

Controlling phase behaviour on gas expansion of fluid mixtures

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The application of moderate pressures (50 bar) of CO₂ to binary liquid solvent mixtures at room temperature can induce changes in phase behaviour; both inducing miscibility and splitting miscible mixtures. The cause of this phase change behaviour was found to be due to the balance between enthalpic and entropic terms that define the Gibbs energy of mixing and, hence, the partition coefficient. In the majority of binary solvent mixtures, the solvents were miscible at ambient pressure with two phases forming upon application of CO₂. For some mixtures, the phase behaviour was found to be very composition dependent and in only five systems did no phase change occur.

Introduction

The use of CO₂ as a pro- or anti-solvent has become popular recently. It has the advantages that it is non-toxic, sustainable and that it can act as a simple barometric switch to induce phase change behaviour. It also has the advantage over supercritical CO₂ that relatively moderate pressures are required and that this effect can be observed at ambient temperatures. This methodology, therefore, has the potential to decrease the overall energy requirements for a process. Several studies have been made on the carbon dioxide–alcohol–water systems in an endeavour to break the azeotropic concentration.^{1–4} Efremova and Shvartz^{5,6} investigated the liquid–liquid and gas–liquid critical end points for the CO₂–methanol (and ethanol)–water systems. Lim and Lee have determined the tie-lines in the two-phase region and three-phase equilibrium compositions at temperatures close to the critical point of carbon dioxide and also for the carbon dioxide–ethanol–water system.⁷

Gas expanded liquids have also started to show ‘promise’ as alternative media for performing catalytic reactions such as oxidations,⁸ hydroformylations,^{9,10} and solid-acid catalysed reactions.¹¹ Most recently Phan *et al.* studied the extraction of soybean oil using CO₂ as a switch to change the polarity of the solvent enabling initially miscibility of the oil with the solvent at high pressure and separation from the solvent at ambient pressure.¹² In terms of understanding the physical properties of such systems, so far researchers have concentrated on determining transport properties. Laird *et al.*¹³ reviewed the calculation of phase equilibria and transport properties of GXs using molecular simulation methods. Sassi *et al.*¹⁴ reported that diffusion coefficients for benzene in CO₂-expanded methanol showed a four-fold increase on expansion with CO₂. Similar expansions have been experienced by Kho *et al.*¹⁵ who noticed a decrease of four-fold in solvent viscosities of CO₂-expanded fluorinated solvents. In the preceding paper, in a detailed study of some of the physical properties of organic solvents expanded

with CO₂, we have shown that liquid density, solubility strength, and both local and bulk polarity properties can be tuned.¹⁶ Lazzaroni *et al.* studied the phase behaviour of THF, acetonitrile and dioxane mixtures with water and CO₂, fitting their phase behaviour to a Peng–Robinson Equation of State with Huron–Vidal type mixing rules. They suggested that these systems may be suitable carrying out catalytic reactions and achieving effective product catalyst separation.¹⁷

In order to optimise the use of CO₂ it is useful to have knowledge of solvent compatibility, in particular for multi-component mixtures. Although some experimental data on CO₂ expanded liquids are now available in the literature,^{18–20} in general, data is still quite sparse. The limiting case of equilibrium between two components (binary systems) presents a suitable starting point for determining multi-component phase behaviour and in the current study, the liquid–liquid equilibrium behaviours for 120 binary solvent systems at room temperature are reported in which the phase behaviours of these systems at ambient pressure and under gas expanded conditions are compared.

Experimental

Pressure was applied using a model P50-series piston controlled pump (Thar Technologies Inc.; Pittsburg, PA, USA) and was monitored (± 2 bar) using a Swagelok manometer. The temperature of the cell was measured using an iron/constantan thermocouple, the tip of which was in contact with the solvent close to the centre of the cell. The temperature was held at a given value (± 0.5 K) using a CAL-9300 controlled heater. The high pressure optical cell was constructed from 316 stainless steel with 1 cm thick sapphire windows. The gas seals were made from Teflon. The cell path length was 6 cm and the cell volume was 70 cm³. The density was determined using an Anton Paar DMA 512P densitometer and an Anton Paar mPDS 1000 evaluation unit designed to make measurements at both atmospheric and high pressures.

