# The direct determination of partial molar volumes and reaction volumes in ultra-dilute non-reactive and reactive multi-component systems using a combined spectroscopic and modified response surface model approach<sup>†</sup>

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Two experimental multi-component organometallic systems were studied, namely, (1) a non-reactive system consisting of  $[Mo(CO)_6]$ ,  $[Mn_2(CO)_{10}]$ , and  $[Re_2(CO)_{10}]$  in toluene under argon at 298.15 K and 0.1 MPa and (2) a reactive system consisting of  $[Rh_4(CO)_{12}] + PPh_3 \rightarrow [Rh_4(CO)_{11}PPh_3] + CO$  in n-hexane under argon at 298.15 K and 0.1 MPa. The mole fractions of all solutes were less than  $140 \times$  $10^{-6}$  in system (1) and less than  $65 \times 10^{-6}$  in system (2). Simultaneous *in-situ* FTIR spectroscopic measurements and on-line oscillatory U-tube density measurements were performed on the multi-component solutions. A newly developed response surface methodology was applied to the data sets to determine the individual limiting partial molar volumes of all constituents present as well as the reaction volume. The limiting partial molar volumes obtained for system (1) were  $176.4 \pm 2.5$ ,  $265.1 \pm$ 2.4, and  $276.8 \pm 2.4$  cm<sup>3</sup> mol<sup>-1</sup> for [Mo(CO)<sub>6</sub>], [Mn<sub>2</sub>(CO)<sub>10</sub>], and [Re<sub>2</sub>(CO)<sub>10</sub>], respectively and are consistent with independent binary experiments. The limiting partial molar volumes obtained for system (2) were  $310.7 \pm 2.7$ ,  $219.8 \pm 2.2$  and  $461.5 \pm 4.5$  cm<sup>3</sup> mol<sup>-1</sup> for [Rh<sub>4</sub>(CO)<sub>12</sub>], PPh<sub>3</sub> and  $[Rh_4(CO)_{11}PPh_3]$ , respectively. In addition, a reaction volume  $\Delta_r V$  equal to  $-17.0 \pm 5.7 \text{ cm}^3 \text{ mol}^{-1}$  was obtained. The present results demonstrate that both partial molar volumes and reaction volumes can be obtained directly from multi-component organometallic solutions. This development provides a new tool for physico-chemical determinations relevant to a variety of solutes and their reactions.

## Introduction

Many organometallic syntheses and homogeneous catalytic syntheses for fine chemicals and pharmaceuticals can be considered highly complex multi-component systems, possessing many product(s) and/or intermediate(s).<sup>1</sup> In-situ spectroscopic studies have shown that many of the observable organic and organometallic species present are in fact non-isolatable transient intermediates.<sup>2-4</sup> Most of these reactions were conducted in a liquid phase, with a very low concentration of the reacting species (in parts per million levels). Recently, advanced signal processing techniques like bandtarget entropy minimization (BTEM) have been successfully deconvoluting, then identifying as well as quantifying the nonisolatable reacting species.5-7 This information has been widely used for kinetic modeling and process optimization. However, the corresponding determination of the associated physico-chemical solution properties of the individual solutes (non-isolatable as well as isolatable) in multi-component systems has not advanced to the same degree, due to combined numerical, analytical and methodological difficulties.

The use of an appropriate *in-situ* spectroscopic measurement (possibly FT-IR, RAMAN, UV/VIS, *etc.*) together with a bulk fluid property measurement would appear to provide sufficient experimental information for determining individual physicochemical solute properties from multi-component solutions. In addition, a robust and general method of analysis involving appropriate design of experiments, model development, and system identification, would be required to solve the corresponding inverse problem,<sup>8</sup> thereby obtaining the individual physico-chemical quantities of interest.

Many bulk physico-chemical properties of solutions are of common interest to physical chemists such as volume, dielectric constant, refractive index and/or refraction, dipole moment etc.9 Among these, volumetric measurements are perhaps one of the most straightforward thermodynamic measurements to obtain and these lead to the determination of partial molar volumes, volumes of interaction, as well as volume of reaction. Traditionally, partial molar volumes have been determined from binary data alone, in other words, from single-solute/solvent systems.<sup>10</sup> Recently, a new and very general approach to the determination of partial molar volumes from multi-component solutions alone (without recourse to binary experiments) was developed and applied to a non-reactive highly-associating system.<sup>11</sup> This new approach relies on the application of a response surface model to the total molar volume of solution. Good experimental design ensured that the composition space was adequately covered and that optimal parameter estimation for the individual partial molar volumes could be achieved.

Department of Chemical and Biomolecular Engineering, 4 Engineering Drive 4, National University of Singapore, Singapore 117576. Email: chemvg@nus.edu.sg; Fax: +65 6779-1936; Tel: +65 6874-6617 † Electronic supplementary information (ESI) available: Raw experimental data for the multi-component non-reactive system. This includes (a) the density differences between the pure solvent and the multi-component solution, and (b) the volume differences Y defined by the left-hand-side of eqn (11) or eqn (12), for each perturbation of the three semi-batch runs as well as (c) compositional data. See DOI: 10.1039/b515298d

In the present contribution, the approach is considerably extended, to permit *in-situ* spectroscopic analysis and to encompass ultra-dilute concentration regimes and reactive solutions. In order to fully demonstrate the utility of the new approach, two experimental multi-component organometallic systems were studied in the present contribution, namely, (1) a non-reactive system consisting of  $[Mo(CO)_6]$ ,  $[Mn_2(CO)_{10}]$ , and  $[Re_2(CO)_{10}]$  in toluene under argon at 298.15 K and 0.1 MPa and (2) a reactive system of ligand substitution of CO with triphenylphosphine, PPh<sub>3</sub> in tetrarhodium dodecacarbonyl,  $[Rh_4(CO)_{12}]$  using n-hexane as a solvent and under argon at 298.15 K and 0.1 MPa.

$$[Rh_4(CO)_{12}] + PPh_3 \rightarrow [Rh_4(CO)_{11}PPh_3] + CO$$
(1)

The concentration regimes were ultra-dilute. The mole fractions of all solutes were less than  $140 \times 10^{-6}$  in system (1) and less than  $65 \times 10^{-6}$  in system (2). The reaction (eqn (1)) is very fast.<sup>12-14</sup> Simultaneous *in-situ* FTIR spectroscopic measurements and online oscillatory U-tube density measurements were performed on both multi-component solutions. A modified response surface model for the ultra-high dilution multi-component solution was proposed. Partial molar volume of each individual solute was determined using the multi-component data alone. In addition, the volume of reaction  $\Delta_r V$  for system (2) was determined. It is important to note that this avoids the reliance on a large pressure variation which is needed in  $\Delta_r V$  studies.<sup>15</sup> To verify the accuracy of the results as well as validate the models used, separate binary studies were carried out in both systems.

The present contribution suggests a wider use of the present approach and a more general applicability to thermodynamic/physico-chemical system identification of very dilute non-reactive as well as reactive systems, especially systems involving non-isolatable but observable and quantifiable species.

## Experimental

## General information

All solution preparations were carried out under argon (Soxal, Singapore, 99.999%) by using standard Schlenk techniques.<sup>16</sup> The solvents n-hexane (Fluka, puriss, 99.6%+) and toluene (Mallinckrodt Chem., ChromAR®HPLC, 99.9%+) were refluxed over sodium–potassium alloy under argon. The argon was further purified prior to use by passage through a column containing 100 g of reduced BTS-catalyst (Fluka AG Buchs, Switzerland) and 100 g of 4 Å molecular sieves to adsorb trace oxygen and water, respectively. The metal complexes [Mo(CO)<sub>6</sub>], [Mn<sub>2</sub>(CO)<sub>10</sub>], and [Re<sub>2</sub>(CO)<sub>10</sub>], and [Rh<sub>4</sub>(CO)<sub>12</sub>] with stated purity of at least 98% for all complexes were obtained from Strem Chemicals (Newport, MA) and triphenylphosphine, PPh<sub>3</sub> with stated purity of greater than 99% obtained from Merck were used without further purification.

