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Solubility, Density, Viscosity, Electrical Conductivity, and Refractive Index of Saturated Solutions of Lithium Hydroxide in Water + Ethanol

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The solubilities, densities, refractive indices, electrical conductivities, and viscosities were determined for a constant ethanol/water mass ratio of 0.1 over the temperature range (288.15 to 308.15) K. Equations are given for these properties as a function of temperature. These properties are useful in the study of the crystallization of lithium hydroxide from aqueous solutions by means of the addition of ethanol.

Introduction

Chile is one of the major production countries of lithium carbonate in the world. The lithium salts are obtained from the brines of Salar de Atacama, located in the north of Chile. These brines are concentrated using a series of solar ponds and later on processed into lithium carbonate.

The monohydrate lithium hydroxide is usually made from the reaction of lithium carbonate and calcium hydroxide in aqueous solution. The monohydrate is used in the production of lubricating greases due to its high resistance to temperature and in the production of inks.[1]

Anhydrous lithium hydroxide is obtained by heating the monohydrate at 110 °C for 2 days. The anhydrous compound is used to purify the air in submarines and space ships.

An alternative to traditional solar extraction is to use chemical extraction by adding a third component in the solution to change the phase equilibria and promote crystallization.

A solution can be made supersaturated, with respect to a given solute, by the addition of a substance that reduces the solubility of the solute in the solvent. This process is called "salting-out". Salting-out has many advantages. For example, highly concentrated initial solutions can be made by dissolving an impure crystalline material in a suitable solvent. It can be processed at room temperature to produce high purity salts. In this case, the important variables to be considered include the miscibility of the additional solvent with the original solution, the limiting solubility of the solute in the additional solvent, economic considerations in separating the organic solvent from the water, and the physical properties of the organic solvent + water + salt system.[1]

A study with a lithium salt was reported by Cartón et al.[2] They obtained data on the solubilities and densities of lithium sulfate in ethanol aqueous solution over the temperature range (282.75 to 323.15) K and at (0 to 0.6) mass fraction of ethanol. In another paper, Cartón et al.[3] presented data on the solubilities, densities, viscosities, conductivities, and refractive indices of saturated solutions of lithium formate in water + ethanol over the temperature range (283.15 to 313.15) K and at (0 to 0.8) mass fraction of ethanol. They reported in both papers equations for these properties as a function of temperature and the mass fraction of ethanol, and they found that the presence of ethanol significantly reduced the solubility and density of the aqueous solutions of lithium sulfate and lithium formate.

Cartón et al.[4] reported data on the densities and viscosities of saturated solutions of lithium potassium sulfate in water + ethanol at 298.15 K. Equations are given for both properties as a function of solubility. They also determined the solubility of this double salt in water and in aqueous ethanol at 298.15 K. In that paper, the range of the ethanol mass fraction was from 0 to 0.4.

We report in this article the solubilities, densities, viscosities, electrical conductivities, and refractive indices for saturated solutions of lithium hydroxide in an aqueous ethanol mixture (0.1 ethanol/water mass ratio) at five different temperatures from (288.15 to 308.15) K. These properties are useful in the study of the crystallization process for the salting-out of LiOH, using ethanol as the second solvent. The 0.1 ethanol/water mass ratio was selected because it allows the crystallization process without increasing significantly the equipment size.

Experimental Section

The reagents used in the experiments are lithium hydroxide monohydrate (+99%, Merck), grade absolute ethanol (+99.5%, Merck), and ultrapure water (conductivity 0.05 $\mu S \cdot cm^{-1}$) obtained by passing distilled water through a Millipore ultrapure cartridge kit. All reagents were used as received commercially.

A rotary, thermostatically controlled water bath was used to obtain phase equilibria, with a holder containing eight 90 mL suitable sealed glass flasks. The central portion of the stoppers in the flasks was made of rubber, such that samples could be extracted from the flask by syringe without losses of solvent by evaporation. The system worked within a range of (283.15 to 363.15) K ± 0.1 K.

Known masses of ethanol, water, and lithium hydroxide were measured on a Mettler Toledo Co. model AX204 analytical balance with a precision of 0.07 mg. The lithium hydroxide was added in excess to ensure the saturation of the solutions. Ethanol was the last reagent to be added to the solution to avoid their evaporation.

