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Short Communication

Electrolyte Solutions: Measurement and Correlation of the Solubility of Et_4NBF_4 in Different Solvents at Temperatures from (263.15 to 323.15) K

Peixin Rui[1], *Jian Xu*[2], *Leiqiang Zhao*[2], *Wei Song*[2], *Li Chao*[3], *Deliang Chen*[3], *Zhenyu Yang*[2,3*]

[1] National Engineering Research Centre for Carbohydrate Synthesis, Jiangxi Normal University, Nanchang, 330022, China.
[2] College of Chemistry, Nanchang University, Nanchang, 330031, China.
[3] School of Material Science and Engineering, Dongguan Univeristy of Technology, Dongguan, 523808, China.
[*]E-mail: zyyang@ncu.edu.cn

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The efficient organic liquid electrolyte for supercapacitors requires the stable solubility of electrolyte salt and the high permittivity solvents over a wide temperature range. The solubilities of tetraethylammonium tetrafluoroborate (Et_4NBF_4) in propylene carbonate (PC), γ-butyrolactone (GBL), N, N-dimethylfomamide (DMF), and acetonitrile (ACN) were determined by a synthetic method at temperatures ranging from (263.15 to 323.15) K under atmospheric pressure. The liquid−solid equilibrium process of these mixture was studied by a laser in-situ observing technique. The experimental solubilities were correlated by the van't Hoff equation, the modified Apelblat and the λh equations. It is found the calculated solubility data shows good consistency with the experimental values. The thermodynamic properties of the solution process, including the Gibbs energy, enthalpy, and entropy were calculated by the van't Hoff analysis and the Gibbs equation. These results concerning the solubility of Et_4NBF_4 in different solvents under atmospheric pressure will provide fundamental data in the commercial application of Et_4NBF_4 in supercapacitors.

Keyword: Organic liquid electrolyte, Tetraethylammonium tetrafluoroborate, Solubilities, Different temperatures, Thermodynamic properties, Supercapacitors

1. INTRODUCTION

Electric double-layer capacitors or supercapacitors have attracted extensive attention recently as rechargeable power sources, because they can provide high power density comparable to that for usual rechargeable chemical batteries [1, 2]. Especially, the high energy density of EDLCs is possible with excellent rechargeability. One of the main ways to increase the energy capacitance of supercapacitors is the development of more nonaqueous organic electrolytes with a operating voltage above 3V. The efficient organic liquid electrolyte for these supercapacitors requires the stable solubility of electrolyte salt and the high permittivity solvents over a wide temperature range.[3]

Tetraethylammonium tetrafluoroborate (Et_4NBF_4) have been extensively studied as electrolyte salt in non-aqueous supercapacitors, because it is stable, safe to use and provides favorable electrical conductivity[4-6]. Some important physical chemical properties of Et_4NBF_4 in various high permittivity solvents (γ-butyrolactone[7], propylene carbonate[8], N,Ndimethylformamide[9,10], acetonitrile[11, 12], and so forth) has been investigated. However, a systematic solubility study of Et_4NBF_4 has not been reported in different permittivity solvents under a wide temperature range.

In this work, the solubilities of Et_4NBF_4 in four high permittivity solvents, acetonitrile (ACN), γ-butyrolactone (GBL), propylene carbonate (PC), and N,N-dimethylfomamide (DMF) at T=(263.15, 273.15, 283.15, 293.15, 303.15, 313.15 and 323.15)K under atmospheric pressure. On this basis, the van’t Hoff equation, the λh equation and the modified Apelblat equation are used to correlate the obtained experimental data. Some importamt thermodynamic property parameters were estimated by van’t Hoff analysis including standard molar Gibbs energy, standard molar enthalpy, and standard molar entropy .

2. EXPERIMENTAL

2.1. Materials

Table 1 lists the chemical reagents used in the experiment, including tetraethylammonium tetrafluoroborate (Et_4NBF_4), acetonitrile (ACN), butyrolactone (γ-GBL), propylene carbonate (PC), and N,N-dimethylfomamide (DMF).

Table 1. Sources and purity of the materials

Materials	Mass fraction purity	Sources
Tetraalkylammonium tetrafluoroborates	≥99.0%	ALDRICH
γ-butyrolactone (GBL)	≥99.0%	J&K Chemical
propylene carbonate (PC)	≥99.5%	J&K Chemical
N,N-dimethylfomamide (DMF)	≥99.8%	J&K Chemical
acetonitrile (ACN)	≥99.9%	J&K Chemical

The water used in all experimental work for solution preparation and dilution was double distilled water (conductivity < 0.1 μs·cm^{-1}) unless otherwise specified.

