Refractive Indices of Sodium, Potassium, and Ammonium Sulfates in Ethanol−Water Solutions

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The refractive indices (sodium line) of sodium, potassium, and ammonium sulfate in water and ethanol + water solutions have been determined experimentally over the temperature range (288.15 to 318.15) K and at atmospheric pressure. Parameters of polynomial equations which represent the composition dependence are gathered. The predicted results show good agreement with the experimental data.

Introduction

The refractive index measurement provides important structural information about liquid mixtures,[1] since the refractive index is very sensitive to changes in molecular organization. Furthermore, the measure of this property has many practical applications such as concentration measurements,[2] phase-change determination,[3] dissociation constant measurement,[4] and the estimation of other physical properties.[5]

The present work continues our research program on the physical characterization of the salt effect in ethanol−water solutions.[6−8] The present paper presents experimental refractive indices of water + ethanol + (ammonium, sodium, or potassium sulfate) mixtures that have been measured as a function of the molality of the salt and the salt-free mass fraction of the solution, at atmospheric pressure and from (288.15 to 318.15) K at 10 K intervals. The refractive index of the mixtures was correlated by an application of a composition-dependent polynomial equation.

Unlike other physical properties, studies about the refractive index of water + alcohol mixed with a salt are very rare, so for the ethanol + water + salt systems treated in this paper no experimental data was found, except for the system containing sodium sulfate.[9]

Experimental Section

Materials. The sodium sulfate (mass fraction > 0.99), ammonium sulfate (mass fraction > 0.995), and potassium sulfate (mass fraction > 0.99) used in this work were from Merck. The chemicals were stored under sun and humidity protection conditions. The water used to prepare solutions was of Milli-Q quality (resistivity, 18.2 MΩ·cm) and was provided by our technical center. The ethanol employed was supplied by Merck (LiChrosolv quality) with a purity better than 0.995, degassed with ultrasound, and stored over freshly activated molecular sieves (type 4a or 3a, 1/16 in., Aldrich cat. no. 20.860-4 or 20.858-2, respectively) for several days before use.

Stock solutions of concentrated sulfates were prepared by mass, using a Mettler AT261 Delta range balance, with an uncertainty better than $\pm 10^{-4}$ g, yielding an uncertainty better than $\pm 5 \cdot 10^{-5}$ in the salt-free mass fraction and salt-free molar fraction and $\pm 5 \cdot 10^{-4}$ mol·kg^{-1} in the molality of the salt.

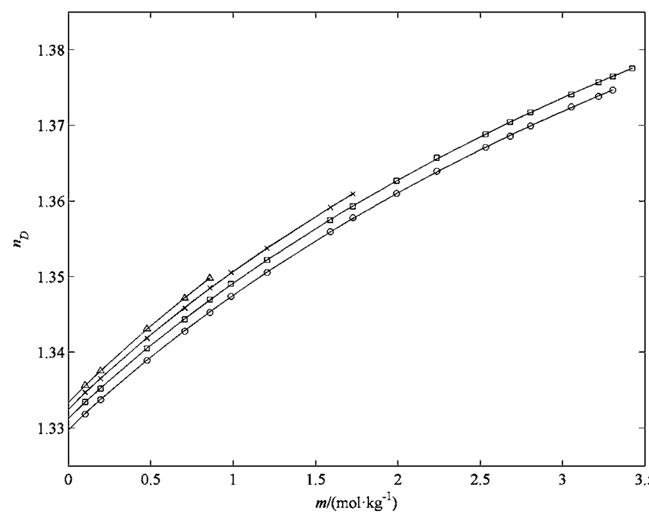

Figure 1. Refractive indices, n_D, vs molality of sodium sulfate in aqueous solution at different temperatures: ○, 318.15 K; □, 308.15 K; ×, 298.15 K; △, 288.15 K.

Measurements. Measurements of the refractive index (589.3 nm, sodium line) of samples were carried out using an automatic refractometer (ABBEMAT-HP Dr. Kernchen) with a precision of $\pm 10^{-5}$. The uncertainty in the temperature measurement was 0.1 K. 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. The relative error of the preparation process, manipulation, and measurement has an accuracy better than 0.00015.

Results and Discussion

The refractive indices for the salt + water binary mixtures were measured from zero to the solubility limit (Table 1). In the case of potassium sulfate and ammonium sulfate in water, its solubility increases with temperature, whereas in the case of sodium sulfate, we found a maximum of solubility between (305.15 and 306.15) K. All salts are insoluble in ethanol. These binary data were fitted to polynomials of the form:[10]

