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PHASE DIAGRAM OF EC–DMC BINARY SYSTEM AND ENTHALPIC DETERMINATION OF ITS EUTECTIC COMPOSITION

M. S. Ding[*], *K. Xu and T. R. Jow*

Army Research Laboratory, 2800 Powder Mill Road, Adelphi, MD 20783, USA

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Abstract

We construct with a differential scanning calorimeter (DSC) a phase diagram for the ethylene carbonate (EC)–dimethyl carbonate (DMC) binary system for its liquid-solid phase equilibria. We determine the eutectic composition of the binary system using an enthalpic method that we devised based on the composition dependence of the enthalpy of solidus melting, with highly consistent results. We also discuss the merits and limitations of this enthalpic method.

Keywords: binary phase diagram, DSC, enthalpic method, eutectic composition

Introduction

Differential scanning calorimetry (DSC) is one of the most effective methods for mapping a liquid-solid phase diagram for a binary system. The usual procedure consists of preparing a series of binary samples with compositions covering the whole composition range, and measuring the phase transition temperatures of the samples during heating. A phase diagram is obtained when these temperatures are properly interpreted and connected to form phase lines [1]. But difficulties arise with this conventional use of DSC when two phase lines at different temperatures converge to the same temperature at a particular composition. The eutectic composition of a simple eutectic binary system is an example of such a composition of convergence, where the liquidus line converges with the solidus line. There are two main reasons for the difficulties. The first one is due to the limited power of DSC to resolve two-phase transitions into distinct thermal peaks when the two transition temperatures are too close to each other. The second and the more serious is the grave imbalance between the quantities of the two phases whose temperatures are to be differentiated in a sample near the composition of convergence. In such a sample, thermal effect of phase transition for the phase of the larger quantity invariably overwhelms that of the

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[*] Author for correspondence: Phone: (301)394-0272; E-mail: mding@arl.mil

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smaller quantity. Because of these reasons, one can only estimate with limited accuracy for the composition of convergence by extrapolating from adjacent measured transition temperatures. However, as we will show with the enthalpic method that we devised for the determination of eutectic composition for the ethylene carbonate (EC)–dimethyl carbonate (DMC) binary system, the accuracy can be significantly improved with a new way of using the DSC data. This new method employs the composition dependence of an enthalpy fraction, instead of the temperature, for the extrapolation of the composition of convergence. It is the main purpose of this paper to demonstrate the use of this new method in the determination of a composition of convergence.

The second purpose is to discuss the merits of such a new way of using the DSC data, as compared to the conventional way of relying only on the transition temperatures determined from the DSC heating curves. The final purpose of this paper is to provide a phase diagram for the EC–DMC binary carbonate solvent, one of many carbonate solvent systems frequently used in making the non-aqueous electrolytes for lithium batteries [1, 2]. There are a number of reasons for the popularity of the binary carbonates as the non-aqueous solvents for lithium batteries. First, most of the individual carbonates have high chemical stability with lithium, which enables carbonates of very different properties to be used as the components for the binary solvent. Second, these carbonates are sufficiently unstructured in their liquid states to form binary solvents approaching ideal mixtures. This means that the dielectric constant and viscosity, among other properties, of a binary carbonate are related to those of its two components by monotonous relationships with its composition. These properties, which are critically important for a binary solvent to be able to form a highly conductive electrolyte with a lithium salt, can therefore be optimized for a binary solvent by choosing two appropriate components and adjusting their relative proportions [1, 3]. Third, a binary carbonate solvent will have a liquidus temperature lower than the melting point of either of its components, as will be shown in the EC–DMC phase diagram we present in this paper and in other binary carbonate phase diagrams [1]. Such a binary solvent will therefore make electrolytes with operating temperature limits lower than those made of either of the components.

Experimental section

Sample preparation

The starting solvent components, EC and DMC, were both manufactured by Grant Chemical (Zachary, LA) to the purities of 99.95 and 99.98%, respectively. They were used without further treatment. The handling of these materials in the preparation of EC–DMC mixtures and DSC samples was performed in a dry box under pure argon to prevent water absorption and contamination. The series of solvent mixtures covered the whole composition range from EC to DMC in an interval of approximately 0.05 mole fraction, by weighing out the appropriate proportions and mixing them in glass vials. DSC samples of these solvent mixtures were made by hermetically sealing a small amount (~10 mg) of a solvent in a small aluminum pan and a lid (0219–0062) supplied by Perkin Elmer Corp. (Norwalk, CT). For EC solvent and EC-rich mixtures that would freeze at room temperatures, we applied gentle heating to keep them in the liquid state for their subsequent handling in the preparation of the solvent mixtures and the DSC samples.

