Refractive Indices of Lithium, Magnesium, and Copper(II) Sulfates in Ethanol−Water Solutions

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The refractive indices of lithium, magnesium, and copper sulfate in ethanol + water solutions were measured over the temperature range (288.15 to 318.15) K and at atmospheric pressure. Also, ethanol + water and single salt + water binary systems were measured. Binary and ternary systems were correlated using polynomial expressions, and the parameters depend on the composition of the mixtures. Data fitting shows good agreement with experimental values.

Introduction

Optical data (refractive index) of electrolyte mixtures provide interesting information related to molecular interactions and structure of the solutions, as well as complementary data on practical procedures, such as concentration measurement[1] or estimation of other properties.[2] The effect of an electrolyte or multicomponent electrolytes dissolved in water or other solvents has potential use in industrial separation processes of liquid chemicals by modified unit operations such as distillation,[3] extraction,[4] extractive distillation,[5] or selective crystallization.[6]

The present work continues our research program on the physical characterization of the salt effect in ethanol−water solutions.[7,8] The principal aim of this work is to present new data on the refractive index of lithium, magnesium, and copper(II) sulfates in water and water + ethanol mixtures at different temperatures. The refractive index of mixing was correlated by the application of a composition-dependent polynomial equation.

Despite the considerable amount of data in the main compilations, only a scarce amount of work has been devoted to electrolyte refractive index studies either over wide temperature ranges or in multicomponent systems. For the systems treated in this article, we have not been able to find more data in the literature on experimental values for these ternary systems, except data on $MgSO_4$ mixtures[1,9] and data on Li_2SO_4 saturated solutions.[10]

Experimental Section

Materials. The chemicals were ethanol (Merck, Lichrosolv quality) with a stated minimum purity of 0.995 (mass fraction), degassed with ultrasound, and stored over freshly activated molecular sieves (type 4a or 3a, 1/16 in., Aldrich catalog no. 20.860-4 or 20.858-2, respectively) for three days before use. The water was Milli-Q quality (resistivity, 18.2 $M\Omega\cdot cm$). Lithium sulfate monohydrate (Merck, mass fraction > 0.99), magnesium sulfate (Aldrich, mass fraction > 0.99), and copper(II) sulfate (Merck, mass fraction > 0.99) were used in sample preparation. The chemicals were stored under sun and humidity protection conditions.

The molality of the $MgSO_4$ and $CuSO_4$ aqueous stock solutions was determined by gravimetric sulfate analysis. Li_2SO_4 stock aqueous solutions were prepared by weight. Final solutions were prepared gravimetrically one by one, by dilutions of water and ethanol. All mixtures were prepared using a Mettler AT261 Delta Range balance with a precision of $\pm 10^{-4}$ g, yielding an error better than $\pm 5\cdot10^{-5}$ in the salt free mass and molar fraction and better than $\pm 5\cdot10^{-4}$ $mol\cdot kg^{-1}$ in the molality of the salt.

Measurements. The refractive indices were measured with an automatic refractometer ABBEMAT-HP Dr. Kernchen with a precision of $\pm 10^{-5}$. Refractometer calibration was performed periodically (Milli-Q quality water and ambient air were used for calibration). The measurement device was thermostatted using a Polyscience controller bath (Model 9510), with a temperature stability of $\pm 10^{-2}$ K.

To provide a test on the functioning of the refractive system, measurements were routinely made at different temperatures in the range of work temperatures for chemicals whose accurate values are available.[11] The relative error of the preparation process, manipulation, and measurement has a precision better than 0.00015.

Results and Discussion

The experimental values of the refractive indices, n_D, of the binary mixture of ethanol with water as a function of weight fraction of ethanol, w_e, are given in Table 1. The deviations of refractive index[12] were used for the correlation of the binary ethanol + water mixtures:

$$\Delta n_{Dew} = n_{Dew} - x_e n_{De} - x_w n_{Dw} \quad (1)$$

where Δn_{Dew} is the deviation of the refractive index for this binary system and n_{Dew}, n_{De}, and n_{Dw} are the refractive index of the binary mixture, refractive index of ethanol, and refractive index of water, respectively. x is the mole fraction. All Δn_{Dew} are positive for the entire range of compositions, and the refractive indices increase with decreasing temperature. The values of Δn_{Dew} are shown in Figure 1. The computed deviations

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Table 1. Refractive Indices and Deviations of Refractive Indices for the Binary Mixtures of Ethanol + Water in the Temperature Range from (288.15 to 318.15) K