## Equipment

The experimental apparatus for non-reactive and reactive system studies consisted of a jacketed glass reactor (Aceglass) equipped with a magnetic stirrer, a Teflon membrane pump (Cole-Parmer) and an Anton-Paar DMA 5000 (precision of better than  $10^{-6}$  g cm<sup>-3</sup>) vibration tube densitometer thermostatically controlled by a built-in Peltier thermostat to within  $\pm 0.001$  K and a Perkin Elmer System 2000 mid-infrared FTIR spectrometer. The fluid was pumped under isobaric (Argon, atmospheric pressure) and isothermal conditions from the reactor through the pump (Temp control Polyscience 9105, with temperature stability  $\pm 0.05$  K), DMA 5000, then high-pressure infrared cell (SS316) with recycle back to reactor. Connections for vacuum and argon were provided. A 2.000 piezo-transducer (PAA-27W, Keller AG, Switzerland) was used throughout for pressure measurements. The entire experimental setup was gas tight, and the approximate liquid phase volume was 100 mL. In order to ensure quantitative working conditions, and hence minimal decomposition of metal complexes and phosphine, the system was thoroughly rinsed with anhydrous solvent under argon and then evacuated to dryness prior to each experiment. In addition, the reactor was fully covered with aluminum foil, thus providing dark reaction conditions.<sup>17</sup>

Before performing density measurements, the DMA 5000 was calibrated using Millipore quality de-ionized water and dry air. Hamilton gas-tight 1.0 mL and 2.5 mL syringes were used for introducing perturbation of solutions into the reactor through a rubber septum. The amounts of solutes in stock solutions were determined by using a balance (Analytical Plus, Ohaus, New Jersey) with a precision of  $\pm 10^{-5}$  g. The high-pressure infrared cell was constructed at the ETH Zürich of SS316 steel and could be heated and cooled. The CaF<sub>2</sub> and KBr single crystal windows used (Korth Monokristalle, Kiel, Germany) had dimensions of diameter 40 mm by thickness 15 mm. Two sets of Viton and Silicone gaskets provided sealing, and Teflon spacers were used between the windows. The construction of the flow through cell is a variation on the design by Noack<sup>18</sup> and differs in some respect from other high-pressure infrared cells.19 The high-pressure cell was situated in a Perkin-Elmer 2000 FTIR infrared spectrometer. The cell chamber was purged with purified nitrogen (Soxal, Singapore, 99.999%). The resolution was set to 4 cm<sup>-1</sup>. A schematic diagram of the experimental setup is shown in Fig. 1.

#### In-situ spectroscopic and density measurement

First, background spectra of the empty high-pressure infrared cell were recorded. Then 100 mL solvent was transferred to the reactor under argon. Pressure was set at 0.1 MPa of argon. The stirrer was turned on and liquid was circulated throughout the entire system. After the vapor–liquid equilibrium (VLE) was established and confirmed by stable density measurements from the DMA 5000, spectra of the argon–solvent solution in the cell were recorded and the density of the pseudo argon–solvent liquid was measured simultaneously.<sup>20</sup> To reduce error, while actually measuring the density with the DMA, the pump was turned off. Thus density measurements were performed under static and not flow conditions. A few minutes were typically needed for a DMA 5000 measurement. After density and absorbance measurement, the pump was turned on and the solution was circulated back to the reactor.

For the non-reactive system, both binary and multi-component semi-batch experiments were performed. First, the apparatus was filled with 100 mL toluene under argon, then stock solutions in toluene of  $[Mo(CO)_6]$  (*ca.* 49.9 mg in 10 mL for binary-1, 50.0 mg in 10 mL for binary-2, and 124.8 mg in 25 mL for multi-component experiment),  $[Mn_2(CO)_{10}]$  (*ca.* 75.0 mg in 10 mL for binary-1,



Fig. 1 Experimental setup for simultaneous *in-situ* FTIR measurements and density measurements. 1. Argon tank; 2. Argon purification column; 3. Pressure transducer; 4. Jacketed continuous stirrer tank reactor (CSTR); 5. Hermetically sealed Teflon pump; 6. FTIR with high pressure flow through cell; 7. Anton Paar DMA 5000 Densitometer; 8. Data acquisition.

75.2 mg in 10 mL for binary-2, and 187.7 mg in 25 mL for multicomponent experiment), [Re<sub>2</sub>(CO)<sub>10</sub>] (ca. 98.9 mg in 10 mL for binary-1, 99.2 mg in 10 mL for binary-2, and 250.5 mg in 25 mL for multi-component experiment) were prepared, and transferred by injection into the reactor containing toluene-argon at 0.1 MPa. Typically, several perturbations using a single stock solution were required for each binary study and optimally planned perturbations using all three stock solutions were required for each multi-component semi-batch experiment (see numerical section). With respect to solution homogeneity, after each perturbation, the solution was stirred and circulated for about 10 minutes before simultaneous density measurements and spectral measurements (in the range of 1000–4000 cm<sup>-1</sup>) were taken. With respect to repeatability, at least 6 readings of density were performed during each perturbation. Two semi-batch experiments of each binary system consisting of [Mo(CO)<sub>6</sub>]-toluene, [Mn<sub>2</sub>(CO)<sub>10</sub>]-toluene, and [Re2(CO)10]-toluene were performed, and for the multicomponent system [Mo(CO)<sub>6</sub>]–[Mn<sub>2</sub>(CO)<sub>10</sub>]–[Re<sub>2</sub>(CO)<sub>10</sub>]–toluene, 3 semi-batch experiments were performed.

For the reactive system, both binary and reactive multicomponent semi-batch experiments were performed. The apparatus was filled with 100 mL n-hexane under argon and stock solutions of [Rh<sub>4</sub>(CO)<sub>12</sub>]-n-hexane (ca. 59.4 mg in 30 mL for binary-1, 59.8 mg in 30 mL for binary-2) and PPh<sub>3</sub>-n-hexane (ca. 102 mg in 10 mL for binary experiment, 31.7 mg in 20 mL for reactive experiment-1 and 31.6 mg in 20 mL for reactive experiment-2) were prepared, and transferred by injection into the reactor containing n-hexane-argon at 0.1 MPa. Typically, several perturbations using a single stock solution were required for each binary study and many perturbations of PPh<sub>3</sub> in substoichiometric amounts were required for each reactive multicomponent semi-batch experiment. With respect to solution homogeneity, after each perturbation, the solution was stirred and circulated for about 10 minutes before simultaneous density measurements and spectral measurements (in the range of 400-4000 cm<sup>-1</sup> using KBr or in the range of 1000-4000 cm<sup>-1</sup> using CaF<sub>2</sub>) were taken.<sup>21</sup> With respect to repeatability, at least 6 readings of density were performed during each perturbation. The binary system consisting of [Rh<sub>4</sub>(CO)<sub>12</sub>]-n-hexane and PPh<sub>3</sub>-nhexane were studied with 2 semi-batch experiments and 1 semibatch experiment respectively. Two semi-batch experiments were performed for the multi-component reactive system.

#### Determination of experimental moles

The simplest volumetric equation which represents the present experiments takes the form eqn (2),

$$\underline{V}(T, P, \boldsymbol{n}) = n_{\rm s} V_{\rm s}^{\rm o} + \sum_{\text{solute-}i} n_i \bar{V}_i^{\infty}$$
(2)

where  $\underline{V}(T, P, n)$  is total volume of solution,  $V_s^\circ$  is the pure molar volume of solvent,  $\overline{V}_i^\infty$  is the partial molar volume of solute at infinite dilution,  $n_s$  is the mole of solvent and  $n_i$  is the mole of solute-*i*. At each perturbation of the system using the stock solutions, each of the mole balances is updated by the increments  $\Delta n_s$  and  $\Delta n_i$ . This multi-linear approximation implicitly assumes, in particular, that the solvent volumetric properties do not vary in the ultra-dilute solutions studied.

#### **Experimental system**

An initial volume of solvent at *ca*. room temperature was added to the experimental system thermostated at 298.15 K and the experimental density measured  $\rho_s^o$ . The experimental volume and experimental density, together with molar mass, result in the initial moles of solvent introduced  $n_s^{init}$  and the molar volume  $V_s^o$ .