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Table 1. 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

m	T/K			
$\text{mol} \cdot \text{kg}^{-1}$	318.15	308.15	298.15	288.15
		K_2SO_4 + Water, n_D		
0.00000	1.32979	1.33128	1.33248	1.33339
0.04559	1.33072	1.33228	1.33359	1.33447
0.13868	1.33251	1.33411	1.33552	1.33636
0.25020	1.33466	1.33625	1.33771	1.33866
0.34090	1.33626	1.33786	1.33945	1.34035
0.41741	1.33763	1.33927	1.34071	1.34183
0.50302	1.33906	1.34077	1.34227	1.34330
0.50934	1.33920	1.34084	1.34230	1.34341
0.57028	1.34022	1.34186	1.34337	1.34451
0.65089	1.34151	1.34324	1.34476	
0.74350	1.34301	1.34478		
0.81064	1.34404			
0.86054	1.34488			
0.90485	1.34557			
		Na_2SO_4 + Water, n_D		
0.00000	1.32979	1.33128	1.33248	1.33339
0.10017	1.33185	1.33342	1.33473	1.33566
0.19375	1.33378	1.33518	1.33653	1.33757
0.47704	1.33896	1.34052	1.34187	1.34311
0.70547	1.34278	1.34434	1.34585	1.34719
0.85779	1.34531	1.34695	1.34855	1.34983
0.98656	1.34742	1.34904	1.35058	
1.20582	1.35057	1.35220	1.35377	
1.58976	1.35598	1.35746	1.35915	
1.72712	1.35778	1.35931	1.36096	
1.99199	1.36102	1.36271		
2.23676	1.36396	1.36573		
2.53241	1.36711	1.36884		
2.68065	1.36857	1.37046		
2.80462	1.36992	1.37172		
3.05340	1.37246	1.37411		
3.21880	1.37386	1.37569		
3.30508	1.37470	1.37649		
3.42297		1.37756		
		$(NH_4)_2SO_4$ + Water, n_D		
0.00000	1.32979	1.33128	1.33248	1.33339
0.27253	1.33544	1.33696	1.33813	1.33934
0.39945	1.33806	1.33941	1.34080	1.34174
0.48762	1.33956	1.34098	1.34227	1.34348
0.80250	1.34521	1.34670	1.34798	1.34905
1.19844	1.35156	1.35300	1.35434	1.35554
1.60363	1.35740	1.35888	1.36025	1.36140
1.99244	1.36252	1.36402	1.36535	1.36659
2.38125	1.36733	1.36878	1.37008	1.37134
2.80082	1.37211	1.37338	1.37472	1.37588
3.19975	1.37611	1.37738	1.37873	1.38006
3.61857	1.38009	1.38126	1.38259	1.38383
3.99732	1.38325	1.38446	1.38596	1.38708
4.39547	1.38647	1.38760	1.38897	1.39018
4.76252	1.38922	1.39031	1.39170	1.39286
5.18081	1.39197	1.39320	1.39451	1.39570
5.60005	1.39461	1.39584	1.39715	1.39836
5.87605	1.39618	1.39750		
6.32794	1.39830			

$$n_{\text{Dsw}} = n_{\text{Dw}} + \sum_{i=1}^{N} A_i m^{(i+1)/2} \tag{1}$$

where n_{Dsw} and n_{Dw} are the refractive index of the salt + water mixture and refractive index of water, respectively, m is the molality of the salt in the solution, A_i are fitting parameters, and N is the number of parameters. These parameters are presented in Table 2. Figures 1 to 3 show that, for any given binary salt + water mixture, the refractive index always decreases with increasing temperature and always increases with increasing molality of salt.

For the ternary systems of salt + water + ethanol solutions (Tables 3 to 5), a polynomial expansion[11] similar to that used for the salt + water solutions was used to represent ternary refractive indices

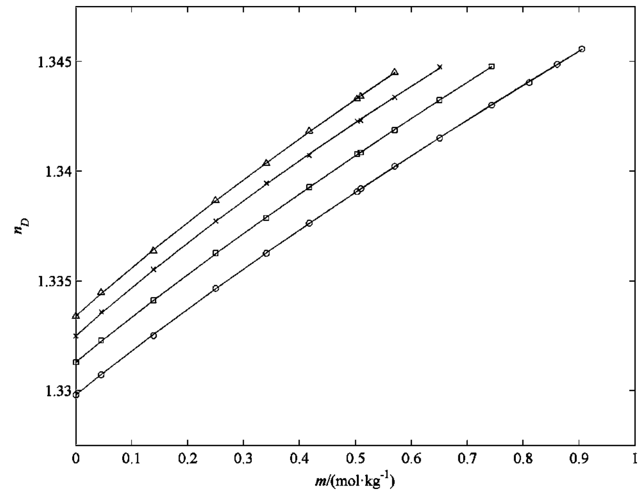

Figure 2. Refractive indices, n_D, vs molality of potassium sulfate in aqueous solution at different temperatures: ○, 318.15 K; □, 308.15 K; ×, 298.15 K; △, 288.15 K.

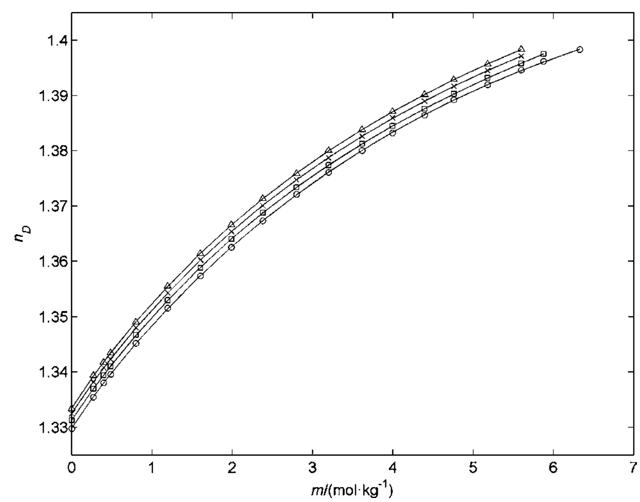

Figure 3. Refractive indices, n_D, vs molality of ammonium sulfate in aqueous solution at different temperatures: ○, 318.15 K; □, 308.15 K; ×, 298.15 K; △, 288.15 K.