	n_D at T/K				Δn_D at T/K			
w_e	318.15	308.15	298.15	288.15	318.15	308.15	298.15	288.15
0.00000	1.32979	1.33128	1.33248	1.33339	0.00000	0.00000	0.00000	0.00000
0.02468	1.33124	1.33282	1.33402	1.33491	0.00125	0.00131	0.00128	0.00123
0.05380	1.33301	1.33455	1.33587	1.33686	0.00277	0.00276	0.00281	0.00282
0.07815	1.33449	1.33619	1.33765	1.33854	0.00403	0.00416	0.00431	0.00419
0.10141	1.33580	1.33771	1.33915	1.34032	0.00513	0.00544	0.00554	0.00566
0.12493	1.33736	1.33923	1.34095	1.34209	0.00647	0.00671	0.00706	0.00711
0.15278	1.33895	1.34104	1.34294	1.34443	0.00778	0.00821	0.00870	0.00906
0.17780	1.34054	1.34272	1.34475	1.34627	0.00912	0.00961	0.01019	0.01054
0.20363	1.34180	1.34435	1.34651	1.34829	0.01011	0.01093	0.01160	0.01217
0.22496	1.34311	1.34551	1.34781	1.34976	0.01119	0.01184	0.01260	0.01331
0.24696	1.34418	1.34682	1.34934	1.35137	0.01202	0.01287	0.01382	0.01456
0.26993	1.34519	1.34790	1.35056	1.35281	0.01276	0.01365	0.01470	0.01562
0.29554	1.34640	1.34922	1.35212	1.35435	0.01367	0.01463	0.01587	0.01672
0.32414	1.34772	1.35053	1.35363	1.35595	0.01463	0.01554	0.01693	0.01781
0.34680	1.34853	1.35164	1.35460	1.35720	0.01515	0.01632	0.01752	0.01864
0.37231	1.34932	1.35252	1.35567	1.35843	0.01560	0.01682	0.01816	0.01938
0.39592	1.34997	1.35342	1.35665	1.35970	0.01592	0.01735	0.01871	0.02018
0.42546	1.35103	1.35448	1.35765	1.36073	0.01655	0.01793	0.01917	0.02059
0.44625	1.35147	1.35501	1.35831	1.36161	0.01667	0.01810	0.01942	0.02102
0.47353	1.35212	1.35566	1.35919	1.36235	0.01689	0.01827	0.01975	0.02114
0.49690	1.35251	1.35620	1.35969	1.36316	0.01690	0.01838	0.01976	0.02140
0.52386	1.35301	1.35667	1.36042	1.36378	0.01694	0.01832	0.01990	0.02135
0.54583	1.35330	1.35731	1.36078	1.36431	0.01683	0.01852	0.01975	0.02131
0.57086	1.35369	1.35770	1.36134	1.36482	0.01675	0.01838	0.01971	0.02115
0.59716	1.35385	1.35801	1.36186	1.36547	0.01639	0.01811	0.01957	0.02105
0.62033	1.35417	1.35825	1.36199	1.36582	0.01624	0.01781	0.01909	0.02072
0.64668	1.35430	1.35839	1.36243	1.36603	0.01580	0.01731	0.01880	0.02010
0.66942	1.35455	1.35867	1.36263	1.36636	0.01553	0.01701	0.01833	0.01969
0.69588	1.35454	1.35875	1.36288	1.36665	0.01488	0.01638	0.01777	0.01907
0.71869	1.35469	1.35892	1.36306	1.36663	0.01446	0.01590	0.01722	0.01822
0.74940	1.35471	1.35895	1.36313	1.36702	0.01366	0.01501	0.01624	0.01743
0.76719	1.35475	1.35902	1.36317	1.36703	0.01320	0.01451	0.01563	0.01672
0.79926	1.35484	1.35879	1.36318	1.36694	0.01233	0.01321	0.01442	0.01525
0.81874	1.35478	1.35887	1.36320	1.36705	0.01165	0.01259	0.01365	0.01447
0.84506	1.35457	1.35860	1.36289	1.36683	0.01056	0.01133	0.01221	0.01298
0.86696	1.35421	1.35844	1.36278	1.36684	0.00942	0.01029	0.01110	0.01187
0.90278	1.35374	1.35782	1.36230	1.36637	0.00757	0.00812	0.00885	0.00942
0.92349	1.35333	1.35743	1.36196	1.36603	0.00630	0.00677	0.00741	0.00784
0.94813	1.35255	1.35677	1.36123	1.36528	0.00443	0.00488	0.00529	0.00553
0.97516	1.35171	1.35590	1.36037	1.36454	0.00231	0.00257	0.00279	0.00294
1.00000	1.35068	1.35477	1.35922	1.36344	0.00000	0.00000	0.00000	0.00000

of refractive indices of the binary mixtures were fitted using the following Redlich−Kister expression:[13]

$$\Delta n_{\mathrm{Dew}} = w_e w_w \sum_{p=0}^{S} B_p (w_e - w_w)^p \qquad (2)$$

where B_p are the adjustable parameters obtained by a least-squares fitting method, w is the mass fraction, and S is the

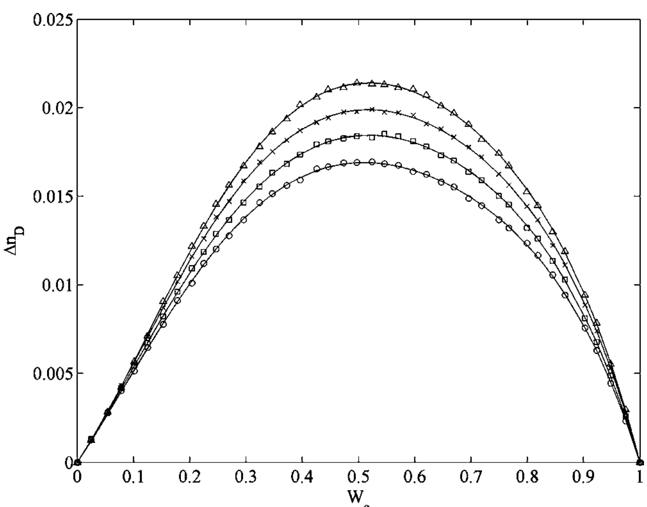

Figure 1. Deviations of refractive index, Δn_D, versus mass fraction of ethanol for the binary mixture with water at different temperatures: ○, 318.15 K; □, 308.15 K; ×, 298.15 K; Δ, 288.15 K.

Table 2. Fitting Parameters of eq 2 and Root Mean Square Deviation (σ) of eq 6 for the Ethanol + Water System

	318.15	308.15	298.15	288.15
B_0	$6.75762 \cdot 10^{-2}$	$7.37048 \cdot 10^{-2}$	$7.94833 \cdot 10^{-2}$	$8.55560 \cdot 10^{-2}$
B_1	$2.39181 \cdot 10^{-3}$	$5.11264 \cdot 10^{-3}$	$5.17144 \cdot 10^{-3}$	$6.26631 \cdot 10^{-3}$
B_2	$5.74731 \cdot 10^{-3}$	$3.44910 \cdot 10^{-3}$	$2.92900 \cdot 10^{-3}$	$-1.53539 \cdot 10^{-3}$
B_3	$2.44240 \cdot 10^{-2}$	$2.40711 \cdot 10^{-2}$	$2.96978 \cdot 10^{-2}$	$3.31109 \cdot 10^{-2}$
σ	$7 \cdot 10^{-5}$	$7 \cdot 10^{-5}$	$7 \cdot 10^{-5}$	$8 \cdot 10^{-5}$

