

Limiting Molar Conductances and Thermodynamic Association Constants for Nickel(II), Cadmium(II), Magnesium(II), and Copper(II) Sulfates in Mixtures of Methanol and Water at 293.15 K

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Electrolytic conductivities of dilute solutions of nickel(II), cadmium(II), magnesium(II), and copper(II) sulfates in binary mixtures of methanol and water have been measured at 293.15 K. The limiting molar conductances (Λ_0) and the ion-association constants (K_A) of the electrolytes have been evaluated by analysis of the conductance data using the Lee and Wheaton conductivity equation in the Pethybridge and Taba modification.

Introduction

The study of transport properties (conductance, viscosity, transference numbers) of electrolytes is important because the values provide information about the solvation behavior of the ions. The use of mixed solvents makes possible the variation of the dielectric constant, so the ion solvation effect can be better studied. Solutions of 2:2 salts in water are electrostatically equivalent to 1:1 salts in a solvent of low dielectric constant (~ 20), implying that an unassociated 2:2 electrolyte is essentially impossible.^{1,2}

In the literature appear reports of conductivity measurements of transition-metal (II) sulfates in mixed solvents such as ZnSO₄ and CuSO₄ in water with dioxan, ethanol, acetone, and ethylene glycol;³ MnSO₄ in methanol + water,⁴ in dioxane + water,⁵ in acetone + water,⁶ in ethylene glycol + water;⁷ MgSO₄ in ethanol + water;⁸ and CuSO₄ and MnSO₄ in ethanol + water.⁹

As a part of an extensive investigation on the transport properties of 2:2 electrolytes in mixed solvents, we report conductance measurements of NiSO₄, CdSO₄, MgSO₄, and CuSO₄ in binary mixtures of methanol + water and in a composition range from 0 to 80% mass of methanol at 293.15 K. The concentration range in which conductance measurements were made was 0.0001–0.0060 mol·dm⁻³. The limiting molar conductivities (Λ_0) and the association constants (K_A) of the electrolytes have been derived. The results indicate the presence of specific ion–solvent and ion–ion forces in the solutions. These are reflected strongly in the values of Λ_0 and K_A .

Experimental Section

Methanol (Merck, 99.5%) with density 0.791 45 g·cm⁻³, viscosity 0.587 mPa·s, and refractive index 1.3294 at 293.15 K was used for the present measurements without further purification. These physical constants are in agreement with the literature values, $\rho = 0.791\ 29\ \text{g}\cdot\text{cm}^{-3}$, $\eta = 0.5929\ \text{mPa}\cdot\text{s}$, and $n_D = 1.3284$.¹⁰ The water was doubly distilled, and the conductance was found to be better than 0.50 μS at 293.15 K.

Nickel sulfate hexahydrate (NiSO₄·6H₂O) (Merck, 99.0%), cadmium sulfate monohydrate (CdSO₄·H₂O) (Fluka, 99.0%), magnesium sulfate anhydrous (MgSO₄) (Sigma, 99.5%),

Table 1. Densities (ρ), Viscosities (η), and Specific Conductivities (κ) of Methanol (1) + Water (2) Mixtures at 293.15 K

x_1	ρ g·cm ⁻³	η mPa·s	$10^6\kappa$ S·cm ⁻¹
0.0000	0.998 22	1.002	0.55
0.0588	0.981 27	1.318	0.76
0.1233	0.966 48	1.618	0.70
0.1942	0.951 59	1.805	0.53
0.2727	0.934 71	1.850	0.52
0.4576	0.894 32	1.612	0.51
0.6923	0.846 57	1.126	0.40
1.0000	0.791 45	0.587	0.15

and copper sulfate anhydrous (CuSO₄) (Fluka, 99.5%) were used without further purification.

The methanol + water mixtures were prepared by mass ($\pm 0.0001\ \text{g}$). The mole fractions were known to ± 0.0001 in all cases. A stock solution for each salt in pure water or the appropriate methanol + water mixture was prepared by mass, and the solutions were prepared by dilution. Molar concentrations of the solutions were obtained from the salt and solution masses and the density values. The accuracy of the molar concentrations was $\pm 0.000\ 01\ \text{mol}\cdot\text{dm}^{-3}$.

