Development of CO₂-Assisted Dispersibility of Organic-Inorganic Hybrid Nanoparticles with Expanded Liquid Solvent Mixtures

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Abstract

Applications of organic-inorganic hybrid nanoparticles (NPs) generally confront a limited number of suitable pure solvents to provide high dispersible NP solutions. In this work, the first objective is to propose a method for selecting suitable solvents and the second objective is to develop a CO₂-expanded liquid system for controlling NP dispersibility. The key parameters for selecting suitable solvents were the dispersion solubility parameter (δ_D) and the van der Waals volume (V_{vdw}), in which favorable ranges were δ_D ($\approx 15 - 17$ MPa$^{0.5}$) and V_{vdw} (< 89 cm^3·mol^{-1}). To validate the favorable ranges, CO₂ was chosen because its δ_D (≈ 15.6 MPa$^{0.5}$) and V_{vdw} (19.7 cm^3·mol^{-1}) values are within the favorable ranges. To demonstrate the role of CO₂ in dispersion, the experiments were conducted by an addition of CO₂ into solutions. The studied conditions were 1wt% hybrid CeO₂ nanoparticles in solutions (decane or cyclohexane solvent), the temperature of 40 °C and pressure from 2 to 6 MPa using a high-pressure observation. It was found that the addition of CO₂ could cause a change of turbid solution to clear solution, namely increasing the dispersibility. These results imply that the δ_D and V_{vdw} favorable ranges can be used to identify a suitable solvent and CO₂-expanded liquid solvent mixtures can be a suitable alternative solvent for NP processing.

Keywords
Solubility parameter, Solvent selection, Nanoparticles

1. Introduction

Inorganic nanoparticles (NPs) have many applications [1], such as medicines, electronics, energy materials and catalysts. Due to the agglomeration of the inorganic NPs that causes difficulty in their processing, the surface modification of the NPs with an organic acid molecule (e.g. carboxylic acid) has been proposed [2] to improve the stability and dispersibility of NPs. The surface-modified NPs are defined as organic-inorganic hybrid nanoparticles that contain inorganic nanoparticles in the center and organic chains on the surface as shown in Fig. 1.

The organic surface chains could improve dispersibility and solubility of the hybrid NPs in a nonpolar solvent (e.g. hexane or cyclohexane) [3] due to molecular interactions between the surface chains and nonpolar solvent via dispersion/polarizability forces, while polar solvents (e.g. ethanol and water) caused agglomeration of the hybrid NPs [3]. However, it comes out the problem of solvent selections in the applications of hybrid NPs because of a small number of suitable pure solvents. To resolve the problem, a methodology should be proposed for quantitively predicting the dispersibility and solubility of the hybrid NPs by enlarging the candidate solvents to a mixed solvent system.
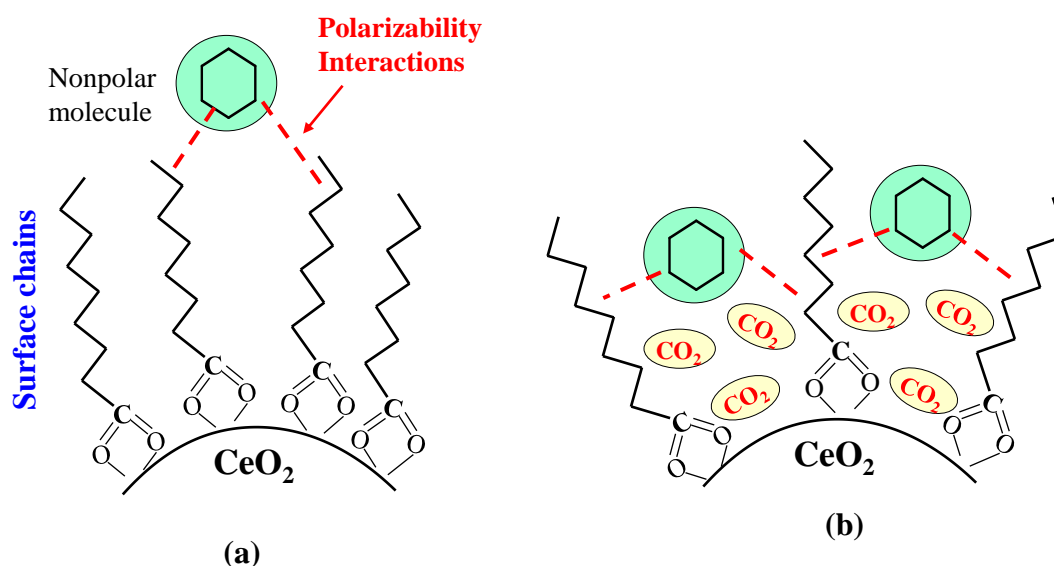

Fig. 1. Molecular interactions of organic-inorganic hybrid CeO_2 nanoparticles with solvent in (a) pure nonpolar solvents and (b) CO_2-expanded liquid solvent mixture.