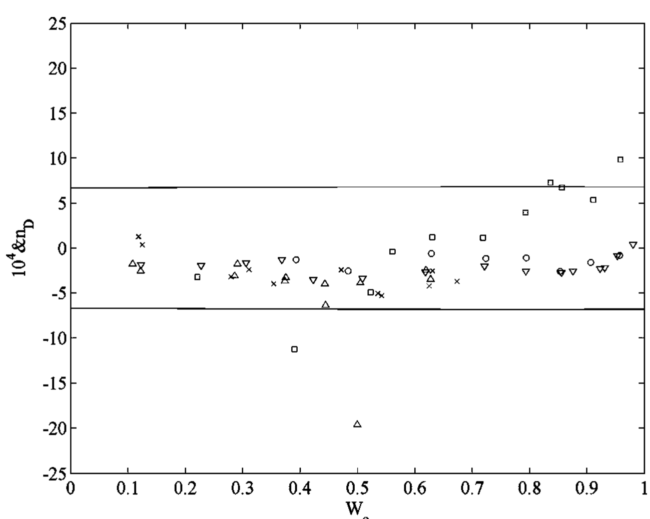

Figure 2. Deviations ($10^4(n_{\mathrm{Dlit}} - n_{\mathrm{Dpred}})$) between the literature data (n_{Dlit}) and the predicted refractive index values (n_{Dpred}) at 298.15 K: ○, Arce et al.;[14] □, Belda et al.;[15] ×, Zhao et al.;[16] Δ, Galleguillos et al.;[17] ▽, Arce et al.[18] The curves enclose deviations falling within $\pm\, 0.0005 \cdot n_{\mathrm{Dpred}}$ (0.05 %).

Table 3. Refractive Index for the Binary Mixtures of Salt + Water as a Function of Molality, in the Temperature Range from (288.15 to 318.15) K

	Li_2SO_4 + Water, n_D at T/K			
m/mol·kg^{-1}	318.15	308.15	298.15	288.15
0.0000	1.32979	1.33128	1.33248	1.33339
0.2520	1.33446	1.33612	1.33727	1.33830
0.4681	1.33812	1.33987	1.34096	1.34212
0.7337	1.34260	1.34419	1.34534	1.34651
0.9917	1.34670	1.34829	1.34944	1.35062
1.2447	1.35056	1.35198	1.35316	1.35440
1.4685	1.35375	1.35518	1.35628	1.35752
1.7564	1.35765	1.35905	1.36011	1.36140
1.7573	1.35767	1.35909	1.36015	1.36143
1.9387	1.35998	1.36134	1.36242	1.36365
2.1241	1.36227	1.36368	1.36472	1.36601
2.3061	1.36453	1.36574	1.36691	1.36812
2.5419	1.36720	1.36850	1.36964	1.37090
2.7977	1.37003	1.37124	1.37243	1.37360
2.9827	1.37206	1.37316	1.37442	1.37551
3.1577				1.37704
3.2201				1.37774
	$MgSO_4$ + Water, n_D at T/K			
0.0000	1.32979	1.33128	1.33248	1.33339
0.2096	1.33491	1.33629	1.33762	1.33858
0.3448	1.33803	1.33930	1.34072	1.34163
0.5911	1.34335	1.34463	1.34594	1.34710
0.7832	1.34735	1.34872	1.35009	1.35115
0.9997	1.35160	1.35295	1.35438	1.35558
1.1898	1.35532	1.35667	1.35810	1.35934
1.3786	1.35894	1.36037	1.36174	1.36292
1.6214	1.36342	1.36468	1.36613	1.36740
1.8675	1.36770	1.36899	1.37039	1.37176
2.1201	1.37185	1.37320	1.37469	1.37600
2.3603	1.37586	1.37709	1.37853	1.37993
2.5923	1.37944	1.38069	1.38211	1.38344
2.8588	1.38352	1.38461	1.38613	
3.0869	1.38662	1.38780	1.38927	
3.3473	1.39026	1.39151		
3.5795	1.39328	1.39450		
3.8067	1.39614			
3.9977	1.39817			
	$CuSO_4$ + Water, n_D at T/K			
0.0000	1.32979	1.33128	1.33248	1.33339
0.1346	1.33371	1.33528	1.33658	1.33752
0.3007	1.33834	1.33987	1.34125	1.34217
0.4408	1.34204	1.34360	1.34510	1.34604
0.5896	1.34587	1.34753	1.34915	1.35008
0.7359	1.34951	1.35129	1.35287	1.35392
0.8590	1.35249	1.35427	1.35606	1.35712
1.0160	1.35632	1.35816	1.36002	1.36104
1.1791	1.36027	1.36209	1.36398	1.36510
1.3008	1.36305	1.36500	1.36700	1.36803
1.4565	1.36664	1.36872	1.37060	
1.5790	1.36952	1.37162		
1.7361	1.37296			
1.8906	1.37632			
2.0580	1.38013			

number of terms in the polynomial. Table 2 shows the adjusted parameters obtained with eq 2 with $S = 3$. The differences between the experimental values from the literature[14−18] and our results fitted for the ethanol + water system with eq 2 are shown in Figure 2. The low solubility of sulfates in ethanol + water mixtures, due to the insolubility of sulfates in ethanol, leads to the use of ethanol mass fraction rather than mole fraction. Below, in a ternary refractive index calculation, both mass fraction and mole fraction of ethanol have low values, but the mass fraction is higher than the mole fraction, so the mass fraction was chosen for refractive index solvent correlation. Another reason is the extended use of salt-free mass fraction and concentration of salt to express solubility of a solute in binary solvents.[19−21]

Refractive indices for the salt + water binary mixtures are tabulated in Table 3. Figures 3, 4, and 5 show that for any given binary salt + water mixture, the refractive index always decreases with increasing temperature and always increases with the increasing molality of salt. The refractive indices were measured from zero to the solubility limit. In the lithium system,

