *et al.*[2] to measure the standard partial molar volumes of C_{60} itself in different solvents. Their densitometric analyses were based upon Liron and Cohen's method[3,4] for determining limiting partial molar volumes of various solutes at infinite dilutions. The inclusion properties of container molecules (cavitands) with guest molecules in general is a subject of considerable current interest[5] and there have been many recent studies reported concerned with the inclusion complexes of C_{60} with various host molecules, such as the calixarenes, resorcinarenes and cyclotriveratrylene.[6] Volumetric studies using high-precision densitometry provide a potentially general and simple experimental method to probe the nature of these "host–guest" interactions in solution;[1,7] however, to date no other studies have been reported.

We have shown previously[8,9] that the *endo*-calix[4]naphthalene (**1**) and its *tert*-butylated derivative (**2**) form stable inclusion complexes with C_{60}. These calix[4]naphthalenes,[10,11] which are the subject of ongoing investigations by our group, are a class of cavitands possessing deeper cavities than those of analogous calixarenes, and so their complexation properties are of interest. It was found that the respective association equilibrium constants (K_{assoc}), of the 1 : 1 supramolecular complexes in benzene, toluene or CS_2 increased in the order benzene, toluene, CS_2, and the hypothesis was presented that this trend could be due to a solvophobic effect.[5] The results obtained from a thermodynamic study[9] on the above systems were consistent with this hypothesis. In order to ascertain whether standard partial molar volume changes could provide further insights into the nature of the inclusion complexation observed, we have employed high-precision densitometry. Our results and their interpretation are presented herein.



1: R = H
2: R = Bu^t

Results and discussion

The partial molar volume of a solute ($\bar{V}_2$) [eqn. (1)] is the

$$\bar{V}_2 = (\partial V/\partial n_2)_{T,p,n_1} \quad (1)$$

differential change in volume of its solution (V) as a function of the change in the number of moles of the solute (n_2) for a given temperature (T), pressure (p) and number of moles of solvent (n_1).

By definition, the standard partial molar volume, $\bar{V}_2^{\ominus}$, is the limiting value of $\bar{V}_2^{\ominus}$ at infinite dilution. Experimental values of $\bar{V}_2^{\ominus}$ can be obtained from eqn. (2) by measuring $V_{\phi,2}$, the

$$V_{\phi,2} = 1/m_2\,[\{(1000 + m_2 M_2)/\rho\} - (1000/\rho_1)] \quad (2)$$

apparent molar volume of the solute,[12] and extrapolating the results to $m_2 = 0$, *i.e.* $\bar{V}_2^{\ominus} = \lim_{m_2\to 0} (V_{\phi,2})$; here m_2 is the molality of the solute, component 2; M_2 is its molar mass; ρ and ρ_1 are the densities of the solution and the solvent, respectively.

Since the solutions employed in our work were very dilute ($m_2 \sim 10^{-4}$ mol kg^{-1}), there was no need to extrapolate $V_{\phi,2}$ to infinite dilution, as was done by Isaacs and Young[7] in their study. At these low molalities, the average of the $V_{\phi,2}$ values obtained could be shown to represent very closely the standard partial molar volume at infinite dilution. The standard partial molar volumes calculated from the average $V_{\phi,2}$ values derived from eqn. (2) (method A) for the cavitands and C_{60} are shown in Tables 1 and 2.

The solutions of the complexes contained a small excess of either the cavitand or C_{60}. Values of the overall apparent molar

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Table 1 Solute standard partial molar volumes ($V_2^{\ominus}$/cm^3 mol^{-1}) of C_{60}, **1** and the C_{60}:**1** complex ($C_{60}\subset\mathbf{1}$) in different solvents and the calculated reaction volumes ($\Delta_r V_2^{\ominus}$/cm^3 mol^{-1})[a]

