

Solubilities of six lithium salts in five non-aqueous solvents and in a few of their binary mixtures

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Abstract

Solubilities were measured from 25 to 45 °C for six lithium salts (LiF, LiCl, LiBr, LiNO₃, LiTFSI and LiPF₆) in five pure non-aqueous solvents (ethanol, acetonitrile, dimethyl carbonate, dimethyl sulfoxide and propylene carbonate) and in a few of their binary mixtures (ethanol + DMSO, DMC + DMSO and DMC + PC). The experimental method uses a Varian inductively-coupled plasma-optical-emission spectrometer (ICP-OES). Solubilities increase with rising temperature. At a given temperature, LiNO₃ shows the highest solubility in all solvents. Salt solubilities follow the order LiNO₃ > LiTFSI > LiBr > LiCl > LiPF₆ > LiF. The dissolving abilities of the solvents are in the order ethanol > DMSO > acetonitrile > PC > DMC. Coupled with the salt's melting temperature and enthalpy of fusion, liquid-phase activity coefficients for salts were obtained from the solubility data.

Keywords: Lithium salts, Solubility, Solvents, Activity coefficient

1. Introduction

Lithium-ion batteries use non-aqueous solvents [1-5]. For design of such batteries it is useful to know lithium-salt solubilities over a range of temperature. For salts, solubility data in water are plentiful [6-12], but solubility data for salts in non-aqueous solvents and their mixtures are not enough [13-17], despite their importance for production of specialty chemicals and pharmaceuticals [18]. Propylene carbonate (PC) is a polar aprotic solvent widely used in battery applications because of its electrochemical stability, high dielectric constant and strong ability to dissolve electrolytes [19]. With similar properties, acetonitrile and dimethyl sulfoxide (DMSO) are also possible solvents for a lithium-ion battery. Dimethyl carbonate (DMC) has a low dielectric constant, but a mixture of DMC and PC gives favorable battery cyclability [20]. Lithium hexafluorophosphate (LiPF₆) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) have high solubility in non-aqueous polar solvents [21]. LiPF₆ shows high solubility and good electrochemical properties in a mixture of dimethoxyethane + PC [22]. These salts and these solvents may be potentially useful for lithium-ion batteries.

LiF, LiCl, LiBr and LiNO₃ are possible electrolytes for batteries; they are also used in the pharmaceutical industry, and in nuclear reactors [23-25].

Compared with LiTFSI and LiPF₆, these lithium salts are attractive because they have a lower price. While salt-solubility studies are not plentiful in the electrochemical literature, we find many reports on the electrochemical properties of lithium salts in nonaqueous solvents. For example, the Li cycling efficiency for LiPF₆ in ethylene carbonate (EC) + DMC solution was investigated by Aurbach [26]. Buss [27] measured the self-diffusion coefficients of LiTFSI in DMSO with pulsed-field-gradient nuclear-magnetic-resonance spectroscopy and calculated conductivities from the Nernst-Einstein relation. Giordani [28] determined the battery voltage of lithium salts in DMSO. Plakhotnyk [29] used ¹⁹F and ³¹P NMR spectroscopy to study the kinetics of the hydrolysis of LiPF₆ in a mixture of PC + DMC + H₂O. These and many other studies focus on battery application of lithium salts in a non-aqueous solvent. However, there are few published data for the solubilities of these lithium salts in these non-aqueous solvents.

In this work, we used a static equilibrium method to measure the solubilities of six lithium salts (LiF, LiCl, LiBr, LiNO₃, LiTFSI and LiPF₆) in five non-aqueous solvents (ethanol, acetonitrile, DMC, DMSO and PC) and in a few of their binary mixtures (ethanol + DMC, DMC + DMSO and DMC + PC) from 25 to 45 °C.

Table 1a
Properties of salts.

Chemicals	Mass fraction Purity	Supplier	Melting point K	Melting enthalpy kJ·mol ⁻¹
KCl	0.995	Aldrich	1044.15 [30]	26.53 [30]
LiF	0.995	Aldrich	1121.35 [30]	27.09 [30]
LiCl	0.995	Alfa Aesar	883.15 [30]	19.9 [30]
LiBr	0.995	Alfa Aesar	825.15 [30]	17.6 [30]
LiNO ₃	0.995	Alfa Aesar	526.15 [30]	26.7 [30]
LiTFSI	0.99	Aldrich	509.15 [31]	13.2 [31]
LiPF ₆	0.99	Aldrich	473.15 [32]	2.6 [32]

Table 1b
Properties of solvents.

