

# Expansivities of the Binary Mixtures Benzene + Pentan-1-ol and Benzene + Pentan-2-ol between 298.15 and 323.15 K

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**Thermal expansion coefficients,  $\alpha$ , are reported for binary mixtures of benzene with pentan-1-ol and with pentan-2-ol. The values, between 298.15 and 323.15 K, are determined from density measurements obtained in a vibrating-tube densimeter. Obtained as well are the values of  $V_m^E$  and  $(\partial V_m^E/\partial t)$  for the systems indicated, correlated with appropriate equations. The data of  $\alpha$  obtained are compared with those evaluated by using some equations of the specific refraction.**

## Introduction

In a previous paper (1) thermal expansion coefficients were determined for benzene with heptan-1-ol between 298.15 and 313.15. Continuing along the same line, the expansivities of benzene with pentan-1-ol and pentan-2-ol are reported in this paper, but now for a wider range of temperatures, namely between 298.15 and 323.15 K. To complete this study we have included in this paper a secondary alcohol in order to contrast its behavior to the primary alcohol. Just as in other papers (1, 2), the values of the average expansivities ( $\bar{\alpha}$ ), in a range of temperature, are obtained for the pure compounds and their binary mixtures by using the empirical formulas reported in the mentioned papers. A comparison between the data obtained empirically and those estimated from the experimental densities is finally made.

## Experimental Section

The benzene as well as the alcohols used were provided by Fluka. Their characteristics were benzene (99.5 mol %), pentan-1-ol (99 mol %), and pentan-2-ol (99 mol %). Prior to use, all products were degassed and dried with molecular

sieves. The procedure and equipment used are the same as in the previous paper (1). There is, however, a difference in the calibration of the densitometer. In some papers (3, 4) water and air were used as pattern substances for calibration, while in others air was substituted by benzene (2), tetrachloromethane (5) or dry nitrogen (6). Of all these, water is the most frequently used substance; however, the densities of air and nitrogen are far too different from those of the organic products. Also, although the densities of  $C_6H_6$  and  $CCl_4$  have been determined sufficiently, they are fairly unstable compounds (high volatility, hygroscopic, etc.). In order to unify the results obtained, in this and future papers we have decided to use degassed and redistilled water, with density taken from ref 7, and nonane as references for calibration. The densities of nonane (Fluka, 74252, >99 mol %) were determined between 263.15 and 323.15 K at the Institute for Measuring Techniques of Dr Stabinger, Graz (Austria), and their values, at the temperatures used in this work, are the following: 713.85 at 298.15, 709.91 at 303.15, 705.96 at 308.15, 698.06 at 318.15, and 694.12  $kg \cdot m^{-3}$  at 323.15 K.

The densities of nonane and water offer a wide working range and, above, all, one much closer to the majority of the densities of the organic products. Also, both compounds are quite stable and their characteristics are easily reproducible.

## Results and Discussion

Experimental densities and refractive indices of the pure compounds are given in Table I along with those found in the literature, for each temperature in our experiments. The values of  $n_D$  for the pure liquids were correlated as a function of temperature ( $^{\circ}C$ ), using a linear relationship

$$n_D = a + bt \quad (1)$$

where the coefficients  $a$  and  $b$  were determined by the method

Table I.  $\rho$  and  $n_D$  at Various Temperatures and Comparison with Those Values Found in the Literature

	298.15 K	303.15 K	308.15 K	318.15 K	323.15 K
$\rho$ , $kg \cdot m^{-3}$	873.47	873.70 (7)	868.14	868.5 (7)	862.74
		873.50 (8)		868.33 (8)	862.96 (8)
		873.78 (1)		868.40 (1)	852.01
		1.4979 (7, 8)	1.4945	1.4948 (8)	846.58
$n_D$	1.4979	1.4976 (1)		1.4943 (1)	1.4914
					1.4908 (1)
					1.4864
					1.4837
$\rho$ , $kg \cdot m^{-3}$	811.08	811.5 (7)	807.79	807.9 (9)	803.47
		811.2 (9)		803.99* (9)	803.99* (9)
		811.2 (9)			795.97
		1.4079 (7)	1.4057	1.4058 (9)	1.4040
$n_D$	1.4079	1.4080 (9)			1.4010
					796.63 (9)
					792.19
					792.9 (9)
$\rho$ , $kg \cdot m^{-3}$	805.16	805.4 (7)	800.97	801.2 (9)	796.79
		805.3 (9)			797.06 (9)
		1.4044 (7, 9)	1.4021	1.4025 (9)	1.4000
					788.26
$n_D$	1.4044				788.51 (9)
					783.75
					784.1 (9)
					1.3944

