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.

Literature Cited

(1) Riddick, J. A.; Bunger, W. B. "Organic Solvents", 3rd ed.; Wiley-Interscience: New York, 1970; *Tech. Chem.* (*N.Y.*), Vol. II, pp 203–12.
(2) Freeman, H. H.; Dubois, R. A. *Tetrahedron Lett.* **1975**, *38*, 3251.
(3) Erickson, J. L. E.; Ashton, W. H. *J. Am. Chem. Soc.* **1941**, *63*, 1769.
(4) Sellers, P. *Acta Chem. Scand.* **1971**, *25*, 2295.
(5) Kusano, K. *J. Chem. Eng. Data* **1978**, *23*, 141.
(6) Huggins, K. L. *J. Am. Chem. Soc.* **1941**, *63*, 115.
(7) Calingaert, G.; Beatty, H. A.; Kuder, R. C.; Thomson, G. W. *Ind. Eng. Chem.* **1941**, *33*, 103.

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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 7×10^{-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 g·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 $\pm 1 \times 10^{-5}$ g·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 ±0.01 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*, 1.41623.

The experimental densities may be expressed by the equation

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

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

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

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

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Table I. Physical Constants of Pure Compounds at 293.15 K

	ρ, g·cm^{-3}		n_D		
	exptl	lit.	exptl	ref *5*	ref *7*
1-hexanol	0.818 71	0.8185 (*6*), 0.8198 (*7*)	1.4178	1.4178	1.4181
2-hexanol	0.813 56	0.8159 (*5*), 0.8144 (*7*)	1.4146	1.4144	1.4147
2-M-1-P	0.821 67	0.8263 (*5*), 0.8242 (*7*)	1.4179	1.4182	1.4190
4-M-2-P	0.806 99	0.8075 (*5*), 0.8076 (*7*)	1.4116	1.4100	1.4112
3-M-3-P	0.827 96	0.8286 (*5*), 0.8281 (*7*)	1.4189	1.4186	1.4186
3-M-2-P	0.835 20	0.8307 (*5*), 0.8291 (*7*)	1.4207	1.4182	1.4197
2-M-2-P	0.818 54	0.8136 (*7*)	1.4100	1.4100	1.4113

Table II. Densities of Hexanol Isomers and Fitting Parameters of Eq 1

	ρ, g·cm^{-3}									
	25 °C									
compd	exptl	ref *8*	ref *7*	27 °C	29 °C	31 °C	33 °C	35 °C	A, g·cm^{-3}	$10^3(-B)$, °C^{-1}
1-hexanol	0.815 15	0.815 29	0.8162	0.813 69	0.812 25	0.810 83	0.809 41	0.807 97	0.833 33	0.88
2-M-1-P	0.817 99	0.817 92	0.8144	0.816 47	0.814 98	0.813 45	0.812 06	0.810 53	0.836 86	0.91
2-hexanol	0.809 61		0.8105	0.808 05	0.806 46	0.804 85	0.803 27	0.801 89	0.829 40	0.97
3-M-2-P	0.831 08	0.830 30	0.8248	0.829 41	0.827 73	0.826 07	0.824 42	0.822 69	0.852 39	1.01
4-M-2-P	0.802 98	0.802 72	0.8033	0.801 29	0.799 64	0.798 01	0.796 38	0.794 69	0.823 99	1.03
3-M-3-P	0.823 63	0.823 00	0.8238	0.821 84	0.819 99	0.818 32	0.816 50	0.814 77	0.846 17	1.08
2-M-2-P	0.814 79		0.8095	0.813 06	0.811 29	0.809 58	0.807 83	0.806 05	0.837 04	1.08

Table III. Refractive Indices of Hexanol Isomers and Fitting Parameters of Eq 2

	n_D								
	25 °C								
compd	exptl	ref 7	27 °C	29 °C	31 °C	33 °C	35 °C	a	$10^4(-b)$, °C
1-hexanol	1.4160	1.4161	1.4152	1.4144	1.4134	1.4127	1.4117	1.4268	4
2-M-1-P	1.4162	1.4172	1.4152	1.4144	1.4134	1.4126	1.4117	1.4273	4
2-hexanol	1.4130	1.4128	1.4121	1.4110	1.4102	1.4090	1.4082	1.4251	5
3-M-2-P	1.4190	1.4179	1.4182	1.4168	1.4160	1.4150	1.4144	1.4309	5
4-M-2-P	1.4094	1.4090	1.4084	1.4075	1.4066	1.4057	1.4047	1.4210	5
3-M-3-P	1.4166	1.4163	1.4157	1.4146	1.4135	1.4126	1.4116	1.4293	5
2-M-2-P	1.4077	1.4089	1.4067	1.4058	1.4048	1.4038	1.4030	1.4197	5

