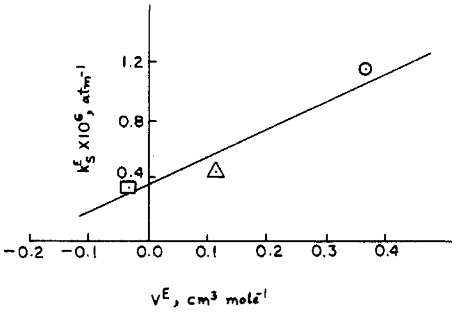

Figure 4. Plot of k_s^E vs. V^E for equimolal mixtures at 303.15 K: (○) C_2Cl_4–benzene; (△) C_2Cl_4–toluene; (□) C_2Cl_4–*p*-xylene.

volumes decrease as the number of CH_3 substituents attached to the aromatic ring increases, and these changes in V^E parallel the changes in the values of k_s^E.

In order to assess the perturbation that will be caused to the molecules of cyclohexane, CCl_4, and *p*-xylene as a result of their interactions with C_2Cl_4, we have estimated the dipole moments of cyclohexane, carbon tetrachloride, and *p*-xylene in C_2Cl_4 from the refractive index, dielectric constant, and specific volume (obtained by using data on excess volumes (*1*, *2*)) data for dilute solutions of cyclohexane, carbon tetrachloride, and *p*-xylene in C_2Cl_4 at 298.15 K, by using the method described by Halverstadt and Kumler (*12*). The dipole moments of cyclohexane, carbon tetrachloride, and *p*-xylene in tetrachloroethylene have been found to be 0.04, 0.26, and 0.12 D, respectively. The dipole moments (*13*) of these substances are normally zero. The value of the dipole moment, 0.04 D, of cyclohexane is negligibly small. The values 0.12 and 0.26 D of the dipole moments of *p*-xylene and carbon tetrachloride, respectively, in tetrachloroethylene suggest the formation of electron donor–acceptor species of C_2Cl_4 with *p*-xylene and CCl_4 in the liquid state.

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Densities and Refractive Indices of Pure Alcohols as a Function of Temperature

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Densities and refractive indices of normal alcohols from methanol to 1-decanol were measured in the temperature range from 20 to 80 °C for the refractive indices and from 20 to 45 °C for the densities. In both cases the data are discussed and compared to the results obtained by other scientists, having been correlated vs. temperature through an empirical relationship. To check the accuracy of experimental densities and refractive indices, the Eykman equation is used within the common interval of temperatures (20–45 °C).

The degree to which the velocity of propagation of an electromagnetic disturbance is affected by the medium through which it travels depends upon the molecular charge distributions that the radiation encounters per unit of its path length. Thus, in a liquid under ordinary ambient conditions, the packing degree of the molecules is one of the determining factors for the refractive index. Therefore, the effect of temperature on the usual refractive index of transparent liquids is primarily due to its influence on the degree of packing of the molecules in the liquid.

The refractive indices of all liquids decrease with increasing temperature. Most organic liquids have temperature coeffcients between −0.000 35 and −0.000 45 °C^{-1}. An average value of −0.000 45 °C^{-1} in applying temperature corrections to data is often recommended by some authors.

Density is a physical property of extreme importance in the characterization, identification and utilization of materials. The wide range of densities covered by the compounds provides a quick way of rough identification or classification of many substances with apparatus that can be carried into the field or plant. Densities of organic liquids range from about 3.3 to 0.6 g cm^{-3}. In general, the density of a substance decreases with increasing temperature.

In this work both properties have been determined for the primary set of normal alcohols at temperatures higher than ambient conditions.

