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Combining *in situ* FTIR spectroscopy, BTEM analysis, bulk density measurements and DFT for two Diels–Alder reactions. A general approach for partial molar volume and reaction volume analyses[†]

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Two organic reactions, namely the reaction of cyclopentadiene (CPD) and dimethyl acetylene dicarboxylate (DMAD) and the dimerization reaction of CPD were conducted in toluene at 298.1 K at atmospheric pressure and measured by *in situ* FTIR spectroscopy. Band-target entropy minimization (BTEM) analyses were employed for obtaining the pure component spectra of the solutes and their corresponding concentrations. The solute concentrations and the bulk density data were used to evaluate the partial molar volumes of the solute constituents. The partial molar volumes evaluated from this multi-component approach were in good agreement with those determined from independent binary solution measurements. The corresponding volumes of reaction for the CPD + DMAD and dimerization CPD + CPD reactions were determined to be -37 ± 3 cm³ mol⁻¹ and -31 ± 2 cm³ mol⁻¹, respectively. For completeness, DFT calculations were performed and used to rationalize the vibration modes corresponding to the BTEM spectral estimates as well as to provide predictions of the molar volumes of the solutes. The present study demonstrates the usefulness of a combined spectroscopic, signal processing, bulk density measurement and DFT approach to the determination of partial molar volumes and volumes of reaction directly from the multi-component reactive systems.

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Introduction

The partial molar volume (PMV) has been a subject of interest in both theoretical and experimental studies for decades.¹⁻⁷ As one of the most investigated physico-chemical properties, PMV gives information on the molecular size or space occupied by a solute molecule and facilitates better understanding of solute behavior in solution *i.e.* solute–solute and solute–solvent interactions.

PMV has also been used to analyze the effect of pressure on chemical reactions. Many classes of organic, inorganic and organometallic reactions are pressure dependent and therefore exhibit non-zero volumes of reaction.⁸⁻¹⁰ In some reactions, the volume of reaction can be very large (on the order of 30–50 cm³ mol⁻¹) and hence such reactions are very sensitive to pressure.⁸ In practical terms, understanding of the volume of reaction can allow optimization in yields and/or selectivity patterns.

The volume of reaction can be experimentally determined in three different ways,⁸ namely (i) from the pressure dependence of the equilibrium constant, (ii) from direct measurement of the volume change of reactants and products employing dilatometry, and (iii) from the measurements of partial molar volumes of all reactants and products. The latter is typically determined from independent binary solutions at temperature 298.1 K and atmospheric pressure.

Recently, due to significant progress in advanced *in situ* spectroscopic techniques and automated bulk-fluid property measurements, new opportunities arise especially for the physico-chemical characterization of multi-component reactive systems.^{11,12} For example, *in situ* spectroscopic measurements allow the accurate evaluation of the solute concentrations even under reaction conditions. When this quantitative information is combined with bulk physico-chemical measurements, the individual solute physico-chemical properties can be readily determined. *In situ* measurements also offer some practical advantages as no sampling is required and no separation/purification is needed to characterize the physico-chemical properties of the reactive species. Indeed, such an approach using FTIR spectroscopy and density measurements has been applied to a very fast, almost

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Fig. 1 Reaction of cyclopentadiene (CPD) and dimethyl acetylene dicarboxylate (DMAD) to produce the adduct, dimethyl bicyclo[2.2.1]-2,5-heptadiene-2,3-dicarboxylate.



Fig. 2 Dimerization reaction of cyclopentadiene (CPD)

instantaneous reaction in order to determine partial molar volumes and volume of reaction.¹³

In the present contribution, FTIR spectroscopic measurements and automated density measurements are applied to two organic reactions namely (i) the reaction of cyclopentadiene (CPD) and dimethyl acetylene dicarboxylate (DMAD) (Fig. 1) and (ii) the dimerization reaction of CPD (Fig. 2).

These reactions were selected for this study as they belong to a broader class of pericyclic reactions, which typically exhibit large volume of reaction. Both reactions were performed in toluene and investigated at temperature 298.1 K and atmospheric pressure. The FTIR spectroscopic data combined with BTEM analysis provided the pure component spectra of the reactive solutes and these were compared to the DFT predicted spectra. In addition, the pure component spectra together with mass balances allowed the determination of the instantaneous concentrations during reaction. The latter were then combined with the bulk density to evaluate the partial molar volumes of the constituents and the corresponding reaction volumes. In this study, DFT calculations were also used to provide predictions for the molar volumes of the reactive solutes.