The samples were agitated for 72 h in order to reach equilibrium at the desired temperature. Following the agitation step, samples were allowed to decant for an additional 24 h. The clear liquid was collected from the flasks using Versapore membrane filters having a nominal

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Table 1. Solubility in Mass % (*s*), Density (*ρ*), Refractive Index (n_D), Electrical Conductivity (*k*), and Viscosity (*η*) of Lithium Hydroxide Saturated Solutions in the Binary System and the Ternary System (Ethanol + Water) at 288.15, 293.15, 298.15, 303.15, and 308.15 K

T/K	s	ρ/kg·m^{-3}	n_D	k/S·m^{-1}	η/mPa·s
		Binary System			
288.15	11.0	1114.35	1.3744	365.0	4.817
	11.0	1114.35	1.3745	364.4	4.962
	11.0	1114.39	1.3744	364.9	4.820
293.15	11.08	1112.93	1.3739	380.0	4.086
	11.08	1112.99	1.3739	379.4	4.181
	11.04	1113.02	1.3739	379.8	4.114
298.15	11.11	1112.02	1.3734	394.8	3.539
	11.11	1111.92	1.3735	394.6	3.579
	11.21	1111.94	1.3734	394.7	3.369
303.15	11.25	1110.94	1.3730	408.1	3.125
	11.25	1110.92	1.3730	407.7	3.104
	11.21	1110.94	1.3730	407.9	3.131
308.15	11.32	1110.24	1.3730	419.1	2.765
	11.35	111023	1.3726	418.8	2.743
	11.32	1110.22	1.3726	419.0	2.777
		Ternary System			
288.15	8.42	1074.72	1.3721	238.4	5.474
	8.52	1075.28	1.3721	238.7	5.304
	8.49	1074.97	1.3721	238.9	5.475
293.15	8.49	1073.35	1.3716	252.5	4.460
	8.52	1073.29	1.3715	251.6	4.511
	8.52	1073.72	1.3716	252.0	4.411
298.15	8.66	1071.99	1.3708	262.4	3.756
	8.70	1071.87	1.3709	262.9	3.737
	8.66	1071.93	1.3709	262.8	3.808
303.15	8.70	1070.70	1.3703	274.4	3.283
	8.63	1070.64	1.3703	274.2	3.186
	8.59	1070.67	1.3703	274.6	3.333
308.15	8.90	1069.32	1.3697	285.5	2.779
	8.97	1069.37	1.3696	286.1	2.834
	8.94	1069.52	1.3697	285.5	2.774

pore size of 0.25 μm. Salt concentrations were determined by chemical analysis. In all cases, the experiments were performed in triplicates for each temperature. For each sample the solubility values are reported in this paper.

The density of each sample was determined using a Mettler Toledo model DE50 vibrating tube densimeter, operating in the static mode, having an uncertainty of 2 × 10^{-2} kg·m^{-3}. Three runs were made for each sample.

Refractive indices for the sodium D line were measured on a Mettler Toledo RE40 refractometer with an uncertainty of 1 × 10^{-4}. The measurements were repeated at least three times without any appreciable variation. The average of these readings was used to calculate the refractive index.

Ultrapure degassed water and air were used as references for calibration of both the densimeter and the refractometer in the temperature range (288.15 to 308.15) K.

Measurements of electrical conductivity were carried out using an Orion model 170 conductimeter, calibrated using a 0.2 M standard KCl solution. The uncertainty was ±0.6 S·m^{-1}.

The kinematics viscosities of the saturated solutions were measured with an automatic Schott-Gerate AVS 310 laser viscosimeter which measures the transit time of the liquid meniscus through a capillary, with a precision of ±0.1 s. A calibrated Micro-Oswald viscosimeter was immersed in a transparent Schott-Gerate CT 52 thermostatic bath, with a temperature precision of ±0.05 K. The dynamic viscosity was obtained by multiplying the kinematic viscosity by the corresponding density. The results are given in Table 1 for the average of three determinations for each solution. The uncertainty of the measured viscosities was better than ±5 × 10^{-3} mPa·s.

Results and Discussion

The solubilities, densities, viscosities, electrical conductivities, and refractive indices of the saturated solutions for the binary system lithium hydroxide + water and the ternary system lithium hydroxide + water + ethanol (0.1 ethanol/water mass ratio) at five different temperatures are given in Table 1.

Measurements of solubility (*s*) for the binary system lithium hydroxide + water agreed with literature values,[5−8] as shown in Table 2.

The mass percentage (*s*) of anhydrous lithium hydroxide may be correlated as a function of temperature, according to the following equation:

$$\ln[s/(\text{kg}/100\text{ kg of solution})] = A^{\text{I}} + B^{\text{I}}(T/\text{K}) \qquad (1)$$

The A^{I} and B^{I} coefficients for eq 1 of the binary system and the ternary system with ethanol mass ratios constant at 0.1 are presented in Table 3.

The mean absolute deviation between the calculated and experimental solubility values is 0.004 g of LiOH/100 g of solution for the binary system and 0.059 g of LiOH/100 g of solution for the ternary system. The maximum absolute deviation is 0.011 g of LiOH/100 g of solution for the binary system and 0.114 g of LiOH/100 g of solution for the ternary system.