Normal alcohols have been the subject of a great deal of study. Actual investigations generally require highly accurate physical properties. Although several sets of density and refractive index data exist for normal alcohols at 20 and 25 °C, in the literature there are few data for higher temperatures. The present work was undertaken to resolve the densities of pure normal alcohols at temperatures higher than 25 °C at atmospheric pressure. Therefore, the densities of normal alcohols from methanol to 1-decanol were determined at 5 °C intervals from 20 to 45 °C. For the same alcohols the refractive indices were measured, but now in a wider range to determine more exactly the coefficient dn_D/dt. These measurements were made at 5 °C intervals between 20 and 80 °C, except for methanol and ethanol, whose refractive indices were obtained up to 50 and 70 °C, respectively.

Both refractive index and density can be checked, for each pure compound or mixture, by means of several empirical equations. In the present work we have preferred Eykman's equation to others more familiar, like the Lorentz-Lorenz equation, even though the latter has a theoretical basis because of its greater simplicity and its smaller average deviation from experimental data.

To faciliate the interpolation of the data, we have derived equations for primary alcohols, in which the effects of temperature on refractive index and density are incorporated.

Experimental Section

Materials. Methanol (analytical reagent Prolabo) was rectified twice through a 120-cm column packed with Rasching rings, its purity being confirmed to be more than 99.8 mol% with gas chromatography. Ethanol, 1-propanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, and 1-decanol (Fluka AG) "puriss" grade material with high purity was used as received. 1-Butanol (Fluka AG) analytical reagent for spectroscopy was purified chromatographically to a purity of >99.8 mass%. 1-Nonanol (Fluka AG) "purum" grade material with a purity of >98.0 mass% was used as received.

The water used for checking the instruments was redistilled and run through an ion-exchange column until it showed an electrical conductivity of $<7 \times 10^{-7}$ mho cm^{-1}. Likewise, the dissolved air was expelled from the water before calibration.

Experimental Measurements. Refractive indices were measured between 20 and 80 °C with a Bausch & Lomb refractometer provided with temperature control by circulating thermostated water through it. The water used came from a bath thermostatically controlled within ±0.1 °C by a Brand thermometer previously calibrated against an NBS certified standard. All measurements were made for a wavelength of 5893 Å for the sodium D line, the refractometer having been frequently rechecked with redistilled water at each temperature. The resultant experimental error was estimated to be about ±0.0001 unit for all experiments.

Densities were determined with a 10-mL Brand pycnometer which was calibrated with the redistilled water at 20 °C by taking 0.9982 g cm^{-3} as the density of water at this temperature. At higher temperatures, the volumes of the pycnometer were corrected by using a standard volume expansion formula and taking a value of 15.6×10^{-6} °C^{-1} for the thermal volumetric coefficient of glass (derived from ref *1*). The pycnometer was maintained in the bath until a constant meniscus level was obtained by removing the excess liquid when necessary. Density measurements were made for all of the alcohols at 5 °C intervals from 20 to 45 °C, and the samples were prepared by weight in a Mettler H10 balance with an accuracy of 0.0001 g. Replications of measured densities of the pure alcohols indicate an estimated precision of ±0.0001 g cm^{-3}.

All of the above measurements were carried out in a constant-temperature room of 20 ± 1 °C and at atmospheric pressure.

Results and Discussion

Refractive indices of pure normal alcohols are given in Table I between 20 and 80 °C and have been plotted against temperature in Figure 1. These experimental values are compared with those found in the literature, when available. Likewise, the values of the parameters of eq 1, used to correlate the refractive indices as a function of temperature, are shown in Table I for each compound.

