



Why is the CO₂–CS₂ non-ideality larger than in CO₂–CCl₄? A Raman scattering study



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ABSTRACT

The dense phases of the CO₂–CCl₄ (I) and CO₂–CS₂ (II) mixtures have been studied by Raman spectroscopy. Mixture I is found almost ideal and II strongly non-ideal. At high CS₂ concentration in II, the local structure of CS₂ is preserved suggesting a nano-segregation of the liquid phase without demixing whereas in CO₂ concentrated mixtures a diversity of species are present. Thermodynamical considerations together with spectroscopic results show that a subtle interplay between attractive and repulsive interactions leads to this non-ideal behaviour. The connection of these results with the liquid–liquid demixing reported for CO₂–CS₂ at lower temperature is discussed.

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1. Introduction

The solvation of CO₂ in molecular liquids and complex fluids is a field of current fundamental interest motivated by the need to assess inter-molecular interactions in these mixtures to design and/or improve *in-fine* its utilisation in industrial processes [1,2]. In this context, we have investigated binary mixtures of CO₂ with organic solvents and ionic liquids using Raman spectroscopy combined with ab-initio calculations [3–6]. We showed that the solvation could be rationalised either from the formation of labile transient dimers formed on a sub-picosecond time scale or involving CO₂ in a chemical reaction.

The high pressure phase diagram of the system CO₂–CS₂ showed that this mixture is non-ideal, belonging to the type II phase diagrams in the classification of Scott and Van Konynenburg [7]. Recently, the pressure–composition diagrams of CO₂–CCl₄ and CO₂–CS₂ have been reported and the ideality of these mixtures discussed according to their deviations from Raoult's law [8]. The system CO₂–CCl₄ (I in the following) was found almost ideal (Figure 1a), whereas in CO₂–CS₂ (system II) a sizeable deviation from the linear dependency up to 0.5 CO₂ mole fraction (m.f.) was observed. At this value the system reaches a plateau (Figure 2a) related to the presence of a liquid–liquid equilibrium (LLE) region with an Upper Critical Solution Temperature (UCST) at lower temperature (290 K) [7]. The values of the partial molar enthalpies and entropies of solvation have been found to be almost identical in the two systems (about –2.41 kcal mol^{–1} and 18.4 cal mol^{–1} K^{–1}, respectively) [8]. Besides these thermodynamics studies, investigations on these

systems are extremely scarce. We may wonder if transient complexes exist in these systems having partial molar enthalpies values close to those found for CO₂–organic liquids mixtures in which complexes are formed. In gaseous phase, a spectroscopic study of the CO₂–CS₂ mixture in helium the formation of a weak complex with a non-planar X-shaped structure (C_{2v} symmetry) has been put in evidence [9]. Furthermore the ideality concept requires that the molecular shapes of the components of the mixture are similar. This criterion is only almost fulfilled in the non-ideal CS₂–CO₂ system leading to an apparent contradiction which demands to be clarified.

These reasons have prompted us to study comparatively the solvation of CO₂ in these systems using Raman spectroscopy to provide, at the molecular level, experimental evidences and criteria to critically discuss the origin of the deviation from an ideal behaviour of a mixture. We have addressed these issues by Raman spectroscopy by studying the strongly active ν₁ – 2ν₂ Fermi dyad of the CO₂ molecule and the ‘forbidden’ ν₂ (II_u) bending modes of CO₂ in system I and CS₂ in system II.

2. Experimental

2.1. Experimental conditions

The polarised I_{VV} and depolarised I_{HV} spectra were recorded on a LabRam HR8000 spectrometer with resolutions 0.5 cm^{–1} (CO₂ Fermi dyad) and 3.8 cm^{–1} (other spectral domains). The pressure bench and the cell equipped with fused silica windows were previously described [6]. The cell windows give a faint polarised feature at about 470 cm^{–1} which is not affected, at constant temperature, by the pressure variation (up to 8 MPa) and has been used as an

