DOI:10.7598/cst2018.1450
ISSN:2278-3458

Chemical Science Transactions
2018, **7(1),** 151-157

RESEARCH ARTICLE

Molar Refraction, Thermal Expansivity and Polarizabilities of Aqueous 1-1 Electrolyte Solutions

RUPALI SETHI[1*], N.K.SONI[2], TANU SRIVASTAVA[1] and
SURENDRA KUMAR VISHWAKARMA[3]

[1]Department of Chemistry, University of Allahabad, Allahabad, India

[2]Department of Chemistry, Govt. P.G. College Charkhari U.P., India

[3]Department of Chemistry, Mahatma Gandhi Chitrakoot Gramodaya Vishvavidyalaya Chitrakoot, Satna, India

sethirupali.au@gmail.com

Received 26 August 2017 / Accepted 9 September 2017

Abstract: The refractive index and density of aqueous solutions of LiCl, NaCl and KCl have been measured at four different temperatures (298.15, 303.15, 313.15 and 318.15 K) in the concentration range of 0.01 to 0.1 molar. From the experimental values of density and refractive index molar refractions of electrolyte solution and electrolyte have been calculated. These data were also utilized to obtain the values of thermal expansion coefficient and polarizability using the relevant equations. The results of investigation were found to be satisfactory.

Keywords: Refractive index, Thermal expansion coefficient, Polarizability, Density

Introduction

Considerable work has been done during recent past on the refractive index and related properties of non-electrolyte solutions. This property can be used to study the molecular interactions and also can be employed to correlate important properties *e.g*. molar refraction, polarizability and thermal expansion coefficient. Various mixing rules[1-7] for refractive index have been proposed from time to time. These mixing rules have been applied and tested by a number of workers for binary and higher order liquid mixtures. However, such study of refractive index has been quite limited for electrolyte solutions, Lee *et al.,*[8] measured refractive index of LiBr + H_2O + 1,3 propane diol system. Knowledge of refractive index (n), molar refraction (R_m), thermal expansion coefficient (α) and polarizabilities (α_p) is useful for predicting many physicochemical properties of electrolyte solutions. There are several correlations between refractive index and some thermophysical properties like critical constants, density, polarizability, equation of state parameters and dielectric permittivity that indicate the importance of this property for the study of electrolytic solutions while a wealth of studies on water and electrolyte solutions by light absorption and scattering experiments have been reported, we pay attention here to study refractive index of aqueous solutions of electrolytes. The polarizabilities of free or gaseous ions are not susceptible to direct experimental determinations[9]. The purpose of the present work is to deduce thermal expansion coefficient, molar refraction and polarizibilities of ions of aqueous electrolyte solutions from the experimental data of density and refractive index. We have employed common mixing rules, Lorentz-Lorenz[5,6] and Eykman (Eyk)[7], for the calculation of thermal expansion coefficient (α) of solutions.

Experimental

Densities of solutions were measured with a single stem Pycnometer which was calibrated by using triple distilled water at 298.15 K. The overall experimental uncertainty in the density measurement was estimated to be ±0.0001 g/cc. Ultrasonic speeds of pure liquids and their solutions were measured using an ultrasonic interferometer supplied by M/S Mittal Enterprise, New Delhi, operating at a frequency of 2MHz. The ultrasonic speeds were measured in pure liquid water, 1-butanol, 2-butanol, 2-methyl-1-propanol and 2-methyl-2 propanol at 298.15 K. These values were compared to the literature values. The maximum error in the speed of sound relative to water at 298.15 K was found to be less than 0.2 ms^{-1}. The refractive index of pure water and electrolytic solutions were measured directly with calibrated and thermostatic instrument called Abbe Refractometer at wavelength of *D*-sodium line 589.3 nm. The instrument was calibrated by using the aforesaid liquids at 298.15 K. A thermostatically controlled bath was used for temperature measurements giving precision of +0.1 K. The electrolytes LiCl, NaCl and KCl used were of A.R. grade. The solutions were proposed in triple distilled water. The details of experimental procedure for measuring density, refractive index and ultrasonic speed are described in earlier papers[7,10].