Chemicals	Mass fraction Purity	Supplier	Density g/cm ³ (at 25 °C)	Dielectric constant (at 25 °C)	Polarity (water = 100)
Acetonitrile	0.995	Aldrich	0.79 [33]	36.7 [34]	46 [33]
Dimethyl carbonate	0.995	Fisher	1.07 [33]	3.2 [35]	3.9 [33]
Dimethyl sulfoxide	0.995	Fisher	1.00 [33]	46.7 [34]	44.4 [33]
Ethanol	0.995	Aldrich	0.79 [33]	24.3 [34]	65.4 [33]
Propylene carbonate	0.995	Fisher	1.20 [33]	64.9 [35]	8.7 [36]
Methanol	0.99	Aldrich	0.79 [33]	32.6 [33]	76.2 [34]

2. Materials and methods

2.1. Materials

Table 1a-b summarizes some properties of the salts and solvents studied in this work [30–36]. The purities of all salts are more than 99% checked by high-performance liquid chromatography. They were stored under vacuum in a desiccator with dry CaCl₂. Prior to measurements, they were dried at 100 °C under vacuum for more than 24 h. Solvent purities are no less than 99.5% checked by gas chromatography; they were used without further purification other than drying.

2.2. Apparatus and method

For each experiment, about 50 mL solvent was injected into a volumetric flask (Pyrex 100 mL). A thermostatically controlled water bath (VWR 1160) was used to control the temperature of the solvent to ± 0.1 °C. The solvent temperature was measured by a thermocouple thermometer (Grainger Type K) with accuracy ± 0.01 °C. Excess solute was added to the volumetric flask. The solution was stirred by a magnetic stir bar; the turbid and cloudy supersaturated solution was stirred for more than 12 h to assure solid-liquid equilibrium. After stirring, the volumetric flask was stored for 6 h to precipitate the undissolved solute. A sample of the clear saturated solution was removed using a glass syringe pre-heated to a little higher than the temperature of the solvent and filtered through a membrane filter (0.22 mm). The filtered solution was transferred into a pre-heated flask; 5 mL of saturated solution were removed with an adjustable-volume pipette (Cole-Parmer 0-1000 mL accuracy is $\pm 0.6\%$) and injected into an Erlenmeyer flask (Pyrex 100 mL). The Erlenmeyer flask was heated in vacuum to evaporate the solvent. The precipitated solid solute was dissolved into 100 mL deionized water giving a 20-times diluted aqueous solution. The K^+ and Li^+ concentration were determined by atomic emission with an inductively-coupled-plasma optical-emission-spectrometer (Varian ICPeOES 720 Series).

The standard deviation of the ICP-OES is less than 3%. Each solubility was measured twice and the average value was recorded. The uncertainties of the solubility are less than 5%. The assessment of uncertainties is summarized in Supplementary Material (Table S1).

Solubilities are expressed by mole fraction x :

$$x = \frac{m/M_1}{m/M_1 + \rho V/M_2} \quad (1)$$

where m is the mass of the solute, M_1 and M_2 , respectively, refer to the molecular weight of solute and solvent; ρ is the mass density of the solvent at 25 °C; V is the volume of solvent, 5 mL.

Table 2

Solubility (mole fraction x) of potassium chloride in methanol at the temperature range from $t = (20\text{--}60)^\circ\text{C}$ under 101.1 kPa.

$t/^\circ\text{C}$	x			$(x_{\text{exp}} - x_{\text{ref}}) / x_{\text{exp}} \times 100$	
	This work	Ref [37]	Ref [38]	Ref [37]	Ref [38]
20		2.26×10^{-3}			
25	2.32×10^{-3}	2.35×10^{-3}	2.32×10^{-3}	-1.37	-0.12
30	2.39×10^{-3}	2.41×10^{-3}	2.39×10^{-3}	-0.82	0.08
35	2.49×10^{-3}	2.49×10^{-3}		-0.21	
40	2.58×10^{-3}	2.59×10^{-3}	2.58×10^{-3}	-0.28	0.05
45	2.66×10^{-3}	2.66×10^{-3}		-0.21	
50		2.74×10^{-3}	2.72×10^{-3}		
55		2.84×10^{-3}			
60		2.90×10^{-3}	2.89×10^{-3}		

Note: Standard uncertainties of u are $u(t) = 0.1^\circ\text{C}$, $u(x) = 5\%$.

