

Scientific paper

# Global Thermodynamic Analysis of Conductivity Data

Matjaž Bončina\* and Marija Bešter-Rogač

Faculty of Chemistry and Chemical Technology, University of Ljubljana, SI-100 Ljubljana Slovenia

\* Corresponding author: E-mail: matjaz.boncina@fkk.uni-lj.si

Received: 01-02-2012

Dedicated to Prof. Dr. Gorazd Vesnaver on the occasion of his 70<sup>th</sup> birthday

## Abstract

Conductivity can serve as a tool to study ion properties in different solvents. In the current study, principles of the global modelling of the conductivity data measured at different concentrations and temperatures are demonstrated. Global model was developed on the basis of two modern conductivity theories; the low concentration chemical model and the Quint-Viallard model. It was tested on three different systems; NaCl in water, NaCl in water-1,4 dioxane mixture and MgSO<sub>4</sub> in water. It turned out, that such approach successfully describes all the measured experimental data simultaneously. The applied global analysis of the experimental data allows determination of the thermodynamic profile of ion pairing process and the transport properties of ions at the same time.

**Keywords:** Conductivity, lcCM model, Quint-Viallard, global model

## 1. Introduction

The temperature and concentration dependence of the electrolyte conductivity is one of the most appropriate and precise methods for studying ion-ion, ion-solvent and solvent-solvent interactions in solutions. It has been intensively applied since the beginning of 20<sup>th</sup> century, but a significant progress has been made during the last decades. Evaluating the conductivity within the framework of present electrolyte theories requires namely high accuracy in measurements which is difficult to achieve over a sufficiently large temperature range. This problem has been successfully solved recently with the help of contemporary equipment.<sup>1,2</sup> Thus, determination of precise temperature-dependent electric conductivity data is nowadays more user-friendly what makes this method interesting and appealing again.

In recent years, important theoretical progress has been made by the implementation of chemical models of electrolyte solutions. Through the years, they have been progressively developed for dilute solutions, starting with the Kohlrausch and the Onsager models to more sophisticated Barthel's low concentration chemical model (lcCM)<sup>3</sup> and the Quint-Viallard (QV)<sup>4</sup> model. First two models can provide information only about limiting molar conductivities while the last two take into account also ion pairing.

Apelblat recently re-examined the conductivity data of diverse electrolyte systems by help of the QV conductivity equations.<sup>5–9</sup> It was observed for symmetrical electrolytes that the limiting molar conductivities of electrolytes at infinite dilution,  $\Lambda_T^0$ , are very similar irrespective of the applied conductivity equation, whereas the derived ion association equilibrium constants,  $K_T$ , can vary considerably.

Despite modern computers and programs, data evaluation is still quite a time consuming procedure. First, one has to analyse data at each temperature separately to obtain  $\Lambda_T^0$  and  $K_T$ . Then, from temperature dependence of  $K_T$ , the standard Gibbs free energy,  $\Delta G_T^\circ$ , enthalpy,  $\Delta H_T^\circ$ , and entropy,  $\Delta S_T^\circ$ , of the ion pairing process can be calculated. In order to reduce the steps in the estimation of the thermodynamic functions of ion association we propose a global analysis of the conductivity data. Global models are usually applied to the set of experimental data obtained from different techniques at different temperatures, concentrations etc. They improve the ratio between the number of experimental points and the number of adjustable parameters and to some extent reduce correlations between adjustable parameters. They have been frequently and successfully used in biophysical field as shown by Lah and Vesnaver.<sup>10–12</sup>

In this paper, we demonstrate a global analysis of the literature conductivity data for diluted solutions of

NaCl in water and in water-1,4 dioxane mixture<sup>13</sup> and MgSO<sub>4</sub> in water<sup>14</sup> reported in the temperature range from 278.15 to 308.15 K. The results, ( $\Lambda_T^0$ ,  $K_T$  and thermodynamic functions of ion pairing process) obtained by the global analysis, are compared to those obtained from the individual fits and discussed in the light of possible advantages and disadvantages of both approaches.

