Refraction and Polarization Properties of Binary Solutions of the Nitrotoluene Isomers with the Xylene Isomers, Chloroform and Cyclohexane

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Densities, refractive indices, dielectric constants, molar refractions, and polarizations of a number of binary systems were obtained for the complete range of concentrations at two temperatures. Such data are often useful in checking theories relating dipole moments with dielectric constants and theories of molecular associations.

PURSUANT of studies relating activity coefficients and molecular interactions, polarization data for a number of binary solutions over the entire concentration range were obtained. The systems include each of the xylene isomers with each of the nitrotoluene isomers, *o*- and *m*-nitrotoluenes with chloroform and cyclohexane, and the *m*-nitrotoluene-*o*-nitrotoluene system. Several of the systems were studied at two temperatures. The properties measured were densities, refractive indices and dielectric constants. From these molar refractions and polarizations were calculated.

EXPERIMENTAL

Purification of Materials. The *o*- and *m*-nitrotoluenes (Eastman White Label) were purified by distilling through a 4-foot column packed with glass helices under reduced pressure and retaining a mid-cut. The *p*-nitrotoluene was recrystallized twice from a 50% ethanol-water solution and then from benzene. The purified product had a melting point of 54.5° C. in agreement with the literature value (*2*) of 54.5° C.

The *m*- and *p*-xylenes (Eastman White Label) were distilled through a packed column. The *o*-xylene (Eastman White Lable) was fractionally frozen several times and then distilled through a packed column.

Chloroform was passed several times through a column of activated alumina and then distilled through a packed column.

Cyclohexane was not further purified since it was of optical grade.

Table I shows the physical properties of these reagents obtained in this laboratory as compared with values reported by other workers.

Apparatus. Dielectric constants were measured with a General Radio Type 821-A Twin-T impedance bridge, a General Radio Type 1001-A standard signal generator, and a Hallicrafter Model S-40A Multiband receiver. The dielectric cell has been described by Leader (*4*). Temperature in the cell was controlled to ± 0.05° C. All measurements were made using 10 megacycle frequency.

Densities were measured in the standard manner using 25-ml. Reischauer pycnometers.

Refractive indices were measured with a Spencer Model 1470 refractometer.

Calculations. Molar refractions of solutions were calculated using Equation 1,

$$R_D = \frac{n^2 - 1}{n^2 + 2} \frac{N_1 M_1 + N_2 M_2}{d} \quad (1)$$

where n is the refractive index of the solution, N_1 and N_2 are mole fractions of the two components M_1 and M_2 are their molecular weights, and d is the density of the solution.

Molar polarizations of the solutions were calculated by Equation 2,

$$P = \frac{D - 1}{D + 2} \frac{N_1 M_1 + N_2 M_2}{d} \quad (2)$$

where D is the dielectric constant of the solution.

Table I. Physical Properties of Reagents at 25° C.

	n_D		d, Grams/Ml.			D	
	This work	Other	This work	Other	Ref.	This work	Other[a]
o-Xylene	1.5025	1.5029	0.8755	0.8757	(*6*)	2.56	2.56
m-Xylene	1.4947	1.4946	0.8601	0.8602	(*6*)	2.35	2.36
o-Xylene	1.4931	1.4932	0.8569	0.8567	(*6*)	2.27	2.26
o-Nitrotoluene	1.5440	1.5440	1.1584	1.1580	(*1*)	26.52	26.6
m-Nitrotoluene	1.5447	1.5445	1.1527	1.1523	(*1*)	26.39	23.8[b]
Chloroform	1.4429	1.4427	1.4795	1.4799	(*7*)	4.77	4.79
Cyclohexane	1.4235	1.4235	0.7739	0.7741	(*3*)	2.02	2.02

[a] All dielectric constant values are those selected by Maryott and Smith (*5*). [b] 20° C.

Table II. Densities, Refractive Indices, Dielectric Constants, Molar Refractions, and Molar Polarizations of Binary Solutions at 25° and 35° C.

