Refractive Indices of Binary Mixtures of Tetrahydrofuran with Aromatic Hydrocarbon at Temperatures from (288.15 to 318.15) K

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The refractive indices n of pure tetrahydrofuran (THF), benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, mesitylene, and those of their binary mixtures with THF as a common component, over the entire composition range expressed by mole fraction x_1 of THF, were measured at temperatures (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, and 318.15) K. From the experimental data, the deviations in refractive index (Δn) have been calculated. It is observed that the extent of deviation in Δn for these mixtures follows the sequence: benzene > toluene > *p*-xylene > *m*-xylene > *o*-xylene > mesitylene.

Introduction

The refractive index is an important physical property of liquids and liquid mixtures, which affects the solution of different problems in chemical engineering in order to develop industrial processes. Knowledge of n of multicomponent mixtures provides information regarding the interactions in these mixtures.[1–3] Prediction of n of multicomponent liquid mixtures is essential for many physicochemical calculations, which include correlation of n with density,[4] excess molar volume,[5] and surface tension.[6] In continuation of our ongoing research[7–11] focusing on experimental and theoretical studies of physicochemical properties of nonaqueous binary liquid mixtures, here we report the results of our study on the binary mixtures of tetrahydrofuran (THF) with six aromatic hydrocarbons (benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, and mesitylene) over the entire composition range at seven different temperatures. A survey of the literature indicates that there has been no study of the refractive index on these systems, except the work of Giner et al.[1] and Oswal et al.[12] who reported refractive indices of THF + benzene mixtures at T/K = 298.15 and THF + benzene/toluene/*m*-xylene mixtures at T/K = 303.15, respectively.

This paper reports the refractive indices of binary mixtures of THF with benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, and mesitylene, including those of pure liquids, at the temperatures (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, and 318.15) K, covering the entire composition range expressed by mole fraction x_1 of THF ($0 \le x_1 \le 1$). The experimental values of n have been used to calculate the deviations in refractive index Δn, and the results were discussed in terms of molecular interactions in these mixtures.

Experimental

THF and the aromatic hydrocarbons (benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, and mesitylene) used in the study were the products from S. D. fine chemicals, India, and were purified by using the methods described in the literature.[13,14] The mass fraction purities as determined by gas chromatography are: THF > 0.996, benzene > 0.998, toluene > 0.998, *o*-xylene > 0.997, *m*-xylene > 0.997, *p*-xylene > 0.997, and mesitylene > 0.995. Before use, the pure chemicals were stored over 0.4 nm molecular sieves for 72 h to remove water, if any, and were degassed at low pressure. The mixtures were prepared by mass and were kept in special airtight stopper glass bottles to avoid evaporation. The weighings were done on an electronic balance with a precision of ± 0.1 mg. The probable error in the mole fraction was estimated to be less than ± 0.0001.

Table 1. Comparison of Experimental Values of Refractive Indices with the Literature Values of Pure Liquids at 298.15 K

	n	
liquid	experimental	literature
tetrahydrofuran	1.4046	1.404642[1]
		1.40496[13]
benzene	1.4980	1.49792[13]
		1.4979[3]
toluene	1.4942	1.49413[13]
		1.4941[3]
o-xylene	1.5029	1.50295[13]
m-xylene	1.4948	1.49494[13]
		1.4946[3]
p-xylene	1.4933	1.49325[13]
mesitylene	1.4969	1.49684[13]

The refractive indices of pure liquids and their binary mixture were measured using a thermostatted Abbe refractometer. The refractometer was calibrated by measuring the refractive indices of triply distilled water and toluene at various temperatures. The values of refractive index were obtained using sodium D light. The uncertainty in refractive index measurements was within ± 0.0001. The temperature of the test liquids between the prisms during the measurements was maintained to an uncertainty of ± 0.01 K by circulating water through the jacket around the prisms from an electronically controlled thermostatic water bath (JULABO, model ME-31A, Germany). The reliability of experimental measurements of n was ascertained by comparing the experimental data of pure liquids with the corresponding literature values[1,3,13] at 298.15 K (Table 1).

