Refraction, Dispersion, and Densities for Methanol Solutions of Benzene, Toluene, Aniline, and Phenol

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The effect of chemical structure, composition, and temperature on refractive index, dispersion, and density measurements is presented using methanol solutions of benzene, toluene, aniline, and phenol. Refractive index measurements for sodium D and hydrogen F and C lines were determined along with the density measurements at 20°, 30°, and 40° C. The use of refractivity intercept plots, $n_D - d/2$ vs. composition, is recommended as a possible means of indicating the presence, in the solution, of impurities with different structures and properties. The use of volume per cent composition in plotting refractivity intercept values gives closer to a linear correlation than weight per cent.

CONTINUING an investigation of the effect of molecular structure on density–refractive index relationships, the present study reports the effect of groups attached to the benzene ring. Furthermore the data presented can be used as an analytical tool in the analysis of the mixtures investigated. Dispersion ($n_F - n_C$) values are useful in determining the presence of impurities. In the case of phenol-methanol mixtures at 20° C., the presence of water in phenol is clearly shown.

EXPERIMENTAL

Purification and Preparation. The chemicals used in this research were obtained in their purest form, meeting ACS specifications, except phenol which contained 12% water. No further purification was necessary but extreme care was taken in handling these chemicals. Amber glass solution bottles were used for aniline and phenol solutions to avoid color change owing to light, and contact with air was kept

Table I. Benzene-Methanol System

Methanol, Wt. %	Composition, Vol. %	Density, d, G./Ml.	Refractive Index Measurements, ±0.00003 n_D	n_F	n_C	Dispersion, $n_F - n_C$	Refractivity Intercept, $n_D - d/2$
			At 20° C.				
0.00	0.00	0.8784	1.50192	1.51518	1.49607	0.01911	1.0627
10.06	11.04	0.8695	1.48281	1.49388	1.47847	0.01541	1.0481
20.33	22.08	0.8592	1.46251	1.47267	1.45862	0.01405	1.0329
29.62	31.85	0.8507	1.44447	1.45363	1.44099	0.01264	1.0191
39.98	42.51	0.8411	1.42553	1.43416	1.42253	0.01163	1.0050
49.72	52.33	0.8316	1.40771	1.41509	1.40490	0.01019	0.9919
60.78	63.24	0.8221	1.38924	1.39570	1.38658	0.00912	0.9782
70.23	72.37	0.8143	1.37433	1.38012	1.37185	0.00827	0.9672
80.09	81.71	0.8064	1.35876	1.36399	1.35675	0.00724	0.9556
90.01	90.91	0.7989	1.34408	1.34815	1.34170	0.00644	0.9446
100.00	100.00	0.7914	...	1.3334	...	0.0054	0.9423
			At 30° C.				
0.00	0.00	0.8680	1.49450	1.50863	1.48929	0.01934	1.0614
10.06	11.03	0.8590	1.47694	1.49051	1.47504	0.01547	1.0475
20.33	22.06	0.8489	1.45686	1.46786	1.45420	0.01366	1.0324
29.62	31.82	0.8402	1.43923	1.44801	1.43572	0.01229	1.0191
39.98	42.48	0.8313	1.42078	1.42793	1.41681	0.01112	1.0051
49.72	52.30	0.8226	1.40260	1.40894	1.39915	0.00979	0.9913
60.78	63.22	0.8134	1.38481	1.38997	1.38099	0.00898	0.9781
70.23	72.34	0.8053	1.37002	1.37371	1.36608	0.00763	0.9674
80.09	81.69	0.7973	1.35453	1.35805	1.35763	0.00642	0.6559
90.01	90.90	0.7898	1.34027	1.34391	1.33781	0.00610	0.9454
100.00	100.00	0.7828	...	...	...	0.0053	0.9348
			At 40° C.				
0.00	0.00	0.8572	1.48937	1.50267	1.48304	0.01963	1.0607
10.06	11.03	0.8492	1.47373	1.48409	1.46874	0.01535	1.0491
20.33	22.05	0.8396	1.45270	1.46213	1.44840	0.01373	1.0329
29.62	31.82	0.8306	1.43402	1.44273	1.43016	0.01257	1.0187
39.98	42.48	0.8209	1.41498	1.42277	1.41156	0.01121	1.0045
49.72	52.30	0.8121	1.39759	1.40460	1.39444	0.01016	0.9915
60.78	63.21	0.8027	1.37939	1.38579	1.37716	0.00863	0.9780
70.23	72.34	0.7958	1.36453	1.36997	1.36192	0.00805	0.9666
80.09	81.69	0.7877	1.35041	1.35429	1.34661	0.00768	0.9566
90.01	90.90	0.7804	1.33583	1.3402	1.33324	0.00691	0.9456
100.00	100.00	0.7732	...	...	...	0.0057	0.9348

