Hypoeutectic Liquid-Solid Phase Diagrams for Ternary Lithium-Ion Battery Electrolytes

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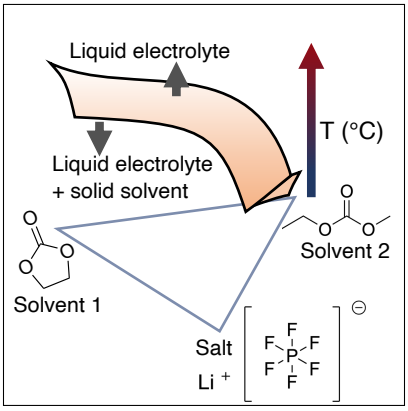
Abstract

One of the current efforts of Li-ion battery technology research is to enable the operation of lithium-ion batteries in low temperature environments ($< 0^\circ$ C). However, the ternary phase diagrams of liquid electrolytes commonly used in lithium-ion cells are generally unknown. We herein study the liquidus surface of a ternary liquid electrolyte — up to 1 m $LiPF_6$ in ethylene carbonate and ethyl methyl carbonate. We find that literature electrochemical and thermodynamic measurements of the composing binary electrolytes, in addition to limited ternary liquidus data, can be used to recover the liquidus surface via appropriate mixing terms.

TOC Graphic



Among the current challenges of Li-ion battery (LIB) technology is improving the low temperature performance.[1] Specifically for the liquid electrolyte, which is generally a ternary or higher order carbonate electrolyte mixture, the liquid-solid equilibria have received little attention. Given that the carbonates used in lithium-ion battery electrolytes freeze by themselves often close to room temperature, the question of the liquid-solid equilibria is well motivated when such carbonates are mixed and when salt is added. In this preliminary work we investigate the liquidus surface of the ternary EC:EMC:$LiPF_6$ (ethylene carbonate:ethyl methyl carbonate:$LiPF_6$) system up to 0.95 molal of $LiPF_6$ (approximately[2] 1 molar), which is of immediate technological interest. The methodology relies on using previous electrochemical characterization of lower order systems and ternary mixing terms informed by limited higher-order thermodynamic measurements. Gibbs-Duhem relationships are also suggested as a useful tool in relating the thermodynamic properties of species.

The most common liquid carbonates used in LIB electrolytes include EC, a cyclic carbonate which is chosen for its high dielectric constant and ability to form a stable passivating interphase at the negative electrode, and EMC, a linear carbonate with a relatively low viscosity.[3] Carbonates without salt have been studied in phase diagrams in their binary, ternary and quaternary mixtures. In their binary mixtures, they generally form a eutectic mixture without any intermediate compounds.[4,5]

Significant work exists on binary electrolytes relevant to LIBs. The phase diagrams of $LiPF_6$ in EC,[6,7] in DMC (dimethyl carbonate),[8] and in other solvents,[9] in addition to other salts such as LiTFSI and $LiBF_4$ in carbonates, ethers, and other solvents have been studied.[9–15] Generally, the investigation of phase behavior of these systems has been limited to small concentration ranges, in part due to the possibility of glass formation. Solid solvates relevant to LIB electrolytes systems such as EC_4LiPF_6(s) have also been characterized,[16,17] although generally their thermodynamic properties (such as formation energies) are as of yet unmeasured.

Thermodynamic properties of binary

electrolytes for LIBs have been investigated via vapor-liquid equilibria, theoretical calculations and electrochemical measurements.[6,18–21] We note that many of the basic thermodynamic properties such as the species' activity coefficients for simple binary electrolyte systems have only been reported within the last five years,[19,20] even for salts and solvents that have been conventional components of LIB electrolytes for decades.

Significant but limited work has investigated the liquid-solid phase equilibria in ternary or more complex LIB liquid electrolytes comprised of salt in two or more solvents. Ding et al. measured the liquidus for three salt concentrations for $LiPF_6$ in EC:EMC 1:1, and at a fixed salt concentration in a quinary system.[22,23] Bauer reported fixed solvent ratio or fixed salt molarity liquidus data for $LiPF_6$ in EC:EMC.[24] Phase behavior can also be predicted from activity coefficient data. Electrochemical measurements of salt activity coefficients $\gamma_\pm$ have previously been reported for $LiPF_6$ in EC:EMC mixtures[6,25–27] and in one higher order system at a fixed solvent composition of PC (propylene carbonate):EC:EMC.[18] Generally the activity coefficient of the salt, or similarly the thermodynamic factor, is measured for limited solvent ratios in the ternary systems while often relying on simplifying assumptions such as treating the multi-solvent system as a single "mean" or "pseudo" solvent. Past and recent work has shown that these assumptions may not be not be sufficiently rigorous to model thermodynamics or transport.[28–30] The limited thermodynamic measurements for higher order systems motivate a methodology to recover higher order liquid-solid phase equilibria from lower order systems where phase-equilibria and thermodynamic properties may be better studied.

