

Densities, Molar Volumes, and Cubic Expansion Coefficients of 78 Aliphatic Ethers

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Densities of 78 aliphatic ethers were measured at 288.15, 298.15, and 308.15 K by the use of a Lipkin-Davison type pycnometer. Molar volumes at these temperatures and cubic expansion coefficients at 298 K were derived from the experimental data. For some homologous series of ethers, molar volumes were expressed as a function of the number of carbon atoms in the alkyl groups. Within any series of isomeric compounds, an ether containing different kinds of *n*-alkyls always has a smaller molar volume than the symmetric ether that has the same alkyl in the molecule, and as the difference between the numbers of carbon atoms in the two alkyls increases their molar volumes decrease. On the other hand, chain branchings of alkyls result in an increase of the molar volume. Throughout a homologous series of ethers having one of the alkyl groups in common, cubic expansion coefficients of the ethers decrease as the number of carbon atoms in the other alkyl groups increases. Within a group of isomeric compounds, however, the cubic expansion coefficients increase almost linearly with an increase in the molar volumes. For both homologous and isomeric series of compounds, the cubic expansion coefficients were correlated with their molar volumes.

Densities, molar volumes, and cubic expansion coefficients of a compound at various temperatures not only are important for practical purposes, but also are necessary for evaluating other thermochemical properties of the compound. Physical constants for some aliphatic ethers are already well-known (1), but few systematic investigations have been carried out for ethers as a class.

This paper is a part of systematic investigations on thermochemical properties of aliphatic ethers and deals with the experimental density measurements of 78 aliphatic ethers at three temperatures including the standard thermochemical temperature of 298.15 K. Molar volumes and cubic expansion coefficients at 298 K which were derived from the observed density data are also dealt with.

Experimental Section

Materials. Symmetric ethers, except di-*sec*-butyl and di-*tert*-butyl ether, and a few asymmetric ones were obtained from commercial sources. The rest of the compounds were synthesized in the laboratory either by means of the standard and/or improved Williamson method or by the use of a dehydration reaction of the corresponding alcohols. For the improved Williamson method, butylammonium hydrogen sulfate was employed as a phase-transfer catalyst (2), while for the dehydration reactions either aqueous solution of sulfuric acid or that containing sodium hydrogen sulfate was used. Di-*tert*-butyl ether was synthesized according to the method described by Erickson and Ashton (3).

Most compounds were purified by repeated fractional distillations over sodium wire until no impurity peaks were found on GLC; but for some compounds impurities were difficult to re-

move by the fractional distillations alone. Thus, they were purified by the use of preparative gas chromatography.

The purity of the samples was determined by GLC fitted with 3 mm \times 3 m columns containing polar and nonpolar stationary phases. The GLC analysis revealed that the purity for most compounds was more than 99.9 mol %. However, impurities in some compounds were difficult to remove even when a preparative gas-chromatographic technique was employed. The purity of such compounds, denoted with asterisks in Table I, was estimated to be about 99.6 mol %.

Water content in the purified samples was examined by the method described by Sellers (4) and was found to be less than 0.01 wt % for all compounds.

Density Measurements. Densities were measured at three temperatures, 288.15, 298.15, and 308.15 K, by the use of a Lipkin-Davison type pycnometer whose inner volume was about 2.1 cm³. The procedures for density measurements and for thermostat temperature establishment were the same as those described in the previous paper (5).

Densities of each compound were measured at least twice at each temperature. A fresh sample was used for each measurement. During thermal equilibration of the pycnometer, samples of low molecular weight became contaminated with water vapor in spite of special precautions taken. The observed densities were, therefore, corrected by the assumption that each sample forms an ideal solution with the dissolved water (5).

For each sample, the final density values obtained from repeated measurements at each temperature agreed within ± 0.0001 g cm⁻³.

Results and Discussion

Throughout the paper the 1979 atomic mass table is used.

Results from the density measurements are summarized in Table I. The recorded density values refer to the air-saturated liquids. Table I also includes molar volumes and cubic expansion coefficients at 298.15 K, where the latter are calculated by taking the first derivatives of the quadratic equations which express the molar volumes as a function of temperature. For diethyl and methyl isopropyl ethers, the coefficients are evaluated merely from their densities observed at 288.15 and 298.15 K, because no measurements of their densities at 308.15 K were available.

