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Osmotic and activity coefficients for five lithium salts in three non-aqueous solvents

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Abstract

To obtain osmotic coefficients, a classic static-view apparatus was used to measure the difference between the vapor pressure of a solvent and that of its salt solution at 25 °C. Vapor-pressure lowering was measured for solutions containing a lithium salt (LiCl, LiBr, LiNO₃, LiPF₆ and LiTFSI) dissolved in a non-aqueous solvent (dimethyl carbonate, dimethyl sulfoxide and acetonitrile) that may be used in a lithium-ion battery. The osmotic-coefficient data are represented by Archer's extended Pitzer equation. Mean ionic activity coefficients for the salts are calculated from the osmotic-coefficient data.

Keywords: Osmotic coefficient, Activity coefficient, Lithium salts, Archer-Pitzer equation, Non-aqueous solvents

1. Introduction

Because the decomposition voltage of water is low and water is easily reacting with the salts in lithium-ion battery, lithium-ion batteries use non-aqueous solvents [1-5]. The electrolyte solutions in such batteries exhibit considerable deviations from ideal behavior, especially at high solute concentrations [6]. For modeling and designing a lithium-ion battery, it is useful to know lithium-salt activity coefficients. Although activity-coefficient data for salts in water are plentiful [7-17], such data for salts in non-aqueous solvents are rare.

Only few activity-coefficient data have been reported for non-aqueous electrolyte solutions, Barthel and Neueder [18-25] made vapor-pressure-lowering measurements for some lithium-salt solutions to obtain activity coefficients in methanol, ethanol, acetone, acetonitrile, dimethoxyethane, and dimethylcarbonate. Nasirzadeh [26] measured activity coefficients for LiBr in acetonitrile that agree well with Barthel's work; he also measured osmotic pressures for lithium bromide in methanol, ethanol and 2-propanol [27-29] from 25 to 75 °C. Zafarani-Moattar reported osmotic and activity coefficients for solutions of LiCl, LiBr, and LiNO₃ in 2-propanol at 25 °C [32]. Javid measured vapor pressures of solutions of CaCl₂ in methanol and in ethanol from 25 to 50 °C [33]. Table 1 lists publications that report salt activity coefficients for salts in non-aqueous solutions. LiCl, LiBr and LiNO₃ are possible electrolytes for batteries; they are also used in the

pharmaceutical industry, and in nuclear reactors [34–36]. However, short-chain alcohols which are widely used in the publications in Table 1 are not useful for lithium-ion batteries. More activity coefficients of lithium salts in battery-using solvents should be measured. Lithium hexafluorophosphate (LiPF_6) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) are commonly used in lithium-ion batteries [6,37].

Propylene carbonate (PC) is a polar aprotic solvent widely used in lithium-ion batteries because of its electrochemical stability, high dielectric constant and strong ability to dissolve electrolytes [38]. With similar properties, acetonitrile (AC) and dimethyl sulfoxide (DMSO) are also possible solvents for a lithium-ion battery [39,40]. Dimethyl carbonate (DMC) has a low dielectric constant but a mixture of DMC and PC gives favorable battery cyclability [41]. These salts and these solvents may be useful for lithium-ion batteries. However, there are few published data for the osmotic pressures and activity coefficients of lithium salts in these and other aprotic solvents.

In this work, we used a static method to measure osmotic coefficients for five salts (LiCl , LiBr , LiNO_3 , LiPF_6 and LiTFSI) in three non-aqueous solvents (DMC, DMSO, and AC) at 25 °C. The osmotic-pressure data are represented by Archer's extension of the Pitzer equation [42,43]. Mean ionic activity coefficients for the salts are calculated from our osmotic-pressure data.

Table 1
Sources for activity-coefficient data for salts in non-aqueous solvents.

Solute	Solvent	$t/^\circ\text{C}$	Reference
LiClO_4	methanol, ethanol, 2-propanol, acetone, acetonitrile, DME, DMC	25	Barthel [18]
Et_4NBr , Pr_4NBr , Bu_4NBr , BpBr	ethanol, 2-propanol	25	Barthel [19,20]
LiBr , Bu_4NBr , Bu_4NClO_4	acetone	25	Barthel [21]
Et_4NBr , Pr_4NBr , Bu_4NCl , Bu_4NBr , Bu_4NI , Am_4NBr	acetonitrile	25	Barthel [22]
NaCl , NaBr , NaI , NaClO_4 , KBr , KI , RbI , CsI	methanol	25	Barthel [23]
Et_4NBr , Bu_4NBr , Bu_4NI , Am_4NBr	methanol	25	Barthel [24]
NaI	ethanol, 2-propanol, acetonitrile	25	Barthel [25]
LiBr	acetonitrile	25–70	Nasirzadeh [26]
LiBr	methanol	25–60	Nasirzadeh [27]
LiBr	ethanol, 2-propanol	25–75	Nasirzadeh [28,29]
LiCl , LiBr	N, N-dimethylacetamide	50–150	Nasirzadeh [30]
NaBr , NaSCN	methanol	25	Nasirzadeh [31]
LiCl , LiBr , LiNO_3	2-propanol	25	Zafarani-Moattar [32]
CaCl_2	methanol, ethanol	25–50	Javid [33]

2. Materials and methods

2.1. Materials

Table 2 reports purities and suppliers of the salts and solvents, and solvent dielectric constants. The purities of all salts are more than 99.0% checked by high-performance liquid phase chromatograph (HPLC Agilent-1260). All salts were used without any additional purification except dried at 100 °C under vacuum for more than 24 h to remove the water before the experiment. The salts were stored under vacuum in a desiccator with dry CaCl_2 . Solvent purities are no less than 99.5% checked by gas chromatography (Agilent HP-6890) except the water. The water was from the deionized water supply system in UCB. The deionized water was distilled and then filtered by a water purifier. These solvents were used without any further purification. Both the

solvents and the solutions are frozen and melted at least twice under high vacuum for degassing. The manometer liquid, *n*-butyl phthalate, was also degassed under high vacuum for more than 24 h. The purities of mercury and *n*-butyl phthalate are stated by the supplier without further check. The densities of the solvents and manometer liquids were measured with pycnometers. Table S1 compares our measured density with those from the literatures in Supplementary Material.

Table 2
Purities of salts and solvents, dielectric constants and densities of solvents.

Chemicals	Mass fraction Purity	Supplier	Dielectric constant (at 25 °C)	Density g ml ⁻¹ (at 25 °C, 101.325 kPa) ^a	Analytical method
NaCl	>0.999	Alfa Aesar			HPLC ^b
LiCl	>0.995	Alfa Aesar			HPLC
LiBr	>0.995	Alfa Aesar			HPLC
LiNO ₃	>0.995	Alfa Aesar			HPLC
LiTFSI	>0.99	Aldrich			HPLC
LiPF ₆	>0.99	Aldrich			HPLC
Mercury	>0.995	Aldrich		13.53	
<i>N</i> -butyl phthalate	>0.995	Aldrich		1.042	
Water	>0.999	UCB	78.3 [7]	0.997	HPLC
Acetonitrile	>0.995	Aldrich	35.96 [19]	0.776	GC ^c
Dimethyl carbonate	>0.995	Fisher	3.09 [19]	1.063	GC
Dimethyl sulfoxide	>0.995	Fisher	46.7 [7]	1.096	GC

^a Relative standard uncertainty of density $u_r(\rho) = 0.11\%$, with corresponding $u(t) = 0.1\text{ °C}$, $u(p) = 1.0\text{ kPa}$.