Experimental section

Materials

The solvent toluene (Sigma Aldrich, CHROMASOLV® for HPLC, 99.9%) was dried over activated molecular sieves type 4 Å (Aldrich). The reactant dimethyl acetylene dicarboxylate, DMAD (Aldrich, 99%) from freshly opened bottles was used without further purification. The reactant cyclopentadiene monomer, CPD was obtained by cracking dicyclopentadiene dimer, DCPD (Fluka, purum, >95%). The CPD monomer was subsequently kept under argon and stored at a temperature of circa -70 °C to prevent its dimerization. Before its usage, the CPD monomer was checked by NMR to ensure its purity (*i.e.* negligible amount of dimer formed). In addition, the crude DCPD dimer was

Table 1 Summary of the experimental runs performed in the study. Mole fractions of the reactants are given in parentheses^a

Reaction	Exp. run	Mass of solvent (g)	CPD (g)	DMAD (g)
CPD + DMAD	1	40.331	0.795 (0.026)	1.083 (0.016)
	2	41.560	1.223 (0.039)	0.819 (0.012)
	3	40.348	1.016 (0.033)	0.793 (0.012)
CPD + CPD	4	37.576	1.458 (0.051)	_ ` `
	5	39.559	1.609 (0.053)	_
	6	43.119	1.601 (0.049)	_

^{*a*} Note: higher CPD concentrations were used in the dimerization reaction due to slow conversion.

purified and separated from its stabilizer by passing it through a column consisting of silica gel. The pure DCPD dimer was used in independent binary experiments in order to obtain a reference value for its partial molar volume at infinite dilution.

The purity of the reactant CPD monomer as well as the purified DCPD dimer were checked by ¹H NMR after dissolution in CDCl₃ (Bruker Avance 400 MHz, equipped with a 5 mm TBI probe with *z* gradient, running a standard Bruker supplied pulse sequence). The integration of the proton resonances provided lower bounds for the purity of freshly cracking CP monomer (>99%) and purified DCPD dimer (>98.5%).

Both the CPD and DMAD reaction and dimerization of CPD were carried out three times. The reactions were performed in dilute toluene at temperature 298.1 K and pressure circa 0.103 MPa (under dry nitrogen). The amount of solvent and solute used for reactions was determined using a balance (Metter Toledo, AB204-S) with a precision of $\pm 10^{-4}$ g. The difference in the masses of the syringes before and after the injection was taken as the mass of the substance injected into the reactor. Experimental details concerning the amount of solvent and solutes used for various runs are summarized in Table 1.

Equipment

The reactions were performed under dry nitrogen at a pressure of circa 0.103 MPa (Keller, LEO 1) in a 50 mL jacketed glass reactor equipped with a magnetic stirrer. The temperature in the reactor was maintained isothermal at 298.1 K (using Polyscience model 9106 circulator, temperature stability ± 0.05 K). The fluid was pumped in a closed loop system from the reactor through the pump (Masterflex® L/S, programmable digital drive) to the density meter (Anton Paar, DMA 5000, accuracy of 10^{-6} g mL⁻¹), to the flow-through cell situated in the infrared spectrometer (Bruker, Equinox 55), then recycled back to the reactor. The flow-rate of the pump was set to circa 12 mL min⁻¹.

Density measurements were necessarily performed under static or non-flow condition in order to reduce measurement error. In this regard, an in-house software was developed using Visual Basic .NET to synchronize the density meter measurement and pump on/off switching time. Briefly, the pump was initially switched on for a predetermined period of time (*i.e.* 4 minutes) to circulate the fluid, and then it was switched off



Fig. 3 Experimental setup for simultaneous on-line FTIR spectroscopy and automated density measurements.

while the density meter was signalled to measure. To ensure that the density meter was able to complete the measurement, the period of non-flow condition was set to be 6 minutes. After each density measurement, the software logged the measured density value and its corresponding measured time. The fluid was re-circulated by switching on the pump for circa 2 minutes before subsequent density measurement was taken (note: recirculation time in the system was circa 60 s). In this setup, the density measurements of the solution were able to be collected automatically circa every 8 minutes.

Mid-infrared spectra in the range 1000–3500 cm⁻¹ and with resolution of 4 cm⁻¹ were collected automatically every 2 min for the reaction CPD + DMAD and every 4 min for dimerization reaction. Co-added scans of 32 spectra were measured in order to ensure good signal-to-noise ratios. The CaF₂ single crystal windows used (Korth Monokristalle, Kiel, Germany) had dimensions of 20 mm diameter by 2 mm thickness. Two sets of Viton gaskets provided sealing and Teflon spacers (25 μ m) were used between the windows. The general experimental setup for simultaneous spectra and density measurements using on-line FTIR spectroscopy coupled with the density meter is shown in Fig. 3.

Due to the inherent acquisition times, the FTIR spectroscopic measurements and the density measurements occurred on two different time-scales. In particular, the FTIR spectra could be acquired rather rapidly (circa every 2 or 4 minutes), whereas, due to temperature stability issues the density measurements were acquired at a slower rate (8 minutes). In order to synchronize the time series between both spectroscopic and density data, the density data were fit to a polynomial function. This function was subsequently used to obtain the densities of solution associated with the spectral acquisition time.