## Perturbations using stock solutions

As mentioned, each stock solution was prepared by dissolving a known mg solute  $m_i^{\text{stock}}$  to a known quantity of solvent. The maximum solute concentrations were *ca*. 2000 × 10<sup>-6</sup>. During each perturbation, a known *volume* of stock solution  $\underline{V}^{\text{inj}}$  was injected into the system. This known volume  $\underline{V}^{\text{inj}}$  was then used to calculate the increments  $\Delta n_s$  and  $\Delta n_i$  according to eqn (3) and (4).

$$\Delta n_{\rm s} \cong \frac{\rho_{\rm s}^{\rm o} \underline{V}^{\rm inj}}{M_{\rm s}} \tag{3}$$

$$\Delta n_i \cong \frac{V^{\rm inj} m_i^{\rm stock}}{V^{\rm stock} M_i} \tag{4}$$

The increments  $\Delta n_s$  and  $\Delta n_i$  are used to update the total moles of solvent  $n_s$  and solute  $n_i$ .

Since all the stock solutions are dilute, *i.e.* maximum *ca.* 2000 × 10<sup>-6</sup>, eqn (3) and (4) are clearly very good first approximations to the incremental quantities. But they are not exact, and accordingly, this is made explicit in the equation with  $\cong$ , the approximately equal to symbol. In eqn (3), it is assumed that the experimental  $\underline{V}^{\text{inj}}$  is a good approximation for the incremental solvent volume and that the solvent molar volume can be approximated by its pure molar volume  $V_s^{\text{s}}$ . In eqn (4), it is assumed that the volume of solvent used in the stock solution is equal to the volume of stock solution  $\underline{V}^{\text{stock}}$ . In either case, the errors in the incremental moles  $\Delta n_s$  and  $\Delta n_i$  are anticipated to be considerably less than 1%. As seen in the results section, the error bounds for partial molar volumes are a little larger than 1%. Therefore, there are other sources of error in this study which are greater than those introduced by the approximations eqn (3) and (4).

Since it is difficult to introduce very small and precise quantities of solutes (accuracy of  $10^{-4}$  g or better) directly into the present system without introducing further mass balance and other errors, the present method of preparing stock solutions was used. This issue will be addressed further in the discussion.

#### Total molar volumes and mole fractions

The primary quantities used in this study for modeling purposes are the total molar volume  $V_m$  and mole fractions. The total molar volume is defined by eqn (5)

$$V_{\rm m} = \frac{(n_{\rm s}^{\rm init} + \sum \Delta n_{\rm s})M_{\rm s} + \sum_{i} (\sum \Delta n_{i})M_{i}}{\rho \left[ n_{\rm s}^{\rm init} + \sum \Delta n_{\rm s} + \sum_{i} (\sum \Delta n_{i}) \right]}$$
(5)

where the experimental solution density  $\rho$  appears in the denominator. Note that the small incremental errors in moles, *i.e.*  $\Delta n_s$  and  $\Delta n_i$ , appear in both the numerator and denominator. This reduces somewhat the accumulation or propagation of error in the value of  $V_m$ . The same situation, namely, presence of incremental errors in both numerator and denominator of mole fractions also occurs.

#### Numerical aspects

For the multi-component  $[Mo(CO)_6]$ – $[Mn_2(CO)_{10}]$ – $[Re_2(CO)_{10}]$ –toluene semi-batch experiments, a recently developed experimental design<sup>11</sup> was used to obtain an optimal distribution of data points throughout the multi-component composition space.

Band-target entropy minimization (BTEM) was used to recover a *normalized* observable pure component spectrum of species-*i* at the wavenumber range v,  $\hat{a}_{i\times v}$  present in the binary and multicomponent solution, for both the non-reactive and the reactive systems.<sup>22</sup>

The concentrations or moles of the species present in the reactive multi-component solutions were determined using i) the raw experimental FTIR absorbance data,  $A_{kexv}$ , where k denotes the number of spectra taken in one step of semibatch experiment, e denotes the number of semibatch steps, ii) the BTEM normalized reconstructed spectra of total species s,  $\hat{a}_{sxv}$ , iii) information on the initial reagent quantities used in the experiment  $N_{kexv}^0$  and iv) the mole balances for Rh and PPh<sub>3</sub>, which are conserved in the

liquid phase to a very good approximation. The procedure used has been discussed in detail elsewhere.<sup>23–24</sup>

The determination of the partial molar volumes of the species present in the ultra-dilute multi-component solutions was achieved using a simplified form of a newly developed response surface approach to total molar volumetric data.<sup>11</sup> The reaction volume was calculated directly *i.e.* from the differences between limiting partial molar volumes of the products and reactants.<sup>15,25</sup>

In the original multi-component response surface model for dilute mixtures of highly interacting solutes (*i.e.* protic solutes undergoing hydrogen bonding), the total molar volume  $V_m$  (T, P, x) can be represented by 3 sets of terms, namely linear, bilinear and higher interaction terms eqn (6).

$$V_{\rm m}(T, P, \mathbf{x}) = \sum_{i=1}^{N} a_i x_i + \sum_{i=1}^{N-1} \sum_{j>i}^{N} a_{ij} x_i x_j + \sum_{i=1}^{N-1} \sum_{j>i}^{N} \gamma_{ij} x_i x_j (x_i - x_j)$$
(6)

Notation T, P, x and N represent temperature, pressure, mole fraction and number of components respectively. Given a set of appropriate experimental values for  $V_m$ , the coefficients  $a_i$ ,  $a_{ij}$ , and  $\gamma_{ij}$  can be solved, and finally, the infinite dilution partial molar volumes and volumes of interaction can be determined.<sup>11</sup>

For the case of ultra dilute multi-component solutions of weakly or negligibly interacting solutes, changes to eqn (6) should be made. First, the bilinear and higher interaction terms can probably be neglected (eqn (7) and (8)).

$$V_{\rm m}(T, P, \mathbf{x}) = \sum_{i=1}^{N} \alpha_i x_i + \sum_{i=1}^{N-1} \sum_{j>i}^{N} \alpha_{ij} x_i x_j \tag{7}$$

$$V_{\rm m}(T, P, \mathbf{x}) = \sum_{i=1}^{N} \alpha_i x_i \tag{8}$$

Secondly, eqn (7) and (8) can be re-arranged, in order to avoid illconditioning<sup>26,27</sup> and to make the computation more numerically stable (see eqn (9a)–(9c) or eqn (10), resectively)

$$Y = V_{\rm m}(T, P, \mathbf{x}) - a_{\rm s} x_{\rm s} = \sum_{\text{solute-}i} a_i x_i + \sum_{\text{solute-}i} a_{i\rm s} x_i x_{\rm s} + \sum_{\text{solute-}i} \sum_{\text{solute-}j > i} a_{i\rm j} x_i x_j \qquad (9a)$$

$$Y = V_{\rm m}(T, P, \mathbf{x}) - a_{\rm s} x_{\rm s} = \sum_{\text{solute-}i} (a_i + a_{i\rm s} x_{\rm s}) x_i$$
$$+ \sum_{\text{solute-}i > i} \sum_{a_{ij} x_i x_j} a_{ij} x_i x_j$$
(9b)

$$Y = V_{\rm m}(T, P, \mathbf{x}) - \alpha_{\rm s} x_{\rm s} = \sum_{\rm solute-i} \alpha_{\rm i} x_{\rm i} + \sum_{\rm solute-i} \sum_{\rm solute-j>i} \alpha_{\rm ij} x_{\rm i} x_{\rm j} \qquad (9c)$$

$$Y = V_{\rm m}(T, P, \mathbf{x}) - \alpha_{\rm s} x_{\rm s} = \sum_{\text{solute-}i} \alpha_i x_i$$
(10)

The difference between total molar volume of solution and the solvent that represents the total molar volume of contributing solutes is defined by Y.