Table II.  $\rho$ ,  $n_D$ , and  $V_m^E$  for the Mixture Benzene + Pentan-1-ol and Benzene + Pentan-2-ol at Various Temperatures

temp, K	$x_1$	$\rho$ , g·cm <sup>-3</sup>	$V_m^E$ , cm <sup>3</sup> ·mol <sup>-1</sup>	$n_D$	temp, K	$x_1$	$\rho$ , g·cm <sup>-3</sup>	$V_m^E$ , cm <sup>3</sup> ·mol <sup>-1</sup>	$n_D$				
<b>C<sub>6</sub>H<sub>6</sub> (1) + C<sub>5</sub>H<sub>11</sub>(OH) (2)</b>													
298.15	0.040 65	0.813 02	0.0215	1.4109	323.15	0.685 75	0.829 20	0.3348	1.4531				
	0.119 85	0.816 84	0.0685			0.727 85	0.831 81	0.3219	1.4571				
	0.171 19	0.819 37	0.0995	1.4198		0.800 45	0.836 56	0.2831	1.4643				
	0.219 51	0.821 76	0.1328	1.4235		0.867 07	0.841 19	0.2311	1.4712				
	0.256 67	0.823 64	0.1568	1.4258		0.903 02	0.843 85	0.1912	1.4751				
	0.319 43	0.826 92	0.1912	1.4297		0.081 78	0.795 39	0.0707	1.4045				
	0.349 98	0.828 56	0.2061	1.4896		0.112 00	0.796 64	0.0921	1.4065				
	0.386 24	0.830 53	0.2237	1.4312		0.212 92	0.800 84	0.1728	1.4134				
	0.419 63	0.832 42	0.2360			0.312 51	0.805 19	0.2442	1.4203				
	0.472 40	0.835 42	0.2535	1.4433		0.398 16	0.809 07	0.3035	1.4266				
	0.499 65	0.837 01	0.2618	1.4458		0.432 95	0.810 74	0.3199	1.4294				
	0.546 75	0.839 81	0.2746	1.4498		0.480 41	0.813 08	0.3387	1.4331				
	0.613 69	0.843 96	0.2833	1.4562		0.508 02	0.814 48	0.3471	1.4353				
	0.667 37	0.847 43	0.2833	1.4615		0.563 50	0.817 40	0.3563	1.4398				
	0.730 77	0.851 75	0.2694	1.4675		0.584 26	0.818 52	0.3582	1.4416				
	0.802 28	0.856 95	0.2329	1.4759		0.693 52	0.824 72	0.3497	1.4514				
0.802 28	0.856 95	0.2329	1.4759	0.756 44	0.828 59	0.3238	1.4574						
0.838 93	0.859 74	0.2074		0.846 32	0.834 48	0.2650	1.4665						
0.934 41	0.867 43	0.1188	1.4896	0.917 70	0.839 63	0.1831	1.4740						
0.964 49	0.870 04	0.0785	1.4927	<b>C<sub>6</sub>H<sub>6</sub> (1) + C<sub>3</sub>H<sub>7</sub>CH(OH)CH<sub>3</sub> (2)</b>									
303.15	0.042 84	0.809 76	0.0238	1.4086	298.15	0.044 46	0.807 14	0.0701	1.4073				
	0.085 97	0.811 77	0.0481	1.4117		0.084 52	0.808 93	0.1359	1.4099				
	0.118 97	0.813 31	0.0691	1.4140		0.130 56	0.811 06	0.2060	1.4131				
	0.202 25	0.817 29	0.1204	1.4201		0.199 11	0.814 40	0.2967	1.4180				
	0.262 17	0.810 21	0.1593	1.4241		0.229 33	0.815 88	0.3390	1.4200				
	0.314 14	0.822 81	0.1910	1.4285		0.276 44	0.818 31	0.3934	1.4240				
	0.363 54	0.825 34	0.2194	1.4322		0.345 25	0.822 00	0.4647	1.4293				
	0.427 70	0.828 73	0.2521	1.4371		0.405 90	0.825 49	0.5080					
	0.483 42	0.831 79	0.2744	1.4410		0.430 61	0.826 97	0.5213	1.4366				
	0.500 63	0.832 76	0.2798	1.4430		0.466 23	0.829 18	0.5342	1.4392				
	0.539 80	0.835 01	0.2900	1.4468		0.515 54	0.832 35	0.5450	1.4439				
	0.585 48	0.837 71	0.2980	1.4508		0.600 62	0.838 12	0.5460	1.4516				
	0.607 10	0.839 03	0.2988	1.4531		0.621 15	0.839 60	0.5395	1.4538				