In previous work on non-electrolyte ternary liquid carbonate systems,[5] ternary phase diagrams were generated from binary interactions described by a Gibbs excess energy term g^{E} implemented via mixing rules and no specific ternary interactions. Herein, we instead thermodynamically describe the activity of the solvents directly, without recourse to a direct description of g^{E}. This provides a more direct path to the liquidus surface. Although it may be possible to

equivalently use a methodology involving g^{E}-based energy minimization with appropriate ternary interactions, we were so far unable to do so.

We first parametrize the solvents' activities (EC and EMC) in all three relevant binary systems ($LiPF_6$ in EC, $LiPF_6$ in EMC, and EC in EMC). Afterwards, we fit the ternary interactions (vide infra) to two lithium concentration series in fixed EC:EMC solvent ratios. This allows us to generate the phase diagram in the entire target composition space. We compare a reported liquidus line at fixed molarity and varying solvent ratios to the corresponding calculated line.[24] Finally, we use the parametrized solvents' data to recover the thermodynamic factor, relevant to the activity of the salt, and compare it to experiment. Our primary goal is to establish a framework to describe the liquidus surface from limited experimental data. Here, the thermodynamic factor is primarily used to evaluate the data obtained.

A proper description of the solvent components' activity allows evaluation of phase equilibria. Freezing point depression (θ), the difference in the freezing point of the neat solvent T^0 and that of the electrolyte T^{m} where the solvent freezes, is of specific interest for low temperature electrolyte engineering. In a liquid electrolyte, θ can be computed from the activity a_{solvent} of the solvent that freezes if the neat solvent freezing temperature T^0 and the enthalpy of fusion $\Delta H^{\circ}_{\mathrm{fus}}$ are known according to:[6,31]

$$\theta = T^0 - T^{\mathrm{m}} = \frac{-2RT^0 \ln a_{\mathrm{solvent}}}{2\Delta H^{\circ}_{\mathrm{fus}}/T^0 - 2R \ln a_{\mathrm{solvent}}} \tag{1}$$

In the above equation, $\Delta H^{\circ}_{\mathrm{fus}}$ is not a function of temperature since it is defined for the neat solvent at the melting temperature. Furthermore, for simplicity, we neglect the heat capacity change upon fusion in this work.

In this work we resort to a practical macroscopic formulation for the activity of species. As such, we effectively describe the activity of species with phenomenological Margules-type expressions.[32] We leave a quantitative nanoscopic accounting of non-idealities[21,33] to further work. Although it is common to use Guggeinheim or Pitzer-type equations to describe the activity of species in liquid electrolytes,[6,32,34–36]

we herein avoid their use as in multisolvent electrolytes, the electrostatic contributions such as the so-called Debye-Huckel terms cannot be easily calculated. LIB electrolytes use a mix of solvents of dramatically different dielectric constants and yield highly variable amounts of ion pairing. As such, the concentration-dependent dielectric constant and ionic strength value, necessary for such electrostatic terms, are a priori unknown. Instead, for an activity a_i of a solvent species i in a binary electrolyte, the dependence on salt molality m is here more simply assumed as a generalized Margules-type expression,[32,37,38] with coefficients $c_{i,\mathrm{salt}}$, $d_{i,\mathrm{salt}}$, $e_{i,\mathrm{salt}}$ and $f_{i,\mathrm{salt}}$:

$$a_i(m) = (1 - \frac{2m}{\frac{1}{M_i} + 2m}) e^{c_{i,\mathrm{salt}} m^{1.5} + d_{i,\mathrm{salt}} m^2 + e_{i,\mathrm{salt}} m^{2.5} + f_{i,\mathrm{salt}} m^3} \quad (2)$$

For a solvent species i in a binary solvent system, the dependence of its activity a_i on the other solvent mole fraction X_j can be written as a four-suffix Margules expression[32]:

$$a_i(X_j) = (1 - X_j) e^{c_{i,j} X_\mathrm{j}^2 + d_{i,j} X_\mathrm{j}^3 + e_{i,j} X_\mathrm{j}^4} \quad (3)$$

For simplicity, a_i is assumed to be independent of temperature.