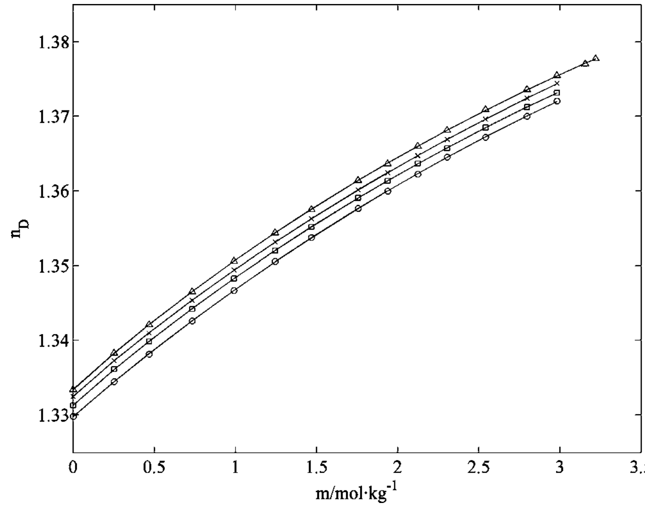

Figure 3. Refractive indices, n_D, versus molality of lithium sulfate in aqueous solution at different temperatures: ○, 318.15 K; □, 308.15 K; ×, 298.15 K; Δ, 288.15 K.

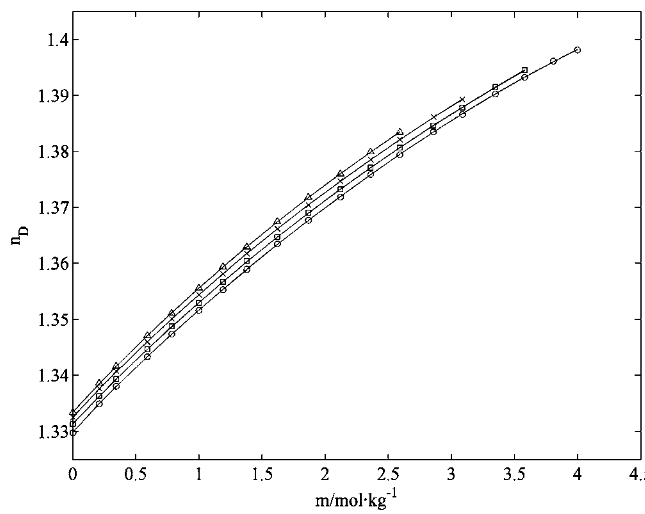

Figure 4. Refractive indices, n_D, versus molality of magnesium sulfate in aqueous solution at different temperatures: ○, 318.15 K; □, 308.15 K; ×, 298.15 K; Δ, 288.15 K.

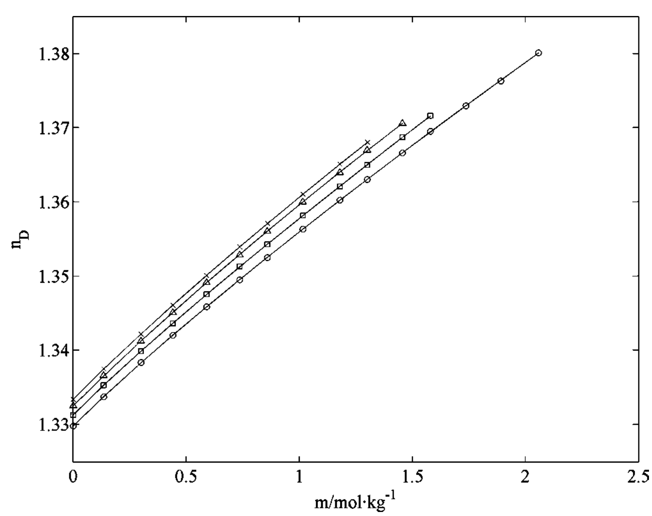

Figure 5. Refractive indices, n_D, versus molality of copper sulfate in aqueous solution at different temperatures: ○, 318.15 K; □, 308.15 K; ×, 298.15 K; Δ, 288.15 K.

the solubility decreases with increasing temperature.[10] These binary systems were fitted to polynomials of the form:[22]

$$n_{\mathrm{Dsw}} = n_{\mathrm{Dw}} + \sum_{i=1}^{N} A_i m^i \qquad (3)$$

where n_{Dsw} is the refractive index of the salt + water system, respectively, m is the molality of the salt in the solution, A_i are the fitting parameters, and N is the number of terms in the polynomial. These parameters are presented in Table 4.

Table 4. Fitting Parameters of eq 3 and Root Mean Square Deviation (σ) of eq 6 for the Salt + Water System

	Li_2SO_4 + Water at T/K			
	318.15	308.15	298.15	288.15
A_1	$1.94981 \cdot 10^{-2}$	$2.06330 \cdot 10^{-2}$	$2.06751 \cdot 10^{-2}$	$2.10609 \cdot 10^{-2}$
A_2	$-1.60822 \cdot 10^{-3}$	$-3.08511 \cdot 10^{-3}$	$-3.37319 \cdot 10^{-3}$	$-3.27914 \cdot 10^{-3}$
A_3	$-8.63030 \cdot 10^{-4}$	$-4.24223 \cdot 10^{-4}$	$-2.67394 \cdot 10^{-4}$	$-4.35981 \cdot 10^{-4}$
σ	$5 \cdot 10^{-5}$	$4 \cdot 10^{-5}$	$4 \cdot 10^{-5}$	$5 \cdot 10^{-5}$
	$MgSO_4$ + Water at T/K			
A_1	$2.73823 \cdot 10^{-2}$	$2.51935 \cdot 10^{-2}$	$2.57660 \cdot 10^{-2}$	$2.59855 \cdot 10^{-2}$
A_2	$-7.28487 \cdot 10^{-3}$	$-2.84235 \cdot 10^{-3}$	$-3.30349 \cdot 10^{-3}$	$-3.17224 \cdot 10^{-3}$
A_3	$2.49858 \cdot 10^{-3}$	$-6.02756 \cdot 10^{-4}$	$-5.01409 \cdot 10^{-4}$	$-5.99128 \cdot 10^{-4}$
A_4	$-7.10707 \cdot 10^{-4}$			
σ	$6 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	$6 \cdot 10^{-5}$	$4 \cdot 10^{-5}$
	$CuSO_4$ + Water at T/K			
A_1	$3.14628 \cdot 10^{-2}$	$3.20895 \cdot 10^{-2}$	$3.16971 \cdot 10^{-2}$	$3.17464 \cdot 10^{-2}$
A_2	$-6.19592 \cdot 10^{-3}$	$-7.11855 \cdot 10^{-3}$	$-4.56543 \cdot 10^{-3}$	$-4.48108 \cdot 10^{-3}$
A_3	$9.06856 \cdot 10^{-4}$	$1.51499 \cdot 10^{-3}$		
σ	$5 \cdot 10^{-5}$	$3 \cdot 10^{-5}$	$4 \cdot 10^{-5}$	$4 \cdot 10^{-5}$