Many parameters (e.g. solubility parameter, solvatochromic parameters and polarity parameter) can be used to quantify the solvent characteristics. Among them, the Hansen solubility parameter is a common useful tool in selecting a suitable solvent for many applications [4]. Hansen solubility parameter (HSP) [5] is defined initially as the square root of cohesion energy density and consists of three components as the dispersion term (δ_D), the polar term (δ_P) and the hydrogen bonding term (δ_H). For example, ethanol polar solvent (Entry 4, Table 1) contains three components of Hansen solubility parameter ($\delta_D = 15.8$, $\delta_P = 8.8$ and $\delta_H = 19.4$), while the dispersion term (δ_D) is the main contribution in nonpolar solvent due to small values in δ_P and δ_H parameters (Entries 9-16, Table 1). According to the dispersibility results, dissolution of the NPs in a solvent might be explained by molecular interactions of surface chains with nonpolar solvent via dispersion/polarizability forces that prevent agglomeration of the NPs (Fig. 1). Thus, the dispersion solubility parameter (δ_D) is expected to be a key term for selecting suitable solvents.

For the surface-modified NPs, the molecular size is expected to be another key parameter for solvent selection because the surface chains are fixed at only one end of which position is arranged from the atomic composition. It is supposed that smaller molecular sizes of solvent are preferable to have better molecular interactions with the surface chains than a bigger molecules (Fig. 1b). To prove this concept, CO_2 is chosen due to nonpolar characteristics and smaller molecular size than nonpolar liquid solvents according to the van der Waals volume (V_{vdw}, Table 1).

We also expected that CO_2 might have an additional role as a plasticizer [6] for enhancing motion of the surface chains because the behavior of the hybrid NP solutions at a high concentration is likely to be a polymer, according to rheology results [7]. In this work, CO_2 is applied in the dispersibility of hybrid NP solutions with two benefits of CO_2 as (i) an increase in dispersion due to small molecular size and high penetration and diffusivity and (ii) a decrease in the amount of liquid organic solvent. The two hypotheses explored in this work are as follows: (i) organic-modified surface chains only interact with a nonpolar solvent and (ii) dispersion solubility parameter (δ_D) and molecular size of nonpolar solvents are key parameters in molecular interactions.

The first objective of this work is to propose a method for selecting suitable solvents by extending the candidate into binary solvent systems. The second objective is to propose a CO_2-expanded liquid process for controlling NP dispersibility. The literature data of NPs and a solvent [3] were analyzed to identify the favorable ranges for selecting suitable solvents, as discussed in section 2. The van der Waals volume (V_{vdw}) was used to represent the molecular size of the solvent molecule. The experiments were conducted by an addition of CO_2 into solutions to demonstrate the role of CO_2 in dispersion. The studied conditions were 1wt% CeO_2 nanoparticles in solutions (decane or cyclohexane solvent), the temperature of 40 °C and pressure from 2 to 6 MPa using a high-pressure observation as discussed in Sections 3 and 4.

2. Proposed solvent selection

Table 1 shows the Hansen solubility parameter (HSP), van der Waals volume (V_{vdw}) and dispersibility experiments for solute (hybrid NPs, Entry 1), pure polar solvents (Entries 2-8), pure nonpolar solvents (Entries 9-17) and binary solvent systems (CO_2-expanded liquid solvent mixtures, Entries 18-23). The HSP and V_{vdw} values of the hybrid NP solute (Entry 1, Table 1) were adopted from those of decane solvent because the decanoic acid was used to modify the surface chains of hybrid NPs studied in this work and the chains only have molecular interactions with a solvent as mentioned in the introduction. The dispersibility experiments of hybrid CeO_2 NPs in pure solvents at 1wt% (Entries 9-16, Table 1) were obtained from the literature, while the experiments in the CO_2-expanded solvent mixtures (Entries 18-23, Table 1) were conducted in this work (discuss later in sections 3 and 4).