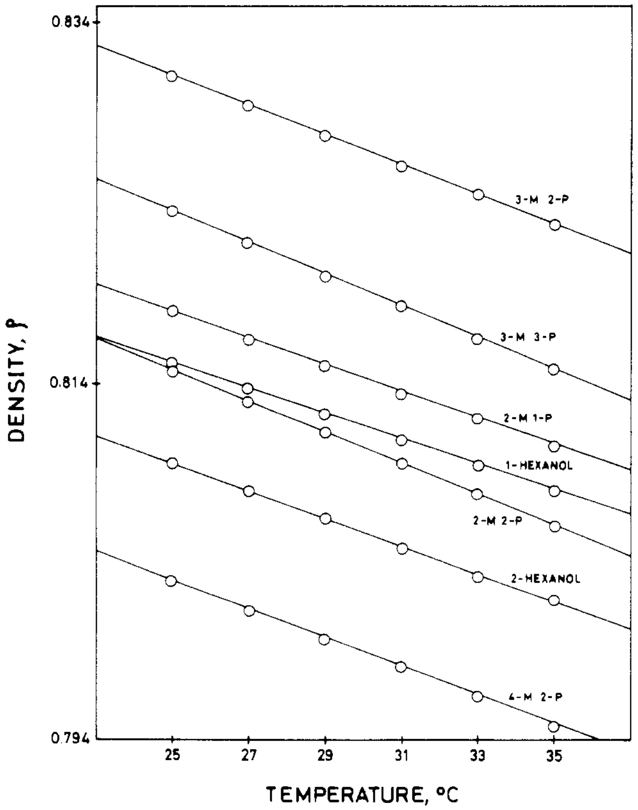

Figure 1. Densities of alcohols as a function of temperature.

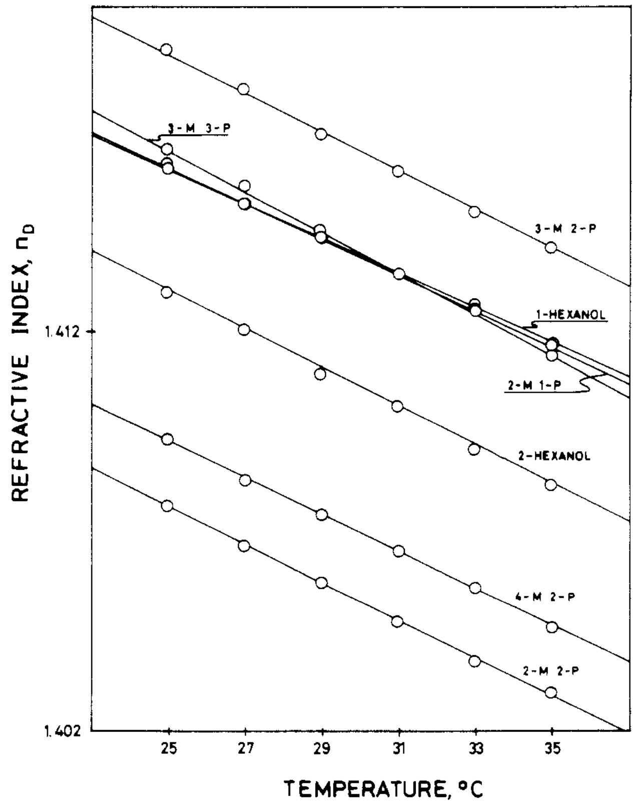

Figure 2. Refractive indices of alcohols as a function of temperature.

This coefficient shows a value of about -5×10^{-4} °C^{-1} for all isomers except for 2-M-1-P and 1-hexanol, whose slopes are nearly -4×10^{-4} °C^{-1} (*6*). Figure 2 and Table III show almost identical values for 1-hexanol and 2-M-1-P; likewise, the straight lines that represent these compounds along with the one for 3-M-3-P coincide at a point around 30 °C. Values of the parameters *a* and *b*, determined by the method of least squares,

Table IV. Average Expansivities of Hexanol Isomers between 25 and 35 °C

	$10^3\alpha$, °C^{-1}			
	$\bar{\alpha}_{\mathrm{exptl}}$	$\bar{\alpha}_{\mathrm{GD}}$	$\bar{\alpha}_{\mathrm{LL}}$	$\bar{\alpha}_{\mathrm{E}}$
1-hexanol	0.88	1.0	0.9	1.0
2-M-1-P	0.91	1.1	0.9	1.0
2-hexanol	0.97	1.2	1.0	1.1
3-M-2-P	1.01	1.1	1.0	1.1
4-M-2-P	1.03	1.1	1.0	1.1
3-M-3-P	1.08	1.2	1.1	1.2
2-M-2-P	1.08	1.2	1.0	1.1
δ		0.13	0.03	0.09

are given in Table III. To correlate both densities and refractive indices a HP-85 computer was used, the goodness of fit being 1.0 for the densities of all compounds and higher than 0.99 for the refractive indices.