2.2. Apparatus and Procedure.

In this work, the solubility of Et_4NBF_4 in four organic solvents was based on the fact that the light intensity penetrating through the solution increases with the dissolution of Et_4NBF_4 at the temperature ranges from (263.15 to 323.15) K under atmospheric pressure of 101.325 kPa. A synthetic method was used to measure the solubilities of Et_4NBF_4 [13]. The measurements were operated in a jacketed glass vessel (~50 mL) with a magnetic stirrer. At the beginning of each measurement, certain masses of Et_4NBF_4 and organic solvents were weighed by a precision Sartorius autobalance (an uncertainty of ± 0.0001 g) and then transfered to the glass vessel at a known temperature. A laser beam was utilized to monitor the dissolution of the solid + liquid mixture. The intensity of the penetrated light decreased with the increase of the amount of solute in the vessel, and the penetrated light intensity reached its saturation value when the last portion of the solid solute just disappeared. The total consumption of the solute and the mass of the total solvent were recorded.

The mole fraction solubility (x_1) of Et_4NBF_4 could be estimated in different pure organic solvents:

$$x_1 = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2} \qquad (1)$$

Where m_1 and m_2 represent the mass of Et_4NBF_4 respectively, M_1 and M_2 are the corresponding molecular weights, respectively.

All of the experiments were investigated at least three times, and the relative uncertainties of the experimental data were within 3 %, obtained from the mass ratio of the additional solute to the dissolved solute.

3. RESULTS AND DISCUSSION

3.1. Solubility data and correlation models

Before the experiment, the accuracy about the equipment and method was confirmed by comparing our solubility data of potassium chloride in water (26.4wt%, 298.15 K) with those in literature [14]. Our experimental data was in agreement with literature values and thus demonstrated that our experimental method was accurate and reliable.

The solubilities of tetraethylammonium tetrafluoroborate (Et_4NBF_4) in pure propylene carbonate (PC), γ-butyrolactone (GBL), N,N-dimethylfomamide (DMF), and acetonitrile (ACN) at different temperature are listed in table 2. The nonlinear van't Hoff equation, λh equation and modified Apelblat equation have been use to described the relationship between mole fraction solubility and temperature in different solvents.

Table 2. Solubilities of tetraethylammonium tetrafluoroborate in different solvent at (263.15 to 323.15) K at 101.325kPa

T/K	10^2x_1	$10^2x_1^v$	10^2RD^V	$10^2x_1^A$	10^2RD^A	$10^2X_1^{\lambda h}$	$10^2RD^{\lambda h}$
GBL							
263.15	5.984	5.786	3.30	5.945	0.65	5.739	4.10
273.15	6.965	7.046	-1.16	7.084	-1.71	7.013	-0.69
283.15	8.495	8.461	0.41	8.3951	1.18	8.440	0.65
293.15	10.244	10.034	2.04	9.899	3.37	10.019	2.19
303.15	11.369	11.767	-3.50	11.616	-2.17	11.747	-3.32
313.15	13.349	13.659	-2.33	13.570	-1.66	13.617	-2.01
323.15	16.058	15.710	2.17	15.784	1.71	15.623	2.71
PC							
263.15	4.869	5.223	-7.27	4.963	-1.92	5.136	-5.48
273.15	6.437	6.407	0.46	6.301	2.10	6.328	1.69
283.15	8.177	7.747	5.23	7.774	4.93	7.674	6.15
293.15	9.206	9.247	-0.45	9.349	-1.55	9.175	0.34
303.15	10.723	10.909	-1.73	10.991	-2.50	10.828	-0.98
313.15	12.469	12.735	-2.13	12.665	-1.57	12.630	-1.29
323.15	14.787	14.724	0.43	14.334	3.07	14.574	1.44
DMF							
263.15	6.554	6.113	6.73	6.497	0.88	6.1271	6.52
273.15	7.237	7.273	-0.49	7.345	-1.49	7.285	-0.66
283.15	8.401	8.547	-1.75	8.378	0.27	8.556	-1.85
293.15	9.539	9.935	-4.15	9.625	-0.90	9.938	-4.18
303.15	11.355	11.433	-0.69	11.125	2.02	11.428	-0.65
313.15	12.879	13.040	-1.25	12.923	-0.34	13.025	-1.13
323.15	15.004	14.753	1.67	15.072	-0.46	14.722	1.88
ACN							
263.15	6.774	6.461	4.63	6.619	2.29	6.418	5.26
273.15	7.839	7.773	0.85	7.690	1.90	7.742	1.24
283.15	9.072	9.229	-1.74	8.945	1.40	9.210	-1.52
293.15	10.590	10.832	-2.28	10.412	1.68	10.816	-2.14

