relating tool, also in the presence of association.

However, the activity coefficients γ_A of acetic acid, calculated from the Wilson expression, show large deviation from the ones evaluated from the experimental data especially at the lowest values of x_A (when $x_A \rightarrow 1$ then $\gamma_A \rightarrow 1$ and deviations are less evident). This seems to indicate difficulties of the Wilson expression in correlating the activity coefficients of the associating substance, though the overall result of the least squares, σ, is acceptable. The second virial coefficients s_1 and s_1' of monomer of A and B, appearing in $(P_k^0)_c$, were calculated with the Wohl formula (*9*) assuming, for acetic acid, that the virial coefficient of the monomer can be estimated from physical properties of the acid (clearly a mixture of at least monomer and dimer). The equilibrium constant k_2 in eq 2 is the same used in ref *9*. In the calculation of s_1 and s_1' the critical values of the components are needed: the ones of acetic acid were taken from ref *15*, whereas for dioxolane they were estimated in a previous work (*16*).

Other forms of associations of the acetic acid in the vapor (such as trimer and tetramer) and A-B associates were not accounted for in this paper, following the conclusions of ref *9* and *10*.

Glossary

A, B	pure components
k_2	equilibrium constant for the acetic acid dimerization
L	latent heat of vaporization
P	pressure on the system, mmHg
s	second virial coefficient
t	temperature, °C
T	temperature, K
x, y	molar fractions in the liquid and vapor phases
y_1, y_1'	molar fractions of monomer of A and B in the vapor phase
$y_1(1)$, $y_1'(1)$	values of y_1 and y_1' at $y_A = 1$ and $y_B = 1$

Greek

α, β	constants in the Clausius-Clapeyron equation
ΔH	liquid-phase enthalpy of mixing
γ	activity coefficient
σ	root-mean-square deviation, mmHg

Registry No. Acetic acid, 64-19-7; 1,3-dioxolane, 646-06-0.

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Thermal Expansion Coefficients of the Mixture Benzene + 1-Heptanol

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The thermal expansion coefficients for the mixtures of benzene with 1-heptanol were determined from density measurements between 298.15 and 313.15 K. The data obtained are compared with those evaluated from equations derived by differentiation of the Gladstone-Dale, Lorentz-Lorenz, and Eykman relationships.

Introduction

The object of the present work is to determine the thermal expansivities of the binary mixtures of benzene with 1-heptanol at moderate temperatures and to verify the applicability to the binary mixtures of the empirical formulas reported in a previous paper (*1*) for some pure substances. This involved measuring the densities and refractive indices of the mixtures mentioned at the entire range of concentration and at temperatures of 298.15, 303.15, 308.15, and 313.15 K.

The results obtained experimentally for the thermal expansion coefficients of the pure compounds and mixtures thereof were then compared with those predicted from empirical equations taken from the Gladstone-Dale, Lorentz-Lorenz, and Eykman relationships. In order to facilitate data analysis, the experimental values of densities and refractive indices of this study were corrleated with the most suitable equations in each case.

Experimental Section

Both the benzene (puriss >99.5 mol %) and 1-heptanol (puriss >99.0 mol %) were from Fluka and were used without further purification.

The densities were measured with an Anton Paar DMA-55 digital vibrating tube densimeter with a reproducibility of ±0.000 01 g·cm.$^{-3}$ The temperature of the vibrating tube was controlled within ±0.01 K by using a thermistor previously calibrated according to the regulation IPTS-68. Before each series of measurements, the instrument was calibrated for each temperature with redistilled and deaerated water and benzene. The values of the densities of water at the different temperatures were derived from ref 2 and those corresponding to benzene (Table I) were confirmed by a precision pycnometer.

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Table I. Experimental Densities and Refractive Indices at Various Temperatures and Comparison with Literature Values at 298.15 K

	298.15	303.15	308.15	313.15
	benzene			
ρ, kg·m^{-3}	873.78, 873.70 (*2*)	868.40	863.04	857.64
n_D	1.4976, 1.49792 (*2*)	1.4943	1.4908	1.4875
	1-heptanol			
ρ, kg·m^{-3}	819.40, 819.5 (*3*)	815.81	812.34	808.66
n_D	1.4222, 1.4216 (*3*)	1.4203	1.4182	1.4161

Refractive indices were measured by a digital readout Abbe refractometer from A.O. with an accuracy of ±0.0001 unit. The working temperatures were observed with an accuracy of ±0.1 K, and the instrument was calibrated with redistilled water, using the values found for n_D in ref 2 at all the temperatures.

In order to maintain the prism of the refractometer and the the densimeter at constant temperature, a current of water was circulated through them which were thermostated by a Heto-Birdkerod ultrathermostat.