			$V_2^{\ominus}$						
Solvent	Run	Method	C_{60}	10^4 c_2	**1**	10^4 c_2	C_{60}:**1**	10^4 c_2	$\Delta_r V^{\ominus}$
Toluene	1	A	370 ± 14	4.0–7.3 (*5*)	548 ± 21	4.6–11.2 (*4*)	1064 ± 59	5.0–10.5 (*4*)	
	2	A	366 ± 10	4.7–7.3 (*5*)	521 ± 19	2.3–6.7 (*4*)	1083 ± 23	1.2–8.5 (*4*)	
		Mean values	368 ± 12		535 ± 20		1074 ± 45		171 ± 51
	1	B	361 ± 23	4.0–7.3 (*5*)	580 ± 15	4.6–11.2 (*4*)	1110 ± 38	5.0–10.5 (*4*)	
	2	B	367 ± 13	4.7–7.3 (*4*)	528 ± 35	2.3–5.5 (*4*)	1075 ± 22	1.2–8.5 (*4*)	
		Mean values	364 ± 19		554 ± 27		1092 ± 31		174 ± 45
Benzene	1	A	363 ± 3	4.0–9.0 (*4*)	560 ± 30	2.7–4.7 (*5*)	837 ± 40	3.0–5.7 (*5*)	
	2	A	355 ± 18	1.7–3.0 (5)	545 ± 25	3.0–8.0 (*5*)	857 ± 26	3.0–9.4 (*5*)	
		Mean values	359 ± 13		552 ± 28		847 ± 34		−64 ± 46
	1	B	371 ± 2	4.0–9.0 (*4*)	542 ± 39	2.7–4.7 (*5*)	841 ± 54	3.0–5.7 (*5*)	
	2	B	349 ± 48	1.7–3.0 (*5*)	559 ± 9	3.0–8.0 (*5*)	879 ± 40	3.0–9.4 (*5*)	
		Mean values	360 ± 34		551 ± 28		860 ± 48		−62 ± 56
CS_2	1	A	345 ± 12	2.0–2.8 (*3*)	458 ± 28	1.4–4.0 (*4*)	784 ± 15	0.80–1.6 (*4*)	
	2	A	348 ± 8	1.6–3.0 (*3*)	480 ± 20	1.0–2.0 (*6*)	813 ± 12	2.7–4.0 (*4*)	
	3	A	342 ± 8	7.0–16.0 (*5*)	491 ± 5	6.0–12.0(6)	812 ± 10	6.0–16.0 (*6*)	
		Mean values	345 ± 10		476 ± 20		803 ± 13		−18 ± 21
	1	B	348 ± 11	2.0–2.8 (*3*)	446 ± 26	1.4–4.0 (*4*)	800 ± 36	0.80–1.6 (*4*)	
	2	B	370 ± 9	1.6–3.0 (*3*)	458 ± 18	1.0–2.0 (*6*)	851 ± 22	2.7–4.0 (*4*)	
	3	B	341 ± 18	7.0–16.0 (*6*)	489 ± 11	6.0–12.0 (*7*)	817 ± 14	6.0–16.0 (*4*)	
		Mean values	353 ± 13		464 ± 19		823 ± 26		−10 ± 34

[a] c_2 = mass fraction; italic figures in parentheses are the number of data points. ± values are standard deviations, derived (for method A) from the statistical treatment (Sigmaplot v 3.0) and (for method B) from a non-linear least-squares analysis (Sigmaplot v 3.0).

Table 2 Solute standard partial molar volumes ($V_2^{\ominus}$/cm^3 mol^{-1}) of C_{60}, **2** and the C_{60}:**2** complex ($C_{60}\subset\mathbf{2}$) in different solvents and the calculated reaction volumes ($\Delta_r V_2^{\ominus}$/cm^3 mol^{-1})[a]