Numerical section

Spectral data analysis - pure component spectra

The infrared spectra for each reaction system were consolidated to provide two absorbance reaction data matrices (consolidation of exp. runs 1-3 and 4-6). The data were then analyzed in two spectral regions, namely a wide spectral region with wavenumber range of 1000-3500 cm⁻¹ and a narrower region with wavenumber range of 1300-2000 cm⁻¹. The wide spectral region was analyzed for qualitative purpose, namely to obtain pure component spectra exhibiting a wide variety of vibrations. In contrast, the spectral data analysis in the narrow region was performed in order to obtain more accurate quantitative information. For each region, Singular Value Decom-(SVD) and thereafter Band-target Entropy position Minimization (BTEM) analysis¹⁴⁻¹⁶ were performed in order to reconstruct the underlying pure component spectra of the reactive species. These reconstructed spectra were then compared to the corresponding DFT predicted spectra.

Concentration of the reactive species

Quantitative spectral analysis was performed with data from the narrow spectral region with wavenumber range of 1300–2000 cm⁻¹. The raw reaction spectra were preprocessed to exclude the spectral contributions from the moisture and to correct the slight baseline shift.¹⁷ The matrix of preprocessed spectra will be denoted as *A*. Subsequently, a dimensionless approach using solvent as internal standard¹⁸ was applied to the preprocessed spectra to eliminate the influence of any changes in reaction volume and in cell path length. It should be noted that this special spectral data treatment is necessary since the change of volume due to reaction is non-negligible in the present systems.

Based on the Lambert–Beer–Bouguer law (LBBL) model, the dimensionless data A_i^{std} can be related to the preprocessed absorbance data A_i as shown in eqn (1), where *V* is the reaction volume, *l* is the optical path length, *s* is number of species, a_{ij} is molar absorptivity, n_j is total number of moles of species *s*, and *i* is wavenumber.

$$\frac{V}{l}A_i = \sum_{j=1}^s \left(a_{ij}n_j\right) = A_i^{\rm dml} \tag{1}$$

The variables *V* and *l* can be eliminated by using internal standard absorbance A_{ω}^{std} , of a reference species (*i.e.* solvent) at a reference wavenumber ω as shown in eqn (2). The substitution of eqn (2) into eqn (1) results in eqn (3).

$$\frac{V}{l} = \frac{a_{\omega}^{\rm std} n_{\rm std}}{A_{\omega}^{\rm std}} \tag{2}$$

$$A_i^{\rm dml} = \frac{a_{\omega}^{\rm std} n_{\rm std}}{A_{\omega}^{\rm std}} A_i = \sum_{j=1}^s \left(a_{ij} n_j \right) \tag{3}$$

The moles of the standard (solvent) n_{std} is known in each experimental run and the internal standard absorbance A_{ω}^{std} is calculable from the peak height of the solvent at a selected reference wavenumber ω . The quantity a_{ω}^{std} (molar absorptivity of the standard) can be set equal to 1 as it is merely a scalable constant (note: its effect will be lumped in the scaling elements $d_{s \times s}$ which will be determined below).

In matrix form, the dimensionless absorbance data $A_{k\times\nu}^{\text{dml}}$ can be rewritten as in eqn (4) and related to $n_{k\times s}$, $\hat{a}_{s\times\nu}$ and $d_{s\times s}$ the moles of the species-*s*, the normalized pure component absorptivities (from BTEM) and the scaling elements, respectively. The subscripts *k* and *v* denote the number of spectra in one experimental run and the number of data channels associated with the spectroscopic wavenumber range, respectively. It can be noted that the scaling elements are needed to relate the real magnitude of the pure component absorptivities and its normalized pure component absorptivities.

$$A_{k\times v}^{\rm dml} = n_{k\times s} d_{s\times s} \hat{a}_{s\times v} \tag{4}$$

Moles of the species can be estimated from (eqn (5)) where $[\hat{a}_{s \times \nu}]^+$ is the pseudo inverse matrix of $\hat{a}_{s \times \nu}$. Proper scaling elements $d_{s \times s}$ must be evaluated in order to evaluate the moles.

$$\mathbf{n}_{k\times s} = \mathbf{A}_{k\times v}^{dml} [\mathbf{\hat{a}}_{s\times v}]^+ (\mathbf{d}_{s\times s})^{-1}$$
(5)

Since the reaction was carried out in a closed system, various mass balances apply. This condition is accordingly used as constraints to evaluate the scaling elements (diagonal $d_{s \times s}$). The following mole balance constraints were used in this study.

In the reaction CPD + DMAD, only three major reactive species are considered, namely CPD, DMAD, and adduct. Based on its reaction stoichiometry, the summation of moles of CPD and adduct and the summation of moles of DMAD and adduct at any reaction time are equal to the initial moles of CPD and DMAD, respectively.

In the dimerization reaction of CPD, only two reactive species are involved, namely CPD and DCPD. Based on its reaction stoichiometry, the summation of moles of CPD and twice the moles of DCPD at any reaction time are equal to the initial moles of CPD.

Using a least square minimization procedure, the scaling elements (diagonal $d_{s \times s}$) of the reactive species (note: 3 elements for CPD + DMAD reaction and 2 elements for dimerization reaction) were evaluated. The resulted scaling elements were subsequently used to calculate the moles of the corresponding species as a function of time using eqn (5).

