

## Phase diagram of $\gamma$ -butyrolactone-dimethyl-carbonate mixtures

A. Chagnes, C. Mialkowski, B. Carre, D. Lemordant, V. Agafonov  
and P. Willmann<sup>1</sup>

*Laboratoire de Physicochimie des Interfaces et des Milieux Réactionnels, EA 2048,  
Université de Tours, Faculté des Sciences, Parc de Grandmont, 37200 Tours, France*

<sup>1</sup> *CNES, 18 avenue E. Belin, 31055 Toulouse cedex, France*

**Abstract.** Using differential scanning calorimetry (DSC) and X-ray diffraction (XRD) at low temperatures we have determined a phase relation between  $\gamma$ -butyrolactone and dimethyl carbonate. Two polymorphs of  $\gamma$ -butyrolactone with a monotropic transformation and two polymorphs of dimethyl carbonate with an enantiotropic transformation induced by BL were observed. The diagram is characterised by an eutectic point for  $x_{\text{DMC}}=0.12$  and  $T=-57.5^\circ\text{C}$ .

### 1. INTRODUCTION

In order to enhance lithium ion batteries performances, and particularly at low temperatures, the formulation of the electrolyte is critical. A new trend in the batteries research is the search of binary or ternary mixtures of solvents thermodynamically stable at low temperature (below  $-20^\circ\text{C}$ ). The mixture of solvents must have a low viscosity in order to enhance ionic mobilities, a high dielectric constant to dissolve the salt as separated ions, a large electrochemical window and a low crystallisation point. Few of studies deal with phase diagrams of mixtures of organic dipolar aprotic solvent. Nevertheless, recently, the phase diagrams of mixtures of cyclic ethylene carbonate (EC) and linear carbonates as dimethylcarbonate (DMC) or ethylmethylcarbonate (EMC) have been studied by Ding [1]. The obtained phase diagrams are simple and characterised by an eutectic point which is close to the compound having the lowest melting point. Moreover, there is no miscibility gap in the liquid state whereas in solid state there is no mutual solubility.

Then, in addition to conductivity and electrochemical stability studies, the thermal stability of the mixed solvent is to be investigated [2]. Unlike the permittivity or the viscosity which can be estimated considering ideal mixtures [3,4], the thermal stability is definitively unpredictable and experimental studies are required. In this paper, we investigate a phase relation of  $\gamma$ -butyrolactone (BL)-DMC mixtures by means of differential scanning calorimetry (DSC) and X rays diffraction (XRD) at low temperature.

The properties of BL are very attractive for Li-batteries applications. In fact, BL has a low melting point [4] and a high boiling point [4]. Its permittivity is high enough to permit an almost complete dissociation of the Li-salt at least when large anions are used [3]. Nevertheless, BL exhibits a relatively high viscosity and for this reason a low viscosity solvent like DMC is added [3,7]. DMC is interesting as co-solvent despite the fact that itself has a low permittivity [7], a high melting point [8] and a low boiling point [6,7]. The main aim of this work is to establish the phase diagram of BL-DMC because it determines the liquid stability of the mixture.

## 2. EXPERIMENTAL

The solvents BL (99.9%) and DMC (99.9%) are from Aldrich. A dry glove box filled with argon is used for the preparation of the binary mixtures. Samples for DSC experiments were prepared by hermetically sealing a small amount (10-20 $\mu$ L) of a liquid mixture in a 50 $\mu$ L aluminium sample pan. The reference used is an aluminium pan. Thermograms are recorded with a Perkin Elmer DSC 6 apparatus equipped with a gas flow system cooled by liquid nitrogen. To prevent water condensation, a stream of nitrogen was continuously flowed around the sample holder. The heating and cooling rate is fixed at 10 $^{\circ}$ C/min. We can notice that during DSC experiments we don't take in account the evolution of pressure in the sealing pan to plot the phase diagram.