Formulation

Density, refractive index and ultrasonic speed data of aqueous LiCl, NaCl and KCl solutions were employed to obtain important and useful properties with the help of relations outlined here.

$$\text{Molar refraction, } R_m = \frac{n^{2-1}}{n^{2+2}}.Vm \quad (1)$$

V_m is the molar volume of electrolytic solution R_m of solute electrolyte can be calculated by the relation,

$$R_{m,(soln.)} = R_{m,(solvent)} + R_{m,(solute)} \quad (2)$$

Hence,

$$R_{m\ (electrolyte)} = R_{m\ ,(soln.)} - R_{m,\ (water)} \quad (3)$$

$R_{m\ (soln)}$ and $R_{m(water)}$ are given by

$$R_{m(soln.)} = \frac{n_{soln.}^2 - 1}{n_{soln.}^2 + 2} . \frac{\sum MiXi}{\rho_{soln.}} \quad (4)$$

Where

$$\frac{\sum MiXi}{\rho_{soln.}} = \frac{M_{salt}X + M_w X_w}{\rho_{soln.}} \quad (5)$$

$$R_{m(w)} = \frac{n_w^2 - 1}{n_w^2 + 2} . \frac{Mw}{\rho w} \quad (6)$$

$$R_{m(salt)} = \frac{n_{salt}^2 - 1}{n_{salt}^2 + 2} \cdot \frac{M_{salt}}{\rho_{salt}} \quad (7)$$

The polarizability, α_p, of the solution is obtained from equation,

$$\alpha_p = \frac{3R_m}{4\pi N} \quad (8)$$

Where N is the Avogadro number, using the temperature dependant data of density, the values of thermal expansion coefficient (α) of solution is obtained from the relation.

$$\alpha = \rho\left(\frac{\partial_{\rho-1}}{\partial T}\right)_P \quad (9)$$

The temperature dependent refractive index data has been employed to calculate α of binary electrolyte solution. This approach has been recently employed[11-13] for binary liquid mixtures. Lorentz-Lorenz (L-L)[4,5] and Eykman (Eyk)[14] mixing rules for refractive index were employed to obtain α using the following equation;

$$\alpha_{L-L} \frac{-6n}{(n^2-1)(n^2+2)}\left(\frac{dn}{dt}\right) \quad (10)$$

$$\alpha_{Eyk} = -\frac{(n^2+0.8n+1)}{(n^2-1)(n+0.4)}\left(\frac{dn}{dt}\right) \quad (11)$$

Results and Discussion

Experimental values of density and refractive index of aqueous solutions of LiCl, NaCl and KCl have been used to calculate molar refraction, polarizability and thermal expansivity at five different temperatures 298.15 K, 303.15 K, 308.15 K, 313.15 K and 318.15 K using various relations. The calculated values of R_m, α_p, α are reported in Tables 1-3. A perusal of Tables 1-3 reveals that the polarizability, thermal expansivity and molar refraction values of solution and solvent decrease with increasing temperature for all the binary electrolytic solutions over the entire concentration range. The values of all the thermodynamic properties also increase with increasing concentration of the solution. The trends of increasing all the properties are the same in all the solutions. Thermal expansion coefficient of electrolyte solution has been determined by using Eqs 8-10. This property is linked with the electrostriction of water in the vicinity of ions and changes in the water structure (hydrogen-bonding equilibrium among water molecules). The decrease in thermal expansivity by raising the temperature is due to the ion-water interactions. Molar refraction has been calculated using Eq. 1.The calculated molar refractions are included in Table 1, the molar refraction values of the electrolyte solutions assuming the rule of mixtures holds, are recorded. In the case of electrolyte solutions only positive values of R_m are observed. R_m values employed to explain interaction effects in electrolytic solutions. From the above, it can be calculated that interactions depend on the concentration and temperature. The polarizability of a compound is a measure of its molecular volume. In the phenomenon of refraction of light it is the loosely bound (called active) electrons of the ions which play a prominent role. Since the electrons of the cation are very firmly held owing to the positive charge and the opposite holds in the case of the anion, it is the latter ion which makes the principal contribution to the molar refraction.