Table I includes many isomeric and homologous series of compounds. In any series of isomeric compounds, it is observed that the molar volume of a normal ether having different kinds of alkyls at each side of the oxygen atom is always smaller than the molar volume of a symmetric normal ether that has the same alkyl in the molecule. And the larger the difference between the numbers of carbon atoms in the two alkyls in the molecule, the smaller the molar volume of the ether. Thus, methyl *n*-alkyl ether in any series of isomeric compounds has the smallest molar volume, and ethyl *n*-alkyl ether follows it.

The existence of a side chain in an alkyl group causes the molar volume to increase. For example, when a *n*-propyl group in an ether is replaced by an isopropyl radical, the molar volume increases about 2 cm³ mol⁻¹ irrespective of the kind of the

[†] Deceased.

Table I. Densities, Molar Volumes, and Cubic Expansion Coefficients of 78 Aliphatic Ethers

compd ^a	ρ /(g cm ⁻³)			$V(298.15\text{ K})/$ (cm ³ mol ⁻¹)	$10^3\alpha(298.15\text{ K})/\text{K}^{-1}$
	288.15 K	298.15 K	308.15 K		
4 C Atoms					
MeOPr	0.7302	0.7185	0.7074	103.16	1.58 ₈
MeO- <i>i</i> -Pr	0.7205	0.7089		104.56	1.61
EtOEt	0.7192	0.7076		104.75	1.61
5 C Atoms					
MeOBu	0.7492	0.7394	0.7291	119.22	1.36 ₀
MeO- <i>i</i> -Bu	0.7375	0.7272	0.7166	121.22	1.43 ₈
MeO- <i>sec</i> -Bu	0.7467	0.7367	0.7262	119.65	1.39 ₃
MeO- <i>t</i> -Bu	0.7453	0.7351	0.7244	119.91	1.42 ₃
EtOPr*	0.7412	0.7307	0.7198	120.64	1.46 ₅
EtO- <i>i</i> -Pr	0.7281	0.7173	0.7061	122.89	1.53 ₄
6 C Atoms					
MeOPe	0.7642	0.7552	0.7456	135.30	1.23 ₃
MeO- <i>i</i> -Pe	0.7584	0.7490	0.7394	136.42	1.26 ₉
EtOBu*	0.7543	0.7449	0.7348	137.17	1.31 ₀
EtO- <i>i</i> -Bu	0.7442	0.7342	0.7241	139.17	1.36 ₉
EtO- <i>sec</i> -Bu	0.7482	0.7383	0.7282	138.39	1.35 ₅
EtO- <i>t</i> -Bu	0.7456	0.7354	0.7250	138.94	1.40 ₁
PrOPr	0.7516	0.7421	0.7320	137.68	1.32 ₂
PrO- <i>i</i> -Pr	0.7425	0.7324	0.7221	139.51	1.39 ₃
<i>i</i> -PrO- <i>i</i> -Pr*	0.7292	0.7189	0.7083	142.13	1.45 ₅
7 C Atoms					
MeOHx	0.7749	0.7663	0.7573	151.64	1.14 ₉
EtOPe*	0.7659	0.7572	0.7477	153.46	1.20 ₃
EtO- <i>i</i> -Pe	0.7613	0.7521	0.7426	154.50	1.24 ₄
PrOBu	0.7633	0.7542	0.7449	154.07	1.22 ₀
PrO- <i>i</i> -Bu	0.7533	0.7440	0.7345	156.19	1.26 ₄