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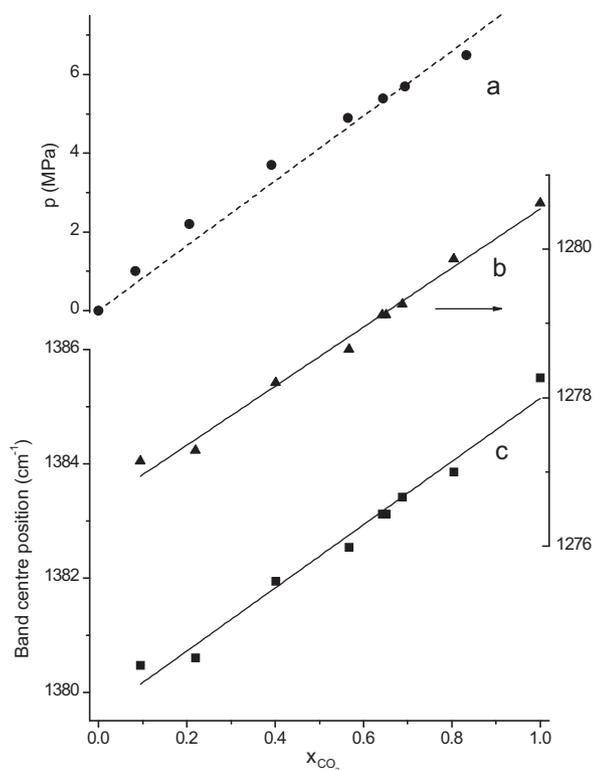


Figure 1. Binary mixture $\text{CO}_2 + \text{CCl}_4$ at 313 K: pressure-composition diagram. The straight line represents the ideal behaviour predicted by Raoult's law (a). Evolution of the band centre position of the Fermi dyad of CO_2 with CO_2 concentration (lower-(b), upper-(c) components).

internal standard for intensity calibration of the bending mode of CS_2 (see [supplementary data, SD](#)). Experiments were performed at 313 K and other experimental details are referred in [supplementary data](#).

2.2. Experimental results

2.2.1. The Fermi dyad of CO_2

The evolution of the band centre position of the Fermi dyad components of CO_2 in CCl_4 as a function of the CO_2 concentration is displayed in [Figure 1b](#) and [c](#). The band centres are continuously shifted towards higher wave number with increasing CO_2 concentration. The overall variation of the shift is almost the same for the two bands and typically of the order of 4 cm^{-1} . The evolutions of the experimental band centres are close to those calculated by assuming that the peak positions vary linearly with the concentration between the two extreme points corresponding to CO_2 infinitely diluted in the mixture and to pure CO_2 at a density close to that of the more concentrated mixture. It is noteworthy that the calculated linear behaviour of the peak positions is expected under the hypothesis of an 'ideal' character of the mixture [10,11]. This result is consistent with the fact that the solubility of CO_2 in the mixture closely follows the Raoult's behaviour ([Figure 1a](#)).

The evolution with CO_2 concentration of the band centre position of the Fermi dyad components of CO_2 in CS_2 is displayed in [Figure 2b](#) and [c](#). The band-centre positions increase non-monotonously presenting a 'plateau-like' region in the concentration range 0.3–0.7 m.f. A marked deviation from the linearity is clearly observed compared with the evolution of the peak positions calculated as done for system (I) ([Figure 2a](#)). We also note that the overall variation of the shift is almost the same for the two bands and typically of the order of 7 cm^{-1} . It is noteworthy, that the