Results and Discussion

The experimental values of refractive index n of the binary mixtures of THF with benzene, toluene, *o*-xylene, *m*-xylene,

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10.1021/je700564c CCC: $40.75
Published on Web 02/22/2008

Table 2. Values of Refractive Index n of THF (1) + Aromatic Hydrocarbon (2) Mixtures at T = (288.15 to 318.15) K as a Function of Mole Fraction x_1

	T/K								T/K						
x_1	288.15	293.15	298.15	303.15	308.15	313.15	318.15	x_1	288.15	293.15	298.15	303.15	308.15	313.15	318.15
							THF + Benzene								
0.0000	1.5042	1.5011	1.4980	1.4949	1.4918	1.4887	1.4856	0.5506	1.4556	1.4528	1.4500	1.4473	1.4445	1.4417	1.4389
0.0754	1.4980	1.4949	1.4918	1.4888	1.4857	1.4826	1.4796	0.6219	1.4487	1.4460	1.4432	1.4405	1.4378	1.4350	1.4323
0.1518	1.4917	1.4886	1.4855	1.4825	1.4794	1.4764	1.4734	0.6884	1.4421	1.4394	1.4367	1.4341	1.4314	1.4287	1.4260
0.2230	1.4855	1.4825	1.4795	1.4765	1.4735	1.4705	1.4675	0.7512	1.4358	1.4332	1.4305	1.4279	1.4253	1.4226	1.4200
0.2962	1.4791	1.4761	1.4732	1.4702	1.4672	1.4642	1.4614	0.8119	1.4295	1.4269	1.4243	1.4218	1.4192	1.4166	1.4140
0.3556	1.4738	1.4709	1.4679	1.4650	1.4621	1.4592	1.4563	0.8792	1.4225	1.4200	1.4174	1.4149	1.4124	1.4098	1.4073
0.4128	1.4686	1.4657	1.4628	1.4599	1.4570	1.4541	1.4513	0.9388	1.4161	1.4136	1.4111	1.4087	1.4062	1.4037	1.4013
0.4812	1.4622	1.4593	1.4565	1.4537	1.4509	1.4480	1.4452	1.0000	1.4094	1.4070	1.4046	1.4023	1.3999	1.3975	1.3951
							THF + Toluene								
0.0000	1.4998	1.4970	1.4942	1.4913	1.4884	1.4855	1.4826	0.5368	1.4587	1.4560	1.4533	1.4505	1.4478	1.4451	1.4424
0.0718	1.4952	1.4923	1.4895	1.4866	1.4837	1.4808	1.4779	0.6067	1.4522	1.4495	1.4468	1.4441	1.4414	1.4387	1.4361
0.1498	1.4898	1.4870	1.4841	1.4812	1.4783	1.4755	1.4726	0.6704	1.4461	1.4434	1.4407	1.4380	1.4353	1.4326	1.4300
0.2283	1.4841	1.4813	1.4784	1.4755	1.4727	1.4698	1.4670	0.7378	1.4392	1.4366	1.4339	1.4313	1.4286	1.4260	1.4234
0.2902	1.4795	1.4766	1.4738	1.4709	1.4681	1.4652	1.4625	0.8018	1.4325	1.4298	1.4272	1.4246	1.4220	1.4194	1.4169