XRD investigations were performed with an INEL CPS 120 diffractometer using the Cu K( $\alpha_1$ ) radiation. Capillaries are sealed to be sure that no hydration phenomenon occurs during XRD investigations at low temperature. Samples are cooled by OXFORD system using liquid nitrogen. The cooling method in DSC and XRD is different and for this reason, the temperature in XRD experiment is slightly different of the temperature in DSC experiment. During the XRD experiment the temperature is estimated with an accuracy of  $\pm 10^{\circ}$ C.

## 3. RESULT AND DISCUSSION

The DSC curves of the pure solvents BL and DMC are reported in figures 1 and 2 respectively. The thermogram reported in figure 1 exhibits a freezing peak at  $-69^{\circ}$ C corresponding to a crystallisation delay. The melting point is attained at  $-43^{\circ}$ C, in fair agreement with literature data [4].

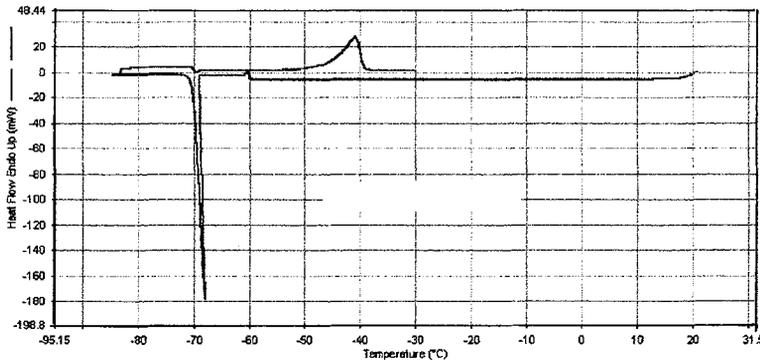


Figure 1 : DSC thermogram of BL at 10 $^{\circ}$ C/min with a pause on cooling at  $-60^{\circ}$ C and on heating at  $-70^{\circ}$ C.

The thermogram of DMC, reported in fig. 2, has a crystallisation peak at  $3^{\circ}$ C which corresponds to the fusion temperature without almost any subcooling phenomenon.

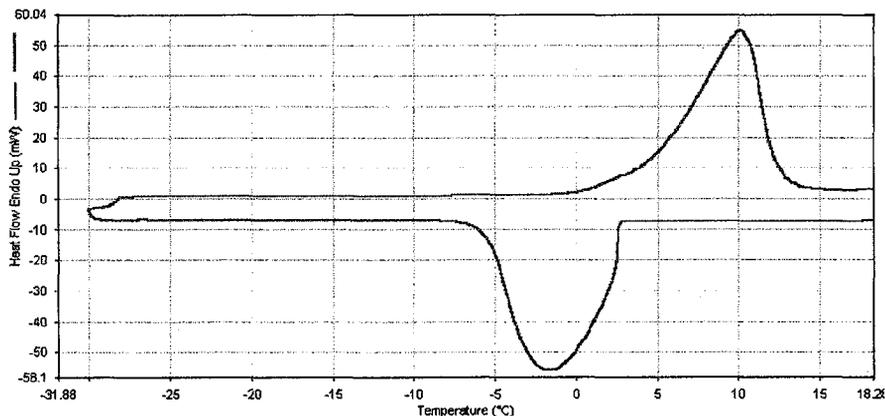


Figure 2 : DSC thermogramm of DMC at 10°C/min.

XRD patterns of BL at  $-93^{\circ}\text{C}$  are reported on figures 3a and 3b. Figure 3a corresponds to XRD pattern obtained for sample quenched down to  $-93^{\circ}\text{C}$ . Figure 3b is obtained when the precedent sample is heated back to  $20^{\circ}\text{C}$  and then cooled in a second step down to  $-93^{\circ}\text{C}$ . For the both samples, the same cooling condition is used and we cannot estimate the cooling rate (about one second to cool down from ambient temperature to  $-103^{\circ}\text{C}$ ). XRD measurements were made by heating up to room temperature for the both patterns. The both patterns are different (we have indexed with two different lattices the both patterns) which proves that BL at the solid state exhibits at least two polymorph forms called as BL1 (more stable) and BL2.

