Mixing Effects on the Protonation of Polycarboxylates. Protonation of Benzenehexacarboxylate in LiCl−KCl, NaCl−KCl, NaCl−LiCl, and LiCl−CsCl Aqueous Solutions at $I = 1\ \text{mol}\cdot\text{L}^{-1}$ and $T = 298.15$ K

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Protonation constants are reported for 1,2,3,4,5,6-benzenehexacarboxylate in the electrolyte mixtures LiCl−KCl, NaCl−KCl, NaCl−LiCl, and LiCl−CsCl at a total ionic strength of 1 mol·L^{-1} and T = 298.15 K, for different molar ratios (y) from 0 to 1. The function $\log_{10} K^{H}$ vs y is not linear and can be expressed by a three-parameter equation derived using the zeroth Guggenheim approximation. Deviation from linearity was interpreted in terms of mixing free energy and mixed-metal complex formation.

Introduction

The simple observations that (i) protonation constants are primary data for the speciation of most of the ligands and (ii) almost all biological fluids and natural waters are multielectrolyte solutions suggest that the study of acid−base properties of different inorganic and organic polyanions in mixed electrolytes are of great interest for the speciation analysis of aqueous solutions.

As a continuation of our investigations of the effects of mixing on protonation constants in mixed electrolytes,[1−4] we report here protonation data for 1,2,3,4,5,6-benzenehexacarboxylate in different alkali metal chloride solutions.

Experimental Section

1,2,3,4,5,6-Benzenehexacarboxylate acid ($h_6$mlt) solutions (Aldrich) were prepared from the solid product without further purification. Their purity was checked alkalimetrically, and in all cases, it was >99 %. Lithium, sodium, potassium, and cesium chloride solutions were prepared by weighing the pure salts (Fluka, puriss.) previously dried at 110 °C.

Measurements were carried out by titrating, in a thermostatted cell at $T = (298.15 \pm 0.1)$ K, (25 or 50) mL of a solution containing the ligands [(2.5−10) mmol·L^{-1}] and LiCl−KCl, NaCl−KCl, NaCl−LiCl, and LiCl−CsCl mixtures at a total ionic strength of 1.0 mol·L^{-1} and at different molar ratios y [for example, in the mixture NaCl−KCl, $y = [\text{Na}^+]/([\text{Na}^+] + [\text{K}^+])$], with standard LiOH, NaOH, or KOH solution. For each set of experimental conditions, at least three replicates were performed. Independent titrations of a hydrochloric acid solution with standard strong base at the same ionic strength as the systems were also carried out to determine the electrode potential ($E\text{ext}^{\circ}$) and the acidic junction potential ($E_j = j_a[\text{H}^+]$). The free hydrogen ion concentration scale was used, i.e., pH = $-\log_{10}$ [H$^+$]. The instrumental apparatus and the procedures followed for the measurements were already described in detail in previous articles.[1−4] Calculation methods and the relative computer programs were already described in detail as well.[5] Protonation constants are expressed as

$$K_i^{H} = \frac{[\text{H}_i\text{L}^{(z-i)-}]}{[\text{H}^+][\text{H}_{i-1}\text{L}^{(z-i+1)-}]}$$

Models for Interpreting Mixing Effects. Young's rule, first formulated for densities in the mixing of solutions of strong electrolytes,[6,7] if applied to protonation constants in MCl + M′Cl aqueous mixtures (where M and M′ are generic cations), can be written as a function of the molar ratio (y)

$$\log_{10} K^{H}_{M-M'} = y \log_{10} K^{H}_{M} + (1-y) \log_{10} K^{H}_{M'} \quad (1)$$

where K^{H}_{M} and $K^{H}_{M'}$ are the protonation constants in the corresponding pure salt solutions. Equation 1 is valid for linear (ideal) mixing, whereas for the protonation constants in mixtures of MCl and M′Cl that do not follow the Young's rule, we used the Guggenheim zeroth approximation,[8] which leads to the three-parameter equation

$$\log_{10} K^{H}_{M-M'} = y^2 \log_{10} K^{H}_{M} + (1-y)^2 \log_{10} K^{H}_{M'} + 2y(1-y) \log_{10} K^{H}_{m} \quad (2)$$