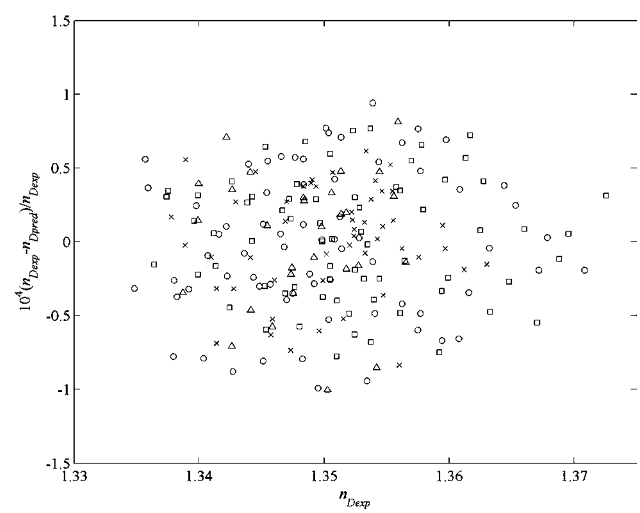

Figure 4. Relative error ($10^4(n_{\text{Dexp}} - n_{\text{Dpred}})/n_{\text{Dexp}}$) between the experimental and the predicted refractive index values for the water + ethanol + sodium sulfate ternary system: ○, 318.15 K; □, 308.15 K; ×, 298.15 K; △, 288.15 K.

Table 2. Fitting Parameters in Equation 1 and Root Mean Square Deviation (σ) of Equation 4 for the Salt + Water System

T/K	318.15	308.15	298.15	288.15
		K_2SO_4 + Water		
A_1/(kg·mol^{-1})	2.15142·10^{-2}	2.20493·10^{-2}	2.43105·10^{-2}	2.39279·10^{-2}
A_2/(kg$^{1.5}$·mol$^{-1.5}$)	−4.31117·10^{-3}	−4.54869·10^{-3}	−6.86625·10^{-3}	−5.90212·10^{-3}
σ	3·10^{-5}	3·10^{-5}	5·10^{-5}	4·10^{-5}
		Na_2SO_4 + Water		
A_1/(kg·mol^{-1})	2.28803·10^{-2}	2.29601·10^{-2}	2.36328·10^{-2}	2.39286·10^{-2}
A_2/(kg$^{1.5}$·mol$^{-1.5}$)	−5.11224·10^{-3}	−5.10265·10^{-3}	−5.42801·10^{-3}	−5.16140·10^{-3}
σ	7·10^{-5}	7·10^{-5}	8·10^{-5}	3·10^{-5}
		$(NH_4)_2SO_4$ + Water		
A_1/(kg·mol^{-1})	2.36659·10^{-2}	2.25206·10^{-2}	2.31541·10^{-2}	2.40360·10^{-2}
A_2/(kg$^{1.5}$·mol$^{-1.5}$)	−4.74581·10^{-3}	−2.35782·10^{-3}	−3.28383·10^{-3}	−4.20629·10^{-3}
A_3/(kg^{2}·mol^{-2})	−4.07402·10^{-4}	−1.98950·10^{-3}	−1.48643·10^{-3}	−1.12787·10^{-3}
A_4/(kg$^{2.5}$·mol$^{-2.5}$)	1.06288·10^{-4}	4.32307·10^{-4}	3.38847·10^{-4}	2.89194·10^{-4}
σ	7·10^{-5}	4·10^{-5}	6·10^{-5}	5·10^{-5}

Table 3. Refractive Index for the Ternary Mixtures of Sodium 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