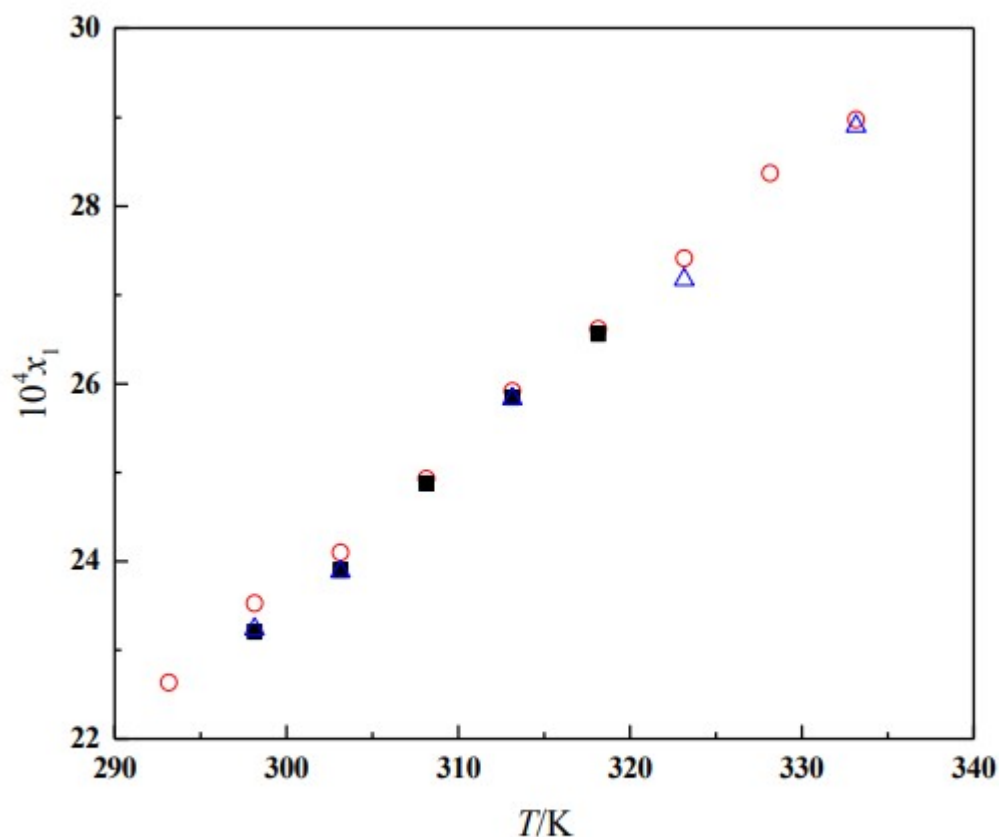


Fig. 1. Comparison of solubilities of potassium chloride in methanol: ■, this work; ○, Li et al. [37]; △, Pinho et al. [38].

Table 3Solubilities (mole fraction x) of six lithium salts in five non-aqueous solvents at the temperature range from $t = (25\text{--}45)^\circ\text{C}$ under 101.1 kPa.