where K^{H}_{m} is an intermediate value that accounts for the nonlinearity of the function $\log K_i^{H} = f(y)$. This equation, also called Högfeldt three-parameter equation,[9,10] was already applied to study the acid−base properties of different polycarboxylates by Crea et al. (see ref 11 and references therein). After simple rearrangement, eq 2 can be written as

$$\log_{10} K^{H}_{M-M'} = y \log_{10} K^{H}_{M} + (1-y) \log_{10} K^{H}_{M'} + 4\Delta y(1-y) \quad (3)$$

where Δ is a measure of the deviation from linearity and, for y = 0.5, it is given by

$$\Delta = \frac{1}{2}(\log_{10} K^{H}_{M} + \log_{10} K^{H}_{M'}) - \log_{10} K^{H}_{M-M'} \quad (4)$$

Negative Δ values indicate the lowering of protonation constants with respect to those calculated by eq 1 at y = 0.5.

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Table 1. Protonation Constants of 1,2,3,4,5,6-Benzenexacarboxylate in Different Mixed Electrolyte Solutions, at $I = 1.0\ \mathrm{mol \cdot L^{-1}}$ and $T = 298.15$ K

y	$\log_{10} K_1^{\mathrm{H}}$	$\log_{10} K_2^{\mathrm{H}}$	$\log_{10} K_3^{\mathrm{H}}$	$\log_{10} K_4^{\mathrm{H}}$
LiCl−KCl				
1.000[a]	5.208 ± 0.004[b]	4.297 ± 0.002[b]	3.572 ± 0.005[b]	2.537 ± 0.008[b]
1.000	5.207 ± 0.004	4.297 ± 0.002	3.572 ± 0.005	2.537 ± 0.008
0.903	5.214 ± 0.003	4.302 ± 0.001	3.571 ± 0.004	2.533 ± 0.007
0.903	5.205 ± 0.003	4.301 ± 0.001	3.572 ± 0.004	2.533 ± 0.007
0.753	5.237 ± 0.003	4.317 ± 0.002	3.569 ± 0.003	2.509 ± 0.006
0.753	5.236 ± 0.003	4.317 ± 0.002	3.569 ± 0.003	2.509 ± 0.006
0.503	5.300 ± 0.004	4.363 ± 0.002	3.572 ± 0.002	2.490 ± 0.005
0.503	5.301 ± 0.004	4.364 ± 0.002	3.571 ± 0.002	2.490 ± 0.005
0.253	5.382 ± 0.003	4.421 ± 0.002	3.589 ± 0.002	2.479 ± 0.005
0.253	5.383 ± 0.003	4.422 ± 0.002	3.588 ± 0.002	2.479 ± 0.005
0.095	5.445 ± 0.002	4.464 ± 0.001	3.603 ± 0.001	2.470 ± 0.006
0.095	5.443 ± 0.002	4.464 ± 0.001	3.601 ± 0.001	2.470 ± 0.006
0	5.482 ± 0.003	4.493 ± 0.002	3.612 ± 0.002	2.459 ± 0.007
0	5.485 ± 0.003	4.495 ± 0.002	3.613 ± 0.002	2.459 ± 0.007
NaCl−KCl				
1.000	5.389 ± 0.005[b]	4.445 ± 0.002[b]	3.601 ± 0.003[b]	2.476 ± 0.009[b]
1.000	5.388 ± 0.005	4.447 ± 0.002	3.599 ± 0.003	2.476 ± 0.009
0.804	5.381 ± 0.003	4.441 ± 0.002	3.595 ± 0.002	2.477 ± 0.007
0.804	5.376 ± 0.003	4.438 ± 0.002	3.596 ± 0.002	2.477 ± 0.007
0.498	5.400 ± 0.004	4.448 ± 0.002	3.592 ± 0.002	2.465 ± 0.005
0.499	5.401 ± 0.004	4.447 ± 0.002	3.593 ± 0.002	2.465 ± 0.005
0.198	5.444 ± 0.002	4.470 ± 0.001	3.602 ± 0.001	2.462 ± 0.006
0.198	5.440 ± 0.002	4.471 ± 0.001	3.601 ± 0.001	2.462 ± 0.006
0	5.482 ± 0.003	4.493 ± 0.002	3.612 ± 0.002	2.459 ± 0.007
0	5.485 ± 0.003	4.495 ± 0.002	3.613 ± 0.002	2.459 ± 0.007
NaCl−LiCl				
1.000	5.394 ± 0.005[b]	4.447 ± 0.002[b]	3.602 ± 0.003[b]	2.476 ± 0.009[b]
1.000	5.393 ± 0.005	4.450 ± 0.002	3.600 ± 0.003	2.476 ± 0.009
0.806	5.347 ± 0.004	4.409 ± 0.002	3.591 ± 0.003	2.490 ± 0.007
0.806	5.341 ± 0.004	4.408 ± 0.002	3.588 ± 0.003	2.490 ± 0.007
0.500	5.282 ± 0.005	4.357 ± 0.003	3.576 ± 0.004	2.499 ± 0.006
0.500	5.280 ± 0.005	4.355 ± 0.003	3.575 ± 0.004	2.499 ± 0.006
0.210	5.243 ± 0.004	4.316 ± 0.002	3.572 ± 0.004	2.512 ± 0.006
0.210	5.243 ± 0.004	4.318 ± 0.002	3.571 ± 0.004	2.512 ± 0.006
0	5.222 ± 0.004	4.302 ± 0.002	3.573 ± 0.005	2.537 ± 0.008
0	5.222 ± 0.004	4.301 ± 0.002	3.573 ± 0.005	2.537 ± 0.008
LiCl−CsCl				
1.000[a]	5.178 ± 0.004[b]	4.289 ± 0.002[b]	3.535 ± 0.005[b]	2.536 ± 0.008[b]
1.000	5.177 ± 0.004	4.289 ± 0.002	3.535 ± 0.005	2.536 ± 0.008
0.903	5.102 ± 0.003	4.264 ± 0.002	3.444 ± 0.004	2.418 ± 0.007
0.903	5.110 ± 0.003	4.270 ± 0.002	3.460 ± 0.004	2.418 ± 0.007
0.754	5.062 ± 0.005	4.273 ± 0.003	3.383 ± 0.004	2.466 ± 0.012
0.754	5.066 ± 0.005	4.275 ± 0.003	3.389 ± 0.004	2.466 ± 0.012
0.500	5.076 ± 0.006	4.282 ± 0.004	3.342 ± 0.005	2.361 ± 0.016
0.500	5.070 ± 0.006	4.276 ± 0.004	3.324 ± 0.005	2.361 ± 0.016
0.252	5.101 ± 0.005	4.320 ± 0.003	3.299 ± 0.004	2.282 ± 0.014
0.252	5.097 ± 0.005	4.321 ± 0.003	3.295 ± 0.004	2.282 ± 0.014
0.096	5.134 ± 0.007	4.361 ± 0.004	3.282 ± 0.006	2.276 ± 0.020
0.096	5.134 ± 0.007	4.359 ± 0.004	3.272 ± 0.006	2.276 ± 0.020
0	5.148 ± 0.010	4.386 ± 0.006	3.250 ± 0.009	2.267 ± 0.028
0	5.148 ± 0.010	4.390 ± 0.006	3.248 ± 0.009	2.267 ± 0.028