0.3452	1.4751	1.4723	1.4695	1.4667	1.4639	1.4611	1.4583	0.8714	1.4248	1.4222	1.4196	1.4171	1.4145	1.4119	1.4095
0.4005	1.4706	1.4678	1.4650	1.4623	1.4595	1.4568	1.4539	0.9368	1.4171	1.4146	1.4121	1.4097	1.4072	1.4047	1.4023
0.4694	1.4647	1.4619	1.4592	1.4565	1.4537	1.4510	1.4482	1.0000	1.4094	1.4070	1.4046	1.4023	1.3999	1.3975	1.3951
							THF + *o*-Xylene								
0.0000	1.5083	1.5055	1.5029	1.5002	1.4975	1.4948	1.4921	0.5310	1.4659	1.4633	1.4607	1.4582	1.4556	1.4530	1.4504
0.0764	1.5032	1.5004	1.4978	1.4951	1.4924	1.4897	1.4870	0.5850	1.4605	1.4579	1.4553	1.4528	1.4502	1.4476	1.4451
0.1504	1.4980	1.4953	1.4926	1.4900	1.4873	1.4846	1.4819	0.6578	1.4529	1.4503	1.4477	1.4452	1.4427	1.4401	1.4375
0.2243	1.4925	1.4898	1.4872	1.4845	1.4818	1.4791	1.4765	0.7322	1.4445	1.4419	1.4394	1.4370	1.4344	1.4319	1.4294
0.2942	1.4870	1.4843	1.4817	1.4790	1.4764	1.4737	1.4711	0.8049	1.4358	1.4333	1.4308	1.4284	1.4259	1.4234	1.4209
0.3660	1.4810	1.4783	1.4757	1.4731	1.4705	1.4678	1.4652	0.8708	1.4275	1.4250	1.4225	1.4201	1.4176	1.4151	1.4127
0.4226	1.4761	1.4734	1.4708	1.4682	1.4656	1.4629	1.4603	0.9392	1.4182	1.4157	1.4133	1.4109	1.4085	1.4061	1.4036
0.4801	1.4708	1.4681	1.4656	1.4630	1.4604	1.4578	1.4551	1.0000	1.4094	1.4070	1.4046	1.4023	1.3999	1.3975	1.3951
							THF + *m*-Xylene								
0.0000	1.4999	1.4974	1.4948	1.4922	1.4896	1.4870	1.4844	0.5476	1.4602	1.4577	1.4552	1.4526	1.4501	1.4476	1.4450
0.0722	1.4956	1.4931	1.4905	1.4879	1.4853	1.4827	1.4801	0.6041	1.4550	1.4525	1.4499	1.4474	1.4449	1.4424	1.4398
0.1486	1.4908	1.4883	1.4857	1.4831	1.4805	1.4779	1.4753	0.6751	1.4480	1.4455	1.4429	1.4405	1.4380	1.4355	1.4329
0.2134	1.4865	1.4840	1.4814	1.4788	1.4762	1.4736	1.4710	0.7396	1.4412	1.4387	1.4362	1.4338	1.4313	1.4288	1.4263
0.2804	1.4818	1.4793	1.4767	1.4741	1.4715	1.4689	1.4664	0.8005	1.4345	1.4320	1.4295	1.4271	1.4246	1.4221	1.4197
0.3536	1.4764	1.4739	1.4713	1.4687	1.4661	1.4636	1.4610	0.8722	1.4260	1.4236	1.4211	1.4187	1.4163	1.4138	1.4114