$t/^\circ\text{C}$	LiBr				
	Acetonitrile	Ethanol	DMC	DMSO	PC
25	4.16×10^{-2}	2.74×10^{-1}	4.02×10^{-3}	2.20×10^{-1}	2.24×10^{-2}
30	4.61×10^{-2}	2.76×10^{-1}	4.15×10^{-3}	2.26×10^{-1}	2.40×10^{-2}
35	4.98×10^{-2}	2.77×10^{-1}	4.26×10^{-3}	2.32×10^{-1}	2.59×10^{-2}
40	5.34×10^{-2}	2.79×10^{-1}	4.41×10^{-3}	2.39×10^{-1}	2.79×10^{-2}
45	5.72×10^{-2}	2.81×10^{-1}	4.60×10^{-3}	2.47×10^{-1}	3.00×10^{-2}
	LiCl				
	Acetonitrile	Ethanol	DMC	DMSO	PC
25	1.32×10^{-3}	2.12×10^{-1}	1.35×10^{-4}	1.58×10^{-1}	8.22×10^{-4}
30	1.38×10^{-3}	2.14×10^{-1}	1.37×10^{-4}	1.64×10^{-1}	9.22×10^{-4}
35	1.45×10^{-3}	2.15×10^{-1}	1.40×10^{-4}	1.70×10^{-1}	1.03×10^{-3}
40	1.52×10^{-3}	2.16×10^{-1}	1.42×10^{-4}	1.76×10^{-1}	1.16×10^{-3}
45	1.58×10^{-3}	2.16×10^{-1}	1.44×10^{-4}	1.82×10^{-1}	1.30×10^{-3}
	LiF				
	Acetonitrile	DMC	DMSO	PC	
25	2.01×10^{-6}	1.07×10^{-5}	1.02×10^{-3}	4.56×10^{-4}	
30	2.23×10^{-6}	1.24×10^{-5}	1.11×10^{-3}	5.34×10^{-4}	
35	2.47×10^{-6}	1.44×10^{-5}	1.26×10^{-3}	6.24×10^{-4}	
40	2.71×10^{-6}	1.67×10^{-5}	1.44×10^{-3}	7.17×10^{-4}	
45	2.95×10^{-6}	1.96×10^{-5}	1.62×10^{-3}	8.31×10^{-4}	
	LiNO ₃				
	Acetonitrile	Ethanol	DMC	DMSO	PC
25	1.74×10^{-2}	1.76×10^{-1}	2.06×10^{-4}	2.32×10^{-1}	1.41×10^{-2}
30	1.85×10^{-2}	1.79×10^{-1}	2.31×10^{-4}	2.41×10^{-1}	1.53×10^{-2}
35	1.95×10^{-2}	1.81×10^{-1}	2.60×10^{-4}	2.51×10^{-1}	1.69×10^{-2}
40	2.06×10^{-2}	1.84×10^{-1}	2.95×10^{-4}	2.61×10^{-1}	1.86×10^{-2}
45	2.16×10^{-2}	1.85×10^{-1}	3.34×10^{-4}	2.70×10^{-1}	2.05×10^{-2}
	LiPF ₆				
	Acetonitrile	DMC	DMSO	PC	
25	6.35×10^{-2}	2.04×10^{-1}	1.42×10^{-1}	2.17×10^{-2}	
30	7.34×10^{-2}	2.15×10^{-1}	1.46×10^{-1}	3.40×10^{-2}	
35	8.52×10^{-2}	2.28×10^{-1}	1.51×10^{-1}	4.92×10^{-2}	
40	9.91×10^{-2}	2.42×10^{-1}	1.56×10^{-1}	6.85×10^{-2}	
45	1.15×10^{-1}	2.59×10^{-1}	1.61×10^{-1}	9.12×10^{-2}	
	LiTFSI				
	DMC	DMSO	PC		
25	1.97×10^{-1}	2.37×10^{-1}	1.83×10^{-1}		
30	2.03×10^{-1}	2.41×10^{-1}	1.90×10^{-1}		
35	2.10×10^{-1}	2.44×10^{-1}	1.97×10^{-1}		
40	2.18×10^{-1}	2.48×10^{-1}	2.05×10^{-1}		
45	2.26×10^{-1}	2.52×10^{-1}	2.14×10^{-1}		

Note: Standard uncertainties of u are $u(t) = 0.1^\circ\text{C}$, $u(x) = 5\%$.

3. Results and discussion

3.1. Experimental results

Before solubility measurements for lithium salts, we checked the reliability of our experimental system by comparing our results with data from the literature. For this purpose, we measured the solubility of potassium chloride in methanol. Table 2 and Fig. 1 compare our solubilities with those from Li [37] and Pinho [38]. Agreement is very good.