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

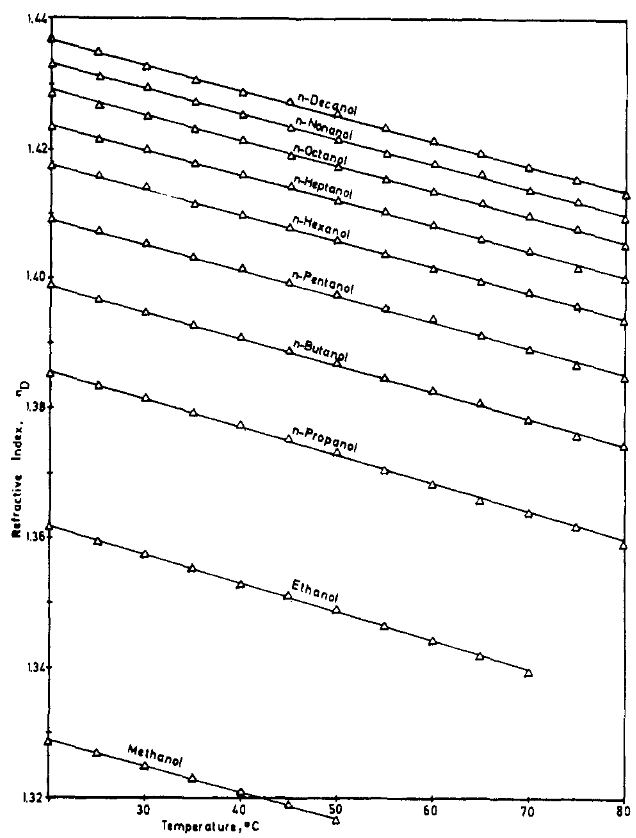

Figure 1. Refractive indices vs. temperature for the normal alcohols.

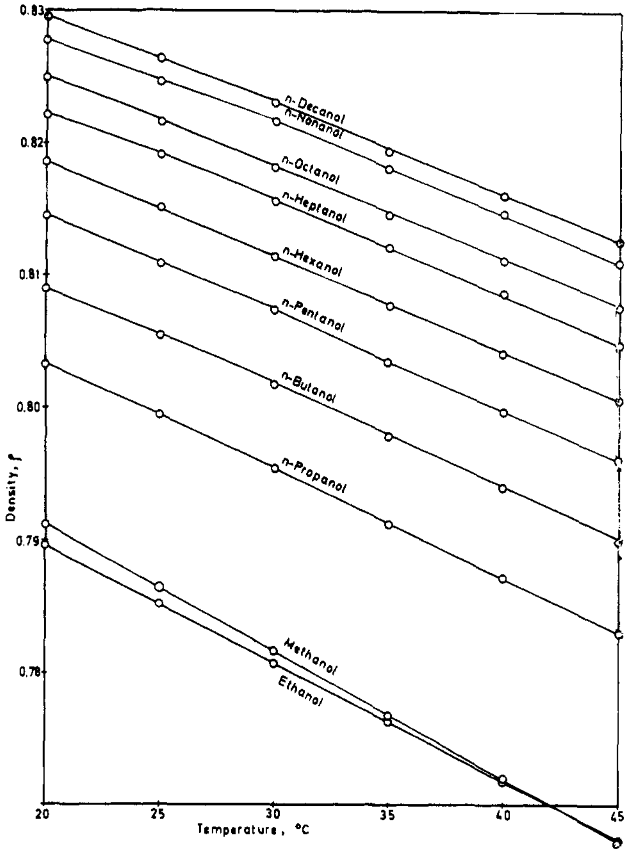

Figure 2. Densities vs. temperature for the normal alcohols.

A closer examination of Table I data shows a constant value of $dn_D/dt = -4 \times 10^{-4}$ °C^{-1} for all alcohols, which is in agreement with those predicted by some authors.