			$V_2^{\ominus}$						
Solvent	Run	Method	C_{60}	10^4 c_2	**2**	10^4 c_2	C_{60}:**2**	10^4 c_2	$\Delta_r V^{\ominus}$
Toluene	1	A	370 ± 14	4.0–7.3 (*5*)	746 ± 15	4.2–15 (*5*)	1178 ± 40	6.0–13 (*5*)	
	2	A	366 ± 10	4.7–7.3 (*4*)	753 ± 48	4.0–12 (*4*)	1139 ± 19	2.0–6.0 (*4*)	
		Mean values	368 ± 12		749 ± 36		1158 ± 31		41 ± 49
	1	B	361 ± 23	4.0–7.3 (*5*)	748 ± 12	4.2–15 (*5*)	1187 ± 36	6.0–13 (*5*)	
	2	B	367 ± 13	4.7–7.3 (*4*)	729 ± 40	4.0–12 (*4*)	1194 ± 26	2.0–6.0 (*4*)	
		Mean values	364 ± 19		739 ± 29		1190 ± 31		87 ± 46
Benzene	1	A	363 ± 3	4.0–9.0 (*4*)	777 ± 44	4.0–5.5 (*3*)	1196 ± 19	3.2–4.6 (*4*)	
	2	A	355 ± 18	1.6–3.0 (*5*)	786 ± 2	3.5–5.5 (*4*)	1190 ± 30	2.5–4.3 (*5*)	
		Mean values	359 ± 13		782 ± 31		1193 ± 25		52 ± 42
	1	B	371 ± 2	4.0–9.0 (*4*)	798 ± 47	4.0–5.5 (*3*)	1229 ± 28	3.2–4.6 (*4*)	
	2	B	349 ± 48	1.6–3.0 (*5*)	812 ± 7	3.5–5.5 (*4*)	1168 ± 44	2.5–4.3 (*5*)	
		Mean values	360 ± 34		805 ± 34		1198 ± 37		22 ± 50
CS_2	1	A	345 ± 12	2.0–2.8 (*3*)	630 ± 20	1.0–1.5 (*4*)	1115 ± 38	1.0–3.0 (*4*)	
	2	A	348 ± 8	1.6–3.0 (*4*)	655 ± 18	1.6–3.3 (*3*)	1104 ± 28	1.0–2.0 (*4*)	
	3	A	342 ± 8	7.0–16.0 (*5*)	640 ± 9	6.5–16.0 (*6*)	1073 ± 33	6.0–16 (*4*)	
		Mean values	345 ± 10		642 ± 16		1097 ± 33		110 ± 39
	1	B	370 ± 9	1.6–3.0 (*4*)	654 ± 38	1.6–3.3 (*3*)	1101 ± 70	1.0–2.0 (*4*)	
	2	B	341 ± 18	7.0–16.0 (*6*)	617 ± 6	6.5–16.0 (*6*)	1035 ± 8	6.0–16 (*4*)	
	3	B	348 ± 11	2.0–2.8 (*3*)	630 ± 36	1.0–1.5 (*4*)	1095 ± 44	1.0–3.0 (*4*)	
		Mean values	353 ± 13		634 ± 30		1077 ± 48		98 ± 69

[a] See Table 1.

volume, V_{ϕ}, were obtained from the general form of eqn. (2) for n solutes.[12] Young's rule[13] [eqn. (3)] was then applied to calculate $V_{\phi,2}$:

$$V_{\phi,2} = \Sigma F_n V_{\phi,n} \tag{3}$$

In eqn. (3), F_n is the molar fraction of each solute in a multicomponent solution of n solutes, for example $F_2 = n_2/(n_2 + n_3)$, and $V_{\phi,n}$ is the apparent molar volume of each individual solute. The apparent molar volumes of the 1 : 1 complexes of C_{60} with **1** and **2** are listed in Tables 1 and 2, respectively. Fig. 1 shows the plots of $V_{\phi,2}$ *versus* molality for the solutions in benzene, of C_{60}, **2** and the C_{60}:**2** (1 : 1) complex, respectively, from which the $V_2^{\ominus}$ values in Table 2 were derived. Table 1 contains the corresponding data for the volumetric studies on the complex formation between C_{60} and **1**.

