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Ionic Conductivity of Selected 2:1 Electrolytes in Dilute Solutions of Mixed Aqueous–Organic Solvents at 298.15 K

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Equivalent conductivities of dilute solutions of calcium nitrate, cadmium nitrate, zinc nitrate, and calcium chloride (c < 0.0021 eq·dm^{-3}) were measured in binary aqueous mixtures containing up to 70 wt % cosolvent (methanol, ethanol, and acetone) at 298.15 K ± 0.1. Data were treated by the Fuoss−Edelson equation, and its parameters, the limiting equivalent conductivity, Λ_0, and the primary association constants, K_{1A}, were evaluated. Variations in Walden products and K_{1A} were interpreted in terms of ionic properties as well as solvent structure and dielectric constant.

Introduction

Modeling complex multicomponent systems such as soil solutions cocontaminated with metals, organic ligands, and solvents as a result of codisposal[1,2] or accidental or direct discharge[3] is partly hindered by the scarcity of data describing ion association (type of ionic species and ionic association constants) in mixed solvents. Such data constitute essential components of mass balance equations and primary inputs of soil chemical models. Ion association data are mostly available for 1:1 electrolytes, particularly alkali halides in binary aqueous–organic solvents.[4–17] Less work is reported on the ionic association of polyvalent unsymmetrical electrolytes in these solvent mixtures. Višic and colleagues carried out potentiometric investigations to determine the stability of cadmium chloride in aqueous mixtures of 2-propanol,[18] acetone,[19] *t*-butanol,[20] 2-butanone,[21] and 2-butanol.[22] Barcynska et al.[23] reported the stability constants of calcium chloride in 1-propanol + water. Baker and Abd El-Wahab Mohamed[24] thoroughly studied the conductivity of some alkaline earth metal salts in dioxane + water mixtures of different composition and at different temperatures. For this purpose and in the absence of published values, studies of electrolytic conductance in binary mixed aqueous methanol, ethanol, and acetone solvents have been initiated to provide experimental data on the primary ion association constant, K_{1A}, of calcium nitrates, cadmium nitrates, zinc nitrates, and calcium chloride. The solvents selected were neutral amphiprotic (methanol and ethanol) and dipolar aprotic (acetone). These electrolytes (cadmium and zinc nitrates) and solvents (ethanol and acetone) are of interest in environmental soil science studies and have been reported as major contaminants in the subsurface environments of a number of Department of Energy sites and leaking underground disposal tanks.[2] Calcium nitrate and chloride were included for comparison.

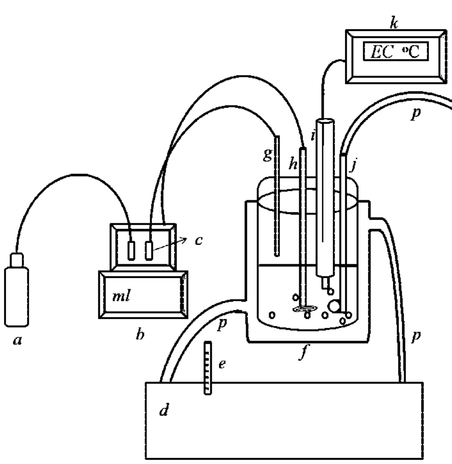

Figure 1. Schematic diagram of the experimental setup: *a*, standardized titrant; *b*, Mettler Toledo DL50 autotitrator; *c*, syringes; *d*, water bath; *e*, thermometer; *f*, water-jacketed reaction cell; *g*, pipet; *h*, stirring rod; *i*, TetraConL conductivity measuring cell equipped with a temperature sensor; *j*, gas diffuser; *k*, LF 3000 microprocessor conductivity meter; *l*, Erlenmeyer flask containing wt % cosolvent; *m*, glass tubes; *n*, nitrogen tank; *o*, nitrogen tank regulator; *p*, insulated polyvinyl tubes.

Table 1. Dielectric Constants ϵ, Densities ρ, and Viscosities η for Cosolvent (1) +Water (2) at T = 298.15 K

100 W_1	ϵ	ρ/(g·cm^{-3})	η/(mPa·s)
	Water[a]		
0	78.48	0.997	0.890
	Methanol (1)[b] + Water (2)		
10	74.21	0.982	1.098
30	65.19[c]	0.951	1.444
50	56.05	0.916	1.572
70	46.90[c]	0.871	1.339
	Ethanol (1)[c] + Water (2)		
8.6	73.08[d]	0.977	1.230[d]
10	72.29[d]	0.982	1.501
26.6	63.01[d]	0.947	2.103[d]
30	61.11[d]	0.954	2.667
46.3	51.99[d]	0.907	2.874[d]
50	49.92[d]	0.914	2.813
67	40.41[d]	0.877	2.701[d]
	Acetone (1)[e] + Water (2)		
10	73.02	0.983	0.952
30	61.04	0.954	1.075
50	48.22	0.916	0.911
70	36.42	0.887	0.747

[a] ϵ and ρ from ref 28, η from ref 29. [b] ϵ from ref 28, ρ from ref 29, η from ref 30. [c] ϵ and η from ref 30, ρ from ref 29. [d] Interpolated values. [e] ϵ and ρ from ref 30, ρ from ref 28.