^b High-performance liquid phase chromatograph.

^c Gas chromatography.

2.2. Apparatus

Fig. 1 shows our classic static-view apparatus, similar to those used by Gibson [44] and by Nasirzadeh [45]. The main part of the apparatus is made of Pyrex glass. All connections are ground-glass coated with high-vacuum grease. The flasks in the water bath are filled with solvent (flask 6) and solution (flask 7) prior to attachment to the upper part of the apparatus. A thermostatically controlled water bath (VWR 1160) controls the temperature to $\pm 0.1\text{ °C}$. Two electromagnetic stirrers (Corning PC-410D) are used to stir the solvent and the solution. The entire apparatus is in an air thermostat. An electric heater inside the air-thermostat is controlled by a temperature-controller (OMRON E5CSV, PID: 0.1). A thermocouple-thermometer (Grainger Type K) is in contact with the temperature-controller to measure the temperature inside the air-bath with accuracy $\pm 0.1\text{ °C}$. A glass window in the air thermostat allows observing the manometer. The apparatus is evacuated by a vacuum pump (Welch 1400B-01, Max. Vacuum = 0.001 torr). A vacuum gauge (Grainger 35W1005P) is used for checking the vacuum. Salts, solvents and solutions are weighed with an electronic balance (Mettler Toledo ME204) with uncertainty $\pm 1\text{ mg}$.

Table 3

Pressure difference between solvent and solution (Δp), osmotic coefficients (ϕ , ϕ_{ref}) for NaCl in water at 25 °C.^a

$m/\text{mol kg}^{-1}$	$\Delta p/\text{Pa}$	ϕ	ϕ_{ref} [7]
0	0	1	1
0.1	10.6	0.932	0.9324
0.2	21.0	0.923	0.9245
0.3	31.4	0.921	0.9215
0.4	41.8	0.921	0.9203
0.5	52.2	0.922	0.9209
0.7	73.1	0.926	0.9288
1.0	105.0	0.936	0.9355
1.2	126.7	0.944	0.9428
1.4	148.6	0.953	0.9513
1.6	170.9	0.962	0.9616
1.8	193.5	0.972	0.9723

^a Standard uncertainties $u(t) = 0.1$ °C, $u(p) = 0.6$ Pa; relative standard uncertainties $u_r(m) = 0.66\%$, $u_r(\phi) = 1.25\%$.

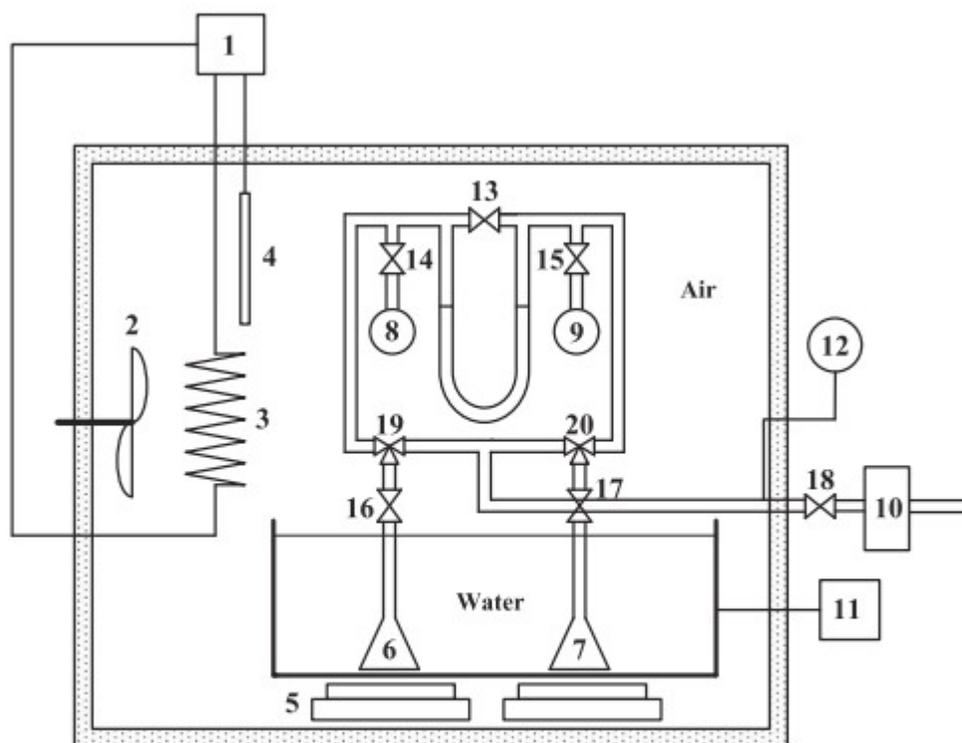


Fig. 1. Experimental system. 1, PID temperature controller; 2, circulating ventilator; 3, heater; 4, thermocouple; 5, electromagnetic stirrer; 6–9, glass flasks with solution or pure solvent; 10, vacuum pump; 11, water bath controller; 12 vacuum gauge; 13–20, stopcocks.

The difference between the vapor pressure of the salt-free solvent and that of the solution, Δp , is determined by a differential manometer. The manometer liquid is *n*-butyl phthalate for low Δp and mercury for high Δp . The density of *n*-butyl phthalate is 1.0418 g/cm³ at 25 °C, much lower than that of mercury, 13.53 g/cm³ at the same temperature. Using *n*-butyl phthalate as the manometer liquid gives Δp with accuracy ± 1 Pa at 25 °C. The very small vapor pressure of *n*-butyl phthalate is 9.7×10^{-3} Pa at 25 °C [46]. The vapor pressure of *n*-butyl phthalate is much lower than that of the solvents and that of the solutions. *N*-butyl phthalate is almost involatile at 25 °C. The tiny concentration of *n*-butyl phthalate in the vapor phase can be ignored. The manometer liquid is replaced by new liquid after ten measurements to prevent contamination from the solvent. The difference between the two liquid levels in the manometer is read by a cathetometer (Wild Heerbugg Switzerland KM347) with uncertainty ± 0.1 mm.

Two flasks filled with solution (flask 8) and solvent (flask 9) are located near the manometer. Because there may be a very small difference in temperature between the air bath and the water bath, the liquids in flask 8 and flask 9 are used to measure the difference in vapor pressure of the solvent and that of the solution. The uncertainties of temperatures in flasks 6 and 7 are less than 0.1 °C. Flasks 6 and 7 are reservoirs to feed flasks 8 and 9.

The range for Δp can be up to 1200 Pa when using *n*-butyl phthalate as manometer liquid and 16 kPa when using mercury. The uncertainty of the measured vapor-pressure difference is less than 0.6 Pa. Table S2 summarizes our assessment of uncertainties in Supplementary Material.

2.3. Experimental procedure

Before the measurement of the vapor pressure, the densities of the manometer liquids and experimental solvents were measured by pycnometers at first. All the density of the liquids were measured at 25 °C and 101.3 kPa. During the measurement process, the atmospheres pressure in the air bath was measured by a barometer (Oliver Hemming W300B105W). The fluctuation of the pressure was less than 1.0 kPa. The manometer liquids and experimental solvents were put into water bath and kept as 25 °C for more than 2 h. The mass of a 20 ml empty pycnometer with its glass cork was measured by the high accuracy electronic balance and recorded as M_p in the air bath at 25 °C. Then the pycnometer was filled with the deionized water, and the water overflow from the cork was cleaned by blotting paper. The pycnometer filled with deionized water was weighed again and recorded the mass as M_w . The density of water was calculated as $(M_w - M_p)/V_p$, here V_p equals to 20 ml. For getting more accurate density, we also used the 50 ml and 100 ml pycnometers to measure the density of the deionized water with the same process. The average of the three results was recorded as the final density of the deionized water. The densities of other solvents and the manometer liquids were measured with the same process.