	0.655 55	0.842 07	0.2960	1.4573		0.675 23	0.843 62	0.5156	1.4594				
	0.699 11	0.844 91	0.2870	1.4613		0.707 47	0.846 15	0.4913	1.4625				
	0.725 36	0.846 66	0.2799	1.4642		0.741 21	0.848 84	0.4654	1.4640				
0.767 00	0.849 54	0.2614	1.4684	0.791 49	0.853 00	0.4183	1.4714						
0.822 63	0.853 54	0.2286	1.4743	0.829 89	0.856 34	0.3715	1.4760						
0.890 49	0.858 68	0.1745	1.4816	0.876 37	0.860 57	0.3033	1.4812						
0.971 48	0.865 40	0.0696	1.4911	0.967 81	0.869 69	0.1147	1.4928						
308.15	0.064 52	0.806 40	0.0352	1.4083	303.15	0.063 59	0.803 82	0.0920	1.4063				
	0.105 02	0.808 27	0.0577	1.4109		0.084 46	0.804 67	0.1355	1.4077				
	0.156 58	0.810 61	0.0967	1.4146		0.123 94	0.806 42	0.2010	1.4103				
	0.186 74	0.812 04	0.1140	1.4167		0.203 30	0.810 06	0.3262	1.4160				
	0.264 66	0.815 71	0.1710	1.4224		0.264 11	0.813 10	0.3985	1.4204				
	0.279 32	0.816 43	0.1794	1.4235		0.319 54	0.815 98	0.4580	1.4246				
	0.320 82	0.818 48	0.2043	1.4265		0.363 23	0.818 30	0.5038	1.4281				
	0.386 70	0.821 84	0.2384	1.4316		0.441 93	0.822 85	0.5523	1.4347				
	0.451 87	0.825 29	0.2666	1.4368		0.486 51	0.825 57	0.5698	1.4385				
	0.479 44	0.826 78	0.2779	1.4391		0.517 41	0.827 52	0.5775	1.4413				
	0.528 07	0.829 50	0.2912	1.4432		0.572 45	0.831 16	0.5784	1.4466				
	0.559 78	0.831 30	0.3000	1.4460		0.596 08	0.832 80	0.5726	1.4488				
	0.632 52	0.835 61	0.3087	1.4526		0.650 46	0.836 67	0.5553	1.4542				
	0.672 15	0.838 10	0.3030	1.4565		0.684 30	0.839 22	0.5333	1.4575				
	0.720 33	0.841 23	0.2904	1.4609		0.740 15	0.843 56	0.4913	1.4633				
	0.752 98	0.843 44	0.2757	1.4641		0.790 16	0.847 68	0.4377	1.4689				
0.797 77	0.846 50	0.2579	1.4687	0.823 05	0.850 48	0.3981	1.4724						
0.852 82	0.850 51	0.2172	1.4746	0.846 34	0.852 50	0.3688	1.4751						
0.906 21	0.854 59	0.1670	1.4804	0.905 66	0.858 01	0.2653	1.4822						
0.966 44	0.859 75	0.0633	1.4875	0.967 68	0.864 28	0.1213	1.4902						
318.15	0.039 13	0.797 58	0.0300		308.15	0.043 80	0.798 59	0.0801	1.4027				
	0.090 35	0.799 73	0.0679	1.4068		0.101 98	0.801 02	0.1868	1.4062				
	0.138 89	0.801 78	0.1067	1.4101		0.154 53	0.803 30	0.2773	1.4102				
	0.180 05	0.803 58	0.1349	1.4127		0.208 18	0.805 79	0.3537	1.4140				
	0.236 02	0.806 05	0.1758	1.4170		0.253 79	0.807 95	0.4180	1.4171				
	0.252 13	0.806 78	0.1862	1.4177		0.340 87	0.812 49	0.4997	1.4239				
	0.321 44	0.809 95	0.2333	1.4230		0.378 70	0.814 54	0.5311	1.4270				
	0.371 29	0.812 30	0.2644	1.4267		0.452 71	0.818 78	0.5746	1.4331				
	0.455 17	0.816 41	0.3091	1.4334		0.489 94	0.820 99	0.5925	1.4363				
	0.475 49	0.817 44	0.3180	1.4351		0.526 47	0.823 28	0.5991	1.4396				
	0.534 90	0.820 57	0.3348	1.4399		0.564 11	0.825 74	0.5979	1.4431				
	0.609 72	0.824 74	0.3406	1.4464		0.609 61	0.828 70	0.6028	1.4474				
	0.632 15	0.826 03	0.3403	1.4484		0.645 77	0.831 34	0.5797	1.4509				