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Table 2. Average Equivalent Conductivity Λ at Concentration *c* of Studied 2:1 Electrolytes in Cosolvent (1) + Water (2) at T = 298.15 K

Methanol (1) + Water (2)

(100 W_1 = 10)		(100 W_1 = 30)		(100 W_1 = 50)	
10^4c ($eq \cdot dm^{-3}$)	$\Lambda \pm \Delta\Lambda$ ($S \cdot cm^2 \cdot eq^{-1}$)	10^4c ($eq \cdot dm^{-3}$)	$\Lambda \pm \Delta\Lambda$ ($S \cdot cm^2 \cdot eq^{-1}$)	10^4c ($eq \cdot dm^{-3}$)	$\Lambda \pm \Delta\Lambda$ ($S \cdot cm^2 \cdot eq^{-1}$)
		Calcium Nitrate			
1.94	106.44 ± 0.01	1.94	78.49 ± 0.00	1.94	70.28 ± 0.07
3.88	105.55 ± 0.02	3.88	77.80 ± 0.00	3.88	69.65 ± 0.05
5.81	104.84 ± 0.01	5.82	77.27 ± 0.06	5.82	69.10 ± 0.03
7.74	104.28 ± 0.00	7.75	76.84 ± 0.05	7.75	68.65 ± 0.01
9.67	103.78 ± 0.01	9.68	76.36 ± 0.04	9.68	68.2 ± 0.01
11.6	103.39 ± 0.01	11.6	76.06 ± 0.04	11.6	67.75 ± 0.01
13.5	102.92 ± 0.01	13.5	75.64 ± 0.03	13.5	67.33 ± 0.04
15.4	102.59 ± 0.01	15.4	75.35 ± 0.02	15.4	66.98 ± 0.08
17.3	102.19 ± 0.02	17.4	75.05 ± 0.01	17.4	66.65 ± 0.03
19.2	101.80 ± 0.01	19.3	74.75 ± 0.06	19.3	66.38 ± 0.03
		Calcium Chloride			
1.99	107.02 ± 0.35	1.99	76.06 ± 0.11	1.99	65.77 ± 0.01
3.97	105.37 ± 0.44	3.97	75.28 ± 0.15	3.97	64.80 ± 0.04
5.95	104.47 ± 0.54	5.95	74.59 ± 0.08	5.95	64.19 ± 0.16
7.92	103.70 ± 0.60	7.93	74.10 ± 0.14	7.92	63.60 ± 0.13
9.89	103.01 ± 0.56	9.90	73.58 ± 0.11	9.89	63.12 ± 0.04
11.9	102.43 ± 0.41	11.9	73.05 ± 0.27	11.9	62.61 ± 0.04
13.8	101.86 ± 0.26	13.8	72.58 ± 0.12	13.8	62.19 ± 0.04
15.8	101.45 ± 0.33	15.8	72.25 ± 0.11	15.8	61.77 ± 0.04
17.7	101.05 ± 0.29	17.7	71.80 ± 0.13	17.7	61.42 ± 0.08
19.7	100.80 ± 0.02	19.7	71.44 ± 0.11	19.7	61.02 ± 0.07
		Cadmium Nitrate			
2.10	92.99 ± 0.02	2.10	68.19 ± 0.00	2.10	61.56 ± 0.04
4.19	92.19 ± 0.04	4.20	67.51 ± 0.02	4.20	60.87 ± 0.10
6.28	91.51 ± 0.06	6.29	66.95 ± 0.04	6.29	60.33 ± 0.08
8.37	91.01 ± 0.01	8.38	66.50 ± 0.03	8.38	59.84 ± 0.06
10.5	90.47 ± 0.01	10.5	66.16 ± 0.01	10.5	59.43 ± 0.11
12.5	90.10 ± 0.02	12.5	65.84 ± 0.04	12.5	58.94 ± 0.03
14.6	89.68 ± 0.00	14.6	65.46 ± 0.06	14.6	58.64 ± 0.03
16.7	89.25 ± 0.02	16.7	65.18 ± 0.06	16.7	58.28 ± 0.06
18.7	88.84 ± 0.00	18.8	64.88 ± 0.05	18.8	57.96 ± 0.09
20.8	88.49 ± 0.01	20.8	64.57 ± 0.01	20.8	57.64 ± 0.08
		Zinc Nitrate			
2.10	94.83 ± 0.01	2.10	68.12 ± 0.00	2.10	62.08 ± 0.01
4.19	93.99 ± 0.05	4.20	67.48 ± 0.01	4.19	61.43 ± 0.05
6.28	93.24 ± 0.08	6.29	66.93 ± 0.06	6.28	60.91 ± 0.02
8.37	92.68 ± 0.10	8.38	66.47 ± 0.04	8.37	60.55 ± 0.02
10.5	92.23 ± 0.04	10.5	66.12 ± 0.02	10.5	60.21 ± 0.05
12.5	91.81 ± 0.01	12.6	65.74 ± 0.01	12.5	59.89 ± 0.04
14.6	91.36 ± 0.02	14.6	65.43 ± 0.01	14.6	59.57 ± 0.02
16.7	90.98 ± 0.04	16.7	65.09 ± 0.01	16.7	59.28 ± 0.06
18.7	90.63 ± 0.01	18.8	64.81 ± 0.04	18.7	58.91 ± 0.06
20.8	90.26 ± 0.01	20.8	64.55 ± 0.00	20.8	58.66 ± 0.05

(100 W_1 = 70)

10^4c ($eq \cdot dm^{-3}$)	$\Lambda \pm \Delta\Lambda$ ($S \cdot cm^2 \cdot eq^{-1}$)	10^4c ($eq \cdot dm^{-3}$)	$\Lambda \pm \Delta\Lambda$ ($S \cdot cm^2 \cdot eq^{-1}$)	10^4c ($eq \cdot dm^{-3}$)	$\Lambda \pm \Delta\Lambda$ ($S \cdot cm^2 \cdot eq^{-1}$)
		Calcium Chloride			
1.98	68.28 ± 0.21	9.87	64.89 ± 0.30	15.7	63.15 ± 0.30
3.96	67.17 ± 0.30	11.8	64.26 ± 0.27	17.7	62.63 ± 0.28
5.93	66.33 ± 0.23	13.8	63.72 ± 0.28	19.6	62.14 ± 0.29
7.90	65.54 ± 0.28				

Ethanol (1) + Water (2)