## 2. Global Model Analysis of Conductivity Data

The ion pair formation of a symmetrical electrolyte XY can be written as



The equilibrium concentrations are equal to  $c_{X^{z+}} = c_{Y^{z-}} = \alpha c$  and  $c_{X^{z+}Y^{z-}} = (1 - \alpha)c$  where  $c$  is the total electrolyte concentration and  $\alpha$  the degree of ion pair dissociation. Thus, the equilibrium association constant,  $K_T$ , can be expressed as

$$K_T = \frac{c_{X^{z+}Y^{z-}} \gamma_{X^{z+}Y^{z-}}}{c_{X^{z+}} \gamma_{X^{z+}} c_{Y^{z-}} \gamma_{Y^{z-}}} = \frac{(1-\alpha)\gamma_{X^{z+}Y^{z-}}}{\alpha^2 c \gamma_{X^{z+}} \gamma_{Y^{z-}}}. \quad (2)$$

The activity coefficients of the individual species in dilute solutions,  $\gamma_i$ , can be approximated by the Debye-Hückel equation

$$\gamma_i = \exp\left(-\frac{\kappa q}{1 + \kappa R_i}\right); \quad \kappa^2 = 16\pi N_A q I; \quad q = \frac{e_0^2}{8\pi\epsilon\epsilon_0 kT} \quad (3)$$

where  $\kappa$  is the Debye parameter,  $I$  the ionic strength,  $R_i$  the ion size parameter,<sup>15</sup>  $e_0$  the proton charge,  $\epsilon$  the relative permittivity of the solvent,  $\epsilon_0$  the permittivity of vacuum and  $T$  the absolute temperature. The other symbols have their usual meaning. It should be noted, that ion pairs are neutral species and therefore  $\gamma_{X^{z+}Y^{z-}}$  is assumed to be unity.

According to the lcCM model, the dependence of molar conductivity  $\Lambda_T$  on concentration at a given temperature  $T$  is defined as<sup>3</sup>

$$\frac{\Lambda_T}{\alpha} = \Lambda_T^0 - S(\alpha c)^{1/2} + E\alpha c \ln(\alpha c) + J_1 \alpha c - J_2 (\alpha c)^{3/2}. \quad (4)$$

Similar expression is used in the Quint-Viallard (QV) model where  $\Lambda_T$  is expressed as the sum of ionic molar conductivities  $\lambda_{i,T}$ <sup>4</sup>

$$\Lambda_T = \sum_i \frac{|z_i| c_i \lambda_{i,T}}{c} \quad (5)$$

$$\lambda_{i,T} = \lambda_{i,T}^0 - S_i I^{1/2} + E_i I \ln I + J_{1i} I - J_{2i} I^{3/2}$$

where  $\lambda_{i,T}^0$  is the limiting molar conductivity of the ion at a given temperature. In the case of 1:1 and 2:2 electrolytes,

the ionic strength is equal to  $I = \alpha c$  and  $I = 4\alpha c$ , respectively. The coefficients  $S$ ,  $E$ ,  $J_1$ ,  $J_2$  and  $S_i$ ,  $E_i$ ,  $J_{1i}$ ,  $J_{2i}$  are rather complex functions of temperature, viscosity,<sup>16</sup> the dielectric constant of pure water,<sup>17</sup> distance parameter  $R$  (or  $a_i$  in the QV model) and valences  $z$ . The explicit expressions for these coefficients are given in detail in the literature.<sup>3,4,18</sup> The distance parameter  $R$  ( $a_i$ ) defines the distance to which ions are regarded as ion-pairs (the upper limit of ion association),  $R = a_i = a + n \cdot s$ . The lower limit of the association is the distance of closest approach of cation and anion (contact distance),  $a = a_+ + a_-$ , where  $a_+$  and  $a_-$  represent the radii of cation and anion,<sup>19</sup>  $s$  is the length of an oriented solvent molecule and  $n$  is an integer. If we assume contact ion pairs  $n = 0$ , for solvent-shared  $n = 1$  and for solvent-separated ion pairs  $n = 2$ . In water,  $s$  is the length of an OH-group,  $s = 0.28$  nm.