Table II (Continued)

temp, K	$x_1$	$\rho$ , $\text{g}\cdot\text{cm}^{-3}$	$V_m^E$ , $\text{cm}^3\cdot\text{mol}^{-1}$	$n_D$	temp, K	$x_1$	$\rho$ , $\text{g}\cdot\text{cm}^{-3}$	$V_m^E$ , $\text{cm}^3\cdot\text{mol}^{-1}$	$n_D$
318.15	0.70467	0.83572	0.5408	1.4568	323.15	0.71693	0.82644	0.5743	1.4533
	0.74904	0.83917	0.5027	1.4614		0.76029	0.82979	0.5317	1.4577
	0.78070	0.84170	0.4724	1.4648		0.80582	0.83333	0.4851	1.4629
	0.83345	0.84612	0.4080	1.4705		0.86745	0.83860	0.3857	1.4698
	0.86198	0.84861	0.3671	1.4737		0.93873	0.84524	0.2315	1.4783
	0.91182	0.85322	0.2759	1.4798		0.06753	0.78634	0.1318	1.3987
	0.96901	0.85908	0.1252	1.4871		0.10827	0.78789	0.2170	1.4013
	0.06801	0.79090	0.1342			0.14804	0.78943	0.2993	1.4039
	0.12420	0.79313	0.2445	1.4044		0.21807	0.79233	0.4251	1.4086
	0.14039	0.79377	0.2777	1.4055		0.27209	0.79479	0.4984	1.4126
	0.21696	0.79710	0.4001	1.4110		0.35612	0.79890	0.5874	1.4189
	0.26360	0.79921	0.4695	1.4142		0.45594	0.80425	0.6540	1.4270
	0.32482	0.80219	0.5398	1.4187		0.50137	0.80691	0.6641	1.4308
	0.35652	0.80385	0.5642	1.4212		0.54851	0.80977	0.6683	1.4349
	0.41883	0.81883	0.6098	1.4261		0.59890	0.81299	0.6600	1.4395
	0.47125	0.81021	0.6291	1.4306		0.69374	0.81945	0.6178	1.4485
	0.53583	0.81412	0.6399	1.4361		0.76201	0.82454	0.5544	1.4555
	0.57951	0.81688	0.6389	1.4400		0.82499	0.82958	0.4715	1.4622
	0.63786	0.82079	0.6221	1.4454		0.91739	0.83770	0.2979	1.4727
	0.68299	0.82398	0.5962	1.4498					

of least squares. The values of  $b = dn_D/dt$  were  $-6 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$  for benzene and  $-4 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$  for pentan-1-ol and pentan-2-ol. Likewise, the densities of all pure products were correlated through an exponential equation