0.4255	1.4707	1.4682	1.4656	1.4631	1.4605	1.4579	1.4554	0.9378	1.4178	1.4153	1.4129	1.4106	1.4081	1.4057	1.4033
0.4864	1.4656	1.4631	1.4605	1.4580	1.4555	1.4529	1.4504	1.0000	1.4094	1.4070	1.4046	1.4023	1.3999	1.3975	1.3951
							THF + *p*-Xylene								
0.0000	1.4985	1.4959	1.4933	1.4907	1.4881	1.4855	1.4830	0.5518	1.4594	1.4568	1.4542	1.4517	1.4491	1.4465	1.4441
0.0840	1.4936	1.4910	1.4884	1.4858	1.4832	1.4806	1.4780	0.6201	1.4531	1.4505	1.4480	1.4454	1.4429	1.4403	1.4378
0.1716	1.4881	1.4855	1.4829	1.4803	1.4777	1.4751	1.4726	0.6825	1.4470	1.4444	1.4419	1.4394	1.4368	1.4342	1.4318
0.2322	1.4842	1.4816	1.4790	1.4764	1.4738	1.4712	1.4686	0.7414	1.4409	1.4383	1.4358	1.4333	1.4308	1.4282	1.4258
0.2934	1.4800	1.4774	1.4748	1.4722	1.4696	1.4670	1.4644	0.8102	1.4333	1.4308	1.4282	1.4258	1.4233	1.4207	1.4183
0.3548	1.4755	1.4729	1.4703	1.4677	1.4651	1.4625	1.4600	0.8756	1.4256	1.4231	1.4206	1.4182	1.4157	1.4132	1.4108
0.4284	1.4698	1.4672	1.4646	1.4621	1.4595	1.4569	1.4544	0.9409	1.4174	1.4149	1.4125	1.4101	1.4077	1.4052	1.4028
0.4896	1.4648	1.4622	1.4596	1.4571	1.4545	1.4519	1.4494	1.0000	1.4094	1.4070	1.4046	1.4023	1.3999	1.3975	1.3951
							THF + Mesitylene								
0.0000	1.5020	1.4995	1.4969	1.4944	1.4918	1.4893	1.4868	0.5496	1.4624	1.4599	1.4573	1.4549	1.4523	1.4498	1.4473
0.0735	1.4977	1.4952	1.4925	1.4900	1.4874	1.4849	1.4823	0.6055	1.4572	1.4547	1.4521	1.4497	1.4471	1.4446	1.4421
0.1513	1.4928	1.4903	1.4877	1.4851	1.4825	1.4800	1.4774	0.6784	1.4499	1.4474	1.4448	1.4424	1.4399	1.4374	1.4349
0.2274	1.4878	1.4852	1.4826	1.4801	1.4775	1.4749	1.4724	0.7516	1.4419	1.4395	1.4370	1.4346	1.4320	1.4295	1.4270
0.2986	1.4827	1.4802	1.4776	1.4751	1.4725	1.4700	1.4675	0.8280	1.4330	1.4305	1.4280	1.4256	1.4231	1.4206	1.4181
0.3672	1.4776	1.4751	1.4725	1.4700	1.4674	1.4649	1.4624	0.8790	1.4265	1.4241	1.4216	1.4192	1.4167	1.4142	1.4118
0.4305	1.4726	1.4701	1.4675	1.4650	1.4625	1.4599	1.4574	0.9412	1.4181	1.4157	1.4132	1.4109	1.4084	1.4059	1.4035
0.4912	1.4675	1.4650	1.4625	1.4600	1.4574	1.4549	1.4524	1.0000	1.4094	1.4070	1.4046	1.4023	1.3999	1.3975	1.3951