Densities were measured with an Anton Paar (DMA 58) microcomputer-controlled precision densimeter with a built-in solid-state thermostat at (293.15 \pm 0.01) K. The estimated uncertainty of the measured densities was $\pm 0.000\ 01\ \text{g}\cdot\text{cm}^{-3}$. Flow times of the solvent mixtures were measured with a viscosity measuring unit (Schott Geräte AVS 310), equipped with an Übbelohde capillary viscometer. The temperature was maintained constant within $\pm 0.03\ \text{K}$. The accuracy in the viscosity measurements was $\pm 0.001\ \text{mPa}\cdot\text{s}$. The measuring procedures for density and viscosity are described in previous papers.^{11,12}

The conductance measurements were carried out using a digital bridge-type conductivity meter (Jenway, PCM 3) working at a frequency of 1 kHz. The accuracy was $\pm 0.5\%$. A dipping type conductance cell with platinized electrodes was used. The cell constant (0.98 \pm 0.01 cm⁻¹) was determined by calibration with a 0.01 mol·dm⁻³ aqueous KCl solution at (293.15 \pm 0.01) K. The temperature of each solution became stable within 10–15 min and remained

Table 3. Limiting Molar Conductances (Λ_0) and Association Constants (K_A) for Copper(II), Magnesium(II), Cadmium(II), and Nickel(II) Sulfates in Methanol (1) + Water (2) Mixtures at 293.15 K

x_1	Λ_0 S·cm ² ·mol ⁻¹	K_A dm ³ ·mol ⁻¹	σ_A
Copper(II) Sulfate			
0.0000	229.3 ± 0.9	253 ± 1	0.321
	266.16 ^b	188 ^b	
0.0588	154.2 ± 0.8	396 ± 1	0.323
0.1233	142.5 ± 0.7	512 ± 1	0.105
0.1942	116.1 ± 0.6	609 ± 1	0.074
0.2727	108.0 ± 0.6	1403 ± 3	0.025
0.4576	73.2 ± 0.4	2978 ± 6	0.022
0.6923	<i>a</i>	<i>a</i>	
Nickel(II) Sulfate			
0.0000	234.4 ± 0.9	139 ± 1	0.558
0.0588	201.0 ± 0.9	342 ± 1	0.408
0.1233	156.2 ± 0.8	437 ± 1	0.155
0.1942	138.9 ± 0.7	753 ± 2	0.121
0.2727	122.7 ± 0.6	1078 ± 2	0.041
0.4576	112.2 ± 0.6	3856 ± 8	0.015
0.6923	66.2 ± 0.3	8281 ± 17	0.011
Cadmium(II) Sulfate			
0.0000	209.9 ± 0.9	222 ± 1	1.137
0.0588	161.9 ± 0.8	262 ± 1	0.657
0.1233	138.4 ± 0.7	564 ± 1	0.375
0.1942	107.2 ± 0.6	525 ± 1	0.446
0.2727	84.5 ± 0.4	612 ± 1	0.222
0.4576	79.1 ± 0.4	3212 ± 6	0.044
0.6923	58.5 ± 0.3	17731 ± 35	0.030
Magnesium(II) Sulfate			
0.0000	225.2 ± 0.9	164 ± 1	1.264
		167.7 ^c	
		210 ^d	
0.0588	179.3 ± 0.9	189 ± 1	0.917
0.1233	149.7 ± 0.8	379 ± 1	0.415
0.1942	125.0 ± 0.6	467 ± 1	0.262
0.2727	115.3 ± 0.6	858 ± 2	0.055
0.4576	85.4 ± 0.4	1226 ± 2	0.110
0.6923	59.9 ± 0.3	4368 ± 9	0.021

^a Copper sulfate was not sufficiently soluble in the methanol rich region of the mixtures. ^b At 298.15 K (Niaz and Hussain, 1994).⁹ ^c At 298.15 K (Pethybridge and Taba, 1977).² ^d At 298.15 K (Quintana et al., 1986).⁸

constant. All data were corrected with the specific conductance of the solvent. The accuracy of the molar conductances was ±0.5%.