PrO- <i>sec</i> -Bu	0.7594	0.7501	0.7406	154.92	1.25 ₄
PrO- <i>t</i> -Bu	0.7562	0.7466	0.7369	155.64	1.29 ₃
<i>i</i> -PrOBu	0.7554	0.7460	0.7364	155.77	1.27 ₄
<i>i</i> -PrO- <i>i</i> -Bu	0.7446	0.7349	0.7253	158.12	1.31 ₃
<i>i</i> -PrO- <i>sec</i> -Bu	0.7490	0.7396	0.7300	157.12	1.28 ₅
<i>i</i> -PrO- <i>t</i> -Bu	0.7460	0.7362	0.7266	157.84	1.31 ₇
8 C Atoms					
MeOHp	0.7838	0.7756	0.7670	167.91	1.08 ₅
EtOHx	0.7777	0.7682	0.7604	169.53	1.12 ₅
PrOPe	0.7740	0.7653	0.7560	170.17	1.13 ₈
PrO- <i>i</i> -Pe	0.7687	0.7601	0.7512	171.33	1.15 ₂
<i>i</i> -PrOPe	0.7681	0.7598	0.7506	171.40	1.15 ₃
<i>i</i> -PrO- <i>i</i> -Pe	0.7634	0.7545	0.7453	172.60	1.20 ₀
BuOBu	0.7725	0.7642	0.7551	170.41	1.14 ₀
BuO- <i>i</i> -Bu	0.7640	0.7552	0.7463	172.44	1.17 ₂
BuO- <i>sec</i> -Bu	0.7696	0.7611	0.7526	171.11	1.15 ₆
BuO- <i>t</i> -Bu	0.7672	0.7581	0.7492	171.78	1.18 ₇
<i>i</i> -BuO- <i>i</i> -Bu	0.7541	0.7452	0.7361	174.76	1.22 ₂
<i>i</i> -BuO- <i>sec</i> -Bu	0.7598	0.7508	0.7419	173.45	1.19 ₂
<i>i</i> -BuO- <i>t</i> -Bu	0.7574	0.7480	0.7386	174.10	1.25 ₇
<i>sec</i> -BuO- <i>sec</i> -Bu	0.7675	0.7588	0.7498	171.63	1.16 ₈
<i>sec</i> -BuO- <i>t</i> -Bu	0.7662	0.7571	0.7481	172.01	1.19 ₅
<i>t</i> -BuO- <i>t</i> -Bu	0.7669	0.7578	0.7487	171.85	1.20 ₁
9 C Atoms					
MeOOc	0.7909	0.7830	0.7748	184.24	1.02 ₉
EtOHp	0.7838	0.7753	0.7672	186.07	1.07 ₀
PrOHx	0.7813	0.7730	0.7647	186.62	1.07 ₄
<i>i</i> -PrOHx*	0.7759	0.7678	0.7591	187.88	1.09 ₅
BuOPe	0.7804	0.7727	0.7637	186.69	1.09 ₀
BuO- <i>i</i> -Pe	0.7758	0.7676	0.7595	187.93	1.09 ₄
<i>i</i> -BuOPe	0.7740	0.7656	0.7570	188.42	1.11 ₁
<i>i</i> -BuO- <i>i</i> -Pe*	0.7677	0.7594	0.7511	189.96	1.11 ₃
<i>sec</i> -BuOPe	0.7772	0.7687	0.7604	187.66	1.09 ₃
<i>sec</i> -BuO- <i>i</i> -Pe	0.7729	0.7643	0.7557	188.74	1.12 ₅
<i>t</i> -BuOPe	0.7751	0.7664	0.7578	188.23	1.12 ₉
<i>t</i> -BuO- <i>i</i> -Pe	0.7705	0.7616	0.7530	189.41	1.14 ₉
10 C Atoms					
MeONy	0.7966	0.7886	0.7808	200.71	1.00 ₂
EtOOc	0.7902	0.7823	0.7741	202.33	1.02 ₉
PrOHp	0.7878	0.7798	0.7717	202.98	1.03 ₃
<i>i</i> -PrOHp	0.7817	0.7736	0.7653	204.61	1.06 ₀
BuOHx*	0.7870	0.7788	0.7708	203.24	1.04 ₀
<i>i</i> -BuOHx	0.7793	0.7712	0.7631	205.24	1.05 ₀
<i>sec</i> -BuOHx	0.7839	0.7758	0.7678	204.03	1.03 ₈