Table II. Toluene-Methanol System

Methanol, Wt. %	Composition, Vol. %	Density, d, G./Ml.	Refractive Index Measurements, ±0.00003 n_D	n_F	n_C	Dispersion, $n_F - n_C$	Refractivity Intercept, $n_D - d/2$
At 20° C.							
0.00	0.00	0.8666	1.49780	1.51127	1.49150	0.01977	1.0645
10.07	10.92	0.8586	1.47984	1.49019	1.47465	0.01554	1.0505
19.76	21.25	0.8512	1.46242	1.47223	1.45849	0.01374	1.0368
30.06	32.01	0.8445	1.44311	1.45234	1.43966	0.01268	1.0208
40.02	42.22	0.8361	1.42289	1.43412	1.42266	0.01146	1.0048
48.63	50.91	0.8292	1.40808	1.41850	1.40805	0.01045	0.9964
60.05	62.21	0.8205	1.38671	1.39856	1.38942	0.00914	0.9815
70.15	72.02	0.8134	1.37510	1.38118	1.37298	0.00820	0.9683
79.94	81.37	0.8058	1.35999	1.36509	1.35797	0.00712	0.9571
90.21	90.99	0.7990	1.34432	1.34900	1.34278	0.00622	0.9448
100.00	100.00	0.7914	...	1.3334	...	...	0.9423
At 30° C.							
0.00	0.00	0.8574	1.49120	1.50559	1.48558	0.02001	1.0625
10.07	10.92	0.8495	1.47431	1.48481	1.47010	0.01471	1.0496
19.76	21.25	0.8421	1.45681	1.46655	1.45312	0.01343	1.0358
30.06	32.01	0.8344	1.43859	1.44727	1.43507	0.01220	1.0214
40.02	42.22	0.8266	1.43082	1.42918	1.41797	0.01121	1.0075
48.63	50.91	0.8203	1.40605	1.41366	1.40324	0.01042	0.9959
60.05	62.21	0.8114	1.38722	1.39366	1.38461	0.00905	0.9815
70.15	72.02	0.8039	1.37075	1.37648	1.36850	0.00798	0.9688
79.94	81.36	0.7972	1.35486	1.36000	1.35297	0.00703	0.9562
90.21	90.99	0.7893	1.34034	1.34500	1.33881	0.00619	0.9457
100.00	100.00	0.7828	...	...	...	...	0.9348
At 40° C.							
0.00	0.00	0.8480	1.48676	1.50022	1.4800	1.02022	1.0627
10.07	10.94	0.8405	1.46955	1.48008	1.46560	0.01448	1.0493
19.76	21.27	0.8330	1.45178	1.46149	1.44814	0.01335	1.0353
30.06	32.04	0.8259	1.43293	1.44216	1.42979	0.01237	1.0200
40.02	42.26	0.8175	1.41565	1.42383	1.41285	0.01098	1.0069
48.63	50.94	0.8108	1.40128	1.40874	1.39855	0.01019	0.9958
60.05	62.24	0.8022	1.38233	1.38878	1.37986	0.00892	0.9812
70.15	72.05	0.7947	1.36620	1.37179	1.36414	0.00765	0.9689
79.94	81.39	0.7874	1.35129	1.35657	1.34932	0.00725	0.9576
90.21	91.00	0.7800	1.33630	1.34128	1.33495	0.00635	0.9463
100.00	100.00	0.7732	...	...	...	...	0.9348