In order to calculate the liquid solid equilibria, the melting temperature T^0 and heat of fusion $\Delta H^\circ_{\mathrm{fus}}$ were taken from literature for the EC and EMC solvents.[4,6] Table 1 shows T^0 and H°_{fus} employed herein. The (frozen) solid solvent is taken as insoluble to other species. We assume in this work that at 0.95 molal $LiPF_6$ and below, we are below the $LiPF_6$-EC eutectic composition in the entire ternary system. We refer to this composition region as hypoeutectic, even as it contains the EC-EMC eutectic composition. In studying exclusively the hypoeutectic region, the enthalpy and entropy of the references states of the ions are inconsequential using the assumption that solid phases possible in this regime are made up of pure solvent. We further note that although the eutectic of the binary system $LiPF_6$ in EC with the relevant solid solvate may be below 0.95 molal,[6] we

Table 1: Neat solvent properties, taken from references.[4,6]

	EC	EMC
Chemical formula	$C_3H_4O_3$	$C_4H_8O_3$
T^0	38.1 °C	-53.8°C
$\Delta H^{\circ}_{\text{fus}}$	13.02 kJ/mol	11.24 kJ/mol

expect that for most of the ternary composition space studied that the eutectic composition relevant to that solid solvate be well above 0.95 molal.

In the ternary system of a salt in a binary-solvent system, there are only two independent compositional variables. We in this work pick a basis of one kilogram of total solvent. Thus, in the ternary system a given molality m_i of one solvent with molar mass M_i fixes the molality m_j of the other solvent of molar mass M_j via the following relationship:

$$m_i M_i + m_j M_j = 1 \tag{4}$$

Furthermore, the composition of the ternary system is fully determined by knowledge of the molality of salt (mol per kilogram of total solvent) and the molality of one solvent. Moreover, in the ternary system, we define the mole fraction of a solvent species X_i as

$$X_i = \frac{m_i}{m_i + m_j + 2m} \tag{5}$$

Electrolyte systems' compositions are often characterized by a solvent fraction X'_i, directly related to the solvent ratio. The solvent fraction of a solvent i in a complex mixture which includes another solvent j can be written as :

$$X'_i = \frac{X_i}{X_i + X_j} \tag{6}$$

Either knowledge of the molality of a solvent species or its solvent fraction is sufficient to determine the molality and solvent fraction of the other solvent species via equations 4, 5 and 6. For the activity of solvent species in the ternary system, we use the following relationship as a function of composition,[38] with coefficients $c_{i,j,\text{salt}}, d_{i,j,\text{salt}}, e_{i,j,\text{salt}}$:

Table 2: Parameter values of binary interactions for the solvent's activity.

	EC:EMC	EMC:EC	EC:$LiPF_6$	EMC:$LiPF_6$
$c_{i,j}$	-0.66992	0.62190	0.042895	0.82629
$d_{i,j}$	4.2840	2.5617	-0.38832	-1.7913
$e_{i,j}$	-2.5671	-2.5672	0.066300	1.7011
$f_{i,j}$	-	-	-0.017291	-0.63441

$$a_i(X'_j, m) = X_i \frac{a_i(X'_j, m=0)}{1 - X'_j} \frac{a_i(X'_j = 0, m)}{1 - \frac{2m}{1/M_i + 2m}} e^{c_{i,j,\mathrm{salt}} m^{1.5} X'^2_{\mathrm{j}} + d_{i,j,\mathrm{salt}} m^{1.5} X'^3_{\mathrm{j}} + e_{i,j,\mathrm{salt}} m^2 X'^2_{\mathrm{j}}} \quad (7)$$

The mole fraction X_i appearing in equation 7 can be calculated with knowledge of the solvent fraction X'_j and the molality of salt via equations 4, 5 and 6. $a_i(X'_j, m = 0)$ and $a_i(X'_j = 0, m)$ are directly calculated via equations 3 and 2, respectively.