Table 2 gives the densities of them. The relative standard uncertainty of density is 0.11%, with corresponding standard uncertainty of temperature is 0.1 °C, uncertainty of pressure is 1.0 kPa. Table S2 summarizes our assessment of uncertainties in Supplementary Material.

The difference in vapor pressure between solvent and solution is determined by measuring the two levels of the manometer liquid. Degassed solvent is used to prepare the solution in flask 7. The mass of salt is M_1 and that of solvent is M_2 . The molality of the solution should be a little lower than that desired because it is further degassed under high vacuum. After this degassing, half of the solution is poured into flask 8. We then measure and record the weight M_3 of solution in flask 7. After vacuuming flask 7, we close stopcock 5. The solvent in flask 6 and that in flask 9 are prepared similarly. The four flasks are attached to the upper part of the apparatus with stopcocks 14, 15, 16 and 17 closed. Flask 6 and flask 7 are immersed in the water bath. They are well-stirred for more than half an hour to insure that the temperatures of solution and solvent are the same as that of the water bath.

At the same time, we open three-way stopcocks 19 and 20 and connect the two legs of the manometer to the vacuum line for at least 30 min. We then open stopcocks 14 and 15 to vacuum the solution and solvent in flask 8 and flask 9 for at least 30 min. After closing stopcocks 13, 14 and 15, we measure and record the two levels of the manometer liquid.

Table 4
Vapor pressures of solvents (p_0) at 25 °C.^a

	Acetonitrile		Dimethyl carbonate		Dimethyl sulfoxide	
	p_0/kPa	$(p_{0,\text{exp}} - p_{0,\text{ref}})/p_{0,\text{exp}} \times 100$	p_0/kPa	$(p_{0,\text{exp}} - p_{0,\text{ref}})/p_{0,\text{exp}} \times 100$	p_0/Pa	$(p_{0,\text{exp}} - p_{0,\text{ref}})/p_{0,\text{exp}} \times 100$
This work	11.812		7.256		80	
Literature	11.795 [47]	0.14	7.253 [51]	0.04	80 [47]	0.00
	11.825 [26]	-0.11	7.284 [52]	-0.39	81 [54]	-1.25
	11.834 [48]	-0.19	7.291 [53]	-0.48	79.65 [55]	0.44
	11.795 [49]	0.14			79.68 [56]	0.40
	11.833 [50]	-0.18			80.23 [57]	-0.29

^a Standard uncertainties $u(t) = 0.1$ °C, and $u(p) = 0.6$ Pa.

The solvent in flask 6 is connected to one leg of the manometer; the other leg, located near flask 9, is connected to the vacuum pump. The difference in the two levels of the manometer liquid indicates p_0 , the vapor pressure of the salt-free solvent. The vapor pressures of three pure solvents shown in Table 4 were measured by this process. Then we close stopcock 20 and open stopcock 15. The difference in vapor pressure between flask 6 and flask 9 is measured by the manometer. The difference in the levels of the manometer liquid gives $\Delta p_{\text{solvent}}$, the difference in vapor pressure between the solvent in the water bath and that in the air thermostat. Similarly, we close stopcocks 15 and 19, then open stopcocks 14 and 20. The solutions in flask 7 and flask 8 are connected to the two legs of the manometer. The difference in the levels of the manometer liquid gives $\Delta p_{\text{solution}}$, the difference in vapor pressure between the solution in the water bath and that in the air thermostat. Because the temperature in the air thermostat and that in the water bath are essentially the same, $\Delta p_{\text{solvent}}$ and $\Delta p_{\text{solution}}$ are usually small enough to be

ignored. The measurements of $\Delta\rho_{\text{solvent}}$ and $\Delta\rho_{\text{solution}}$ provide only a check to determine a possible effect of temperature difference between water bath and air bath. If the $\Delta\rho_{\text{solution}}$ and $\Delta\rho_{\text{solvent}}$ are significant, we give more time to make sure that the temperature of the solution in the air bath and that in the water bath become essentially identical. The decrease of the mass due to degassing is very small in both flask 7 and flask 8.

Table 5
Pressure difference between solvent and solution (Δp), osmotic coefficients (ϕ , ϕ_{P4} , ϕ_{Pitzer} , ϕ_{Archer}) and activity coefficients (γ_{\pm} , $\gamma_{\pm, \text{Archer}}$) of lithium salts in non-aqueous solutions at 25 °C.^a

$m/\text{mol kg}^{-1}$	$\Delta p/\text{Pa}$	ϕ	ϕ_{P4}	ϕ_{Pitzer}	ϕ_{Archer}	$\gamma_{\pm, \text{Archer}}$
LiBr in AC						
0	0	1	1	1	1	1
0.014	9.2	0.677	0.701	0.708	0.696	0.429
0.035	20.4	0.602	0.612	0.603	0.598	0.281
0.056	31.6	0.584	0.575	0.568	0.570	0.224
0.082	44.9	0.566	0.552	0.552	0.559	0.188
0.117	62.3	0.550	0.539	0.546	0.555	0.160
0.155	81.7	0.545	0.534	0.543	0.549	0.140
0.209	107.2	0.531	0.531	0.537	0.537	0.121
0.252	126.6	0.521	0.529	0.530	0.526	0.109
0.311	153.1	0.511	0.525	0.520	0.512	0.098
0.406	196.0	0.502	0.512	0.504	0.495	0.084
0.509	240.9	0.493	0.495	0.489	0.486	0.074
0.623	290.0	0.486	0.478	0.480	0.485	0.067
0.714	327.7	0.480	0.471	0.477	0.487	0.062
0.805	369.6	0.481	0.474	0.479	0.486	0.059
0.912	419.6	0.483	0.494	0.488	0.478	0.055
LiPF₆ in AC						
0	0	1	1	1	1	1
0.024	16.3	0.702	0.724	0.723	0.711	0.420
0.060	37.8	0.650	0.645	0.651	0.643	0.291
0.085	52.1	0.633	0.620	0.633	0.628	0.253
0.157	91.9	0.606	0.587	0.607	0.608	0.196
0.214	122.5	0.593	0.577	0.595	0.596	0.171
0.280	156.2	0.579	0.570	0.582	0.582	0.151
0.341	186.8	0.570	0.565	0.572	0.571	0.138
0.373	202.2	0.564	0.562	0.567	0.565	0.132
0.435	232.8	0.557	0.557	0.560	0.557	0.122
0.492	261.4	0.554	0.552	0.554	0.551	0.115
0.541	284.8	0.550	0.548	0.549	0.547	0.110
0.626	326.7	0.546	0.540	0.544	0.544	0.102
0.781	404.3	0.543	0.530	0.540	0.543	0.092
0.865	446.2	0.542	0.528	0.540	0.544	0.088
0.945	487.0	0.543	0.529	0.541	0.545	0.085
1.013	521.7	0.543	0.533	0.543	0.545	0.082
1.079	556.4	0.545	0.540	0.546	0.545	0.080
1.125	580.9	0.546	0.546	0.548	0.543	0.078
LiTFSI in AC						
0	0	1	1	1	1	1
0.035	26.5	0.783	0.797	0.791	0.788	0.501
0.067	49.0	0.756	0.751	0.750	0.750	0.415
0.114	79.6	0.723	0.715	0.719	0.722	0.351
0.227	148.0	0.677	0.673	0.678	0.681	0.274
0.338	212.4	0.654	0.652	0.653	0.653	0.234
0.427	261.4	0.638	0.640	0.639	0.637	0.212
0.489	294.0	0.628	0.633	0.631	0.629	0.200
0.562	333.9	0.621	0.627	0.624	0.622	0.188
0.676	397.2	0.616	0.618	0.616	0.615	0.174
0.781	455.3	0.613	0.612	0.612	0.612	0.164
0.865	502.3	0.612	0.609	0.610	0.612	0.158
1.013	586.0	0.612	0.607	0.610	0.613	0.149
1.125	649.3	0.612	0.609	0.611	0.613	0.143
1.267	730.0	0.613	0.618	0.615	0.614	0.136
LiPF₆ in DMC						
0	0	1	1	1	1	1
0.035	23.5	0.514	0.571	0.517	0.515	0.033
0.078	45.9	0.452	0.453	0.442	0.445	0.021
0.113	60.2	0.409	0.403	0.411	0.415	0.016
0.235	109.2	0.358	0.329	0.359	0.362	0.010
0.341	149.1	0.338	0.313	0.337	0.338	0.007
0.468	196.0	0.325	0.311	0.322	0.321	0.006
0.59	239.9	0.316	0.317	0.316	0.314	0.005
0.703	283.8	0.315	0.323	0.315	0.312	0.004
0.814	327.7	0.316	0.330	0.317	0.314	0.004
0.960	386.9	0.317	0.338	0.324	0.322	0.004
1.100	459.4	0.330	0.346	0.334	0.333	0.003
1.235	539.1	0.351	0.354	0.346	0.346	0.003
1.563	740.2	0.382	0.379	0.385	0.387	0.003
1.799	929.1	0.423	0.407	0.418	0.421	0.003
1.902	1010.8	0.438	0.423	0.435	0.437	0.003
2.015	1112.9	0.459	0.444	0.453	0.455	0.003
2.148	1233.3	0.482	0.473	0.476	0.477	0.003
2.378	1423.2	0.508	0.538	0.519	0.515	0.003