Finally, further physical significance can be attached by recognizing that eqn (9c) and eqn (10) are equivalent to eqn (11) and eqn (12),

$$Y = V_{\rm m}(T, P, \mathbf{x}) - x_{\rm s} V_{\rm s}^{\rm o} = \sum_{\rm solute-i} x_i \bar{V}_i^{\infty} + \sum_{\rm solute-i} \sum_{\rm solute-j>i} \alpha_{ij} x_i x_j \qquad (11)$$

$$Y = V_{\rm m}(T, P, \mathbf{x}) - x_{\rm s} V_{\rm s}^{\rm o} = \sum_{\text{solute-}i} x_i \bar{V}_i^{\infty}$$
(12)

respectively, where  $V_s^{\circ}$  (cm<sup>3</sup> mol<sup>-1</sup>) is the molar volume of solvent and  $\bar{V}_i^{\infty}$  (cm<sup>3</sup> mol<sup>-1</sup>) is the limiting partial molar volumes of solutes-*i*. The resulting equations, namely eqn (11) represents a model with linear and bilinear terms which accounts for slight interactions and eqn (12) represents a model with linear terms only (strictly no interaction). It can be noted that precedence exists for such substitutions and re-arrangements, and this basic approach (resulting in a truncated form somewhat similar to eqn (10)) was used previously by Young and Smith for simple 2 solute systems.<sup>28</sup>

## Results

#### Non-reactive binary system

Three different semi-batch binary experiments, namely  $[Mo(CO)_6]$ ,  $[Mn_2(CO)_{10}]$ , and  $[Re_2(CO)_{10}]$  in toluene under argon, were carried out at 298.15 K and 0.1 MPa. Density as well as FTIR spectra of these binary systems were measured. Two experimental runs for each of these binary systems were performed.

From FTIR absorbance spectra, the pure component spectra of  $[Mo(CO)_6]$ ,  $[Mn_2(CO)_{10}]$ , and  $[Re_2(CO)_{10}]$  were obtained by using BTEM from these binary experiments, and the results are shown in Fig. 2. The BTEM analysis did not indicate the presence of any further organometallic impurities. The spectra compare very well with literature references, where maxima at 1983 cm<sup>-1</sup> for  $[Mo(CO)_6]$ ,<sup>29,30</sup> 1976, 2010, 2045 cm<sup>-1</sup> for  $[Mn_2(CO)_{10}]^{31}$  and 1970, 2011, 2070 cm<sup>-1</sup> for  $[Re_2(CO)_{10}]^{32}$  are observed. These spectra were later used for comparison with pure component spectra obtained using BTEM from the multi-component solutions.

The average density measurements (from at least six measurements) for each perturbation were used to determine the apparent molar volumes of  $[Mo(CO)_6]$ ,  $[Mn_2(CO)_{10}]$ , and  $[Re_2(CO)_{10}]$  in toluene at 298.15 K and 0.1 MPa. The apparent molar volume of solute-*i*,  $\phi_i^{33}$  was determined using eqn (13),

$$\phi_i = \frac{V_{\rm m}(T, P, \mathbf{x}) - x_{\rm s} V_{\rm s}^{\rm o}}{x_i} \tag{13}$$

where  $V_{\rm m}(T, P, x)$  was simply calculated from the experimental solution density and total mass in the solution. The molar volume of toluene  $V_{\rm s}^{\rm o}$  was determined from the experimental density of pure toluene and molar mass.

The concentration ranges of the studies (in mole fractions) and the limiting apparent molar volume (extrapolated to zero concentration using a linear regression of the apparent molar volume *versus* mole fraction),<sup>34</sup>  $\phi_i^{\circ}$  of those three solutes are tabulated in Table 1. As shown in Table 1, it was possible to determine these quantities with typically about 1% error, and inter-experimental reproducibility is also very high. These binary systems were measured (a) in order to establish the sensitivity and accuracy of the measurement method in the ultra dilute solute region ( $x_{solute-i}$  less than 152  $\times$  10<sup>-6</sup>), (b) in order to establish



**Fig. 2** The pure component spectra of (1)  $[Mo(CO)_6]$ , (2)  $[Mn_2(CO)_{16}]$  and (3)  $[Re_2(CO)_{16}]$  in toluene obtained from experimental binary absorbance data using BTEM.

**Table 1** Data for binary experiments and limiting apparent molar volumes in toluene at T = 298.15 K and P = 0.1 MPa

Solute- <i>i</i>	Exp	Range of mole fraction $(\times 10^{-6})^{\alpha}$	$\phi_i^{\mathrm{o}}/\mathrm{cm}^3 \mathrm{mol}^{-1}$
[Mo(CO) <sub>6</sub> ] [Mn <sub>2</sub> (CO) <sub>10</sub> ]	1 2 1 2	19.9–149.2 (8) 20.0–149.3 (8) 20.3–151.7 (8) 20.3–151.9 (8)	$175.5 \pm 1.8 \\ 176.6 \pm 0.5 \\ 264.9 \pm 0.8 \\ 266.3 \pm 3.3 \\ 266.$
$[\operatorname{Re}_2(\operatorname{CO})_{10}]$	1 2	16.0-119.5(8) 16.0-120.0(8)	$278.8 \pm 1.3$ $276.9 \pm 0.9$

<sup>*a*</sup> Values in parentheses show number of semi-batch perturbations (data points).

reproducibility, and (c) for comparison purposes with the partial molar volumes obtained from the multi-component solutions and thus to confirm the validity of the utility of the presently developed multi-component approach.

#### Non-reactive multi-component system

It has been shown that experimental design is a crucial factor in utilizing the response surface model for direct determination of partial molar volume of each individual species from multicomponent systems.<sup>11</sup> Therefore, a similar approach is taken in the present study. Three sets of experiments consisting of 12 different compositions each were pre-designed prior to the experimental work. All experiments were started with pure toluene as a major component (solvent) under argon, and subsequently adding one stock solution at a time to change the solution composition. The constraints imposed for the dilute solution region in the current study are shown in eqn (14), (15) and (16),

$$0 \le x_i \le 0.000140 \text{ for } i = 1, 2, 3 \tag{14}$$

$$0.9997 \le x_4 \le 1 \tag{15}$$

$$\sum_{i=1}^{N} x_i = 1$$
(16)

where *N* is the total number of components (in this study, N = 4), subscript-*i* refers to the solutes [Mo(CO)<sub>6</sub>] (1), [Mn<sub>2</sub>(CO)<sub>10</sub>] (2), [Re<sub>2</sub>(CO)<sub>10</sub>] (3) and the major component, toluene (4).

The raw experimental results of the multi-component experiments are shown in Table S1 (ESI<sup>†</sup>). The mole fractions of the three organometallic solutes [Mo(CO)<sub>6</sub>], [Mn<sub>2</sub>(CO)<sub>10</sub>], and [Re<sub>2</sub>(CO)<sub>10</sub>] were calculated from the actual experimental mass balance of the perturbations used in the experiments.<sup>35</sup> Also, (a) the density differences between the pure solvent and the multi-component solution, and (b) the volume differences *Y* defined by the lefthand-side of eqn (11) or eqn (12), for each perturbation of the three semi-batch runs are tabulated in Table S1.<sup>†</sup> The 3-dimensional plots generated by the composition data and the volume difference *Y* data constitute the response surface maps for these systems, and form the basis for the analytical approach.

For every perturbation/injection, the absorbance spectra of the mixtures were measured. An example of the multi-component absorbance spectra (taken from step 12 of semi-batch run-1) before and after preconditioning (*e.g.* background and solvent subtraction<sup>36</sup> as well as baseline correction<sup>37</sup>) is given in Fig. 3. The pure component spectra reconstruction results *via* BTEM are shown in Fig. 4(a). The inner product(s) between unit vectors of reconstructed pure component spectra of [Mo<sub>(</sub>CO)<sub>6</sub>], [Mn<sub>2</sub>(CO)<sub>10</sub>], and [Re<sub>2</sub>(CO)<sub>10</sub>] and their references (Fig. 2) are 0.9993, 0.9920, and 0.9970, respectively. Since the pure component spectra are accurate, the relative concentrations of these solutes



Fig. 3 Absorbance spectra of multi-component non-reactive system of  $[Mo(CO)_6]$ ,  $[Mn_2(CO)_{10}]$ , and  $[Re_2(CO)_{10}]$  in toluene (i) before and (ii) after preconditioning (run I, step 12).

can be obtained reliably, even from these highly overlapping spectral data, using a least squares fitting procedure. Fig. 4(b) shows the concentration profiles obtained from the corresponding perturbations in a multi-component experiment (run I). BTEM analysis did not indicate the formation of any new additional carbonyls during these experiments.