In order to fit the ternary parameters, we combined a selection of collected differential scanning calorimetry data (DSC) and published literature data. We used lithium concentration series at two solvent mole ratios: EC:EMC 1:1 and EC:EMC 1:2. For EC:EMC 1:2, data was collected as described in a previous publication.[21] The data was smoothed via use of a linear fitting function, as was done for the same composition series in Bauer's thesis.[24] For EC:EMC 1:1, the data was taken from Ding et al.,[22] and here molality was approximated as the reported molarity.[2] We also compare a solvent-ratio series at 1 M taken from Bauer's work[24] to the generated liquidus surface. We expect systematic errors on the liquidus data, both published and collected herein, on the order of 3°C.[24] As the goal of this work is not to experimentally collect extensive ternary data but to establish a methodology to generate a liquidus surface from binary and limited ternary data, we leave more extensive and precise data collection to further work.

Table 3: Parameter values of ternary interactions for the solvents' activity.

	EC:EMC:$LiPF_6$	EMC:EC:$LiPF_6$
$c_{i,j,\text{salt}}$	2.7936	-
$d_{i,j,\text{salt}}$	-7.8747	-
$e_{i,j,\text{salt}}$	1.7636	-

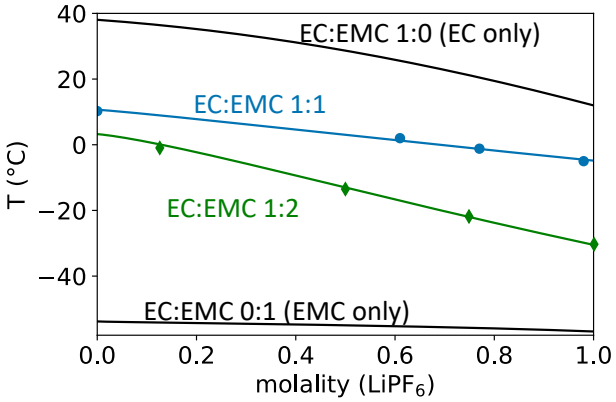


Figure 1: Calculated liquidus data as a function of salt molality at fixed solvent compositions (lines). Two binary electrolyte systems are shown in black. The experimental data (symbols) for 1:1 EC:EMC is taken from Ding et al.,[22] while the EC:EMC 1:2 data is collected in the present work.

The parameters used for the binary interactions are shown in Table 2. These were found via fits to reported electrochemical and thermodynamic data[6,20] with the formulas from equations 2 and 3. For the EC:EMC binary the fit followed that of Ding et al.[4] We note that for the coefficients $c_{i,j}, d_{i,j}, e_{i,j}$, the coefficients $c_{j,i}, d_{j,i}, e_{j,i}$ are fixed by the appropriate Gibbs-Duhem relationships.[32] Figure 1 shows the calculated liquidus data of binary $LiPF_6$ in EC and $LiPF_6$ in EMC (black lines) using equation 1 and the parameters shown in Table 2. For $LiPF_6$ in EC, the calculated liquidus line reproduces previous reported experiments.[6,7] This suggests that the use of equation 1 for the freezing point depression calculation is reasonable, including its use of temperature-independent activities. For EMC-$LiPF_6$, we are unaware of any experimental data of the liquidus line. However, the much less significant freezing point depression than for EC is consistent with that observed for $LiPF_6$ in another linear carbonate, DMC (dimethyl carbonate).[8,21] This is due to the much higher activity of the linear carbonate than the polar carbonate for the same salt concentration. This arises in part due to much higher amount of ion pairing of salt in the linear carbonate from dilute up to moderate salt concentrations.[21]

Figure 1 also shows the liquidus data of ternary systems at fixed solvent ratios. The ternary terms for a_{EC}, as appearing in equation 7, were fit to reproduce this liquidus

data. We find that the ternary terms allow for a good fit to the 1:1 and 1:2 EC:EMC solvent ratios. The fitted terms are listed in Table 3. We expect the ternary interactions to account for preferential solvation of the Li^+ cation by EC over EMC[39–42] and the decrease in ion pairing as we increase the more polar EC solvent fraction. We further expect these to be competing effects, which we speculate are the origin of the negative sign on the $d_{\mathrm{EC,EMC,LiPF6}}$ term and the positive signs for the $c_{\mathrm{EC,EMC,LiPF6}}$ and $e_{\mathrm{EC,EMC,LiPF6}}$ terms. We note that for the EC:EMC 1:2 ternary data, the liquidus data from Bauer[24] yielded similar results as the the collected DSC data used here.