Table I. Refractive Indices of Normal Alcohols at Several Temperatures and the Fitting Parameter of Eq 1

t, °C	n_D				a	$10^4(-b)$, °C^{-1}
	exptl	ref *3*	ref *4*	ref *5*		
			Methanol			
20	1.3284	1.32840	1.3288	1.3288	1.3366	4
25	1.3267	1.32652				
30	1.3247					
35	1.3229					
40	1.3207					
45	1.3187					
50	1.3165					
			Ethanol			
20	1.3615	1.36143	1.3615	1.3611	1.3706	4
25	1.3593	1.35941				
30	1.3573					
35	1.3553					
40	1.3533					
45	1.3512					
50	1.3491					
55	1.3464					
60	1.3444					
65	1.3418					
70	1.3394					
			1-Propanol			
20	1.3850	1.38556	1.3854	1.3850	1.3943	4
25	1.3832	1.38370				
30	1.3814					
35	1.3793					
40	1.3774					
45	1.3752					
50	1.3732					
55	1.3704					
60	1.3684					
65	1.3661					
70	1.3641					
75	1.3617					
80	1.3591					
			1-Butanol			
20	1.3988	1.3993	1.3991	1.39931	1.4071	4
25	1.3967	1.3973				
30	1.3947					
35	1.3927					
40	1.3908					
45	1.3889					
50	1.3867					
55	1.3846					
60	1.3827					
65	1.3807					
70	1.3783					
75	1.3758					
80	1.3742					
			1-Pentanol			
20	1.4090	1.4100	1.4101	1.4101	1.4175	4
25	1.4074	1.4079				
30	1.4052					
35	1.4033					
40	1.4015					
45	1.3994					
50	1.3974					
55	1.3955					
60	1.3937					
65	1.3913					
70	1.3892					
75	1.3868					
80	1.3847					
			1-Hexanol			
20	1.4172	1.4181	1.4133	1.4178	1.4254	4
25	1.4157	1.4161				
30	1.4137					
35	1.4114					
40	1.4098					
45	1.4078					
50	1.4057					
55	1.4039					
60	1.4015					

Table I (*Continued*)

	n_D					
t, °C	exptl	ref *3*	ref *4*	ref *5*	a	$10^4(-b)$, °C^{-1}
65	1.3998					
70	1.3980					
75	1.3958					
80	1.3936					
			1-Heptanol			
20	1.4232		1.4233 (22.4 °C)	1.4249	1.4315	4
25	1.4216					
30	1.4200					
35	1.4179					
40	1.4160					
45	1.4142					
50	1.4121					
55	1.4103					
60	1.4082					
65	1.4062					
70	1.4044					
75	1.4016					
80	1.4001					
			1-Octanol			
20	1.4285	1.4295	1.4304 (20.5 °C)	1.4295	1.4364	4
25	1.4267	1.4275				
30	1.4250					
35	1.4230					
40	1.4213					
45	1.4194					
50	1.4173					
55	1.4152					
60	1.4135					
65	1.4117					
70	1.4098					
75	1.4077					
80	1.4053					
			1-Nonanol			
20	1.4328		1.4311	1.4333	1.4407	4
25	1.4309					
30	1.4294					
35	1.4273					
40	1.4253					
45	1.4232					
50	1.4215					
55	1.4194					
60	1.4177					
65	1.4162					
70	1.4138					
75	1.4120					
80	1.4094					
			1-Decanol			
20	1.4367		1.4372	1.43719	1.4441	4
25	1.4345					
30	1.4323					
35	1.4303					
40	1.4285					
45	1.4272					
50	1.4252					
55	1.4233					
60	1.4213					
65	1.4194					
70	1.4173					
75	1.4152					
80	1.4132					

Density data at 20, 25, 30, 35, 40, and 45 °C for normal alcohols are given in Table II. This also presents the values derived from the literature for the same compounds and the parameters of eq 2 used to correlate the experimental densities

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

vs. temperature. The experimentally determined densities and the correlation obtained as a function of temperature are shown for normal alcohols in Figure 2. The B parameter of eq 2 coincides with the average coefficient of thermal expansion for the normal alcohols cited $(-\delta \ln \rho/\delta t)_p$. It can be observed in Table II that this coefficient does not remain constant for all alcohols. This value decreases slowly with increasing normal-alcohol molecular weight, varying from 1.23×10^{-3} °C^{-1} for methanol to 0.82×10^{-3} °C^{-1} for 1-decanol.