Table 5. Refractive Index for the Ternary Mixtures of Copper Sulfate for Various Mass Fractions w_e in w_e Ethanol + (1 − w_e)Water at a Temperature Range from (288.15 to 318.15) K

		n_D at T/K			
w_e	m/mol·kg^{-1}	318.15	308.15	298.15	288.15
0.02643	0.1786	1.33633	1.33811	1.33928	1.34042
0.02462	0.3327	1.34060	1.34210	1.34352	1.34467
0.02524	0.4959	1.34498	1.34650	1.34791	1.34918
0.02475	0.6614	1.34918	1.35071	1.35214	1.35350
0.02435	0.8149	1.35299	1.35453	1.35610	1.35753
0.02494	0.9772	1.35707	1.35884	1.36023	1.36168
0.05125	0.1471	1.33687	1.33864	1.33996	1.34103
0.05089	0.3071	1.34137	1.34294	1.34448	1.34558
0.05113	0.4528	1.34530	1.34691	1.34827	1.34964
0.05142	0.6033	1.34921	1.35086	1.35228	1.35368
0.05009	0.7539	1.35284	1.35446	1.35607	1.35744
0.07523	0.1221	1.33760	1.33942	1.34095	1.34208
0.07539	0.2387	1.34081	1.34274	1.34412	1.34540
0.07533	0.3570	1.34411	1.34576	1.34729	1.34852
0.07166	0.4517	1.34636	1.34797	1.34959	1.35090
0.07549	0.6047	1.35045	1.35223	1.35379	1.35513
0.09975	0.1143	1.33886	1.34083	1.34230	1.34362
0.09923	0.2197	1.34164	1.34365	1.34511	1.34649
0.10053	0.3281	1.34482	1.34652	1.34814	1.34945
0.10033	0.4432	1.34771	1.34962	1.35115	1.35270
0.11893	0.0834	1.33928	1.34124	1.34280	1.34417
0.11859	0.1667	1.34138	1.34344	1.34500	1.34644
0.11887	0.2405	1.34341	1.34546	1.34708	1.34849
0.12549	0.3349	1.34636	1.34821	1.35010	1.35149
0.14991	0.0735	1.34085	1.34294	1.34467	1.34609
0.15173	0.1644	1.34325	1.34544	1.34723	1.34875
0.15014	0.2427	1.34550	1.34731	1.34931	1.35081
0.17534	0.0538	1.34174	1.34404	1.34583	1.34744
0.17588	0.1151	1.34336	1.34563	1.34753	1.34918
0.17523	0.1728	1.34498	1.34715	1.34910	1.35068
0.19970	0.0620	1.34319	1.34572	1.34784	1.34955
0.20089	0.1226	1.34492	1.34749	1.34958	1.35127
0.02528	1.1943	1.36240	1.36418	1.36548	
0.05495	0.9581	1.35831	1.35992	1.36133	
0.07780	0.7385	1.35413	1.35577	1.35725	
0.10017	0.5503	1.35061	1.35235	1.35384	
0.12465	0.4223	1.34868	1.35050	1.35216	
0.15034	0.3242	1.34767	1.34959	1.35133	
0.17494	0.2481	1.34711	1.34921	1.35096	
0.19960	0.1806	1.34675	1.34889	1.35087	

Table 6. Refractive Index for the Ternary Mixtures of Magnesium Sulfate for Various Mass Fractions w_e in w_e Ethanol + (1 − w_e)Water at a Temperature Range from (288.15 to 318.15) K