The pure polar solvents selected (Entries 2-8, Table 1) are poor solvents for NPs that causes agglomeration in the NP solutions (turbid solution). The reason might be attributed to the dipole-induced dipole interactions in the surface chains by a polar solvent that promotes the attractive forces (agglomeration) in the surface chains. On the other hand, pure nonpolar solvents with smaller molecular size ($V_{vdw} \leq 88.7$ cm^3·mol^{-1}, Entries 9-12, Table 1) are suitable solvents for providing high dispersibility in the NPs (clear solution) because the mutual interactions of the surface chains with nonpolar solvent via dispersion/polarizability forces (Fig. 1) prevent the agglomeration from the surface chains.

Since dispersion/polarizability forces are short-range interactions, the nonpolar solvents having higher molecular size ($V_{vdw} \geq 88.7$ cm^3·mol^{-1}, Entries 13-16, Table 1) are unable to have the effective mutual interactions with the surface chains that cause agglomeration in the

NP solutions. The dispersion results in pure solvents (Entries 2-16, Table 1) showed that the two key parameters for proving high dispersibility in the NPs are (i) dispersion/polarizability interactions and (ii) the molecular size of the nonpolar solvents. In this work, these parameters can be quantified by the dispersion solubility parameter (δ_D) and van der Waals volume (V_{vdw}), respectively.

Fig. 2 shows the plots of the δ_D and V_{vdw} values of solute (NP surface chains), pure nonpolar solvents and alternative binary solvent systems (CO_2-expanded liquid decane and cyclohexane solvent). The favorable ranges for providing high dispersibility were identified from the suitable solvents (nonpolar solvents, Entries 13-16, Table 1), assuming that the δ_D and V_{vdw} values of alternative solvents should be similar to those values of the suitable solvents. In this work, the favorable ranges were defined as δ_D ($\approx 15 - 17$ MPa$^{0.5}$) and V_{vdw} (≤ 89 cm$^3 \cdot$mol^{-1}) as shown in Fig. 2 in the green area.
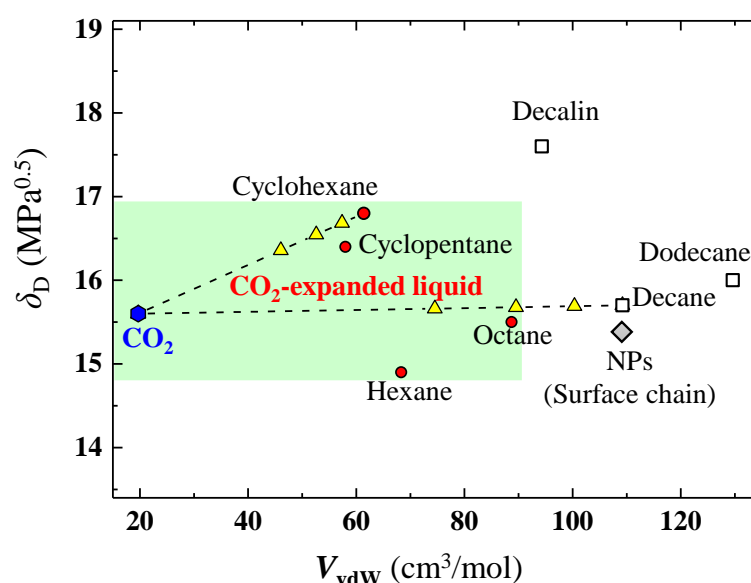

Fig. 2. Plot of dispersion solubility parameter (δ_D) and van der Waals volume (V_{vdw}) of organic-inorganic hybrid CeO_2 nanoparticles, pure nonpolar solvents and CO_2-expanded liquid solvent mixtures. Filled symbols represent a clear solution. Open symbols represent a turbid solution.

According to the δ_D and V_{vdw} parameters, CO_2 at 25 °C and 0.1 MPa (Entry 17, Table 1) is expected to be a promising alternative solvent because its δ_D and V_{vdw} values are within the favorable ranges (Fig. 2). The δ_D and V_{vdw} values of CO_2 (Entry 17, Table 1) were evaluated from experimental solubility of CO_2 in organic liquid solvents at 25 °C and 0.1 MPa [5] and were adopted to validate the favorable range in CO_2-expanded liquid solvent mixtures studied in this work.