303.15	12.481	12.579	-0.78	12.122	2.88	12.558	-0.62
313.15	14.48	14.469	0.08	14.111	2.55	14.429	0.35
323.15	16.663	16.499	0.99	16.420	1.46	16.422	1.45

The nonlinear van't Hoff equation [15-16] was proposed to correlate the experimental data as follows :

$$\ln\left(x_1\right)=A+\frac{B}{T} \qquad (2)$$

Where x_1 and T are the mole fraction of the solute and absolute temperature, respectivel, and A and B are the parameters of the equation. The parameter values of A and B are given in table 3.

Table 3. Parameters of the van't hoff equation for tetraethylammonium tetrafluoroborate in the selected organic solvents

Solvent	A	B	10^3rmsd
GBL	2.53	-1415.67	2.58
PC	2.63	-1468.94	2.46
DMF	1.95	-1248.57	2.59
ACN	2.31	-1328.76	1.78

The absolute temperature T dependence of the experimental solubility (x^e) of Et_4NBF_4 in selected solvents can be well-correlated by the modified Apelblat equation derived from the Williamson equation [17, 18].

$$\ln\left(x_1\right)=A+\frac{B}{T}+C\ln T \qquad (3)$$

Where is the mole fraction solubility of Et_4NBF_4, T is temperature in K, and A, B and C are regression curve parameters which are summarized in table 4.

Table 4. Parameters for tetraethylammonium tetrafluoroborate in the different solvents obtained by the modified apelblat equation

Solvent	A	B	C	10^3rmsd
GBL	-33.63	188.07	5.40	2.17
PC	64.69	-4204.71	-9.28	2.74
DMF	-88.30	2734.14	13.49	1.08
ACN	-58.60	1361.26	9.10	2.44

The form of the λh equation has been shown as follows [19-21] eq (4):

$$\ln\left[1+\frac{\lambda\left(1-x_1\right)}{x_1}\right]=\lambda h\left[\frac{1}{T/K}-\frac{1}{T_m/K}\right] \quad (4)$$

Where x_1 is the mole fraction solubility of Et_4NBF_4, T is the experimental temperature of Et_4NBF_4 in K, Tm is the normal melting temperature of Et_4NBF_4 and λ and h are two constants of the λh model. λ is identified as the association number of solute molecules in associating solution, and its value is a reflection of the nonideality of the solution. h equals the ratio of the enthalpy of solution to the gas constant R, so it can be used to estimate the enthalpy of solution .The λ and h are the model parameters which are listed in table 5.

Table 5. Parameters for tetraethylammonium tetrafluoroborate in different solvents obtained by the λh equation

Solvent	λ	h	10^3rmsd
GBL	1.70	870.46	2.72
PC	1.73	888.54	2.45
DMF	1.05	1188.86	2.60
ACN	1.52	909.30	1.98

The values of model parameters for van't Hoff equation, modified Apelblat and λh equations were obtained through regression of the experimental solubility data and are listed respectively in table 3–5 together with root-mean-square deviations (rmsd), described as:

$$rmsd=\left(\frac{1}{N}\sum_{i=1}^{N}\left(x_1^c-x_1^e\right)^2\right)^{1/2} \quad (5)$$

Where N denotes the number of solubility data points measured in each solvent; x_1^c and x_1^e refer to the calculated solubility and experimental solubility, respectively.

The relative deviations (RD) between the calculated solubility and the experimental solubility are given in table 2.

$$RD=\frac{x_1^e-x_1^c}{x_1^e} \quad (6)$$

As we can see from table 2, the calculated data of Et_4NBF_4 in the four pure organic solvents show good agreement with the experimental data from small rmsds. The solubility data could be successfully correlated using the van't Hoff equation, the modified Apelblat equation and the λh equation. Meanwhile, the solubilities data of Et_4NBF_4 in different solvents at the temperature range of (263.15 to323.15) K are shown in Fig. 1.