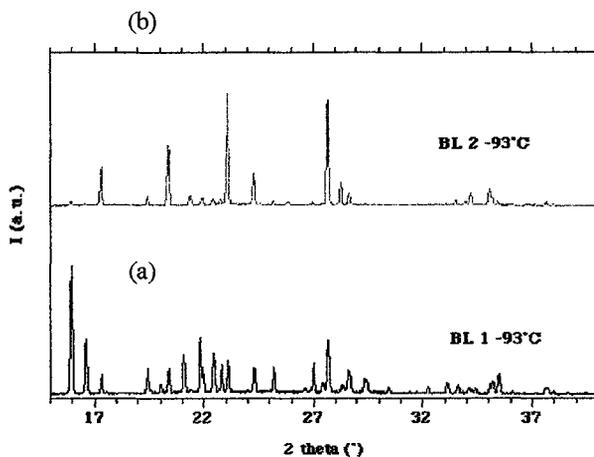
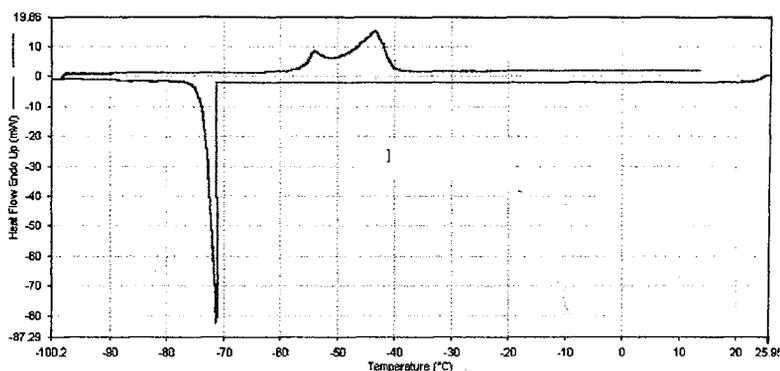


Figure 3 : XRD patterns of BL at  $-93^{\circ}\text{C}$  (a) sample quenched down to  $-93^{\circ}\text{C}$  (b) precedent sample heated back to  $20^{\circ}\text{C}$  and then cooled in a second step down to  $-93^{\circ}\text{C}$ .

The DSC curves of BL – DMC mixtures at different molar fractions in DMC have been determined in order to obtain the phase diagram of the system. As an example we have reported in figures 4a and 4b, the DSC thermogramms of the BL-DMC mixtures at  $x_{\text{DMC}}=0.04$  and  $x_{\text{DMC}}=0.92$  respectively.

(a)



(b)

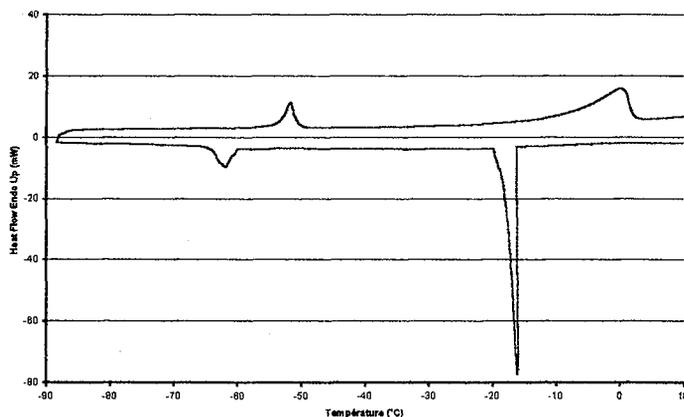
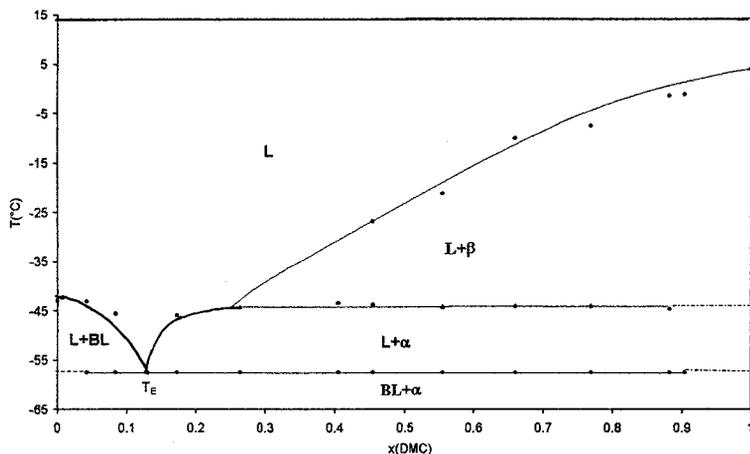