Instruments

A Perkin Elmer DSC 7, equipped with an Intracooler 2 as the cooling mechanism and Pyris 3.01 Software for the instrument control and data acquisition and analysis, was used to determine the temperature and heat of phase transition. During a measurement, we continuously purged the sample cell with helium gas and the refrigerated parts with nitrogen gas, mainly to prevent water condensation.

Calibration

Hexatriacontane (72.14°C, solid phase transition) and *n*-decane (–29.66°C, melting) were used for the temperature calibration of the DSC, and indium (28.45 J g^{-1}, melting) was used for its calibration of heat-flow [4]. The calibration employed a heating rate of 2°C min^{-1}, as would be subsequently used for the measurement of temperature and heat of phase transition.

Determination of temperature of phase transition

The equilibrium temperatures of the phase transitions of a sample material were determined from the DSC curve of the sample at a heating rate of 2°C min^{-1}. Figure 1 shows such a DSC heating curve for an EC-DMC sample with 0.854 mole fraction of EC, from which a solidus and a liquidus temperature were determined. As shown in the figure with the tangent lines to the DSC curve, the solidus temperature was identi-

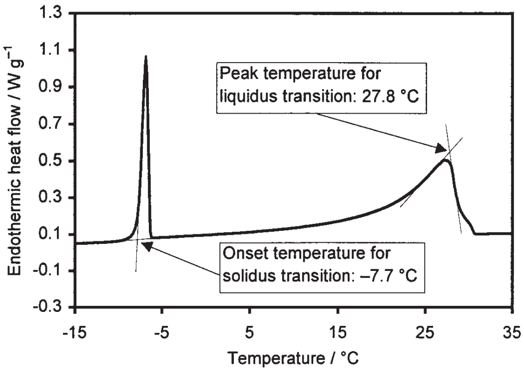

Fig. 1 A DSC heating curve of an EC–DMC binary sample of 0.854 mole fraction of EC, demonstrating how the onset temperature of a solidus transition thermal peak is determined for the solidus temperature and how the peak temperature of a liquidus transition thermal peak is determined for the liquidus temperature

fied with the onset temperature of the endothermic peak associated with the solidus phase transition, and the liquidus temperature with the peak temperature of the endothermic peak associated with the liquidus phase transition. The thermal peak of the solidus transition is a sharp one because in this phase transition, a finite amount of eutectic liquid is generated from solid EC and DMC at a fixed temperature – the solidus, or eutectic, temperature. The liquidus transition, on the other hand, involves partial melting of solid EC that starts at the solidus temperature and ends at the liquidus temperature, which results in the broad endothermic peak shown in Fig. 1. The peak temperature of this peak marks the point where solid EC is in equilibrium with the liquid of the overall composition of the sample and was thus identified with the liquidus temperature of the sample material.

Determination of heat of phase transition

The heats absorbed by a sample material during its phase transitions were also determined from the DSC heating curve of the sample. For such a determination, a straight line was first established that was the common tangent to both the pre-transition and post-transition heat-flow curves, as shown in Fig. 2. This is the baseline heat-flow of the sample in the temperature range and mainly reflects the heat-flow due to the heat capacity of the sample. We then calculated the heat of the phase transition by integrating the total heat-flow minus the baseline heat-flow in the time domain between the two tangent points. The subtraction of the baseline heat-flow ensures the elimination of the capacitive heat effect of the sample material in a phase transition whose occurrence spans a finite temperature range, such as the liquidus transition indicated in the figure. With this procedure, we evaluated the heat of solidus transition from the solidus peak and its baseline heat-flow, and the total heat from the solidus and liquidus peaks and the baseline heat-flow of the liquidus peak, as shown in Fig. 2. The heat of the liquidus transition was the difference between the total heat and the heat of solidus transition.