Table 5 (continued)

$m/\text{mol kg}^{-1}$	$\Delta p/\text{Pa}$	ϕ	ϕ_{P4}	ϕ_{Pitzer}	ϕ_{Archer}	$\bar{\gamma}_{\pm}$ Archer
LiTFSI in DMC						
0	0	1	1	1	1	1
0.010	8.2	0.625	0.742	0.618	0.611	0.066
0.027	19.4	0.550	0.622	0.564	0.570	0.042
0.127	80.7	0.489	0.427	0.450	0.477	0.018
0.243	139.9	0.445	0.385	0.423	0.443	0.012
0.376	200.1	0.413	0.384	0.411	0.417	0.009
0.452	232.8	0.400	0.390	0.407	0.406	0.008
0.589	297.1	0.394	0.403	0.404	0.393	0.007
0.711	355.3	0.392	0.415	0.404	0.390	0.006
0.865	432.9	0.395	0.427	0.409	0.394	0.006
1.020	514.6	0.400	0.437	0.417	0.405	0.005
1.131	593.2	0.419	0.443	0.425	0.417	0.005
1.298	719.0	0.446	0.452	0.440	0.440	0.005
1.546	909.7	0.481	0.467	0.469	0.480	0.004
1.862	1188.4	0.533	0.500	0.515	0.535	0.004
2.175	1485.5	0.585	0.559	0.573	0.587	0.004
2.320	1625.4	0.607	0.597	0.603	0.608	0.004
2.583	1876.5	0.643	0.689	0.663	0.641	0.004
LiBr in DMSO						
0	0	1	1	1	1	1
0.102	1.02	0.806	0.813	0.804	0.805	0.424
0.202	2.04	0.819	0.815	0.823	0.823	0.380
0.301	3.06	0.830	0.824	0.831	0.831	0.358
0.398	4.08	0.842	0.834	0.835	0.835	0.343
0.502	5.10	0.841	0.843	0.840	0.840	0.332
0.602	6.13	0.847	0.852	0.848	0.848	0.325
0.704	7.15	0.851	0.864	0.859	0.859	0.321
0.789	8.17	0.873	0.876	0.872	0.872	0.320
0.955	10.21	0.915	0.908	0.909	0.909	0.325
1.038	11.23	0.933	0.929	0.932	0.932	0.331
1.183	13.27	0.981	0.978	0.983	0.983	0.346
1.371	16.34	1.066	1.066	1.068	1.068	0.378
1.481	18.38	1.128	1.132	1.127	1.127	0.404
LiCl in DMSO						
0	0	1	1	1	1	1
0.107	1.02	0.768	0.773	0.767	0.768	0.370
0.211	2.04	0.784	0.779	0.786	0.785	0.323
0.314	3.06	0.796	0.791	0.795	0.794	0.300
0.422	4.08	0.795	0.801	0.800	0.800	0.284
0.518	5.10	0.815	0.810	0.806	0.806	0.275
0.624	6.13	0.817	0.819	0.815	0.816	0.268
0.822	8.17	0.838	0.845	0.847	0.847	0.264
0.99	10.21	0.883	0.885	0.890	0.889	0.268
1.049	11.23	0.923	0.904	0.909	0.908	0.272
1.204	13.27	0.964	0.970	0.967	0.968	0.286
LiNO ₃ in DMSO						
0	0	1	1	1	1	1
0.112	1.02	0.734	0.745	0.737	0.735	0.324
0.221	2.04	0.749	0.733	0.742	0.747	0.275
0.443	4.08	0.757	0.753	0.756	0.756	0.233
0.663	6.13	0.769	0.780	0.776	0.772	0.216
0.870	8.17	0.792	0.803	0.800	0.797	0.209
1.048	10.21	0.834	0.822	0.822	0.823	0.207
1.243	12.25	0.856	0.844	0.848	0.851	0.207
1.461	14.29	0.862	0.873	0.876	0.878	0.208
1.623	16.34	0.901	0.899	0.896	0.893	0.208

^a Standard uncertainties $u(t) = 0.1$ °C, $u(p) = 0.6$ Pa, relative standard uncertainties $u_r(m) = 0.66\%$, $u_r(\phi) = 1.25\%$.

We connect flask 6 and flask 7 to the manometer and measure Δp , the difference in vapor pressure between the solvent and that of the solution. After the measurement, we reweigh mass M_4 of the solution in flask 7.

The molality m of the solution is:

$$m = \frac{M_1 M_3}{M^* (M_1 M_4 + M_2 M_4 - M_1 M_3)} \quad (1)$$

where M^* is the molecular weight of the salt. Each Δp is measured at least three times; the average is recorded as the final result. Table S2 in Supplementary Material shows the uncertainty of the vapor pressure, temperature and molality.

The reliability of the apparatus and procedure were obtained by measuring the osmotic pressure for NaCl solutions in water and for LiBr solutions in acetonitrile at 25 °C and comparing our results with those in the literatures. Tables 3 and 5, and Fig. 2 show the vapor pressures of aqueous NaCl and those of LiBr in acetonitrile. Our results agree very well with those reported by Robinson [7] and those reported by Nasirzadeh [26].