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Results and discussion

The gas expanded liquid–liquid phase behaviour of 120 binary solvent systems was determined at 25 °C and 50 bar of CO₂ in a high pressure view cell. The results are shown in Fig. 1, where 16 different organic solvents were compared for miscibility/immiscibility with each other at both ambient and pressurised conditions. Clearly, in any ternary system phase behaviour will be dependent upon not only temperature and pressure, but also composition, and it is impossible to map all compositions and all constituents. Total immiscibility is also rarely obtained in any system and so the term immiscible here refers to systems which are predominantly although not totally immiscible. In this work, therefore, a simplified comparison was undertaken where equal volumes (2.5 cm³) of liquid molecular solvents were used at fixed CO₂ pressure.

Fig. 1 illustrates that the alcohol–water equilibrium shifts reported previously^{1–4} under CO₂ pressure are not unique. In fact, phase change behaviour could be induced in 115 of the 120 systems studied in this work by the application of modest CO₂ pressure (* in Fig. 1 highlight the 5 combinations that remained miscible under all conditions). This is a remarkable result, as it demonstrates the almost universal ability of CO₂ to bring about phase change in binary liquid mixtures.

In a limited number of cases, CO₂ acts as a pro-solvent but in the majority of cases it acts as an anti-solvent. In Fig. 1(a)/(b) the highlighted combinations (at either ambient or 50 bar pressure) that represent immiscibility demonstrate an apparently random impact of gas expansion on the miscibility of these binary solvent mixtures. For example, with toluene (14 out of 15 combinations) or 1,2-dichloroethane (14 out of 15 combinations) phase separation predominately occurs on gas expansion, whilst with cyclohexane phase separation (for some solvent combinations) or miscibility (for others) occurs, apparently dependent on the polarity of the partner solvent. The situation is further complicated (Fig. 1(c) and 2) where changing the total solvent volume and/or the component ratios affords phase separation on gas expansion for previously miscible systems; e.g. cyclohexane and ethanol are miscible under ambient conditions and stay miscible when pressurised, but phase separation could be induced when the conditions were changed.

Fig. 2a shows that cyclohexane and ethanol at 50 bar of CO₂ under the experimental conditions (1.0 cm³ total volume of solvent in a 9 cm³ volume vessel) are clearly miscible. In Fig. 2b, the change in behaviour when the volume of initial liquid solvent is increased to 1.5 cm³ is apparent, and in Fig. 2c phase immiscibility is seen when the solvent volume is increased further to 2 cm³. In these 3 cases a dye was used (phenol blue) to distinguish between the two phases but since it is only present in micromolar concentrations it is not thought to affect the phase behaviour. As can be seen from the thermodynamic discussion below, both the amount of solvent and their relative interactions with each other will affect the phase behaviour.

The addition of CO₂ will have several effects on the systems being studied;¹⁶ it will:

- Change the system density
- Decrease the dielectric constant
- Decrease the polarisability of the solvent