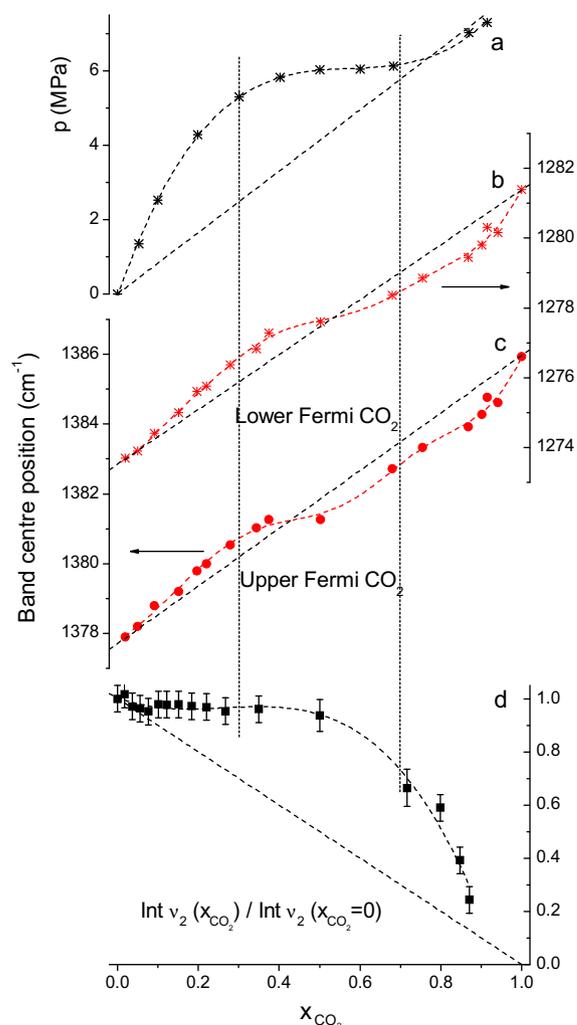


Figure 2. Binary mixture $\text{CO}_2 + \text{CS}_2$ at 313 K: pressure-composition diagram fitted with a third order polynomial to guide the eye. The straight line represents the ideal behaviour predicted by Raoult's law (a). Evolution with the CO_2 concentration of the band centre positions of the lower (b) and upper (c) components of the Fermi dyad of CO_2 . Evolution with the CO_2 concentration of the scattering intensity of the I_{VV} profiles of the ν_2 mode of CS_2 scaled to that of pure CS_2 (d). The line obtained by fitting a third order polynomial is given to guide the eye. The straight line corresponds to a linear evolution of the normalised intensity with the CO_2 concentration.

plateau region observed in the band-centre evolution (delimited by vertical lines in [Figure 2](#)) is closely correlated with the plateau-like region existing on the pressure-composition ($P - x$) curve. This sizeable non-linear behaviour observed on the Fermi dyad peak positions of system II has never been reported so-far for CO_2 -organic solvents and strongly contrasts with the linear trend observed for system I.

2.2.2. The ν_2 bending mode of CO_2

The ν_2 bending vibration of CO_2 is normally Raman inactive for the isolated molecule. In the dense phase of the mixture of CO_2 with an organic liquid, the weak activity of this degenerate mode and its splitting has been shown as an indicator of the formation of a hetero-dimer between CO_2 and the organic molecule [4–6,12,13].

In the CO_2 - CCl_4 mixture, the presence of this hetero-dimer is clearly observed on the polarised I_{VV} and depolarised I_{HV} spectra of the mixture which show the presence of a new weak band absent in neat CCl_4 and which does not correspond to the weak, broad

feature observed in pure CO₂ and ascribed to the CO₂ homo-dimers formation (Figure 3a) [14]. The band centre positions of the I_{VV} and I_{HV} profiles of the new feature are found to be equal and centred at about 657 cm⁻¹. The band is slightly polarised with a depolarisation ratio of about 0.6. The band shapes of the polarised and depolarised profiles are close to Lorentzian profiles having the same width varying between about 10 cm⁻¹ to 16 cm⁻¹ as the CO₂ concentration increases from 2 to 6.5 MPa.

The existence of the hetero-dimer formation in this system has been further confirmed by the observation of a faint polarised feature detected at about 1325 cm⁻¹ in the spectral domain between the dyad peaks (Figure 3b) and which has been demonstrated to be another signature of the presence of weak transient complexes formation in CO₂-organic liquid mixtures [2–4,15]. In the CO₂-CS₂ mixture, the presence of the intense Raman ν_1 mode of CS₂ in the spectral domain of the weak ‘induced’ ν_2 band of CO₂ precludes a direct discussion of the complex formation. However, a very weak, broad and polarised feature which is absent in pure CS₂ is observed at about 1330 cm⁻¹ between the Fermi dyad (Figure 4). This feature is the signature of transient CO₂-CS₂ hetero-dimers. So, we can conclude that in system I and II, transient CO₂ hetero-dimers are formed, presenting spectral characteristics different from that observed for CO₂ homo dimers in pure CO₂ [14].