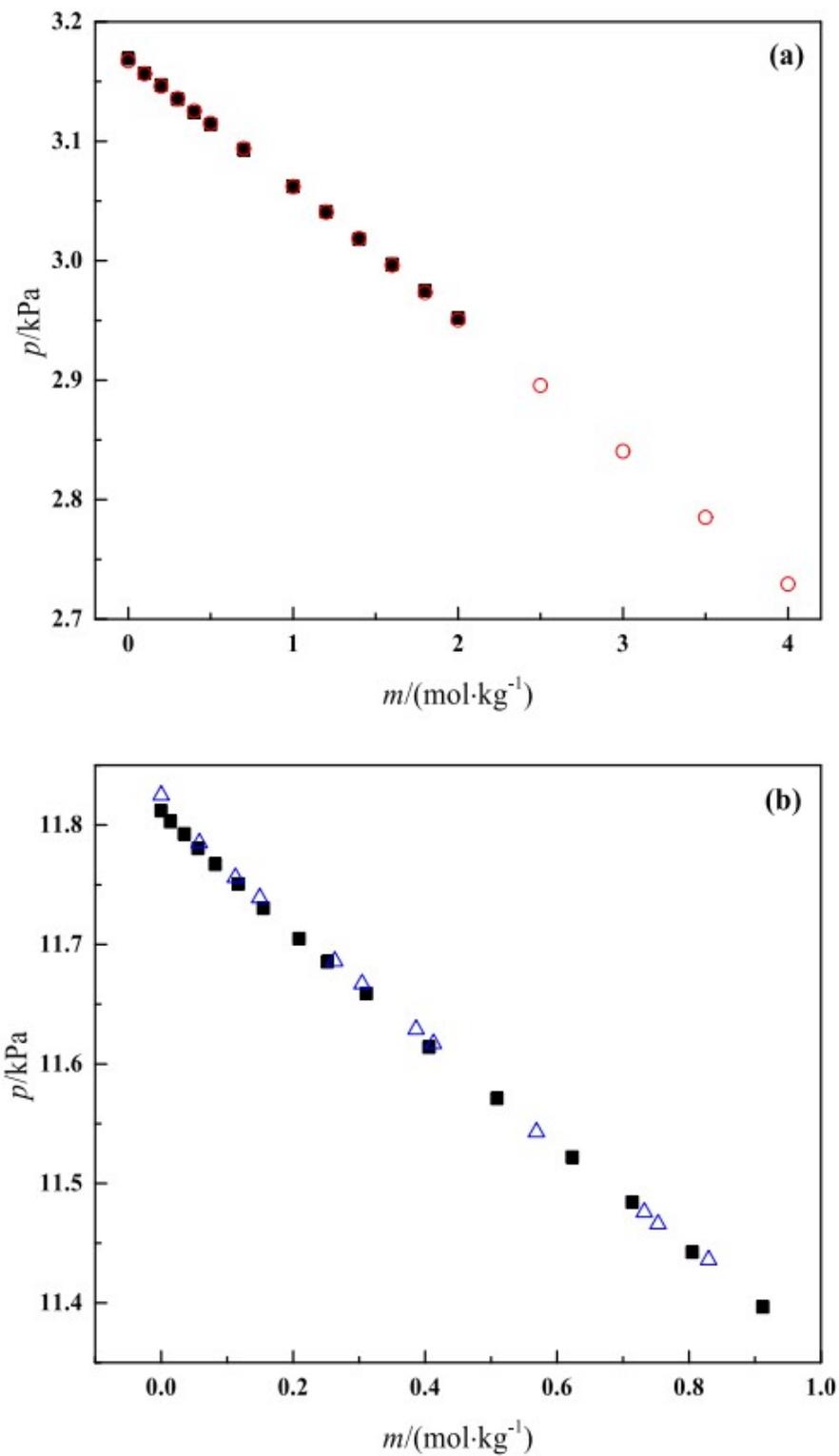


Fig. 2. Vapor–pressures for: (a), NaCl in water ■, this work; ○, Robinson et al. [7]; (b), LiBr in acetonitrile ■, this work; △, Nasirzadeh et al. [26].

3. Results and discussion

3.1. Experimental results

We first measured the vapor pressures of the salt-free solvents. Table 4 compares our vapor pressures with those from NIST [47] and those from the literature [26,48-56]. Agreement is very good. Fig. S1 gives the comparison of the deviation for the vapor pressure in Supplementary Material.

Table 5 gives the differences of vapor pressure Δp , between solvent (AC, DMC and DMSO) and its salt solution for each of five lithium salts (LiCl, LiBr, LiNO₃, LiPF₆ and LiTFSI) at 25 °C. Activities of solvent and osmotic coefficients are calculated from our measurements using basic thermodynamic relations [7]:

$$a_s = 1 - \frac{\Delta p}{p_0} \quad (2)$$

$$\phi = -\frac{\ln a_s}{\nu m M_s^*} \quad (3)$$

where a_s is the activity of the solvent and ϕ is the osmotic coefficient; ν is the stoichiometric number of the salt; m is the molality of the salt solution with unit mol kg⁻¹; M_s^* is the molar mass of the solvent with unit kg mol⁻¹. For a 1-1 salt, $\nu = 2$. Osmotic coefficients ϕ are shown in Table 5 and Figs. 3-5.

3.2. Thermodynamic analysis

3.2.1. Osmotic-coefficient data

The osmotic coefficients of the solution are fitted to a polynomial of the fourth degree in $m^{1/2}$,

$$\phi_{p4} = 1 + am^{1/2} + bm + cm^{3/2} + dm^2 \quad (4)$$

Table S3 gives parameters a , b , c and d in Supplementary Material. Table 5 shows the correlated results ϕ_{p4} from Eq. (4).

The equation of Pitzer and Mayorga [58] relates the osmotic coefficient to the salt molality. For a 1-1 salt, the osmotic coefficient is represented by

$$\phi - 1 = f^\phi + mB^\phi + m^2C^\phi \quad (5)$$

$$f^\phi = \frac{-A_\phi I^{1/2}}{1 + bI^{1/2}} \quad (6)$$

$$A_\phi = \frac{1}{3} (2\pi N_A d_s)^{1/2} \left(\frac{e^2}{4\pi\epsilon_0\epsilon_r kT} \right)^{3/2} \quad (7)$$

$$B^\phi = \beta^{(0)} + \beta^{(1)} e^{-\alpha_1 I^{1/2}} + \beta^{(2)} e^{-\alpha_2 I^{1/2}} \quad (8)$$

where $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^ϕ are Pitzer's temperature-dependent ion-ion interaction parameters. A_ϕ is the Debye-Hückel constant; I is the ionic strength $1/2 \sum m_i z_i^2$; m_i is the molality of ion i and z_i is its charge. In Eq. (7), d_s is the mass density of the solvent, N_A is Avogadro number, e is the elementary charge, ϵ_0 is the permittivity of free space, ϵ_r is the relative permittivity (dielectric constant) of the solvent, and k is Boltzmann's constant. A_ϕ is calculated from the density and dielectric constant shown in Table 2. A_ϕ equals 1.112 for AC, 51.647 for DMC, and 0.893 for DMSO with the unit $\text{mol}^{-1/2} \text{kg}^{1/2}$.