The solubilities of CO_2 in a liquid solvent by pressurization were calculated using the Peng-Robinson equation of state with the van der Waals one fluid model, where the binary interaction parameters were estimated by literature vapor−liquid equilibrium data [8, 9]. Table 1 (Entries 18-23) tabulates the solubility of CO_2 in liquid solvent in terms of volume fraction (ϕ_1) along with the δ_D^{mix} and V_{vdw}^{mix} values of CO_2-expanded liquid solvent mixtures that were calculated by taking volume fraction averages (Eqs. (1) and (2)). The dashed lines (Fig. 2) show the δ_D^{mix} and V_{vdw}^{mix} values of CO_2-expanded liquid solvents at the pressure from 2 to 6 MPa that leans a trajectory within the favorable ranges (the green area, Fig. 2).

$$\delta_D^{mix} = \phi_1\delta_1 + \phi_2\delta_2 \tag{1}$$

$$V_{vdw}^{mix} = \phi_1 V_{vdw1} + \phi_2 V_{vdw2} \tag{2}$$

The ϕ_i is the volume fraction of component i and subscripts of 1 and 2 denote liquid solvent and CO_2, respectively. Please note that although the experiments were performed at the temperature of 40 °C and pressure from 2 to 6 MPa (sections 3 and 4), the calculations of δ_D parameters of CO_2-expanded liquid solvent were made carried out based on conditions at 25 °C and 0.1 MPa for liquid solvent. The CO_2 density at 25 °C saturated liquid condition was used to convert mole fraction to volume fractions, where the mole fractions were determined via VLE calculation at 40 °C and each pressure.

3. Experimental
3.1. Materials
Carbon dioxide (> 99.99 %) was purchased from Showa Denko Gas Products Co. Ltd. Decane (99.0%) and cyclohexane (99.7+%) were obtained from Fujifilm Wako Pure Chemical Industries, Ltd, respectively. The hybrid CeO_2 nanoparticles with decanoic acid-modified surface were kindly provided by Prof. Tadafumi Adschiri and co-workers. The detail synthesis of hybrid CeO_2 nanoparticles can be found in the literature [2, 11, 12]. The solvent and CeO_2 nanoparticles were used as received without further purification.

3.2. Apparatus and Procedure
Fig. 3 shows a schematic diagram of the observation apparatus at high-pressure conditions. The observation apparatus mainly consisted of a SUS vessel, cylindrical sapphire window and glass tube. The SUS vessel was set in a thermostated water bath for temperature control within ±0.1 °C. The details of the observation apparatus have been described in our previous work [13]. The samples were prepared at 1wt% hybrid CeO_2 nanoparticles in a solvent.

The sample solution ($\approx$ 0.1 g) was filled into the glass tube, and then CO_2 was introduced into the observation apparatus with a syringe pump (ISCO model 260D) at a temperature of 40 °C and pressure from 2 to 6 MPa. The pressure was monitored with a pressure sensor (Krone Corporation, Tokyo, KDM30, accuracy 0.05 MPa). During experiments, equilibration was promoted by a magnetic stirrer and was generally reached in about 10-20 min. After equilibration, photographs of the sample solutions were recorded with a video camera (Panasonic, HC-V480MS).
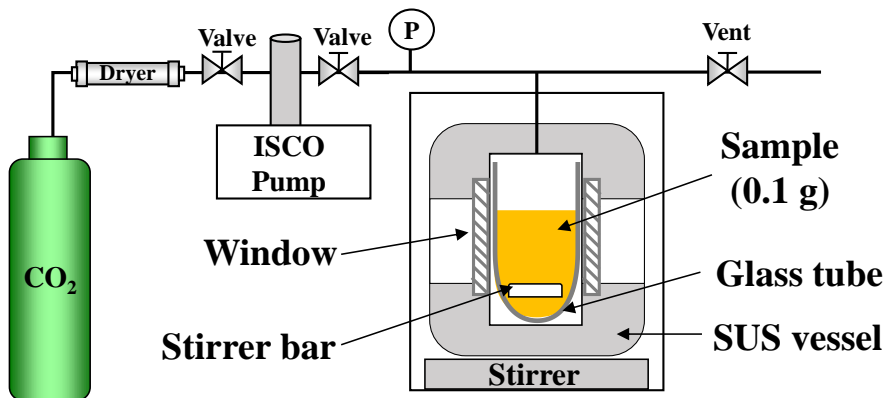

Fig. 3. Schematic diagram of high-pressure observation apparatus.