2.2.3. The ν_2 bending mode of CS₂

The polarised and depolarised spectra of the ν_2 mode of CS₂ although originating from collision-induced (CI) scattering are intense and easily detected in the pure fluid [16–19]. The corrected polarised spectra, centred at about 395 cm⁻¹, are broad, slightly asymmetric and have the same band-shape as shown from the comparison of the I_{VV} with the I_{HV} profile multiplied by a constant factor (namely the reciprocal value of the depolarisation factor $\rho = 0.40 \pm 0.06$) (Figure 5).

Upon dilution of CS₂ by CO₂, it is found that all the previous characteristics features of the ν_2 spectra, namely, the bandshape, the band-centre position and the depolarisation ratio remain almost unaffected. This remarkable result is observed in a very broad concentration domain ranging from pure CS₂ to a state point in which CS₂ is very diluted ($x_{\text{CO}_2} \sim 0.7$) (Figure 5).

The evolution with the CO₂ concentration of the intensity of the polarised profiles scaled as discussed before (see SD) and normalised

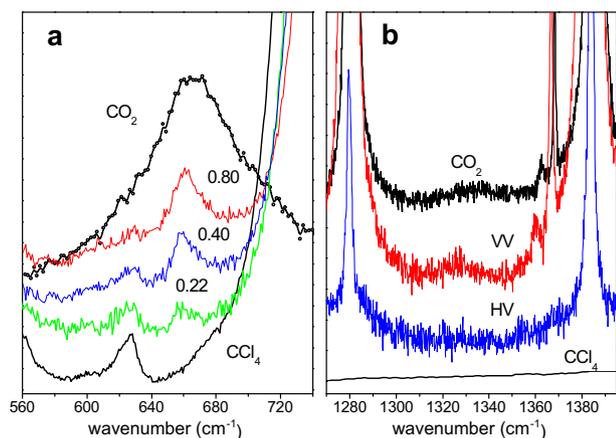


Figure 3. Binary mixture CO₂+CCl₄ at 313 K: Polarized Raman spectra in the spectral domain of the ν_2 bending mode of CO₂ at different CO₂ concentrations (m.f.). The polarized spectra of pure CO₂ (27 MPa) and of pure CCl₄ are also reported at 313 K (a). Polarized I_{VV} and depolarized I_{HV} Raman spectra in the spectral domain between the CO₂ Fermi dyad $x_{\text{CO}_2} = 0.80$. The polarised spectrum of CO₂ (27 MPa) and of pure CCl₄ at 313 K are given for comparison (b).

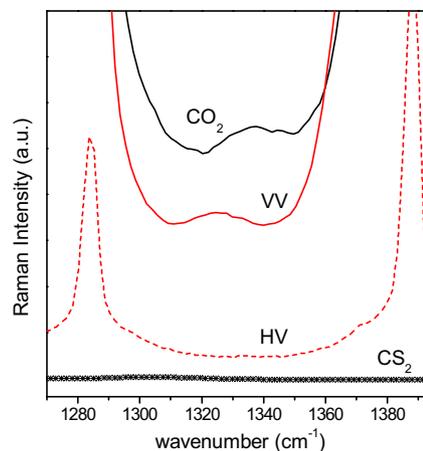


Figure 4. Polarised I_{VV} and depolarised I_{HV} Raman profiles in the spectral domain between the CO₂ Fermi dyad peaks in the CO₂-CS₂ mixture ($x_{\text{CO}_2} = 0.91$) at 313 K. The polarised spectra of CO₂ (13 MPa) and of pure CS₂ (*) at 313 K are given for comparison.

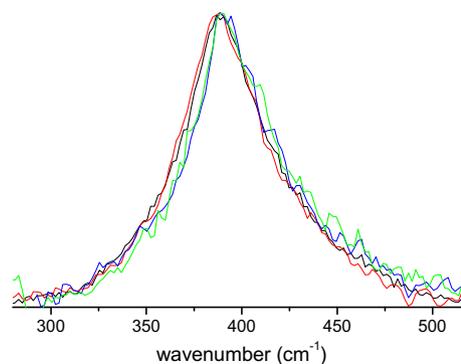


Figure 5. The corrected I_{VV} (black) and the I_{HV} (red) profiles (see Supplementary data) of the ν_2 mode in pure CS₂ at 313 K. The depolarised profile has been multiplied by the value of reciprocal depolarisation factor (0.40). The corrected I_{VV} (blue) and the I_{HV} (green) profiles of the ν_2 mode in the mixture ($x_{\text{CO}_2} = 0.70$) scaled to the I_{VV} profile of pure CS₂ are displayed.