Total molar volume and partial molar volume

The primary quantities used in this study for modeling purposes are the total molar volume and mole fractions. The total molar volume $V_{\rm m}$ is obtained using eqn (6), where *n*, *M*, ρ and *x* are mole, molar mass, density of solution and mole fraction, respectively. Subscripts solv. and *i* refer to the solvent and the solutes.

$$V_{\rm m} = \frac{n_{\rm solv} M_{\rm solv} + \sum_{\rm solute-i} n_i M_i}{\rho \left(n_{\rm solv} + \sum_{\rm solute-i} n_i M_i \right)} = \frac{x_{\rm solv} M_{\rm solv} + \sum_{\rm solute-i} x_i M_i}{\rho}$$
(6)

In dilute solution the total molar volume can be related to the molar volume of the solvent $V_{\text{solv}}^{\text{o}}$ and the partial molar volumes at infinite dilution of the solutes- $i \bar{V}_i^{\infty}$ using eqn (7).¹¹

$$V_m = x_{\text{solv}} V_{\text{solv}}^{\text{o}} + \sum_{\text{solute}-i} x_i \overline{V}_i^{\infty}$$
(7)

Since the molar volume of the solvent is calculable from solvent mass and solvent density, eqn (7) can be re-arranged to eqn (8). The partial molar volumes at infinite dilution of the reactive solutes– $i \ \bar{V}_i^{\infty}$ were determined using multivariate regression.

$$V_{\rm m} - x_{\rm solv} V_{\rm solv}^{\rm o} = \sum_{\rm solute-i} x_i \overline{V}_i^{\infty}$$
(8)

DFT calculations

The DFT calculations were performed with Gaussian 09 version A.02.19 The reactive species CPD, DMAD, adduct and dimer DCPD were modelled and calculations were carried out in order to obtain the fully optimized geometries and the corresponding predicted infrared spectra. As well, the molar volumes can be estimated based on the van der Waals surface of the molecules.20 B3LYP functional and cc-pVTZ basis set was used by taking into account the dielectric constants of the solvent toluene. All the DFT calculations were carried out at temperature 298 K. SCRF model IEFPCM was used to account for the solvent effect in the geometric optimization and the subsequent infrared spectral prediction while SCRF model IPCM was used in the molar volume calculations. The present infrared spectral calculation takes a similar computational approach as previously used to predict the infrared spectrum of CPD,²¹ namely, (a) frequencies are reported directly as provided by the DFT calculations (with chosen functional and basis set) without recourse to scaling (correcting for systematic shifts using a known reference compound) and (b) graphical spectra are generated using the above mentioned frequencies as well as line widths consistent with the average experimentally observed line widths.

Results and discussion

Reaction of CPD and DMAD

The reaction between CPD and DMAD (see Fig. 1) was carried out in toluene at temperature 298.1 K. Three reaction runs were performed with different reactant ratios (see Table 1). The reaction was monitored simultaneously using FTIR spectroscopy and density meter. From all 3 reaction runs, a total of 595 *in situ* FTIR reaction spectra were recorded. From the spectroscopic measurements, several spectral changes were observed during reactions and some major changes occurring in the wavenumber range of 1300–1800 cm⁻¹ are shown in Fig. 4.

The major bands of CPD at 1365 cm⁻¹ and DMAD at 1731 cm⁻¹ are shown decreasing with time. Further inspection shows that the band of limiting reactant DMAD at 1731 cm⁻¹ decreases more rapidly than the band of CPD at 1365 cm⁻¹. The bands at 1322, 1628, and 1717 cm⁻¹ which are seen increasing with time correspond to the vibrations of the adduct. A rather distinct spectral change is noted at circa 1435 cm⁻¹. Although this band is decreasing with time, it does not appear to be strictly correlated with the bands at 1365 cm⁻¹ and 1727 cm⁻¹. This observation indicates that there could be some overlapping



Fig. 4 Ten representative infrared reaction spectra of the reaction between CPD and DMAD for the first 6 hours (time progression is shown from red to blue). The spectrum of the solvent toluene is indicated by the dashed line.

bands present at this position between the reactants and the product.

The reaction progress was also monitored by the density meter. The density changes observed during the three experimental runs are shown in Fig. 5. It can be noted that the initial density values and the reaction rates are very sensitive to the initial reactant concentrations. More specifically, the second and third reaction runs have low initial densities due to the higher concentration of CPD (lowest density component) used.

During the automated density measurements, a few outlier density data were generated (see the omitted points in Fig. 5). This is primarily due to the occasional formation of bubbles in the density cell. These outliers were easily identified and accordingly excluded in the analyses.



Fig. 5 The density monitoring of reaction between CPD and DMAD carried out in three experimental runs (exp. run 1 − \oplus ; exp. run 2 − \forall ; exp. run 3 − \blacksquare).

Spectral analysis

A wide range spectral deconvolution of reactive species in the wavenumber range of 1000–3500 cm^{-1} was performed using BTEM. This analysis was used in order to confirm the identity of species present. The reconstructed pure component spectra of the reactants DMAD and CPD as well as the product in the wide spectral range are presented in Fig. 6 and 7, respectively. These spectra are also compared with the corresponding DFT predicted spectra.