Table 3 and Fig. 2 give solubilities of six lithium salts (LiF, LiCl, LiBr, LiNO₃, LiTFSI and LiPF₆) in five non-aqueous solvents (acetonitrile, ethanol, DMC, DMSO and PC) from 25 to 45 °C. The solubilities of these lithium salts show a strong dependence on temperature. Three models are used to relate the solubilities to temperature. The accuracies are shown in Supplementary Material (Table S3–S5). Table 4 shows experimental solubilities of LiCl, LiBr and LiNO₃ in a few mixtures of two solvents. The solvent mixtures are

prepared based on mole fraction. The solubilities are presented as the mole fraction of the solution.

Table 3 and Fig. 2 show that all solubilities increase with rising temperature, indicating that the dissolution process is endothermic. Solubilities of halogenated lithium and lithium nitrate decrease in the order: ethanol > DMSO > acetonitrile > PC > DMC. However, the solubility of LiF in acetonitrile is less than that in PC and the solubility of LiNO₃ in ethanol is less than that in DMSO.

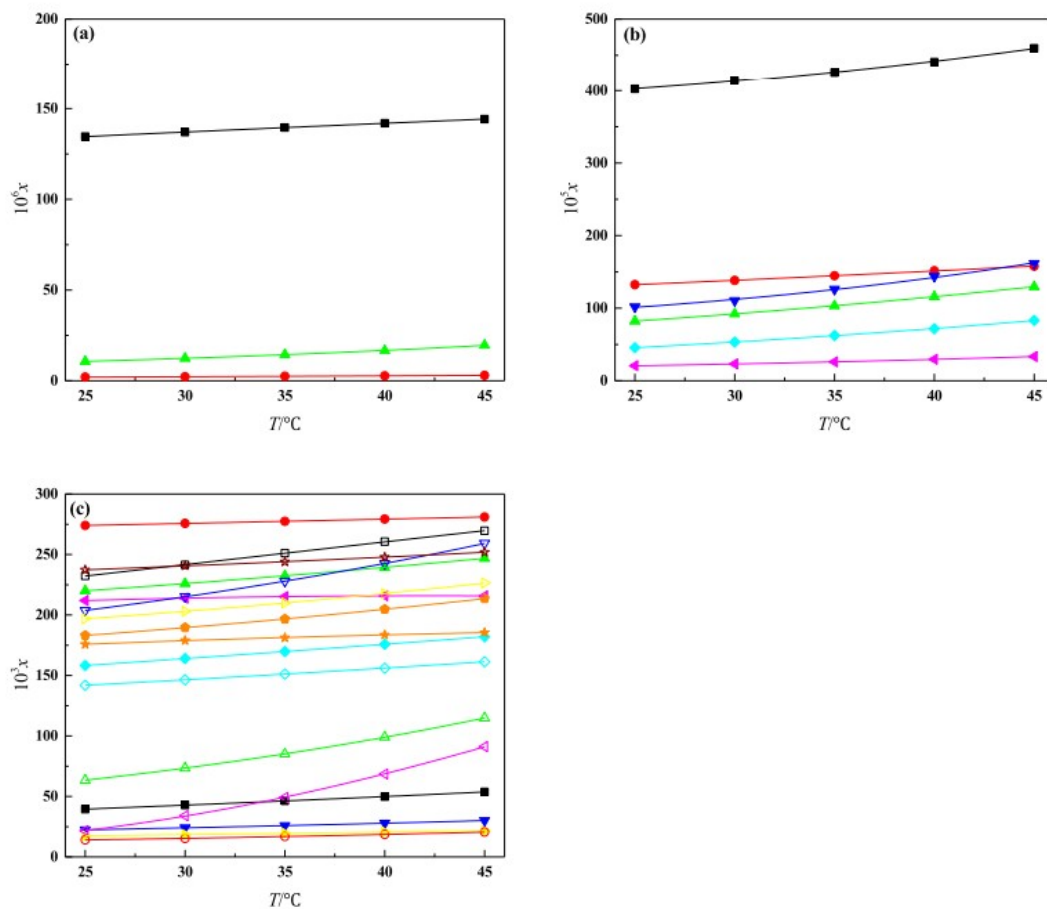


Fig. 2. Solubilities of lithium salts in non-aqueous solvents: (a) ■, LiCl in DMC; ●, LiF in Acetonitrile; ▲, LiF in DMC; (b) ■, LiBr in DMC; ●, LiCl in Acetonitrile; ▲, LiCl in PC; ▼, LiF in DMSO; ◆, LiF in PC; ◆, LiNO₃ in DMC; (c) ▲, LiBr in Acetonitrile; ●, LiBr in Ethanol; ▲, LiBr in DMSO; ▼, LiBr in PC; ◆, LiCl in DMSO; ◆, LiCl in Ethanol; ◆, LiNO₃ in Acetonitrile; ★, LiNO₃ in Ethanol; □, LiNO₃ in DMSO; ○, LiNO₃ in PC; △, LiPF₆ in Acetonitrile; ▽, LiPF₆ in DMC; ◇, LiPF₆ in DMSO; ◊, LiPF₆ in PC; ◆, LiTFSI in DMC; ☆, LiTFSI in DMSO; ◆, LiTFSI in PC.

Solvent properties are shown in Table 1b. The dielectric constants decrease in the order PC > DMSO > acetonitrile > ethanol > DMC. Only the salt solubilities in DMSO, acetonitrile and DMC follow this order, indicating that lithium-salt solubilities are affected by other factors such as hydrogen-bond formation and dispersion forces. Ma [39] reported that the solvent's polarity has a significant influence on solubility. Table 1b gives solvent polarities, decreasing in the order: ethanol > acetonitrile > DMSO > PC > DMC. This order is the same as that for the solubilities except acetonitrile and DMSO. The lithium salts used here seem to be more easily dissolved into solvents with higher polarity. Although PC has a higher dielectric constant than those