With the binary parameters obtained from previous thermodynamic and electrochemical data, and ternary parameters obtained via a fit to limited ternary data, it is possible to draw out the hypoeutectic liquidus surface. Figure 2 shows the liquidus surface as a function of mole fraction (top), up to 0.95 molal. The same data is also shown for different molalities of salt in Figure 2 (bottom).

Given the low EC content of the eutectic composition in the EC-EMC binary (< 0.1 mole fraction) and the resulting low EC content in the respective eutectic line in the ternary composition, electrolytes at 1:2 EC:EMC are in the liquidus region determined by the EC activity. Moreover, with increasing salt concentration, the EC activity decreases substantially along with the liquidus temperature.

A fixed salt concentration liquidus data series at 1 M is plotted as circles in Figure 2 (bottom) and shows fair agreement against the 0.95 m calculated liquidus line (within 5°C). No fitting was done for the concentrations plotted here. This suggests limited ternary data may allow accurate reproduction of the liquidus surface via the methodology described herein, and is likely limited by the accuracy of the calorimetric data.

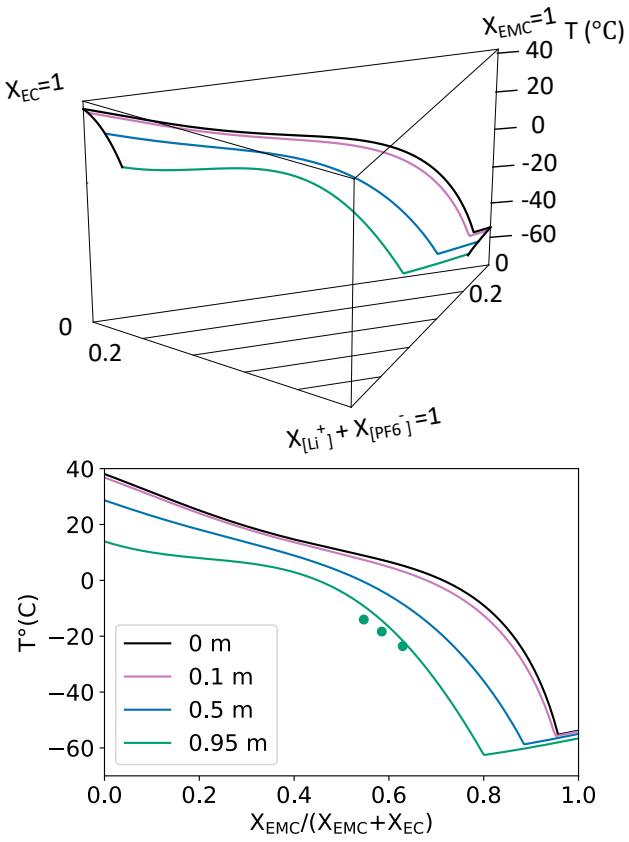


Figure 2: Calculated ternary liquidus temperature as a function of component mole fraction, for various molalities (top). The same liquidus lines as a function of mole fraction of EMC per mole fraction of total solvent (bottom). The data points (circles) are taken from Bauer,[24] for 1 M $LiPF_6$ in EC and EMC in different ratios.

The approach for calculating activities in binary liquid electrolyte systems generally relies on obtaining the salt activity coefficient via knowledge of the solvent activity, or vice-versa. In ternary systems all three components activities are related. The Gibbs-Duhem relationship for a three component (i, j, k) system can be written as :

$$m_i d(\ln(a_i)) + m_j d(\ln(a_j)) + m_k d(\ln(a_k)) = 0 \tag{8}$$

Following the work of Davis et al.,[37] it is possible to use the above expression to relate the activity of the salt to the activities of the two other solvent components:

$$-\int m \frac{\partial[\ln(a_{\text{salt}})]}{\partial m} dm = m_{\text{EMC}} \ln[\frac{a_{\text{EMC}}(m, X'_{\text{EMC}})}{a_{\text{EMC}}(m=0, X'_{\text{EMC}})}] + m_{\text{EC}} \ln[\frac{a_{\text{EC}}(m, X'_{\text{EMC}})}{a_{\text{EC}}(m=0, X'_{\text{EMC}})}] \tag{9}$$