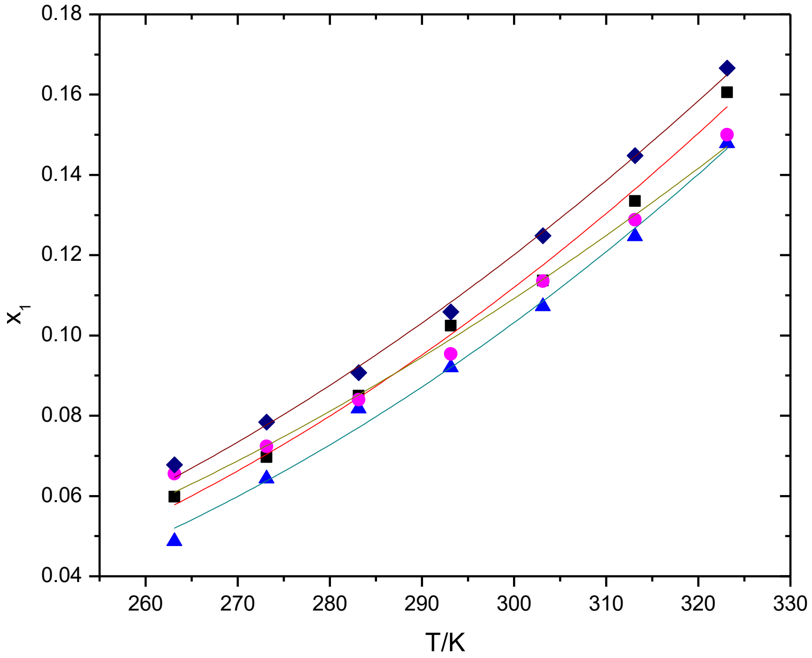

Figure 1. Mole fraction solubility (x_1) of tetraethylammonium tetrafluoroborate versus temperature (t) in the selected pure solvents: ■, GBL; ▲, PC; ●, DMF; ◆, ACN.. Solid lines, calculated from equation 2.

From table 2 and figure 1, we can see that the solubility of Et_4NBF_4 in the four organic solvents are dependent on the temperature, and the solubility data of Et_4NBF_4 are increased with the increase of temperature, but the increment of solubility with temperatures different in different pure solvents.

3.2. Thermodynamic parameter for the solution properties

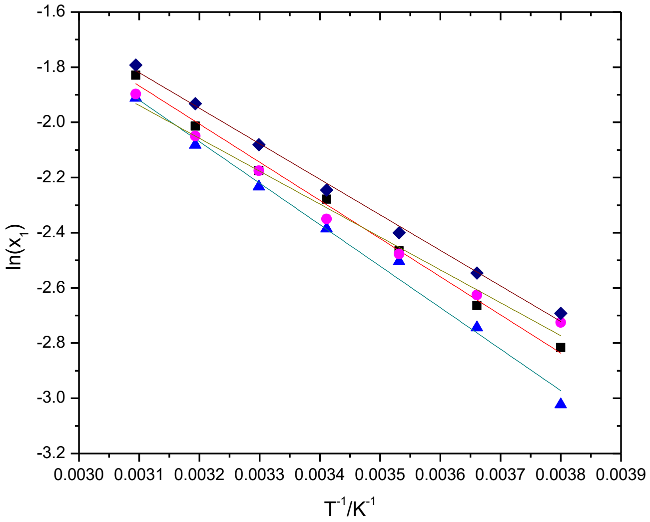

Figure 2. A van't hoff plot of the mole fraction solubility ($\ln(x_1)$) of tetraethylammonium tetrafluoroborate in the selected pure solvents against t^{-1} with a straight line to correlate the data: ■, GBL; ▲, PC; ●, DMF; ◆,ACN.