Figure 4 : DSC thermogram of BL – DMC mixture at 10°C/min: (a)  $x_{DMC}=0.04$  and (b)  $x_{DMC}=0.92$

The thermogram in figure 4a exhibits a sharp exothermic peak at  $-72^{\circ}\text{C}$  corresponding to the crystallisation of the liquid. The surfusion is evidenced as, on the reverse scan, fusion is only achieved at  $-43^{\circ}\text{C}$ . The first endothermic peak at  $-57.5^{\circ}\text{C}$  observed on the reverse scan corresponds to the fusion of the eutectic.

Unlike the preceding mixture, the BL-DMC mixture with  $x_{DMC}=0.92$  reported in figure 4b, exhibits clearly two successive exothermic peaks. The first one at  $-16^{\circ}\text{C}$  corresponds to the crystallisation of the subcooled liquid and consequently the second peak at  $-63^{\circ}\text{C}$  can be attributed to an enantiotropic transition. On the reverse scan, two endothermic peaks are successively observed: the first one, at  $-55^{\circ}\text{C}$ , is the eutectic fusion peak (refer to the thermogram reported in figure 4a), the second extended peak corresponds to the complete fusion of the mixture which ends at  $-1.1^{\circ}\text{C}$ . For  $x_{DMC}=0.92$ , no enantiotropic transition is observed at  $-43^{\circ}\text{C}$  as it has been observed in thermograms for  $x_{DMC}<0.92$ .

The phase transition temperatures obtained by DSC are plotted against the mole fraction in DMC in the BL-DMC mixtures in figure 5.



**Figure 5 : Phase diagram of BL – DMC mixture**

This phase diagram is characterised by an eutectic point at  $-57.5^{\circ}\text{C}$  and  $x_{\text{DMC}}=0.12$  which is effectively close to the pure compound which has the lowest melting point. Below  $-57.5^{\circ}\text{C}$ , an heterogeneous mixture of pure solid BL and DMC is obtained as, by summing the individual XRD spectra of BL and DMC, the spectrum of the heterogeneous solid mixture is obtained, independently of the composition.

In order to determine the nature of the phase transition observed by mean of DSC measurements, the XRD pattern of BL – DMC mixtures with  $x_{\text{DMC}}=0.04$  and  $x_{\text{DMC}}=0.92$  have been reported in figures 6 and 7 respectively.

The pattern reported in figure 6 confirms the existence at  $x_{\text{DMC}}=0.04$  of a liquid phase above  $-43^{\circ}\text{C}$ , a mixture of solid BL and liquid between  $-53^{\circ}\text{C}$  and  $-63^{\circ}\text{C}$ , and a mixture of two solids (almost pure BL and DMC) below  $-63^{\circ}\text{C}$ .