	m	n_D at T/K					m	n_D at T/K			
w_e	mol·kg^{-1}	318.15	308.15	298.15	288.15	w_e	mol·kg^{-1}	318.15	308.15	298.15	288.15
0.03065	0.16180	1.33481	1.33640	1.33778	1.33871	0.12459	0.77618	1.35036	1.35246	1.35426	
0.02432	0.34996	1.33799	1.33960	1.34097	1.34220	0.12429	1.03960	1.35406	1.35610		
0.02361	0.69281	1.34395	1.34536	1.34700	1.34840	0.11916	1.30523	1.35752	1.35942		
0.02524	1.11568	1.35047	1.35201	1.35376		0.11842	1.47609	1.35942	1.36170		
0.02897	1.50506	1.35623	1.35781	1.35948		0.15368	0.07260	1.34035	1.34262	1.34451	1.34586
0.02525	1.79066	1.35976	1.36134	1.36302		0.14559	0.19117	1.34216	1.34423	1.34603	1.34755
0.02492	2.08363	1.36321	1.36479			0.13925	0.38509	1.34511	1.34720	1.34904	1.35060
0.02539	2.43287	1.36717	1.36881			0.14587	0.56930	1.34836	1.35045	1.35238	
0.02544	2.78210	1.37084	1.37256			0.14660	0.76766	1.35134	1.35348	1.35547	
0.05577	0.13695	1.33590	1.33753	1.33888	1.33998	0.14577	0.95321	1.35390	1.35610		
0.05212	0.35742	1.33978	1.34132	1.34277	1.34409	0.14602	1.24851	1.35750	1.35992		
0.04871	0.72370	1.34570	1.34733	1.34895	1.35030	0.17421	0.07098	1.34159	1.34386	1.34575	1.34744
0.05086	1.08731	1.35139	1.35298	1.35469		0.16805	0.31368	1.34541	1.34765	1.34959	1.35138
0.05139	1.43707	1.35624	1.35792	1.35969		0.17080	0.61542	1.35015	1.35245	1.35463	
0.04912	1.80160	1.36078	1.36250			0.17050	0.92949	1.35438	1.35698		
0.04815	2.09784	1.36441	1.36602			0.20093	0.05944	1.34271	1.34532	1.34732	1.34921
0.05058	2.40332	1.36785	1.36956			0.19889	0.21113	1.34511	1.34782	1.34991	1.35178
0.08155	0.04716	1.33570	1.33741	1.33892	1.33993	0.19844	0.42134	1.34827	1.35103	1.35328	
0.07492	0.20304	1.33822	1.33992	1.34140	1.34266	0.19696	0.62883	1.35125	1.35398		
0.07748	0.49780	1.34363	1.34525	1.34690	1.34835	0.20060	0.79646	1.35343	1.35645		
0.07077	0.81243	1.34834	1.34989	1.35154		0.22414	0.08052	1.34434	1.34691	1.34935	1.35136
0.07543	1.09995	1.35281	1.35442	1.35622		0.22630	0.24752	1.34699	1.34985	1.35226	
0.07462	1.46024	1.35772	1.35924	1.36120		0.22507	0.44759	1.34983	1.35282	1.35530	
0.07342	1.78237	1.36158	1.36330			0.24878	0.06919	1.34547	1.34803	1.35068	1.35276
0.07553	2.09146	1.36531	1.36703			0.24373	0.17920	1.34682	1.34968	1.35220	1.35420
0.10516	0.09663	1.33795	1.33993	1.34140	1.34262	0.24151	0.35486	1.34919	1.35232	1.35473	
0.10118	0.25084	1.34069	1.34243	1.34409	1.34545	0.24841	0.44902	1.35084	1.35375		
0.09978	0.49750	1.34483	1.34666	1.34835	1.34981	0.27624	0.05892	1.34653	1.34938	1.35203	1.35445
0.10146	0.74542	1.34885	1.35066	1.35241		0.27012	0.14936	1.34767	1.35047	1.35322	1.35557
0.10036	1.09716	1.35390	1.35578	1.35756		0.27505	0.32378	1.35036	1.35320	1.35601	
0.09994	1.38842	1.35770	1.35969			0.30233	0.04890	1.34749	1.35050	1.35336	1.35591
0.09786	1.63970	1.36085	1.36277			0.30056	0.09964	1.34832	1.35102	1.35409	1.35656
0.12677	0.08974	1.33917	1.34117	1.34292	1.34416	0.29836	0.20115	1.34951	1.35247	1.35553	
0.12518	0.26180	1.34223	1.34424	1.34586	1.34736	0.30068	0.27586	1.35082	1.35369		
0.12406	0.51873	1.34656	1.34852	1.35019	1.35179						

$$n_D = n_{Dew} + \sum_{i=1}^{P} C_i m^{(i+1)/2} \qquad (2)$$

where n_D and n_{Dew} are the refractive index of the ternary solution and of the ethanol + water solution, respectively, C_i are fitting parameters, and P is the number of parameters, in these cases. These parameters are dependent on the ethanol mass fraction of the salt-free system

$$C_i = A_i + \sum_{j=1}^{Q} C_{ij} w_e^j \qquad (3)$$

where w_e is the ethanol mass fraction of the salt free solution, C_{ij} are adjustable parameters, which are in Table 6, Q is the number of terms in the polynomial, and A_i are the parameters of the salt + water solutions, corresponding to $w_e = 0$. These latter parameters are collected from Table 2. In this way, binary systems (salt + water, ethanol + water) are perfectly represented in the equation of the ternary solution. The necessary refractive indices of ethanol + water mixtures are collected in a previous work.[8] The relative error between the experimental and the predicted refractive index values for the ternary systems is shown in Figures 4 to 6.

For the ternary salt systems measured, it was observed that the refractive index decreased with an increase in temperature or mass fraction of ethanol, and it is also seen that the refractive index increased with the molality of the salt. The same behavior was observed for all systems.