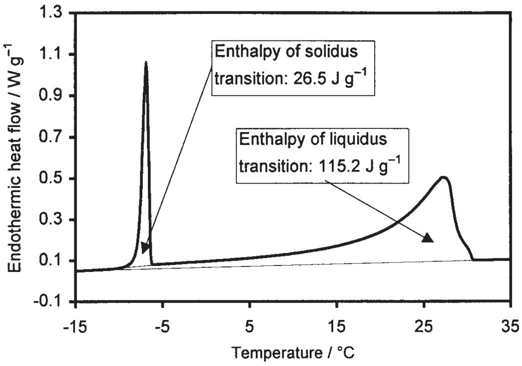

Fig. 2 A DSC heating curve of an EC–DMC binary sample of 0.854 mole fraction of EC, demonstrating how the heats of solidus and liquidus transitions are determined from their thermal peaks and their respective baseline heat-flows

Results and discussion

Change of temperature and heat of phase transition with composition

The DSC heating curve of an EC–DMC sample changes systematically in its basic features with the composition of the sample. As shown in Fig. 3, which plots DSC heating curves for some EC-rich samples of the EC–DMC mixtures, the peak temperature of the curves for the liquidus transition shifts progressively toward low temperature with lower EC content, while the onset temperature of the solidus transition remains essentially unchanged. These trends manifest the constancy of the solidus temperatures and the downward movement of the liquidus temperatures for the binary mixtures as their compositions become less EC-rich. They also anticipate the convergence of the two transition temperatures. It can also be seen that the heat absorbed in the solidus transition gets progressively larger with decreasing EC content, while that in the liquidus transition becomes smaller. These observations clearly demonstrate the two difficulties in the determination of a composition of convergence described in the introductory section.

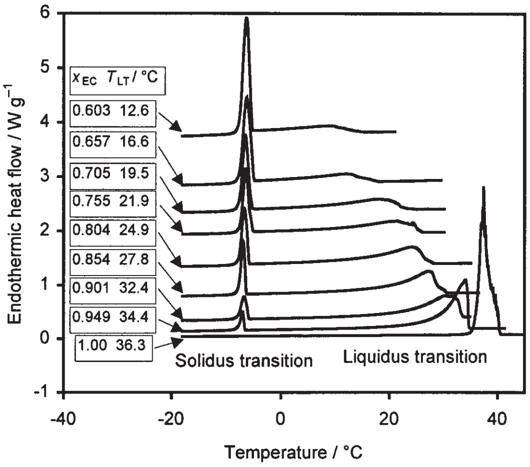

Fig. 3 DSC heating curves for some EC-rich samples of EC–DMC binary mixtures, demonstrating the dependence of the liquidus temperature and the independence of the solidus temperature on the composition, and the relative change of the heats of solidus and liquidus phase transitions. The curves have been shifted in their value of heat-flow for clarity, and x_{EC} and T_{LT} stand for the mole fraction of EC and the liquidus transition temperature, respectively

Table 1 summarizes the temperatures and enthalpies of phase transition experimentally determined from the DSC heating curves of all the samples, except for the eutectic temperature and composition. The eutectic composition of 0.292 has been obtained independently through an enthalpic method, the details of which will be described in a later section. The eutectic temperature of –7.6°C is merely the average of all the other solidus temperatures listed in the table. The need for such an enthalpic method arises from the difficulty of determining the eutectic composition by the temperature measurements. It is for the same reason that we determined some values without a great deal of certainty and failed to determine the liquidus temperature for one sample, as indicated in the table.

Table 1 Values of the temperature and the heat of phase transition of all the EC–DMC binary samples as determined from their DSC heating curves

Sample composition/ x_{EC}	Transition temperature/°C			Transition enthalpy/J g^{-1}		
	solidus	DMC-liquid	liquid-EC	total	solidus	f_S [a]
1.000	–	–	36.3[b]	148.1	0.0	0.000
0.949	–7.7	–	34.4	145.1	9.2	0.063
0.901	–7.8	–	32.4	131.6	16.7	0.127
0.854	–7.7	–	27.8	141.7	26.5	0.187
0.804	–7.7	–	24.9	147.2	37.8	0.257
0.755	–7.5	–	21.9	134.6	45.1	0.335
0.705	–7.6	–	19.5	140.3	55.8	0.398
0.657	–7.5	–	16.6	140.3	65.9	0.469
0.603	–7.6	–	12.6	136.0	75.2	0.553
0.545	–7.5	–	9.8	144.5	91.6	0.634
0.503	–7.7	–	7.9	140.3	96.0	0.684
0.454	–7.6	–	5.0	142.6	106.3	0.745
0.397	–7.5	–	1.2[c]	140.3	118.0	0.841
0.355	–7.5	–	–2.5[c]	127.4	–	–
0.299	–7.5	–	[d]	–	–	–
0.292[e]	–7.6[f]	–7.6[f]	–7.6[f]	–	–	–
0.256	–7.6	–5.1	–	132.5	–	–
0.203	–7.4	–3.2	–	131.6	89.0	0.676
0.154	–7.3	–1.1	–	131.9	68.5	0.520
0.105	–7.5	0.5	–	130.5	45.5	0.349
0.051	–7.8	2.9	–	135.5	21.1	0.156
0.000	–	4.9 [g]	–	131.1	0.0	0.000