In the pattern reported in figure 7 relative to the mixture rich in DMC ( $x_{\text{DMC}}=0.92$ ), the peak at  $2\theta=15.92^{\circ}$  attributed to BL disappears. This may be due to two phenomena : the melting of the eutectic composition composed mainly of BL and the diffusion of BL in the lattice. The presence of liquid phase was not observed by XRD but it has been evidenced by DSC measurements via to the existence of the eutectic point. On figure 7 we can observe shifts which may be due to the phase transition, the effect of temperature or a small solubility of BL in DMC. As at low temperature the solubility of organic compounds is very low, the shifts will be preferentially attributed to the phase transition.

XRD patterns shows us the existence of two forms of DMC ( $\alpha$  and  $\beta$ ). The peaks at  $2\theta=20.42^{\circ}$  and  $2\theta=21.22^{\circ}$  disappear completely at  $-53^{\circ}\text{C}$  (the XRD's temperature corresponds to the DSC sample temperature within an accuracy of  $10^{\circ}\text{C}$ ). We observe an enantiotropic transformation induced by the presence of BL from  $\alpha$  to  $\beta$  form of DMC which is less organised than  $\alpha$  form.

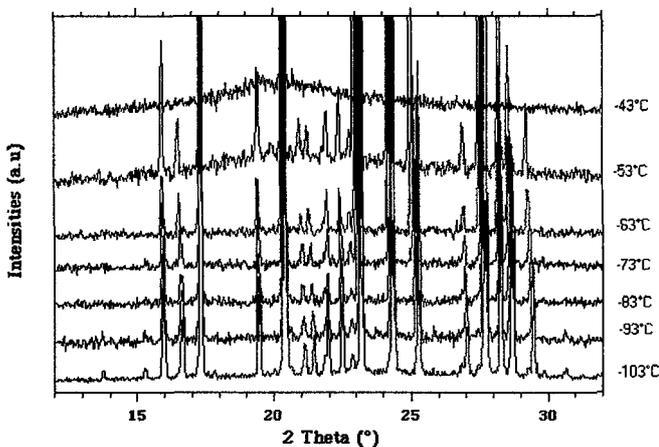


Figure 6 : Evolution with the temperature of the XRD pattern of BL -DMC mixture with  $x_{\text{DMC}}=0.04$

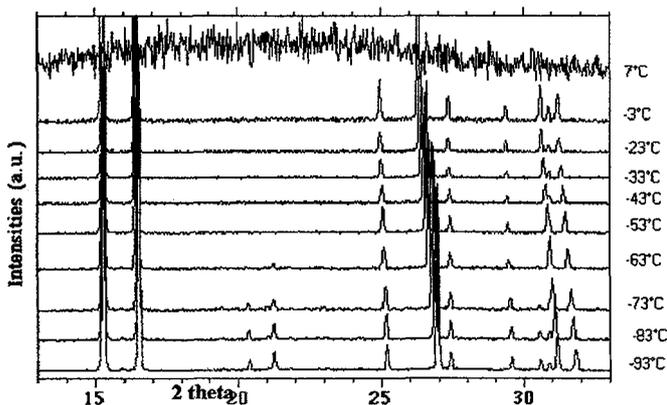


Figure 7 : Evolution with the temperature of the XRD pattern of BL -DMC mixture with  $x_{\text{DMC}}=0.92$

#### 4. CONCLUSION

The thermal stability of the solvent mixtures is very attractive for the formulation of electrolyte for lithium batteries. The study of BL – DMC mixtures by DSC and XRD permit us to propose a phase diagram. It is characterised by an eutectic point for  $x_{\text{DMC}}=0.12$  and  $T_E=-57.5^\circ\text{C}$ . By XRD measurements, the existence of two polymorphs of BL is proved corresponding to a monotropic transformation. Two forms of DMC are obtained and the enantiotropic transformation is induced by BL: the phase  $\alpha$  obtained at lower temperature is more organised than the  $\beta$  phase.

The BL – DMC mixture at  $x_{\text{DMC}}=0.12$  is the most thermal stable. The electrolyte bases on this mixture is interesting for application in the field of Li-ion batteries since it exhibits a low viscosity and a high relative permittivity.

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