p-xylene, and mesitylene as a function of mole fraction x_1 of THF at different temperatures are listed in Table 2. The deviations in refractive index, Δn, have been calculated by using the following relation[15]

$$\Delta n = n - (\phi_1 n_1 + \phi_2 n_2) \quad (1)$$

where ϕ is the volume fraction (calculated using the molar volumes of the pure components obtained from the density data from our earlier work[16]) and the subscripts 1 and 2 represent pure components, THF and aromatic hydrocarbon, respectively. The values of Δn were fitted to a Redlich–Kister type[17] polynomial equation of the form

$$\Delta n = \phi_1(1-\phi_1)\sum_{i=1}^{5} A_i(1-2\phi_1)^{i-1} \quad (2)$$

The values of coefficients A_i evaluated by the method of least-squares, together with the corresponding standard deviation σ, are listed in Table 3. The variations of Δn with composition (in terms of volume fraction) of the mixture along with

Table 3. Coefficients, A_i, of Equation 2 of $100 \cdot \Delta n$ and Standard Deviations, σ, for THF + Aromatic Hydrocarbon Mixtures at Different Temperatures

T/K	A_1	A_2	A_3	A_4	A_5	$100 \cdot \sigma$
			THF + Benzene			
288.15	0.6572	0.0208	0.0788	−0.0447	−0.0653	0.0012
293.15	0.6286	0.0223	0.0692	−0.0523	−0.1354	0.0010
298.15	0.6008	0.0211	0.0087	−0.0373	−0.1305	0.0017
303.15	0.5748	0.0239	−0.0274	−0.0435	−0.1424	0.0013
308.15	0.5458	−0.0024	−0.0274	0.0314	−0.1521	0.0013
313.15	0.5162	−0.0075	−0.0559	0.0744	−0.1555	0.0018
318.15	0.5072	0.0497	−0.0957	0.0100	−0.0777	0.0011
			THF + Toluene			
288.15	0.5956	0.0952	0.2008	0.0124	−0.0591	0.0015
293.15	0.5529	0.1184	0.0593	−0.0376	0.0180	0.0014
298.15	0.5101	0.1411	−0.0808	−0.0864	0.0945	0.0022
303.15	0.4680	0.1735	−0.1045	−0.1209	0.0176	0.0031
308.15	0.4449	0.2170	−0.2059	−0.1427	0.0845	0.0037
313.15	0.4213	0.2602	−0.3089	−0.1630	0.1537	0.0047
318.15	0.3996	0.2173	−0.1754	−0.1646	0.0531	0.0022
			THF + *o*-Xylene			
288.15	0.2145	0.0948	0.1076	−0.0138	−0.0507	0.0006
293.15	0.2003	0.0974	0.0644	−0.0245	−0.0163	0.0006
298.15	0.1823	0.0932	0.0621	−0.0245	−0.0401	0.0004
303.15	0.1694	0.0850	0.0532	−0.0107	0.0401	0.0007
308.15	0.1583	0.0846	0.0489	−0.0157	−0.0608	0.0007
313.15	0.1469	0.0835	0.0298	−0.0151	−0.0500	0.0005
318.15	0.1377	0.0861	0.0234	−0.0225	−0.0561	0.0005
			THF + *m*-Xylene			
288.15	0.2585	0.1469	0.0126	−0.0666	0.0426	0.0008
293.15	0.2388	0.1482	0.0178	−0.0835	−0.0119	0.0007
298.15	0.2225	0.1376	−0.0136	−0.0710	0.0282	0.0007
303.15	0.2063	0.1299	−0.0191	−0.0690	0.0026	0.0006
308.15	0.1934	0.1308	−0.0177	−0.0749	0.0317	0.0005
313.15	0.1825	0.1311	−0.0413	−0.0846	−0.0153	0.0005
318.15	0.1728	0.1203	−0.0625	−0.0763	−0.0022	0.0005
			THF + *p*-Xylene			
288.15	0.3659	0.0996	0.0628	−0.0748	−0.1343	0.0013
293.15	0.3365	0.1127	0.0392	−0.0748	−0.1048	0.0012
298.15	0.3092	0.1408	−0.0008	−0.1037	−0.0527	0.0011
303.15	0.2805	0.1417	−0.0160	−0.1099	−0.0419	0.0010
308.15	0.2518	0.1605	−0.0350	−0.2101	−0.0238	0.0008
313.15	0.2224	0.1738	−0.0580	−0.1198	0.0053	0.0011
318.15	0.2194	0.1642	−0.0202	−0.1788	−0.0983	0.0005
			THF + Mesitylene			
288.15	−0.3568	−0.1243	−0.0795	−0.0307	0.1343	0.0004
293.15	−0.3733	−0.1148	−0.0942	−0.0673	0.1060	0.0007
298.15	−0.3922	−0.1294	−0.0935	−0.0481	0.0628	0.0008
303.15	−0.4100	−0.1285	−0.0922	−0.0519	−0.0047	0.0009
308.15	−0.4271	−0.1251	−0.1247	−0.0601	−0.0243	0.0013
313.15	−0.4477	−0.1053	−0.1358	−0.0844	−0.0960	0.0010
318.15	−0.4696	−0.0757	−0.1092	−0.1398	−0.2535	0.0011

smoothed values by using eq 2, at (298.15 and 318.15) K, are shown in Figure 1.