(100 W_1 = 10)		(100 W_1 = 30)		(100 W_1 = 50)	
10^4c ($eq \cdot dm^{-3}$)	$\Lambda \pm \Delta\Lambda$ ($S \cdot cm^2 \cdot eq^{-1}$)	10^4c ($eq \cdot dm^{-3}$)	$\Lambda \pm \Delta\Lambda$ ($S \cdot cm^2 \cdot eq^{-1}$)	10^4c ($eq \cdot dm^{-3}$)	$\Lambda \pm \Delta\Lambda$ ($S \cdot cm^2 \cdot eq^{-1}$)
		Calcium Nitrate			
1.94	101.49 ± 0.21	1.94	62.95 ± 0.06	1.94	50.29 ± 0.06
3.87	100.69 ± 0.25	3.88	62.36 ± 0.00	3.87	49.70 ± 0.01
5.80	100.07 ± 0.14	5.81	62.01 ± 0.05	5.80	49.31 ± 0.03
7.73	99.52 ± 0.18	7.74	61.66 ± 0.04	7.73	48.92 ± 0.01
9.65	99.08 ± 0.13	9.67	61.27 ± 0.02	9.65	48.55 ± 0.06
11.6	98.68 ± 0.17	11.6	60.94 ± 0.01	11.6	48.27 ± 0.04
13.5	98.28 ± 0.19	13.5	60.65 ± 0.01	13.5	48.01 ± 0.04
15.4	97.87 ± 0.21	15.4	60.38 ± 0.01	15.4	47.67 ± 0.08
17.3	97.51 ± 0.23	17.3	60.16 ± 0.04	17.3	47.47 ± 0.03
19.2	97.15 ± 0.23	19.2	59.89 ± 0.01	19.2	47.21 ± 0.01
		Calcium Chloride			
1.99	97.41 ± 0.25	1.98	60.33 ± 0.13	1.99	47.20 ± 0.05
3.97	96.46 ± 0.23	3.95	59.33 ± 0.08	3.97	46.38 ± 0.08
5.94	95.64 ± 0.36	5.92	58.67 ± 0.07	5.95	45.80 ± 0.13
7.92	94.96 ± 0.33	7.89	58.25 ± 0.07	7.92	45.32 ± 0.04
9.89	94.33 ± 0.38	9.86	57.71 ± 0.07	9.90	44.93 ± 0.03
11.9	93.74 ± 0.36	11.8	57.21 ± 0.06	11.9	44.56 ± 0.10
13.8	93.19 ± 0.34	13.8	56.75 ± 0.01	13.8	44.20 ± 0.24
15.8	92.68 ± 0.32	15.7	56.39 ± 0.11	15.8	43.87 ± 0.10
17.7	92.18 ± 0.31	17.7	55.98 ± 0.06	17.7	43.46 ± 0.13
19.7	91.71 ± 0.30	19.6	55.61 ± 0.03	19.7	43.09 ± 0.15
		Cadmium Nitrate			
2.10	88.75 ± 0.00	2.10	54.54 ± 0.03	2.10	44.16 ± 0.00
4.19	87.95 ± 0.02	4.20	53.92 ± 0.01	4.20	43.56 ± 0.00
6.28	87.43 ± 0.04	6.29	53.52 ± 0.01	6.30	43.08 ± 0.01
8.36	86.69 ± 0.04	8.38	53.19 ± 0.00	8.39	42.73 ± 0.02
10.4	86.37 ± 0.03	10.5	52.82 ± 0.00	10.5	42.33 ± 0.03
12.5	85.87 ± 0.02	12.5	52.51 ± 0.01	12.6	42.13 ± 0.04

Table 2 Continued

Ethanol (1) + Water (2)

$(100\ W_1 = 10)$		$(100\ W_1 = 30)$		$(100\ W_1 = 50)$	
10^4c ($eq \cdot dm^{-3}$)	$\Lambda \pm \Delta\Lambda$ ($S \cdot cm^2 \cdot eq^{-1}$)	10^4c ($eq \cdot dm^{-3}$)	$\Lambda \pm \Delta\Lambda$ ($S \cdot cm^2 \cdot eq^{-1}$)	10^4c ($eq \cdot dm^{-3}$)	$\Lambda \pm \Delta\Lambda$ ($S \cdot cm^2 \cdot eq^{-1}$)
14.6	85.46 ± 0.01	14.6	52.30 ± 0.01	14.6	41.82 ± 0.02
16.6	85.24 ± 0.01	16.7	52.04 ± 0.01	16.7	41.45 ± 0.02
18.7	84.79 ± 0.02	18.8	51.80 ± 0.02	18.8	41.25 ± 0.05
20.7	84.45 ± 0.01	20.8	51.61 ± 0.01	20.8	40.93 ± 0.01
Zinc Nitrate					
2.10	87.51 ± 0.10	2.10	54.21 ± 0.01	2.10	44.43 ± 0.01
4.20	86.69 ± 0.00	4.19	53.64 ± 0.03	4.20	43.84 ± 0.03
6.29	86.14 ± 0.01	6.29	53.20 ± 0.06	6.30	43.41 ± 0.01
8.37	85.63 ± 0.07	8.37	52.82 ± 0.03	8.39	43.01 ± 0.05
10.5	85.12 ± 0.06	10.5	52.52 ± 0.00	10.5	42.66 ± 0.03
12.5	84.77 ± 0.02	12.5	52.22 ± 0.04	12.6	42.36 ± 0.01
14.6	84.37 ± 0.02	14.6	51.98 ± 0.03	14.6	41.96 ± 0.01
16.7	84.03 ± 0.03	16.7	51.70 ± 0.01	16.7	41.72 ± 0.00
18.7	83.68 ± 0.02	18.7	51.46 ± 0.04	18.8	41.41 ± 0.04
20.8	83.37 ± 0.02	20.8	51.24 ± 0.01	20.8	41.18 ± 0.01

$(100\ W_1 = 70)$

10^4c ($eq \cdot dm^{-3}$)	$\Lambda \pm \Delta\Lambda$ ($S \cdot cm^2 \cdot eq^{-1}$)	10^4c ($eq \cdot dm^{-3}$)	$\Lambda \pm \Delta\Lambda$ ($S \cdot cm^2 \cdot eq^{-1}$)	10^4c ($eq \cdot dm^{-3}$)	$\Lambda \pm \Delta\Lambda$ ($S \cdot cm^2 \cdot eq^{-1}$)
1.99	42.34 ± 0.06	9.90	39.57 ± 0.06	15.8	38.24 ± 0.04
3.97	41.37 ± 0.02	11.9	39.08 ± 0.05	17.7	37.88 ± 0.07
5.95	40.65 ± 0.07	13.8	38.67 ± 0.05	19.7	37.54 ± 0.06
7.92	40.07 ± 0.08				