In Fig. 6(a), the BTEM reconstructed spectrum of DMAD is shown to be in good agreement with the DFT predicted spectrum. The strong bands at 1263 cm⁻¹ and 1731 cm⁻¹ and medium bands at 1042 cm⁻¹ and 1435 cm⁻¹ are in excellent agreement with the bands reported in the literature.²² Based on the DFT calculations, these four bands are associated with the



Fig. 6 The BTEM and DFT infrared spectra of (a) DMAD and (b) CPD in
 toluene. Artifact arising due to strong absorption of the solvent toluene at wavenumber 1496 cm⁻¹ is noted.



Fig. 7 The pure component infrared spectra of the adduct reconstructed using BTEM (bottom) and predicted from DFT calculations (top). Inset: comparison spectra in the wavenumber range of 1280–2000 cm⁻¹. Artifact arising due to strong absorption of the solvent toluene at wavenumber 1496 cm⁻¹ is noted.

vibrations of C–C–O stretching, C=O stretching, C–O–C stretching and CH_3 bending, respectively. Some weak bands appearing in the range of 2800–3100 cm⁻¹ correspond to some C–H stretching vibrational modes.

In Fig. 6(b), the BTEM reconstructed spectrum of CPD is compared to the corresponding DFT predicted spectrum. This spectrum is also compared with the spectral bands of liquid CPD reported in the literature.²³ The strong band at 1365 cm⁻¹ and medium weak to medium bands at 1089, 1238, 1292, 1590, 1626, 2734, 2884, 2900, 3043, 3075, 3105 cm⁻¹ are in excellent agreement with those bands reported in literature.^{23,24} From the DFT calculations, it is possible to assign that the strong band at 1365 cm⁻¹ to the CH₂ scissoring vibration mode. Similarly, bands at 1089 and 1292 cm⁻¹ correspond to CH bending modes and the band at 1238 cm⁻¹ corresponds to the CH₂ wagging mode. Bands at 1590 and 1626 cm⁻¹ are related to the combination vibrations of CH bending and C=C stretching. The bands in the region of 2700–3100 cm⁻¹ are associated with the CH stretching vibrations.

The pure component spectrum of the adduct reconstructed using BTEM is presented in Fig. 7. The spectrum of the adduct is much more complex than either of the reactants. This is expected as the adduct has more atoms and lower symmetry. The DFT predicted spectrum is also shown in Fig. 7.

Although there are some discrepancies in relative intensities, the DFT predicted spectrum is still useful to confirm the identity of the adduct as the predicted frequencies are fairly consistent with those of experimental spectrum. A closer look in the fingerprint region of 1280–2000 cm⁻¹ (see the inset of Fig. 7) shows a good agreement between BTEM and DFT predicted spectra. The fingerprint bands at 1293, 1322, 1434, 1561, 1628, 1717, 1739 cm⁻¹ are consistent with those predicted spectral bands. Based on the DFT calculations, the bands at 1293, 1322, and 1434 cm⁻¹ correspond to C–O stretching, C–C stretching, and CH₃ symmetric bending, respectively. Bands at 1561 and 1628 cm⁻¹ correspond to the C=C stretching and bands at 1717 and 1739 cm⁻¹ correspond to the C=O stretching. The bands in the region of 2800–3200 cm⁻¹ are associated with the CH stretching vibrations.

BTEM analysis was also attempted to identify and reconstruct the pure component spectra of other species, in particular the dimer DCPD which could be formed due to slow dimerization of CPD in the solution. The analysis was restricted to the spectral datasets which were collected during the first 3 hours of reaction. BTEM analysis could not identify and reconstruct the pure spectrum of the dimer DCPD from the data in this short reaction time. This indicates that the formed dimer DCPD, if any, should be in very small amount and therefore can be neglected.

Quantitative spectral analysis

The reaction spectra in the narrower wavenumber range of $1300-2000 \text{ cm}^{-1}$, which covers numerous strong vibrations arising from the reactive species (see Fig. 4) were chosen for quantitative analysis. BTEM analysis was re-utilized to reconstruct the underlying pure component spectra of the three reactive species from the reaction spectra. The resulting pure component spectra are presented in Fig. 8(a).

Subsequently, using the dimensionless approach detailed in Numerical section, the moles and hence the mole fractions of the three reactive species were determined. In this procedure, the solvent toluene was selected as an internal standard, with its peak height at 1496 cm⁻¹ taken as the reference. The mole fractions of each reactive species resulting from this quantitative spectral analysis are shown in Fig. 8(b).

As will be noted (*vide infra*), that the dimerization product DCPD was directly identifiable in the independent dimerization experiments and detectable in the CPD + DMAD reaction at longer reaction times *i.e.* greater than circa 3 hours. Therefore, for the partial molar volume evaluation, analysis will be restricted to short reaction times *i.e.* less than 2 hours.

Partial molar volumes of reactive species

The measured densities and the mole fractions of the constituents in the solution were used to calculate the total molar volume of the solution using eqn (6). The partial molar volumes at infinite dilution of each individual solute were subsequently determined from the total molar volume and the mole fractions of individual reactive species using eqn (8).