[a] $y = [\mathrm{Li^+}]/([\mathrm{Li^+}] + [\mathrm{K^+}])$. [b] Value ± standard deviation.

Table 2. Protonation Constants of 1,2,3,4,5,6-Benzenexacarboxylate in Pure Salts, at $I = 1.0\ \mathrm{mol \cdot L^{-1}}$ and $T = 298.15$ K

i[a]	$\log_{10} K_{\mathrm{Li}}^{\mathrm{H}}$	$\log_{10} K_{\mathrm{Na}}^{\mathrm{H}}$	$\log_{10} K_{\mathrm{K}}^{\mathrm{H}}$	$\log_{10} K_{\mathrm{Cs}}^{\mathrm{H}}$
1	5.194 ± 0.004[b]	5.388 ± 0.005[b]	5.484 ± 0.003[b]	5.178 ± 0.010[b]
2	4.293 ± 0.002	4.446 ± 0.002	4.494 ± 0.002	4.392 ± 0.006
3	3.554 ± 0.005	3.600 ± 0.003	3.612 ± 0.002	3.282 ± 0.009
4	2.524 ± 0.008	2.477 ± 0.009	2.460 ± 0.007	2.261 ± 0.028

[a] Equilibrium refers to the reaction $\mathrm{H^+ + H_{(i-1)}L^{(6-i+1)-} = H_iL^{(6-i)-}}$. [b] Value ± standard deviation.