Acetone (1) + Water (2)

$(100\ W_1 = 10)$		$(100\ W_1 = 30)$		$(100\ W_1 = 50)$	
10^4c ($eq \cdot dm^{-3}$)	$\Lambda \pm \Delta\Lambda$ ($S \cdot cm^2 \cdot eq^{-1}$)	10^4c ($eq \cdot dm^{-3}$)	$\Lambda \pm \Delta\Lambda$ ($S \cdot cm^2 \cdot eq^{-1}$)	10^4c ($eq \cdot dm^{-3}$)	$\Lambda \pm \Delta\Lambda$ ($S \cdot cm^2 \cdot eq^{-1}$)
Calcium Chloride					
1.98	110.06 ± 0.18	1.98	84.67 ± 0.47	1.99	73.06 ± 0.02
3.96	108.86 ± 0.11	3.96	83.12 ± 0.40	3.97	71.10 ± 0.23
5.94	107.84 ± 0.06	5.94	81.74 ± 0.26	5.95	69.82 ± 0.41
7.91	107.01 ± 0.22	7.91	80.65 ± 0.28	7.92	68.71 ± 0.30
9.88	106.49 ± 0.38	9.88	79.67 ± 0.07	9.89	67.62 ± 0.16
11.8	105.85 ± 0.37	11.8	78.83 ± 0.24	11.9	66.79 ± 0.25
13.8	105.20 ± 0.27	13.8	78.00 ± 0.41	13.8	66.03 ± 0.25
15.8	104.55 ± 0.28	15.8	77.40 ± 0.36	15.8	65.25 ± 0.31
17.7	104.04 ± 0.25	17.7	76.60 ± 0.40	17.7	64.49 ± 0.11
19.7	103.54 ± 0.14	19.7	76.06 ± 0.32	19.7	63.82 ± 0.13

$(100\ W_1 = 70)$

10^4c ($eq \cdot dm^{-3}$)	$\Lambda \pm \Delta\Lambda$ ($S \cdot cm^2 \cdot eq^{-1}$)	10^4c ($eq \cdot dm^{-3}$)	$\Lambda \pm \Delta\Lambda$ ($S \cdot cm^2 \cdot eq^{-1}$)	10^4c ($eq \cdot dm^{-3}$)	$\Lambda \pm \Delta\Lambda$ ($S \cdot cm^2 \cdot eq^{-1}$)
Calcium Chloride					
1.99	70.97 ± 0.11	9.89	63.33 ± 0.36	15.8	60.20 ± 0.35
3.97	68.33 ± 0.37	11.9	62.18 ± 0.41	17.7	59.34 ± 0.26
5.95	66.34 ± 0.37	13.8	61.17 ± 0.25	19.7	58.51 ± 0.28
7.92	64.63 ± 0.36				

Experimental Section

Chemicals. HPLC grade methanol (CAS: 67-56-1, Fisher Scientific, Pittsburgh, PA), acetone (CAS: 67-64-1, Fisher Scientific, Pittsburgh, PA) and reagent grade SDA_1 anhydrous ethanol (95.27 %, CAS: 64-17-5, Fisher Scientific, Pittsburgh, PA) solvents were used without further purification. The electrical conductivity of each solvent was measured, and the reported values were [0.39 (double-distilled and deionized water), 0.04 (methanol), 0.1 (ethanol), and 0.01 (acetone)] $\mu S \cdot cm^{-1}$. All cosolvent fractions were prepared by weight using a Sartorious E2000D 3 places balance.

Certified reagent grade $Ca(NO_3)_2 \cdot 4H_2O$ (CAS: 13477-34-4, Fisher Scientific, Pittsburgh, PA), $Cd(NO_3)_2 \cdot 4H_2O$ (CAS: 10022-68-1, Fisher Scientific, Pittsburgh, PA), $Zn(NO_3)_2 \cdot 6H_2O$ (CAS: 7779-88-6, Fisher Scientific, Pittsburgh, PA), and $CaCl_2$ (CAS: 10043-52-4, Fisher Scientific, Pittsburgh, PA) were used to prepare titrant stock solutions. The exact concentrations of all titrant stock solutions were obtained by colorimetric titration against a standard 0.01 $mol \cdot dm^{-3}$ EDTA solution and Calgamite indicator. [25]

Apparatus and Procedure. Conductivity measurements in mixed aqueous–organic solvents are highly sensitive to atmospheric pressure and carbon dioxide.[26] Therefore special care was taken to ensure complete isolation of the system from the atmosphere. Before each run, the water-jacketed reaction cell was rinsed several times with the solvent of interest and then flushed for approximately 10 min with highly purified nitrogen gas (Ultra Pure nitrogen, Airgas, Bowling Green, KY) which bubbled through the solvent just before entering the cell.[27] A known volume of cosolvent, V_s (weighed and corrected for density), was carefully transferred to the cell and purged with solvent-saturated nitrogen until the measured electrical conductivity, EC, stabilized. This value was recorded and subtracted from all subsequent EC readings. After thermal equilibrium had been attained ($T = 298.15$ K ± 0.1), and the solvent EC determined, an exact volume of titrant, V, was added using a Mettler Toledo DL50 autotitrator, and the solution was allowed to equilibrate for 3 min before the specific conductivity and the solution temperature were recorded using an LF 3000 Microprocessor Conductivity meter equipped with a TetraConL conductivity measuring cell (WTW). At all times during the titration, the solution was continuously stirred and a solvent-saturated $N_2(g)$ pressure head was maintained. Temperature was kept constant by allowing water from a water bath to circulate through the water-jacketed reaction cell. The temperature of the water bath was continuously adjusted so that the temperature inside the reaction cell was maintained at $T = 298.15$ K ± 0.1. Each titration was generally completed within one hour and was

