

Degrees of Dissociation and Hydration Numbers of Alkali Halides in Aqueous Solutions at 25 °C (Some up to Saturation)*

Rajalakshmi Heyrovská

*Academy of Sciences of the Czech Republic, J. Heyrovský Institute of Physical
Chemistry, Dolejškova 3, Praha 8, Czech Republic.*

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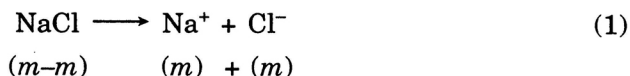
Systematic researches in recent years have revived the earlier ideas of ionic association/dissociation and hydration as causes of non-ideality in solutions of strong electrolytes. Fundamental properties like vapour pressures, e.m.f. of concentration cells, equivalent conductivities, diffusion coefficients and molal volumes/densities of solutions were shown to be simple functions of the ionic molalities (not ionic activities) and hydration numbers, over large ranges of concentrations. Recently, the work was extended to cover the whole range of concentrations from zero to saturation for a strong electrolyte like NaCl(aq). This paper deals with the interpretations of osmotic and activity coefficients in terms of degrees of dissociation (α) and hydration numbers for all the alkali halides. Tables of α and relevant graphs are provided.

INTRODUCTION

Sixty five years ago, the near-success of the Debye-Hückel (DH) inter-ionic interaction theory in explaining the properties of dilute solutions, led theorists to assuming complete dissociation of strong electrolytes at all concentrations. However, as properties of concentrated solutions deviated from those expected on the basis of the DH limiting equations, the latter were extended by the additions of more terms and parameters to fit the data for

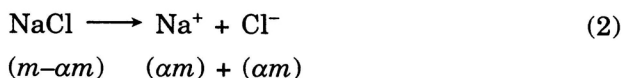
* Dedicated to Marko Branica on the occasion of his 65th birthday.

higher concentrations, see *e.g.* Ref. 1. A recent review² of the equations for the osmotic (ϕ) and mean ionic activity (γ_{\pm}) coefficients (non-ideality parameters) and molar volumes of NaCl(aq), based on the assumption of complete dissociation,



where m is the molality, illustrates the complexity of the extended DH equations tailored to fit the experimental data for large ranges of concentrations. Such equations do not give a unified interpretation of the properties over the entire concentration range, and only serve as »mathematical representations« of experimental data rather than as »explanations of their physical significance«. For other recent criticisms, see Refs. 3–6.

On the other hand, the earlier ideas^{7,8} of partial dissociation,



where $\alpha \leq 1$ is the degree of dissociation, $m[(1-\alpha) + 2\alpha] = im$ is the total number of moles of solute and i is the van't Hoff factor, have now been successfully revived over the last decade.^{3,9,10} Degrees of dissociation (α) and hydration numbers, evaluated from the available ϕ data, were shown to explain the concentration dependence of many other properties of mono and multivalent strong electrolytes over large ranges of concentrations. The DH limiting laws for very dilute solutions were shown³ to be asymptotic laws for complete dissociation at infinite dilution. Recently, X-ray diffraction studies¹¹ and molecular dynamic simulations¹² of saturated alkali halide solutions have pointed to the presence of about 20–30% ion pairs. This fact has been a great support for all the past and present advocates of the idea of partial dissociation.

The author's earlier work^{3,9,10} on the solution properties of NaCl(aq) for the concentration range from 0 to about 4 m , were recently extended^{13,14} to cover the whole range of concentrations up to saturation. The concentration dependences of osmotic and activity coefficients and solution densities/molal volumes of NaCl(aq) from zero to saturation were explained quantitatively (for the first time) in terms of α and hydration numbers. (The molal volumes could be accounted for quantitatively using the molar volume of the crystal for the undissociated form.¹⁴ This indicates that NaCl forms contact ion-pairs in solution.) This paper deals with the partial dissociation and hydration of all the alkali halides¹⁵ in aqueous solutions, on the same lines as for NaCl(aq).^{13,14} As the method and details can be found in Ref. 14, only the main points are outlined below.

Degrees of Dissociation (α) from Osmotic Coefficients (ϕ)

As shown¹⁴ for NaCl(aq), the following equation holds for the osmotic pressure, π_{os} of a solution of molality m ,

$$\pi_{os} = iRT/V_{Afb} = iRTmd_{Afb} / (1 - mn_b/55.51) = vm\phi RTd_{Afb} \quad (3)$$

where V_{Afb} is the volume of 'free' (f) solvent (A) in the bulk (subscript b) per mole of solute, d_{Afb} is the corresponding density, and v ($= 2$ for alkali halides) is the number of moles of ions into which one mole of the electrolyte dissociates and n_b is the hydration number in the bulk. From Eq. (3), one gets for the concentration dependence of ϕ the simple equation,

$$v\phi = 55.51(i/n_{Afb}) \quad (4)$$

where $n_{Afb} = 55.51 - mn_b$ is the molality of 'free' water in the bulk. Eq. (4) shows that $\phi \neq 1$ because of partial dissociation and hydration of the electrolyte. (Note that $\phi = 1$ for complete dissociation at infinite dilution.)