Table 4. Refractive Indices for the Ternary Mixtures of Potassium Sulfate for Various Mass Fractions w_e in w_e Ethanol + (1 − w_e) Water at a Temperature Range from (318.15 to 288.15) K

	m	n_D at T/K					m	n_D at T/K			
w_e	mol·kg^{-1}	318.15	308.15	298.15	288.15	w_e	mol·kg^{-1}	318.15	308.15	298.15	288.15
0.02786	0.40000	1.33895	1.34060	1.34190	1.34310	0.09970	0.36919	1.34267			
0.02414	0.10242	1.33328	1.33490	1.33607	1.33712	0.12067	0.06751	1.33844	1.34030	1.34188	1.34321
0.02491	0.20319	1.33533	1.33690	1.33810	1.33913	0.12307	0.14107	1.33997	1.34185	1.34347	1.34477
0.02305	0.30436	1.33706	1.33867	1.33993	1.34105	0.12729	0.21289	1.34138	1.34332	1.34497	
0.02022	0.50204	1.34042	1.34190	1.34325		0.12749	0.28368	1.34263			
0.02301	0.59805	1.34219	1.34368	1.34505		0.15358	0.05409	1.34001	1.34216	1.34395	1.34544
0.02710	0.69812	1.34401				0.15174	0.06549	1.34012	1.34225	1.34403	1.34551
0.05155	0.10052	1.33488	1.33658	1.33789	1.33891	0.15228	0.12533	1.34135	1.34350	1.34527	1.34669
0.04965	0.20006	1.33665	1.33820	1.33961	1.34074	0.14714	0.17602	1.34189	1.34395	1.34568	
0.05009	0.29962	1.33849	1.34019	1.34156	1.34265	0.14744	0.23304	1.34299			
0.05412	0.40384	1.34061	1.34218	1.34358		0.17460	0.05111	1.34109	1.34332	1.34532	1.34696
0.05191	0.50643	1.34216	1.34383			0.17523	0.10241	1.34228	1.34445	1.34633	1.34803
0.05106	0.57358	1.34326				0.17052	0.16716	1.34312	1.34530		
0.07558	0.08784	1.33616	1.33778	1.33915	1.34036	0.19972	0.04556	1.34237	1.34479	1.34696	1.34874
0.07252	0.18265	1.33768	1.33945	1.34084	1.34197	0.20477	0.08505	1.34340	1.34584	1.34808	1.34989
0.07841	0.30231	1.34020	1.34187	1.34334		0.20112	0.13101	1.34398	1.34644		
0.07419	0.37060	1.34112	1.34279	1.34428		0.22770	0.04327	1.34381	1.34647	1.34879	1.35085
0.07449	0.45251	1.34270				0.22283	0.09139	1.34440	1.34694	1.34928	
0.09990	0.08150	1.33737	1.33930	1.34078	1.34201	0.25005	0.02590	1.34472	1.34752	1.34994	1.35205
0.10053	0.16111	1.33898	1.34080	1.34222	1.34354	0.24256	0.04993	1.34480	1.34750	1.34989	1.35196
0.10018	0.23698	1.34033	1.34215	1.34364		0.24354	0.08253	1.34538	1.34802		
0.10184	0.30220	1.34159	1.34342								

Table 5. Refractive Indices for the Ternary Mixtures of Ammonium 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