The molar refractions of substances have been evaluated by several empirical formulas of which only the Lorentz–Lorenz (LL) relation has a sound theoretical basis. However, it has been shown that the Gladstone–Dale (GD) and Eykman (E) formulas are as successful as that of Lorentz–Lorenz in giving a temperature-independent molar refraction. If the molar refraction were strictly a function of temperature, then the differential form of Gladstone–Dale, Lorentz–Lorenz, and Eykman formulas would imply a direct relation between coefficient isobaric thermal expansion, α, and the temperature dependence of refractive index. These expressions would be (*10*)

$$\alpha_{\mathrm{GD}} = \frac{-1}{n-1}\left|\frac{dn}{dt}\right| \tag{3}$$

$$\alpha_{\mathrm{LL}} = \frac{-6n}{(n^2-1)(n^2+2)}\left|\frac{dn}{dt}\right| \tag{4}$$

$$\alpha_{\mathrm{E}} = \frac{-(n^2+0.8n+1)}{(n^2+1)(n+0.4)}\left|\frac{dn}{dt}\right| \tag{5}$$

Table IV shows the average expansivities of the alcohols directly obtained from densities between 25 and 35 °C along with those evaluated by means of eq 3–5. These values are in agreement with those found in the literature for 1-hexanol (0.89 (*6*), 0.89 (*7*), 0.87 (*11*)), 2-M-1-P (0.91 (*7*), 0.9 (*11*), 2-hexanol (0.99 (*7*)), 4-M-2-P (1.05 (*7*), 1.01 (*11*)), 3-M-3-P (1.08 (*7*)), and 2-M-2-P (1.05 (*7*)), the largest discrepancy appearing for 3-M-2-P with a difference of 4 × 10^{-5} °C^{-1}.

A survey of Table IV data shows that α_{GD}, α_{LL}, and α_{E} are higher than the experimental values; however, the discrepancy is greater for α_{GD} and α_{E} than α_{LL}.

The mean deviation, $\delta = \sum|\alpha_{\mathrm{calcd}} - \alpha_{\mathrm{exptl}}|/10^{-3}N$, is 0.13, 0.03, and 0.09 for the thermal expansivities calculated from eq 3–5, respectively. The errors of the values calculated through expression 4 oscillate around 2% except for 2-M-2-P, where the error is higher than 7%, which permits one to reproduce sufficiently the data of the isobaric thermal expansion coefficients of these pure substances.

Glossary

A, B	parameters of eq 1
a, b	parameters of eq 2
N	number of experimental points
n	refractive index
t	temperature, °C

Greek Letters

α	thermal expansivity, °C^{-1}
δ	mean deviation
ρ	density, g·cm^{-3}

Registry No. 2-M-1-P, 105-30-6; 3-M-2-P, 565-60-6; 4-M-2-P, 108-11-2; 3-M-3-P, 77-74-7; 2-M-2-P, 590-36-3; 1-hexanol, 111-27-3; 2-hexanol, 626-93-7.

Literature Cited

(1) Lorentz, H. A. *Wied. Ann.* **1880**, *9*, 641.
(2) Lorenz, L. *Wied. Ann.* **1880**, *11*, 70.
(3) Dale, D.; Gladstone, F. *Philos. Trans. R. Soc. London* **1958**, *148*, 887.
(4) Eykman, J. F. *Recl. Trav. Chim. Pays-Bas* **1895**, *14*, 185.
(5) Weast, R. C. "Handbook of Chemistry and Physics", 55th ed.; Chemical Rubber Publishing Co.: Boca Raton, FL, 1974.
(6) Ortega, J. *J. Chem. Eng. Data*, **1982**, *27*, 312.
(7) TRC Tables. "Selected Values of Properties of Chemical Compounds"; Thermodynamic Research Center Data Project: College Station, TX, 1983.
(8) Bravo, R.; Pintos, M.; Baluja, M. C.; Paz Andrade, M. I. *J. Chem. Thermodyn.* **1984**, *16*, 73.
(9) Kimura, F.; Benson, G. C. *J. Chem. Eng. Data* **1984**, *29*, 72.
(10) Rao, K. J.; Helphay, D. B.; Angell, C. A. *Phys. Chem. Glasses* **1973**, *14*, 26.
(11) Riddick, J. A.; Bunger, W. B. "Organic Solvents", 3rd ed.; Wiley-Interscience: New York, 1970; Vol. 2.

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Association of Acridine Orange in Nonaqueous Solutions

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The dimerization constants of acridine orange (AO) in various organic solvents have been measured spectrophotometrically at 20 °C. These constants are 2–3 orders of magnitude lower than in water. The peculiar role of water as a dye solvent has been stressed.

Introduction

The association process of metachromatic dyes in aqueous solution has been the subject of a wide literature (*1*, *2*, and references therein). On the other hand, to our knowledge, the behavior of these dyes in nonaqueous medium has never been particularly studied.

In the concentration range 10^{-5}–10^{-4} mol/L drastic spectral changes are observed in aqueous solution. These changes have been interpreted in terms of multiple association of dye ions that interact through the π-electron orbital system of the aromatic rings, stacking in a sandwichlike mode (*3–6*). Thermodynamic data of association are available in the literature for a variety of dyes (*2*).

On the contrary, in nonaqueous medium very limited changes are shown by the absorption spectra, in the same concentration range, and dye solutions essentially obey Beer's law.

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