The values for saturation density were correlated as a function of temperature, according to the following equation:

$$\ln \rho/(\text{kg/m}^3) = A^{\text{II}} + B^{\text{II}}/(T/\text{K}) \qquad (2)$$

The A^{II} and B^{II} coefficients for eq 2 of the binary system and the ternary system with ethanol mass ratios constant at 0.1 are presented in Table 3.

Table 2. Comparisons of Solubility Data with Literature Values

T/K	this study	Habashi[5]	I.C.T[6]	Kirk−Othmer[7]	Linke−Seidell[8]
288.15	11.00		11.28	10.84	10.89
293.15	11.07	11.00	11.30	10.90	10.99
298.15	11.16	11.05	11.34	11.00	11.14
303.15	11.23	11.10	11.38	11.10	11.27
308.15	11.33	11.15	11.43	11.20	11.48

Table 3. Coefficients for eqs 1−5

system	A^{I}	A^{II}	A^{III}	A^{IV}	A^{V}
LiOH + H_2O	1.9794	6.9585	1.3991	1204.6	−7.3215
LiOH + H_2O + ethanol	1.3681	6.8997	1.4073	955.76	−8.5498

system	B^{I}	B^{II}	$10^2\,B^{\text{III}}$	$10^{-2}\,B^{\text{IV}}$	B^{V}
LiOH + H_2O	0.0015	16.530	−0.0086	−2417.4	2563.3
LiOH + H_2O + ethanol	0.0026	23.141	−0.0122	−2065.5	2948.2

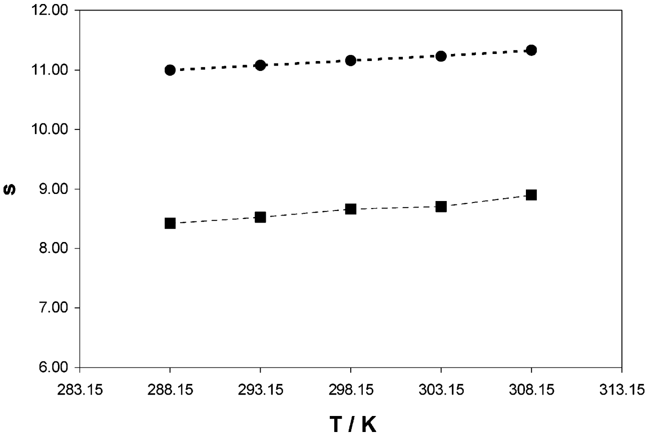

Figure 1. Mass % Solubility (s) of lithium hydroxide in the binary system (●) and the ternary system (ethanol + water) (■).

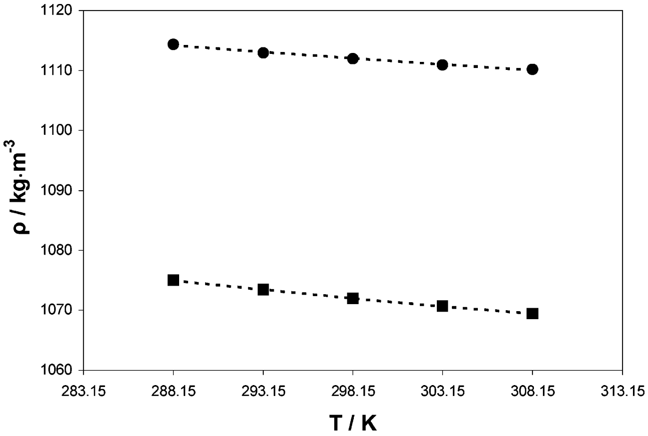

Figure 2. Density of lithium hydroxide in the same systems used in Figure 1.

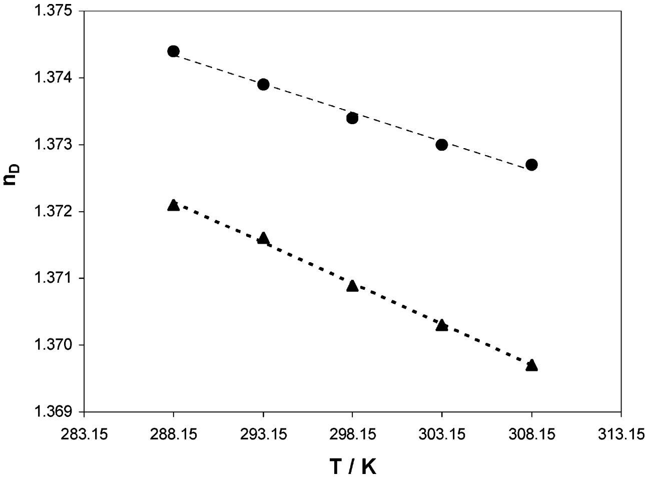

Figure 3. Refractive index of lithium hydroxide in the same systems used in Figure 1.