		n_D at T/K			
w_e	m/mol·kg^{-1}	318.15	308.15	298.15	288.15
0.02281	0.4484	1.34151	1.34291	1.34427	1.34528
0.02308	0.8817	1.35046	1.35194	1.35320	1.35440
0.02296	1.3241	1.35891	1.36036	1.36169	1.36311
0.02291	1.7444	1.36660	1.36782	1.36929	1.37055
0.02273	2.2050	1.37418	1.37547	1.37689	1.37825
0.02366	2.6465	1.38109	1.38229	1.38371	
0.02446	3.0584	1.38704	1.38824		
0.05006	0.4512	1.34312	1.34459	1.34595	1.34710
0.05054	0.9085	1.35252	1.35399	1.35547	1.35658
0.04937	1.3637	1.36101	1.36244	1.36391	1.36528
0.05248	1.7989	1.36895	1.37021	1.37178	1.37315
0.04954	2.2893	1.37679	1.37810	1.37962	1.38110
0.04907	2.7282	1.38351	1.38468		
0.07604	0.4078	1.34364	1.34525	1.34670	1.34771
0.07726	0.7816	1.35145	1.35298	1.35447	1.35578
0.07563	1.1966	1.35931	1.36089	1.36236	1.36363
0.07518	1.5715	1.36596	1.36747	1.36913	1.37049
0.07580	1.9718	1.37294	1.37431	1.37585	1.37747
0.07599	2.3891	1.37972	1.38095		
0.10022	0.4204	1.34531	1.34704	1.34853	1.34990
0.10057	0.8250	1.35352	1.35525	1.35682	1.35830
0.10009	1.2552	1.36176	1.36328	1.36489	1.36630
0.10016	1.6685	1.36900	1.37041	1.37202	1.37369
0.10001	2.0738	1.37562	1.37721		
0.14959	0.3377	1.34626	1.34841	1.35015	1.35167
0.14999	0.6766	1.35318	1.35515	1.35702	1.35865
0.15070	1.0195	1.35980	1.36164	1.36350	1.36517
0.15064	1.3362	1.36533	1.36733	1.36919	1.37096
0.14886	1.6953	1.37134	1.37311		
0.19879	0.3291	1.34890	1.35102	1.35323	1.35507
0.19874	0.6396	1.35474	1.35705	1.35929	1.36132
0.19663	0.9716	1.36075	1.36304	1.36502	1.36726
0.20154	1.3005	1.36660	1.36892		
0.24851	0.2583	1.34962	1.35239	1.35481	1.35686
0.24727	0.5172	1.35459	1.35713	1.35966	1.36187
0.24701	0.7846	1.35928	1.36201		
0.30004	0.1729	1.35014	1.35290	1.35592	1.35845
0.29776	0.3345	1.35308	1.35594	1.35868	1.36138
0.30230	0.5151	1.35632	1.35924		
0.12711	0.4923	1.34823	1.35008	1.35190	1.35319
0.12441	0.9894	1.35782	1.35973	1.36144	1.36291
0.12494	1.4860	1.36686	1.36854	1.37041	1.37188
0.17347	0.3805	1.34865	1.35052	1.35254	1.35431
0.17436	0.7539	1.35591	1.35803	1.36006	1.36187
0.17380	1.1261	1.36271	1.36480	1.36678	1.36863
0.22410	0.3917	1.35117	1.35377	1.35598	1.35802
0.22281	0.7885	1.35851	1.36094	1.36312	1.36543
0.27099	0.2458	1.35045	1.35321	1.35586	1.35812
0.27262	0.4901	1.35493	1.35786	1.36046	1.36276
0.32169	0.2499	1.35248	1.35531	1.35831	1.36096

For the ternary systems of the salt + water + ethanol solutions (Tables 5, 6, and 7), a polynomial expansion[23] similar to that obtained for the salt + water solutions was used to represent ternary refractive indices

$$n_D = n_{\mathrm{Dew}} + \sum_{i=1}^{P} C_i m^i \qquad (4)$$

n_D is the refractive index of the ternary solution, C_i are the parameters, and P is the number of terms in the polynomial. In these cases, these parameters are dependent on the mass fraction of the salt-free system

$$C_i = A_i + \sum_{j=1}^{Q} C_{ij} w_e^j \qquad (5)$$

w_e is the ethanol mass fraction of the salt free solution, C_{ij} are adjustable parameters, which are given in Table 8, Q is the

Table 7. Refractive Index for the Ternary Mixtures of Lithium Sulfate for Various Mass Fractions w_e in w_e Ethanol + (1 − w_e)Water at a Temperature Range from (288.15 to 318.15) K

		n_D at T/K			
w_e	m/mol·kg^{-1}	318.15	308.15	298.15	288.15
0.05347	1.1046	1.35138	1.35270	1.35411	1.35540
0.04750	0.2962	1.33803	1.33967	1.34088	1.34195
0.05298	0.5924	1.34343	1.34489	1.34623	1.34740
0.05167	0.8736	1.34773	1.34925	1.35056	1.35175
0.05830	1.4548	1.35670	1.35794	1.35935	1.36061
0.05346	1.7394	1.36005	1.36152	1.36281	1.36406
0.05339	2.0475	1.36394	1.36530	1.36659	1.36793
0.04698	2.3969	1.36781	1.36893	1.37031	1.37160
0.10323	0.2773	1.34104	1.34281	1.34431	1.34560
0.09911	0.5374	1.34516	1.34686	1.34838	1.34966
0.09865	0.8088	1.34937	1.35110	1.35253	1.35393
0.09859	1.0729	1.35345	1.35478	1.35655	1.35787
0.09778	1.3449	1.35703	1.35868	1.36033	1.36165
0.10139	1.6297	1.36105	1.36262	1.36418	1.36563
0.10225	1.8970	1.36448	1.36612	1.36756	1.36901
0.15091	0.2481	1.34336	1.34534	1.34705	1.34867
0.15110	0.5034	1.34738	1.34950	1.35129	1.35286
0.14914	0.7484	1.35108	1.35300	1.35497	1.35662
0.14764	1.0063	1.35497	1.35657	1.35850	1.36006
0.14861	1.2650	1.35836	1.36018	1.36203	1.36383
0.14843	1.4959	1.36142	1.36316	1.36512	1.36676
0.20371	0.2063	1.34538	1.34788	1.34993	1.35184
0.20368	0.4516	1.34936	1.35169	1.35365	1.35567
0.19783	0.6776	1.35259	1.35458	1.35686	1.35861
0.20336	0.8948	1.35571	1.35784	1.35999	1.36217
0.19916	1.1280	1.35889	1.36088	1.36304	1.36500
0.25263	0.2196	1.34791	1.35063	1.35310	1.35535
0.25549	0.4298	1.35137	1.35380	1.35643	1.35878
0.25274	0.6441	1.35445	1.35681	1.35907	1.36162
0.25341	0.8669	1.35743	1.35976	1.36201	1.36424
0.35031	0.1560	1.35079	1.35385	1.35676	1.35981
0.35391	0.3099	1.35316	1.35629	1.35907	1.36199
0.35279	0.4625	1.35535	1.35827	1.36113	1.36387
0.30369	0.1647	1.34942	1.35206	1.35494	1.35752
0.30705	0.3356	1.35209	1.35491	1.35742	1.36026
0.30550	0.5007	1.35423	1.35696	1.35981	1.36215
0.30787	0.6721	1.35679	1.35919	1.36199	1.36435
0.40406	0.1136	1.35196	1.35504	1.35841	1.36142
0.40205	0.2189	1.35345	1.35661	1.35979	1.36275
0.40405	0.3394	1.35504	1.35802	1.36119	1.36406
0.50173	0.0726	1.35352	1.35696	1.36061	1.36397
0.50578	0.1693	1.35507	1.35825	1.36182	1.36511
0.05096	2.5582	1.36964	1.37092	1.37226	1.37368
0.15392	1.6490	1.36360	1.3654	1.36732	1.36892
0.20490	1.3100	1.36143	1.36353	1.36551	1.36739
0.25171	1.0193	1.35932	1.36157	1.36378	1.36601
0.30155	0.7852	1.35812	1.36041	1.36285	1.36553
0.34819	0.5940	1.35703	1.35967	1.36238	1.36499
0.40409	0.4036	1.35587	1.35891	1.36195	1.36479
0.45439	0.1045	1.35314	1.35642	1.35966	1.36300
0.45485	0.2434	1.35505	1.35805	1.36140	1.36451