to that of pure CS₂ is displayed in Figure 2d. The intensity of the profile remains almost unaffected by the large variation of the CO₂ concentration up to equimolar mixture. It is beyond this state point that the intensity decreases markedly. This trend is clearly seen from the comparison with the straight line passing between points corresponding to pure CS₂ and infinitely diluted in CO₂ for which the intensity is expected to almost vanish. The Raman spectrum of the ν_2 mode of liquid CS₂ has been considerably studied theoretically and experimentally [16–23]. It has been established that its Raman activity is mainly due to a dipole-induced quadrupole interaction ($A'-\alpha$) mechanism [18,21,24] and that the bandshape and intensity depend upon rotational and translational contributions in which a subtle balance between two and three body terms associated with the interaction mechanism exist. Such a framework has been extended to binary mixtures but investigations in this domain are scarce in view of the complexity of the expressions and lack of knowledge of molecular parameters [22,25–27]. In the present study, we will retain as main physical result the fact that the ν_2 mode being induced is a particularly sensitive probe of the perturbation of the CS₂ molecule by its environment. Upon dilution of CS₂ with CO₂, we normally expect that the composition of the neighbouring shell of molecules surrounding a tagged CS₂ molecule should be modified. Moreover, this composition variation and the replacement of CS₂-CS₂ interactions by the CO₂-CS₂ ones should affect the degree

of cancellation between two and three body terms leading to a sizeable perturbation of the band-shape and intensity of the ν_2 mode. However, this prediction is not experimentally verified as the ν_2 band-shape and its integrated intensity are almost unaffected by the dilution in CO_2 up to equimolar mixture (Figure 5). Incidentally, we note that experimental studies have reported that CI scattering of the CS_2 diluted in cyclopentane was independent of the concentration of this solvent [26,27].

Therefore, in the context of the CI theoretical framework, the previous results may be only understood by contending that the dilution does not affect significantly the local translational and orientational ordering probed by the ν_2 mode on the time scales and distances involved in the interaction mechanism. This is indeed a remarkable conclusion which allows giving a picture of the mixing process. Thus, at very low CO_2 concentration, the conventional view of mixing in which CO_2 molecules start filling the voids existing or formed in the liquid phase of CS_2 should apply. However, as the CO_2 concentration is increased, the preservation of the local structure of CS_2 implies that the incoming new CO_2 molecules should be accommodated in the vicinity of the existing CO_2 molecules leading to the progressive formation of co-existing local aggregates of CS_2 and CO_2 . The size of the CS_2 aggregates should be such that the local ordering existing in the pure fluid is almost retained to lead to CI profiles keeping band-shapes similar to those in pure CS_2 . Because, the induced band shapes are conditioned by two and three body interaction, we may suppose that such CS_2 aggregates should be constituted, at least by three molecules. Therefore, the mixing process should lead to a ‘micro segregation’ of the liquid phase but without leading to a phase separation. Incidentally, the non-ideality of CS_2 -long-chain n -alkane ($n = 14$ and 16) mixtures that has been ascribed to the existence of two distinct environments in which isolated CS_2 aggregates are present has been suggested by femtosecond optical Kerr effect/Raman-induced Kerr effect studies [28].

At higher CO_2 concentration ($x_{\text{CO}_2} > 0.5$) the intensity of the ν_2 profile clearly decreases to reach at ‘infinite dilution’ the expected vanishing value (Figure 2d). Therefore, as the CO_2 concentration increases, the CS_2 neighbours around a CS_2 molecule become progressively substituted by CO_2 and that a second regime is reached in which a diversity of species comprising small CS_2 oligomers, CS_2 - CO_2 hetero-dimers (as discussed above) exist in a ‘bath’ of monomers and dimers of CO_2 . The existence of these two regimes probed by the ν_2 mode together with the non-linear evolution of the band centre position of the CO_2 Fermi dyad reflects at the molecular level the non-ideal behaviour of the CO_2 - CS_2 mixture put in evidence by thermodynamics studies (Figure 2a). Moreover, the transition between the two regimes giving rises to the plateau-like region on the concentration evolution of the spectroscopic observations is clearly correlated with the corresponding plateau-like region observed in the same concentration domain on the pressure-composition diagram at 313 K.