	25° C.					35° C.				
N_1	d, grams/ml.	n_D	D	R_D, ml.	P, ml.	d, grams/ml.	n_D	D	R_D, ml.	P, ml.
					o-Xylene–*o*-Nitrotoluene					
1.0000	0.8755	1.5025	2.56	35.82	41.49	0.8672	1.4971	2.53	35.83	41.35
0.9037	0.9032	1.5053	4.03	35.86	60.72	0.8946	1.5003	3.91	35.90	60.07
0.8009	0.9319	1.5108	5.77	36.10	74.00	0.9233	1.5059	5.59	36.14	73.57
0.7074	0.9586	1.5141	7.53	36.19	82.36	9.9499	1.5093	7.27	36.26	82.04
0.5995	0.9894	1.5176	9.79	36.29	89.34	0.9806	1.5129	9.41	36.32	89.12
0.5023	1.0169	1.5220	11.97	36.46	93.88	1.0080	1.5171	11.48	38.49	93.77
0.4031	1.0443	1.5273	14.41	36.71	97.54	1.0354	1.5228	13.80	38.76	97.53
0.3021	1.0726	1.5313	17.10	36.87	100.42	1.0635	1.5265	16.34	38.91	100.49
0.2006	1.1018	1.5359	20.04	37.05	102.65	1.0925	1.5309	19.10	37.07	102.80
0.1060	1.1281	1.5392	22.96	37.18	104.39	1.1187	1.5348	21.86	37.24	104.60
0.0000	1.158	1.5440	26.52	37.37	105.94	1.1491	1.5391	25.19	37.39	106.18
					m-Xylene–*o*-Nitrotoluene					
1.0000	0.8601	1.4947	2.35	35.98	38.31	0.8517	1.4894	2.34	36.00	38.49
0.8968	0.8911	1.5000	3.92	36.10	60.53	0.8824	1.4948	3.82	36.13	60.04
0.8006	0.9194	1.5049	5.56	36.23	73.70	0.9106	1.4996	5.39	36.26	73.28
0.7080	0.9468	1.5092	7.30	36.34	82.43	0.9381	1.5043	7.04	36.38	82.05
0.5927	0.9816	1.5150	9.71	36.49	90.00	0.9728	1.5100	9.34	36.52	89.80
0.4740	1.0168	1.5209	12.44	36.66	95.41	1.0078	1.5161	11.94	36.71	95.35
0.3950	1.0402	1.5242	14.47	36.75	98.20	1.0312	1.5200	13.82	36.82	98.15
0.3043	1.0670	1.5292	16.86	36.92	100.65	1.0579	1.5242	16.15	36.95	100.76
0.2018	1.1018	1.5343	19.90	37.07	102.87	1.0888	1.5292	18.96	37.08	103.00
0.1064	1.1281	1.5389	22.87	37.22	104.48	1.1169	1.5340	21.83	37.25	104.74
0.0000	1.1584	1.5440	26.52	37.37	105.94	1.1491	1.5391	25.19	37.39	106.18
					p-Xylene–*o*-Nitrotoluene					
1.0000	1.4947	1.4931	2.27	36.01	36.85	0.8484	1.4879	2.25	36.05	36.81
0.8985	1.5010	1.4983	3.81	36.13	59.58	0.8787	1.4931	3.68	36.16	58.69
0.7959	0.9181	1.5037	5.56	36.26	73.90	0.9095	1.4985	5.37	36.28	73.33
0.6945	0.9486	1.5089	7.50	36.39	83.27	0.9398	1.5039	7.20	36.42	82.91
0.5940	0.9790	1.5139	9.60	36.51	89.91	0.9702	1.5091	9.20	36.55	89.60
0.4944	1.0087	1.5189	11.89	36.65	94.69	0.9998	1.5141	11.36	36.69	94.48
0.3948	1.0388	1.5240	14.38	36.79	98.22	1.0297	1.5195	13.75	36.85	98.20
0.2974	1.0685	1.5290	17.02	36.92	100.84	1.0593	1.5242	16.24	36.96	100.90
0.1975	1.0977	1.5339	19.87	37.09	102.98	1.0885	1.5292	18.94	37.13	103.12
0.0972	1.1288	1.5390	23.17	37.22	104.66	1.1193	1.5345	22.05	37.28	104.88