	m	n_D at T/K					m	n_D at T/K			
w_e	mol·kg^{-1}	318.15	308.15	298.15	288.15	w_e	mol·kg^{-1}	318.15	308.15	298.15	288.15
0.02882	0.61670	1.34348	1.34494	1.34631	1.34741	0.20071	0.37020	1.34858	1.35059	1.35290	1.35477
0.02722	1.24301	1.35341	1.35488	1.35641	1.35761	0.20172	0.76254	1.35486	1.35704	1.35897	1.36087
0.02736	1.87213	1.36216	1.36360	1.36512	1.36638	0.19840	1.12945	1.36015	1.36177	1.36398	1.36575
0.02585	2.57255	1.37048	1.37185	1.37332	1.37462	0.20248	1.51956	1.36501	1.36687	1.36909	1.37078
0.02780	3.14176	1.37648	1.37781	1.37928	1.38059	0.20057	1.88087	1.36910	1.37110	1.37306	1.37484
0.02496	3.72341	1.38169	1.38311	1.38447	1.38582	0.20093	2.20976	1.37239	1.37479	1.37650	1.37827
0.02508	4.39067	1.38729	1.38845	1.38991	1.39115	0.22927	0.59208	1.35348	1.35581	1.35799	1.35997
0.02626	4.98435	1.39160	1.39283	1.39414	1.39545	0.20898	1.10118	1.36010	1.36201	1.36401	1.36577
0.05008	0.63292	1.34487	1.34638	1.34766	1.34882	0.22582	1.80116	1.36879	1.37096	1.37291	1.37477
0.04936	1.29312	1.35530	1.35675	1.35814	1.35950	0.22526	1.19088	1.36182	1.36368	1.36574	1.36785
0.05134	1.91119	1.36369	1.36519	1.36676	1.36798	0.24420	0.35233	1.35007	1.35256	1.35490	1.35722
0.05082	2.56756	1.37151	1.37281	1.37427	1.37565	0.24831	0.70307	1.35591	1.35830	1.36060	1.36279
0.04646	3.19957	1.37781	1.37906	1.38062	1.38187	0.24707	1.06406	1.36070	1.36282	1.36520	1.36743
0.05035	3.86284	1.38387	1.38523	1.38666	1.38795	0.24782	1.38870	1.36469	1.36686	1.36912	1.37134
0.05106	4.47175	1.38869	1.39010	1.39136	1.39274	0.25166	1.72444	1.36832	1.37071	1.37291	1.37503
0.07763	0.62566	1.34624	1.34791	1.34928	1.35038	0.27541	0.45485	1.35306	1.35579	1.35819	1.36055
0.07684	1.23933	1.35606	1.35749	1.35885	1.36007	0.27770	0.89134	1.35948	1.36187	1.36417	1.36655
0.07684	1.87815	1.36464	1.36612	1.36744	1.36875	0.27586	1.33489	1.36456	1.36721	1.36937	1.37166
0.07757	2.51313	1.37209	1.37353	1.37486	1.37612	0.29620	0.24961	1.35063	1.35350	1.35626	1.35862
0.07643	3.13060	1.37808	1.37976	1.38090	1.38227	0.29672	0.50109	1.35468	1.35735	1.35979	1.36252
0.07524	3.75927	1.38376	1.38527	1.38643	1.38780	0.29772	0.74673	1.35789	1.36059	1.36313	1.36575
0.07811	4.19720	1.38739	1.38880	1.39022	1.39162	0.29766	1.00058	1.36117	1.36368	1.36639	1.36866
0.10282	0.58637	1.34714	1.34873	1.35034	1.35156	0.29996	1.31390	1.36444	1.36753	1.36986	1.37227
0.10271	1.20546	1.35679	1.35830	1.35999	1.36124	0.32172	0.39079	1.35363	1.35663	1.35936	1.36221
0.10284	1.77934	1.36459	1.36605	1.36752	1.36899	0.32285	0.78945	1.35902	1.36191	1.36456	1.36725
0.10236	2.37897	1.37163	1.37305	1.37437	1.37595	0.34931	0.14943	1.35082	1.35410	1.35705	1.35987
0.10440	2.98801	1.37768	1.37939	1.38084	1.38222	0.34768	0.30316	1.35336	1.35622	1.35924	1.36201
0.10031	3.47906	1.38216	1.38366	1.38504	1.38639	0.34980	0.45977	1.35549	1.35866	1.36150	1.36419
0.12741	0.69870	1.35034	1.35193	1.35362	1.35500	0.34876	0.60824	1.35744	1.36049	1.36311	1.36592
0.12978	1.38490	1.36059	1.36224	1.36382	1.36522	0.35101	0.80959	1.35982	1.36295	1.36575	1.36836
0.12762	2.08320	1.36919	1.37071	1.37231	1.37365	0.37568	0.29610	1.35406	1.35703	1.36009	1.36296
0.12994	2.75691	1.37616	1.37815	1.37944	1.38094	0.37340	0.59452	1.35767	1.36082	1.36377	1.36671
0.14895	0.48774	1.34782	1.34972	1.35149	1.35303	0.39740	0.10440	1.35158	1.35523	1.35827	1.36134
0.14970	0.95302	1.35541	1.35715	1.35889	1.36045	0.39628	0.20099	1.35322	1.35636	1.35972	1.36266
0.15244	1.43286	1.36231	1.36396	1.36562	1.36719	0.39983	0.35696	1.35543	1.35863	1.36171	1.36466
0.15182	1.91303	1.36818	1.36981	1.37153	1.37299	0.39699	0.45122	1.35639	1.35975	1.36288	1.36575
0.15271	2.40083	1.37341	1.37525	1.37677	1.37836	0.42416	0.17854	1.35345	1.35694	1.36014	1.36334
0.15143	2.69928	1.37619	1.37812	1.37967	1.38127	0.42539	0.36109	1.35578	1.35925	1.36257	1.36538
0.17842	0.69658	1.35291	1.35478	1.35669	1.35834	0.44730	0.09917	1.35288	1.35653	1.35987	1.36295
0.17905	1.39783	1.36290	1.36470	1.36654	1.36807	0.45019	0.20427	1.35456	1.35805	1.36130	1.36450
0.17723	2.09539	1.37074	1.37273	1.37448	1.37599	0.44733	0.30490	1.35577	1.35908	1.36259	1.36561

All parameters were obtained using an unweighted least-squares method applying a fitting algorithm due to Marquardt.[12] The root-mean-square deviation at each correlation is enclosed as a measurement of the validity of the

Table 6. Fitting Parameters of Equations 2 and 3 and the Standard Deviation (σ) of Equation 4 for Salt + Ethanol + Water Ternary Systems