Results and Discussion

The densities (ρ) and refractive indices (n_D) of the pure compounds experimentally determined in this work are given in Table I along with values at 298.15 K from the literature, for comparison purposes. The physical properties of these materials did not differ significantly from those determined by us.

The experimental densities of the pure liquids were correlated by the equation

$$\rho = Ae^{Bt} \tag{1}$$

where t is the temperature in degrees Celsius. In both cases the fitting of experimental data gave a regression coefficient (r^2) equal to unity. It is known that the negative of the B parameter coincides with the isobaric thermal expansion coefficient $\alpha = -(\partial \ln \rho/\partial t)_p$. The values of the B parameter (average thermal expansion coefficient between 298.15 and 313.15 K) are 0.001 24 and 0.000 88 °C^{-1} for benzene and 1-heptanol, respectively, and are in good agreement with those found in the literature (0.001 22 (*4*); 0.000 86 (*3*)).

On the other hand, the refractive indices of the pure substances with regard to the temperature were fitted by using a linear relationship of the type

$$n_D = a + bt \tag{2}$$

where b is the temperature coefficient (dn_D/dt), presenting a value of -7×10^{-4} °C^{-1} for benzene (−0.000 64 (*2*)) and of -4×10^{-4} °C^{-1} for 1-heptanol (−0.0004 (*3*)). The coefficients of linear regression for the refractive index data were higher than 0.999. With the data of n_D obtained with the pure liquids along with the slopes of the function $n_D = \psi(t)$, the expansivities of benzene and 1-heptanol were estimated from the equation obtained by differentiation with regard to the temperature from the Gladstone–Dale, Lorentz–Lorenz, and Eykman formulas. These equations offer a direct relationship between the coefficient of isobaric thermal expansion, α, and the dependence of refractive indices. These relationships are the following

$$\alpha_{G-D} = \frac{-1}{n-1}\left(\frac{dn}{dt}\right) \tag{3}$$

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

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

The average values of α estimated between 298.15 and 313.15 K through these equations were $\bar{\alpha}_{G-D} = 0.001\,38$ °C^{-1}; $\bar{\alpha}_{L-L} = 0.001\,20$ °C^{-1}; $\bar{\alpha}_E = 0.00129$ °C^{-1} for benzene and $\bar{\alpha}_{G-D} = 0.000\,98$ °C^{-1}; $\bar{\alpha}_{L-L} = 0.000\,85$ °C^{-1}; $\bar{\alpha}_E = 0.000\,92$ °C^{-1} for 1-heptanol. It was observed that the values obtained by using eq 4—derived from the Lorentz–Lorenz eq—are in better agreement with those obtained from the densities and those found in the literature, already mentioned at the beginning of this section. The applicability of the same equations to the liquid binary mixture of benzene + 1-heptanol in the same range of temperatures will now be discussed.

Table II shows the experimental densities, refractive indices, and excess volumes of the mixtures benzene + 1-heptanol as a function of the composition of benzene between 298.15 and 313.15 K. The experimental densities and refractive indices were fitted at each temperature as a function of the molar fraction of benzene, using the equation

$$\rho = \sum_{i=0}^{i=3} c_i x^i \tag{6}$$

$$n_D = n_{D_1} x + n_{D_2}(1-x) + \sum_{i=0}^{i=3} d_i x_i \tag{7}$$

These correlations were excellent in all cases with a regresion parameter close to the unit.

The values of V_m^E given in Table II were fitted to an equation already used by the author in a previous paper (*5*), which in this case produced a better adjustment than others such as the Redlich–Kister equation

$$V_m^E = C[Z(1-Z)]^h \tag{8}$$

where Z is related to the molar fraction of the mixture through the expression

$$Z = \frac{x}{x + R(1-x)} \tag{9}$$

The parameters obtained for eq 8 at each temperature and the respective standard deviations are shown in Table III, together with the values obtained for the coefficients of eq 6 and 7. To complete the analysis of this work it was necessary to have values of densities and refractive indices of the mixture at 0.1 mole fractions of the benzene. The corresponding values of ρ and n_D were therefore determined from eq 6 and 7 at intervals of x equal to 0.1 from zero to one. This process was repeated at each temperature and independently for ρ and n_D.

The values of α can be obtained from densities as mentioned above or by addition of the contributions of the expansivities of each component of the mixture. In order to verify the data obtained, this second possibility will now be analyzed.