Table 3. Limiting Equivalent Conductivity Λ_0 and Ionic Association Constants K_{1A} for Studied 2:1 Electrolytes in Cosolvent (1) + Water (2) at T = 298.15 K

100 W_1	$\Lambda_0\Delta\Lambda_0$/S·cm^2·eq^{-1}	$K_{1A} \pm \Delta K_{1A}$
	Calcium Nitrate + Methanol (1) + Water (2)	
0	130.96[a]	$10^{-4.80}$[b]
10	108.21 ± 0.01	10.8 ± 0.2
30	79.99 ± 0.01	14.4 ± 0.3
50	71.95 ± 0.02	23.0 ± 0.2
	Calcium Nitrate + Ethanol (1) + Water (2)	
10	103.17 ± 0.18	10.8 ± 0.3
30	64.14 ± 0.01	17.2 ± 0.1
50	51.50 ± 0.03	22.9 ± 0.1
	Cadmium Nitrate + Methanol (1) + Water (2)	
0	125.85[a]	2.04[b]
10	94.80 ± 0.01	12.4 ± 0.1
30	69.61 ± 0.01	14.8 ± 0.9
50	63.14 ± 0.07	28.0 ± 0.1
	Cadmium Nitrate + Ethanol (1) + Water (2)	
10	90.38 ± 0.03	13.0 ± 0.2
30	55.59 ± 0.01	18.3 ± 0.0
50	45.36 ± 0.02	34.1 ± 1.1
	Zinc Nitrate + Methanol (1) + Water (2)	
0	124.86[a]	2.51[b]
10	96.60 ± 0.06	12.1 ± 0.6
30	69.56 ± 0.02	14.9 ± 0.0
50	63.35 ± 0.01	28.8 ± 0.2
	Zinc Nitrate + Ethanol (1) + Water (2)	
10	89.09 ± 0.02	11.3 ± 0.1
30	55.29 ± 0.04	19.5 ± 0.2
50	45.69 ± 0.01	36.8 ± 0.2
	Calcium Chloride + Methanol (1) + Water (2)	
0	135.7[a]	2.63[b]
10	108.60 ± 0.32	27.4 ± 0.1
30	77.75 ± 0.13	31.5 ± 0.3
50	67.40 ± 0.06	43.0 ± 0.1
70	70.59 ± 0.23	61.4 ± 2.2
	Calcium Chloride + Ethanol (1) + Water (2)	
10	99.33 ± 0.28	28.7 ± 0.7
30	61.64 ± 0.05	55.9 ± 0.1
50	48.51 ± 0.02	58.9 ± 0.3
70	44.11 ± 0.05	84.6 ± 0.7
	Calcium Chloride + Acetone (1) + Water (2)	
10	112.16 ± 0.16	38.2 ± 1.8
30	87.25 ± 0.35	150.0 ± 0.4
50	76.16 ± 0.22	219.4 ± 1.9
70	76.03 ± 0.26	487.5 ± 13.6

[a] Values for Λ_0 of the studied electrolytes in water were computed from ionic equivalent conductance data (S^{-1}·cm^2·eq^{-1}) using Kohlrausch's Law of Independent Migration of Ions ($\Lambda_0 = \nu_+\lambda_+^0 + \nu_-\lambda_-^0$) where $\gamma^0_{Ca^{2+}}$ = 119.0; $\gamma^0_{Cl^-}$ = 76.36; $\gamma^-_{NO3}{}^0$ = 71.46 (Atkins);[34] $\lambda^0_{Zn^{2+}}$ = 106.8 (Bešter-Rogač et al.);[35] and $\lambda^0_{Cd^{2+}}$ = 108.78 (Barthel et al.).[36] [b] Values for K_{1A} for water were obtained from Smith and Martell.[37]

replicated twice. A schematic diagram of the experimental setup is presented in Figure 1.

Results and Discussion

The physical properties (dielectric constant ϵ, density ρ, and viscosity η) of cosolvent + water mixtures[28–30] are summarized in Table 1. The experimental equivalent conductivities, Λ, of the studied dilute 2:1 electrolyte solutions as functions of equivalent concentration c in cosolvent + water at T = 298.15 K are given in Table 2. In this table, average values of Λ along with the corresponding standard deviation $\Delta\Lambda$ are presented.

The conductance data were treated with the Fuoss and Edelson method.[31] For a given set of conductivity values (c_i, Λ_i, i = 1,. . ., n), two adjustable parameters, the limiting equivalent conductivity Λ_0 and the primary association constant K_{1A}, were derived from the following set of equations

$$\Lambda F = \Lambda_0 - XK_{1A}/\Lambda_0 \quad (1)$$

where

$$X = c\gamma_M \Lambda F(\Lambda F - \Lambda_0/2) \quad (2)$$

$$F = \{1/(1 - \delta c^{0.5}) + (\Lambda_0 - \lambda_0)/2\Lambda\}/\{1 + (\Lambda_0 - \lambda_0)/2\Lambda_0\} \quad (3)$$