The picture of a segregated liquid phase in which CS_2 and CO_2 aggregates co-exist in the first solvation regime may be supported by the report of a LLE phase diagram with an UCST at 290 K [7]. Although at 313 K the system is above the UCST and thus, no demixing of the mixture occurs, it is still very close to the liquid-liquid critical point and the phase instability, although not macroscopically observable, is nevertheless still present at the molecular level. Interestingly, the existence of the two regimes also allows rationalising the trend of the solubility of CO_2 in CS_2 . In the first regime, the presence of two rather distinct domains is a witness of the difficulty to mix the components as a great and steep pressure variation up to a certain threshold is required. In contrast, after this threshold, which corresponds to the second regime, a rather modest pressure variation is sufficient to easily concentrate the mixture in CO_2 .

3. Discussion

Although neither of these mixtures is ideal (hetero-dimers also exist in CO_2 - CCl_4), it will be worthwhile to rationalise the difference between the solubility of CO_2 in the two systems on the ground of the criteria used to discuss the ideality of a mixture composed of A and B molecules. The first criterion is that the values of the homo (AA and BB) and hetero (AB) binary interaction energies are of the same order of magnitude. This amounts to say that the interchange energy $\Delta = 2E_{\text{AB}} - E_{\text{AA}} - E_{\text{BB}} = 0$. The calculated ab-initio interaction energy in system I and II and the value of the interchange energy are reported in Table 1 [29]. The Δ values slightly greater than zero for system I and more than twice for system II confirm that the solution I is almost ideal whereas mixture II departs more sizeably from this behaviour. Moreover in system II, because Δ is positive with a non-negligible value, together with the fact that the interaction energy between CS_2 molecules is the greatest, confirm the tendency of the CS_2 molecules to cluster. Incidentally we remind that in gaseous phase CS_2 clusters have been put in evidence [30,31]. We may contend that the CS_2 and CO_2 coexisting clusters (aggregates) should have a rather barrel like arrangement, in accordance with the structure reported for these neat liquids [32] and interact through their interfaces. These interactions occur with a non-negligible energy as shown from the energy value of the hetero-dimer (Table 1). It is certainly this stabilizing interaction which forbids the demixing of the solution. Clearly, energetic considerations are consistent with the interpretation of the spectroscopic findings. The second criterion involved in the ideality concept is that the A and B molecular shapes should be similar. There is a contradiction here as this hypothesis is almost fulfilled in the non-ideal system II and not in system I. Insights can be obtained from the swelling of the organic solvent by CO_2 [33]. This effect is quantified by the evolution with the CO_2 concentration of the relative volume expansion of the liquid phase $\Delta V/V$ at pressure P and temperature T according to:

$$\Delta V/V = (V_{\text{mixt}}(T, P, x_{\text{CO}_2}) - V_{\text{solv}}(T, P_0)) / V_{\text{solv}}(T, P_0) \quad (1)$$

in which V is the volume of the mixture (mixt) or the solvent (solv) and P_0 is the reference pressure (0.1 MPa) [34].

The evolution of $\Delta V/V$ with the CO_2 concentration at 313 K for the systems I and II is reported in Figure 6. At equimolar concentration, the volume of the liquid phase has increased by about 50% in system I and 100% in system II. It is clear that mixture I presents a shrunken volume compared to mixture II. Furthermore, the relative volume expansion in mixture II is found to closely follow the variation calculated for an expanded mixture in which the volumes of the components of the mixture are additive (Figure 6). These new findings and this comparison have two implications. Firstly, the volume additivity observed for system II is consistent with the tendency to have in this system a segregated liquid phase in which CS_2 and CO_2 aggregates co-exist in the first solvation regime.

Table 1

Binding energy of the most stable dimers calculated at the MP2 level of perturbation using augmented correlation-consistent polarized Valence Triple Zeta basis set and corrected from BSSE contribution. The interchange energy $\Delta = 2E_{\text{AB}} - E_{\text{AA}} - E_{\text{BB}}$ is reported.