To correlate both refractive indices and densities, a linear-regression procedure was used on a Hewlett-Packard 9830A computer, the goodness of fit being higher than 0.999 for the

Table II. Densities for Normal Alcohols at Several Temperatures and the Fitting Parameters of Eq 2

	ρ							
t, °C	exptl	ref *2*	ref *3*	ref *4*	ref *5*	ref *6*	A, g cm^{-3}	$10^3(-B)$, °C^{-1}
				Methanol				
20	0.7911		0.791 29	0.791	0.7914	0.791 32	0.8108	1.23
25	0.7864	0.786 64[a]	0.786 64			0.786 54		
30	0.7816					0.781 81		
35	0.7767	0.777 16				0.777 10		
40	0.7720					0.772 32		
45	0.7671	0.767 59				0.767 53		
				Ethanol				
20	0.7894		0.789 37	0.789 34	0.7893	0.789 34	0.8080	1.15
25	0.7852	0.785 09[a]	0.785 04	0.785 06		0.785 06		
30	0.7807			0.780 75		0.780 75		
35	0.7763	0.776 5				0.776 4		
40	0.7718					0.772 0		
45	0.7673	0.767 8				0.767 7		
				1-Propanol				
20	0.8033		0.803 75	0.804	0.8035	0.803 5	0.8205	1.02
25	0.7995	0.799 75[a]	0.799 75					
30	0.7955							
35	0.7913	0.791 85						
40	0.7872							
45	0.7830	0.783 59						
				1-Butanol				
20	0.8089		0.809 7	0.810	0.8098		0.8246	0.95
25	0.8054	0.806 0[a]	0.806 0			0.805 67		
30	0.8018							
35	0.7979	0.708 02						
40	0.7940							
45	0.7900	0.790 18						
				1-Pentanol				
20	0.8144		0.815 1	0.817	0.8144		0.8296	0.91
25	0.8109	0.811 5[a]	0.811 5					
30	0.8074							
35	0.8035	0.803 61						
40	0.7998							
45	0.7961	0.796 05						
				1-Hexanol				
20	0.8185		0.819 6	0.820	0.8136		0.8333	0.89
25	0.8151	0.815 9[a]	0.815 9					
30	0.8114							
35	0.8078	0.808 54						
40	0.8041							
45	0.8006	0.801 23						
				1-Heptanol				
20	0.8221			0.817 (22.4 °C)	0.8219		0.8368	0.86
25	0.8195	0.818 6[a]						
30	0.8157							
35	0.8121	0.812 28						
40	0.8112							
45	0.8048	0.805 10						
				1-Octanol				
20	0.8249		0.825 55	0.826 (20.5 °C)	0.827		0.8392	0.85
25	0.8216	0.822 2[a]	0.822 09					
30	0.8182							
35	0.8146	0.815 52						
40	0.8112							
45	0.8076	0.808 42						
				1-Nonanol				
20	0.8277			0.828	0.8273		0.8416	0.83
25	0.8246	0.824 7[a]						
30	0.8216							
35	0.8181	0.817 58						
40	0.8147							
45	0.8110	0.810 62						
				1-Decanol				
20	0.8295			0.83	0.8297		0.8435	0.82
25	0.8263	0.826 5[a]						
30	0.8230							
35	0.8194	0.819 46						
40	0.8161							
45	0.8126	0.812 58						

[a] Extracted from ref *2*.