In the global analysis an expression for temperature dependence of limiting molar conductivity  $\Lambda_T^0$ ,  $\lambda_{i,T}^0$  is needed. In principle, Walden's rule<sup>3</sup> or Eyring approach<sup>20</sup> could be used for this purpose but unfortunately both approaches fail to successfully describe temperature dependence of limiting molar conductivity (see supporting information for details). Therefore,  $\Lambda_T^0$  or  $\lambda_{i,T}^0$  are approximated by a simple expression<sup>21</sup>

$$\Lambda_T^0 = \Lambda_{T_0}^0 + A(T - T_0) + B(T - T_0)^2$$

$$\lambda_{i,T}^0 = \lambda_{i,T_0}^0 + A_i(T - T_0) + B_i(T - T_0)^2 \quad (6)$$

where  $\Lambda_{T_0}^0$  is the limiting molar conductivity at the reference temperature  $T_0 = 298.15$  K and  $A$  and  $B$  are the temperature independent coefficients. In the QV model the temperature dependence of limiting molar conductivity of cation and anion,  $\lambda_{i,T_0}^0$  and coefficients  $A_i$  and  $B_i$  ( $i = X^{z+}$ ,  $Y^{z-}$ ) must be defined.

The ion association process can be described in terms of changes of standard thermodynamic parameters: the Gibbs free energy,  $\Delta G_{T_0}^\circ$ , and enthalpy,  $\Delta H_{T_0}^\circ$ , at the reference temperature  $T_0 = 298.15$  K and the corresponding heat capacity  $\Delta C_p^\circ$  (assumed to be temperature independent). These parameters define  $\Delta G_T^\circ$  and  $\Delta H_T^\circ$  at any  $T$  through the Gibbs-Helmholtz relation and Kirchhoff's law:

$$\Delta G_T^\circ = \Delta G_{T_0}^\circ \frac{T}{T_0} + \Delta H_{T_0}^\circ \left(1 - \frac{T}{T_0}\right) + \Delta C_p^\circ \left(T - T_0 - T \ln\left(\frac{T}{T_0}\right)\right) \quad (7)$$

$$\Delta H_T^\circ = \Delta H_{T_0}^\circ + \Delta C_p^\circ (T - T_0)$$

Thus, a single set of (adjustable) parameters  $\Delta G_{T_0}^\circ$ ,  $\Delta H_{T_0}^\circ$  and  $\Delta C_p^\circ$  defines  $K_T = \exp(-\Delta G_T^\circ / RT)$  and  $\alpha$  (eq. 2) at any  $T$ . Global fitting of the model function (eq. 4 for the lcCM model and eq. 5 for the QV model) to the experimental conductivity data, measured at various  $T$ , was based on the non-linear regression procedure by minimizing  $\sum_i \sum_j (\Lambda_{\exp(i,T)} - \Lambda_{\text{calc}(i,T)})^2$  where  $\Lambda_{\exp(i,T)}$  is the  $i$ -th experimental molar conductivity at temperature  $T$  and  $\Lambda_{\text{calc}(i,T)}$  is

the  $i$ -th calculated value from the model at temperature  $T$ . Since it is known that  $\Delta C_T^\circ$  is close to zero in such processes,<sup>22–23</sup> five adjustable parameters were used in the lcCM minimization process:  $\Delta G_{T_0}^\circ$ ,  $\Delta H_{T_0}^\circ$ ,  $\Lambda_{T_0}^0$ ,  $A$  and  $B$  and eight in the QV:  $\Delta G_{T_0}^\circ$ ,  $\Delta H_{T_0}^\circ$ ,  $\lambda_{1,T_0}^0$ ,  $A_i$  and  $B_i$  ( $i = X^{z+}, Y^{z-}$ ).