Table 3. Smoothed Protonation Constants (Eq 3) of 1,2,3,4,5,6-Benzenexacarboxylate in Different Mixed Electrolyte Solutions, at $I = 1.0\ \mathrm{mol \cdot L^{-1}}$ and $T = 298.15$ K

y	$\log_{10} K_1^{\mathrm{H}}$	$\log_{10} K_2^{\mathrm{H}}$	$\log_{10} K_3^{\mathrm{H}}$	$\log_{10} K_4^{\mathrm{H}}$
LiCl−KCl				
0.100[a]	5.441 ± 0.002[b]	4.463 ± 0.001[b]	3.602 ± 0.001[b]	2.467 ± 0.006[b]
0.250	5.383 ± 0.003	4.421 ± 0.002	3.590 ± 0.002	2.476 ± 0.005
0.400	5.331 ± 0.003	4.384 ± 0.002	3.579 ± 0.002	2.486 ± 0.005
0.500	5.301 ± 0.004	4.363 ± 0.002	3.572 ± 0.002	2.492 ± 0.005
0.600	5.273 ± 0.003	4.344 ± 0.002	3.567 ± 0.002	2.499 ± 0.005
0.750	5.238 ± 0.003	4.320 ± 0.002	3.560 ± 0.003	2.508 ± 0.006
0.900	5.209 ± 0.003	4.302 ± 0.001	3.556 ± 0.003	2.518 ± 0.007
NaCl−KCl				
0.100	5.461 ± 0.002[b]	4.481 ± 0.001[b]	3.606 ± 0.001[b]	2.462 ± 0.006[b]
0.250	5.432 ± 0.003	4.465 ± 0.001	3.599 ± 0.001	2.464 ± 0.006
0.400	5.410 ± 0.003	4.453 ± 0.002	3.594 ± 0.002	2.467 ± 0.005
0.500	5.399 ± 0.004	4.447 ± 0.002	3.592 ± 0.002	2.469 ± 0.005
0.600	5.391 ± 0.003	4.443 ± 0.002	3.592 ± 0.002	2.471 ± 0.006
0.750	5.384 ± 0.003	4.441 ± 0.002	3.593 ± 0.002	2.473 ± 0.007
0.900	5.384 ± 0.004	4.443 ± 0.002	3.596 ± 0.002	2.476 ± 0.008
NaCl−LiCl				
0.100	5.211 ± 0.003[b]	4.304 ± 0.002[b]	3.558 ± 0.004[b]	2.520 ± 0.007[b]
0.250	5.238 ± 0.004	4.322 ± 0.002	3.565 ± 0.004	2.513 ± 0.006
0.400	5.265 ± 0.005	4.342 ± 0.002	3.572 ± 0.004	2.506 ± 0.005
0.500	5.284 ± 0.005	4.356 ± 0.003	3.577 ± 0.004	2.501 ± 0.006
0.600	5.304 ± 0.004	4.372 ± 0.002	3.581 ± 0.004	2.496 ± 0.006
0.750	5.334 ± 0.004	4.398 ± 0.002	3.588 ± 0.003	2.489 ± 0.007
0.900	5.366 ± 0.004	4.426 ± 0.002	3.596 ± 0.002	2.482 ± 0.008
LiCl−CsCl				
0.100[a]	5.133 ± 0.007[b]	4.358 ± 0.004[b]	3.275 ± 0.006[b]	2.273 ± 0.020[b]
0.250	5.084 ± 0.005	4.319 ± 0.003	3.279 ± 0.004	2.298 ± 0.015
0.400	5.060 ± 0.006	4.290 ± 0.003	3.300 ± 0.004	2.329 ± 0.015
0.500	5.056 ± 0.006	4.278 ± 0.004	3.324 ± 0.005	2.354 ± 0.016
0.600	5.063 ± 0.006	4.271 ± 0.004	3.355 ± 0.005	2.382 ± 0.015
0.750	5.092 ± 0.005	4.270 ± 0.003	3.415 ± 0.004	2.430 ± 0.012
0.900	5.146 ± 0.003	4.280 ± 0.002	3.492 ± 0.004	2.484 ± 0.008

[a] $y = [\mathrm{Li^+}]/([\mathrm{Li^+}] + [\mathrm{K^+}])$. [b] Value ± standard deviation.