of the other solvents, the solutes used here are more soluble in ethanol because of its higher polarity. Solvent polarity can explain why LiF solubility in acetonitrile is lower than that in PC. The F^- anion is much smaller than the Cl^- and Br^- ions; the lattice energy of LiF is smaller than LiCl and LiBr, it's more difficult for LiF to separate into cation and anion dissolving into polar solvents. The main factor affecting the solubility of LiF in a polar solvent is the dielectric constant. The polarities of acetonitrile and DMSO are nearly the same, but the dielectric constant of DMSO is much larger than that of acetonitrile; therefore, salt solubilities in DMSO exceed those in acetonitrile.

Fig. 3 presents solubilities of LiF, LiCl, LiBr, $LiNO_3$, LiTFSI and $LiPF_6$ in DMSO. They decrease in the order: $LiNO_3 > LiTFSI > LiBr > LiCl > LiPF_6 > LiF$. The solubilities of halogenated lithium salts decrease with rising atomic radii of the F^- , Cl^- and Br^- ions.

Fig. S1 presents solubilities of LiCl, LiBr and $LiNO_3$ in mixtures (ethanol + DMC, DMC + DMSO and DMC + PC) in Supplementary Material. The solubilities of these lithium salts in a solvent mixture are very nearly linearly with temperature. Fig. 4 shows the solubility-composition projections for LiBr in DMSO, ethanol and their mixtures. The solubilities are not linear with composition; the better solvent influences the solubility more than the poorer solvent. This influence is also shown in the solubilities of other lithium salts in the solvent mixtures studied here.

3.2. Thermodynamic analysis

Solubility depends not only on the activity coefficient of the solute in the solvent but also on the fugacity of the standard state to which that activity coefficient refers and on the fugacity of the pure solid. Assuming negligible solubility of the solvent in the solid phase, the equilibrium equation is [40]:

$$f_2^{\zeta} = x_2 \gamma_2 f_2^{\theta} \quad (2)$$

where subscript 2 stands for the solute, f_2^{ζ} is the fugacity of the pure solid, x_2 is the solubility in mole fraction, γ_2 is the liquid-phase activity coefficient, and f_2^{θ} is the standard-state fugacity. Here f_2^{θ} is defined as f_2^L the fugacity of the pure, subcooled liquid at solution temperature T under its saturation pressure.