T/K	318.15	308.15	298.15	288.15
		K_2SO_4 + Ethanol + Water		
C_{11}/(kg·mol^{-1})	$1.06099 \cdot 10^{-2}$	$-3.17795 \cdot 10^{-3}$	$-2.30101 \cdot 10^{-2}$	$-1.45432 \cdot 10^{-2}$
C_{12}/(kg·mol^{-1})	$-1.28624 \cdot 10^{-1}$	$-4.74993 \cdot 10^{-2}$		
σ	$7 \cdot 10^{-5}$	$7 \cdot 10^{-5}$	$7 \cdot 10^{-5}$	$7 \cdot 10^{-5}$
		Na_2SO_4 + Ethanol + Water		
C_{11}/(kg·mol^{-1})	$-2.07529 \cdot 10^{-2}$	$-2.01121 \cdot 10^{-2}$	$-2.19955 \cdot 10^{-2}$	$-1.77344 \cdot 10^{-2}$
C_{12}/(kg·mol^{-1})	$3.42428 \cdot 10^{-1}$	$8.63054 \cdot 10^{-2}$	$2.67212 \cdot 10^{-2}$	$6.69712 \cdot 10^{-2}$
C_{13}/(kg·mol^{-1})	-2.80573	$-2.39347 \cdot 10^{-1}$		
C_{14}/(kg·mol^{-1})	5.59348			
C_{21}/(kg$^{1.5}$·mol$^{-1.5}$)	$1.14289 \cdot 10^{-2}$	$8.46688 \cdot 10^{-3}$	$1.24445 \cdot 10^{-2}$	$2.04054 \cdot 10^{-2}$
C_{22}/(kg$^{1.5}$·mol$^{-1.5}$)	$-2.65150 \cdot 10^{-1}$	$-6.59977 \cdot 10^{-2}$	$-5.40337 \cdot 10^{-2}$	$-2.06747 \cdot 10^{-1}$
C_{23}/(kg$^{1.5}$·mol$^{-1.5}$)	1.70957	$6.93240 \cdot 10^{-2}$		
C_{24}/(kg$^{1.5}$·mol$^{-1.5}$)	-3.01810			
σ	$7 \cdot 10^{-5}$	$6 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	$6 \cdot 10^{-5}$
		$(NH_4)_2SO_4$ + Ethanol + Water		
C_{11}/(kg·mol^{-1})	$7.10207 \cdot 10^{-3}$	$-1.06009 \cdot 10^{-2}$	$-1.15213 \cdot 10^{-2}$	$-2.54224 \cdot 10^{-2}$
C_{12}/(kg·mol^{-1})	$-1.84902 \cdot 10^{-1}$	$-1.62783 \cdot 10^{-2}$	$-5.21095 \cdot 10^{-2}$	$7.55857 \cdot 10^{-2}$
C_{13}/(kg·mol^{-1})	$2.80134 \cdot 10^{-1}$	$2.22900 \cdot 10^{-2}$	$1.01193 \cdot 10^{-1}$	$-1.10267 \cdot 10^{-1}$
C_{21}/(kg$^{1.5}$·mol$^{-1.5}$)	$-2.11077 \cdot 10^{-2}$	$-5.35182 \cdot 10^{-4}$	$-5.83808 \cdot 10^{-4}$	$1.67868 \cdot 10^{-2}$
C_{22}/(kg$^{1.5}$·mol$^{-1.5}$)	$2.63374 \cdot 10^{-1}$	$1.17405 \cdot 10^{-2}$	$6.20004 \cdot 10^{-2}$	$-1.03140 \cdot 10^{-1}$
C_{23}/(kg$^{1.5}$·mol$^{-1.5}$)	$-4.01581 \cdot 10^{-1}$	$-5.28261 \cdot 10^{-2}$	$-1.62468 \cdot 10^{-1}$	$6.66101 \cdot 10^{-2}$
C_{31}/(kg^{2}·mol^{-2})	$7.24449 \cdot 10^{-3}$	$1.45760 \cdot 10^{-3}$	$1.78093 \cdot 10^{-3}$	$-2.96082 \cdot 10^{-3}$
C_{32}/(kg^{2}·mol^{-2})	$-8.30893 \cdot 10^{-2}$	$-2.79403 \cdot 10^{-3}$	$-2.45166 \cdot 10^{-2}$	$1.83531 \cdot 10^{-2}$
C_{33}/(kg^{2}·mol^{-2})	$6.09966 \cdot 10^{-2}$	$5.21523 \cdot 10^{-3}$	$5.29275 \cdot 10^{-2}$	$2.42889 \cdot 10^{-2}$
σ	$8 \cdot 10^{-5}$	$8 \cdot 10^{-5}$	$8 \cdot 10^{-5}$	$8 \cdot 10^{-5}$

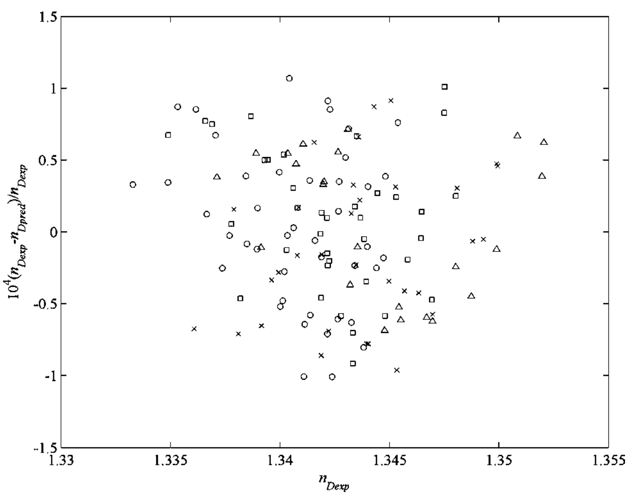

Figure 5. Relative error ($10^4(n_{Dexp} - n_{Dpred})/n_{Dexp}$) between the experimental and the predicted refractive index values for the water + ethanol + potassium sulfate ternary system: ○, 318.15 K; □, 308.15 K; ×, 298.15 K; △, 288.15 K.