	Binding energy (kcal mol ⁻¹)	Δ (kcal mol ⁻¹)
CCl_4 - CCl_4	-2.97 (D_{3d} -symmetry) ^a	
CCl_4 - CO_2	-1.9 (C_s -symmetry)	0.47
CO_2 - CO_2	-1.3 (slipped parallel, C_{2h} -symmetry)	
CS_2 - CS_2	-3.3 (slipped parallel, C_{2h} -symmetry)	
CS_2 - CO_2	-1.7 (slipped parallel, C_s -symmetry)	1.2

^a This value is taken from Li et al. [29].

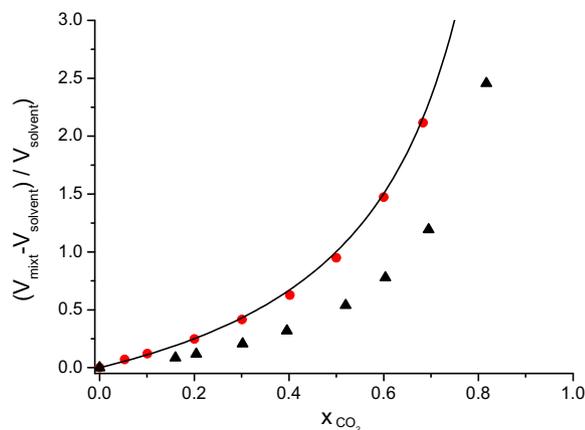


Figure 6. Evolution with the CO_2 concentration of the volume expansion of the solvent in CS_2 - CO_2 (●) and CO_2 - CCl_4 at 313 K (▲). The calculated volume expansion of a mixture in which the volumes of the components are additive is given by the black line.

The second implication is that the hypothesis of volume additivity (or stated otherwise the absence of excess volume) upon mixing is fulfilled in the non-ideal system II and therefore is a necessary but not sufficient condition of ideality.

Understanding the origin of the difference between the volumes expansion in the two mixtures demand to consider the intermolecular interactions. We have already discussed the role of the attractive forces in favouring the clustering of CS_2 molecules in system II and a more random mixing in system I. However, repulsive forces which govern the short range local ordering in liquids and contribute to the packing of molecules via the molecular shape must play a relevant role. The calculated free volumes [35] of liquids CS_2 and CCl_4 by molecule are about 28 and 48 \AA^3 , respectively, whereas it is about 38 \AA^3 for CO_2 . These estimations show that the CO_2 molecules can hardly penetrate the CS_2 compact structure and that a random mixing situation is unfavoured in comparison with a segregated one. Thus the apparent volume additivity observed in the non-ideal system II is very different from that obeyed by ideal mixtures which results from a random mixing of the constituents. Clearly there is sufficient free volume in CCl_4 to accommodate CO_2 molecules hence suggesting that the conditions of a random mixing are favoured in this system and therefore the total volume of the mixture should be shrunken compared to that expected for an ideal solution.

4. Conclusion

The spectroscopic study of the CO_2 Fermi dyad and the ν_2 mode of CS_2 show that CO_2 - CS_2 is strongly non-ideal whereas CO_2 - CCl_4 can be considered as almost ideal. In both systems transient hetero-dimers have been put in evidence. The solvation in CO_2 - CS_2 is characterised by the existence of two regimes. At high CS_2 concentration (regime I), the local structure of CS_2 is preserved suggesting a nano-segregation of the liquid phase without demixing whereas in CO_2 concentrated mixtures (regime II) a diversity of species (CS_2 oligomers, CS_2 - CO_2 hetero-dimers) are present in a 'bath' of CO_2 monomers and dimers. Finally, considerations on the energetics and on the volume expansion and molecular free

volume of the mixtures together with the spectroscopic results show that in CS_2 - CO_2 a subtle interplay between attractive and repulsive interactions lead to a non-ideal behaviour. The micro-segregation picture is supported by the report of a liquid-liquid equilibrium phase diagram with an UCST at lower temperature (290 K). Although at 313 K the system is above the UCST and thus without demixing, it is still very close to the liquid-liquid critical point and the phase instability, although not macroscopically observable, is nevertheless still present at a molecular level.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cplett.2013.07.061>.

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