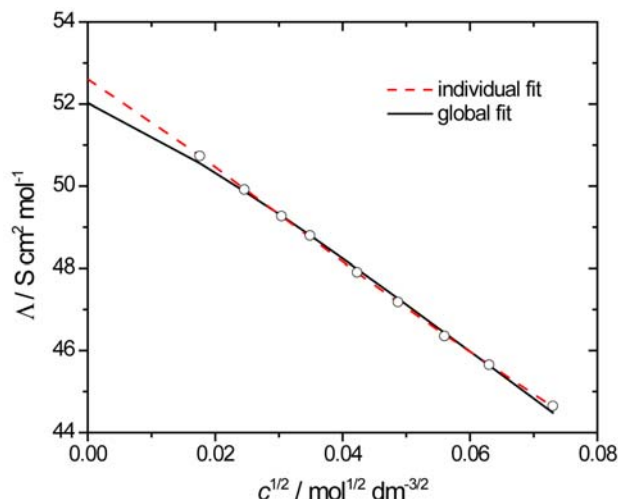
### 3. Results and Discussion

Global model analysis based on the lcCM or the QV set of equations was tested on three sets of conductivity data: NaCl in water, NaCl in water-1,4 dioxane mixture with 20 mass percent of 1,4 dioxane ( $x_D = 0.20$ )<sup>13</sup> and  $MgSO_4$  in water.<sup>14</sup> The conductivity data for all the investigated systems are reported in the temperature range from 278.15 to 308.15 K in steps of 5 K. The results obtained from individual and global analysis for NaCl in water and water-1,4 dioxane mixture based on the lcCM are presented in Table 1 and Figure 1. The distance parameter  $R$  was set to  $R = a + 2s = 0.839$  nm ( $a = 0.279$  nm). Other parameters needed to calculate the model function are presented in Ref. 13. Table 1 reveals that individual and global fit give almost identical limiting molar conductivity of NaCl,  $\Lambda_{T_0}^0$ , quite similar constant of association,  $K_{T_0}$ , but in some examples (NaCl in water) very different values for  $\Delta H_{T_0}^\circ$  and  $T\Delta S_{T_0}^\circ$  accompanying the ion pairing process.

**Table 1.** The thermodynamic and transport properties of NaCl in water and water-1,4dioxane mixture ( $x_D = 0.20$ ) at  $T_0 = 298.15$  K obtained from individual<sup>13</sup> and global analysis of conductivity data. The results correspond to lcCM model.

	water		water-1,4 dioxane mixture	
	individual fit <sup>13</sup>	global fit	individual fit <sup>13</sup>	global fit
$K_{T_0}$	$2.38 \pm 0.44$	$2.63 \pm 0.08$	$23.7 \pm 1.0$	$18.9 \pm 0.2$
$\Delta G_{T_0}^\circ / \text{kJ mol}^{-1}$	-2.92	$-2.40 \pm 0.07$	-8.55	$-7.29 \pm 0.03$
$\Delta H_{T_0}^\circ / \text{kJ mol}^{-1}$	8.88	$1.5 \pm 2.2$	7.72	$8.1 \pm 1.1$
$T\Delta S_{T_0}^\circ / \text{kJ mol}^{-1}$	11.80	$3.9 \pm 2.3$	16.27	$15.4 \pm 1.1$
$\Lambda_{T_0}^0 / \text{S cm}^2 \text{ mol}^{-1}$	$126.54 \pm 0.02$	$126.50 \pm 0.01$	$52.61 \pm 0.03$	$52.06 \pm 0.03$
$A / \text{S cm}^2 \text{ mol}^{-1} \text{ K}^{-1}$	/	$2.635 \pm 0.001$	/	$1.270 \pm 0.003$
$B / \text{S cm}^2 \text{ mol}^{-1} \text{ K}^{-2}$	/	$(9.81 \pm 0.07) 10^{-3}$	/	$0.0077 \pm 0.0001$

In Table 2 we present the results obtained from individual and global analysis (the lcCM and the QV model) for  $MgSO_4$  in water. The results correspond to the distance parameter equal to  $R = a + 2s = 0.896$  nm ( $a = 0.336$  nm). In the QV model the limiting molar conductivity of cation and anion may be treated as adjustable parameters. However, these two parameters are highly correlated therefore the exact physical meaning may be questionable when both of them are used as adjustable parameters. For this reason, the limiting molar conductivity of cation at 298.15 K ( $1/2 \cdot \lambda_{Mg^{2+},T_0}^0 = 52.7 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$ )<sup>5</sup> was set as fixed parameter and only  $A_{Mg^{2+}}$  and  $B_{Mg^{2+}}$  coefficients describing its temperature dependence were fitted. The proposed global model gives excellent



**Figure 1.** Molar conductivities of NaCl in water-1,4dioxane mixture at 298.15 K. Experimental data are presented by symbols while the lines refer to the individual and global analysis based on the lcCM.