In this study, the results from three experimental runs (exp. runs 1–3) were evaluated simultaneously in order to provide some compositional as well as volumetric variations for the reactants and the adduct. The partial molar volumes at infinite dilution of the reactive species, namely DMAD, CPD and adduct obtained from eqn (8) are summarized in Table 2. These values are compared to the corresponding partial molar volumes independently determined from binary solution experiments. The partial molar volume of the adduct can be compared to the





Fig. 8 (a) The BTEM pure component spectra of the reactants DMAD, CPD and the adduct in the wavenumber range of $1300-2000 \text{ cm}^{-1}$. (b) The mole fractions of DMAD (∇), CPD (\odot) and adduct (\blacksquare) evaluated from exp. run 1 (black), exp. run 2 (grey) and exp. run 3 (white). Note: the mole fractions in the initial mixing period are not shown.

Table 2	Partial	molar	volumes	of	reactants	and	product	of	CPD	ł
DMAD re	action	in tolu	ene at 29	8.1	К					

	$ar{V}^{\infty}_i \pm \delta(ar{V}^{\infty}_i) ~(ext{cm}^3 ~ ext{mol}^{-1})$				
Species	From reaction	From binary ^a	literature		
DMAD	124.6 ± 0.5	122.4 ± 0.2	124.3^{b}		
CPD	83.3 ± 0.2	82.3 ± 0.1	82.4^{c}		
Adduct	170.0 ± 0.7	n/a	172.4^{d}		

^{*a*} From separate binary solution measurements performed in this study. ^{*b*} Ref. 26, in solvent toluene. ^{*c*} Ref. 27, in solvent toluene. ^{*d*} Calculated from volume of reaction data $(-33.6 \text{ cm}^3 \text{ mol}^{-1})^{25}$ and \bar{V}_i^{∞} of CPD and DMAD obtained from the present binary measurements. partial molar volume value calculated from the volume of reaction taken from literature.²⁵ As can be seen, the partial molar volumes at infinite dilution of the three reactive species determined from multi-component reactive system are in good agreement with those determined from binary solution or calculated from literature data.

Dimerization reaction of CPD

The dimerization reaction of CPD was carried out in toluene at temperature 298.1 K and atmospheric pressure. The reaction was monitored simultaneously using FTIR spectroscopy and the density meter. From the spectroscopic measurements, some spectral changes were observed due to reaction. The spectral changes occurring in the wavenumber range of $1300-1420 \text{ cm}^{-1}$ are shown in Fig. 9. In Fig. 9(a), the band of the reactant CPD at 1365 cm^{-1} and the band of the dimer product DCPD at 1340 cm^{-1} are seen decreasing and increasing with time, respectively. The very slow conversion of this reaction is indicated by the relatively subtle spectral changes in the period of 24 hours.

The progress of the dimerization reaction was also monitored using the density meter. The density changes during the 10 hour reaction time are shown in Fig. 9(b). Since the density is increasing almost linearly with time, it suggests that the rate of this reaction is nearly constant within this period. This is consistent with the limited conversion occurring during the measurement period for this second order reaction.

Reaction spectra and wide range spectral deconvolution

The deconvoluted spectra of the reactive species in the wide wavenumber range of 1000–3500 cm⁻¹ was performed using BTEM analysis. The analysis was successfully employed to reconstruct the underlying pure component spectra for both monomer CPD and dimer DCPD. The BTEM pure component infrared spectrum of monomer CPD is not shown as it is very similar to the result presented in Fig. 6(b).

The BTEM pure component spectrum of the dimer DCPD is presented in Fig. 10 and compared with the corresponding DFT predicted spectrum. As seen in Fig. 10, the BTEM reconstructed spectrum of DCPD is in good agreement with the DFT predicted spectrum. Noteworthy is the comparison of spectra in the fingerprint region of 1000–1800 cm⁻¹ (see inset). The band at 1340 cm⁻¹ as well as other weaker bands at 1023, 1132, 1160, 1252, 1439 cm⁻¹ obtained from this study are also in excellent agreement with those bands reported in literature.²³ Based on the DFT calculations, the bands at 1023, 1132, 1160, 1252, 1340, 1439 cm⁻¹ correspond to C–C stretching, C–H bending, CH₂ twisting, C–C stretching, C–H bending, CH₂ scissoring, respectively. The bands around 1600 cm⁻¹ corresponds to the C=C stretching vibrations and bands around 2800–3100 cm⁻¹ correspond to the C–H stretching vibrations.

Quantitative spectral analysis

Quantitative analysis was carried out based on the spectra in the wavenumber range of $1300-2000 \text{ cm}^{-1}$. BTEM analysis was re-



Fig. 9 (a) Infrared reaction spectra of the dimerization reaction of CPD in the solution (shown in the period of 24 hours). Spectrum of solvent toluene is shown with the dashed line (b) density monitoring of dimerization reaction.

utilized to reconstruct the underlying pure component spectra of two reactive species from the reaction spectra. The pure component spectra of the monomer CPD and dimer DCPD obtained using BTEM in the narrower region are shown in Fig. 11(a).