$$\rho = Ae^{Bt} \quad (2)$$

where the parameter  $B = -\alpha$  is the thermal expansion coefficient, with a minus sign, of the substance considered. The values obtained for this parameter by using an appropriate fitting method were 0.00125, 0.00095, and 0.00108  $^\circ\text{C}^{-1}$  for benzene, pentan-1-ol, and pentan-2-ol, respectively. In a previous paper (1) the value found for benzene was 0.00124; however, we must indicate that, in this work, the range of temperatures has been increased by 10  $^\circ\text{C}$ ; therefore, the minimum differences observed are considered acceptable. The estimated figures for  $dn_D/dt$  and  $\alpha$  are average values in the temperature range of 298.15–323.15 K; average thermal expansion coefficients are indicated by  $\bar{\alpha}$ .

The application of the empirical formulas already used in previous papers (1, 2) gave the following results for the average thermal expansion coefficients:  $\bar{\alpha}_{G-D} = 0.00114$ ,  $\bar{\alpha}_{L-L} = 0.00097$ , and  $\bar{\alpha}_E = 0.00107 \text{ }^\circ\text{C}^{-1}$  for benzene  $\bar{\alpha}_{G-D} = 0.00084$ ,  $\bar{\alpha}_{L-L} = 0.00074$ , and  $\bar{\alpha}_E = 0.00079 \text{ }^\circ\text{C}^{-1}$  for pentan-1-ol;  $\bar{\alpha}_{G-D} = 0.00098$ ,  $\bar{\alpha}_{L-L} = 0.00086$ , and  $\bar{\alpha}_E = 0.00092 \text{ }^\circ\text{C}^{-1}$  for pentan-2-ol. The  $\bar{\alpha}$  values, evaluated here empirically, are noted to be quite smaller than those estimated previously for benzene by the author using the same relationships (1). This is due to  $\bar{\alpha}$  being directly proportional to the slope ( $dn_D/dt$ ), and in this work, the experimental measurements of  $n_D = n_D(t)$  gave a somewhat smaller slope value.

As indicated in the preceding work, the isobaric thermal expansion coefficients of a binary mixture can be obtained, at a specified concentration, either from the densities as a function of the temperature, or by adding the contributions of the expansivities of each component in the mixture. The application of this second method requires using the expression

$$\alpha = \frac{1}{V_m} \left[ \sum \frac{M_i x_i}{\rho_i} \alpha_i + \left( \frac{\partial V_m^E}{\partial T} \right)_{p,x} \right] \quad (3)$$

where  $V_m$  is the average value of the molar volume of the mixture at each concentration, and  $\rho_i$ ,  $\alpha_i$ ,  $M_i$ , and  $x_i$  are respectively the average value of density and expansivity, the molecular mass and the concentration of component  $i$ . The average values for the magnitudes indicated are understood to be within the range of temperature used in this work. The

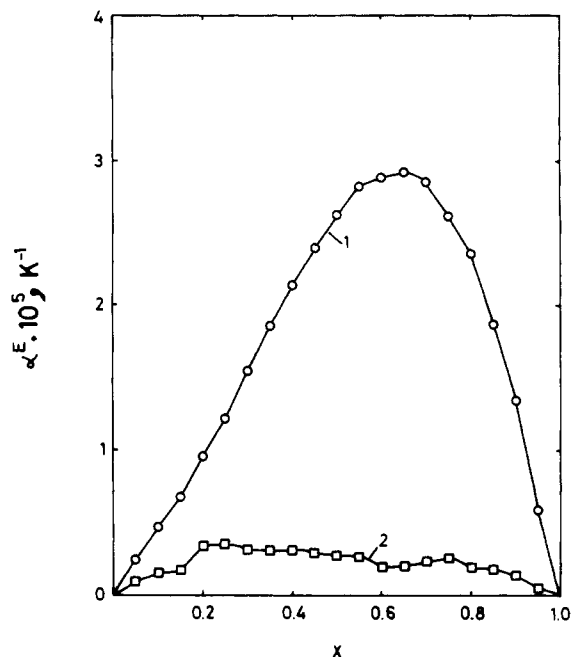


Figure 1. Average excess expansivities evaluated for  $x\text{C}_6\text{H}_6 + (1-x)\text{C}_5\text{H}_{11}(\text{OH})$  (1) and  $+ (1-x)\text{C}_7\text{H}_{15}(\text{OH})$  (derived from ref 1) (2), at every 0.05 units.