In all cases the measurements were repeated twice with different stock solutions to obtain reproducible results.

The dielectric constants of the binary and of the pure solvents were taken from the literature.^{13,14}

Results and Discussion

Densities, viscosities, and specific conductivities of pure water and methanol + water mixtures are reported in Table 1. The viscosity and specific conductance values show a significant change (maximum) with the change in the solvent composition of the mixed solvent, indicating that the methanol + water mixture exhibits nonideal behavior. The addition of methanol to water promotes a breakdown of the water structure so the oxygen centers of the water molecules become free for interaction with the protons of methanol molecules.¹⁵

The molar conductances of each electrolyte in the methanol + water mixtures are given in Table 2.

The experimental data were analyzed with the Lee and Wheaton^{16, 17} conductivity equation in the form suggested

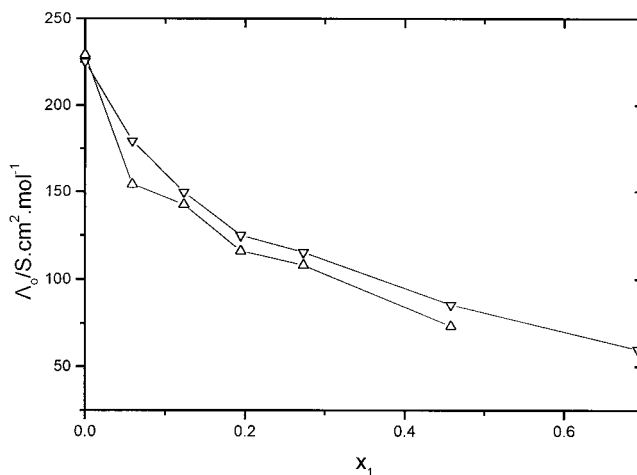


Figure 1. Variation of limiting molar conductivities with mole fraction for CuSO₄ (Δ) and MgSO₄ (∇) in methanol (1) + water (2) mixtures at 293.15 K.

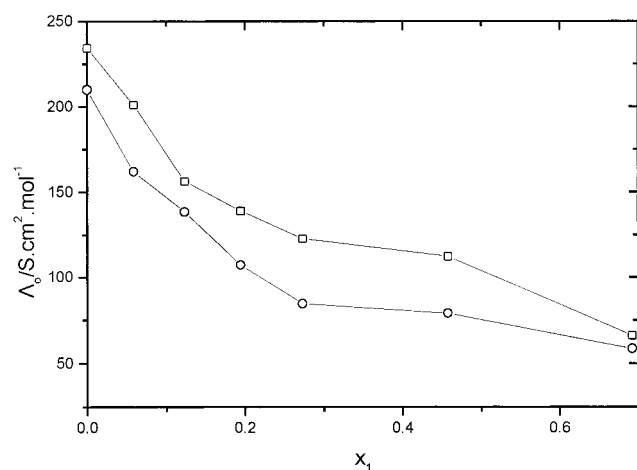


Figure 2. Variation of limiting molar conductivities with mole fraction for CdSO₄ (○) and NiSO₄ (□) in methanol (1) + water (2) mixtures at 293.15 K.

by Pethybridge and Taba,¹⁸ and the following set of equations was used

$$\Lambda = \gamma \left[\Lambda_0 \left(1 + \frac{\Delta x}{x} \right) - \Delta \Lambda_e \right] \quad (1)$$

$$K_A = \frac{(1 - \gamma)}{\gamma^2 f_{\pm}^2 c} \quad (2)$$

$$-\ln f_{\pm} = \frac{\beta \kappa}{2(1 + \kappa R)} \quad (3)$$

where $\Delta x/x$ and $\Delta \Lambda_e$ are the relaxation and electrophoretic terms, respectively, β is twice the Bjerrum's distance, and κ^{-1} is the Debye length. The values of R were actually equal to Bjerrum's critical distance, a procedure which is mentioned by other researchers.¹⁹⁻²³ The other symbols have their usual meanings.