**Fig. 4** (a) Pure component spectra of (1)  $[Mo(CO)_6]$ , (2)  $[Mn_2(CO)_{10}]$  and (3)  $[Re_2(CO)_{10}]$  in toluene from a multi-component study using BTEM. (b) Relative concentration profile of pertinent component of run I.

Since these multi-component experiments were conducted in the ultra-dilute range, the full response surface model eqn (6) was reasonably truncated. Two truncated models, namely models with linear and bilinear terms (linear-bilinear model), eqn (11), and models with linear terms only (linear model), eqn (12), were used to describe the response surface map in this ultradilute range for the multi-component organometallic solutions. The parameters describing the response surface map contain the volumetric information of each solute in the infinite dilution. Thus, the individual limiting partial molar volume of each species can be determined simultaneously from the multi-component system.

The data in Table S1,<sup>†</sup> with the exclusion of the binary composition data, were used in the analysis, and a least squares method was applied to determine the parameters,  $\bar{V}_i^{\infty}$  in linear model eqn (12) and  $\bar{V}_i^{\infty}$  as well as  $a_{ij}$  in the linear-bilinear model eqn (11). The limiting partial molar volumes of the solutes-*i* are provided by the parameters  $\bar{V}_i^{\infty}$  for both models as shown in eqn (11), (12). A comparison of the values resulting from the binary and multi-component studies can be seen in Table 2.

As can be seen in Table 2, the limiting partial molar volumes for  $[Mo(CO)_6]$  and  $[Mn_2(CO)_{10}]$  obtained from the multi-component solutions (linear model) are in agreement with those obtained from the binary solutions, but the data for  $[Re_2(CO)_{10}]$  is slightly outside the confidence limits. This indicates the limitations of determining the partial molar volumes from this multi-component solution using a linear model alone. Table 2 also shows that the limiting partial molar volumes of all the solutes in the multi-component solutions (linear–bilinear model) are in agreement with those obtained from the binary solutions. This indicates that the determination of the partial molar volumes from this multi-component solution is possible using the more robust linear–bilinear model which correctly captures the curvature of

**Table 2** Comparison of limiting partial molar volume,  $\bar{V}_i^{\infty}$  (cm<sup>3</sup> mol<sup>-1</sup>) in toluene at T = 298.15 K and P = 0.1 MPa determined from binary and multi-component studies

	Limiting partial molar volume, $ar{V}^{\infty}_i/ ext{cm}^3  ext{ mol}^{-1}$				
		Multi-component			
Solute	Binary <sup>a</sup>	Linear	Linear and bilinear		
[Mo(CO) <sub>6</sub> ]	$176.1 \pm 1.9$	178.7 ± 1.1 (1.48)	$176.4 \pm 2.5 \ (0.17)$		
$[Mn_2(CO)_{10}]$	$265.6 \pm 3.4$	$261.9 \pm 1.1 (1.39)$	$265.1 \pm 2.4 (0.19)$		
$[\text{Re}_2(\text{CO})_{10}]$	$277.9 \pm 1.6$	$269.9 \pm 1.1$ (2.88)	$276.8 \pm 2.4 (0.40)$		

" Average value from binary experiments 1 and 2 as listed in Table 1. Values in parentheses show the percentage deviations from binary studies results.

the response surface. The average uncertainty in the determined partial molar volumes is *ca*. 1%, and the values obtained from binary and multi-component data differ by only *ca*. 0.3%. This is further verified by analysis of the response surface curvature coefficients  $a_{ij}$ , determined to be  $a_{12} = 33183 \pm 31990$  (cm<sup>3</sup> mol<sup>-1</sup>),  $a_{13} = -57561 \pm 30913$  (cm<sup>3</sup> mol<sup>-1</sup>),  $a_{23} = -89926 \pm 31609$  (cm<sup>3</sup> mol<sup>-1</sup>). From these coefficients, it is clear that the presence of component 3, the [Re<sub>2</sub>(CO)<sub>10</sub>], gives rise to non-negligible non-linearities in the multi-component data. In straightforward physical-chemical terms, association between some of the solutes is occurring.

## Multi-component reactive organometallic system

**Binary reference experiments.** Two different semi-batch binary experiments, with either  $[Rh_4(CO)_{12}]$  or PPh<sub>3</sub> in n-hexane under argon, were carried out at 298.15 K and 0.1 MPa. Density as well as FTIR spectra of these binary systems were measured. The purpose of these binary studies was (i) to identify and/or quantify the impurities that might be present, (ii) to obtain pure component reference spectra and (iii) for later comparison with the partial molar volumes obtained from the multi-component solutions. Two experimental runs and one experimental run were carried out for the binary studies of  $[Rh_4(CO)_{12}]$  and PPh<sub>3</sub> in n-hexane, respectively.

FTIR absorbance spectra of the binary system of  $[Rh_4(CO)_{12}]$  in n-hexane were investigated in the metal carbonyl vibrational range 1800–2200 cm<sup>-1</sup>. BTEM was applied and maxima for [Rh<sub>4</sub>(CO)<sub>12</sub>] were observed at 1886s, 2044s, 2070vs and 2074vs cm<sup>-1</sup>.<sup>6,12,13,38</sup> In addition, the presence of the high nuclearity cluster  $[Rh_6(CO)_{16}]$ , an impurity, was indicated by vibrational bands at 1819s and 2075vs cm<sup>-1</sup>.<sup>6,39</sup> Quantitative analysis shows that the maximum concentrations of [Rh<sub>6</sub>(CO)<sub>16</sub>] throughout experiment-1 and experiment-2 are less than  $0.2 \times 10^{-6}$  and  $0.15 \times 10^{-6}$  mole fractions, respectively. The extremely low amount of  $[Rh_6(CO)_{16}]$ is, in part, the result of good experimental procedure, in order to minimize oxygen/water/light present in the reactor system. In this study, in both binary and multi-component reactive systems, the amount of impurity present was very small, and its presence will not significantly alter the volumetric analysis. Further details of the numerical analysis are provided in the following section.

In the binary experiment with  $PPh_3$  in n-hexane, the spectroscopic analysis was performed by focusing on both the far-infrared region in the range of 550–850 cm<sup>-1</sup> and in mid-infrared region in the range of 1800–2200 cm<sup>-1</sup> using KBr windows. BTEM showed

**Table 3** Data for binary experiments and limiting apparent molar volume  $\phi_i^{\circ}$  (cm<sup>3</sup> mol<sup>-1</sup>) in n-hexane at T = 298.15 K and P = 0.1 MPa

Solute- <i>i</i>	Exp	Range of mole fraction $(\times 10^{-6})^{a}$	$\phi_i^{ m o}/{ m cm}^3~{ m mol}^{-1}$
$[Rh_4(CO)_{12}]$	1 2	30–65 (5) 30–65 (5)	$313.2 \pm 4.6^{b}$ $310.8 \pm 6.4^{b}$
PPh <sub>3</sub>		40-380 (8)	$219.8\pm2.2$

<sup>*a*</sup> Values in parentheses show the number of semi-batch perturbations (data points). <sup>*b*</sup> These limiting apparent molar volumes were obtained from average values of the apparent molar volume within the concentration range.

that the free PPh<sub>3</sub> had vibrations at 696 and 742 cm<sup>-1</sup> in the range of 550–850 cm<sup>-1</sup> as well as 1808, 1879, 1893, 1948 and 1963 cm<sup>-1</sup> in the range of 1800–2200 cm<sup>-1</sup>.<sup>40</sup> It did not indicate other species, including the most probable degradation product OPPh<sub>3</sub> (triphenylphosphine oxide) with bands at 698, 725, 753 and 759 cm<sup>-1</sup>.<sup>41</sup>

The average density measurements (from at least six measurements) for each perturbation were used to determine the apparent molar volumes  $\phi_i$  of [Rh<sub>4</sub>(CO)<sub>12</sub>] and PPh<sub>3</sub> in n-hexane from the binary experiments under argon at 298.15 K and 0.1 MPa using eqn (13).