The dependence of the solubilities to temperature can find by some related equations. According to the van't Hoff equation, the standard molar enthalpy of solution (ΔH^0_{soln})[22-24]of Et_4NBF_4 in the solvents are estimated from eq (7):

$$\frac{\Delta H^0_{soln}}{R} = -\left(\frac{\partial \ln x_1}{\partial(1/T)}\right) \tag{7}$$

Where x_1 is the mole fraction solubility, R is the universal gas constant (8.314 $J{\cdot}mol^{-1}{\cdot}K^{-1}$) and T is the corresponding temperature in K. From eq (2), eq (7) can be simplified to

$$\Delta H^0_{soln} = -BR \tag{8}$$

Over a limited temperature interval, the standard molar enthalpy of solution ΔH^0_{soln} would be valid for the mean temperature [25, 26]. Equation (9) can be written as:

$$\frac{\Delta H^0_{soln}}{R} = -\left(\frac{\partial \ln x_1}{\partial(1/T - 1/T_{mean})}\right) \tag{9}$$

For clarity, ΔH^0_{soln} can also be obtained from the slope of the solubility curve where ln (x_1) is plotted versus (1/T - 1/Tmean). Figure 3 shows the linear.

The standard molar Gibbs energy of solution (ΔG^0_{soln}), the standard molar entropy of solution (ΔS^0_{soln}) can be calculated according to [27, 28]:

$$\Delta G^0_{soln} = -RT_{mean} \times intercept \tag{10}$$

$$\Delta S^0_{soln} = \frac{\Delta H^0_{soln} - \Delta G^0_{soln}}{T_{mean}} \tag{11}$$

The standard thermodynamic parameters for the solution process in the selected solvents are listed in table 6. As shown in table 6, the positive values of ΔH^0_{soln} for all cases suggest that the dissolution process of Et_4NBF_4 in different solvent systems is endothermic. The standard molar Gibbs energy (ΔG^0_{soln}) values for all cases are positive, which demonstrates that the process is nonspontaneous.

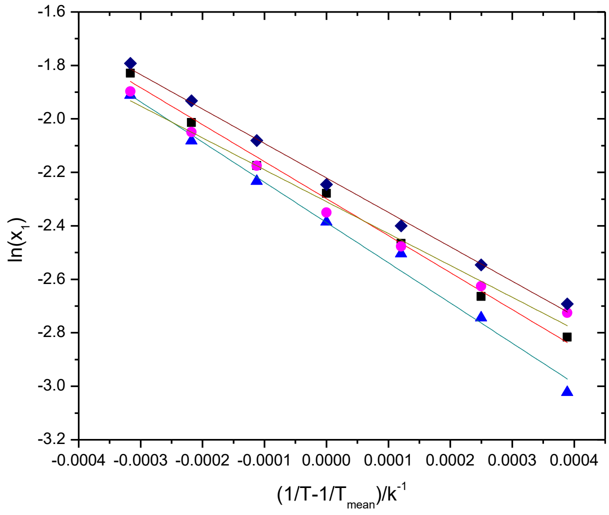

Figure 3. The solubility (ln(x_1)) of tetraethylammonium tetrafluoroborate in different pure solvent systems vs. (1/t-1/t_{mean}) to correlate the data by a straight line: ■, gbl; ▲, pc; ●, dmf; ◆,acn.

Table 6. Thermodynamic properties related to the dissolution process of tetraethylammonium tetrafluoroborate in different solvent systems

Solvent	$\Delta G^{0}_{so\ln} / KJ \cdot mol^{-1}$	$\Delta H^{0}_{so\ln} / KJ \cdot mol^{-1}$	$\Delta S^{0}_{so\ln} / J \cdot mol^{-1} \cdot K^{-}$
GBL	5.61	11.50	20.12
PC	5.83	12.51	22.79
DMF	5.63	9.91	14.60
ACN	5.41	10.71	18.08

The values of $\Delta S^{0}_{so\ln}$ is positive in all the solvents, which shows the dissolution process was entropically favorable.

Therefore, the obtained thermodynamic properties for the dissolution process of Et_4NBF_4 in such four organic solvents including Gibbs energy, enthalpy and the entropy suggests the dissolution of of Et_4NBF_4 are dependent on the temperature, and the solubilities of Et_4NBF_4 are increased with the increase of temperature. The experimental data is in good agreement with the van't Hoff equation and the Gibbs equation. These results will help to deeply understand the dissolution behaviors of Et_4NBF_4 in different solvents and provide fundamental data for the commercial application of Et_4NBF_4.