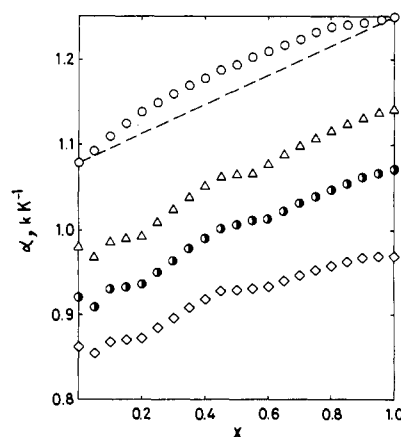
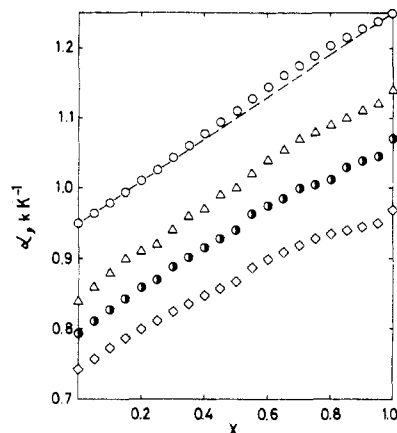


Figure 2.  $\bar{\alpha}$ -Values for  $x\text{C}_6\text{H}_6 + (1-x)\text{C}_5\text{H}_{11}(\text{OH})$ : (O) average experimental values evaluated from densities; ( $\Delta$ ),  $\bar{\alpha}_{G-D}$ ; ( $\square$ ),  $\bar{\alpha}_E$ ; ( $\diamond$ ),  $\bar{\alpha}_{L-L}$ .

Table III. Parameters of Eq 4-6 and Standard Deviations for the Fit of  $V_m^E$  by Eq 6 at Various Temperatures

T, K	$c_0$	$c_1$	$c_2$	$c_3$	$d_0$	$d_1$	$d_2$	$d_3$	R	$A_0$	$A_1$	$A_2$	$A_3$	$A_4$	$\sigma(V_m^E),$ $\text{cm}^3\text{-mol}^{-1}$
C <sub>6</sub> H <sub>6</sub> + C <sub>5</sub> H <sub>11</sub> (OH)	298.15	0.81103	0.04827	0.00074	0.01307	0.0003	-0.0259	0.0207	0.0040	4.3110	0.5348	3.9181	-6.6709	5.1870	0.0035
	303.15	0.80752	0.04536	0.00274	0.01228	-0.0001	-0.0196	0.0052	0.0144	3.7000	0.5231	4.0046	-6.7640	5.2841	0.0006
	308.15	0.80341	0.04631	-0.00254	0.01542	-0.0001	-0.0211	0.0091	0.0121	0.9236	0.4421	1.9889	-2.2616	1.9496	0.0034
	318.15	0.79588	0.04297	-0.00249	0.01544	-0.0003	-0.0200	0.0083	0.0116	1.5450	0.7789	0.6954	4.2101	-9.1806	0.0013
C <sub>6</sub> H <sub>6</sub> + C <sub>7</sub> H <sub>15</sub> CH- (CH) <sub>3</sub>	298.15	0.79206	0.04142	-0.00282	0.01571	-0.0001	-0.0206	0.0074	0.0131	1.1086	0.9660	-1.1209	10.2625	10.9434	0.0018
	303.15	0.80512	0.04448	0.00772	0.01592	-0.0002	-0.0277	0.0154	0.0115	2.7835	1.6279	3.5492	-6.9794	6.0624	0.0024
	308.15	0.80097	0.04298	0.00758	0.01627	0.0001	-0.0288	0.0182	0.0103	2.2420	1.5359	4.8704	-10.0401	8.0462	0.0056
	318.15	0.79668	0.04197	0.00732	0.01640	-0.0002	-0.0280	0.0187	0.0086	3.4600	1.9506	2.7349	-4.7104	4.9095	0.0044
323.15	0.78816	0.03890	0.00890	0.01571	-0.0005	-0.0244	0.0087	0.0161	1.7200	2.0385	3.1311	-7.0865	6.7142	0.0038	
	0.78387	0.03495	0.01689	0.00969	0.0001	-0.0289	0.0196	0.0080	1.2475	1.8984	4.7370	-10.6789	8.7925	0.0054	