Table 1. Molar refraction of aqueous solutions and electrolyte ($R_{m,\ elec}$) of LiCl, NaCl and KCl, as a function of concentration and temperature

Conc., mL^{-1}	298.15 K		303.15 K		308.15 K		313.15 K		318.15 K	
	Soln.	Elec.	Soln.	Elec.	Soln.	Elec.	Soln.	Elec.	Soln.	Elec.
LiCl										
0.1	10.0659	6.4267	10.0613	6.4315	10.0503	6.4223	10.0251	6.3973	9.9714	6.3386
0.09	10.0623	6.423	10.0605	6.4307	10.0379	6.4099	10.0168	6.389	9.9811	6.3484
0.08	10.0577	6.4184	10.0574	6.4276	10.0327	6.4047	10.0103	6.3825	9.9782	6.3455
0.07	10.0541	6.4148	10.0533	6.4234	10.0353	6.4073	10.0187	6.3909	9.9924	6.3596
0.06	10.0523	6.413	10.0478	6.418	10.0405	6.4125	10.0239	6.3961	10.0114	6.3787
0.05	10.0525	6.4132	10.0541	6.4242	10.0447	6.4167	10.0273	6.3995	10.0211	6.3884
0.04	10.0587	6.4194	10.0536	6.4238	10.0461	6.4181	10.0279	6.4001	10.0334	6.4006
0.03	10.0639	6.4246	10.0629	6.4331	10.0465	6.4185	10.0361	6.4083	10.0446	6.4119
0.02	10.0653	6.426	10.0651	6.4353	10.0507	6.4228	10.0424	6.4146	10.0551	6.4223
0.01	10.0657	6.4265	10.0704	6.4406	10.0562	6.4282	10.0527	4.4249	10.0637	6.431
NaCl										
0.1	10.1342	6.4949	10.1212	6.4914	10.0859	6.4579	10.0569	6.4291	10.085	6.4523
0.09	10.1192	6.4799	10.0933	6.4635	10.0822	6.4542	10.0504	6.4226	10.0958	6.4631
0.08	10.1063	6.4671	10.083	6.4532	10.074	6.446	10.0468	6.419	10.0972	6.4645
0.07	10.1017	6.4624	10.0738	6.444	10.0784	6.4504	10.0591	6.4313	10.0949	6.4622
0.06	10.0981	6.4588	10.072	6.4422	10.077	6.449	10.0605	6.4327	10.1024	6.4697
0.05	10.0927	6.4534	10.0559	6.426	10.0607	6.4327	10.0639	6.4361	10.1047	6.472
0.04	10.0959	6.4567	10.0555	6.4256	10.0639	6.4359	10.0692	6.4414	10.1069	6.4742
0.03	10.1012	6.4619	10.0619	6.4321	10.0682	6.4402	10.0795	6.4517	10.1084	6.4756
0.02	10.1055	6.4662	10.0613	6.4315	10.0628	6.4348	10.0668	6.439	10.0897	6.4569
0.01	10.091	6.4517	10.055	6.4252	10.0625	6.4345	10.0667	6.4389	10.0771	6.4443
KCl										
0.1	10.0732	6.4339	10.0499	6.42	10.0096	6.3816	9.9975	6.3697	9.9904	6.3577
0.09	10.0517	6.4124	10.0293	6.3995	10.0022	6.3742	9.9939	6.366	10.0247	6.3919
0.08	10.048	6.4088	10.0285	6.3987	10.0013	6.3733	9.992	6.3642	10.0281	6.3953
0.07	10.0472	6.4079	10.0239	6.3941	10.0005	6.3725	9.9874	6.3596	10.0293	6.3965
0.06	10.0398	6.4005	10.0221	6.3922	9.9997	6.3717	10.0055	6.3777	10.0288	6.3961
0.05	10.0295	6.3902	10.0146	6.3848	9.9989	6.3709	9.9953	6.3675	10.0261	6.3934
0.04	10.0231	6.3838	10.0198	6.39	10.0101	6.3821	10.0081	6.3803	10.0304	6.3976
0.03	10.0194	6.3801	10.03	6.4002	10.0143	6.3863	10.0145	6.3867	10.0326	6.3998
0.02	10.0168	6.3775	10.0342	6.4044	10.0225	6.3945	10.0187	6.3909	10.0409	6.4081
0.01	10.034	6.3948	10.0366	6.4068	10.0307	6.4027	10.0302	6.4024	10.0453	6.4126