0.0000	1.1584	1.5440	26.52	37.37	105.94	1.1491	1.5391	25.19	37.39	106.18
					o-Xylene–*m*-Nitrotoluene					
1.0000	0.8755	1.5025	2.56	35.82	41.49	0.8672	1.4971	2.53	35.83	41.35
0.9038	0.9027	1.5066	4.32	35.96	63.51	0.8943	1.5015	4.24	35.99	63.37
0.8036	0.9304	1.5109	6.33	36.14	77.19	0.9219	1.5058	6.13	36.16	76.83
0.6965	0.9605	1.5153	8.56	36.30	86.13	0.9520	1.5104	8.34	36.33	86.17
0.5994	...	1.5197	10.73	...	...	...	1.5149	...	...	...
0.5070	1.0131	1.5233	12.89	36.63	95.71	1.0044	1.5185	12.46	36.67	95.81
0.3991	1.0428	1.5279	15.49	36.84	99.13	1.0341	1.5229	14.99	36.85	99.35
0.3035	1.0689	1.5320	18.03	37.03	101.60	1.0601	1.5272	17.32	37.05	101.78
0.1993	1.0979	1.5362	20.88	37.21	103.64	1.0889	1.5316	19.99	37.24	103.86
0.1043	1.1235	1.5400	23.38	37.39	105.09	1.1143	1.5353	22.48	37.43	105.44
0.0000	1.1527	1.5447	26.39	37.60	106.40	1.1434	1.5399	25.35	37.63	106.79
					m-Xylene–*m*-Nitrotoluene					
1.0000	0.8601	1.4947	2.35	35.98	38.31	0.8517	1.4894	2.34	36.00	38.49
0.8918	0.8920	1.5002	4.33	36.12	64.59	0.8835	1.4950	4.22	36.15	64.17
0.7953	0.9206	1.5050	6.26	36.25	77.82	0.9121	1.5000	6.09	36.28	77.60
0.6932	0.9503	1.5100	8.43	36.40	86.70	0.9418	1.5051	8.17	36.43	86.58
0.6033	0.9764	1.5149	10.44	36.58	92.06	0.9678	1.5099	10.09	36.60	92.02
0.5025	1.0063	1.5199	12.82	36.72	96.35	0.9976	1.5150	12.37	36.75	96.42
0.3976	1.0369	1.5251	15.44	36.90	99.67	1.0280	1.5201	14.85	36.92	99.80
0.2998	1.0651	1.5299	17.96	37.07	101.99	1.0560	1.5249	17.26	37.10	102.21
0.1969	1.0952	1.5350	20.75	37.25	103.87	1.0862	1.5301	19.94	37.27	104.14
0.1045	1.1225	1.5391	23.35	37.37	105.17	1.1134	1.5343	22.44	37.40	105.50
0.0000	1.1527	1.5447	26.39	37.60	106.40	1.1434	1.5399	25.35	37.63	106.79
					p-Xylene–*m*-Nitrotoluene					
1.0000	0.8569	1.4931	2.27	36.01	36.85	0.8484	1.4879	2.25	36.05	36.81
0.8956	0.8878	1.4987	4.19	36.16	63.49	0.8793	1.4934	4.07	36.18	62.92
0.7920	0.9190	1.5040	6.26	36.28	78.02	0.9105	1.4990	6.04	36.31	77.53
0.6889	0.9492	1.5092	8.47	36.44	87.05	0.9406	1.5045	8.15	36.50	86.72
0.5870	0.9791	1.5145	10.76	36.60	92.92	0.9703	1.5097	10.37	36.61	92.86
0.4851	1.0094	1.5199	13.21	36.77	97.11	1.0006	1.5151	12.69	36.80	97.11
0.3861	1.0387	1.5249	15.68	36.93	100.06	1.0298	1.5203	15.07	36.98	100.19
0.2897	1.0670	1.5299	18.22	37.10	102.29	1.0581	1.5251	17.50	37.13	102.49
0.1922	1.0956	1.5348	20.89	37.27	104.04	1.0865	1.5300	20.05	37.29	104.30
0.0969	1.1241	1.5395	23.54	37.41	105.31	1.1150	1.5350	22.64	37.45	105.64
0.0000	1.1527	1.5447	26.39	37.60	106.40	1.1434	1.5399	25.35	37.63	106.79