4. CONCLUSION

The solubilities of tetraethylammonium tetrafluoroborate (Et_4NBF_4) in the four organic solvents were determined at temperatures ranging from (263.15 to 323.15) K under atmospheric pressure by employing the synthetic method. The following conclusions can be drawn: (1) the solubilities of Et_4NBF_4 in the four organic solvents are dependent on the temperature, and the solubility data of Et_4NBF_4 are increased with the increase of temperature, but the increment of solubility with temperature is different in different pure solvents; (2) the experimental data is in good agreement with the van't Hoff equation, the modified Apelblat equation and the λh equation; (3) the thermodynamic properties for the solution process including Gibbs energy, enthalpy and the entropy were obtained by the van't Hoff analysis and the Gibbs equation. These results concerning the solubility of Et_4NBF_4 in different solvents will provide fundamental data for the commercial application of Et_4NBF_4.

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References

1. A.D. Pasquier, I. Plitz, J. Gural, F. Badway,G.G. Amatucci, *J. Power Sources,* 136 (2004) 160–170.
2. P.. Erdogan, H. Zengin, A. Yavuz, *Solid State Ionics*, 352(2020) 115362.
3. L Zhang, S. Yang, J. Chang, *Frontiers in Chemistry,* 8 (2020) 413.
4. G.W. Sun, W.H. Song, X.J. Liu, D.H. Long, W.M. Qiao, L.C Ling, *Electrochimica Acta,* 56 (2011) 9248-9256
5. L. Kiss, J. Iranian Chem. Soc., 17 (2020) 67-71.
6. D. Cericola, R. Kötz, A. Wokaun, *J. Power Sources*, 196 (2017) 3114-3118
7. M.Ue, K.Ida, S.Mori, *J.Electrochem.Soc.,* 141 (1994) 2989-2996.
8. E.G. See, Gmelin Handbook, 8th Edn. Boron compounds, 2nd Supplement, 2 (1982) 53–56.
9. A. Chagnes, B. Carre´, P. Willmann, D. Lemordant, *Electrochim. Acta,* 46 (2001) 1783-1791.
10. E.Y. Tyunina, V.N. Afanasiev, M.D. Chekunova, *J. Chem. Eng. Data*., 56 (2011) 3222-3226.
11. L.P. Safonova, D.V. Sakharov, L.E. Shmukler, A.M. Kolker, *J.Phys.Chem*., 3 (2018) 819-823.
12. R. Sharma, B. Pradhan, D. Subba, *J. Chem. Eng. Data,* 54 (2009) 2902-2905.
13. J. Barthel, L. Iberl, J. Rossmaier, H. J. Gores, B. Kaukal, *J. Solution Chem.,* 19 (1990) 321–327.
14. K. Wang, Y. Hu, W. Yang, J. Chem. Thermodyn., 55 (2012) 50-55.
15. X.W. Hu, Y.L. Wang, C. Xie, G. Wang, H.X. Hao, *J. Chem. Eng. Data*., 58 (2013) 2028-2034.
16. S.P. Pinho, E.A. Macedo, *Fluid Phase Equilib*., 116 (1996) 209-216.
17. M. Xiao, Y.D. Shao, W.D. Yan, Z.Z. Zhang, *J. Chem. Thermodyn*., 43 (2019) 240-243.
18. Y. Zhang, H.Wang, S. Wei, J. Chem. Eng. Data, 60 (2015) 941-946.
19. A. Apelblat, E. Manzurola, *J. Chem. Thermodyn*., 31 (1999) 85-91.
20. A.T. Williamson, *Trans. Faraday Soc*., 40 (1944) 421-436.
21. F. Chen, J. Hu, Z. Chen, Z. Yang, *J. Chem. Eng. Data*., 59 (2014) 1614-1618.
22. H. Buchowski, A. Ksiazczak, S. Pietrzyk, *J. Phys. Chem*., 84 (1980) 975-979.
23. H. Buchowski, A. Khiat, *Fluid Phase Equilib*., 25 (1986) 273-278.
24. S. Liang, H. Li, L. Shen, *Electrochim. Acta,* 630 (2016) 1-10.
25. D.W. Wei, H. Li, Y.N. Li, J. Zhu, *Fluid Phase Equilibr*., 316 (2012) 132-134.
26. A.R. Holguin, D.R. Delgado, F. Martinez, Y. Marcus, *J. Solution, Chem*., 40 (2011) 1987-1999.
27. M.A. Ruidiaz, D.R. Delgado, F. Martinez, Y. Marcus, *Fluid Phase Equilibr*., 299 (2010) 259-265.
28. W. Song, H. Zhang, Z. Yang, Z. Phys. Chem., 232 (2018) 127-151.