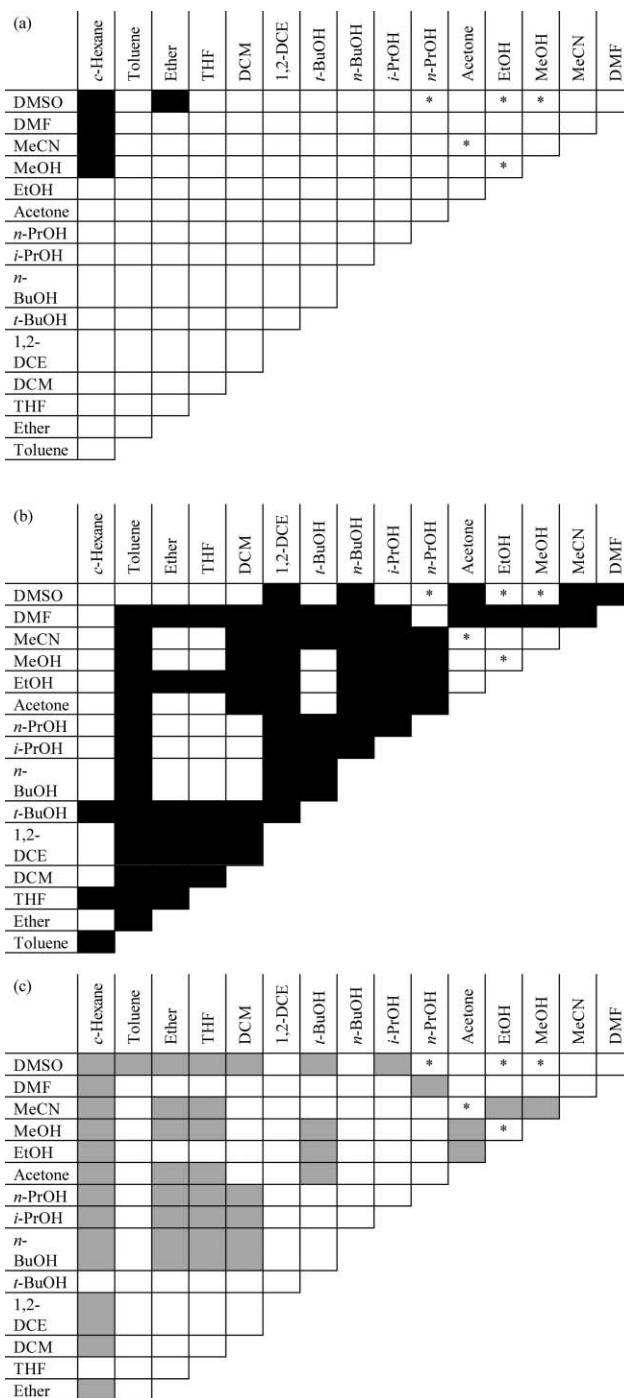


Fig. 1 Phase behaviour results for binary solvent systems where a white box represents solvents that are ‘miscible’ and a black box represents solvents that are ‘immiscible’. (a) ambient temperature and pressure; (b) ambient temperature and 50 bar CO₂; (c) ‘grey’ boxes reveal solvent systems which were initially shown to be miscible when pressurised with CO₂, but can be made ‘immiscible’ if the ratio of the two solvents is altered. *Highlights those solvent mixtures that remain miscible throughout.

- Decrease the packing density and affect the entropy and the free volume
- Change the volume expansion ratios depending on the CO₂ solubility

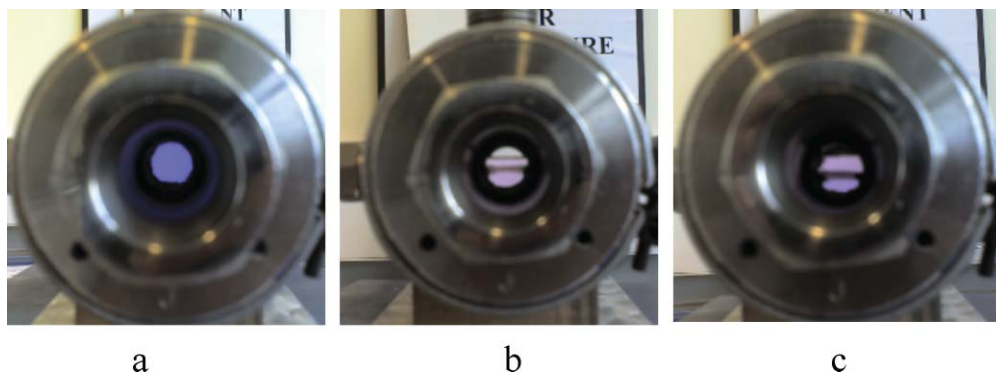


Fig. 2 The series of pictures taken represent changes in phase behaviour of the binary system cyclohexane–ethanol upon expansion. (Dye = phenol blue).

Using the physical parameters reported for these systems in the previous paper it is possible to compare the changes in dielectric constant, density and local polarisability upon pressurisation to determine the possible causes of phase changes. It was shown that pressurising the solvents in Fig. 1 with CO₂ caused a decrease in dielectric constant and local polarisability as would be expected given the low polarity of CO₂.¹⁶ In all cases CO₂ brought the dielectric constant of each component closer together which would be predicted to cause all the solvents to become more miscible in the pressurised form as they become more alike; *i.e.* CO₂ acts as a pro-solvent. In reality, however, the opposite is true and most of the solvent mixtures separate. In the same way, the observed phase behaviours cannot be argued on any polarity, density or solubility grounds and, hence, the only way of explaining this phenomenon is in terms of the thermodynamics of mixing.

Thermodynamics of solvent mixing

Miscibility of molecular liquid solvents is controlled by the Gibbs Energy of mixing, and both enthalpic and entropic contributions will be important. The Gibbs Energy of mixing $\Delta_{\text{mix}}G$ is given by;²¹

$$\Delta_{\text{mix}}G = nRT(x_A \ln x_A + x_B \ln x_B + x_A x_B \beta) \quad (1)$$