Figure 3.  $\alpha$ -Values for  $x\text{C}_6\text{H}_6 + (1-x)\text{C}_5\text{H}_7\text{CH}(\text{OH})\text{CH}_3$ : (O) average experimental values evaluated from densities; ( $\Delta$ ),  $\alpha_{G-D}$ ; ( $\bullet$ ),  $\alpha_{Ei}$ ; ( $\diamond$ ),  $\alpha_{L-L}$ .

application of eq 3 demands that, at a particular concentration, we have the numerical values for the parameters shown in it. For this reason, it was necessary to obtain adequate relations for  $\rho = \rho(x)$ ,  $n_D = n_D(x)$  and  $V_m^E = V_m^E(x)$ . Table II shows the  $\rho$ ,  $n_D$ , and  $V_m^E$  for the mixtures as a function of the composition of benzene between 298.15 and 323.15 K. Densities and refractive indices were correlated, at each temperature, as a function of the concentration of benzene,  $x$ , using the following polynomial equations:

$$\rho = \sum c_i x^i \quad (4)$$

$$n_D = n_{D_1} x + n_{D_2} (1-x) + \sum d_i x^i \quad (5)$$

As the excess molar volumes present a nonsymmetrical distribution, a polynomial form of the equation of  $Z(1-3)$  was used to correlate the  $V_m^E$  values. Now, this equation is presented as

$$V_m^E = x(1-x) \sum A_i Z^i \quad (6)$$

where

$$Z = x/[x + R(1-x)] \quad (7)$$

The parameters of all these equations appear in Table III at each temperature. Once the parameters of eq 4-6 were defined, the values of  $\rho$ ,  $n_D$ , and  $V_m^E$ , at every 0.05 units of the molar fraction of benzene,  $x$ , were estimated for each temperature. Then, with  $x$  constant, the relationships of  $\rho = \rho(t)$ ,  $n_D = n_D(t)$ , and  $V_m^E = V_m^E(t)$  were obtained through expressions similar to (1) and (2). Knowing these equations and ( $\partial V_m^E / \partial t$ ), we can evaluate the  $\alpha$  values of our binary mixtures using eq 3. In order to analyze the behavior of benzene + alcohol mixtures and compare the results obtained, all these equations applied to benzene + pentan-1-ol and benzene + heptan-1-ol (derived from ref 1) were processed on a mini-computer, and represented in Figure 1 are the  $\alpha^E$ 's calculated at every 0.05 units between  $x = 0$  and  $x = 1$ . The distribution of  $\alpha^E$  is seen even better if the points evaluated are joined by means of the broke line, such as appears in Figure 1.  $\alpha^E$ 's were calculated from  $\alpha^E = \alpha - \sum \Phi_i \alpha_i$ , where  $\Phi_i$  is the corresponding fraction in volume of component  $i$ , given by  $\Phi_i = x_i V_{m,i} / V_m$ .

We continue to be interested in contrasting these results with those obtained from the empirical relationships derived by differentiation of the Gladstone-Dale, Lorentz-Lorenz, and Eykman equations (ref 2). To achieve this, it is necessary to have a great deal of experimental data for pure products and mixtures in order to obtain a better comparison between the empirical and experimental results. Figures 2 and 3 show the graphic comparison of the data for the two systems in this work

using on the one hand eq 3, and on the other, the empirical relationships previously mentioned and derived from ref 1 and 2. The data represented have been evaluated at every 0.05 units of the molar fraction of benzene,  $x$ .