Table 2. Experimental and calculated values (from *Eq. 10 and #Eq.11) of thermal expansion coefficient of aqueous solutions of LiCl, NaCl, KCl, as a function of concentration and temperature

C mol /Lit	LiCl														
	298.15 K			303.15 K			308.15 K			313.15 K			318.15 K		
	Exp.	Cal.*	Cal.#	Exp.	Cal.*	Cal.#	Exp.	Cal.*	Cal.#	Exp.	Cal.*	Cal.#	Exp.	Cal.*	Cal.#
0.1	3.0975	4.3066	4.5007	3.0978	4.3096	4.5036	3.0988	4.317	4.5108	3.0997	4.332	4.5252	3.1143	4.3486	4.5411
0.09	2.9982	4.3096	4.5036	2.9985	4.311	4.505	2.9993	4.3245	4.518	3.0006	4.338	4.531	3.0181	4.3546	4.547
0.08	2.8986	4.3125	4.5065	2.8993	4.314	4.5079	2.9003	4.329	4.5223	2.9012	4.3425	4.5353	2.9155	4.3562	4.5484
0.07	3.0191	4.2034	4.3922	3.0197	4.2049	4.3936	3.0236	4.2209	4.4091	3.0254	4.2327	4.4204	3.0391	4.2445	4.4317
0.06	3.6793	4.0927	4.2764	3.6807	4.097	4.2805	3.6874	4.1098	4.2928	3.6896	4.1212	4.3038	3.7088	4.1327	4.3149
0.05	3.8804	4.2626	4.4538	3.8843	4.267	4.458	3.8905	4.2803	4.4709	3.8936	4.2938	4.4838	3.9137	4.3057	4.4953
0.04	3.8639	4.2641	4.4552	3.8673	4.2715	4.4623	3.8732	4.2833	4.4737	3.8771	4.2982	4.4881	3.8966	4.3072	4.4967
0.03	3.907	4.2655	4.4566	3.9121	4.2729	4.4637	3.9157	4.2863	4.4766	3.9216	4.2997	4.4895	3.9398	4.3087	4.4982
0.02	3.9699	4.2685	4.4595	3.9743	4.2744	4.4652	3.9787	4.2878	4.478	3.9855	4.3012	4.491	4.004	4.3118	4.5011
0.01	4.2331	4.2715	4.4623	4.2387	4.2759	4.4666	4.2446	4.2908	4.4809	4.2527	4.3027	4.4924	4.2713	4.3163	4.5054
	NaCl														
0.1	3.2967	5.0462	5.2773	3.297	5.0548	5.2857	3.2984	5.0793	5.3091	3.299	5.0986	5.3277	3.311	5.1039	5.3328
0.09	3.0975	4.2786	4.4739	3.0981	4.2934	4.4881	3.0991	4.3008	4.4952	3.0997	4.3187	4.5124	3.1163	4.3232	4.5167
0.08	3.0079	3.8407	4.0154	3.0085	3.8526	4.0269	3.01	3.8593	4.0333	3.0103	3.8727	4.0461	3.028	3.8767	4.0500
0.07	3.0182	3.5648	3.7268	3.0191	3.5784	3.7398	3.023	3.5821	3.7434	3.0248	3.5933	3.7541	3.0382	3.597	3.7577
0.06	3.4586	3.5116	3.6709	3.4593	3.5237	3.6826	3.4659	3.5298	3.6884	3.468	3.5396	3.6978	3.4844	3.542	3.7002
0.05	3.4797	2.8456	2.9745	3.4835	2.8624	2.9906	3.4891	2.8664	2.9944	3.4912	2.8674	2.9954	3.5063	2.8684	2.9964
0.04	3.4217	2.7348	2.8586	3.4262	2.7528	2.8759	3.431	2.7548	2.8778	3.4337	2.7557	2.8787	3.4476	2.7567	2.8796
0.03	3.4245	2.7918	2.918	3.4303	2.8111	2.9367	3.4334	2.8121	2.9376	3.4382	2.8131	2.9385	3.45	2.815	2.9404
0.02	3.3467	3.9097	4.0864	3.3517	3.9382	4.1138	3.3551	3.9423	4.1177	3.3602	3.9477	4.123	3.3707	3.9519	4.1270
0.01	3.6101	3.9205	4.0968	3.6145	3.9436	4.1191	3.6192	3.9464	4.1217	3.6268	3.9546	4.1296	3.6367	3.9629	4.1376
	KCl														
0.1	2.9964	4.1778	4.3666	2.997	4.1908	4.3791	2.9976	4.2126	4.4001	2.9982	4.2199	4.4072	3.0003	4.2273	4.4142
0.09	2.9967	3.8085	3.9797	2.9976	3.8203	3.9911	2.9979	3.8336	4.0039	2.9988	3.839	4.0091	3.0114	3.8443	4.0142
0.08	2.9973	3.8111	3.9823	2.9982	3.8217	3.9924	2.9985	3.8349	4.0052	2.9991	3.8403	4.0103	3.0142	3.847	4.0168
0.07	2.9979	3.8124	3.9835	2.9985	3.8243	3.995	2.9991	3.8363	4.0065	2.9994	3.843	4.0129	3.0154	3.8483	4.0181
0.06	2.9982	3.8725	4.046	2.9988	3.8819	4.055	2.9997	3.8941	4.0667	3.0006	3.8927	4.0654	3.0178	3.909	4.0811
0.05	2.9985	3.6531	3.8163	2.9991	3.6607	3.8236	3.0003	3.6696	3.8322	3.006	3.6798	3.842	3.0187	3.685	3.8470
0.04	2.9991	3.3193	3.4673	3.0015	3.3239	3.4717	3.0045	3.332	3.4795	3.009	3.339	3.4862	3.0208	3.346	3.4930
0.03	2.9997	3.2653	3.4107	3.0054	3.2687	3.414	3.0066	3.2767	3.4217	3.0127	3.2847	3.4294	3.0224	3.2904	3.4349
0.02	3.0006	3.1549	3.2952	3.0075	3.1571	3.2973	3.0099	3.1648	3.3047	3.0148	3.1725	3.3122	3.0257	3.178	3.3175
0.01	3.0066	3.2687	3.414	3.0099	3.2721	3.4173	3.0133	3.2789	3.4238	3.0199	3.2881	3.4327	3.0288	3.2938	3.4382