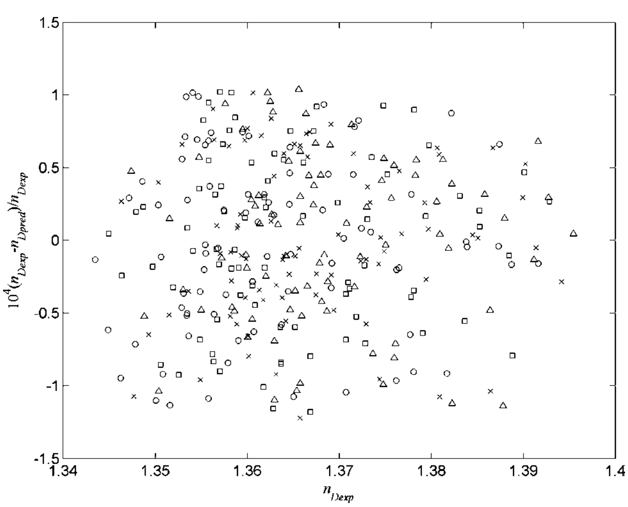

Figure 6. Relative error ($10^4(n_{Dexp} - n_{Dpred})/n_{Dexp}$) between the experimental and the predicted refractive index values for the water + ethanol + ammonium sulfate ternary system: ○, 318.15 K; □, 308.15 K; ×, 298.15 K; △, 288.15 K.

gathered fitting parameters, and the equation applied is expressed by eq 4.

$$\sigma = \sqrt{\frac{\sum_{i}^{n} (z_{i,\text{experimental}} - z_{i,\text{predicted}})^2}{n - p}} \quad (4)$$

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.

Conclusions

In this paper, refractive indices of (sodium, ammonium, or potassium) sulfate in water and ethanol + water mixtures were experimentally determined from (288.15 to 318.15) K and at atmospheric pressure. A decrease in all measured refractive indices was observed with an increase in temperature or mass fraction of ethanol, and an increase was observed with an increase in molality of the salt. For all systems, the index of refraction is described adequately by these equations, and these polynomials can be used for the refractive index prediction to salt saturation.

Literature Cited

(1) Jimenez, R. J.; Philipp, M.; Ramos, M. A.; Krüger, J. K. Concentration and Temperature Dependence of the Refractive Index of Ethanol-Water Mixtures: Influence of Intermolecular Interactions. *Eur. Phys. J. E* **2009**, *30*, 19–26.

(2) Genceli, F. E.; Himawan, C.; Witkamp, G. J. Inline Determination of Supersaturation and Metastable Zone width of $MgSO_4 \cdot 12H_2O$ with Conductivity and Refractive Index Measurement Techniques. *J. Cryst. Growth* **2005**, *275*, e1757–e1762.

(3) Mohsen-Nia, M.; Rasa, M.; Modarress, H. Cloud-Point Measurements for (Water-Poly(ethylene glycol) + Salt) Ternary Mixtures by Refractometry Method. *J. Chem. Eng. Data* **2006**, *51*, 1316–1320.

(4) Grunwald, E.; Haley, J. F. Acid Dissociation Constant of Trifluoroacetic Acid in Water Measured by Differential Refractometry. *J. Phys. Chem.* **1968**, *69*, 1123–1129.

(5) Heller, W. Remarks on Refractive Index Mixture Rules. *J. Phys. Chem.* **1965**, *76*, 1944–1948.

(6) Hervello, M. F.; Sánchez, A. Densities of Univalent Cation Sulphates in Ethanol - Water Solutions. *J. Chem. Eng. Data* **2007**, *52*, 752–756.

(7) Hervello, M. F.; Sánchez, A. Densities of (Lithium, Magnesium or Copper Sulphates(II)) in Ethanol - Water Solutions. *J. Chem. Eng. Data* **2007**, *52*, 906–909.

(8) Urréjola, S.; Sánchez, S.; Hervello, M. F. Refractive Indices of Lithium, Magnesium and Copper (II) Sulfates in Ethanol - Water solutions. *J. Chem. Eng. Data* **2010**, *55*, 482–487.
(9) Padova, J. Ion-Solvent Interaction in Mixed Solvents. Part III. The Molar Refraction of Electrolytes. *Can. J. Chem.* **1965**, *43*, 458–462.
(10) Lo Surdo, A.; Alzola, E. M.; Millero, F. J. The (p, V, T) Properties of Concentrated Aqueous Electrolytes I. Densities and Apparent Molar Volumes of NaCl, Na_2SO_4, $MgCl_2$, and $MgSO_4$ Solutions from 0.1 $mol\cdot kg^{-1}$ to Saturation and from 273.15 to 323.15 K. *J. Chem. Thermodyn.* **1982**, *14*, 649–662.
(11) Comesaña, J. F.; Otero, J. J.; Camesella, E.; Correa, A. Densities and Viscosities of Ternary Systems of Water + Fructose + Sodium Chloride from 20 to 40 °C. *J. Chem. Eng. Data* **2001**, *46*, 1153–1155.
(12) Marquardt, D. W. An Algorithm for Least-Squares Estimation of Nonlinear Parameters. *J. Soc. Ind. Appl. Math.* **1963**, *11*, 431–441.

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