$V_2^{\ominus}$ may also be derived from the limiting partial specific volume $v_{s,2}$ of the solute, which can be calculated (method B) from a plot of the specific volume of the solution, $v_s = 1/\rho$, *versus* the mass fraction of solute (c_2).[2,3] $V_2^{\ominus}$ is related to $v_{s,2}$ by eqn. (4).[2,3]

$$V_2^{\ominus} = M_2 \cdot v_{s,2} \tag{4}$$

We employed the same data points used to calculate the partial molar volumes from eqn. (2) above, to calculate $V_2^{\ominus}$ (method B) from eqn. (4). The standard partial molar volumes calculated by both methods show good agreement within experimental error. The experimental curves shown in Fig. 2 (which are typical), were obtained directly from the density measurements of benzene solutions having known mass fractions respectively, of each of the solutes C_{60}, **2**, and the C_{60}:**2** (1 : 1) complex.

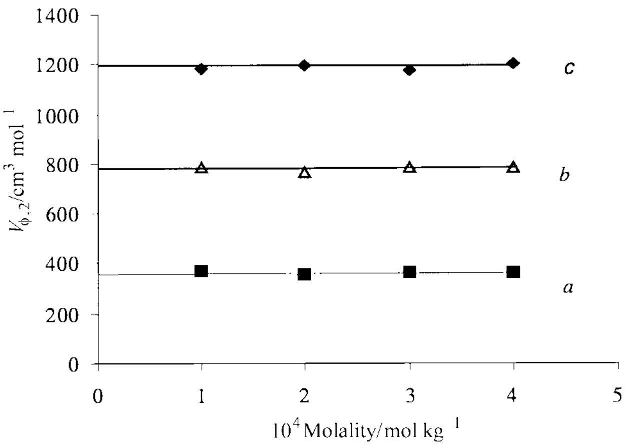

Fig. 1 Apparent molar volume ($V_{\phi,2}$) of solutes (■, C_{60}; △, **2**; ◆, $C_{60}\subset$**2**) *vs.* their molality in benzene.

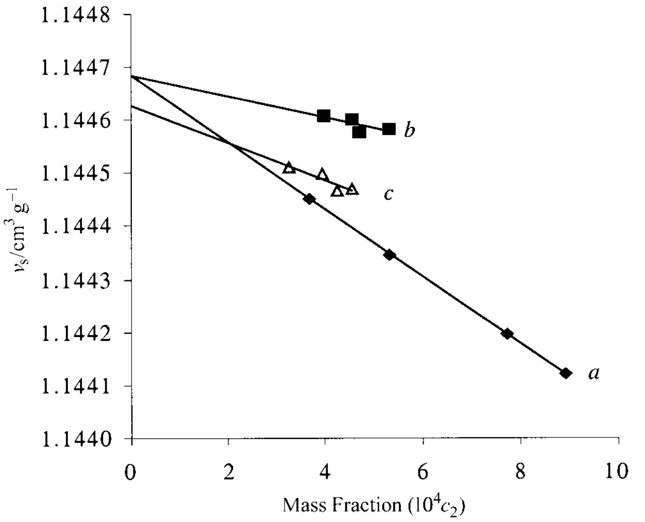

Fig. 2 Specific volume (v_s) of solutions in benzene of solutes (◆, C_{60}; ■, **2**; △, $C_{60}\subset$**2**) *vs.* their mass fraction (c_2).

The following discussion is based upon the results calculated using method A since they contain corrections for the excess, presumably uncomplexed, solute in the respective solutions, although the results obtained using both methods are in close agreement. When the error limits for the mean values obtained from our assays are taken into account, our data for the partial molar volume of C_{60} itself in each of the three solvents are basically in agreement with those reported by Ruelle *et al.*[2] and with the values obtained in toluene by Isaacs *et al.*[1]

Using the mean values obtained from method A, a trend can be seen in the partial molar volumes of *tert*-butylcalix[4]-naphthalene (**2**) (Table 2), being largest in benzene (782 ± 31), followed by toluene (749 ± 36) and CS_2 (642 ± 16) cm^3 mol^{-1}. A similar trend can be seen in the partial molar volumes of calix[4]naphthalene (**1**) (Table 1) measured in the same respective solvents, being 552 ± 28 in benzene, 535 ± 20 in toluene and 476 ± 20 cm^3 mol^{-1} in CS_2.