Table I (Continued)

compd ^a	$\rho/(\text{g cm}^{-3})$			$V(298.15 \text{ K})/(\text{cm}^3 \text{ mol}^{-1})$	$10^3\alpha(298.15 \text{ K})/\text{K}^{-1}$
	288.15 K	298.15 K	308.15 K		
PeOPe*	0.7870	0.7792	0.7708	203.14	1.04 ₀
PeO- <i>i</i> -Pe	0.7831	0.7751	0.7669	204.21	1.04 ₅
<i>i</i> -PeO- <i>i</i> -Pe*	0.7794	0.7715	0.7632	205.16	1.05 ₀
11 C Atoms					
MeODe	0.8015	0.7936	0.7859	217.12	0.98 ₃
EtONy	0.7956	0.7879	0.7799	218.70	0.99 ₇
PrOOc	0.7939	0.7859	0.7781	219.25	1.00 ₅
<i>i</i> -PrOOc*	0.7879	0.7799	0.7719	220.94	1.02 ₆
BuOHp	0.7928	0.7851	0.7773	219.48	1.00 ₇
PeOHx*	0.7923	0.7843	0.7765	219.70	1.00 ₇
12 C Atoms					
EtODe	0.8002	0.7924	0.7848	235.15	0.97 ₂
PrONy	0.7986	0.7910	0.7832	235.57	0.96 ₇
BuOOc	0.7975	0.7897	0.7821	235.96	0.97 ₅
PeOHp	0.7974	0.7897	0.7820	235.96	0.97 ₅
HxOHx*	0.8000	0.7923	0.7847	235.18	0.96 ₆

^a Abbreviations: Me, methyl; Et, ethyl; Pr, propyl; Bu, butyl; Pe, pentyl; Hx, hexyl; Hp, heptyl; Oc, octyl; Ny, nonyl; De, decyl; *i*, iso; *sec*, secondary; *t*, tertiary.

other alkyl group. Similar volume expansion is observed when a *n*-butyl or *n*-pentyl group is replaced by either a secondary or tertiary group, but its extent is smaller than that of the propyl group.

Therefore, it can be concluded that if the molar volume of a normal ether having the same alkyl group on both sides of the oxygen atom is taken as a standard in the isomeric series of compounds, molar volume deviations of the isomers from the standard one are considered to be made up of two factors: (1) the difference between the numbers of carbon atoms in the two alkyls in the molecule that causes the molar volume to decrease, and (2) the existence of side chains in the alkyls that leads to the molar volume increase.

For a series of homologous compounds where one of the alkyls is held to be in common, molar volumes of the homologues relate almost linearly to the total number of carbon atoms in the alkyls. And the relation is expressed by a similar equation proposed by Huggins for *n*-alkanes (6)

$$V/(\text{cm}^3 \text{ mol}^{-1}) = a + bn + cn^{-1} \quad (1)$$

where *a*, *b*, and *c* are the empirical constants to be determined from the experimental data, and *n* stands for the number of carbon atoms in the molecules. The last term in eq 1 represents the deviation of the observed molar volumes from linearity for lower members in the series.

Other equations to trace the deviation from linearity were also examined. For example, an equation proposed by Calingaert et al. (7), which contained a term of cn^{-2} instead of cn^{-1} in eq 1, was tested but it gave rather poor fittings compared with that of eq 1.

The empirical constants of eq 1 evaluated by the use of the least-squares method for 13 series of homologous compounds are tabulated in Table II, where one of the alkyls in any series was maintained in common.

As can be seen in Table II, within any series of homologue, where R represents another alkyl without a side chain, all constants change regularly with temperature provided that the number of data points employed in the calculation are the same at all temperatures. In addition, it is found that the constant *a* for *n*-alkyl ethers increases regularly as the number of carbon atoms in the common alkyls increases, while the constants *b* and *c* decrease. These facts show that the observed molar volumes as well as the density data can be reliable.

Table II also includes errors expressed by the maximum deviation calculated as $\delta_{\max} = |V_{\text{obsd}} - V_{\text{calcd}}|$, and twice the percent standard deviation evaluated as $2\sigma = 2\{[(V_{\text{obsd}} - V_{\text{calcd}})/V_{\text{calcd}}]/(N - 1)]^{1/2}$ between the observed and calculated

values, where *N* stands for the number of data points employed in the calculation. As can be seen in the table, δ_{\max} 's are less than $0.4 \text{ cm}^3 \text{ mol}^{-1}$ or 0.3% for every series of normal compounds and are slightly larger for branched-alkyl ethers. These facts indicate that uncertainties of molar volumes obtained in this investigation are believed to be less than 0.25%.