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Table II. Densities, Refractive Indices, Dielectric Constants, Molar Refractions, and Molar Polarizations of Binary Solutions at 25° and 35° C. (*Continued*)

	25° C.					35° C.				
N_1	d, grams/ml.	n_D	D	R_D, ml.	P, ml.	d, grams/ml.	n_D	D	R_D, ml.	P, ml.
					o-Xylene–*p*-Nitrotoluene					
1.0000	0.8755	1.5025	2.56	35.82	41.49	0.8672	1.4971	2.53	35.83	41.35
0.8858	0.9074	1.5080	4.86	36.04	68.02	0.8989	1.5030	4.77	36.07	67.96
0.8039	0.9296	1.5119	6.70	36.22	79.10	0.9212	1.5070	6.48	36.26	78.73
0.7229	0.9520	1.5161	8.55	36.41	86.25	0.9436	1.5109	8.27	36.42	86.08
0.6097	0.9833	1.5215	11.19	36.65	92.91	0.9748	1.5163	10.82	36.66	92.92
0.5363	1.0034	1.5251	13.05	36.82	96.17	0.9947	1.5200	12.58	36.83	96.20
					m-Xylene–*p*-Nitrotoluene					
1.0000	0.8601	1.4947	2.35	35.98	38.31	0.8517	1.4894	2.34	36.00	38.49
0.8931	0.8916	1.5110	4.37	36.17	64.96	0.8830	1.4954	4.30	36.18	64.94
0.7920	0.9206	1.5065	6.66	36.37	79.94	0.9120	1.5011	6.51	36.38	79.94
0.7092	0.9447	1.5111	8.61	36.53	87.44	0.9362	1.5059	8.34	36.54	87.33
0.6256	0.9690	1.5158	10.58	36.69	92.54	0.9604	1.5107	10.22	36.71	92.51
0.5164	0.0005	1.5219	13.28	36.92	97.31	0.9919	1.5169	12.81	36.94	97.39
					p-Xylene–*p*-Nitrotoluene					
1.0000	0.8569	1.4931	2.27	36.01	36.85	0.8484	1.4879	2.25	36.05	36.81
0.8990	0.8866	1.4989	4.32	36.19	64.76	0.8780	1.4940	4.19	36.24	64.15
0.8151	0.9111	1.5039	6.12	36.36	77.43	0.9026	1.4990	5.91	36.40	76.95
0.7241	0.9382	1.5091	8.19	36.51	86.27	0.9296	1.5043	7.89	36.56	85.96
0.6332	0.9644	1.5141	10.31	36.69	92.16	0.9557	1.5095	9.92	36.75	92.02
0.5141	0.9690	1.5211	13.26	36.95	97.48	0.9904	1.5166	12.73	37.00	97.46
0.4702	1.0005	1.5238	14.26	37.06	98.80	1.0029	1.5191	13.82	37.10	99.04
					Chloroform–*o*-Nitrotoluene					
1.0000	1.4795	1.4429	4.77	21.39	44.94					
0.9159	1.4444	1.4566	7.30	22.78	56.69					
0.8312	1.4104	1.4689	9.62	24.16	64.37					
0.7335	1.3728	1.4811	12.09	25.73	71.16					
0.4295	1.2708	1.5126	18.70	30.61	87.14					
0.3291	1.2419	1.5210	20.65	32.19	91.72					
0.2053	1.2083	1.5302	22.91	34.14	97.17					
0.1188	1.1864	1.5365	24.47	35.52	100.91					
0.0000	1.1584	1.5440	26.52	37.37	105.94					
					Chloroform–*m*-Nitrotoluene					
1.0000	1.4795	1.4429	4.77	21.39	44.94					
0.9190	1.4436	1.4560	7.66	22.75	57.71					
0.8345	1.4086	1.4681	10.31	24.15	65.68					
0.7350	1.3697	1.4811	13.02	25.79	72.50					
0.6372	1.3328	1.4922	15.38	27.40	78.11					
0.5098	1.2905	1.5050	18.06	29.44	84.41					
0.4059	1.2581	1.5148	20.04	31.13	89.22					
0.3090	1.2306	1.5228	21.36	32.67	93.24					
0.2179	1.2062	1.5289	23.17	34.07	97.32					
0.1231	1.1813	1.5365	24.63	35.65	101.37					
0.0000	1.1527	1.5447	26.39	37.60	106.40					
					Cyclohexane–*o*-Nitrotoluene					
1.0000	0.7739	1.4235	2.02	27.72	27.59					
0.8999	0.8141	1.4358	3.66	28.72	51.64					
0.8158	0.8473	1.4452	5.23	29.51	64.85					
0.6059	1.3274	1.4956	15.04	27.79	78.45					
0.4998	1.2932	1.5061	17.29	29.47	83.76					
0.7250	0.8834	1.4573	7.16	30.46	75.16					
0.6268	0.9219	1.4694	9.44	31.42	83.17					
0.5321	0.9589	1.4810	11.81	32.33	88.94					
0.4225	1.0010	1.4941	14.69	33.38	94.03					
0.3243	1.0384	1.5059	17.39	34.32	97.65					
0.2163	1.0786	1.5190	20.36	35.36	100.88					
0.1123	1.1169	1.5310	23.28	36.34	103.51					
0.0000	1.1584	1.5440	26.52	37.37	105.94					
					Cyclohexane–*m*-Nitrotoluene					
1.0000	0.7739	1.4235	2.02	27.72	27.59					
0.9000	0.8130	1.4351	3.90	28.72	54.08					
0.8091	0.8487	1.4464	5.79	29.64	68.30					
0.7101	0.8873	1.4593	8.08	30.68	78.78					
0.6135	0.9251	1.4709	10.43	31.61	85.81					
0.5095	0.9646	1.4840	13.09	32.67	91.48					
0.4025	1.0050	1.4969	15.88	33.71	95.90					
0.3127	1.0394	1.5066	18.27	34.50	98.83					
0.1999	1.0804	1.5213	21.23	35.68	102.00					
0.1089	1.1136	1.5318	23.57	36.54	104.12					
0.0000	1.1527	1.5447	26.39	37.60	106.40					