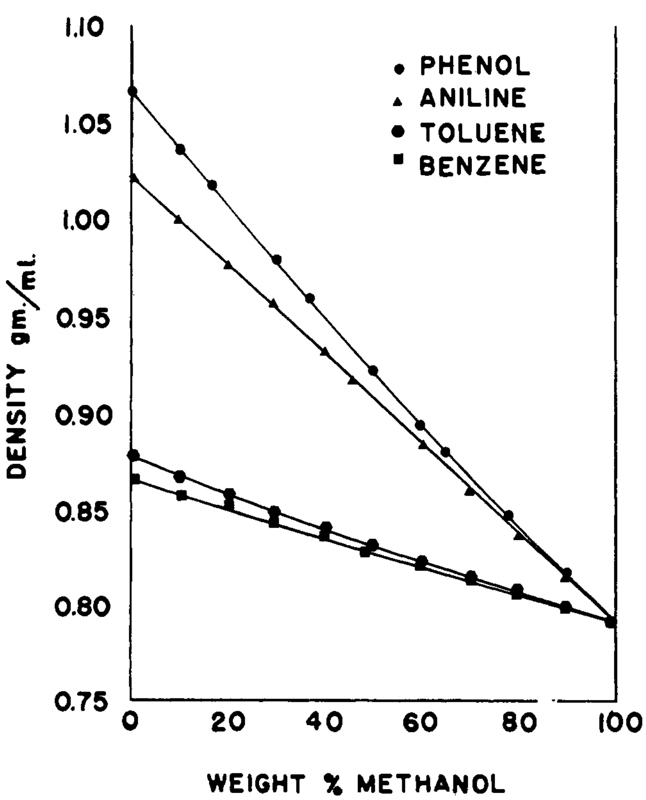

Figure 1. Densities for methanol solutions of benzene, toluene, aniline, and phenol at 20° C.

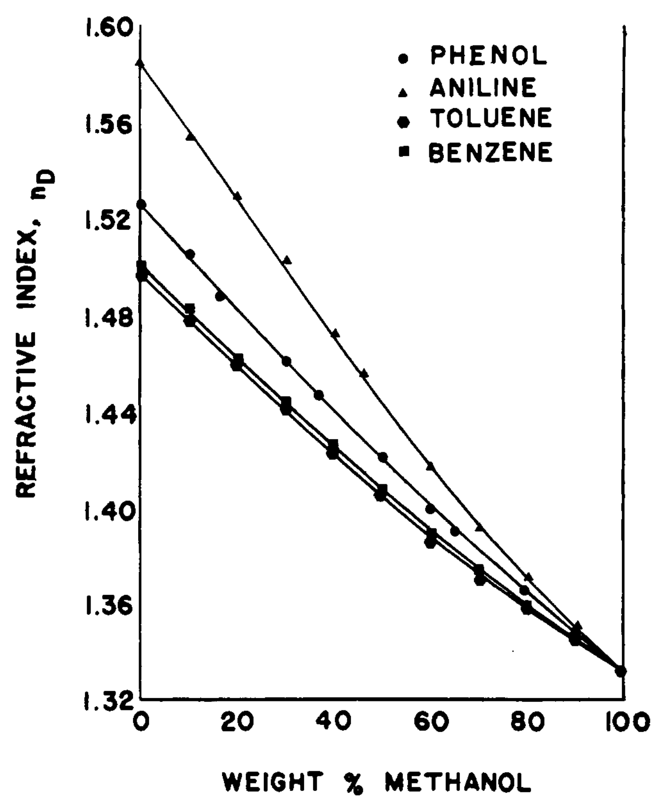

Figure 2. Refractive indices for methanol solutions of benzene, toluene, aniline, and phenol at 20° C.