It may be generally expected that the lower members in a homologous series of compounds have larger expansion coefficients than those of the higher ones. Examination of the results by the present observation for each homologous series of compounds shows that the cubic expansion coefficients of ethers are expressed by the following equation:

$$\log(\alpha/\text{K}^{-1}) = A + B(V/(\text{cm}^3 \text{ mol}^{-1}))^{-1} + C(V/(\text{cm}^3 \text{ mol}^{-1}))^{-2} \quad (2)$$

where α represents the cubic expansion coefficient of a compound, and *A*, *B*, and *C* are the empirical constants to be determined from the experimental results. The evaluated constants are tabulated in Table III together with δ_{\max} 's and 2σ 's for every series, where the latter have the same meaning as those given in Table II. Relatively small errors are obtained for the series of *n*-alkyl ethers as well as for the series of ROR, but somewhat larger errors are observed for those of branched-alkyl ethers.

It is further noted that all constants for the series of *n*-alkyl ethers increase regularly with an increase in the number of carbon atoms in the common alkyls and that the differences of every constant between PrOR and *i*-PrOR are almost the same as those between BuOR and *i*-BuOR.

Table III also shows that the constant *C* diminishes gradually as the number of carbon atoms in the homologous compounds increases. This fact implies that the greater the molecular weight of a compound, the lower the contribution of the ratio of the free volume to the intrinsic one of the molecule to its cubic expansion coefficient.

In Figure 1 α 's for all of the investigated compounds are plotted against their molar volumes. Within any series of isomeric ethers, it is found that cubic expansion coefficients relate almost linearly to their molar volumes, and the relation is given by

$$\alpha/\text{K}^{-1} = A' + B'(V/(\text{cm}^3 \text{ mol}^{-1})) \quad (3)$$

where *A'* and *B'* are again the empirical constants. The evaluated constants are summarized in Table IV. Both constants decrease with the increase in the number of total carbon atoms in the ethers in every series, except isomers of *n* = 4,

Table II. Empirical Constants a , b , and c for Eq 1, and Errors Expressed by the Maximum Deviation, δ_{\max} , and Twice the Percent Standard Deviation, 2σ , between the Observed and Calculated Molar Volumes

T/K	N^a	a	b	c	$\delta_{\max}/(\text{cm}^3 \text{mol}^{-1})$	$2\sigma/\%$
ROR						
288.15	5	42.390	15.9810	-13.200	0.24	0.18
298.15	5	42.830	16.1110	-10.248	0.22	0.15
308.15	4	48.702	15.9336	-28.540	0.17	0.14
MeOR						
288.15	8	34.870	16.3278	+5.423	0.07	0.06
298.15	8	34.523	16.5122	+10.433	0.05	0.05
308.15	8	35.602	16.5996	+11.221	0.06	0.06
EtOR						
288.15	9	36.642	16.3207	+4.368	0.21	0.21
298.15	9	37.544	16.4240	+5.806	0.19	0.18
308.15	8	38.436	16.5274	+7.555	0.34	0.23
PrOR						
288.15	9	44.925	15.8748	-27.164	0.29	0.24
298.15	9	45.863	15.9762	-25.021	0.28	0.21
308.15	9	46.757	16.0983	-24.694	0.35	0.30
<i>i</i>-PrOR						
288.15	8	48.078	15.7417	-31.247	0.51	0.48
298.15	8	49.335	15.8204	-30.633	0.67	0.65
308.15	7	40.281	16.5393	+10.215	0.37	0.32
BuOR						
288.15	8	49.085	15.7022	-48.692	0.28	0.25
298.15	8	50.173	15.8019	-48.802	0.30	0.28
308.15	8	52.841	15.8019	-53.598	0.33	0.28
<i>i</i>-BuOR						
288.15	6	56.992	15.2669	-68.555	0.43	0.32
298.15	6	58.993	15.3030	-70.846	0.44	0.29
308.15	6	61.572	15.3013	-74.715	0.42	0.32
<i>sec</i>-BuOR						
288.15	6	59.399	15.0211	-80.976	0.53	0.56
298.15	6	61.796	15.0591	-85.944	0.56	0.49
308.15	6	64.255	15.0590	-89.297	0.61	0.49
<i>t</i>-BuOR						
288.15	5	73.387	14.0633	-126.487	0.35	0.36
298.15	5	77.128	13.9859	-134.980	0.31	0.38
308.15	5	80.931	13.8920	-142.679	0.43	0.42
PeOR						
288.15	7	54.092	15.4647	-82.785	0.39	0.26
298.15	7	56.434	15.5422	-85.108	0.39	0.26
308.15	7	60.514	15.4706	-96.524	0.39	0.26
<i>i</i>-PeOR						
288.15	5	68.205	14.6788	-129.042	0.12	0.10
298.15	5	72.053	14.5914	-138.815	0.14	0.12
308.15	5	73.549	14.6750	-139.994	0.21	0.18
HxOR						
288.15	6	75.652	14.4177	-186.958	0.26	0.16
298.15	6	80.283	14.3279	-202.807	0.25	0.16
308.15	6	80.970	14.4531	-201.488	0.24	0.16
HpOR						
288.15	5	83.278	14.2567	-249.020	0.12	0.10
298.15	5	87.430	14.2086	-264.874	0.19	0.15
308.15	5	88.602	14.3109	-265.821	0.18	0.14