The Λ_0 and K_A values were obtained as the best fit parameters which minimize the standard deviation

$$\sigma_{\Lambda}^2 = \frac{\sum (\Lambda_{\text{cald}} - \Lambda_{\text{obsd}})^2}{(n - 2)} \quad (4)$$

The values of Λ_0 and K_A for NiSO₄, CdSO₄, MgSO₄, and CuSO₄ in methanol + water mixtures, together with σ_{Λ} ,

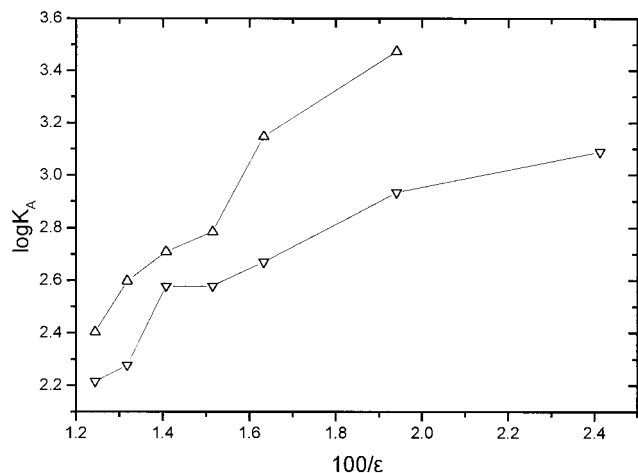


Figure 3. Variation of association constants with the inverse dielectric constant for CuSO_4 (Δ) and MgSO_4 (∇) in methanol (1) + water (2) mixtures at 293.15 K.

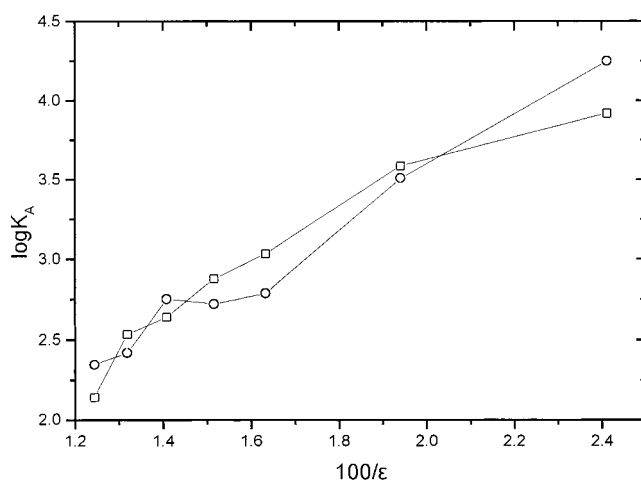


Figure 4. Variation of association constants with the inverse dielectric constant for CdSO_4 (\circ) and NiSO_4 (\square) in methanol (1) + water (2) mixtures at 293.15 K.

are summarized in Table 3. The values given in the literature are also listed in Table 3.

The values of Λ_0 for the electrolytes in methanol + water mixtures are represented graphically in Figures 1 and 2 and the dependence of the $\log K_A$ values on the inverse of the dielectric constant of the binary solvent is represented in Figures 3 and 4.

The limiting molar conductivities decrease rapidly, and the association constants increase, as the methanol content of the mixture increases. The values of the association constants show that these salts do not exist in a completely dissociated form even in the aqueous solutions. The bivalent cations form ion pairs and water-separated pairs with the sulfate ions. As the methanol content is increased (dielectric constant of the solvent mixture decreases), the hydration becomes less strong and a short range interaction is possible. Therefore, it can be clearly considered that electrostatic ion pairs are formed. An examination of molecular models suggests that when methanol solvates the ions, perhaps a steric hindrance occurs.²⁴ Because of this steric hindrance, the oxygen atoms of methanol are not in direct contact with the ions; consequently, the ions move freely and they have a tendency to associate through ion-ion interactions.

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