Handa and Benson[14] have noted that the volume changes observed on mixing two liquids can be the result of any of several factors, such as (i) differences in sizes and shapes of the component molecules, (ii) structural changes, (iii) differences in the intermolecular interaction energy between like and unlike molecules, and/or (iv) formation of new chemical species. Using these considerations, as well as observations noted by Ruelle *et al.* and others,[15–17] it is possible to rationalize the changes that we observed for **1** or **2** with the different solvents, as follows.

Firstly, the trend in the solubilities (mg cm^{-3}) of **1** and **2** in each of the three solvents decreases in the following order: CS_2 (>10) > toluene (1.8) > benzene (1.7) for **1** and CS_2 (>10) > toluene (3.5) > benzene (2.6) for **2**. Increases in the limiting partial molar volume changes of solutes in various solvents are known to be roughly inversely proportional to their solubilities in the respective solvents.[15–17] This is indeed the trend that we noted above, with the smallest partial molar volumes of either **1** or **2** being in CS_2, the solvent in which both calixnaphthalenes have the highest solubilities.

A second factor to consider is the difference in size and shape of the component molecules in each case, outlined as factor (i) above, and which Ruelle *et al.* considered in their intensive study of C_{60} itself in different solvents. These authors determined a good correlation between the solvent molar volume and the variation in the size of C_{60} in solution. For our calixnaphthalene compounds, however, this does not appear to be the case since, whilst CS_2 has the smallest reported molar volume, followed by benzene, then toluene, the trend in partial molar volumes in these solvents follows a different order: benzene > toluene > CS_2. An additional factor, outlined as factor (iv) above, could account for this apparent anomaly between benzene and toluene as solvents of either **1** or **2**. This could be the intermolecular π···methyl interaction that might occur between the naphthalene rings and the methyl group of toluene, but would not be present when benzene is the solvent. This supposition is supported by the well-known fact that a stable toluene:*tert*-butylcalixarene clathrate forms, as first reported by Andreetti *et al.*[18]

The partial molar volumes of the 1 : 1 complexes $C_{60}\subset$**1** and $C_{60}\subset$**2** in the respective solvents were also determined in the same way, and calculated using method A. However, it should be noted that the sparing solubilities of the calixnaphthalenes in benzene or toluene limited the concentration ranges that could be employed and resulted in uncertainties of the order of 3–6%, which are nevertheless comparable to the findings reported by Isaacs *et al.*[1]

The calculated reaction volumes ($\Delta_r V_2^{\ominus}$)[7] for the C_{60} : **2** complex formation are +110 in CS_2, +52 in benzene and +41 cm^3 mol^{-1} in toluene. Based on the molar volumes of each of the solvents, these reaction volumes are roughly equivalent to the partial molar volumes of 2, 0.6 and 0.4 molecules of the respective solvents which, as interpreted by Isaacs *et al.*,[1] are displaced upon complex formation. The trend is consistent with our earlier hypothesis[8] that a solvophobic effect (*i.e.* that a larger number of molecules of CS_2 are displaced from the cavitand cavity upon complex formation) is a driving force in the complex formation processes studied.

For C_{60} : **1** complex formation, the calculated reaction volumes ($\Delta_r V^{\ominus}_{2,\mathrm{calc}}$) are −18 in CS_2, −64 in benzene and +171 cm^3 mol^{-1} in toluene. These values do not support the solvophobic effect hypothesis, since in CS_2 and in benzene they are lower than expected when compared with the corresponding values obtained for the $C_{60}\subset$**2** complex. Thus, for the $C_{60}\subset$**1** complex, for which a deeper penetration of C_{60} into the cavity is possible relative to the $C_{60}\subset$**2** complex, solvation of the complex by CS_2 and benzene could therefore be stronger, thus negating a possible solvophobic effect. For toluene as the solvent, approximately two molecules of toluene are displaced upon complex formation, similar to the finding observed by Isaacs *et al.*[1] in their system.