^a N means the number of data points employed to evaluate the constants.

for which only three data points of less accuracy have been available.

Although maximum uncertainties of α and V are estimated to be about $\pm 0.02 \times 10^{-3} \text{ K}^{-1}$ and $\pm 0.05 \text{ cm}^3 \text{ mol}^{-1}$, respectively, it is found that the plots for isopropyl and isobutyl ethers barely keep the linear relations, and their α 's are rather small for their molar volumes. It is further noted that within the investigated compounds molar volumes of *tert*-butyl ethers are

Table III. Empirical Constants A , B , and C for Eq 2 Expressing Cubic Expansion Coefficients of Homologous Series as a Function of Their Molar Volumes

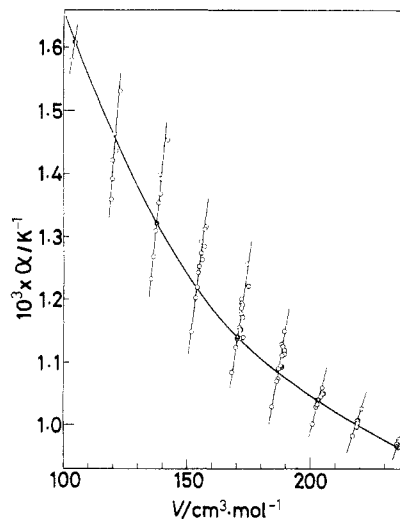
homo- logue	N^a	A	B	C	$10^3 \delta_{\max}/\text{K}^{-1}$	$2\sigma/\%$
ROR	5	-3.263	64.902	-1649.2	0.010	0.47
MeOR	8	-3.137	20.377	+1448.5	0.013	0.47
EtOR	9	-3.204	44.835	-135.1	0.027	0.60
PrOR	9	-3.268	66.743	-1861.7	0.027	0.87
<i>i</i> -PrOR	8	-3.413	113.708	-5090.4	0.046	1.6
BuOR	8	-3.308	85.882	-3915.4	0.021	0.63
<i>i</i> -BuOR	6	-3.465	133.333	-6993.7	0.013	0.56
<i>sec</i> -BuOR	6	-3.534	153.904	-8680.9	0.020	0.86
<i>t</i> -BuOR	5	-3.120	34.456	-11.4	0.058	2.8
PeOR	7	-3.361	108.587	-6385.5	0.013	0.58

^a N indicates the number of data points used for the evaluation of the constants.

Table IV. Empirical Constants A' and B' for Eq 3 Expressing the Cubic Expansion Coefficients of Isomeric Ethers as a Function of Their Molar Volumes

n^a	N^b	$10^3 A'$	$10^3 B'$	$10^3 \delta_{\max}/\text{K}^{-1}$	$2\sigma/\%$
4	3	-0.0519	15.89	0.002	0.2
5	6	-3.7262	42.80	0.027	2.8
6	9	-3.3493	33.94	0.034	2.4
7	11	-2.6059	24.85	0.031	2.2
8	16	-2.7035	22.57	0.030	2.5
9	12	-2.3481	18.36	0.027	2.2
10	10	-1.9039	10.48	0.010	1.1
11	6	-1.2447	10.25	0.013	0.9
12	5	-0.7608	7.35	0.004	0.6

^a Number of carbon atoms in the ether isomers. ^b Number of data points used for the calculation of the constants.