ϕ and the solvent activity, a_A (which is the vapor pressure ratio, p_A/p_A°) are related by definition,¹

$$v\phi = -(55.51/m) \ln(a_A). \quad (5)$$

In Refs. 3, 8–10, 13–15, a_A was interpreted as the mole fraction N_{Afs} of 'free' water,

$$a_A = N_{Afs} = n_{Afs} / (n_{Afs} + im) \quad (6)$$

where $n_{Afs} = 55.51 - mn_s$ and n_s is the hydration number at the surface (vapor/solution interface).^{13–15}

Eq. (6) is a modified form of Raoult's law, which takes into account the incomplete dissociation and hydration of the electrolyte. It was found^{3,9,10} that Eq. (6) is valid for over 100 strong electrolytes over large ranges of concentrations.

Note that Eq. (4) involving a bulk property and Eq. (6), a surface property involve the same values of i , but differing hydration numbers. On realizing^{13,14} that this difference could be due to the difference in the solute-solvent dispositions and interactions in the two regions, Eqs. (4) and (6) were combined and i was eliminated to obtain the ratio,^{13–15}

$$R_{Af} = -a_A \ln a_A / (1 - a_A) = n_{Afs}/n_{Afb}. \quad (7)$$

The value of R_{Af} , which can be calculated by using the available a_A (or ϕ , cf. Eq. (5)) data, represents the ratio of the molality of 'free' water in the surface to that in the bulk. For alkali halides at 25 °C, R_{Af} was calculated

using the ϕ data in Refs. 1 and 16. By a computer linear best-fit plot of $n_{\text{Afs}}/R_{\text{Af}}$ vs. m the values of n_s giving the best correlation coefficient for an intercept of 55.51, and n_b as the slope, were obtained. See *e.g.*, the linearity in Figure 1 for NaCl(aq) from zero to saturation.¹⁴ The concentration ranges over which this linearity holds can be seen from the values of m (the first column) in Tables I–III. The values of n_s and n_b are also given in the same Tables. The values and trend of hydration numbers are close (± 1) to those given in Refs. 1, 17 (best-fitting values for their equation for activity coefficient based on the idea of complete dissociation), as pointed out earlier.⁹ For salts with higher hydration numbers like the lithium halides, the concentration range of linearity is less than for other halides with lower hydration numbers. A possible reason for this is that the hydration number of the Li halides probably decreases at higher concentrations. For NaF and CsI (and also for HF,¹⁸ and several nitrates^{18–20}) the hydration numbers are negative and n_s is less negative than n_b . It is speculated that ion-pair formation¹⁹ (which was neglected by¹⁹) and depolymerization of water²⁰ could be the causes for the negative hydration numbers. On the other hand, as in these cases both n_{Afs} and n_{Afb} are > 55.51 , water is probably appreciably ionized¹⁴. (Conversely, in the other cases, where n_{Afs} and n_{Afb} are both < 55.51 , water can be considered to be associated.)

The above values of n_b and n_s and the ϕ data from¹⁶ were used in Eqs. (4) and (6) respectively, to calculate α from these equations. Nearly identical (± 0.001) values of α for a given value of m were obtained from the two equations, for the entire concentration ranges given in Tables I–III. Conversely,

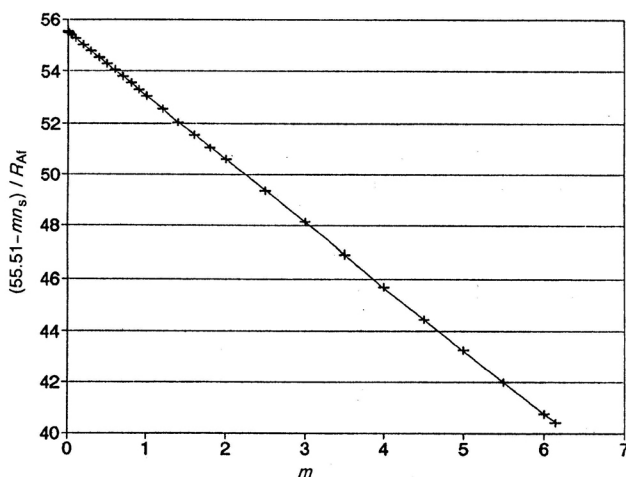


Figure 1. The linear dependence of the ratio $n_{\text{Afs}}/R_{\text{Af}}$ on m for NaCl(aq) at 25 °C, from zero to saturation,¹⁴ (Slope = n_b and y -intercept = 55.51.) (This Figure is reproduced with permission from the J. Electrochem. Soc.)

α (Eq. (4)) and α (Eq. (6)) perfectly reproduce (up to ± 0.001) the ϕ values from Eqs. (6) and (4) respectively. The degrees of dissociation of all the alkali halides (evaluated from the osmotic coefficient data in¹⁶) at various molalities are presented in Table I–III.