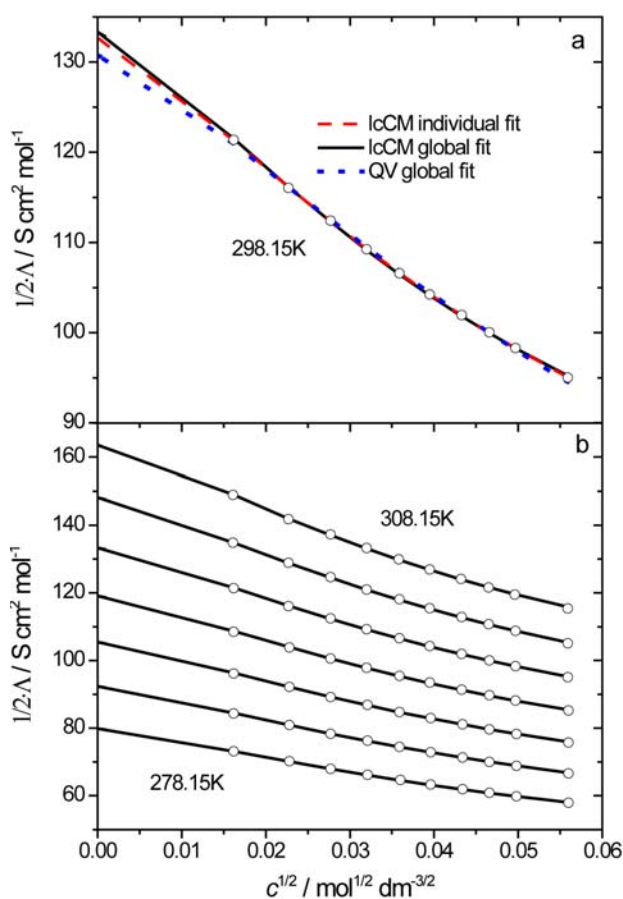
agreement with the experimental molar conductivities which is evident from Figure 2. Comparison of the results obtained from individual and global fit give the same conclusions as for NaCl systems, i.e. almost identical limiting molar conductivity,  $\Lambda_{T_0}^0$ , and slight differen-

ces in  $\Delta G_{T_0}^\circ$ ,  $\Delta H_{T_0}^\circ$ ,  $T\Delta S_{T_0}^\circ$  accompanying the ion pair formation. However, there is one major difference between individual and global analysis: the former gives  $\Delta C_p^\circ = 0.37 \text{ kJ mol}^{-1} \text{ K}^{-1}$  while the latter  $\Delta C_p^\circ = 0.00 \text{ kJ mol}^{-1} \text{ K}^{-1}$ . It should be noted that according to the literature data  $\Delta C_p^\circ$  effects accompanying the ion pair formation are close to zero.<sup>22</sup> Moreover, global analysis allows us to reduce high correlation between adjustable parameters, close to 1 or -1. For instance, correlation between  $K_{T_0}$  and  $\Lambda_{T_0}^0$  in case of individual fit of  $MgSO_4$  in water is -0.93 which can be reduced to -0.88 with global analysis. Correlation matrix corresponding to the lcCM global model analysis of the  $MgSO_4$  conductivity data is presented in Table 3.

**Table 2.** The thermodynamic and transport properties of MgSO<sub>4</sub> in water at T<sub>0</sub> = 298.15 K obtained from individual<sup>14</sup> and global analysis of conductivity data.

	individual fit <sup>14</sup>	global fit lcCM	global fit QV
K <sub>T<sub>0</sub></sub>	157.2 ± 2.1	176.3 ± 0.8	138.8 ± 1.6
ΔG <sub>T<sub>0</sub></sub> <sup>o</sup> / kJ mol <sup>-1</sup>	-12.55	-12.83 ± 0.01	-12.23 ± 0.03
ΔH <sub>T<sub>0</sub></sub> <sup>o</sup> / kJ mol <sup>-1</sup>	6.65	4.1 ± 0.3	3.9 ± 0.7
T ΔS <sub>T<sub>0</sub></sub> <sup>o</sup> / kJ mol <sup>-1</sup>	19.2	16.9 ± 0.3	16.2 ± 0.7
ΔC <sub>p</sub> <sup>o</sup> / kJ mol <sup>-1</sup> K <sup>-1</sup>	0.37	0.00	0.00
1/2 Λ <sub>T<sub>0</sub></sub> <sup>o</sup> / S cm <sup>2</sup> mol <sup>-1</sup>	132.70 ± 0.08	133.31 ± 0.06	130.7 ± 0.2
A / S cm <sup>2</sup> mol <sup>-1</sup> K <sup>-1</sup>	/	2.906 ± 0.005	/
B / S cm <sup>2</sup> mol <sup>-1</sup> K <sup>-2</sup>	/	0.0116 ± 0.0002	/