Subsequently, the moles and hence the mole fractions of the reactive species were determined using the dimensionless approach (see Numerical section). In this calculation, the solvent toluene was chosen as an internal standard with its peak height at wavenumber 1496 cm^{-1} was taken as a reference. The mole fractions of two reactive species resulted from this quantitative spectral analysis are shown in Fig. 11(b).



Fig. 10 The BTEM and DFT infrared spectrum of dimer DCPD in toluene (inset: comparison spectra in the wavenumber range of $1000-1800 \text{ cm}^{-1}$). Artifacts due to absorption of solvent toluene at circa 1496 cm⁻¹ are noted.

Partial molar volumes of reactive species

The obtained densities and the mole fractions of the constituents in the solution were used to calculate the total molar volume of the solution using eqn (6). The partial molar volumes at infinite dilution of each individual reactive solute \bar{V}_i^{∞} were subsequently determined from total molar volume and the mole fractions of reactive species using eqn (8). The results are shown in Table 3.

In order to validate the reproducibility of the present determination, two additional experimental runs (exp. runs 5 and 6) were carried out. The spectroscopic and volumetric analyses were performed in a similar manner. The results of the three experimental runs are shown in Table 3. The results obtained from three experimental runs are reproducible and the deviations of the partial molar volumes obtained for different runs are considered small (circa 0.1 and 1% for CPD and DCPD, respectively).

The partial molar volumes of the CPD and DCPD obtained directly from multi-component reactive system were also compared to the partial molar volumes independently determined from binary solution measurements as well as to the literature value. As can be seen, the partial molar volumes determined from multi-component solution are reliable as they are in excellent agreement with those determined from binary measurements.

Calculation method - molar volume of solutes

A simple procedure based on the Monte Carlo method for calculating molar volume for a variety of organic molecules has been proposed by Wong *et al.*²⁰ This method (now available in the Gaussian software package) was utilized in this study to



Fig. 11 (a) The BTEM pure component infrared spectra of the monomer CPD and dimer DCPD in the wavenumber range of 1300–2000 cm⁻¹. (b) The mole fractions of CPD (\bullet) and DCPD (\checkmark). Artifact due to absorption of solvent toluene at circa 1496 cm⁻¹ is noted.

estimate the molar volume of the solutes. In the present calculation, B3LYP functional and cc-pVTZ basis set was used and the effect of solvent as a polarisable continuum medium was treated by employing SCRF model IPCM. Four reactive species involved in the CPD + DMAD and dimerization reactions namely CPD, DMAD, adduct and dimer DCPD were modeled accordingly in the respective solvent used. The optimized geometries of these species are given in Fig. 12.

The volumes of the solutes obtained from the calculation method above are summarized in Table 4. As shown by the previous study of Wong *et al.*,²⁰ the calculated volumes of many solutes follow a simple empirical relationship (linear) with their corresponding experimental volumes. As shown in their study,

Table 3 Partial molar volumes of reactant and product of dimerization reaction in toluene at 298.1 $\rm K^a$

	$ar{V}_i^\infty \pm \delta\left(ar{V}_i^\infty ight) \left(\mathrm{cm}^3 \ \mathrm{mol}^{-1} ight)$					
Species	From reaction	From binary ^b	literature			
CPD	82.3 ± 0.1 (exp. run 4) 82.2 ± 0.1 (exp. run 5) 82.2 ± 0.1 (exp. run 6) Ave = 82.23 ± 0.06	82.3 ± 0.1	82.4 ^c			
DCPD	133.4 ± 0.6 (exp. run 4) 134.9 ± 2.4 (exp. run 5) 132.1 ± 2.9 (exp. run 6) Ave = 133.47 ± 1.40	135.1 ± 0.1				

^{*a*} The volumetric analyses were performed using density and mole fraction data taken from the first 10 h reaction time. ^{*b*} From separate binary measurements performed in this study. ^{*c*} Ref. 27, in solvent toluene.

the ratio of the calculated volume and the experimental volume ranges from 0.71 to 0.83 for a variety of organic molecules. On the average, a ratio of 0.75 can be selected as an empirical value which relates the calculated volume and the experimental molar volume of many solutes. The molar volume of solutes calculated based on this ratio are shown in Table 4 and compared to their corresponding experimental partial molar volume values obtained from the reaction studies.

As can be seen, the predicted molar volumes of solutes are in relatively good agreement with the experimental values. A greater deviation between the predicted molar volumes of solutes and experimental partial molar volumes is noticed for those molecules with more complex structures. For adduct and dimer DCPD, the deviation can be up to 15% of the



Fig. 12 Optimized geometries of various species. (a) CPD (b) DMAD and (c) adduct (d) DCPD. The atomic assignments are: carbon (dark grey), hydrogen (light grey), oxygen (red).