TABLE I

Degrees of dissociation ($\alpha \pm 0.001$) of Li & Na halides at molalities m in aq. solns. at 25 °C; hydration numbers $n(s)$ and $n(b)$; slopes (δ_A) and intercepts of Figures 7 and 8.

m	LiCl	LiBr	LiI	NaF	NaCl	NaBr	NaI
0.0	1.000	1.000	1.000	1.000	1.000	1.000	1.000
0.1	0.861	0.865	0.882	0.856	0.857	0.857	0.863
0.2	0.843	0.845	0.887	0.832	0.833	0.835	0.846
0.3	0.837	0.839	0.892	0.820	0.819	0.824	0.839
0.4	0.837	0.833	0.898	0.814	0.808	0.815	0.837
0.5	0.836	0.830	0.899	0.811	0.801	0.813	0.838
0.6	0.837	0.828	0.902	0.811	0.797	0.810	0.838
0.7	0.840	0.828	0.900	0.813	0.794	0.808	0.840
0.8	0.842	0.831	0.904	0.814	0.792	0.807	0.842
0.9	0.843	0.833	0.904	0.818	0.789	0.808	0.843
1.0	0.846	0.835	0.910		0.788	0.806	0.844
1.2	0.849	0.843	0.913		0.785	0.804	0.846
1.4	0.854	0.847	0.915		0.784	0.808	0.851
1.6	0.857	0.849	0.916		0.786	0.811	0.854
1.8	0.858	0.850			0.789	0.815	0.857
2.0	0.858	0.848			0.791	0.820	0.858
2.5					0.800	0.828	0.866
3.0					0.811	0.833	0.881
3.5					0.824	0.838	0.881
4.0					0.835	0.847	
4.5					0.845		
5.0					0.854		
5.5					0.860		
6.0					0.862		
m (satd)				0.983	6.144		
α (satd)				0.818	0.863		
$n(s)$	6.091	7.218	7.376	-1.567	3.360	4.084	4.774
$n(b)$	5.174	6.305	6.427	-2.469	2.470	3.187	3.856
δ_A	0.972	0.988	0.999	0.905	0.947	0.955	0.973
Std.Err.	0.005	0.007	0.008	0.005	0.003	0.004	0.006
$-\Delta E^\circ/V$	0.191	0.196	0.199	0.170	0.183	0.185	0.190
Std.Err.	0.001	0.001	0.001	0.001	0.001	0.001	0.001
r°	0.0218	0.0210	0.0207	0.0258	0.0233	0.0230	0.0224

Note the minima in the α vs. m data. This shows that the minima occurring in the ϕ vs. m and γ_{\pm} vs. m curves are reflections of the dissociation minima. A survey of the literature shows that the phenomenon of 'dissociation minimum' was already pointed out by Davies.²⁰ He discusses the con-

TABLE II

Degrees of dissociation ($\alpha \pm 0.001$) of K & Rb halides at molalities m in aq. solns. at 25 °C; hydration numbers $n(s)$ and $n(b)$; slopes (δ_A) and intercepts of Figures 9 and 10.

m	KF	KCl	KBr	KI	RbF	RbCl	RbBr	RbI
0.0	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
0.1	0.851	0.850	0.852	0.860	0.860	0.843	0.842	0.840
0.2	0.820	0.818	0.825	0.836	0.841	0.808	0.806	0.803
0.3	0.803	0.800	0.809	0.823	0.835	0.786	0.788	0.785
0.4	0.792	0.788	0.797	0.817	0.835	0.773	0.776	0.770
0.5	0.784	0.778	0.789	0.813	0.836	0.762	0.766	0.760
0.6	0.777	0.772	0.786	0.811	0.837	0.755	0.760	0.753
0.7	0.744	0.767	0.782	0.809	0.841	0.750	0.753	0.745
0.8	0.772	0.763	0.780	0.810	0.842	0.746	0.747	0.740
0.9	0.769	0.759	0.778	0.810	0.845	0.741	0.743	0.736
1.0	0.769	0.755	0.776	0.810	0.848	0.738	0.741	0.731
1.2	0.769	0.751	0.774	0.811	0.850	0.733	0.735	0.726
1.4	0.769	0.747	0.775	0.814	0.851	0.730	0.732	0.721
1.6	0.770	0.745	0.773	0.817	0.850	0.728	0.730	0.719
1.8	0.770	0.744	0.775	0.822		0.727	0.730	0.718
2.0	0.771	0.744	0.776	0.826		0.726	0.731	0.721
2.5	0.774	0.747	0.784	0.837		0.726	0.732	0.721
3.0	0.781	0.751	0.790	0.844		0.730	0.733	0.724
3.5	0.787	0.754	0.796	0.851		0.736	0.737	0.730
4.0	0.797	0.761	0.804	0.855		0.743	0.743	0.735
4.5		0.767	0.812	0.851		0.745	0.747	0.741
5.0			0.819			0.753	0.755	0.744
5.5			0.821					
6.0								
$m(\text{satd})$		4.803	5.755					
α (satd)		0.772	0.818					
$n(s)$	3.658	2.052	2.040	2.173	3.939	1.878	1.526	1.652
$n(b)$	2.786	1.193	1.235	1.270	2.476	1.030	0.676	0.807
δ_A	0.936	0.922	0.927	0.915	0.935	0.912	0.905	0.906
Std.Err.	0.002	0.002	0.001	0.002	0.001	0.002	0.003	0.003
$-\Delta E^0/V$	0.180	0.176	0.177	0.174	0.179	0.174	0.172	0.172
Std.Err.	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001
r^0	0.0237	0.0243	0.0243	0.0247	0.0241	0.0244	0.0247	0.0248

ditions for α -minimum in terms of the ionic strength and activity coefficient. In Refs. 13 and 14 it was shown for NaCl(aq) that at the dissociation minimum, the e.m.f. of concentration cells, ΔE , (which is¹ nF times the Gibbs free energy), is zero; equivalently, that the mean ionic activity ($m\gamma_{\pm}$) is unity.