The mean absolute deviation between all the calculated and experimental density values is 0.136 kg·m^{-3} for the binary system and 0.034 kg·m^{-3} for the ternary system.

The maximum absolute deviation is 0.171 kg·m^{-3} for the binary system and 0.059 kg·m^{-3} for the ternary system.

The refractive index (n_D) results may be correlated as a function of temperature, according to the following equation:

$$n_D = A^{III} + B^{III}(T/K) \qquad (3)$$

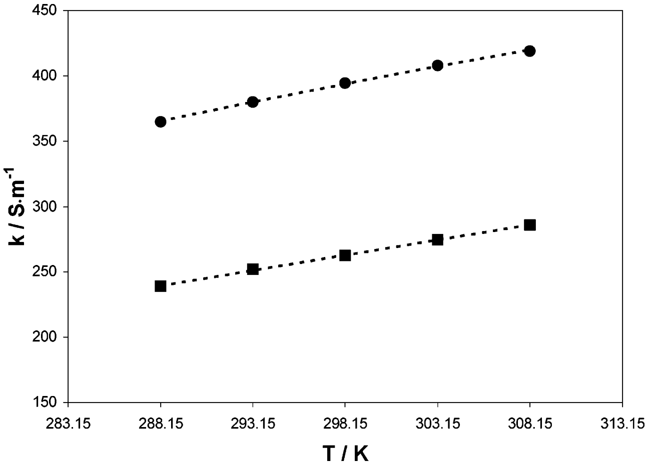

Figure 4. Conductivity of lithium hydroxide in the same systems used in Figure 1.

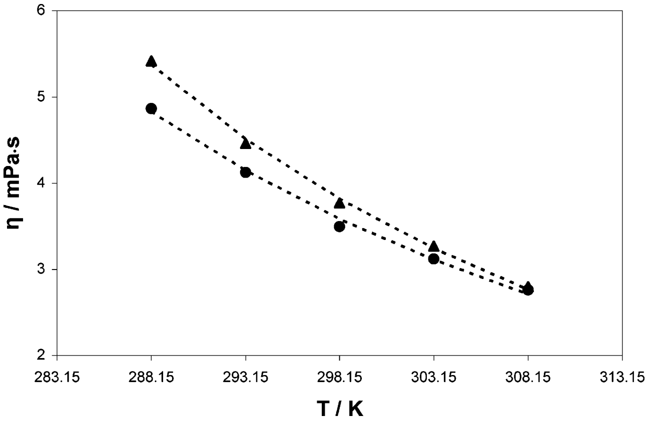

Figure 5. Viscosity of lithium hydroxide in the same systems used in Figure 1.

The A^{III} and B^{III} coefficients for eq 3 of the binary system and the ternary system with ethanol mass ratios constant at 0.1 are presented in Table 3.

The mean absolute deviation between all the calculated and experimental refractive index values is 0.0001 for both systems. The maximum absolute deviation is 0.0001 for the binary system and 0.000 07 for the ternary system.

The electrical conductivity (k) results may be correlated as a function of temperature, according to the following equation:

$$\kappa/(\mathrm{S{\cdot}m^{-1}}) = A^{IV} + B^{IV}/(T/K) \qquad (4)$$

The A^{IV} and B^{IV} coefficients for eq 4 of the binary system and the ternary system with ethanol mass ratios constant at 0.1 are presented in Table 3.

The mean absolute deviation between all experimental and calculated conductivity values is 0.7 S·m^{-1} for the binary system and 0.4 S·m^{-1} for the ternary system. The maximum absolute deviation is 1.1 S·m^{-1} for the binary system and 0.8 S·m^{-1} for the ternary system.

The viscosity (η) results of the saturated solution may be correlated as a function of temperature, according to the following equation:

$$\ln \eta/(\mathrm{mPa{\cdot}s}) = A^{V} + B^{V}/(T/K) \qquad (5)$$

The A^{V} and B^{V} coefficients for eq 5 of the binary system and the ternary system with ethanol mass ratios constant at 0.1 are presented in Table 3.

The mean absolute deviation between the experimental and calculated viscosity values is 0.042 mPa·s for the binary system and 0.04 mPa·s for the ternary system. The maximum absolute deviation is 0.09 mPa·s for the binary system and 0.05 mPa·s for the ternary system.

These results showed a good fit among the experimental values for concentrations of the salt and the physical properties of the saturated solutions at five temperatures, in both systems.

A better visualization of the experimental data and fitting results from eqs 1−5 is presented as solid lines in Figures 1−5. In these figures, the experimental values are an average of three measurements, which are presented in Table 1.

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