[a] f_S=enthalpy of solidus transition/total enthalpy; [b] Melting temperature of pure EC; [c] With large uncertainty; [d] Indeterminable; [e] Eutectic composition, enthalpically extrapolated; [f] Average of all the other solidus temperatures; [g] Melting temperature of pure DMC

Phase diagram of EC–DMC

When the values of phase transition temperature in Table 1 are plotted against the composition of the EC-DMC samples, a phase diagram forms for the EC-DMC binary system. This diagram is shown in Fig. 4 with the experimental data represented by the open dots and their fitting curves by the solid lines. Of the two curves bounding the liquid region, the one on the right traces the change of composition with temperature of the EC–DMC liquid in equilibrium with solid EC, and the one on the left, with solid DMC. They are therefore the solubility curves of EC in DMC and of DMC in EC, respectively. They also form the liquidus line of the binary system, since a binary material above this line contains no solid phase. Such a liquidus line of a binary solvent system is of particular importance in the electrolyte applications, because it provides a basis from which an electrolyte made of a solvent in the system can be readily estimated for its low-temperature limit of operation [5]. The two solubility curves of Fig. 4 meet at the eutectic point (0.292, –7.6°C), where a liquid coexists with solid EC and DMC. As a binary system under constant pressure is invariant at such a point, the solidus equilibria are represented by a horizontal line passing through the eutectic point. This is the solidus line of the system, below which a binary material exists as a heterogeneous mixture of solid EC and solid DMC. Between the liquidus and the solidus lines are the regions where a liquid and a solid coexist [6]. The pattern of this phase diagram is typical of a simple eutectic system, of which the two components are mutually soluble in their liquid states and insoluble in their solid states. Many other binary carbonate systems have been found to belong to this category [1].

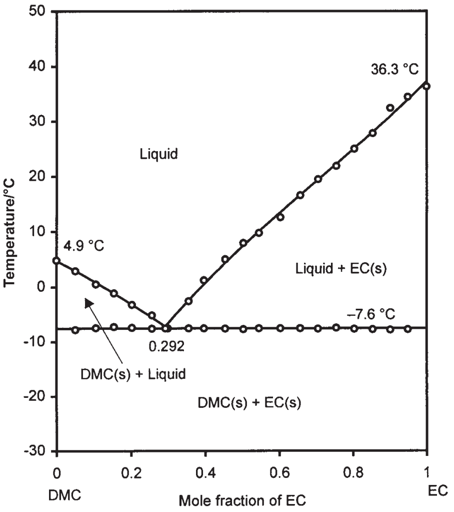

Fig. 4 Liquid-solid phase diagram of EC–DMC binary system, as constructed from the temperatures of phase transition determined from the DSC heating curves of the EC–DMC binary samples

Enthalpic determination of eutectic composition

To overcome the difficulties and improve the accuracy in the determination of the eutectic composition of the EC–DMC binary system, we devised a new procedure, which we now describe in detail. We first define a new quantity, which we call the enthalpy fraction of solidus melting and denote with f_S. This is the fraction that the heat of solidus melting makes in the total heat of solidus and liquidus melting. Operationally, it is the heat enclosed by the solidus thermal peak and its baseline heat-flow, divided by the heat enclosed by both the solidus and the liquidus thermal peaks and the baseline heat-flow of the liquidus thermal peak, as depicted in Fig. 2. For each DSC heating curve on which two thermal peaks can be readily distinguished, as those shown in Fig. 3, both the heat of solidus melting and the total heat can be evaluated. The heats thus determined are listed in Table 1, along with the f_S values that are just the solidus transition heat divided by the total heat. When these f_S values are plotted against the composition of the samples, Fig. 5 results. As can be seen in the figure, the values of f_S as represented by the open dots form two sets, each closely following a straight line. The line on the right represents the composition dependence of f_S for the binary samples richer in EC than a eutectic sample, and the one on the left, poorer in EC. Extrapolation of these two lines intersects at a composition of 0.292 and an f_S value of 0.980. We take this composition as the eutectic composition.