For the liquid-phase activity coefficient, the equilibrium equation becomes:

$$\gamma_2 = \left(\frac{1}{x_2} \right) / \left(\frac{f_2^L}{f_2^{\zeta}} \right) \quad (3)$$

The ratio f_2^L / f_2^{ζ} can be expressed by Refs. [40-42]:

$$\ln \frac{f_2^L}{f_2^S} = \frac{\Delta_{\text{fus}}h}{RT_t} \left(\frac{T_t}{T} - 1 \right) - \frac{\Delta c_p}{R} \left(\frac{T_t}{T} - 1 \right) + \frac{\Delta c_p}{R} \ln \frac{T_t}{T} \quad (4)$$

where R is the gas constant ($8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$), T_t and $\Delta_{\text{fus}}h$ are the triple-point temperature that is very close to melting temperature T_m and the melting enthalpy shown in Table 1b; Δc_p is the molar heat capacity of the liquid phase minus that of the solid. Because the two terms containing Δc_p are less important than the first term and because they approximately cancel, we used a simplified form of Eq. (4):

$$\ln \frac{f_2^L}{f_2^S} = \frac{\Delta_{\text{fus}}h}{RT_t} \left(\frac{T_t}{T} - 1 \right) \quad (5)$$

$$\gamma_2 = \frac{1}{x_2} / \exp \left[\frac{\Delta_{\text{fus}}h}{RT_t} \left(\frac{T_t}{T} - 1 \right) \right] \quad (6)$$

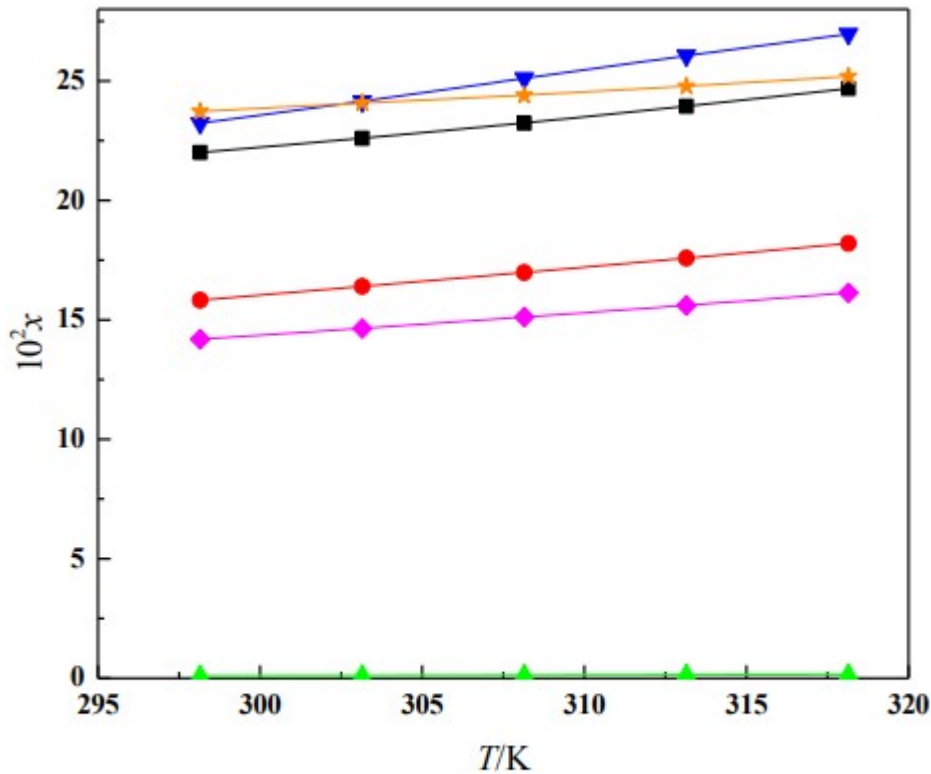


Fig. 3. Solubilities of lithium salts in DMSO: ■, LiBr; ●, LiCl; ▲, LiF; ▼, LiNO₃; ◆, LiPF₆; ★, LiTFSI.