Table. 1 Dispersibility results of organic-inorganic hybrid CeO_2 nanoparticles (NPs) with pure solvent and solvent-pairs along with Hansen solubility parameter (HSP) [5] and van der Waals volume (V_{vdw}) [10] at 25 °C (otherwise noted).

Entry	System	HSP parameters (MPa$^{0.5}$)				V_{vdw} (cm^3·mol^{-1})	Dispersion[a]	Ref.[b]
		δ_D	δ_P	δ_H	δ			
Solute								
1	Hybrid NPs (surface chains)	15.7	0	0	15.7	109.2	N.A.	N.A.
Pure polar solvent								
2	Acetone	15.5	10.4	7.0	19.9	39.0	×	[3]
3	n-butanol	16.0	5.7	15.8	23.2	52.4	×	[3]
4	Ethanol	15.8	8.8	19.4	26.5	31.8	×	[3]
5	Water	15.5	16	42.	47.8	12.4	×	[3]
6	Benzene	18.4	0	2.0	18.5	48.4	×	[3]
7	Toluene	18.0	1.4	2.0	18.2	59.5	×	[3]
8	Ethylbenzene	17.8	0.6	1.4	17.9	69.7	×	[3]
Pure nonpolar solvent								
9	Cyclohexane	16.8	0	0.2	16.8	61.4	o	[3]
10	Cyclopentane	16.4	0	1.8	16.5	58.0	o	[3]
11	Hexane	14.9	0	0	14.9	68.3	o	[3]
12	Octane	15.5	0	0	15.5	88.7	o	[3]
13	Bicyclohexyl	17.0	0	0	17.0	N.A.	×	[3]
14	Decane	15.7	0	0	15.7	109.2	×	[3]
15	Cis-Decalin	17.6	0	0	17.6	94.3	×	[3]
16	Dodecane	16.0	0	0	16.0	129.6	×	[3]
17	CO_2 (25 °C, 0.1 MPa)	15.6	5.2	5.8	17.4	19.7	N.A.	N.A.
CO_2-expanded liquid solvent mixtures								
Condition at constant temperature (40 °C)								
Decane (1) - CO_2 (2)								
18	P = 2 MPa, ϕ_2 = 0.10	15.7	0.5	0.6	15.9	100.4	×	*
19	P = 4 MPa, ϕ_2 = 0.22	15.6	1.1	1.3	16.1	89.4	o	*
20	P = 6 MPa, ϕ_2 = 0.39	15.6	2.0	2.2	16.4	74.5	o	*
Cyclohexane (1) - CO_2 (2)								
22	P = 2 MPa, ϕ_2 = 0.10	16.0	0.5	0.7	16.9	57.4	o	*
22	P = 4 MPa, ϕ_2 = 0.21	16.0	1.1	1.4	16.9	52.6	o	*
23	P = 6 MPa, ϕ_2 = 0.37	15.9	1.9	2.3	17.0	46.0	o	*

Footnote

[a]The appearances of the NP solutions in a solvent: o = clear solution, × = turbid solution
[b]Dispersibility experiments: asterisks refer to obtain from this work, N.A. = not available.

4. Results and discussion

Fig. 4 shows photographs of the hybrid NP solutions in pure decane at atmospheric pressure (Fig. 4a) and in CO_2-expanded liquid decane mixtures at the pressure of 2-6 MPa (Fig. 4b-4d). Similar conditions for the NP solutions in pure cyclohexane and CO_2-expanded liquid cyclohexane mixtures are given in Fig. 5. Table 1summarizes experimental dispersibility results for both CO_2-expanded liquid decane mixtures (Entries 18-20) and CO_2-expanded liquid cyclohexane mixtures (Entries 21-23) along with δ_D^{mix} and V_{vdw}^{mix} values.