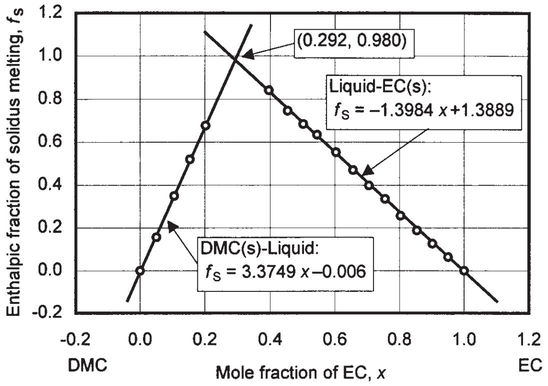

Fig. 5 Changes of the enthalpy fraction of solidus melting with composition for the EC–DMC samples, demonstrating the evaluation of the eutectic composition of the EC–DMC binary system by the enthalpy extrapolation and the consistency of the results by such an enthalpic method

A number of reasons exist for us to believe that the eutectic composition determined by the enthalpy extrapolation carries a higher accuracy than that by the temperature extrapolation. The first reason is the high linearity of the two lines in Fig. 5 as compared to those liquidus curves in Fig. 4, since a linear extrapolation normally produces results with higher certainty than a non-linear one. The second is the higher degree of consistency of the f_S data than that of the temperature data, as evidenced by the lower degree of data scattering shown in Fig. 5 than in Fig. 4. This lower scattering in the f_S–x data could be due to two reasons. One, the enthalpy quantities used in the enthalpic method are integral quantities of the heat-flow of DSC curves, while the temperatures are determined from differential quantities – the tangent lines to the heat-flow. Two, the values used in the enthalpic extrapolation is a fractional quantity, which further improves the reliability by eliminating the weighing errors involved in the preparation of the DSC samples. A further evidence for the reliability of the enthalpic method is seen in the consistency of the extrapolation results shown in Fig. 5. Ideally, f_S should attain a value of unity at the eutectic composition, since such a sample would yield only the heat of solidus transition when heated. As indicated in the figure, the value of extrapolation from the two f_S–x lines is 0.980, only 2% off the ideal value. Or if we use f_S=1 for the extrapolation of the eutectic composition with the two f_S–x lines, we obtain 0.278 and 0.298 with the f_S–x lines on the right and left, respectively. These values are off of 0.292 by less than 5%. Such an extrapolation with only one f_S–x line becomes necessary when the eutectic composition is too close to one of the pure components.

It is important to note that the enthalpic method just described is largely based on the empirical facts observed for the EC–DMC system; its applicability to other binary systems is yet to be demonstrated. However, there seems to be some theoretical basis to this method, for if we use certain equations to fit the two f_S–x lines of Fig. 5, we obtain consistent results for the eutectic composition. Fitting equation $f_S \approx (1-x_0)/(1-x_E)$, where x_0 and x_E are respectively the overall sample composition and the eutectic composition, to the f_S–x line on the right yields for x_E 0.285 from the slope of x_0 and 0.280 from the constant. And fitting $f_S \approx x_0/x_E$ to the f_S–x line on the left yields 0.296 for x_E. These enthalpically fitted values for the eutectic composition fall within 4% of the extrapolated value of 0.292. Furthermore, the two fitting equations can be arrived at through thermodynamic calculations with certain assumptions and approximations [7].

Conclusions

A liquid-solid phase diagram can be readily constructed for a binary system with the DSC technique by measuring the temperatures of phase transition for samples of different compositions. However, the eutectic composition of such a system cannot be determined directly with this method but rather must be extrapolated with limited accuracy from the measured temperatures nearby. The accuracy of such a determination can be much improved by extrapolating the DSC data of the enthalpy fraction of solidus melting instead of the temperature. For EC–DMC binary mixtures, the enthalpy fraction of solidus melting exhibited a linear dependence on the composition of the mixtures with little data scattering. Its extrapolation yielded highly consistent results for the eutectic composition.

References

1 M. S. Ding, K. Xu and T. R. Jow, J. Electrochemical Soc., 147 (2000) 1688.
2 S. Hossain, in Handbook of Batteries, 2nd ed., D. Linden (Ed.), McGraw-Hill, New York 1995, p. 36.8.
3 G. E. Blomgren, in Lithium Batteries, J.-P. Gabano, (Ed.), Academic Press, London 1983, p. 18.
4 Perkin Elmer Corp, Help documents to Pyris 3.01 Thermal Analysis Software, Norwalk, CT.

5 S. P. Ding, K. Xu, S. S. Zhang, T. R. Jow, K. Amine and G. L. Henriksen, J. Electrochem. Soc., 146 (1999) 3974.

6 A. Prince, Alloy Phase Equilibria, Elsevier Publishing Co., Amsterdam 1966.

7 M. S. Ding, Unpublished results.