**Figure 1. Cubic expansion coefficients vs. molar volumes for aliphatic ethers at 298.15 K.**

almost the same as those of the corresponding isobutyl ethers, but cubic expansion coefficients of the former are about 15% greater on average than those of the latter.

Registry No. MeOPr, 557-17-5; MeO-*i*-Pr, 598-53-8; EtOEt, 60-29-7; MeOBu, 628-28-4; MeO-*i*-Bu, 625-44-5; MeO-*sec*-Bu, 6795-87-5; MeO-*t*-Bu, 1634-04-4; EtOPr, 628-32-0; EtO-*i*-Pr, 625-54-7; MeOPe, 628-80-8; MeO-*i*-Pe, 626-91-5; EtOBu, 628-81-9; EtO-*i*-Bu, 627-02-1; EtO-*sec*-Bu, 2679-87-0; EtO-*t*-Bu, 637-92-3; PrOPr, 111-43-3; PrO-*i*-Pr, 627-08-7; *i*-PrO-*i*-Pr, 108-20-3; MeOHx, 4747-07-3; EtOPe, 17952-11-3; EtO-*i*-Pe, 628-04-6; PrOBu, 3073-92-5; PrO-*i*-Bu, 15268-49-2; PrO-*sec*-Bu, 61962-23-0; PrO-*t*-Bu, 29072-93-3; *i*-PrOBu, 1860-27-1; *i*-PrO-*i*-Bu, 78448-33-6; *i*-PrO-*sec*-Bu, 18641-81-1; *i*-PrO-*t*-Bu, 17348-59-3; MeOHp, 629-32-3; EtOHx, 5756-43-4; PrOPe, 18641-82-2; PrO-*i*-Pe, 17071-48-6; *i*-PrOPe, 5756-37-6; *i*-PrO-*i*-Pe, 92096-99-6; BuOBu, 142-96-1; BuO-*i*-Bu, 17071-47-5; BuO-*sec*-Bu, 999-65-5; BuO-*t*-Bu, 1000-63-1; *i*-BuO-*i*-Bu, 628-55-7; *i*-BuO-*sec*-Bu, 92097-00-2; *i*-BuO-*t*-Bu, 33021-02-2; *sec*-

BuO-*sec*-Bu, 6863-58-7; *sec*-BuO-*t*-Bu, 32970-45-9; *t*-BuO-*t*-Bu, 6163-66-2; MeOOC, 929-56-6; EtOHp, 1969-43-3; PrOHx, 53685-78-2; *i*-PrOHx, 18636-65-2; BuOPe, 18636-66-3; BuO-*i*-Pe, 17071-52-2; *i*-BuOPe, 92097-01-3; *i*-BuO-*i*-Pe, 92097-02-4; *sec*-BuOPe, 92097-03-5; *sec*-BuO-*i*-Pe, 92097-04-6; *t*-BuOPe, 10100-95-5; *t*-BuO-*i*-Pe, 92097-05-7; MeONy, 7289-51-2; EtOOC, 929-61-3; PrOHp, 71112-89-5; *i*-PrOHp, 86724-25-6; BuOHx, 54459-71-1; *i*-BuOHx, 92097-06-8; *sec*-BuOHx, 65270-00-0; PeOPe, 693-65-2; PeO-*i*-Pe, 92097-07-9; *i*-PeO-*i*-Pe, 544-01-4; MeODE, 7289-52-3; EtONy, 16979-32-1; PrOOC, 29379-41-7; *i*-PrOOC, 68975-45-1; BuOHp, 71112-90-8; PeOHx, 32357-83-8; EtODE, 16979-29-6; PrONy, 92097-08-0; BuOOC, 53839-23-9; PeOHp, 74398-40-6; HxOHx, 112-58-3.