Comparison of the results obtained from individual and global analysis reveals differences in thermodynamic quantities, mostly in ΔH<sub>T<sub>0</sub></sub><sup>o</sup>, TΔS<sub>T<sub>0</sub></sub><sup>o</sup> and ΔC<sub>p</sub><sup>o</sup> accompanying the ion pairing process. It should be noted that these contributions were obtained from the temperature dependence of ΔG<sub>T</sub><sup>o</sup><sup>13,14,24,25</sup> in the case of individual analysis and such procedure may lead to large errors.

**Figure 2.** Molar conductivities of aqueous MgSO<sub>4</sub> solutions from 278.15 to 308.15 K (steps of 5 K) in the concentration range  $2 \cdot 10^{-4} < c/\text{mol dm}^{-3} < 3 \cdot 10^{-3}$ . Experimental data are presented by symbols while the lines refer to the corresponding best global fit of the model function (the lcCM model eq. 4 and the QV model eq. 5). a) Comparison of individual and global analysis at 298.15 K. b) Results of the lcCM global fit.**Table 3.** Correlation matrix corresponding to the lcCM global model analysis of the MgSO<sub>4</sub> conductivity data.

	K <sub>T<sub>0</sub></sub>	ΔH <sub>T</sub> <sup>o</sup>	Λ <sub>T</sub> <sup>o</sup>	A	B
K <sub>T<sub>0</sub></sub>	1.00				
ΔH <sub>T<sub>0</sub></sub> <sup>o</sup>	-0.05	1.00			
Λ <sub>T<sub>0</sub></sub> <sup>o</sup>	-0.88	0.04	1.00		
A	-0.19	-0.83	0.12	1.00	
B	-0.01	-0.37	-0.25	0.68	1.00

## 4. Conclusions

Global model analysis based on the low concentration chemical model (lcCM) and also the Quint-Viallard set of equations was successfully applied to the conductivity data for the first time. Model was tested on three different systems and results were compared to those obtained from the individual fits. It turned out, that this approach successfully describes all the measured experimental data simultaneously. Therefore, the applied global analysis of experimental data allows determination of the thermodynamic profile of ion pairing process (Gibbs free energy, enthalpy, entropy, heat capacity) and transport properties of ions at the same time. Moreover, the global model improves the ratio between the number of fitting parameters and the number of experimental points, reduces correlation between adjustable parameters and therefore gives more reliable results. The weakest point of the global model is that the temperature dependence of limiting molar conductivity is not based on thermodynamic relationship like association constant which is based on the Gibbs-Helmholtz relation and Kirchhoff's law but it is simple described with a second order polynomial.

As it has been already observed by Apelblat,<sup>5</sup> the limiting conductivities of electrolytes at infinite dilution are very similar irrespective to the applied conductivity equation, whereas the derived ion association constants can vary considerably. The ion association constants and thus also all the derived thermodynamic functions are therefore of doubtful physical value and should be rather treated just as fitting parameters.

## 5. Acknowledgments

M. B. and M. B. R. would like to acknowledge Prof. Dr. Gorazd Vesnaver for his appreciated collaboration and helpful scientific advices. The authors also acknowledge the financial support of the Slovenian Research Agency (ARRS) through Program P1-0201.