$$\delta = \alpha\Lambda_0 + \beta \quad (4)$$

$$\alpha = 5.60 \cdot 10^6 q/\{(\epsilon T)^{1.5}(1 + q^{0.5})\} \quad (5)$$

$$\beta = 123.8/[\eta(\epsilon T)^{0.5}] \quad (6)$$

$$q = (2/3)(1 + \lambda_0/\Lambda_0)^{-1} \quad (7)$$

In these equations, δ represents the Onsager's slope for a 2:1 electrolyte divided by $\Lambda_0\lambda_0$, the limiting anionic conductivity, and T, the absolute temperature in K. The ion activity coefficient of M^{2+}, γ_M, was calculated using the extended Debye–Hückel equation.[32] In all cosolvent fractions, the ion size parameter, a_i, for calcium and zinc was assumed equal to 6 Å and 5 Å for cadmium, the values that are used in water.[33] The conductance parameters were computed using an iterative procedure until their values became constant. The initial values of Λ_0 in cosolvent + water were obtained from an extrapolation of the Kohlrausch plots (Λ vs $c^{0.5}$) except for water where Λ_0 values of the studied electrolytes were computed from ionic equivalent conductance data (S^{-1}·cm^2·eq^{-1}) using Kohlrausch's Law of Independent Migration of Ions (Table 3). The values of $\lambda_0(NO_3)^-$ and $\lambda_0(Cl)^-$ were taken as equal to their values in the pure solvents; that is, for nitrate, these were (60.95 and 24.82) S^{-1}·cm^2·eq^{-1} in methanol and ethanol, respectively, and for chloride, these were (52.38, 21.85, and 109.30) S^{-1}·cm^2·eq^{-1} in methanol, ethanol, and acetone, respectively (ref 38 and references therein), primarily because no data were available for the λ_0's of all the studied electrolytes at the various mixed aqueous–organic solvent concentrations. The only data for λ_0's were available for chloride ions in ethanol + water mixtures at T = 298.15 K by Spivey and Shedlovsky[39] and Hawas and Kay.[40] However, they were not adopted in this study for consistency and because the computation of these values, according to Spivey and Shedlovsky,[39] involved large errors and "their use is subject to considerable uncertainty". Nevertheless, λ_0 does not strongly influence the values of K_{1A} and Λ_0.[41] The lack of data also prevented the use of transport numbers for the calculation of λ_0's.

In the development of the Fuoss−Edelson equation, the following equilibria were considered $M^{2+} + L^- \overset{K_{1A}}{\Leftrightarrow} ML^+$ and $ML^+ + L^{-1} \overset{K_{2A}}{\Leftrightarrow} ML_2$ where $K_{1A} >> K_{2A}$. To test for this hypothesis, ΛF values were plotted as a function of X (eq 1) for the studied 2:1 electrolytes in the various cosolvents + water at T = 298.15 K (Figures 2 and 3). These plots represent individual data replicates. The linear variations in ΛF with X ($R^2 \geq 0.958$) for all studied systems, except for $CaCl_2$ in 10 wt % methanol + water ($R^2 = 0.740$), suggest that the formation of pairs other than the monovalent one is minor.[31]

The percent experimental error, % EE, was also calculated (data not shown) according to the following equation

$$\% \text{ EE} = 100 * \frac{(\Lambda - \Lambda_{calcd})}{\Lambda_{calcd}} \quad (8)$$

where Λ_{calcd} presents the final value of Λ in the iteration process. For all nitrate electrolytes, values of % EE ranged from (0.01

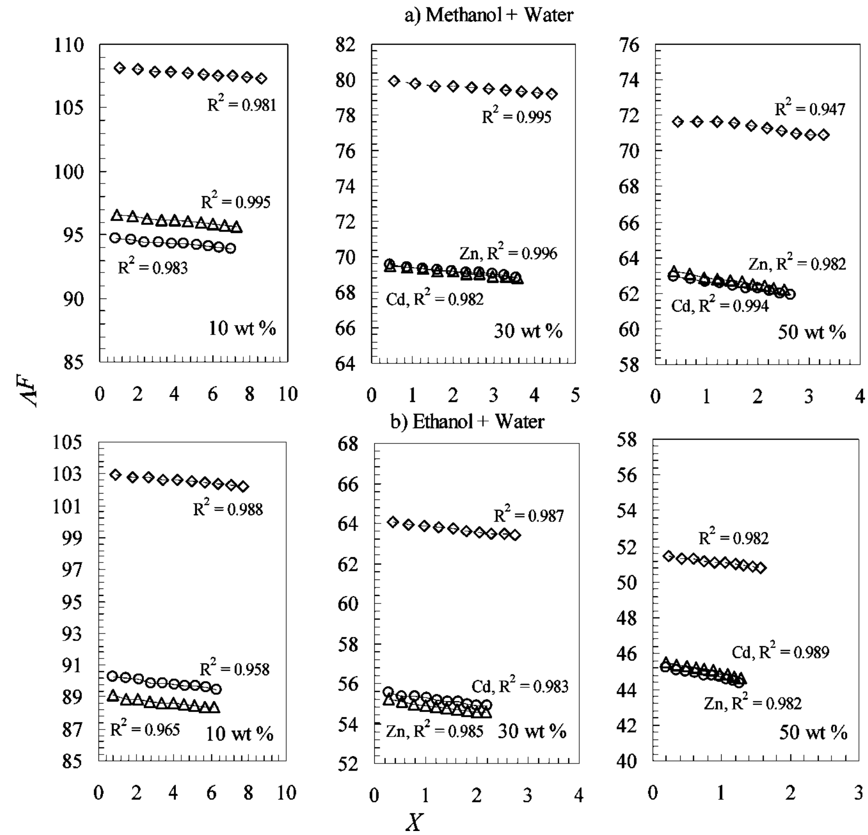

Figure 2. Fuoss−Edelson plots for ◇, $Ca(NO_3)_2$; ○, $Cd(NO_3)_2$; and Δ, $Zn(NO_3)_2$ in cosolvent + water systems at T = 298.15 K.