Results

The protonation constants of 1,2,3,4,5,6-benzenehexacarboxylate ($h_6$mlt), obtained in different electrolyte mixtures and at different molar ratios, are reported in Table 1. Only the first four protonation steps were taken into account because the last two constants are quite low[12] and are fairly independent of the alkali metal mixture. The observed deviation from linearity for the protonation constants is fairly dependent on the pair of electrolytes considered; the maximum deviation is observed for the mixture LiCl−CsCl, whereas for LiCl−NaCl, as the molar ratio was varied from 0 to 1, an almost linear variation of protonation constants was observed. To determine the effects of mixing on the acid−base properties of $h_6$mlt, the protonation constants in pure salt solutions were also determined in the four supporting electrolytes at $I = 1.0\ \mathrm{mol \cdot L^{-1}}$, and these values are reported in Table 2. The protonation constants in electrolyte mixtures were fitted to eq 3, and some smoothed values are reported in Table 3. Table 4 reports the values of the Δ parameter, which defines the deviation of the protonation constants from linearity (ideal mixing), as well as the free energy of mixing (ΔG_{mix}). A first inspection of this table leads to the following observations: (a) Δ_i values are always negative (or zero in some cases); (b) the statistical parameters (standard deviations on the parameters and on the fit) are very good and support the reliability of the model; (c) the higher the difference in the nature of the supporting electrolyte cations, the higher the value of Δ; and (d) for the same charge of $\mathrm{H}_{i-1}\mathrm{mlt}^{(z-i+1)}$, the Δ trend is Δ(LiCl−CsCl) > Δ(LiCl−KCl) > Δ(NaCl−KCl) > Δ(NaCl−LiCl).

Table 4. Parameters of Eq 3 obtained for 1,2,3,4,5,6-Benzenexacarboxylate in Mixed LiCl−KCl, NaCl−KCl, NaCl−LiCl, and LiCl−CsCl Solutions at $I = 1.0\ \mathrm{mol \cdot L^{-1}}$ and Free Energy of Mixing for the Protonation at $T = 298.15$ K

LiCl−KCl	NaCl−KCl	NaCl−LiCl	LiCl−CsCl
$\log_{10} K_1^{\mathrm{H}}$			
$\Delta_1 = -0.038 \pm 0.005$[a] $\Delta G_{\mathrm{mix}} = 0.22 \pm 0.03$ $\sigma_{(\mathrm{fit})}$[b] $= 0.006$	$\Delta_1 = -0.037 \pm 0.005$[a] $\Delta G_{\mathrm{mix}} = 0.21 \pm 0.03$ $\sigma_{(\mathrm{fit})}$[b] $= 0.002$	$\Delta_1 = -0.006 \pm 0.006$[a] $\Delta G_{\mathrm{mix}} = 0.04 \pm 0.03$ $\sigma_{(\mathrm{fit})}$[b] $= 0.014$	$\Delta_1 = -0.130 \pm 0.009$[a] $\Delta G_{\mathrm{mix}} = 0.74 \pm 0.05$ $\sigma_{(\mathrm{fit})}$[b] $= 0.024$
$\log_{10} K_2^{\mathrm{H}}$			
$\Delta_2 = -0.031 \pm 0.003$ $\Delta G_{\mathrm{mix}} = 0.18 \pm 0.02$ $\sigma_{(\mathrm{fit})} = 0.002$	$\Delta_2 = -0.023 \pm 0.002$ $\Delta G_{\mathrm{mix}} = 0.13 \pm 0.01$ $\sigma_{(\mathrm{fit})} = 0.001$	$\Delta_2 = -0.014 \pm 0.003$ $\Delta G_{\mathrm{mix}} = 0.08 \pm 0.02$ $\sigma_{(\mathrm{fit})} = 0.004$	$\Delta_2 = -0.064 \pm 0.005$ $\Delta G_{\mathrm{mix}} = 0.37 \pm 0.03$ $\sigma_{(\mathrm{fit})} = 0.006$
$\log_{10} K_3^{\mathrm{H}}$			
$\Delta_3 = -0.010 \pm 0.004$ $\Delta G_{\mathrm{mix}} = 0.06 \pm 0.02$ $\sigma_{(\mathrm{fit})} = 0.009$	$\Delta_3 = -0.014 \pm 0.002$ $\Delta G_{\mathrm{mix}} = 0.08 \pm 0.01$ $\sigma_{(\mathrm{fit})} = 0.0009$	$\Delta_3 = 0$ $\Delta G_{\mathrm{mix}} = 0$ $\sigma_{(\mathrm{fit})} = 0.010$	$\Delta_3 = -0.094 \pm 0.008$ $\Delta G_{\mathrm{mix}} = 0.54 \pm 0.04$ $\sigma_{(\mathrm{fit})} = 0.026$
$\log_{10} K_4^{\mathrm{H}}$			
$\Delta_4 = 0$ $\Delta G_{\mathrm{mix}} \approx 0$ $\sigma_{(\mathrm{fit})} = 0.008$	$\Delta_4 = 0$ $\Delta G_{\mathrm{mix}} \approx 0$ $\sigma_{(\mathrm{fit})} = 0.002$	$\Delta_4 = 0$ $\Delta G_{\mathrm{mix}} \approx 0$ $\sigma_{(\mathrm{fit})} = 0.006$	$\Delta_4 = -0.038 \pm 0.023$ $\Delta G_{\mathrm{mix}} = 0.22 \pm 0.13$ $\sigma_{(\mathrm{fit})} = 0.030$