## 6. References

1. J. Barthel, R. Wachter, H.-J. Gores, in: B. E. Conway, J. O'M. Bockris (Ed.): *Modern Aspects of Electrochemistry* No. 13, Plenum Press, New York, **1979**, pp. 1–79.
2. M. Bešter-Rogač, D. Habe, *Acta Chim. Slov.* **2006**, *53*, 391–395.
3. J. Barthel, H. Krienke, and W. Kunz, *Physical Chemistry of Electrolyte Solutions-Modern Aspects*, Steinkopff/Darmstadt, and Springer, New York, **1998**.
4. J. Quint, A. Viillard, *J. Solution Chem.* **1987**, *7*, 533–548.
5. A. Apelblat, *J. Solution Chem.* **2011**, *40*, 1209–1233.
6. A. Apelblat, *J. Solution Chem.* **2011**, *40*, 1724–1734.
7. A. Apelblat, *J. Solution Chem.* **2011**, *40*, 1291–1316.
8. A. Apelblat, *J. Solution Chem.* **2011**, *40*, 1234–1257.
9. A. Apelblat, *J. Solution Chem.* **2011**, *40*, 1544–1562.
10. J. Lah, I. Drobnak, M. Dolinar, G. Vesnaver, *Nucleic Acids Res.* **2008**, *30*, 897–904.
11. I. Drobnak, G. Vesnaver, J. Lah, *J. Phys. Chem. B* **2010**, *114*, 8713–8722.
12. J. Lah, M. Bešter-Rogač, T. M. Perger, G. Vesnaver, *J. Phys. Chem. B* **2006**, *110*, 23279–23291.
13. M. Bešter-Rogač, R. Neueder, J. Barthel, *J. Solution Chem.* **1999**, *28*, 1071–1085.
14. M. Tomšič, M. Bešter-Rogač, A. Jamnik, R. Neueder, J. Barthel, *J. Solution Chem.* **2002**, *31*, 19–31.
15. J. Kielland, *J. Am. Chem. Soc.* **1937**, *59*, 1675–1678.
16. L. Korson, W. Drost-Hansen, F. J. Millero, *J. Phys. Chem.* **1969**, *73*, 34–39.
17. B. B. Owen, R. C. Miller, C. E. Miller, H. L. Cogan, *J. Phys. Chem.* **1961**, *65*, 2065–2070.
18. A. Apelblat, R. Neueder, J. Barthel, *Electrolyte Data Collection, Electrolyte Conductivities, Ionic Conductivities and Dissociation Constants of Aqueous Solutions of Organic Monobasic Acids*. Chemistry Data Series, vol. XII, Part 4a. Dechema, Frankfurt am Main, **2004**.
19. V. M. Goldschmidt, *Chem. Ber.* **1927**, *60*, 1263–1296.
20. S. B. Brummer, G. J. Hills, *J. Chem. Soc. Faraday Trans.* **1961**, *5*, 1816–1837.
21. H. S. Harned, B. B. Owen, *The Physical Chemistry of Electrolytic Solutions*, 3rd edn. Reinhold, New York, **1958**.
22. M. Bončina, J. Lah, J. Reščič, and V. Vlachy, *J. Phys. Chem. B* **2010**, *114*, 4313–4319.
23. K. A. Sharp, B. Madan, *J. Phys. Chem. B* **1997**, *101*, 4343–4348.
24. M. Bončina, A. Apelblat, M. Bešter-Rogač, *J. Chem. Eng. Data* **2010**, *55*, 1951–1957.
25. M. Bončina, A. Apelblat, J. Barthel, M. Bešter-Rogač, *J. Solution Chem.* **2008**, *37*, 1561–1574.

## Povzetek

Z merjenjem električne prevodnosti raztopin elektrolitov spomočjo različnih modelov proučujemo lastnosti ionov v različnih topilih. V tem delu smo prikazali možnost uporabe globalne analize podatkov za električno prevodnost razredčenih raztopin elektrolitov v širokem temperaturnem območju. Globalni model smo razvili na podlagi dveh modernih teorij s področja prevodnosti, t.i. kemijskega modela (lcCM) in Quint-Viillardovega modela. Ustreznost globalnega modela smo preverili na treh različnih sistemih: NaCl v vodi, NaCl v mešanici vode in 1,4 dioksana ter MgSO<sub>4</sub> v vodi. Izkazalo se je, da globalni model uspešno popiše eksperimentalne podatke izmerjene pri različnih koncentracijah in temperaturah in določi termodinamski profil procesa tvorbe ionskih parov skupaj s transportnimi lastnostmi ionov.