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Densities and Thermal Expansivities of Hexanol Isomers at Moderate Temperatures

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Densities and thermal expansion coefficients are reported for 1-hexanol and six of its isomers every two degrees between 25 and 35 °C, at atmospheric pressure. The coefficients of thermal expansion are contrasted with those obtained from an empirical equation where both the density and the refractive index are related.

As part of a continuing study on the thermophysical properties of alcohols we have measured the densities and refractive indices of 1-hexanol, 2-methyl-1-pentanol (2-M-1-P), 4-methyl-2-pentanol (4-M-2-P), 2-hexanol, 3-methyl-3-pentanol (3-M-3-P), 3-methyl-2-pentanol (3-M-2-P), and 2-methyl-2-pentanol (2-M-2-P) at six temperatures from 25 to 35 °C. The Lorentz-Lorenz (1, 2), Gladstone-Dale (3), and Eykman (4) equations were differentiated with regard to temperature and subsequently used for determining the thermal expansion coefficients, the results being compared with those obtained from experimental densities.

Experimental Section

Materials. All the alcohols were provided by Fluka (AG) and could be used without further purification given their high grade of purity. The water used for densimeter calibration and refractometer adjustments was redistilled, run through an ion-exchange column, and deaerated by boiling several times, showing an electrical conductivity of $7 \times 10^{-7} \Omega^{-1} \cdot \text{cm}^{-1}$.

Both the observed physical constants of each alcohol and corresponding data found in the literature are summarized in Table I. These data are presented at 293.15 K because at this temperature a greater number of experimental values in the literature were found for all compounds. The densities of some alcohols differ significantly from literature values. Ours are higher than literature values for 2-M-2-P and 3-M-2-P but are lower for 2-hexanol and 2-M-1-P with a maximum difference of $0.0061 \text{ g} \cdot \text{cm}^{-3}$ between our experimental value and that derived from ref 7 for 3-M-2-P. The refractive indices of hexanol isomers did not present as much discrepancy as densities except for 3-M-2-P with a maximum difference of 0.0025 unit with regard to the value found in ref 5.

Instrumental Section. Measurements of densities and refractive indices were made in the temperature range 298.15–308.15 K for all compounds. The densities were

measured by an Anton Paar DMA-55 digital densimeter with an estimated accuracy of $\pm 1 \times 10^{-5} \text{ g} \cdot \text{cm}^{-3}$, which is based on measuring the period of oscillation of a vibrating U-shaped tube which is filled with liquid substances. In the present study, the reference samples used for calibration were redistilled water and air, whose densities were derived from ref 5 at each temperature. Refractive indices were measured with a Bausch and Lomb refractometer with an accuracy of ± 0.0001 unit. All measurements of refractive indices were made for a wavelength of 5893 Å for the sodium D line, having been checked with pure water at each temperature. Both the digital densimeter and the refractometer were thermostated by a Heto Birdkerod ultrathermostat which controlled the temperature within $\pm 0.01 \text{ K}$ using a digital precision thermometer Anton Paar DT-100 with a thermistor calibrated previously.

Results

The densities (ρ) and refractive indices (n_D) of the pure alcohols are given in Tables II and III along with those experimental values found in the literature. Likewise, these values (ρ and n_D) have been plotted against the temperature in Figures 1 and 2, respectively. The densities determined by us at 298.15 K offer a larger discrepancy if our values are compared with those derived from ref 7; however, they do not differ significantly from others published more recently (8). For the refractive indices there also exist some important differences with respect to the values reported in the literature (7), the values differing by 0.0010 and 0.0012 unit for 2-M-1-P and 2-M-2-P, respectively. However, the refractive index for 2-M-1-P agrees satisfactorily with that reported in ref 9, 1.416 23.

The experimental densities may be expressed by the equation

$$\rho = Ae^{Bt} \quad (1)$$

where t is the temperature in degrees Celsius. The fitting parameters A and B are given in Table II. The B parameter coincides with the average coefficient of isobaric thermal expansion, $\alpha = (\partial \ln \rho / \partial t)_p$, in the temperature range of our experiments. Likewise, the experimental refractive indices were correlated by an equation of type

$$n_D = a + bt \quad (2)$$

where b coincides with the temperature coefficient (dn_D/dt) .