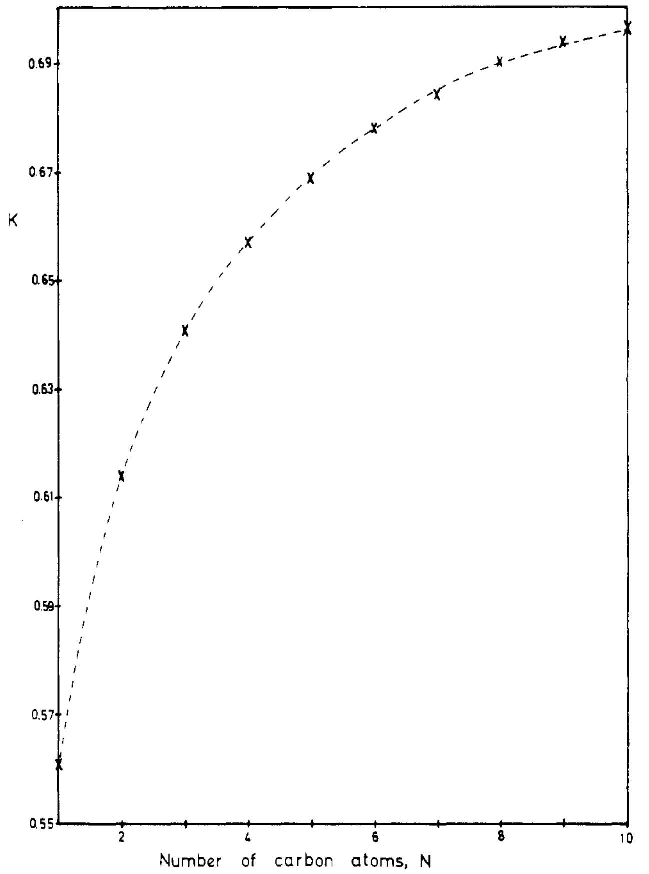

Figure 3. K values (eq 3) vs. number of carbon atoms, N.

refractive indices and higher than 0.998 for the densities. The empirical equation of Eykman (*1*, *3*), eq 3, offers an accurate

$$\frac{n_D^2 - 1}{n_D + 0.4}\frac{1}{\rho} = K \qquad (3)$$

way not only to check the accuracy of experimental densities and refractive indices but also to calculate one from the other. n_D is the refractive index, ρ the density at the same temperature, and K a constant. Eykman stated that the constant K is independent of temperature, and this fact was also observed in this work, the average deviation between the K values for any alcohol always being smaller than ±0.0004 unit. The values found for this constant at each temperature initialy increase faster than the number of carbon atoms (N) of the alcohol, and then more slowly than N increases. Figure 3 shows the representation of the K values vs. N, where it can be seen that the theoretical line joining the calculated points corresponds approximately to a logarithmic-type equation.

Glossary

a, b	parameters of eq 1
A, B	parameters of eq 2
K	constant of Eykman equation
N	number of carbon atoms
n_D	refractive index
t	temperature, °C
ρ	density, g cm^{-3}

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Adsorption of a Gaseous Mixture of Ethylene and Propylene on a Carbon Molecular Sieve

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The adsorption of a binary gaseous mixture of ethylene and propylene on the carbon molecular sieve MSC-5A was measured at temperatures of 1.7, 30, and 50 °C and at a pressure of 100 mmHg. The strong selectivity for propylene from mixtures was observed as in the case of the mixture of ethane and propane. The prediction calculation presented by Suwanayuen and Danner was applied to this system. The agreement between the experimental and calculated values was not satisfactory except for the total amount of adsorption.

The adsorption of a binary gaseous mixture on a microporous adsorbent often deviates from the predicted values that use the isotherms of pure components, as previously reported for the system of ethane–propane–carbon molecular sieve (MSC·5A) (*1*). In this paper, the adsorption equilibria for the system of ethylene–propylene–MSC·5A was measured at temperatures of 1.7, 30, and 50 °C at a pressure of 100 mmHg. The experimental results were compared with the predicted values from the Suwanayued–Danner method (*4*, *5*).

Experimental Section

The apparatus for the measurement of adsorption is quite similar to the one previously reported (*1*) except for the fact that the pressure was measured by an electric pressure gage (Baratron 221A-1000) with a digital and analoge millivoltmeter

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