[a] Value ± standard deviation. [b] Standard deviation in the fit of eq 3.

Table 5. Mean Values of Mixing Parameters at $I = 1.0\ \mathrm{mol \cdot L^{-1}}$ and $T = 298.15$ K

		ΔG_{mix}		ΔG_X
z	Δ	$\mathrm{kJ \cdot mol^{-1}}$	$\log_{10} \beta_X$	$\mathrm{kJ \cdot mol^{-1}}$
1	-0.015 ± 0.008[a]	0.08 ± 0.05[a]	-1.29 ± 0.09[a]	7.3 ± 0.6[a]
2	-0.016 ± 0.008	0.09 ± 0.04	-1.23 ± 0.07	7.0 ± 0.4
3	-0.019 ± 0.007	0.11 ± 0.04	-1.13 ± 0.07	6.5 ± 0.4
4	-0.023 ± 0.005	0.13 ± 0.03	-1.00 ± 0.08	5.7 ± 0.5
5	-0.030 ± 0.005	0.17 ± 0.03	-0.82 ± 0.12	4.7 ± 0.7
6	-0.038 ± 0.006	0.22 ± 0.04	-0.61 ± 0.15	3.5 ± 0.9
$\partial X/\partial(z^2 - 1)$	-0.0009 ± 0.0002	0.005 ± 0.001	0.019 ± 0.003	-0.11 ± 0.02

[a] 95 % confidence interval.

The deviation from linear mixing can be expressed by the free energy of mixing

$$\Delta G_{\mathrm{mix}} = -2.303RT\Delta \qquad (5)$$

The values of ΔG_{mix} (in $\mathrm{kJ \cdot mol^{-1}}$) are reported in Table 4. The lowering of protonation constants in mixed alkali metal chloride solutions can be also interpreted in terms of the formation of mixed-metal complexes[3]

$$\mathrm{MH}_i\mathrm{mlt} + \mathrm{M}' = \mathrm{MM}'\mathrm{H}_i\mathrm{mlt}$$

whose stability is proportional to the parameter[13]

$$K_X = (10^{-\Delta} - 1)/(2I)$$

For $\mathrm{h_6mlt}$ in different MCl−M′Cl mixtures, log K_X ranges between −0.5 and −0.9 for $I = 1.0\ \mathrm{mol \cdot L^{-1}}$.

By considering as a whole the mixing effects in alkali metal solutions studied in this laboratory (succinate,[3] 1,2,3-propanetricarboxylate,[3] citrate,[1] 1,2,3,4-butantetracarboxylate,[3] and mellitate), we were able to determine an average value of mixing parameters as a function of z (charge of the anion) according to the equation

$$X = a + b(z^2 - 1)$$

where $X = \Delta$, ΔG_{mix}, log K_X, and ΔG_X and a and b are empirical parameters. Table 5 reports the X values at $I = 1.0\ \mathrm{mol \cdot L^{-1}}$ for $z = 1$ to 6 and the values of $\partial X/\partial(z^2 - 1)$ parameters, which define the variation of X with anion charge. Note that these values must be considered as rough estimates, independent of alkali metal mixture.

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