Table 3. Polarizability of aqueous solution and electrolytes of LiCl, NaCl, and KCl as a function of concentration and temperature

Conc., mol/Lit	LiCl									
	298.15 K		303.15 K		308.15 K		313.15 K		318.15 K	
	Soln.	Elec.	Soln.	Elec.	Soln.	Elec.	Soln.	Elec.	Soln.	Elec.
0.1	3.992	2.549	3.99	2.551	3.986	2.547	3.976	2.537	3.954	2.514
0.09	3.99	2.547	3.99	2.55	3.981	2.542	3.972	2.534	3.958	2.518
0.08	3.989	2.545	3.988	2.549	3.979	2.54	3.97	2.531	3.957	2.516
0.07	3.987	2.544	3.987	2.547	3.98	2.541	3.973	2.534	3.963	2.522
0.06	3.986	2.543	3.985	2.545	3.982	2.543	3.975	2.536	3.97	2.53
0.05	3.986	2.543	3.987	2.548	3.983	2.545	3.977	2.538	3.974	2.533
0.04	3.989	2.546	3.987	2.547	3.984	2.545	3.977	2.538	3.979	2.538
0.03	3.991	2.548	3.991	2.551	3.984	2.545	3.98	2.541	3.983	2.543
0.02	3.992	2.548	3.992	2.552	3.986	2.547	3.982	2.544	3.988	2.547
0.01	3.992	2.549	3.994	2.554	3.988	2.549	3.987	2.548	3.991	2.55
	NaCl									
0.1	4.019	2.576	4.014	2.574	4	2.561	3.988	2.55	3.999	2.559
0.09	4.013	2.57	4.003	2.563	3.998	2.56	3.986	2.547	4.004	2.563
0.08	4.008	2.565	3.999	2.559	3.995	2.556	3.984	2.546	4.004	2.564
0.07	4.006	2.563	3.995	2.555	3.997	2.558	3.989	2.55	4.003	2.563
0.06	4.005	2.561	3.994	2.555	3.996	2.557	3.99	2.551	4.006	2.566
0.05	4.002	2.559	3.988	2.548	3.99	2.551	3.991	2.552	4.007	2.567
0.04	4.004	2.561	3.988	2.548	3.991	2.552	3.993	2.554	4.008	2.567
0.03	4.006	2.563	3.99	2.551	3.993	2.554	3.997	2.559	4.009	2.568
0.02	4.008	2.564	3.99	2.551	3.991	2.552	3.992	2.554	4.001	2.561
0.01	4.002	2.559	3.988	2.548	3.99	2.552	3.992	2.553	3.996	2.556
	KCl									
0.1	3.995	2.551	3.985	2.546	3.97	2.531	3.965	2.526	3.962	2.521
0.09	3.986	2.543	3.977	2.538	3.967	2.528	3.963	2.525	3.975	2.535
0.08	3.985	2.542	3.977	2.538	3.966	2.527	3.963	2.524	3.977	2.536
0.07	3.984	2.541	3.975	2.536	3.966	2.527	3.961	2.522	3.977	2.537
0.06	3.981	2.538	3.974	2.535	3.966	2.527	3.968	2.529	3.977	2.536
0.05	3.977	2.534	3.971	2.532	3.965	2.526	3.964	2.525	3.976	2.535
0.04	3.975	2.532	3.974	2.534	3.97	2.531	3.969	2.53	3.978	2.537
0.03	3.973	2.53	3.978	2.538	3.971	2.533	3.971	2.533	3.979	2.538
0.02	3.972	2.529	3.979	2.54	3.975	2.536	3.973	2.534	3.982	2.541
0.01	3.979	2.536	3.98	2.541	3.978	2.539	3.978	2.539	3.984	2.543