Table 4Comparison of calculated molar volumes of solutes and theircorresponding partial molar volumes in toluene at 298.1 K

$V_{\text{calc}}^{a} (\text{cm}^3 \text{ mol}^{-1})$	$V_{\mathrm{m,est}}^{b} (\mathrm{cm}^3 \mathrm{mol}^{-1})$	$\bar{V}_i^{\infty c} (\mathrm{cm}^3 \mathrm{mol}^{-1})$
61.5	82.0(-1.6%)	83.3
95.0	126.7 (1.7%)	124.6
146.0	194.7 (14.5%)	170.0
61.5	82.0 (-0.2%)	82.2
111.8	149.1 (11.7%)	133.5
	$\frac{V_{calc}^{\ a} \ (cm^3 \ mol^{-1})}{61.5}$ 61.5 95.0 146.0 61.5 111.8	$\begin{array}{c} V_{calc}{}^{a}\left(cm^{3}\ mol^{-1}\right) & V_{m,est}{}^{b}\left(cm^{3}\ mol^{-1}\right) \\ \hline 61.5 & 82.0 \left(-1.6\%\right) \\ 95.0 & 126.7 \left(1.7\%\right) \\ 146.0 & 194.7 \left(14.5\%\right) \\ 61.5 & 82.0 \left(-0.2\%\right) \\ 111.8 & 149.1 \left(11.7\%\right) \end{array}$

^{*a*} From DFT using SCRF model IPCM. ^{*b*} $V_{m,est} = V_{calc}/0.75$, deviation to the corresponding PMV is shown in parenthesis. ^{*c*} PMV obtained from multi-component reaction system. ^{*d*} From CPD + DMAD reaction. ^{*e*} From CPD + CPD dimerization reaction.

experimental values. This deviation is expected since the predicted method employing a SCRF model only regards the solvent as a dielectric continuum. This model neither accounts for solvent spatial reorganization around solute molecules nor accounts for any specific chemical interactions with solutes. Despite this inadequacy to model a real solution, this predicted method is still quite useful and can be considered as a viable alternative for estimating the molar volume of solutes in solution. Detailed molecular dynamics simulations often provide a much more reliable and realistic approximation to molar volumes (and partial molar volumes) but this extension is beyond the scope of the present contribution.

For completeness, it can be noted that the adduct clearly has numerous conformations in solution. Thus, in the DFT calculations, the fully optimized structure was determined for the adduct as well as some of the more likely, energically low lying conformations. These optimized structures are all graphically presented in the ESI,† as well as their corresponding energies. In addition, DFT with SCRF model SCI + IPCM was used to estimate the molar volumes. The average deviation between the estimated molar volumes for the various approaches and the measured partial molar volumes were (1) 27.1% using IPCM alone (2) 5.9% using IPCM scaled according to the procedure of Wong *et al.*²⁰ and (3) 9.9% using SCI + IPCM. The individual results using the latter procedure are provided in the ESI.†

Calculation of volume of reaction

The information on the individual partial molar volumes of reactants and products obtained from the reaction studies can be readily used to calculate the corresponding volume of reaction. The volume of reaction, were subsequently determined in this study from the difference between partial molar volumes of products and reactants as given by eqn (9), where a_i and b_i are the stoichiometric coefficients of the corresponding reaction.

$$\Delta_{\rm r} V = \sum_{i} b_i \overline{V}_i^{\infty} (\text{products}) - \sum_{i} a_i \overline{V}_i^{\infty} (\text{reactants})$$
(9)

The volume of reaction for the CPD + DMAD and CPD + CPD dimerization reactions calculated using eqn (9) are -37 ± 3 cm³ mol⁻¹ and -31 ± 2 cm³ mol⁻¹, respectively. These values can be compared favorably with the literature values of -33.6 cm³

 mol^{-1} (ref. 25) and $-36.1 \text{ cm}^3 \text{ mol}^{-1}$ (in solvent ethyl acetate)²⁸ for the CPD + DMAD reaction and $-31.4 \text{ cm}^3 \text{ mol}^{-1}$ for the dimerization CPD + CPD reaction (in solvent *n*-butyl chloride),²⁹ which were obtained from high pressure reaction studies. The present determination shows that the volume of reaction of both CPD + DMAD and the dimerization reactions are negative.

Conclusions

This study demonstrates the utility of combined on-line FTIR spectroscopy and automated density measurements to determine partial molar volume of reactive solutes as well as the volume of reaction in the multi-component reactive system. In this regard, BTEM spectral analyses were employed for obtaining the pure component spectra of the solutes and their corresponding concentrations. The obtained solute concentrations were combined with the bulk density data to evaluate the partial molar volumes of the solute constituents. The partial molar volume values evaluated from this approach are subsequently used to calculate the corresponding volume of reaction. The volumes of reaction of the CPD + DMAD and dimerization reactions determined from this study are $-37 \pm 3 \text{ cm}^3 \text{ mol}^{-1}$ and $-31 \pm 2 \text{ cm}^3 \text{ mol}^{-1}$, respectively. The DFT calculations performed in this study were useful for the assignment of the structures and vibration modes corresponding to the experimental spectral estimates as well as to provide predictions of the molar volume of the solutes. In general, the method developed in this study opens a new avenue for the *in situ* physicochemical characterization in particular partial molar volumes and volume of reaction from the multi-component reactive system.

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