Table III. Aniline-Methanol System

Methanol, Wt. %	Composition, Vol. %	Density, d, G./Ml.	Refractive Index Measurements, ± 0.00003			Dispersion, $n_F - n_C$	Refractivity Intercept, $n_D - d/2$
			n_D	n_F	n_C		
			At 20° C.				
0.00	0.00	1.0220	1.58660	1.60448	1.57991	0.02457	1.0756
10.38	13.01	0.9999	1.55598	1.57880	1.55619	0.02261	1.0560
20.09	24.51	0.9768	1.52961	1.55375	1.53417	0.01958	1.0412
29.38	34.95	0.9558	1.50255	1.52606	1.50810	0.01796	1.0246
40.61	46.90	...	1.47246	1.49351	1.47800	0.01551	...
45.74	52.13	0.9182	1.45727	1.47801	1.46388	0.01413	0.9982
60.72	66.63	0.8840	1.41911	1.43837	1.42638	0.01199	0.9771
70.13	75.20	0.8600	1.39209	1.41254	1.40210	0.01044	0.9621
79.51	83.37	0.8381	1.37217	1.38448	1.37498	0.00950	0.9562
89.80	91.92	0.8141	1.35041	1.35976	1.35307	0.00669	0.9434
100.00	100.00	0.7914	...	1.3334	...	...	0.9423
			At 30° C.				
0.00	0.00	1.0125	1.58143	1.59950	1.57519	0.02431	1.0752
10.38	13.02	0.9916	1.55229	1.57276	1.55045	0.02231	1.0565
20.09	24.54	0.9702	1.52742	1.54884	1.52913	0.01971	1.0423
29.38	34.98	0.9482	1.49974	1.52479	1.50680	0.01799	1.0256
40.61	46.93	0.9222	1.47142	1.48896	1.47312	0.01584	1.0103
45.74	52.17	0.9128	1.44886	1.47349	...	...	0.9925
60.72	66.66	0.8780	...	1.43238	1.42044	0.01194	...
70.13	75.22	0.8550	1.39171	1.40609	1.39597	0.01012	0.9642
79.51	83.39	0.8305	1.37448	1.38305	1.37426	0.00879	0.9592
89.80	91.93	0.8061	1.34850	1.35593	1.34902	0.00691	0.9455
100.00	100.00	0.7828	...	...	...	...	0.9348
			At 40° C.				
0.00	0.00	1.0045	1.58096	1.59431	1.56988	0.02443	1.0787
10.38	13.08	0.9844	1.55115	1.56726	1.54501	0.02225	1.0596
20.09	24.62	0.9641	1.52538	1.54243	1.52237	0.02006	1.0433
29.38	35.08	0.9436	...	1.53129	1.51247	0.01882	...
40.61	47.04	0.9179	1.47142	1.48316	1.46737	0.01579	1.0125
45.74	52.28	0.9051	...	1.46777	1.45303	0.01474	...
60.72	66.76	0.8712	1.41845	1.42714	1.41502	0.01208	0.9830
70.13	75.31	0.8480	...	1.40386	1.39406	0.00980	...
79.51	83.45	0.8243	1.37244	1.38071	1.37364	0.00708	0.9604
89.80	91.96	0.8002	1.34496	1.35236	1.34587	0.00649	0.9448
100.00	100.00	0.7732	...	...	...	...	0.9348

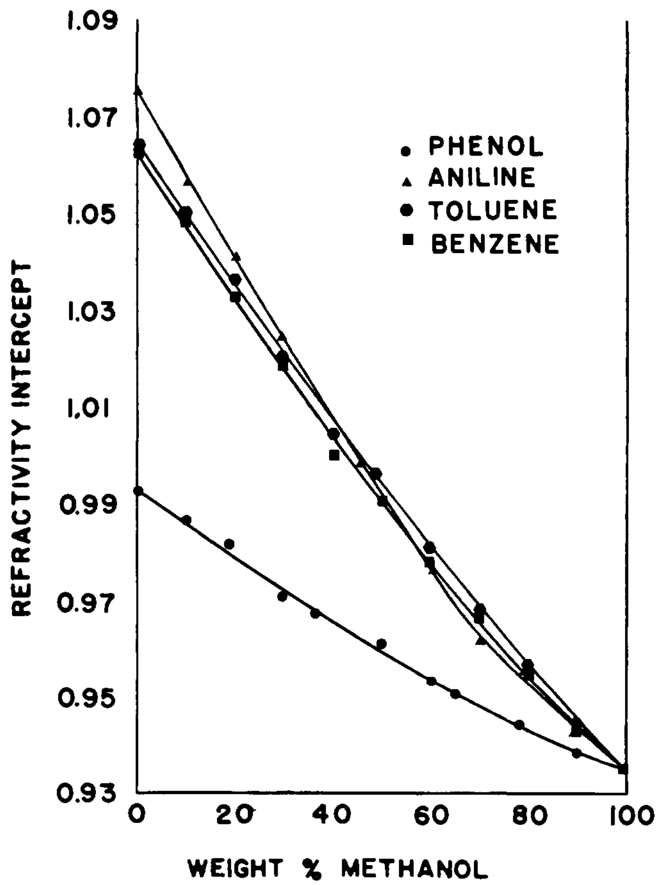

Figure 3. Refractivity intercepts for methanol solutions of benzene, toluene, aniline, and phenol at 20° C.—plotted vs. weight per cent

to a minimum. The densities and refractive indices of the pure compounds were compared with those reported in the literature (*1*, *4*) and were in good agreement.