When the toluene data for the two complexation processes are compared, more solvent molecules are displaced on formation of the $C_{60}\subset$**1** complex than the $C_{60}\subset$**2** complex. This is also consistent with our earlier rationalization[9] that, in the case of $C_{60}\subset$**1** we have deep-cavity inclusion. By contrast, a shallower penetration of the C_{60} guest molecule may be occurring in the case of the $C_{60}\subset$**2** complex, since the *tert*-butylmethyl···C_{60}π interactions may sterically inhibit the potentially more effective interactions between C_{60} and the naphthalene rings.

There appears to be no simple direct correlation between the stability constants, K_{assoc}, which we determined earlier,[9] and the reaction volume changes. On the other hand, a positive correlation is found for the volume changes and $\Delta_r S^\ominus$ values determined earlier for the formation of the $C_{60}\subset\mathbf{1}$ complex and a negative correlation for the formation of the $C_{60}\subset\mathbf{2}$ complex.

Connors published an extensive review in 1997 on cyclodextrin complexes in solution.[19] In this review he points out that interpretations based upon small calculated molar volume changes having relatively large uncertainties should be considered with care and that only after the collection of very many experimental results for a wide range of substrate types will accurate patterns emerge. This holds true for calixarene-based host–guest complexation processes, and we are continuing to design and study other calixnaphthalenes.

In conclusion, the results presented herein show that apparent molar volume measurements can be employed to study host–guest complexation processes and can provide some information as to how deep the inclusion of a guest into the substrate can occur. However, it is important to also take into account additional information, such as the solvation of all of the individual species concerned, solvent molar volumes and other factors identified by Handa and Benson,[14] which may require additional physical methodologies.

Experimental

Toluene (BDH, Scintillation Grade) was distilled over sodium metal with benzophenone prior to use. Benzene (ACP Chemicals Inc., A.C.S. grade, 99%) and CS_2 (Aldrich Chemical Company, Inc., Spectrophotometric Grade, 99+%) and anhydrous ethanol (Commercial Alcohols Inc.) were used without further purification. C_{60} (99.5%) was purchased from Aldrich. Calix[4]naphthalenes **1** and **2** were prepared according to methods previously described.[10,11] For all the solvents tested 4–6 solution samples with decreasing mass fraction were prepared from a specific amount of a pre-prepared stock solution of known mass fraction by dilution with a known mass of solvent. In the case of the complex mixtures, an exact mass of the stock solution of **1** or **2** was mixed with the exact mass of C_{60} stock solution to give a 1 : 1 molar ratio, then this mixture was diluted with a known mass of solvent. All solutions were weighed with a precision of $\pm 10^{-5}$ g. The high-precision density measurements were carried out at 25.00 ± 0.01 °C using a vibrating-tube densitometer (Sodev Model D03), capable of measuring relative densities $(\rho - \rho_1)$ to a precision of $\pm 5 \times 10^{-6}$ g cm^{-3}. Before each series of measurements, the instrument was calibrated with absolute ethanol and the solvent system used in the experiment, whose densities (g cm^{-3}) at 25.00 °C were taken from published data:[20] ρ_1 (ethanol) = 0.78509, ρ_1 (toluene) = 0.86222, ρ_1 (benzene) = 0.87366, ρ_1 (CS_2) = 1.25585. In a typical experiment, approximately 2.0 cm^3 of the tested solution was injected into the densitometer using a glass syringe. The apparent molar volume, V_ϕ, at each molality was calculated using the general form of eqn. (2), then $V_{\phi,2}$ was determined by applying Young's rule. The standard partial molar volume, $V_2^\ominus$, was calculated from the average of all the data points in that experiment (method A). The same data points were analyzed by plotting the specific volume $(1/\rho)$ of a series of solutions against the mass fractions. From these plots, the partial molar volumes could also be calculated using eqn. (4) (method B). Measurements in each solvent were conducted in duplicate or triplicate. Statistical analyses were conducted using *Sigmaplot v 3.0* and curve fitting was conducted using *Excel 97*.

Acknowledgements

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