



Solid-liquid equilibria and thermo-physical properties of liquid electrolyte systems for lithium ion batteries

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ABSTRACT

Alkyl carbonate and γ -butyrolactone (GBL) are attractive organic electrolyte materials that are stable over a wide range of operating voltages and ethylene sulfite (ES) is used as a supplementary film-forming electrolyte additive for lithium ion batteries (LIBs). This paper reports the solid-liquid phase equilibrium (SLE) data and the thermo-physical mixture properties such as the density, refractive index, excess and deviation properties for organic liquid electrolyte solutions of carbonate-based or GBL electrolytes containing ES. The SLE data were correlated with two activity coefficient models: NRTL and UNIQUAC. In addition, the extent to which the excess volume (V^E) and molar refraction deviation (ΔR) of each of the binary systems correlated with the values calculated using the Redlich-Kister polynomial equations was determined.

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1. Introduction

The high electropositivity of lithium and the fact that it is the lightest metal among the solid elements have, together with its high energy density and high specific current capacity, led to the consideration of several combinations of organic solvents and lithium salts as the most promising liquid electrolyte materials for rechargeable batteries. Consequently, research and development of lithium ion batteries (LIBs), which have found use in various applications such as a power source for electric vehicles and as storage medium for electric energy generated by solar and wind sources, has been underway all over the world [1,2]. Research pertaining to LIBs focuses on the three basic components of these batteries: the anode, cathode, and electrolyte. In reality, even though in LIBs the electrodes are responsible for energy storage, the electrodes function in collaboration with a liquid or solid electrolyte capable of conducting lithium. Additionally, the electrolyte (or combination of electrolyte materials) largely contributes to characterizing LIBs in terms of their specific power, safety, life time, and performance at both low and high temperatures [3–6]. Therefore, the subsequent intensification of research into electrolytes and their additives, as one of the core elements of LIB technology, has been a major driving

force behind the technological progress of LIBs [7].

A liquid electrolyte generally consists of a lithium salt, such as LiPF_6 or $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ combined with linear and alkyl carbonates, because several lithium salts are highly soluble in these carbonates and the resulting conductivities are adequate for batteries. In addition, small amounts of other components, known as electrolyte additives, are incorporated in the electrolyte to improve its properties. For instance, ethylene sulfite (ES) or vinyl ethylene sulfite (VES), a film-forming electrolyte additive, are included in electrolyte formulations to increase the dielectric strength and enhance the electrode stability by facilitating the formation of a solid electrolyte interface (SEI) layer [8–10]. The selection of solvents for use in electrolyte formulations is therefore crucial to enhance the performance of LIBs. In practice, these solvent mixtures mainly contain ethylene carbonate (EC) or propylene carbonate (PC), which are used in combination with at least one of the following organic carbonates as co-solvents: dimethyl carbonate (DMC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC), etc. The permittivity of these electrolyte mixtures is sufficiently high to allow lithium salts to dissociate in the mixture; furthermore, the low melting point of these electrolytes make them suitable for low-temperature applications. Apart from the aforementioned linear carbonates, γ -butyrolactone (GBL) is another preferred electrolyte solvent for LIBs because of its similar electrochemical performance. However, its boiling point is much higher compared to that of linear carbonates such as DMC, DEC, and EMC and it would therefore be expected to enhance battery safety.

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Many studies have used theoretical or empirical approaches to examine the properties of different electrolyte solutions. The results of these studies laid the foundation for subsequent advances in equilibrium and solution thermodynamics. Determining the dependence of the phase equilibrium and properties of solutions on the composition and temperature of these solutions remains an ongoing challenge for researchers in the chemical and physical sciences. This is because knowledge of these properties is of great importance to study the separation and interaction between the components of solutions [11]. Therefore, a good understanding of the phase equilibrium and thermodynamic properties of electrolyte mixtures for LIBs remains of interest and is helpful toward their utilization as electrolytes. In the present work, we determined the solid-liquid equilibrium (SLE) density (ρ), refractive index (n_D), excess volume (V^E), and molar refraction deviation (ΔR) at atmospheric pressure and different temperatures for the binary systems: DMC + ES, EC + ES, EMC + ES, GBL + ES. To the best of our knowledge, the experimental SLE and thermo-physical properties of the systems considered in this work have not yet been reported.

The determined SLE data were correlated with the data calculated by the activity coefficient models NRTL [12] and UNIQUAC [13]. In addition, the calculated excess and deviation properties were modeled by known polynomial equations, namely the Redlich-Kister equations for binary fractions [14].

2. Experiment

2.1. Materials

DMC and EMC were purchased from Sigma Aldrich (USA, >99%) and GBL was provided by Junsei (Japan, >99%), whereas EC and ES were supplied by Acros Organics (USA, EC: >99%, ES: >98%). All of these chemicals were dried with 0.3 nm molecular sieves and used without any further purification. Subsequently these chemical compounds were analyzed by gas chromatography (GC) and their final purities were determined to exceed 99.9 mass %. The water contents of the chemicals were also checked using Karl-Fischer titrator (Metrohm 684 KF-Coulometer) and were found to be less than $5 \times 10^{-5} \text{ g g}^{-1}$. The physical measurements of the chemicals are provided in Table 1 where they are compared with the values reported in the literature [15–18].