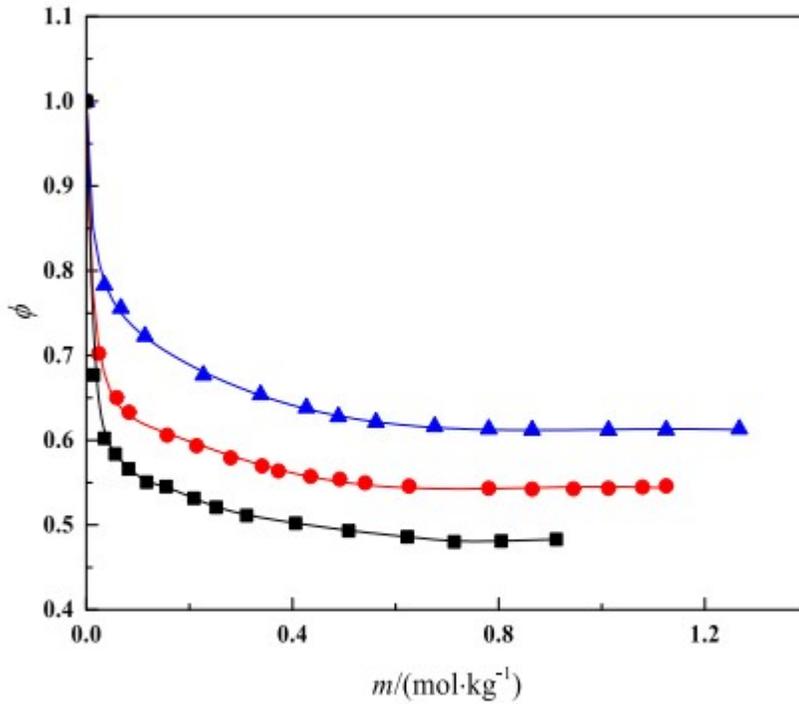


Fig. 3. Experimental osmotic coefficients for lithium salts in acetonitrile (AC): ■, LiBr; ●, LiPF₆; ▲, LiTFSI.

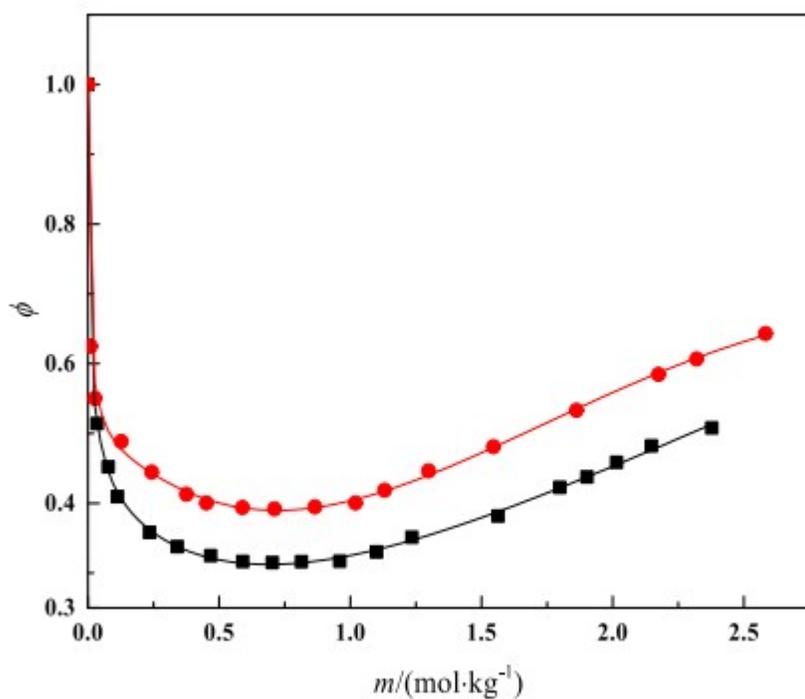


Fig. 4. Experimental osmotic coefficients for lithium salts in dimethyl carbonate (DMC): ■, LiPF_6 ; ●, LiTFSI .

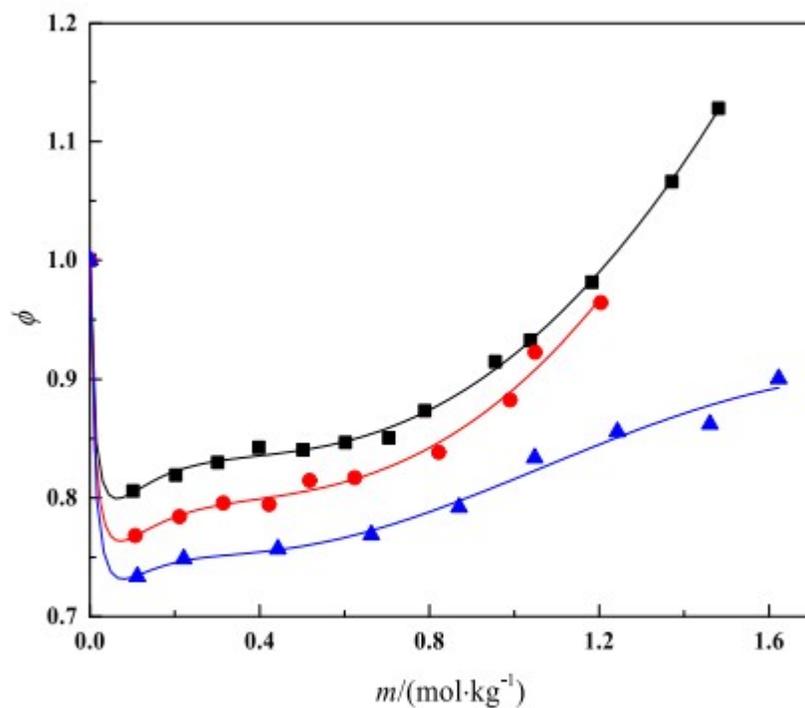


Fig. 5. Experimental osmotic coefficients for lithium salts in dimethyl sulfoxide (DMSO): ■, LiBr ; ●, LiCl ; ▲, LiNO_3 .

Table 6
Parameters for Archer's Equation.

solution	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$c^{(0)}$	$c^{(1)}$	AAD%	RMSD
LiBr in AC	-5.153	6.743	-49.716	-2.061	16.392	0.064	0.008
LiPF ₆ in AC	-1.332	0.641	-30.420	-0.451	4.098	0.406	0.003
LiTFSI in AC	-0.869	0.515	-12.339	-0.221	2.443	0.220	0.002
LiPF ₆ in DMC	-0.244	-0.767	68.064	0.012	0.539	0.808	0.004
LiTFSI in DMC	-1.196	1.968	72.943	-0.033	2.458	0.943	0.007
LiBr in DMSO	-0.241	0.822	-18.233	0.310	-0.124	0.303	0.004
LiCl in DMSO	0.155	-0.265	-21.364	0.390	-1.095	0.598	0.007
LiNO ₃ in DMSO	-0.756	0.839	-26.094	-0.172	2.296	0.680	0.007

From fitting the osmotic-coefficient data, $b = 3.2 \text{ mol}^{-1/2} \text{ kg}^{1/2}$, $\alpha_1 = 2.0 \text{ mol}^{-1/2} \text{ kg}^{1/2}$, $\alpha_2 = 10 \text{ mol}^{-1/2} \text{ kg}^{1/2}$ for AC and DMSO solutions. For DMC solutions, $b = 95 \text{ mol}^{-1/2} \text{ kg}^{1/2}$, $\alpha_1 = 2.0 \text{ mol}^{-1/2} \text{ kg}^{1/2}$, $\alpha_2 = 20 \text{ mol}^{-1/2} \text{ kg}^{1/2}$. Parameters b , α_1 and α_2 for AC and DMC are also recommended by Barthel et al. [19]. Table S4 shows the ion-ion interaction parameters in Supplementary Material. Table 5 also gives the correlated results ϕ_{Pitzer} .