Solutions covering the entire composition range were prepared at approximately 10 weight % intervals using a Sartorius electronic balance.

Density Measurements. Densities of the prepared solutions were determined in duplicate at 20°, 30°, and 40° C. using 10-ml. calibrated Weld-type capped specific gravity bottles. Temperature control was provided by a Fisher Isotemp constant temperature bath which held temperatures to within $\pm 0.02°$ C. Calibrations of the specific gravity bottles were performed at each temperature, using boiled demineralized water.

The density-composition plot at 20° C. is shown in Figure 1. Curves for all four organic solutions show slight curvature but absence of any maxima or minima (Tables I to IV).

Unlike some other systems (*5*, *7*), density measurements may be used in analysis of these binary systems. Nevertheless, the smaller the density difference between the two compounds, the more the chance of an error.

Table IV. Phenol-Methanol System

Methanol, Wt. %	Composition, Vol. %	Density, d, G./Ml.	Refractive Index Measurements, ±0.00003 n_D	n_F	n_C	Dispersion, $n_F - n_C$	Refractivity Intercept, $n_D - d/2$
			At 20° C.				
0.00	0.00	1.0666	1.52623	1.53530	1.52159	0.01371	0.9930
10.00	13.02	1.0358	1.50471	1.51472	1.50006	0.01466	0.9868
19.70	20.99	1.0070	1.48795	1.49404	1.47888	0.01516	0.9845
29.92	36.54	0.9795	1.46158	1.47125	1.45799	0.01326	0.9718
36.86	44.04	0.9590	1.44737	1.45633	1.44379	0.01254	0.9679
49.98	57.39	0.9201	1.42198	1.42948	1.41854	0.01094	0.9619
60.47	67.34	0.8938	1.40088	1.40834	1.39863	0.00971	0.9540
65.36	71.78	0.8808	1.39148	1.39802	1.38938	0.00864	0.9511
78.32	82.96	0.8474	1.36651	1.37368	1.36601	0.00767	0.9444
90.53	92.80	0.8165	1.34688	1.35158	1.34457	0.00701	0.9387
100.00	100.00	0.7914	...	1.3334	...	...	0.9423
			At 30° C.				
0.00	0.00	1.0590	1.52216	1.53357	1.51778	0.01579	0.9927
10.00	13.06	1.0280	1.50110	1.51249	1.49651	0.01598	0.9871
19.70	21.04	1.0067	1.47979	1.49024	1.47528	0.01496	0.9764
29.92	36.63	0.9707	1.45942	1.46963	1.45582	0.01381	0.9741
36.86	44.13	0.9512	1.44423	1.45428	1.44165	0.01263	0.9686
49.98	57.48	0.9148	1.41891	1.42739	1.41661	0.01078	0.9615
60.47	67.42	0.8865	1.39831	1.40505	1.39615	0.00890	0.9551
65.36	71.85	0.8724	1.38878	1.39539	1.38666	0.00873	0.9526
78.32	83.01	0.8390	1.36620	1.37040	1.36401	0.00639	0.9467
90.53	92.82	0.8094	1.34419	1.34951	1.34444	0.00507	0.9395
100.00	100.00	0.7828	...	...	...	...	0.9348
			At 40° C.				
0.00	0.00	1.0510	1.51968	1.53164	1.51507	0.01657	0.9942
10.00	13.12	1.0200	1.49775	1.50938	1.49312	0.01626	0.9878
19.70	21.12	0.9982	1.47538	1.48675	1.47158	0.01517	0.9763
29.92	36.73	0.9626	1.45564	1.46464	1.45150	0.01314	0.9743
36.86	44.24	0.9431	1.44035	1.44919	1.43698	0.01221	0.9688
49.98	57.60	0.9061	1.41416	1.42206	1.41141	0.01065	0.9611
60.47	67.52	0.8793	1.39421	1.40120	1.39177	0.00943	0.9546
65.36	71.95	0.8651	1.38417	1.39005	1.38187	0.00818	0.9516
78.32	83.08	0.8331	1.36073	1.36642	1.35913	0.00729	0.9442
90.53	92.85	0.8000	1.34163	1.34515	1.33848	0.00667	0.9416
100.00	100.00	0.7732	...	...	...	...	0.9348