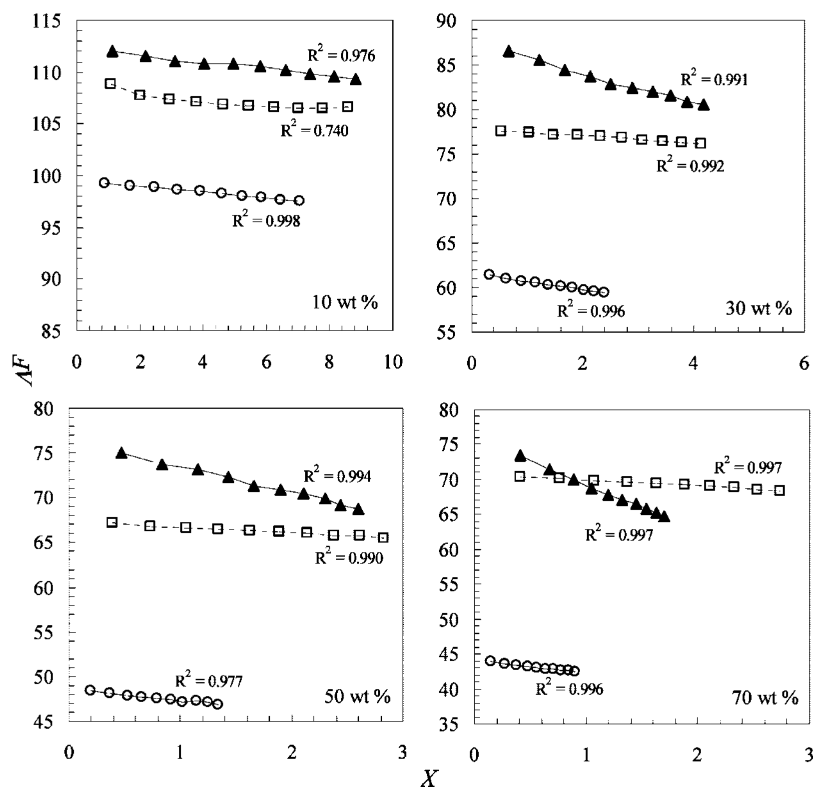

Figure 3. Fuoss−Edelson plots for $CaCl_2$ in □, methanol + water; ○, ethanol + water; and ▲, acetone + water systems at T = 298.15 K.

to 0.99) %. For $CaCl_2$, these values were higher and reached a maximum of 8.12 % in 70 wt % acetone + water.

The derived conductivity parameters (K_{1A} and Λ_0) for the various electrolytes in cosolvent + water systems at T = 298.15 K are presented in Table 3. The values of K_{1A} in water were taken from the literature.[41] Other values of K_{1A} in water are reported elsewhere, and they range from −1 to 0.98.[42] The large variation in these values reflects the differences in the methods (potentiometric, spectrophotometric, NMR, etc.) as well as the assumptions (ionic strength, activity vs concentration constants,

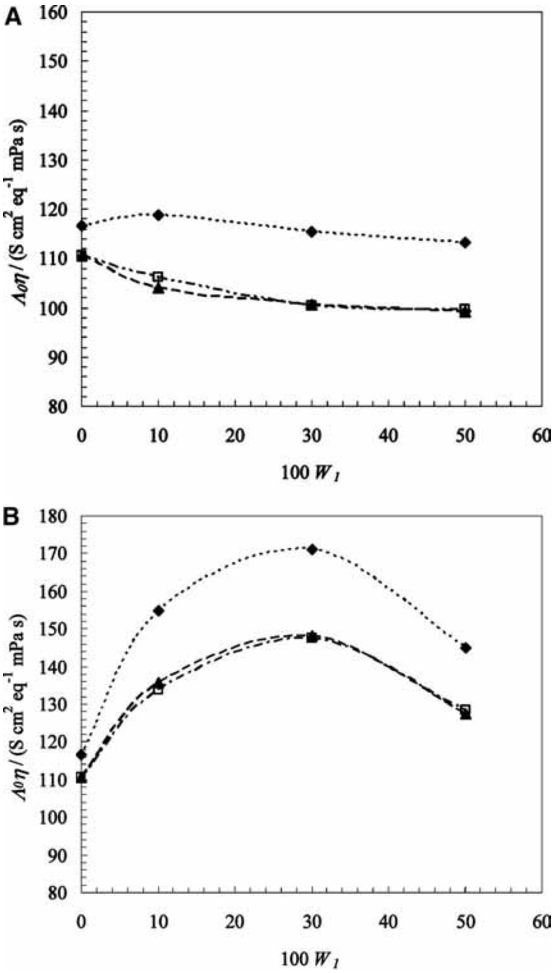

Figure 4. (a) Variation of the Walden products, $\Lambda_0\eta$, with percent weight cosolvent for: ♦, $Ca(NO_3)_2$; □, $Zn(NO_3)_2$; ▲, $Cd(NO_3)_2$ in methanol + water at $T = 298.15$ K. (b) Variation of the Walden products, $\Lambda_0\eta$, with percent weight cosolvent for: ♦, $Ca(NO_3)_2$; □, $Zn(NO_3)_2$; ▲, $Cd(NO_3)_2$ in ethanol + water solvents at $T = 298.15$ K.

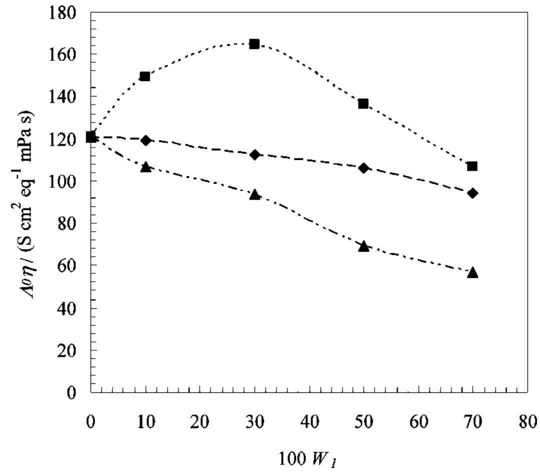

Figure 5. Variation of the Walden products, $\Lambda_0\eta$, of $CaCl_2$ with percent weight cosolvent in: ♦, methanol + water; ■, ethanol + water; and ▲, acetone + water solvents at $T = 298.15$ K. (Error bars smaller than data points.)