TABLE III

Degrees of dissociation ($\alpha \pm 0.001$) of Cs halides at molalities m in aq. solns. at 25 °C; hydration numbers $n(s)$ and $n(b)$; slopes (δ_A) and intercepts of Figure 11.

m	CsF	CsCl	CsBr	CsI
0.0	1.000	1.000	1.000	1.000
0.1	0.869	0.831	0.832	0.836
0.2	0.850	0.788	0.787	0.797
0.3	0.841	0.762	0.757	0.770
0.4	0.838	0.739	0.737	0.753
0.5	0.837	0.724	0.719	0.742
0.6	0.837	0.711	0.708	0.735
0.7	0.838	0.702	0.698	0.732
0.8	0.840	0.695	0.690	0.729
0.9	0.844	0.691	0.683	0.726
1.0	0.846	0.686	0.677	0.723
1.2	0.855	0.678	0.670	0.721
1.4	0.863	0.672	0.663	0.721
1.6	0.872	0.668	0.658	0.721
1.8	0.881	0.666	0.658	0.723
2.0	0.890	0.670	0.657	0.725
2.5	0.904	0.669	0.658	0.730
3.0		0.671	0.659	0.735
3.5		0.678	0.662	
4.0		0.681	0.669	
4.5		0.688	0.672	
5.0		0.691	0.676	
5.5		0.696		
6.0		0.700		
m (satd)			5.67	3.29
α (satd)			0.657	0.724
$n(s)$	4.692	1.753	1.592	-0.166
$n(b)$	3.783	0.934	0.780	-1.017
δ_A	0.957	0.893	0.893	0.880
Std.Err.	0.003	0.004	0.005	0.007
$-\Delta E^\circ/V$	0.187	0.169	0.169	0.164
Std.Err.	0.001	0.001	0.001	0.001
r°	0.0223	0.0251	0.0251	0.0266

From the α vs. m data in Tables I–III, the actual single »ionic molalities, αm « (of either the alkali or the halide ion) as well as the »ion-pair molalities, $(1 - \alpha)m$ « were calculated. The variation of these with the molality m of the alkali halides can be seen in Figures 2–6. In these Figures are also shown the lines with »unit slope« expected for the single ionic molalities on the assumption of complete dissociation. Thus note from the Figures that no alkali halide is dissociated completely at any concentration (except infinite dilution).

The above interpretation of ϕ in terms of Eqs. (4) and (6) is thus simple. On the other hand, the idea of complete dissociation yields² for ϕ the complicated Eq. (7) in Ref. 2.

*The Linear Dependence of the E.M.F, ΔE , of Concentration Cells
on $\ln(am/n_{\text{Afs}})$*

The above values of α (see Tables I–III) have now enabled^{13–15} the extension to high concentrations (even up to saturation in some cases) of the earlier interpretation^{3,9,10} of ΔE by the equation,

$$\Delta E = -\delta_A(2RT/F) \ln[(am/n_{\text{Afs}}) / (am/n_{\text{Afs}})^0]. \quad (9)$$

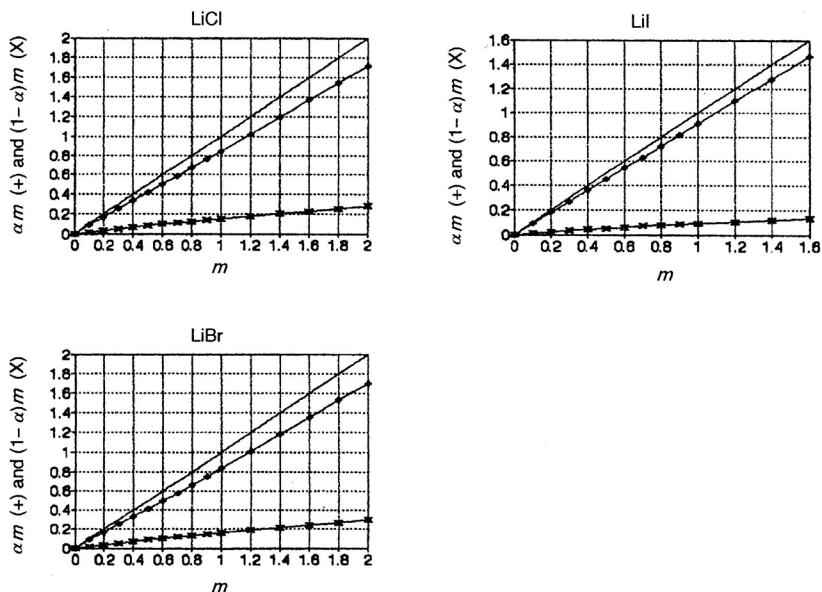


Figure 2. The single »ionic molality«, αm (upper curve) and the »ion pair molality«, $(1 - \alpha)m$ (lower curve) at various molalities, m of lithium halides in aqueous solutions at 25 °C. (The line with 45° slope in Figures 2–6 gives the ionic molality based on the idea of complete dissociation.)