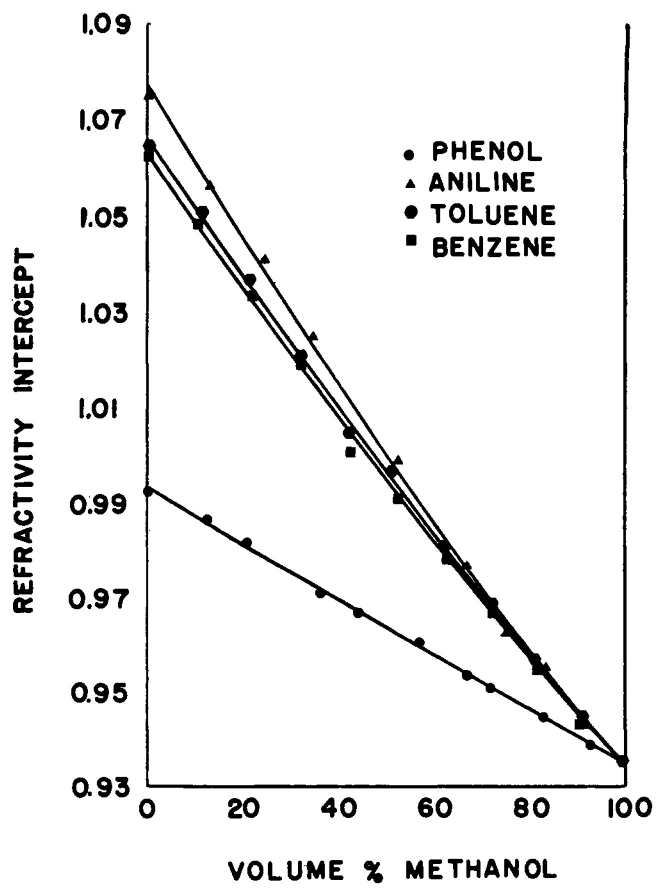

Figure 4. Refractivity intercepts for methanol solutions of benzene, toluene, aniline, and phenol at 20° C.—plotted vs. volume per cent

Refractive Index Measurements. Refractive index values were observed at 20°, 30°, and 40° C. using a Bausch & Lomb precision refractometer fitted with a thermometer calibrated to 0.1° C. Sodium and hydrogen lamps were used as the light sources. Temperature was controlled by a Fisher Isotemp constant temperature bath which was used to circulate water around the prisms. The tubing for the water was insulated to reduce temperature drop between the constant temperature bath and the refractometer. The red (C) and blue (F) lines obtained from the hydrogen lamp (2) were relatively brighter than that of the yellow line of the sodium lamp.

Data obtained for the systems are presented in Tables I to IV along with the calculated dispersions. A plot of refractive index (n_D) *vs.*, composition is presented in Figure 2.

Refractive index readings can be used effectively in the analysis of these binary systems. The refractive index technique is faster, safer, and requires less handling of the solutions.

Table V. Constants for Pure Compounds

Equation	Temp., ° C.	Benzene	Toluene	Aniline	Phenol	Methanol
Eykman	20	0.7516	0.7560	0.7473	0.6471	0.5639
	30	0.7514	0.7547	0.7481	0.6470	0.5653
	40	0.7521	0.7565	0.7535	0.6490	0.5664
Gladstone-Dale	20	0.5714	0.5744	0.5740	0.4934	0.4186
	30	0.5708	0.5724	0.5742	0.4931	0.4197
	40	0.5709	0.5740	0.5783	0.4944	0.4203
Lorentz-Lorenz	20	0.3360	0.3381	0.3286	0.2879	0.2586
	30	0.3362	0.3379	0.3294	0.2881	0.2595
	40	0.3368	0.3390	0.3317	0.2891	0.2602
Newton	20	1.4296	1.4348	1.4846	1.2464	0.9758
	30	1.4242	1.4272	1.4824	1.2436	0.9772
	40	1.4211	1.4274	1.4927	1.2459	0.9773
Kurtz refractivity intercept	20	1.0627	1.0645	1.0756	0.9930	0.9359
	30	1.0614	1.0625	1.0752	0.9927	0.9372
	40	1.0607	1.0627	1.0787	0.9942	0.9384