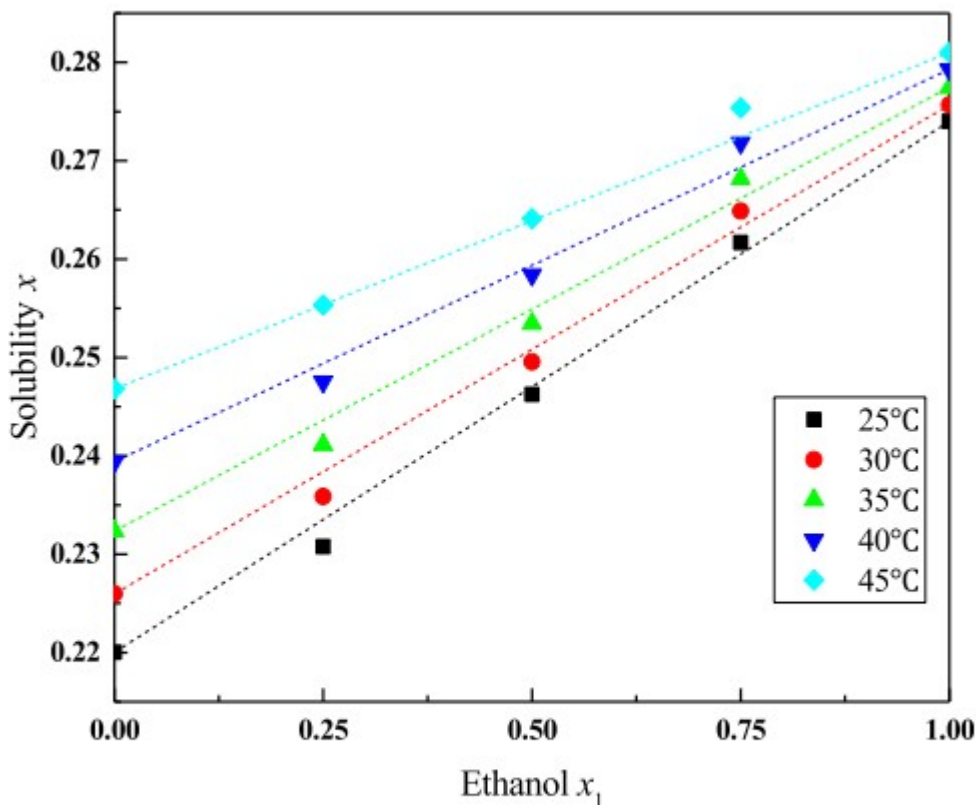


Fig. 4. Solubilities x of LiBr in Ethanol (x_1) + DMSO (x_2) mixtures: (a) ■, 25 °C; ●, 30 °C; ▲, 35 °C; ▼, 40 °C; ◆, 45 °C; ---, linearly changing line.

With measured solubilities x_2 , activity coefficients at saturation γ_2 were calculated, they are shown in the Supplementary Material (Table S2). All γ_2 increase with rising temperature except for LiPF₆. This unexpected result may be due to the small melting enthalpy of LiPF₆. In high-polarity solvents (methanol, ethanol and DMSO), where only dispersion forces are important, γ_2 is generally larger than unity and the solubility is small. But in low-polarity solvents (DMC and PC), where polar forces are important, γ_2 may be less than unity with correspondingly higher solubility. However, for LiTFSI and LiPF₆, this trend is not evident.

The Margules equation [43,44] relates the activity coefficient of the solute to its mole fraction:

$$\ln \gamma_2 = \frac{A}{RT}(1 - x_2)^2 \quad (7)$$

where $A \text{ J} \cdot \text{mol}^{-1}$ is a parameter that reflects the solute-solvent interaction. A/RT is a dimensionless parameter shown in Supplementary Material (Table S6). All A/RT increase with rising temperature except for LiPF₆. For one salt in different solvents at the same temperature, the solubility increases with declining A/RT . The unusual behavior of LiPF₆ may follow from its small

melting enthalpy; a small uncertainty in this enthalpy can cause a large change in A/RT .

4. Conclusion

New measurements are reported for the solubilities of six lithium salts in five non-aqueous solvents and in a few of their binary mixtures from 25 to 45 °C. Toward interpreting the solubilities, activity coefficients were obtained using the salts' melting temperatures and enthalpies of fusion. When these activity coefficients are fitted to the Margules equation, we obtain a dimensionless parameter A/RT that reflects solute-solvent interactions. Attempts to relate these parameters to the solvent's dielectric constant and polarity are only partially successful.

The experimental results reported here may be useful for development of lithium-ion batteries.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.fluid.2017.12.034>.

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