number of terms in the polynomial, and A_i are the parameters of the salt + water solutions, corresponding to $w_e = 0$. These parameters are collated from Table 4. In this way, binary systems (salt + water, ethanol + water) are perfectly represented in the equation of the ternary solution. For the ternary system of lithium, the refractive indices were measured to the solubility limit at all temperatures. For the other two systems, the refractive index was measured to the solubility limit at 308.15 K.

For the ternary salt systems measured, the values of the refractive index increased with concentration of the salt at a constant salt-free mass fraction and temperature. At constant composition, the refractive index decreased with an increase in temperature. At a constant molality of the salt and temperature, the increase in the salt-free mass fraction of ethanol led to a decrease of the refractive indices. The same behavior was observed for all systems.

Table 8. Fitting Parameters of eqs 4 and 5 and Standard Deviation (σ) of eq 6 for Salt + Ethanol + Water Ternary Systems

	318.15	308.15	298.15	288.15
	$CuSO_4$ + Ethanol + Water			
C_{11}	$-7.93162 \cdot 10^{-3}$	$-3.52555 \cdot 10^{-2}$	$-2.46700 \cdot 10^{-2}$	$-2.59260 \cdot 10^{-3}$
C_{12}	$-2.45138 \cdot 10^{-1}$	$1.16473 \cdot 10^{-1}$	$-2.04843 \cdot 10^{-2}$	$-7.66286 \cdot 10^{-2}$
C_{13}	$1.19049 \cdot 10^{-1}$			
C_{21}	$2.92658 \cdot 10^{-2}$	$3.85229 \cdot 10^{-2}$	$9.14327 \cdot 10^{-3}$	$8.90523 \cdot 10^{-3}$
C_{22}	$-2.62959 \cdot 10^{-1}$	$-1.99110 \cdot 10^{-1}$	$5.76286 \cdot 10^{-2}$	$-8.36155 \cdot 10^{-2}$
C_{23}	3.24642			
σ	$8 \cdot 10^{-5}$	$8 \cdot 10^{-5}$	$8 \cdot 10^{-5}$	$7 \cdot 10^{-5}$
	$MgSO_4$ + Ethanol + Water			
C_{11}	$-4.51012 \cdot 10^{-3}$	$-8.45216 \cdot 10^{-3}$	$-1.31808 \cdot 10^{-2}$	$-1.40177 \cdot 10^{-2}$
C_{12}	$-6.27409 \cdot 10^{-2}$	$5.12104 \cdot 10^{-3}$	$1.84793 \cdot 10^{-3}$	$2.91175 \cdot 10^{-2}$
C_{13}	$1.27355 \cdot 10^{-1}$	$-2.64599 \cdot 10^{-2}$	$7.14817 \cdot 10^{-2}$	$-2.16246 \cdot 10^{-2}$
C_{21}	$-2.14030 \cdot 10^{-3}$	$-1.08852 \cdot 10^{-4}$	$1.68948 \cdot 10^{-3}$	$4.20675 \cdot 10^{-3}$
C_{22}	$6.05722 \cdot 10^{-2}$	$1.05266 \cdot 10^{-2}$	$3.42377 \cdot 10^{-2}$	$-1.25970 \cdot 10^{-2}$
C_{23}	$-2.26480 \cdot 10^{-1}$	$-9.48625 \cdot 10^{-2}$	$-2.65638 \cdot 10^{-1}$	$-9.59827 \cdot 10^{-2}$
σ	$7 \cdot 10^{-5}$	$7 \cdot 10^{-5}$	$7 \cdot 10^{-5}$	$7 \cdot 10^{-5}$
	Li_2SO_4 + Ethanol + Water			
C_{11}	$1.39348 \cdot 10^{-2}$	$-1.05590 \cdot 10^{-3}$	$-1.37961 \cdot 10^{-2}$	$-8.08137 \cdot 10^{-3}$
C_{12}	$-1.40444 \cdot 10^{-1}$	$-2.73886 \cdot 10^{-2}$	$-1.51251 \cdot 10^{-2}$	$-3.16854 \cdot 10^{-3}$
C_{13}	$1.74112 \cdot 10^{-1}$	$-7.83714 \cdot 10^{-2}$	$-5.51537 \cdot 10^{-2}$	$-5.94686 \cdot 10^{-2}$
C_{21}	$-1.63982 \cdot 10^{-2}$	$-8.53294 \cdot 10^{-3}$	$1.52369 \cdot 10^{-2}$	$-1.11405 \cdot 10^{-3}$
C_{22}	$9.73594 \cdot 10^{-2}$	$-4.17535 \cdot 10^{-2}$	$-4.39347 \cdot 10^{-2}$	$1.35587 \cdot 10^{-2}$
C_{23}	$-8.76030 \cdot 10^{-2}$	$3.51921 \cdot 10^{-1}$	$2.97002 \cdot 10^{-1}$	$8.29126 \cdot 10^{-2}$
C_{31}	$3.37381 \cdot 10^{-3}$	$2.30465 \cdot 10^{-3}$	$-7.30448 \cdot 10^{-3}$	$1.72703 \cdot 10^{-3}$
C_{32}	$-2.08016 \cdot 10^{-2}$	$6.36297 \cdot 10^{-2}$	$5.74887 \cdot 10^{-2}$	$5.49739 \cdot 10^{-3}$
C_{33}	$9.40728 \cdot 10^{-3}$	$-3.12953 \cdot 10^{-1}$	$-3.28585 \cdot 10^{-1}$	$-1.61740 \cdot 10^{-1}$
σ	$8 \cdot 10^{-5}$	$8 \cdot 10^{-5}$	$8 \cdot 10^{-5}$	$7 \cdot 10^{-5}$