Conclusion

Density and refractive index of aqueous solutions of four 1-1 electrolytes have been accurately measured at 298.15, 303.15, 313.15 and 318.15 K. These data were employed to obtain molar refraction and polarizability of solutions. The results are discussed in terms of ion-solvent interactions.

References

1. Heller W, *J Phys Chem.,* 1965, **69(4)**, 1123-1129; DOI:10.1021/j100888a006
2. Dale D and Gladstone F, *Phil Trans.,* 1858, **148**, 887-894; 1863, **153**, 317; DOI:10.1098/rstl.1858.0002
3. Wiener O, *Zur Theorie der Refraktionskonstanten Ber. Verh. Koniglich Sachisischen Ges. Wiss. Leipzig Math Phys.,* 1910, **62**, 256-277.
4. Lorenz L V, *Ann der Phys.,* 1880, **11**, 70.
5. Lorentz H A, *Ann Phys.,* 1880, 245(**9**), 641-655.
6. Aralaguppi M I, Aminabhavi T M, Ramachandra H B and Harogoppad S B, *J Chem Eng Data,* 1992, **37(3)**, 298-303; DOI:10.1021/je00007a006
7. Pandey J D, Rai R D, Shukla R K, Tiwari K P and Shukla A K, *Ind J Pure Appl Phys.,* 1992, **30**, 94-96.
8. Lee J W, Kim J S, Lee Y W, Baek Y S and Pang H S, *J Chem Thermodyn.,* 2001, **33(11)**, 1527-1534; DOI:10.1006/jcht.2001.0866
9. Pauling L, *Proc R Soc London, Ser A,* 1927, **114**, 181-211.
10. Pandey J D, Jain P, Vyas V, *Can J Chem.,* 1994, **72(12)**, 2486-2492; DOI:10.1139/v94-315
11. Pal A and Kumar H, *J Chem Thermodyn.,* 2004, **36(3)**, 173-182; DOI:10.1016/j.jct.2003.11.003
12. Hosoda H, Mori H, Sogoshi N, Nagasawa A and Nakabayashi S, *J Phys Chem.,* 2004, **108(9)**, 1461-1464; DOI:10.1021/jp0310145
13. Salanne M, Vuilleumier, Madded PA, Simon C, Turq P and Guillot B, *J Phys Condens Matter.,* 2008, **20**, 494207; DOI:10.1088/0953-8984/20/49/494207
14. Giner B, Lafuente C, Villares A, Haro M and Lopez M C, *J Chem Thermodyn.,* 2007, **39(1)**, 148-157; DOI:10.1016/j.jct.2006.05.003