The concentration ranges of these binary studies (given in mole fractions) and the limiting apparent molar volume  $\phi_i^{\circ}$  are tabulated in Table 3. As shown in Table 3, the limiting apparent molar volumes of both binary systems could be determined with typically less than 1% error, and inter-experimental reproducibility for two binary runs of [Rh<sub>4</sub>(CO)<sub>12</sub>] in n-hexane is considered very high.

**Multi-component reactive experiments.** The ligand substitution reaction eqn (1) was conducted in n-hexane solvent at 298.15 K and 0.1 MPa under argon. The reaction was run in semibatch mode by introducing perturbations PPh<sub>3</sub> into the reactor in sub-stoichiometric amounts. The reaction is very fast.<sup>12-14</sup> Free PPh<sub>3</sub> was not observed in any of the *in-situ* FTIR reaction spectra. The mono-substituted product [Rh<sub>4</sub>(CO)<sub>11</sub>PPh<sub>3</sub>] was totally soluble in n-hexane in the range of concentrations used (less than  $65 \times 10^{-6}$  mole fraction). During the experiments, both density and FTIR spectroscopic measurements were performed. The changes in the metal carbonyl vibrational bands in the range 1800– 2200 cm<sup>-1</sup> during one of the semi-batch runs is shown in Fig. 5.

Spectral preconditioning, namely subtraction of background and n-hexane<sup>36</sup> and baseline drift correction<sup>37</sup> were initially performed before further analysis (*e.g.* reconstructed pure component spectra by BTEM and quantitative analysis). As an example, one selected absorbance spectra of one reaction mixture before and after preconditioning are presented in Fig. 6.

Next, BTEM was applied to the preconditioned spectra to reconstruct all the pure component spectra involved in the reaction. The spectra of the major pure components, namely reactant  $[Rh_4(CO)_{12}]$  and the product  $[Rh_4(CO)_{11}PPh_3]$ , as well as the minor pure components  $[Rh_6(CO)_{16}]$  and the di-substituted product  $[Rh_4(CO)_{10}(PPh_3)_2]$  were successfully recovered with high signal to noise ratio and are presented in Fig. 7. The reconstructed spectra of minor products  $[Rh_6(CO)_{16}]$  and  $[Rh_4(CO)_{10}(PPh_3)_2]$  have lower signal to noise ratios as they exist in trace amounts in solution. BTEM analysis did not indicate the presence of any



**Fig. 5** *In-situ* FTIR reaction spectra of the ligand substitution reaction of  $[Rh_4(CO)_{12}]$  with PPh<sub>3</sub> at 298.15 K and 0.1 MPa (under argon) in the range 1800–2200 cm<sup>-1</sup> during a 12 perturbation semi-batch experiment. The nominal rhodium concentration is *ca.* 65 × 10<sup>-6</sup> mole fraction.



Fig. 6 Absorbance spectra of reaction (i) before and (ii) after preconditioning.

other metal carbonyls nor free PPh<sub>3</sub> during these experiments using mid-infrared spectroscopy. Additional experiments were carried out, focusing on the far-infrared region 550–850 cm<sup>-1</sup> using a cell with KBr windows, and these experiments further confirmed the absence of free PPh<sub>3</sub>. The FTIR spectra of mono-substituted product [Rh<sub>4</sub>(CO)<sub>11</sub>PPh<sub>3</sub>] at 1856m, 1875m, 1906vw, 2011w, 2022ms, 2031s, 2054vs, 2057vs, and 2087s cm<sup>-1</sup> and di-substituted product [Rh<sub>4</sub>(CO)<sub>10</sub>(PPh<sub>3</sub>)<sub>2</sub>] at 1822mw, 1859mw, 2004m, 2016ms, 2021m, 2044s, and 2069s cm<sup>-1</sup> are in good



Fig. 7 Recovered pure component spectra obtained by BTEM: (i)  $[Rh_4(CO)_{12}]$ , (ii)  $[Rh_4(CO)_{11}PPh_3]$ , (iii)  $[Rh_4(CO)_{10}(PPh_3)_2]$  and (iv)  $[Rh_6(CO)_{16}]$ .

agreement with those reported in the literature.<sup>12,13</sup> The spectral deconvolution of the latter species is slightly sub-optimal due to its very low concentrations and the limited variation in its concentrations (variance of signals).

Further *in-situ* quantitative spectroscopic analysis was carried out by using spectroscopy and mass balances based on injected mass. The results of these quantitative analyses for both the binary and reaction systems are presented in Fig. 8(a) and (b), respectively. It can be seen that satisfactory results for  $[Rh_4(CO)_{12}]$ are observed in both binary and reaction systems. However, a noticeable discrepancy between the two approaches is observed in Fig.8(b) for [Rh<sub>4</sub>(CO)<sub>11</sub>PPh<sub>3</sub>] at high concentrations. The calculation based on injected mass alone, neglects the influence of the side-reaction, and thus overestimates the real moles of [Rh<sub>4</sub>(CO)<sub>11</sub>PPh<sub>3</sub>] in the solution. Whyman also noticed the formation of di-substituted product,  $[Rh_4(CO)_{10}(PPh_3)_2]$  when he added mole ratio  $PPh_3$  :  $[Rh_4(CO)_{12}] = 1 : 1.^{12}$  These deviations became more pronounced at mole ratios  $PPh_3$ :  $[Rh_4(CO)_{12}]$  greater than 0.7:1 where the second substitution product becomes non-negligible. Throughout experiment-1 and experiment-2, the maximum concentrations of  $[Rh_4(CO)_{10}(PPh_3)_2]$  were less than  $2.2 \times 10^{-6}$  and  $3.3 \times 10^{-6}$  in mole fractions, respectively.

Another species which can be considered as an unavoidable impurity, namely [Rh<sub>6</sub>(CO)<sub>16</sub>], was also monitored in the present study. Quantitative analysis showed that the maximum concentrations of [Rh<sub>6</sub>(CO)<sub>16</sub>] throughout experiment-1 and experiment-2 were less than  $0.23 \times 10^{-6}$  and  $0.14 \times 10^{-6}$  in mole fractions, respectively.

Quantitative analysis of the first few perturbations, where mole ratio PPh<sub>3</sub> : [Rh<sub>4</sub>(CO)<sub>12</sub>] = 0.0–0.7 : 1 showed that the maximum concentration of [Rh<sub>4</sub>(CO)<sub>10</sub>(PPh<sub>3</sub>)<sub>2</sub>] in experiment-1 and experiment-2 were less than  $1.4 \times 10^{-6}$  and  $2.4 \times 10^{-6}$  mole fractions, respectively. These concentrations are considered sufficiently low so that the assumption that the contribution of the minor component is negligible can be reasonably applied.



Fig. 8 Mole(s) comparison determined from spectra prediction (solid symbols) and mass injection (open symbols) of (a) binary system of  $[Rh_4(CO)_{12}]$  and (b) reaction system. Symbols:  $\bullet$ ,  $[Rh_4(CO)_{12}]$ ;  $\bullet$ ,  $[Rh_$ 

Accordingly, the error induced by this assumption becomes imbedded in the determination of limiting partial molar volume of  $[Rh_4(CO)_{11}PPh_3]$ .

The bulk density of the solutions increased noticeably as a function of mole ratio PPh<sub>3</sub> :  $[Rh_4(CO)_{12}]$  as shown in Fig. 9. Especially at mole ratio PPh<sub>3</sub> :  $[Rh_4(CO)_{12}] = 0.0-0.7 : 1$ , the reaction system can be approximated/modeled as a 2 solute system, namely the reactant  $[Rh_4(CO)_{12}]$  and the major product  $[Rh_4(CO)_{11}PPh_3]$  in the pseudo multi-component solution consisting of n-hexane– argon with dissolved CO<sup>42</sup> and in the presence of two trace components  $[Rh_6(CO)_{16}]$  and  $[Rh_4(CO)_{10}(PPh_3)_2]$ . In principle, either eqn (11) or eqn (12) can be applied to determine the limiting partial molar volume of  $[Rh_4(CO)_{12}]$  and  $[Rh_4(CO)_{11}PPh_3]$ in this multi-component reactive solution. However, due to the more limited concentration range used ( $65 \times 10^{-6}$  mole fraction compared to  $140 \times 10^{-6}$  mole fraction in the non-reactive multicomponent), and few data points measured, the use of eqn (12) with linear terms only was considered more appropriate.