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Table II. Densities, Refractive Indices, Dielectric Constants, Molar Refractions, and Molar Polarizations of Binary Solutions at 25° and 35° C. (*Continued*)

	25° C.					35° C.				
N_1	d, grams/ml.	n_D	D	R_D, ml.	P, ml.	d, grams/ml.	n_D	D	R_D, ml.	P, ml.
					m-Nitrotoluene–*o*-Nitrotoluene					
1.0000	1.1527	1.5447	26.39	37.60	106.40					
0.8963	1.1536	1.5447	26.61	37.57	106.37					
0.7959	1.1540	1.5446	26.61	37.55	106.37					
0.6948	1.1544	1.5446	26.69	37.53	106.37					
0.5969	1.1547	1.5445	26.77	37.52	106.38					
0.4967	1.1555	1.5444	26.80	37.49	106.32					
0.3897	1.1564	1.5443	26.80	37.45	106.23					
0.2967	1.1568	1.5442	26.78	37.43	106.19					
0.1952	1.1572	1.5441	26.73	37.42	106.13					
0.1014	1.1576	1.5441	26.64	37.40	106.05					
0.0000	1.1584	1.5440	26.52	37.37	105.94					

RESULTS

Table II gives the composition, density, refractive index, dielectric constant, molar refraction (R_D), and molar polarization (P) of the binary solutions of each of the nitrotoluene isomers with each of the sylene isomers and of the *o*- and *m*-nitrotoluene isomers with chloroform and cyclohexane, as well as the solution of *o*-nitrotoluene with *m*-nitrotoluene, in most cases at two temperatures, 25° and 35° C. In the composition column the mole fraction listed is that of the first named of the binary components. The systems containing *p*-nitrotoluene do not cover the complete range of composition due to the limited solubility of this isomer.

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Effect of Polar Components on the Relative Volatility of the Binary System *n*-Hexane–Benzene

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Vapor liquid equilibrium data are presented for the binary systems *n*-hexane–1-propanol, benzene–1-propanol and *n*-hexane–benzene at 760 mm. of mercury pressure. In addition ternary data are presented at selected compositions with respect to the 1-propanol in the 1-propanol, benzene, *n*-hexane system at 760 mm. The results indicate the relative volatility of *n*-hexane relative to benzene increases appreciably with addition of 1-propanol.

THE RAPID growth of the petrochemical industry has led to the wide application of extractive distillation as a means of separating closely boiling compounds. One of the problems in the field of extractive distillation is to find a quantitative method of assessing solvents, in terms of the physical properties of the constituents, in order to select the most efficient solvent for a particular process. This investigation is another in a series (*8, 10, 11, 14, 16, 18*) initiated to determine experimentally the effect of polar components on the relative volatility of binary systems. Anderson (*1*), Gerster (*4*), Prausnitz (*15*), and Pierotti (*13*) have reported some investigations in this area.

The binary system studied in this work was composed of *n*-hexane and benzene. These hydrocarbons are difficult to separate because of closeness of boiling points. 1-Propanol was used as a solvent. Vapor-liquid equilibria of the binary systems *n*-hexane–benzene, *n*-hexane–1-propanol, benzene–1-propanol, and of the ternary system *n*-hexane–benzene–1-propanol were determined at 760 mm. of mercury absolute, using a modified Colburn still (*9*). The