The analysis of the figures permits us to establish the following: while for benzene + heptan-1-ol, the distribution of the  $\bar{\alpha}$  values presented a negative deviation in relation to the straight line  $\bar{\alpha}_1x + \bar{\alpha}_2(1-x)$ , now, for benzene + pentan-1-ol and benzene + pentan-2-ol, the deviation is positive. Likewise, it is interesting to observe the shift that has taken place in the distribution of the points empirically and in a direction totally contrary to that of the  $\bar{\alpha}$ -values. The shifting of  $\bar{\alpha}_{G-D}$ ,  $\bar{\alpha}_{L-L}$ , and  $\bar{\alpha}_E$  has the same order in both systems as those of the benzene + heptan-1-ol mixture (see ref 1), giving the impression of having moved  $\bar{\alpha}$ -axis. While for the system  $C_6H_6 + C_7H_{15}(OH)$  the empirical equation that produced the least deviation from experimental data was that derived from Lorentz-Lorenz, in this work that equation was that which caused the greatest differences due to the translation of the  $\bar{\alpha}$ -axis previously mentioned. These differences are due to the particular behavior of each mixture. The mean errors obtained from the empirical equa-

tions in relation to the experimental ones are respectively for benzene + pentan-1-ol and benzene + pentan-2-ol 9.73% and 12.21% with  $\bar{\alpha}_{G-D}$ ; 15.05% and 16.41% with  $\bar{\alpha}_E$ ; 21.46% and 22.59% with  $\bar{\alpha}_{L-L}$ .

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## Densities, Viscosities, and Refractive Indexes for the Methyl Isobutyl Ketone + Pentanols Systems. Measurements and Correlations

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In order to facilitate interpolation of the data, empirical single equations for density, viscosity, and refractive index as functions of composition and temperature were obtained by using the experimental results for the methyl isobutyl ketone + 1-pentanol, + 2-pentanol, + isoamyl alcohol, and + *tert*-amyl alcohol binary systems at 25, 30, 35, and 40 °C. The properties calculated through the empirical relations are in fairly good agreement with the experimental data.

Many industrial chemical processes or laboratory works need experimental data of density, viscosity, and refractive index at any given temperature and composition for binary liquid mixtures. Keeping in mind this problem, we are developing equations in which temperature and composition are incorporated to facilitate the interpolation data for these properties of the methyl isobutyl ketone (MIK) + 1-pentanol ( $P_1$ ), + 2-pentanol ( $P_2$ ), + isoamyl alcohol (IA), and + *tert*-amyl alcohol (TA) systems.

#### Experimental Section

**Materials.** The components were supplied by Merck-Darmstadt (A.R. grade). All species were dried with anhydrous  $K_2CO_3$  and fractionally distilled. The middle fraction was collected in each case and kept out from humidity with 3 Å molecular sieves for the pentanols and 4 Å for the methyl isobutyl ketone. The samples were maintained over molecular sieves to prevent water absorption. The physical properties of chem-

icals used here are compared with those reported in the literature in Table I.

**Procedure.** Mixtures were prepared by mixing accurately weighed quantities of pure liquids. Caution was taken to prevent evaporation. The Anton Paar DMA 46 calculating density meter with a built-in thermostat, a Cannon-Fenske viscosimeter, and a Jena dipping refractometer were used to obtain the density, viscosity, and refractive index, respectively. The accuracy of the measurements of these properties reported here is reproducible to within  $\pm 0.0001 \text{ g cm}^{-3}$ ,  $\pm 0.5\%$ , and  $\pm 0.00002$ , respectively. In all cases, a thermostatically controlled bath to  $\pm 0.01 \text{ }^\circ\text{C}$  was used.

#### Results and Discussion

The experimental results of densities, viscosities, and refractive indexes at several temperatures and compositions for the systems (MIK +  $P_1$ ), (MIK +  $P_2$ ), (MIK + IA), and (MIK + TA) are summarized in Tables II, III, IV, and V, respectively.

The following functional relationships of density, viscosity, and refractive index of the mixtures with the temperature were assumed (4-6).

$$\rho = A_1 e^{\beta_1 t} \quad (1)$$

$$\eta = A_2 e^{\beta_2 t/T} \quad (2)$$

$$n_D = A_3 e^{\beta_3 t} \quad (3)$$