Fig. 9 Density of reaction mixture at T = 298.15 K and P = 0.1 MPa.

Total molar volume  $V_m(T, P, x)$  was calculated from the experimental solution density and total mass in the solution (*e.g.* total mass of solvent, major and minor components). The molar volume of n-hexane  $V_s^o$  was determined from the experimental

density of pure n-hexane and molar mass. Two major solutes are considered in the modified response surface model, namely  $[Rh_4(CO)_{12}]$  and  $[Rh_4(CO)_{11}PPh_3]$ . In order to retain a tractable problem and avoid unnecessary propagations in error, these two quantities were treated as lumped parameters, whereby the mole fractions of  $[Rh_4(CO)_{12}]$  and the impurity  $[Rh_6(CO)_{16}]$  were combined and the mole fractions of  $[Rh_4(CO)_{11}PPh_3]$  and the impurity  $[Rh_4(CO)_{10}(PPh_3)_2]$  were combined. All mole fractions used for this analysis are based on Fig. 8(b). The present study did not attempt to include minor trace species explicitly in a 4 solute problem since their concentrations are very low and thus the inverse problem becomes severely ill-conditioned.

A comparison of the resulting limiting partial molar volume determined from multi-component reactive solutions with separate binary study of  $[Rh_4(CO)_{12}]$  in n-hexane–argon alone, are summarized in Table 4.

It can be seen from Table 4 that the two multi-component reaction experiments are quite consistent. The limiting partial molar volumes of  $[Rh_4(CO)_{12}]$  obtained from binary and multi-component are very close, especially for experiment-1. The values are statistically overlapping within the 95% confidence limit. Limiting partial molar volumes of  $[Rh_4(CO)_{11}PPh_3]$  obtained from multi-component reaction solutions are slightly different. The discrepancy is probably due to the fact that the maximum concentration of the trace impurity  $[Rh_4(CO)_{10}(PPh_3)_2]$  is slightly higher in experiment-2 (*ca.* 2.4 × 10<sup>-6</sup>) compared to experiment-1

**Table 4** Mole fraction range and limiting partial molar volume,  $\bar{V}_i^{\infty}$  (cm<sup>3</sup> mol<sup>-1</sup>) of [Rh<sub>4</sub>(CO)<sub>12</sub>] and [Rh<sub>4</sub>(CO)<sub>11</sub>PPh<sub>3</sub>]

Solute- <i>i</i>	Exp	Mole fraction range ( $\times 10^{-6}$ )	$\bar{V}_i^{\infty}/\mathrm{cm}^3 \mathrm{mol}^{-1}$
[Rh <sub>4</sub> (CO) <sub>12</sub> ]	1 2	20–65 20–65	$310.7 \pm 2.7$ $303.3 \pm 2.2$
[Rh <sub>4</sub> (CO) <sub>11</sub> PPh <sub>3</sub> ]	1 2	0–42 0–42	$312.0 \pm 5.4^{a}$ $461.5 \pm 4.5$ $473.8 \pm 2.3$

" Average value from two binary experiments given in Table 3.

(*ca.*  $1.3 \times 10^{-6}$ ). This fact suggested that the limiting partial molar volume of pure [Rh<sub>4</sub>(CO)<sub>11</sub>PPh<sub>3</sub>] must be slightly smaller than the values obtained from this study.

The reaction volume for eqn (1) can be directly determined by using the differences of the limiting partial molar volumes of products and limiting partial molar volumes of reactants as shown in eqn (17).<sup>15,25</sup>

$$\Delta_{\rm r} V = \bar{V}_{\rm Rh_4(CO)_{11}PPh_3}^{\infty} + \bar{V}_{\rm CO}^{\infty} - \bar{V}_{\rm Rh_4(CO)_{12}}^{\infty} - \bar{V}_{\rm PPh_3}^{\infty}$$
(17)

The more reliable limiting partial molar volumes of [Rh<sub>4</sub>(CO)<sub>12</sub>] and [Rh<sub>4</sub>(CO)<sub>11</sub>PPh<sub>3</sub>] obtained from experimental run-1 were selected to calculate the volume of reaction. The limiting partial molar volume of PPh<sub>3</sub> from the binary study was used since it could not be observed and thus determined directly from a multicomponent study. A partial molar volume of CO,  $\bar{V}_{CO}^{\infty}$  equal to 52 cm<sup>3</sup> mol<sup>-1</sup> reported by Connoly and Kandalic was used.<sup>43</sup> As a result, the reaction volume determined by eqn (17) is equal to  $-17.0 \pm 5.7$  cm<sup>3</sup> mol<sup>-1</sup>.

## Discussion

## Multi-component non-reactive system

It was shown that using three semi-batch experiments pre-designed prior to experimental work, compositional data can be optimally distributed in the composition space of this quaternary system of three solutes. This experimental design methodology was crucial to ensure that the response surface would capture the needed system characteristics, such as sufficient information on the surface curvature in the limit of infinite dilution as well as the nonlinearities that might arise due to interactions between solutes and/or solvent. In addition, the optimal distribution will also be cost effective, as fewer experiments are needed, and such a distribution allows more easily discernable outliers in the data set.<sup>44</sup>

In this multi-component organometallic study, density measurements were performed based on the above experimental design in a region of ultra-dilute concentration (*ca.*  $x_i$  less than  $140 \times 10^{-6}$ mole fraction). Such dilute solutions are a very common situation in organometallic chemistry and homogeneous catalysis due to the limited solubility of many of the compounds involved as well as frequent cost constraints. The very dilute concentrations used introduce a new and serious complication in the computations, and this arises due to the fact that the concentration *range* of solvent and solutes spans many orders of magnitude.

In the most general approach (see ref. 11), total molar volume  $V_{\rm m}$  (T, P, x) is a response directly obtained from the bulk density measurements. However, for very dilute solutions it cannot be directly applied without modification due to the very different range of concentrations spanned by the solvent and the solutes *i.e.*  $x_{\rm solvent} \approx 0.99999-0.999999$  and  $x_{\rm solute} \approx 0.00001-0.000001$  that appear on the right hand side of eqn (6). This creates a problem of *numerical ill-conditioning*. In order to circumvent this problem, eqn (6) was rearranged, to generate a new modified response surface Y defined by eqn (11) and (12), so that only solute concentrations are required on the right hand side.

Two closely related response surface models, linear and linear– bilinear, were developed to describe Y from the multi-component data. Both the linear and the linear–bilinear models provided good limiting partial molar volumes of each solute. This conclusion was based on comparison with separate determinations of limiting partial molar volume performed in binary experiments. The average error in the linear model was about 2%. We consider this error to be quite acceptable, indeed very small, when the sensitivity of organometallics and their very high dilution are taken into consideration. Moreover, the average error in the linear-bilinear model was considerably lower at 0.3%. This suggests that genuine non-linearities in the data are present, and that intermolecular interactions might exist.

The above analysis of the "non-reactive" multi-component system would be null-and-void if some degradation/reaction of the species present had occurred. Therefore, sensitive on-line FTIR measurements were made in order to confirm that no new complexes had been formed. Formation of any new complexes would definitely cause the misinterpretation of the volumetric results. The FTIR measurements did not indicate the presence of any new species. In addition, band-target entropy minimization (BTEM) was also applied to the data set in order to identify any new spectroscopic features. BTEM did not indicate the presence of any complexes other than the three solutes used.