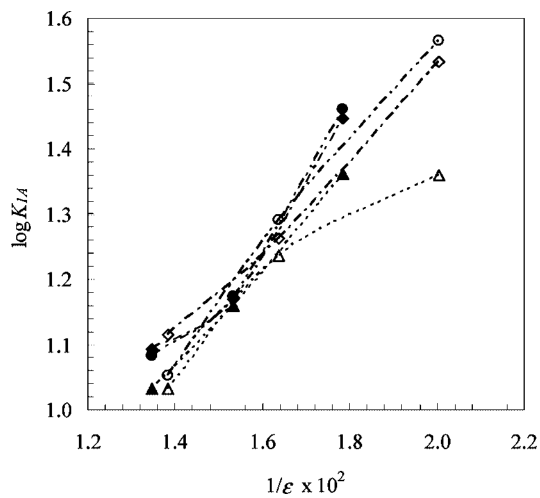

Figure 6. Plot of log K_{1A} vs the reciprocal of the dielectric constant of methanol (filled symbols) and ethanol (empty symbols) + water systems at $T = 298.15$ K for: Δ, $Ca(NO_3)^+$; ◇, $Cd(NO_3)^+$; and ○, $Zn(NO_3)^+$.

etc.) used for their determination. For all studied electrolytes, these values are lower than what we would expect if we extrapolate our data to zero cosolvent fraction but are within the range of values found in the literature.

Figures 4 and 5 show the variation of the Walden products, $\Lambda_0\eta$, for dilute nitrate and chloride electrolytes in cosolvent + water systems at $T = 298.15$ K. For both methanol and ethanol + water systems, the Walden products for $Zn(NO_3)_2$ and $Cd(NO_3)_2$ are nearly identical. These ions have similar ionic sizes, and their properties are largely masked by the strong acid properties of the solvents. The higher mobility of Ca(II) and NO_3^- is attributed to the smaller hydrated radius of the Ca(II) ion. In methanol + water, $\Lambda_0\eta$ values for all three nitrate electrolytes are largely independent of cosolvent composition (Figure 4a). This indicates that the mobility of these ions (Ca(II), Cd(II), Zn(II), and NO_3^-) in methanol + water is primarily determined by the solvent bulk viscosity and that the ion size parameter does not vary with cosolvent composition (Stoke's Law). In ethanol + water mixtures (Figure 4b), the variation in $\Lambda_0\eta$ as a function of cosolvent composition suggests that the mobility of Ca(II), Cd(II), Zn(II), and NO_3^- is not solely dependent on the solvent bulk viscosity but also depends on ion solvation. The observed maxima in $\Lambda_0\eta$ for the three electrolytes at about 30 wt % ethanol (same composition as the maxima in the viscosity)[43] agree with the results reported by Spivey and Shedlovsky[39] and are interpreted as the result of the large disruption caused by the addition of ethanol on the water structure in the vicinity of the ions.[43] Ion solvation might also be responsible for the decrease in the Walden products of $CaCl_2$ in methanol, ethanol, and acetone + water systems (Figure 5). Again, a structure enhancement is observed around (20 to 30) wt % ethanol.

The variations in log K_{1A} for the studied nitrate and chloride electrolytes as a function of the reciprocal dielectric constant of methanol, ethanol, and acetone + water mixtures are depicted in Figures 6 and 7. For nitrate salts (Figure 6), this relationship is almost linear ($R^2 = 0.91$ for $Ca(NO_3)^+$; 0.96 for $Cd(NO_3)^+$; and 0.97 for $Zn(NO_3)^+$), suggesting that the ionic association of these electrolytes in the studied cosolvents is primarily determined by electrostatic attractions between oppositely charged ions.[18–20,40,44,45] The large difference between log K_{1A} of $Ca(NO_3)^+$ (only observed at lower solvent dielectric constant or ~ 50 wt %) and log K_{1A} of $Cd(NO_3)^+$ or $Zn(NO_3)^+$ indicates the lower pairing potential of Ca(II) ions and may be the consequence of the harder Lewis acid character of Ca(II).[45] The primary association constants for $CaCl^+$ were larger than those for $Ca(NO_3)^+$ in both solvents and at all cosolvent concentrations (Figure 7). In methanol + water mixtures, log K_{1A} for $CaCl^+$ increased linearly ($R^2 \geq 0.99$) with the reciprocal of the

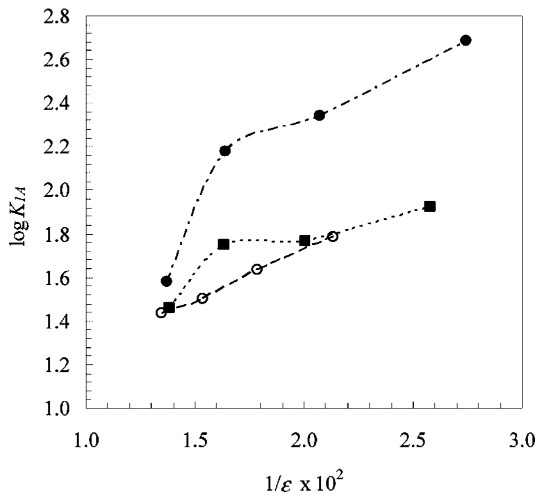

Figure 7. Plot of log K_{1A} vs the reciprocal of the dielectric constant, 100/ϵ, for $CaCl^+$ at $T = 298.15$ K in: ○, methanol + water; ■, ethanol + water; and •, acetone + water solvents.

solvent dielectric constant, suggesting that the ion-pair formation is largely regulated by the mixed solvent dielectric constant. In ethanol ($R^2 = 0.86$) and acetone + water mixtures ($R^2 = 0.81$), other specific solvent–solute interactions are apparent, especially at low acetone concentrations.[46]

Conclusions

The primary association constants of $CaCl^+$ and $M(NO_3)^+$ (M = Ca, Cd, and Zn) in aqueous binary mixtures of methanol, ethanol, and acetone as determined by conductometric titration seem to involve, in addition to electrostatic interactions, specific solvent–solute interactions. These appear to be related to the acid–base character of both the solvent and the solute. The mobility of M(II) and NO_3^- in methanol + water mixtures, at infinite dilution, as shown by the variation in the Walden product with solvent composition, seems to be solely dependent on the bulk viscosity of the solvent. In ethanol + water, solvent−solvent interactions such as ion solvation and water structure disruption seem to occur. This conclusion also applies to Ca(II) and Cl^- mobility at infinite dilution in all three cosolvents (methanol, ethanol, and acetone) + water systems.

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