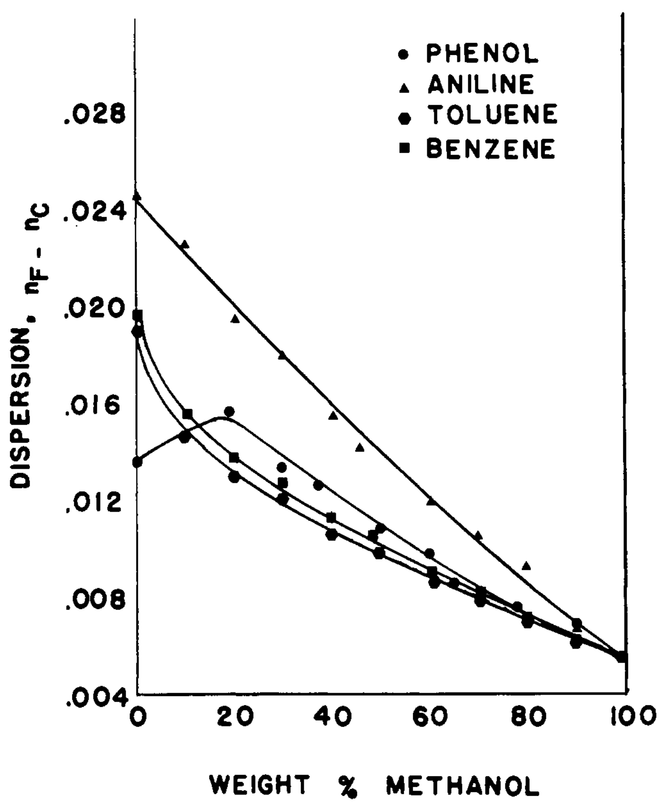

Figure 5. Dispersions for methanol solutions of benzene, toluene, aniline, and phenol at 20° C.

DISCUSSION

Using an IBM 1410 computer and 14 point accuracy, equations suggested by Newton, $n^2 - 1/d$, Gladstone-Dale, $n - 1/d$, Lorentz-Lorenz, $(n^2 + 1)/(n^2 + 2) \times 1/d$, Eykman $(n^2 + 1)/(n + 0.4) \times 1/d$, and Kurtz, refractivity intercept, $n - d/2$, were checked over the temperature range used. Of the five relationships tested, that of Eykman seemed to give the best constancy with change in temperature. Table V shows the results for the pure compounds. These relationships are useful in calculating refractive indices especially for light sensitive and toxic solutions.

Refractivity intercept values were determined as suggested by Kurtz and Ward (*3*) and presented by Rouleau and Thompson (*5*) at the temperatures used. When plotted *vs.* composition (Figure 3), phenol shows unusual deviation from the rest of the systems. This could be attributed to the water content of phenol, 12%, necessary to liquefy it. This might imply that refractivity intercept plots can be used effectively to indicate the presence of impurities with different molecular structures.

Refractivity intercepts are plotted *vs.* weight and volume per cent as shown in Figures 3 and 4, respectively. Although weight per cent would have a better practical application, volume per cent is more useful from a theoretical standpoint. The change from weight to volume per cent seems to smooth the data and avoids any intersection of curves.

Dispersion data $(n_F - n_C)$ obtained from hydrogen F and C lines can be used not only as a criterion of purity but also as an indication of structure. The use of specific dispersion in detecting aromatics in hydrocarbon mixtures (*8*) and in the purification of alkylbenzenes (*6*) has been advocated among other applications.

Since dispersion is a differential value, it is reasonably independent of errors in calibration, etc. For small temperature ranges, dispersion is relatively constant. These properties would indicate that the use of dispersion as a physical constant should find a wide variety of applications.

In the systems analyzed, $(n_F - n_C)$ dispersion increased slightly with the temperature while the ratio of the two indices (n_F/n_C) remained constant. Specific dispersion, on the other hand, is more sensitive to temperature change.

Dispersion is plotted *vs.* composition in Figure 5. The phenol-methanol system shows a behavior different from the rest of the curves at 20° C. The maximum present at 20° C. is reduced at 30° C. and disappears at 40° C. This can be observed in Table IV.

LITERATURE CITED

(1) American Petroleum Institute Research Project 44, April 30, 1962.
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RECEIVED for review December 6, 1966. Accepted April 28, 1967.