#### Multi-component reactive system

The determination of the limiting partial molar volumes of reactive species from a multi-component reactive solution appears possible using the present methodological approach, at least for relatively simple systems like those present here. However, in order to achieve accurate parameter estimation, simultaneous spectroscopic and density measurements are necessary. The former measurements together with signal processing/multivariate analysis permit the accurate quantitative determination of concentrations needed for the proper construction of the response surface model. As shown in the Results section, the spectroscopy analysis resulted in the identification of two impurities/side products in the system, namely, [Rh<sub>6</sub>(CO)<sub>16</sub>] and [Rh<sub>4</sub>(CO)<sub>10</sub>(PPh<sub>3</sub>)<sub>2</sub>]. The simultaneous application of at least one spectroscopic tool and one bulk fluid property measuring instrument, appear to be a pre-requisite for the accurate determination of the physico-chemical properties of reactive species in a multi-component reactive system.

The determined limiting partial molar volumes of the solutes in this multi-component reactive system compared well with those that could be determined from separate binary measurements (*e.g.* [ $Rh_4(CO)_{12}$ ]). The ability to determine the volumetric characteristics of reacting organometallics presents a host of new opportunities (*vide infra*). Moreover, the reaction volume could also be determined and the sign was negative. Under conditions where an observable equilibrium situation might exist, increasing pressure will shift the equilibrium to the product side. The uncertainty in the value of the reaction volume is actually quite large, and this has occurred due to the accumulation of the uncertainties of all the limiting partial molar volumes involved. This is an area where future improvement in the methodology can and should be made.

#### Corresponding solid state molar volumes

The volumetric behavior of a dissolved species, *i.e.* a metal complex in solution at infinite dilution, should be expected to

be different from its corresponding solid-state molar volume, obtained from its crystallographic data. In solution, the volumetric behavior of a solute is characterized by its limiting partial molar volume, which can be conveniently partitioned into intrinsic and solvation parts.45 The intrinsic part is represented by the van der Waals radius of species and the solvation part is believed to represent all changes associated with changes in polarity, electrostriction, and dipole interactions.<sup>46</sup> In this regard, the solidstate molar volumes of the following metal carbonyl clusters are calculated from their solid state density and respective molar mass: [Mo(CO)<sub>6</sub>] (134.69 cm<sup>3</sup> mol<sup>-1</sup>),<sup>47,48</sup> [Mn<sub>2</sub>(CO)<sub>10</sub>] (213.11 cm<sup>3</sup> mol<sup>-1</sup>),<sup>49</sup> and [Re<sub>2</sub>(CO)<sub>10</sub>] (224.23 cm<sup>3</sup> mol<sup>-1</sup>),<sup>49</sup> and [Rh<sub>4</sub>(CO)<sub>12</sub>] (296.73 cm<sup>3</sup> mol<sup>-1</sup>).<sup>50</sup> As noted in this study, the first three metal carbonyl complexes showed an increase in their volumes when they are dissolved in toluene at infinite dilution of ca. 31%, 25%, and 24%, respectively, while the latter carbonyl complex only increases its volume by about 6% when it is dissolved in n-hexane. The results apparently indicate that there are distinctly different volumetric aspects associated with the process of dissolution/solvation since such dissimilar behavior occurs.

It should be noted that these results appear to be consistent with the theory developed by Lee<sup>51</sup> for the partial molar volume of a solute in infinitely dilute hard-sphere binary mixtures. In this theory, the increase of the volume in solution depends primarily on the size of solvent molecule and the packing density of the solvent. The greater the solute-to-solvent radius ratio, the smaller the increased volume is achieved. However, no clear-cut conclusions can be drawn from the present results. Too many physico-chemical issues are associated with dissolution/solvation such as polarity, dipole–dipole interactions,<sup>46</sup> and issues of solute– solvent volumetric dissimilarity.<sup>52</sup>

#### Sensitivity analysis

The present contribution appears to be the first attempt to determine limiting partial molar volumes of ultra-dilute dissolved organometallic compounds experimentally, in both non-reactive and reactive multi-component systems. The limiting partial molar volumes were determined by using two primary experimental measurements, namely density and weight, which have accuracies of  $1 \times 10^{-6}$  in g cm<sup>-3</sup> and  $10^{-5}$  in g, respectively. Assuming that other possible errors are insignificant, and applying the standard propagation of error method to determine the uncertainty in the values of apparent molar volume,53,54 the estimated upper bound limits of accuracies based on the average range of concentrations listed in Tables 2 and 3 are ca. 2% to 3% for [Mo(CO)<sub>6</sub>],  $[Mn_2(CO)_{10}]$ , and  $[Re_2(CO)_{10}]$ , ca. 1% for PPh<sub>3</sub> and ca. 6% for  $[Rh_4(CO)_{12}]$ . The relatively low accuracy of metal cluster concentration is clearly due to the ultra dilute concentration range selected for measurement. In future studies, the accuracy of measurement can be substantially improved by selecting a higher concentration range for study (within the solubility range).

#### Sampling versus online techniques

In the present study for "non-reactive" and "reactive" systems, a closed system with on-line density measurements and *in-situ* spectroscopic measurements were used throughout. The reasons are self evident. (1) Measurements as precise as possible were needed in the present study (in order to have good fits to the

polynomial models), and system sampling is known to introduce significant genuine-replicate error,<sup>55</sup> even in systems involving stable solutes and low vapor pressure solvent. (2) Closed systems with on-line/*in-situ* measurements are the most frugal with resources since a much larger number of measurements can be made with a minimum amount of material. (3) Some of the organometallics used, even in the "non-reactive" experiments were sensitive to moisture, oxygen, light, *etc.*, so extra and unnecessary manipulations are not advisable. (4) Finally, the logistics of on-line/*in-situ* data acquisition is particularly well suited to reactive studies.

#### Classical $(\partial \ln K_{eq} / \partial P)_T$ versus response surface approach

The classic ( $\partial \ln K_{eq}/\partial P$ )<sub>T</sub> for the determination of reaction volumes is well suited to reactions having an observable equilibrium and has been used extensively to study and classify inorganic, organic and organometallic reactions.<sup>56</sup> Normally, significant pressure intervals, *ca.* 1000 bar must be used. This classical approach typically results in rather precise determinations of reaction volumes (accuracy *ca.* 0.2 cm<sup>3</sup> mol<sup>-1</sup>). However, as pointed out by Kiselev *et al.*, applied pressure affects both the free energy of reaction and changes in the solute–solvent and solvent–solvent interactions, and therefore, artifacts in the determined volumes of reaction may occur.<sup>57</sup>

The present response surface approach does not require a system with an observable equilibrium and the reaction volume can be determined at isobaric conditions. Moreover, the present method affords information on the individual partial molar volumes at a particular temperature and pressure, and in principal the volumes of interaction as well. The determination of reaction volume is based on the differences between partial molar volumes of the products and reactants. However, at the moment and as shown in these examples, typical errors in the reaction volume are of the order of 5 cm<sup>3</sup> mol<sup>-1</sup>, due in part to the accumulation of error in the partial molar volumes. This is an issue which requires further consideration in future studies.

## Conclusion

The present response surface methodology provides a general framework for determining the partial molar volumes of solutes in both non-reactive and reactive multi-component solutions. The methodology relies on compositional data together with measurement of the total liquid volume in order to determine the volumetric contributions of each constituent present. In contrast to previous methods, the present approach does not require any binary information what-so-ever. Accordingly, this provides the opportunity to study reactive systems and non-isolatable species. The potential applications of the new approach are numerous. Issues concerning propagation of error, during the determination of reaction volumes, and extension to systems possessing many simultaneous solutes are areas for future study.

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- 21 (a) KBr windows were used in a separate qualitative study to differentiate free and bound PPh<sub>3</sub>. Free PPh<sub>3</sub> has vibrations at 696vs and 742vs cm<sup>-1</sup> in the range of 550–850 cm<sup>-1</sup> as well as 1808vw, 1879vw, 1893vw, 1948vw and 1963vw cm<sup>-1</sup> in the range of 1800–2200 cm<sup>-1</sup>. Bound PPh<sub>3</sub> has a very strong split band at 694 and 705 cm<sup>-1</sup> and at 743vs cm<sup>-1</sup>; (b) CaF<sub>2</sub> windows were used in all quantitative measurements.
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