The results presented in Figure 1 indicate that Δn values are positive over the entire composition range and at all temperatures investigated for THF + benzene/toluene/*o*-xylene/*m*-xylene/*p*-xylene mixtures and are negative for THF + mesitylene mixtures. The extent of deviation in Δn from linear dependence on composition follows the sequence: benzene > toluene > *p*-xylene > *m*-xylene > *o*-xylene > mesitylene. In general, the positive deviations in Δn values (on volume fraction dependence basis) are considered due to the presence of significant interactions in the mixtures, whereas positive deviations in Δn values indicate weak interactions between the components of the mixture.[6,15] The observed trends (Figure 1) of Δn values indicate the presence of significant interactions in THF + benzene/toluene/*o*-xylene/*m*-xylene/*p*-xylene mixtures and the presence of weak interactions in THF + mesitylene mixtures, which follows the order: benzene > toluene > *p*-xylene > *m*-xylene > *o*-xylene > mesitylene. The Δn values decrease with an increase in temperature for all six binary mixtures, indicating that the interactions between unlike molecules weaken with a rise in temperature. This further reinforces our earlier conclusions regarding the intermolecular interactions from the variations of V^E_m and Δk_s values[16,18] of these mixtures. Also, the deviations in Δn values are found opposite to the sign of excess molar volumes V^E_m for all six binary mixtures,[16] which is in agreement with the view proposed by Brocos et al.[6,15]

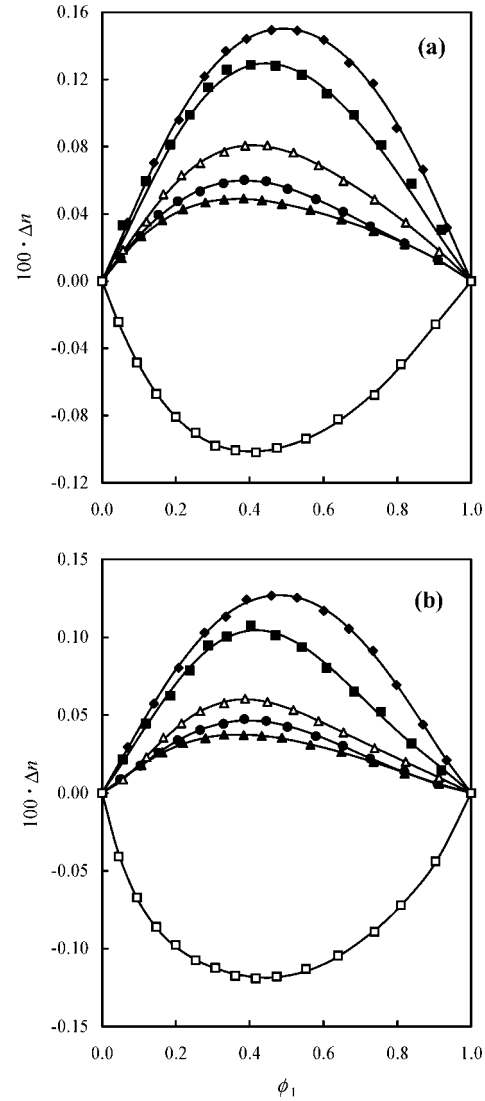

Figure 1. Deviations in refractive index Δn vs volume fraction ϕ_1 of tetrahydrofuran (THF) for the binary mixtures (a) at T/K = 298.15 and (b) at T/K = 318.15. ♦, THF + benzene; ■, THF + toluene; ▲, THF + *o*-xylene; ●, THF + *m*-xylene; Δ, THF + *p*-xylene; □, THF + mesitylene; —, calculated from eq 2.

Acknowledgment

The author is thankful to Dr. I. S. Bakshi, Principal, Dyal Singh College (University of Delhi), New Delhi, for encouragement and providing facilities.

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Received for review September 28, 2007. Accepted January 31, 2008.

JE700564C