Recognizing $\ln(a_{\text{salt}}) = 2\ln(m\gamma_{\pm})$, we can use the above relation to write an equivalent relationship in terms of the thermodynamic factor $1 + \frac{\partial[\ln(\gamma_{\pm})]}{\partial \ln m}$:

$$1+\frac{\partial[\ln(\gamma_{\pm})]}{\partial \ln m}=-\frac{1}{2}\frac{\partial}{\partial m}\Big(m_{\mathrm{EMC}}\ln[\frac{a_{\mathrm{EMC}}(m,X'_{\mathrm{EMC}})}{a_{\mathrm{EMC}}(m=0,X'_{\mathrm{EMC}})}]+m_{\mathrm{EC}}\ln[\frac{a_{\mathrm{EC}}(m,X'_{\mathrm{EMC}})}{a_{\mathrm{EC}}(m=0,X'_{\mathrm{EMC}})}]\Big) \quad (10)$$

Figure 3 shows the thermodynamic factor calculated as a function of concentration using equation 10. We believe the quantitative disagreement originates from limitations of the current methodology and not the limitations of the measured values. We do not expect a perfect agreement as in this work we did not include any ternary interactions for the linear carbonate solvent given the limited data where the liquidus surface is determined by the EMC solvent activity. We would expect the EMC activity ternary interaction contributions to become more significant at higher salt concentrations and lower EMC solvent fraction. More DSC data in the region where EMC freezes or alternative ways of measuring or predicting solvent activity could improve the accuracy of the calculated thermodynamic factor. We further note that the liquidus data to which the a_{EC} ternary terms are fit may be sufficiently accurate to reproduce phase stability but accurate inference of the thermodynamic factor may require higher DSC accuracy.

The relationship described by equation 10 suggests interesting possibilities: with sufficient thermodynamic factor data in the ternary composition space it may be possible to properly parametrize the activity of the salt, and recover the otherwise unknown activity of a solvent species if the other solvent's activity is known. Moreover, if the thermodynamic factor could be predicted from the liquidus surface with sufficient accuracy, it could allow determination of transport properties such as transference numbers from liquid junction potential measurements.[30]

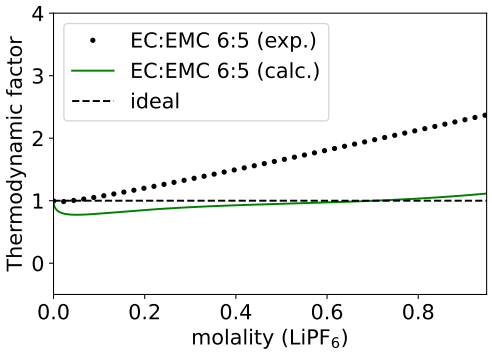


Figure 3: Thermodynamic factor for $LiPF_6$ in EC:EMC 6:5 (1:1 wt%). The experimental data is from Stewart and Newman.[6]

Further work is underway on expanding the reported phase diagram beyond the hypoeutectic region by considering the thermochemistry of the solid salt solvates, as well as alternative solvent and salt systems.

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Nomenclature

X_i' solvent fraction of species i

$1 + \frac{\partial[\ln(\gamma_\pm)]}{\partial \ln m}$ thermodynamic factor

$\Delta H^\circ_{\text{fus}}$ enthalpy of fusion of neat solvent at freezing temperature

$\gamma_\pm$ mean molal activity coefficient of salt

θ freezing point depression

a_i activity of species i

$c_{i,j,k}$ coefficient for activity of species i in a ternary mixture with species j and k

$c_{i,j}$ coefficient for activity of species i in a binary mixture with species j

$d_{i,j,k}$ coefficient for activity of species i in a ternary mixture with species j and k

$d_{i,j}$ coefficient for activity of species i in a binary mixture with species j

$e_{i,j,k}$ coefficient for activity of species i in a ternary mixture with species j and k

$e_{i,j}$ coefficient for activity of species i in a binary mixture with species j

$f_{i,j}$ coefficient for activity of species i in a binary mixture with species j

g^{E} Gibbs excess energy

m molality of salt in mixture

M_i molar mass of species i

m_i molality of species i

R gas constant

T temperature

T^0 freezing temperature of neat solvent

T^m freezing temperature of solvent in a mixture

X_i mole fraction of species i

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