Where x_A is the mole fraction of each component and the other symbols have their usual meaning. The parameter, β , is given by

$$\beta = \frac{w}{RT} \quad (2)$$

and is a measure of the activity coefficient, γ , of each solute

$$\ln \gamma_A = x_B^2 \beta \text{ and } \ln \gamma_B = x_A^2 \beta \quad (3)$$

The parameters w and γ are difficult to quantify but the former can be related to the excess enthalpy of mixing. This in turn is related to the pair-wise interaction parameters, ε for the like-unlike ε_{AB} and like-like molecular interactions, ε_{AA} and ε_{BB} where

$$w_{AB} \propto 2\varepsilon_{AB} - \varepsilon_{AA} - \varepsilon_{BB} \quad (4)$$

The limited collections of published data make quantification of the mixing process impossible, however some qualitative inferences can be drawn from the magnitude of the mixing

enthalpy. For the mixtures studied in this work the enthalpy of mixing may be endothermic or exothermic, but is numerically small and is generally in the order of ± 100 to 500 J mol^{-1} .^{22,23} Remembering that ε values are always negative, for such binary systems it is easy to understand why like solvents *e.g.* ethanol and methanol mix since $\varepsilon_{AA} \approx \varepsilon_{BB} \approx \varepsilon_{AB}$ resulting in $|w_{AB}|$ being small (either positive or negative). This means that $x_A \ln x_A + x_B \ln x_B + x_A x_B \beta$ is negative leading to negative Gibbs energy. Similarly, for unlike solvents $\varepsilon_{AB} > \varepsilon_{AA} \approx \varepsilon_{BB}$, w_{AB} is larger and positive leading to positive Gibbs energy.

When a third component C is added (in this case CO₂) the picture becomes much more complex, since the phase behaviour will depend upon the relative Gibbs energies of mixing. We have shown¹⁶ that for the majority of solvents in this study that as mixing occurs, C is the dominant component in the system with x_A and x_B decreasing significantly. In the three phase system, one phase will predominate if $\Delta_{\text{mix}}G_{ABC} < \Delta_{\text{mix}}G_{AC} + \Delta_{\text{mix}}G_{BC}$ and eqn (1) and (4) become:

$$\Delta_{\text{mix}}G = nRT (x_A \ln x_A + x_B \ln x_B + x_C \ln x_C + x_A x_B x_C \beta) \quad (5)$$

and

$$w_{ABC} \propto 3\varepsilon_{ABC} - 2\varepsilon_{AB} - 2\varepsilon_{BC} - 2\varepsilon_{AC} - \varepsilon_{AA} - \varepsilon_{BB} - \varepsilon_{CC} \quad (6)$$

It is informative to illustrate how this relates to the three binary w parameters:

$$w_{ABC} \propto 3\varepsilon_{ABC} - w_{AB} - w_{BC} - w_{AC} - 3\varepsilon_{AA} - 3\varepsilon_{BB} - 3\varepsilon_{CC} \quad (7)$$

The phase behaviour of the various systems can be more clearly understood by splitting the observations in Fig. 1 into three general cases.

Case 1: Miscible at ambient pressure–immiscible at 50 bar CO₂. Fig. 1 shows that this is the most common case. While the excess enthalpy of mixing has been measured for many of the liquid solvents, those for the liquid solvents with CO₂ have not. One example that can be quantified, CO₂–toluene–methanol, illustrates the underlying thermodynamics in these systems. The excess enthalpy of mixing toluene and methanol is small and endothermic, *ca.* 500 J mol^{-1} ,²⁴ such that, as mentioned above, w_{AB} is small and the two solvents mix. In contrast, the excess enthalpy of mixing of CO₂ and methanol²⁵ is *ca.* -3500 J mol^{-1} whilst that of CO₂ and toluene is *ca.* -2800 J mol^{-1} ,²⁶ such that both w_{AC} and w_{BC} will be large and negative. Hence, from eqn (2)

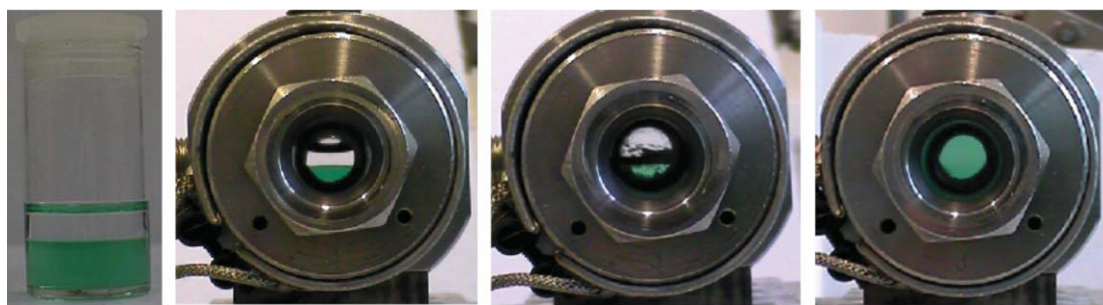


Fig. 3 Phase behaviour of cyclohexane–DMSO binary solvent system. Under ambient pressure (in sample vial, and view cell picture 1), during pressurisation, and after reaching an equilibrated state. (Dye = Reichardt's dye $E_T(33)$).