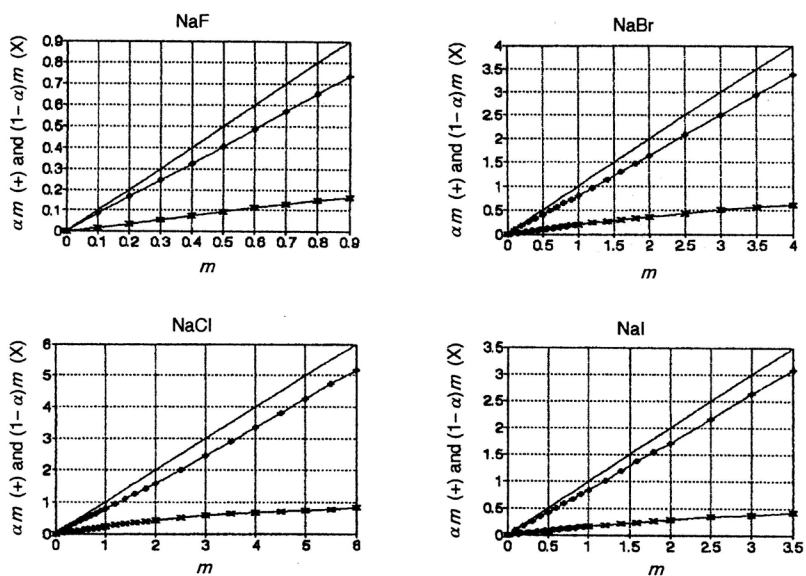


Figure 3. The single »ionic molality«, αm (upper curve) and the »ion pair molality«, $(1-\alpha)m$ (lower curve) at various molalities m of sodium halides in aq. solutions at 25 °C.

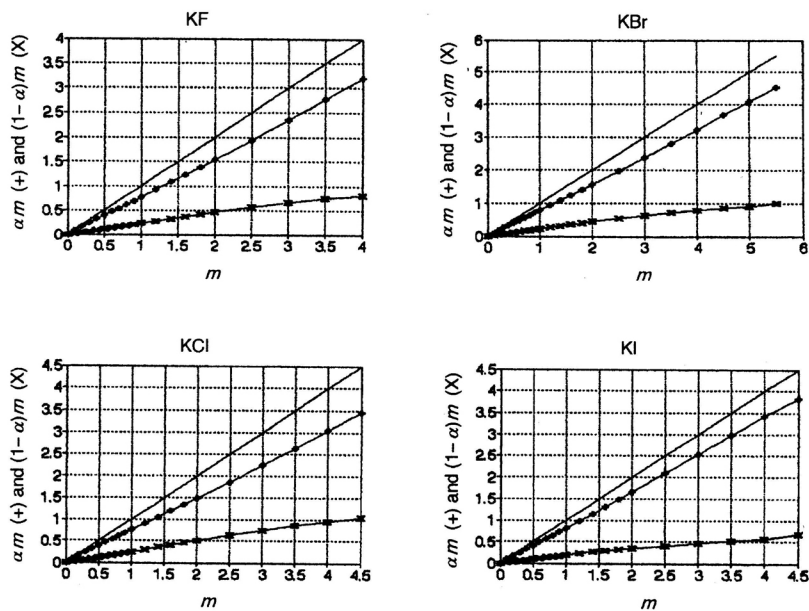


Figure 4. The single »ionic molality«, αm (upper curve) and the »ion pair molality«, $(1-\alpha)m$ (lower curve) at various molalities m of potassium halides in aq. solutions at 25 °C.

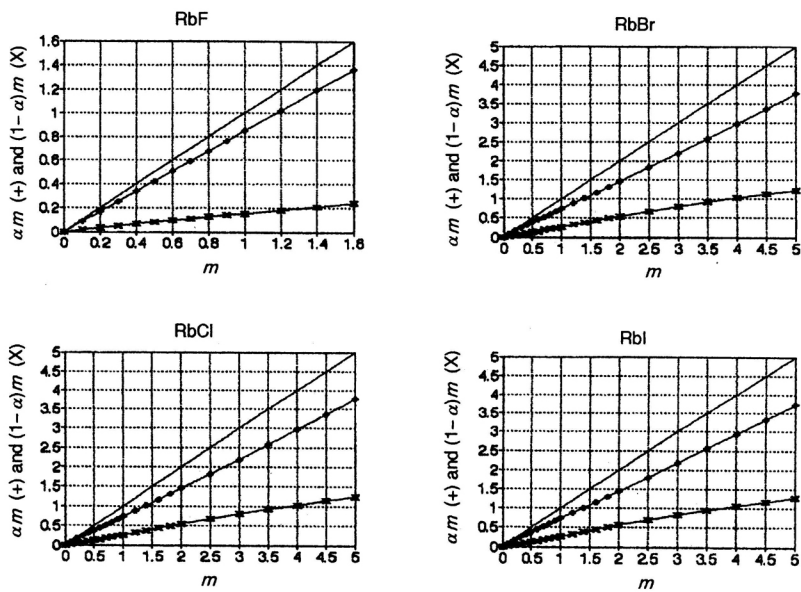


Figure 5. The single »ionic molality«, αm (upper curve) and the »ion pair molality«, $(1 - \alpha)m$ (lower curve) at various molalities m of rubidium halides in aq. solutions at 25 °C.