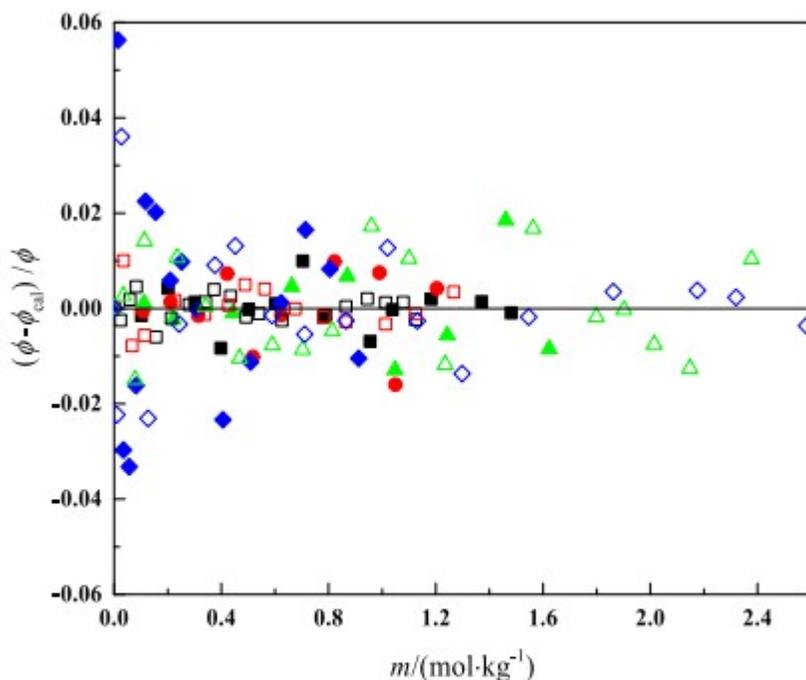


Fig. 6. Deviations of the correlated osmotic coefficients of lithium salts in non-aqueous solutions $(\phi - \phi_{\text{cal}})/\phi$: ■, LiBr in DMSO; ●, LiCl in DMSO; ▲, LiNO₃ in DMSO; ◆, LiBr in AC; □, LiPF₆ in AC; ○, LiTFSI in AC; △, LiPF₆ in DMC; ◇, LiTFSI in DMC.

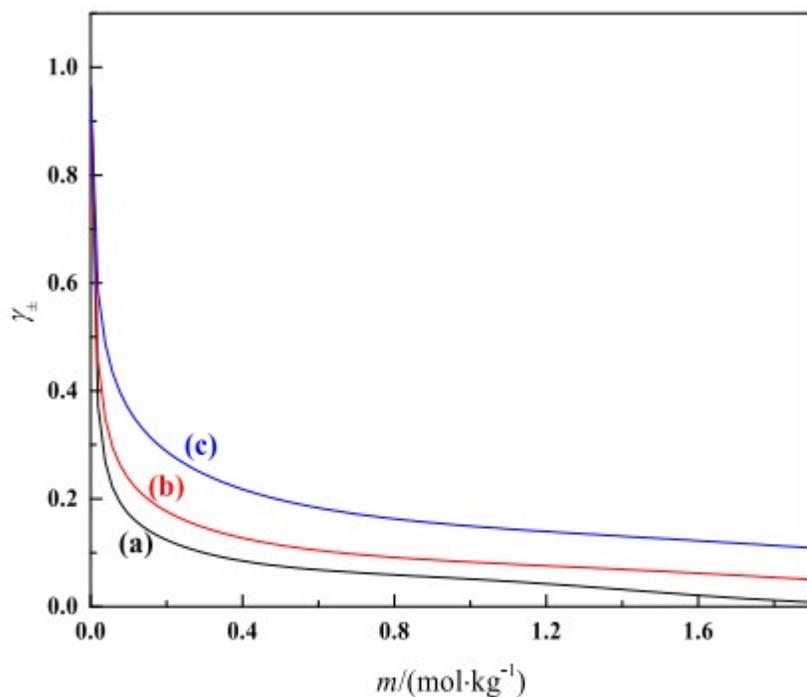


Fig. 7. Mean ionic activity coefficients for lithium salts in acetonitrile (AC) calculated from Archer's equation: (a), LiBr; (b), LiPF₆; (c), LiTFSI.

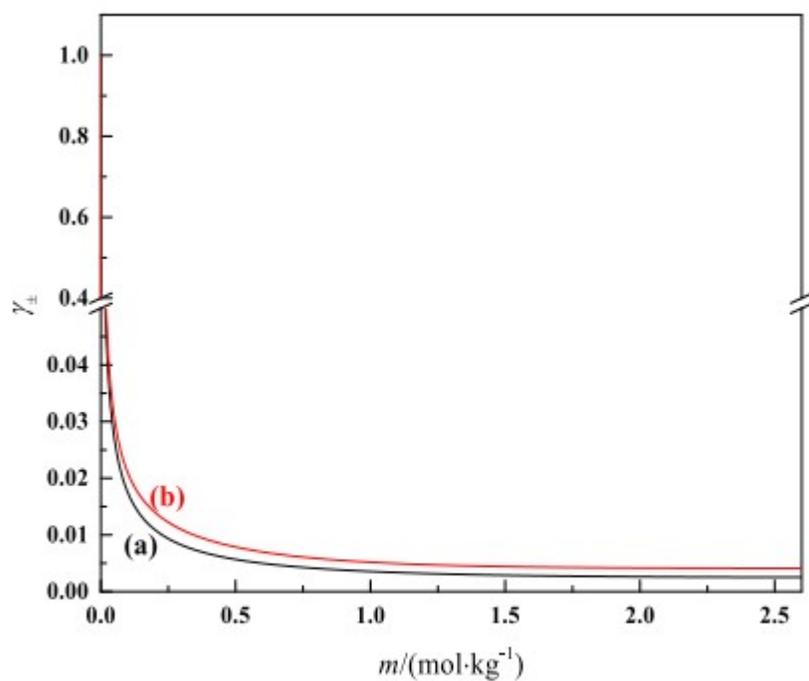


Fig. 8. Mean ionic activity coefficients for lithium salts in dimethyl carbonate (DMC) calculated from Archer's equation: (a), LiPF₆; (b), LiTFSI.