2.2. Apparatus and procedure

The SLE determination was carried out using a cryostat and a

customized self-built triple-glass jacketed still, which enables the melting or freezing process of a solid sample to be visually observed. The outermost exterior glass column of the glass jacket was maintained under vacuum to prevent moisture from freezing on the surface. The cooling/heating media were circulated through the center jacket of the glass still. The innermost equilibrium cell was not only heated or cooled but also insulated from the environment via the circulated cooling/heating media. The equilibrium cell was purged with nitrogen gas for dehumidification [19,20]. First, the mole fraction of each of the binary samples was gravimetrically determined using an A&D microbalance (HA202, Japan) with an accuracy of $\pm 1 \times 10^{-5} \text{ g}$. The standard uncertainty of the determined mole fraction was estimated to be less than $\pm 1 \times 10^{-4}$. The SLE point for the given composition was determined visually at the moment at which the last crystal of the mixture disappeared. The temperature at this SLE point was measured with a platinum resistance thermometer and a digital temperature readout box (ASL F250, UK). The standard uncertainty of the SLE temperature measurement was considered to be less than $\pm 0.02 \text{ K}$.

The values of V^E and ΔR were calculated from the directly measured densities and refractive indices, respectively. The ρ of the pure components and those in mixtures were measured using a vibrating U-tube densitometer (Anton Paar model DMA 5000) under atmospheric pressure. This U-tube densitometer was calibrated using standard bi-distilled water and dried air before every measurement. According to the manufacturer's specification, the accuracy of ρ is $\pm 5 \times 10^{-6} \text{ g cm}^{-3}$ between 0 and 3 g cm^{-3} and that of the temperature is $\pm 0.01 \text{ K}$. The sample mixtures were prepared in narrow-mouth stoppered glass vials using a microbalance with a precision of $\pm 1 \times 10^{-5} \text{ g}$. The high-boiling-point component was first added to the vial to minimize evaporation losses. The experimental procedure was described in detail elsewhere [21]. The experimental systematic error in the ρ and mass measurements was estimated to be less than $1 \times 10^{-5} \text{ g cm}^{-3}$ and 1×10^{-4} in the mole fraction, respectively.

The n_D was determined using a digital precision refractometer (KEM, model RA-520 N, Kyoto, Japan). The manufacturer stated the accuracy of the refractometer to be $\pm 5 \times 10^{-5}$ and $\pm 1 \times 10^{-4}$ in the ranges of 1.32–1.40 and 1.40–1.58 of refractive index values, respectively, and the accuracy of the temperature is $\pm 5 \times 10^{-2} \text{ K}$. The experimental procedure was described in detail elsewhere [22]. The values of ΔR were obtained from the measured n_D data. The reproducibility of the measurement was checked with bi-distilled water and the standard uncertainty (u) was estimated as $u(n_D) = 1.5 \times 10^{-4} \text{ g} \cdot \text{cm}^{-4}$, $u(T) = 0.05 \text{ K}$.

Table 1

Purity and physical properties of the chemicals at $P = 101.3 \text{ kPa}$.

Chemical	Water content (ppm)	CAS-No.	GC analysis (wt. %)	$\rho / \text{g cm}^{-3}$ at 298.15 K		n_D at 298.15 K	
				Exp.	Ref.	Exp.	Ref.
dimethyl carbonate	47.0	616-38-6	>99.9	1.06087	1.06328 ^e	1.3662	1.3671 ^e
ethyl methyl carbonate	41.0	623-53-0	>99.9	1.00688	–	1.3754	–
ethylene carbonate ^a	13.0	96-49-1	>99.9	1.31570 ^d	1.32199 ^f	1.4172 ^d	–
ethylene sulfite ^b	7.0	3741-38-6	>99.9	1.43217	1.4158 ^g	1.4449	–
γ -butyrolactone ^c	43.0	96-48-0	>99.9	1.12497	1.12454 ^h	1.4349	1.4350 ^h

Standard uncertainties u are $u(\rho) = 6 \times 10^{-5} \text{ g} \cdot \text{cm}^{-3}$, $u(T) = 0.01 \text{ K}$.

Standard uncertainties u are $u(n_D) = 1.5 \times 10^{-4} \text{ g} \cdot \text{cm}^{-4}$, $u(T) = 0.05 \text{ K}$.

^a IUPAC name: 1,3-dioxolan-2-one.

^b IUPAC name: 1,3,2-Dioxathiolane 2-oxide.

^c IUPAC name: Oxolan-2-one.

^d At 318.15 K.

^e Ref [15].

^f Ref [16].

^g Ref [17].

^h Ref [18].

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