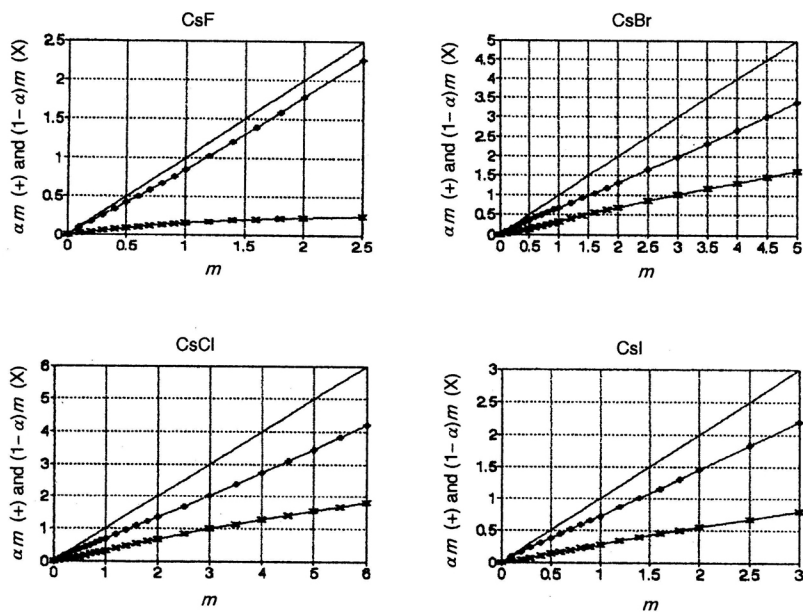


Figure 6. The single »ionic molality«, αm (upper curve) and the »ion pair molality«, $(1 - \alpha)m$ (lower curve) at various molalities m of cesium halides in aq. solutions at 25 °C.

The values of ΔE could be calculated by using the available γ_{\pm} data¹⁶ in the equation defining^{1,21} γ_{\pm} ,

$$\Delta E = (-2RT/F) \ln(m\gamma_{\pm}). \quad (10)$$

Note that the difference in e.m.f., $[\Delta E + (2RT/F) \ln(m)]$, from which γ_{\pm} is evaluated, is the (non-ideal) e.m.f. deficit or excess over that, $-(2RT/F) \ln(m)$, for (ideal) complete dissociation (at infinite dilution, where $\gamma_{\pm} = 1$). (Note also that γ_{\pm} was in fact originally²¹ considered as the thermodynamic degree of dissociation!)

The linear dependence of ΔE on $\ln(am/n_{\text{Afs}})$ for the alkali halides (for the same concentration ranges as in Figures 2–6) is shown in Figures 7–11. In these Figures, the mole ratio $(\alpha m/n_{\text{Af}})$ is denoted by r . From the slope, δ_A (see Eq. (9) and its values in Tables I–III), a constant close to unity is obtained. $\delta_A < 1$ probably due to the solvent-solute polarization. The intercept on the y -axis gives ΔE° at $\ln(r) = 0$ and that on the x -axis at $\Delta E = 0$ gives $-k \ln(r^{\circ})$, where $r^{\circ} = (\alpha m/n_{\text{Afs}})^{\circ}$. $\Delta E = 0$ corresponds to concentrations when α is (around) the minimum and ΔE is of opposite sign on either side of the α -minimum. Eq. (9) reproduces the ΔE values to $\pm 2\text{mV}$ over the entire concentration ranges given in Tables I–III. (Note: for NaF, KCl, KBr, RbCl, RbBr, RbI, CsCl, CsBr and CsI, Eq. (9) involves n_{Afb} .)

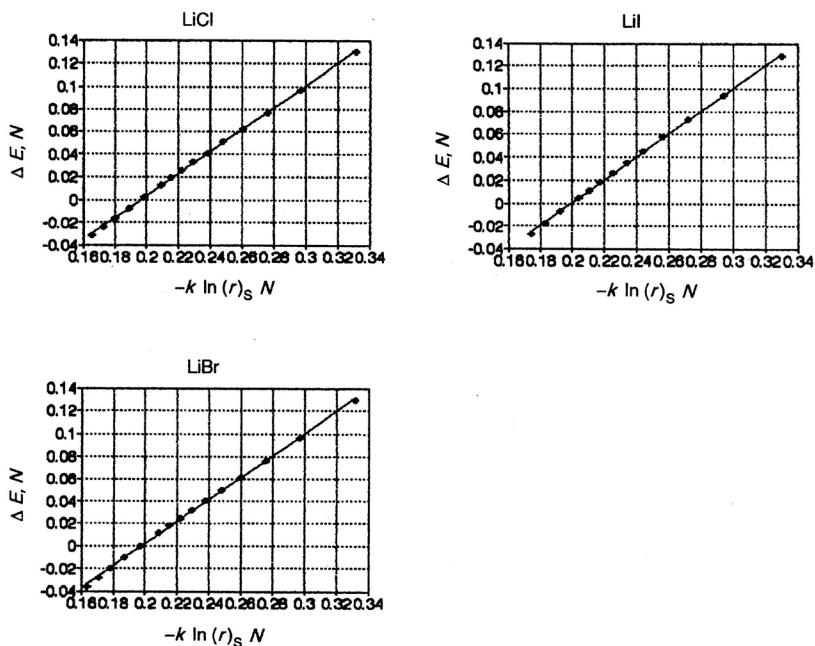


Figure 7. The linear dependence of the e.m.f. of concentration cells, ΔE , on $\ln(r)_s$ for lithium halides in aq. solutions at 25 °C. [$k = 2RT/F$ and $(r)_s = (\alpha m/n_{\text{Afs}})$.]