The turbid NP solutions (Fig. 4a) were obtained from pure decane at atmospheric pressure (without CO_2, Entry 14 and Table 1). The addition of CO_2 into pure decane could change the turbid NP solutions (Fig. 4a) to clear solution (Fig. 4c-4d and Entries 19-20 in Table 1), namely increasing the dispersibility of the NPs. On the other hand, the addition of CO_2 into a clear solution (cyclohexane, Fig. 5a) does not cause agglomeration of the hybrid NPs, namely with keeping clear solutions during CO_2 addition (Fig. 5b-5d).
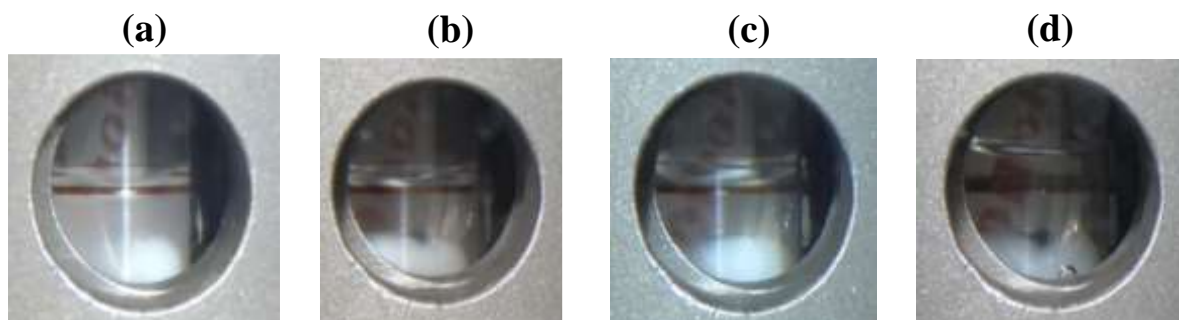
(a)   **(b)**   **(c)**   **(d)**

Fig. 4. Photographs of the hybride CeO_2 nanoparticle solutions in (a) pure decane solvent and (b) – (d) CO_2-expanded liquid decane mixtures at pressure of 2, 4 and 6 MPa, respectively.
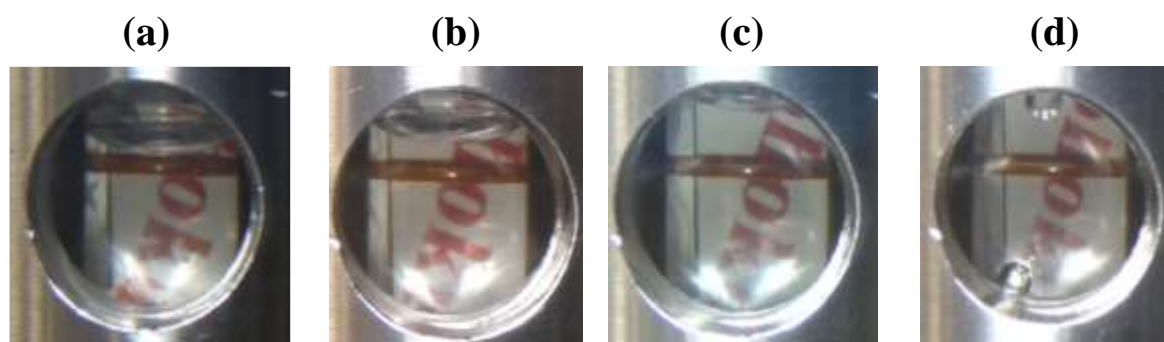
(a)   **(b)**   **(c)**   **(d)**

Fig. 5. Photographs of the hybride CeO_2 nanoparticle solutions in (a) pure cyclohexane solvent and (b) – (d) CO_2-expanded liquid cyclohexane mixtures at pressure of 2, 4 and 6 MPa, respectively.

Fig. 6 shows the estimated values of dispersion solubility parameter (δ_D) and van der Waals volume (V_{vdw}) of CO_2-expanded liquid decane and cyclohexane as a function of pressure. When CO_2 is added into liquid solvents ($P < 6$ MPa, Fig. 6), the δ_D and V_{vdw} values tended to have a slight decrease. Beginning from atmospheric pressure ($P = 0.1$ MPa), the turbid NP solutions were observed in pure decane (Fig. 4a) and in CO_2-expanded liquid decane at 2 MPa (Fig. 4b). These results can be related to their V_{vdw} values (Fig. 6b) that are out of the favorable window (< 89 cm$^3 \cdot$mol^{-1}). With increasing pressure over than 2 MPa, the turbid NP solutions (Fig. 4a and 4b) were changed to clear solutions (Fig. 4c-4d) due to the V_{vdw} values (Fig. 6b) within the favorable window. In the case of CO_2-expanded liquid cyclohexane, the clear solutions (Fig. 5) were obtained over entire pressure ranges, according to the δ_D and V_{vdw} values within the favorable window (Fig.6). These results could support favorable ranges that are reliable to identify a suitable alternative solvent for NP processing.