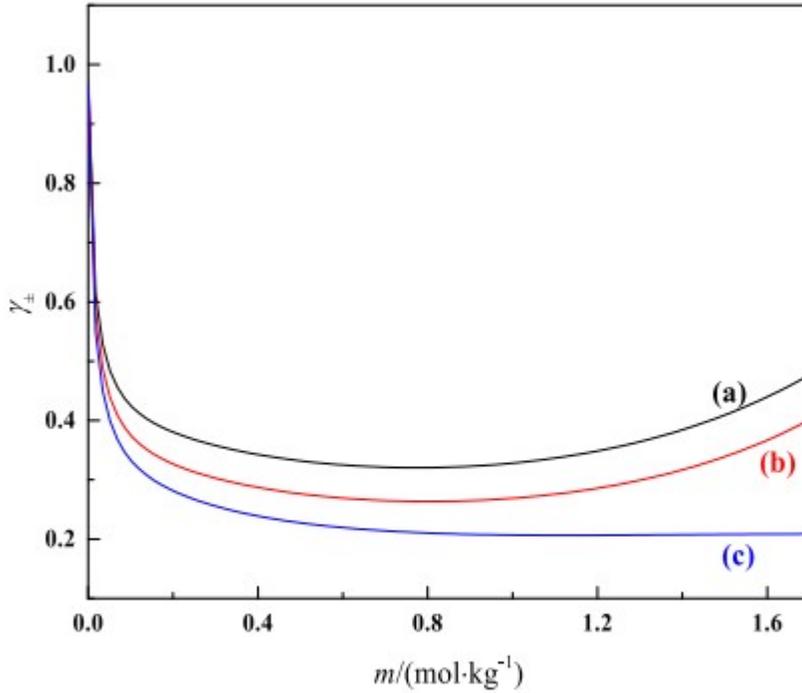


Fig. 9. Mean ionic activity coefficients for lithium salts in dimethyl sulfoxide (DMSO) calculated from Archer's equation: (a), LiBr; (b), LiCl; (c), LiNO₃.

The equation of Pitzer and Mayorga was extended by Archer [59]; his equation includes a third virial coefficient in Eq. (5) for better accuracy at high salt concentrations:

$$\phi - 1 = \frac{-A_\phi I^{1/2}}{1 + bI^{1/2}} + m \left(\beta^{(0)} + \beta^{(1)} e^{-\alpha_1 I^{1/2}} + \beta^{(2)} e^{-\alpha_2 I^{1/2}} \right) + m^2 \left(C^{(0)} + C^{(1)} e^{-\alpha_3 I^{1/2}} \right) \quad (9)$$

where $\alpha_3 = 1 \text{ mol}^{-1/2} \text{ kg}^{1/2}$. Constants A_ϕ , b , α_1 and α_2 are the same as those in Pitzer and Mayorga's equations (Eqs. (5)–(8)). Table 6 shows ion–interaction parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, $C^{(0)}$ and $C^{(1)}$. Table 5 gives the correlated results for ϕ_{Archer} .

The average absolute deviations (AAD) as well as the corresponding root-mean square deviations (RMSD) of Eqs. (4), (5) and (9) are calculated using:

$$AAD = \frac{1}{n} \sum_{i=1}^n \left| \frac{x_{i,exp} - x_{i,cal}}{x_{i,exp}} \right| \quad (10)$$

$$RMSD = \sqrt{\frac{\sum_{i=1}^n (x_{i,exp} - x_{i,cal})^2}{n}} \quad (11)$$

Table S5 gives the AAD and RMSD for Eqs. (4), (5) and (9) in Supplementary Material. Both the fourth degree polynomial (Eq. (4)) and the Pitzer's equation (Eqs. (5)–(8)) use four parameters. Comparing the AAD and RMSD, Pitzer's equation shows better accuracy with AAD less than 0.026 and RMSD less than 0.015. But Archer's equation (Eq. (9)) is better than those two equations, especially for the LiTFSI-acetonitrile solution where the osmotic coefficients decrease sharply at low concentration. The AAD of Archer's equation is 0.220 and the RMSD is 0.002. Figs. 3–5 show the osmotic coefficient curves from Archer's equation. These curves reveal the typical concentration dependence of the osmotic coefficients. They show a sharp decrease at low concentration. For lithium-salt solutions in DMC and DMSO, the osmotic-coefficient curves rise at high concentration.

Fig. 6 gives the relative deviations between the experimental osmotic coefficients data and results from Archer's equation. The relative deviations of osmotic coefficients are all between $\pm 4.0\%$. Most of the relative deviations of osmotic coefficients are between $\pm 2.0\%$, with only a few deviations larger than $\pm 2.0\%$ but smaller than $\pm 4.0\%$.

For the lithium-salt solutions of DMC and AC, the osmotic coefficients decrease in the order $\text{LiTFSI} > \text{LiPF}_6 > \text{LiBr}$, probably because the molecular weights of the salts decrease in the same order. The larger the ion size, the larger the repulsion between them; the repulsive force gives higher osmotic coefficients. But the osmotic coefficients of LiBr , LiCl , LiNO_3 in DMSO decrease in the order $\text{LiBr} > \text{LiCl} > \text{LiNO}_3$ although the molecular weight of LiNO_3 is higher than that of LiCl . This order of osmotic coefficients also appears for lithium salts in 2-propanol [60] suggesting that in DMSO, ion pairing of LiCl is higher than that of LiNO_3 .

Comparing the osmotic coefficients of the same salt in different solvents, LiBr in AC and DMSO, LiPF_6 in AC and DMC, LiTFSI in AC and DMC, the osmotic coefficients decrease in the order $\text{DMSO} > \text{AC} > \text{DMC}$. This order suggests that there is increasing ion-ion attractive interaction from DMSO to AC, to DMC, the same as the order of decreasing dielectric constants $\text{DMSO} > \text{AC} > \text{DMC}$.

3.2.2. Mean ionic activity coefficients

From data for the osmotic coefficient it is readily possible to calculate the mean ionic activity coefficient using the Gibbs-Duhem equation. The mean

ionic activity coefficient γ_{\pm} is calculated using the parameters of Archer's equation for the osmotic coefficient. For 1-1 salts:

$$\ln\gamma_{\pm} = -A_{\phi} \left[\frac{m^{1/2}}{1 + bm^{1/2}} + \frac{2}{b} \ln(1 + bm^{1/2}) \right] + m(2\beta^{(0)} + A_1 + A_2) + \frac{m^2}{2}(3C^{(0)} + A_3) \quad (12)$$

$$A_1 = \frac{2\beta^{(1)}}{\alpha_1^2 m} \left[1 - \left(1 + \alpha_1 m^{1/2} - \frac{\alpha_1^2 m}{2} \right) e^{-\alpha_1 m^{1/2}} \right] \quad (13)$$

$$A_2 = \frac{2\beta^{(2)}}{\alpha_2^2 m} \left[1 - \left(1 + \alpha_2 m^{1/2} - \frac{\alpha_2^2 m}{2} \right) e^{-\alpha_2 m^{1/2}} \right] \quad (14)$$

$$A_3 = \frac{4C^{(1)}}{\alpha_3^4 m^2} \left[6 - \left(6 + 6\alpha_3 m^{1/2} + 3\alpha_3^2 m + \alpha_3^3 m^{3/2} - \frac{1}{2}\alpha_3^4 m^2 \right) e^{-\alpha_3 m^{1/2}} \right] \quad (15)$$

Table 6 shows parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, $C^{(0)}$ and $C^{(1)}$. Table 5 and Figs. 7-9 show c_{\pm} , Archer calculated from Eqs. (12)-(15). Activity coefficients $\gamma_{\pm, \text{Archer}}$ for salts in DMC are much lower than those in DMSO and AC, probably because the low dielectric constant of DMC encourages ion pairing. This result is also shown in the $\text{LiClO}_4 + \text{DMC}$ solution reported by Barthel [19].

4. Conclusion

This work reports osmotic coefficients for lithium salts in non- aqueous solvents. Osmotic and activity coefficients are presented for five salts (LiCl, LiBr, LiNO_3 , LiPF_6 and LITFSI) in three solvents (DMC, DMSO, and AC) at 25 °C. The osmotic coefficients are well correlated using the Archer-Pitzer equation. With that equation, activity coefficients are obtained using the Gibbs-Duhem equation.

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jct.2018.12.016>.

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