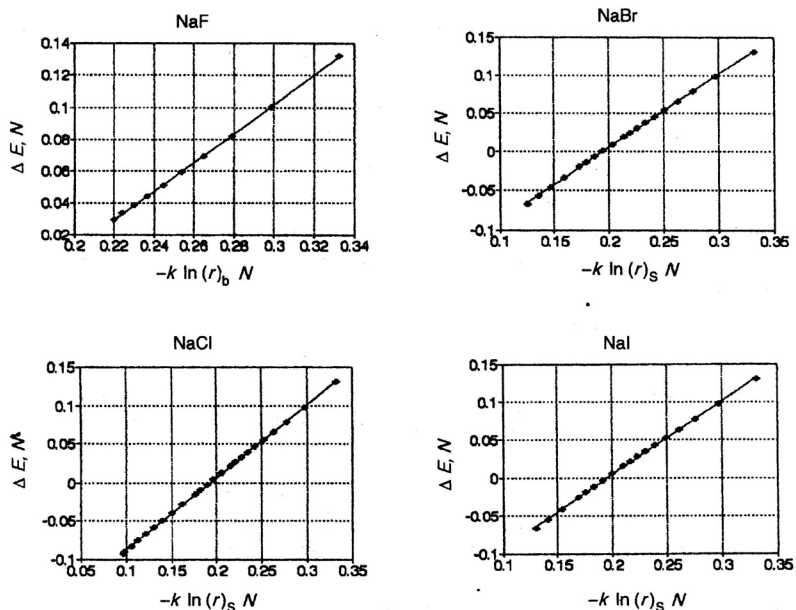


Figure 8. The linear dependence of the e.m.f. of concentration cells, ΔE , on $\ln(r)$ for sodium halides in aq. solutions at 25 °C. $[(r)_b = (am/n_{Afb})]$.

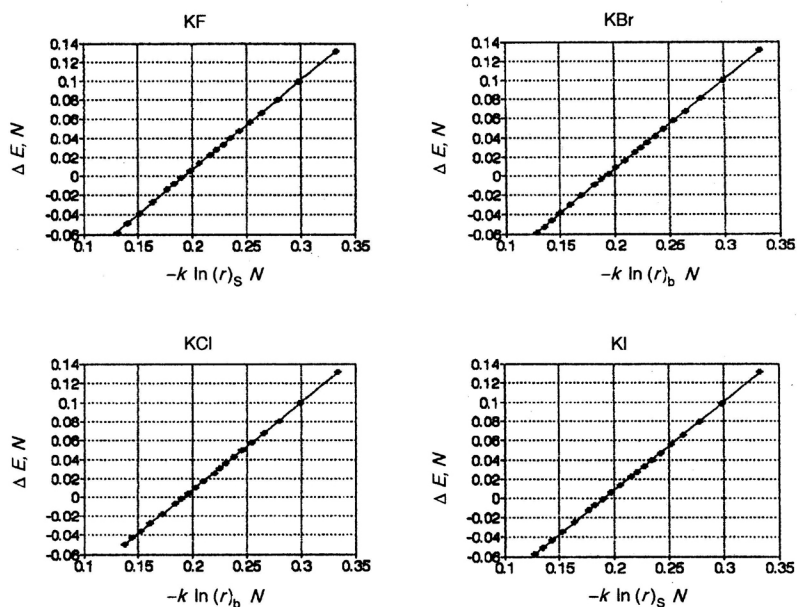


Figure 9. The linear dependence of the e.m.f. of concentration cells, ΔE , on $\ln(r)$ for potassium halides in aq. solutions at 25 °C.

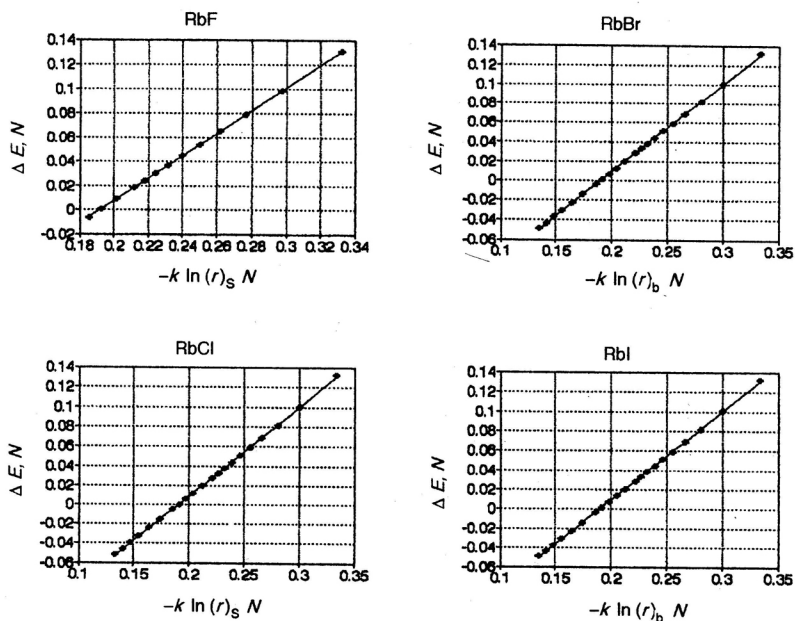


Figure 10. The linear dependence of the e.m.f. of concentration cells, ΔE , on $\ln(r)$ for rubidium halides in aq. solutions at 25 °C.