We supposed that CO_2 has two primary roles in the dispersibility of the NPs. The first role is the direct interactions of CO_2 with the surface chains of NPs via dispersion/polarizability forces (Fig. 1b). Another role of CO_2 is a plasticizer for increasing the motion of the surface

chains. Although the experimental results studied in this work are not enough to verify, it is worth to note that the plasticizing effect might facilitate the interactions between the nonpolar liquid solvent and the surface chains.

5. Conclusion

The method for selecting a suitable solvent being used in the dispersibility of organic-inorganic hybrid nanoparticles was proposed. The method uses the dispersion solubility parameter (δ_d) and the van der Waals volume (V_{vdw}) and it was found that favorable ranges for solvent selections were δ_d ($\approx 15 - 17$ MPa$^{0.5}$) and V_{vdw} (< 89 cm$^3 \cdot$mol^{-1}). CO_2-expanded liquid solvent mixtures were developed to validate the favorable ranges and propose an alternative solvent for NP processing. Further, the solvent selection method and CO_2-expanded liquid solvent mixtures proposed in this work can be used to study the dispersibility of other organic-inorganic hybrid nanoparticles.
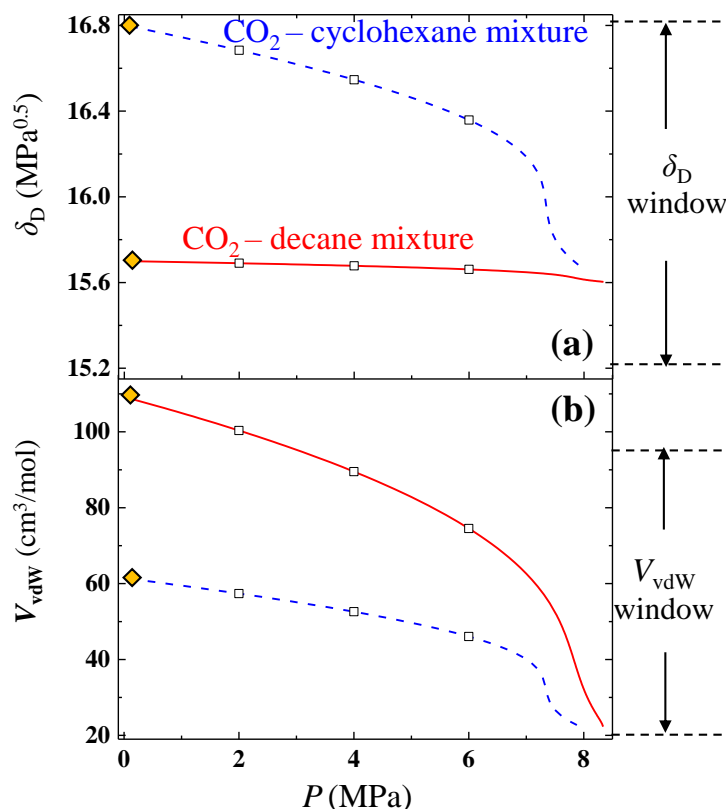

Fig. 6. Plots of (a) dispersion solubility parameter (δ_D) and (b) van der Waals volume (V_{vdw}) of CO_2-expanded liquids for decane (red solid line) and cyclohexane (blue dashed line) as a function of pressure. Solubility parameter window ($\delta_{Dwindow}$) and van der Waals volume window ($V_{vdw\ window}$) denote the favorable range of dispersibility of organic-inorganic hybrid CeO_2 nanoparticles in pure solvents at atmospheric pressure that estimated from Fig. 2. Lines were estimated with eqs. (1) and (2). Filled symbols denote the δ_D and V_{vdw} values of pure components at 25 °C and atmospheric pressure. Unfilled symbols denote the δ_D and V_{vdw} values CO_2-expanded liquids at 40 °C and pressure from 2 to 6 MPa.

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