## Supporting information

As already mentioned in the main text, temperature dependence of limiting molar conductivity may be described with Walden's rule

$$\Lambda_T^0 \eta = \text{const} \quad (1\text{-SI})$$

or Eyring approach

$$\ln(\Lambda_T^0 d^{2/3}) = -\frac{\Delta H^\ddagger}{RT} + \text{const} \quad (2\text{-SI})$$

where  $\eta$  is the viscosity of pure water,<sup>1</sup>  $d$  the density of pure water,<sup>2</sup>  $\Delta H^\ddagger$  temperature independent Eyring's enthalpy of activation of the charge transport which depends only on the solvent properties and  $\text{const}$  temperature independent constant which has no physical meaning. Equations apply to limiting molar conductivity of the salt used in lcCM model, however, same expressions can be used also for modeling temperature dependence of limiting molar conductivity of cation and anion needed in QV model. If Walden's rule was used to model temperature dependence of  $\Lambda_T^0$ , three adjustable parameters were used in the global lcCM minimization process:  $\Delta G_{T_0}^\circ$ ,  $\Delta H_{T_0}^\circ$  and  $\text{const}$  while in the case of Eyring approach four adjustable parameters were used:  $\Delta G_{T_0}^\circ$ ,  $\Delta H_{T_0}^\circ$ ,  $\Delta H^\ddagger$  and  $\text{const}$ .

Models describing temperature dependence of limiting molar conductivity do not affect the thermodynamics of ion pairing process. However, they have big impact on limiting molar conductivities (Table 1-SI) and quality of the fit, especially at low (278.15 K) and high (308.15 K) temperatures (Table 2-SI). Table 1-SI reveals that Walden's rule is the least suitable for this purpose. Same conclusion may be drawn from all three investigated systems.

**Table 1-SI.** Limiting molar conductivities of NaCl in water obtained from individual and global analysis of conductivity data. In the case of global analysis, temperature dependence of  $\Lambda_T^0$  was described with polynomial expression, Walden's rule and Eyring approach. The results correspond to lcCM model.

$T / \text{K}$	individual	global		
		polynomial expression eq. 6	Walden's rule eq. 1-SI	Eyring approach eq. 2-SI
		$\Lambda_T^0 / \text{S cm}^2 \text{mol}^{-1}$		
278.15	77.71	77.74	74.98	79.23
283.15	89.12	89.19	87.16	89.43
288.15	101.09	101.14	100.08	100.53
293.15	113.57	113.58	113.68	112.59
298.15	126.54	126.50	127.95	125.65
303.15	139.95	139.92	142.84	139.74
308.15	153.78	153.83	158.32	154.90

Best fit parameters obtained from global analysis:

Walden's rule:  $\text{const} = 1.139 \cdot 10^{-2} \text{ S kg m mol}^{-1} \text{ s}^{-1}$

Eyring approach:  $\Delta H^\ddagger = 15.8 \text{ kJ mol}^{-1}$ ;  $\text{const} = 11.218$

**Table 2-SI.** Experimental and calculated molar conductivities obtained from global analysis of NaCl in water at 278.15 K. Temperature dependence of  $\Lambda_T^0$  was described with polynomial expression, Walden's rule and Eyring approach. The results correspond to lcCM model.

$10^3 m / \text{mol kg}^{-1}$	$\Lambda_{\text{exp}}$	polynomial expression eq. 6	Walden's rule eq. 1-SI	Eyring approach eq. 2-SI
		$\Lambda_{\text{calc}} / \text{S cm}^2 \text{mol}^{-1}$		
0.1778	77.00	77.03	74.32	78.52
0.3359	76.81	76.77	74.08	78.26
0.5695	76.53	76.48	73.83	77.96
0.8645	76.27	76.19	73.58	77.67
1.2066	75.94	75.91	73.35	77.39
1.5044	75.74	75.70	73.18	77.18
1.9519	75.47	75.42	72.96	76.90
2.5393	75.15	75.10	72.72	76.57

## References

1. L. Korson, W. Drost-Hansen, F.J. Millero, *J. Phys. Chem.* **1969**, 73, 34-39.
2. E. F. G. Herington, *Pure Appl. Chem.* **1976**, 45, 1-9.