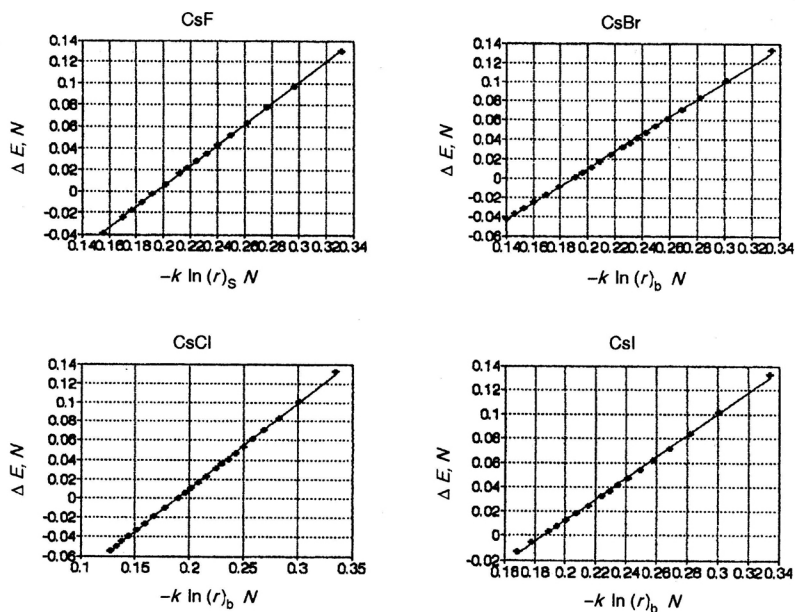


Figure 11. The linear dependence of the e.m.f. of concentration cells, ΔE , on $\ln(r)$ for cesium halides in aq. solutions at 25 °C.

The validity of Eq. (9), and hence of the interpretation of ΔE shows that the α values (and hence n_s and n_b as well) evaluated from the ϕ data (see the first section) are meaningful. Moreover, Eq. (9) based on the idea of partial dissociation and hydration affords a *simple and unified interpretation of ΔE over the entire concentration range.*

For comparison with the simple Eq. (9) above, please see the elaborate Eq. (8) in Ref. 2 for $\ln(\gamma_{\pm})$ (equivalently, for ΔE) based on complete dissociation.

*The Linear Relation Between the Surface (n_s) and Bulk (n_b)
Hydration Numbers*

Figure 12 shows the linear relation between the surface and bulk hydration numbers. The straight line follows the relation,

$$n_s = 1.011n_b + 0.85 . \quad (11)$$

Note that the slope (1.011 ± 0.003) is nearly unity and that the intercept (0.85 ± 0.03) is independent of the electrolyte. A plot of n_s vs. n_b for 44 1:1 electrolytes gives 1.007 ± 0.001 and 0.88 ± 0.03 as the slope and intercept respectively.¹⁸ This shows that n_s is the sum of the hydration number of the electrolyte at the surface (which is $1.007 n_b$), and a constant (= 0.88), which pertains to water. The latter is probably due to the fact that the water molecules at the interface have not only to keep the solute in solution but also to maintain the equilibrium with the molecules of its own kind in the vapor phase.

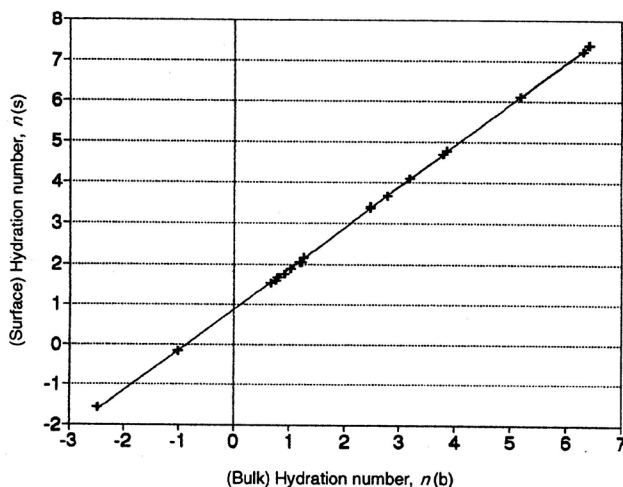


Figure 12. The linear dependence of n_s (surface hydration number) on n_b (bulk hydration number) for alkali halides in aq. solutions.

In conclusion, the author hopes that the results in this paper would be of some help to Marko Branica's marine science and that the question of mixed electrolytes would be solved before his 70th birthday!

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SAŽETAK**Stupanj disocijacije i hidratacijski brojevi alkalijskih halogenida u vodenim otopinama pri 25 °C (nekih do zasićenja)***Rajalakshmi Heyrovská*

Sustavna istraživanja posljednjih godina oživjela su ideje o ionskoj asocijaciji/disocijaciji i hidrataciji kao uzrocima neidealnosti otopina jakih elektrolita. Pokazano je da su temeljna svojstva poput tlaka para, EMS koncentracijskih članaka, molarne provodnosti, difuzijskih koeficijenata i molarnih volumena (gustoća) otopina jednostavne funkcije njihovih ionskih molaliteta (ne ionskih »aktiviteta«) i hidratacijskih brojeva u širokom rasponu koncentracija. Istraživanja su nedavno proširena na cijelo područje koncentracija, od nule do zasićenja, za jake elektrolite poput NaCl(aq). U ovom su radu osmotski koeficijenti i aktivnosni koeficijenti interpretirani u smislu stupnja disocijacije (α) i hidratacijskih brojeva za sve alkalijske halogenide. Priložene su tablice α vrijednosti i odgovorajući grafovi.