Table 1 Density measurements of four mixed solvent pairs (1 : 1 ratio) at ambient pressure, and when pressurised with CO_2 at 50 bar. 'Expected' densities are also included; these are determined by taking an average of the density values for the pure components. Expected densities for the expanded systems are taken from an average of the expanded density values determined for expanded solvents with published data¹⁵

Solvent Pair	Density at Ambient Pressure/ g cm^{-3}		Density at 50 bar $\text{CO}_2/\text{g cm}^{-3}$	
	<i>expected</i>	<i>actual</i>	<i>expected</i>	<i>actual</i>
EtOH MeOH	0.788	0.787	0.811	0.847
DMSO EtOH	0.941	0.950	0.957	0.973
DMSO MeOH	0.943	0.958	0.946	0.976
Acetone MeCN	0.782	0.782	0.858	0.879

and (7), β will be positive and under the conditions in Table 1 this is sufficient to make $\Delta_{\text{mix}}G$ positive such that the equilibrium tends to the two separate phases, toluene + CO_2 and methanol + CO_2 .

Case 2: Immiscible at ambient pressure–miscible at 50 bar CO_2 . The systems which are immiscible at ambient pressure are generally those with large differences in polarity; *e.g.* DMSO and cyclohexane ($2\varepsilon_{\text{AB}} > \varepsilon_{\text{AA}} + \varepsilon_{\text{BB}}$; ΔH_{mix} is endothermic). However, despite the fact that cyclohexane and DMSO are at opposite ends of any polarity scale, they become miscible upon pressurisation, as shown in Fig. 3. Unfortunately, a quantitative illustration of this process cannot be carried out due to the lack of CO_2 expansion thermodynamics; however, the key difference between Cases 1 and 2 is that, here, w_{AB} is large and positive. This leads to smaller w_{ABC} and β and under the conditions in Table 1, this must be sufficient to make $\Delta_{\text{mix}}G$ negative, leading to a single phase.

Case 3: Always miscible. The above discussion clearly explains the majority of cases, where a phase change occurs upon pressurisation, but there are a few exceptions, which are listed in Table 1, where the solvents are miscible before and after pressurisation. In these cases, both liquid components are polar and good hydrogen bond donors and acceptors. The ΔH_{mix} values for these liquids are, however, endothermic (typically 1–1.5 kJ mol^{-1}),²⁶ which should tend towards those systems in case 1 and, therefore, suggests that entropic factors are more significant and govern the phase behaviour. Table 1 shows that the density change upon pressurisation for those solvents that do not phase separate is larger than expected from the average of the two individual components. This suggests that in these

ternary mixtures the entropy changes on mixing are larger than those for CO_2 mixing with either of the individual components, ε_{ABC} becomes more significant than in either case 1 or 2, w_{ABC} will be small, affording a single phase on pressurisation.

It must, however, be stressed that Fig. 1 only shows a qualitative assessment of the phase behaviour of two and three component systems. In the real case, the separate phases will contain mixtures of components, *i.e.* the partition coefficient will be dependent upon ΔG_{mix} . Pressurisation with CO_2 will not cause total splitting of the components but it will drive the equilibrium towards separation of the two binary phases. This could potentially be used for the reversible homogenisation of reagents in biphasic reactions. It could also be used for simple barometric control over solvent or solute separation where conventional distillation methods are extremely energy intensive.

Conclusions

This work has assessed the change in phase behaviour of mixed binary solvents on expansion with 50 bar of CO_2 at ambient temperature. It was noted that 115 of the 120 system studies showed the ability to undergo phase inversion when pressurised. This showed that GXLs can act as both pro- and anti-solvents, and can therefore be used to induce miscibility (for example in phase transfer applications), or be used in phase separation studies, such as the precipitation of solids, in extractions, separations and to replace distillation methods. It was shown that the phase behaviour resulted from a complex mixture of enthalpic and entropic components.

Secondary studies of those solvents which did not show any change in phase behaviour showed that if experimental conditions were optimised and volume ratios of the components were altered, then conditions could be achieved where phase behaviour could be inverted, such as that reported earlier with the case of cyclohexane–ethanol– CO_2 .

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