All parameters were obtained by an unweighted least-squares method applying a fitting algorithm because of Marquardt.[24] The root-mean-square deviation at each correlation is enclosed as a measurement of the validity of the gathered fitting parameters and an equation applied, which is expressed by eq 6.

$$\sigma = \sqrt{\frac{\sum_i^n (z_{i,\text{experimental}} - z_{i,\text{predicted}})^2}{n - p}} \qquad (6)$$

In this equation the value of the property, the number of experimental data, and the number of parameters are represented by z, n, and p, respectively. The root-mean-square deviation values between the experimental data of this work and the

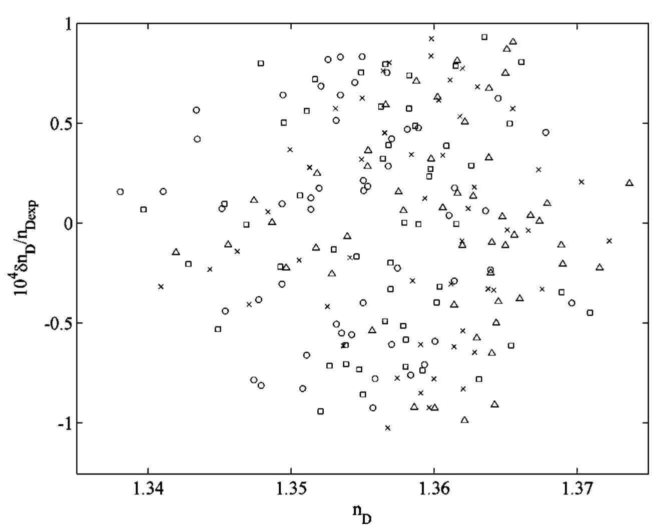

Figure 6. Relative error ($10^4(n_{Dexp} - n_{Dpred})/n_{Dexp}$) between the experimental and the predicted refractive index values for the water + ethanol + lithium sulfate ternary system: ○, 318.15 K; □, 308.15 K; ×, 298.15 K; Δ, 288.15 K.

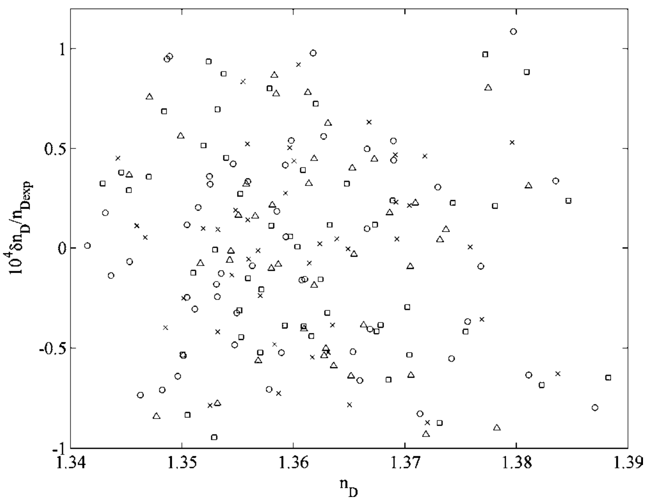

Figure 7. Relative error ($10^4(n_{Dexp} - n_{Dpred})/n_{Dexp}$) between the experimental and the predicted refractive index values for the water + ethanol + magnesium sulfate ternary system: ○, 318.15 K; □, 308.15 K; ×, 298.15 K; Δ, 288.15 K.

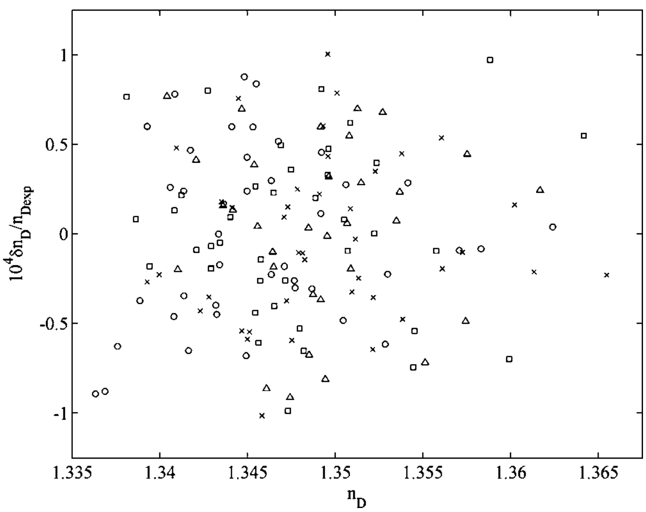

Figure 8. Relative error ($10^4(n_{Dexp} - n_{Dpred})/n_{Dexp}$) between the experimental and the predicted refractive index values for the water + ethanol + copper sulfate ternary system: ○, 318.15 K; □, 308.15 K; ×, 298.15 K; Δ, 288.15 K.

corresponding ones from the proposed equations show good agreement (Figures 6, 7, and 8).

Conclusion

This paper reports experimental data for the refractive index of (lithium, magnesium, or copper(II)) sulfate in ethanol + water mixtures from 288.15 to 318.15 K. These data were correlated by a method of least-squares to polynomials. For all systems, the root-mean-square deviation values between the experimental data of this work and the corresponding ones from the proposed equations show good agreement, and all values are less than 10^{-4} at all temperatures. So, the refractive index solutions are described adequately by these equations, and these polynomials can be used for refractive index prediction to salt saturation.

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