It is known that the isobaric thermal expansion coefficient of the mixture can be calculated from its molar volume V_m, whiich is given by where V_i is the molar volume of the pure

$$V_m = \sum x_i V_i + V_m^E \tag{10}$$

component i and V_m^E is the molar excess volume in the mixture. Differentiating in relation to the temperature and dividing by V_m gives

$$\frac{1}{V_m}\left(\frac{\partial V_m}{\partial T}\right)_{p,x} = \frac{1}{V_m}\sum x_i\left(\frac{\partial V_i}{\partial T}\right)_{p,x_i} + \frac{1}{V_m}\left(\frac{\partial V_m^E}{\partial T}\right)_{p,x} \tag{11}$$

which can be written in terms of the expansivities of the mixture as α, and of the pure components as α_i plus a last sum that can be considered as the excess thermal expansion of the mixture. However, it must be stated that this last sum is not exactly the corresponding excess property, α^E, but a term that indicates a deviation from an ideal behavior.

Once the values of $(\partial V_m^E/\partial T)_{p,x}$ were calculated at all the concentrations and in order to simplify the problem of comparing data, average values of α were evaluated for the small

Table II. Values of Densities, Refractive Indices, and Excess Volumes for the Mixture Benzene (1) + 1-Heptanol (2) at Various Temperatures

x_1	ρ, g·cm^{-3}	V^E, cm^3·mol^{-1}	n_D	x_1	ρ, g·cm^{-3}	V^E, cm^3·mol^{-1}	n_D
	298.15 K				308.15 K		
0.060 08	0.821 24	0.0450	1.4248	0.059 96	0.813 99	0.0544	1.4208
0.114 80	0.822 94	0.0940	1.4272	0.109 76	0.815 39	0.1042	1.4229
0.149 95	0.824 04	0.1304	1.4290	0.173 40	0.817 30	0.1607	1.4259
0.209 85	0.826 05	0.1819	1.4319	0.236 67	0.819 28	0.2160	1.4290
0.254 61	0.827 64	0.2165	1.4342	0.287 81	0.821 03	0.2546	1.4310
0.305 04	0.829 51	0.2542	1.4367	0.339 54	0.822 87	0.2912	1.4341
0.365 38	0.831 87	0.2965	1.4403	0.386 01	0.824 60	0.3228	1.4364
0.414 35	0.833 91	0.3259	1.4431	0.454 51	0.827 36	0.3575	1.4408
0.454 65	0.835 65	0.3507	1.4458	0.472 29	0.828 11	0.3655	1.4420
0.534 46	0.839 43	0.3798	1.4511	0.501 58	0.829 38	0.3776	1.4438
0.568 20	0.841 16	0.3857	1.4538	0.557 61	0.831 98	0.3903	1.4477
0.592 18	0.842 43	0.3890	1.4555	0.608 89	0.834 52	0.3965	1.4512
0.653 29	0.845 89	0.3858	1.4602	0.671 08	0.387 85	0.3936	1.4561
0.685 81	0.847 85	0.3799	1.4631	0.716 39	0.840 50	0.3796	1.4598
0.736 23	0.851 15	0.3546	1.4674	0.779 46	0.844 53	0.3438	1.4656
0.799 24	0.855 59	0.3148	1.4736	0.811 61	0.846 76	0.3169	1.4689
0.840 29	0.858 78	0.2735	1.4779	0.869 35	0.815 05	0.2585	1.4746
0.881 75	0.862 16	0.2307	1.4825	0.924 41	0.855 61	0.1797	1.4811
0.929 47	0.866 44	0.1609	1.4881	0.966 80	0.859 52	0.0977	1.4863
0.981 00	0.871 62	0.0559	1.4950				
					313.15 K		
	303.15 K			0.059 54	0.810 23	0.0554	1.4186
0.061 88	0.817 60	0.0533	1.4229	0.103 66	0.811 42	0.0997	1.4204
0.105 33	0.818 91	0.0902	1.4248	0.151 11	0.812 75	0.1463	1.4224
0.193 70	0.821 68	0.1702	1.4288	0.190 44	0.813 94	0.1766	1.4242
0.247 77	0.823 51	0.2130	1.4316	0.233 70	0.815 28	0.2118	1.4265
0.304 62	0.825 52	0.2582	1.4345	0.273 72	0.816 57	0.2429	1.4283
0.355 46	0.827 41	0.2969	1.4374	0.325 44	0.818 29	0.8246	1.4305
0.399 74	0.829 19	0.3207	1.4398	0.384 47	0.820 38	0.3268	1.4342
0.439 32	0.830 82	0.3446	1.4421	0.426 23	0.821 93	0.3555	1.4366
0.476 31	0.832 44	0.3606	1.4446	0.470 35	0.823 72	0.3726	1.4395
0.509 94	0.833 95	0.3765	1.4468	0.522 52	0.825 94	0.3911	1.4424
0.562 41	0.836 49	0.3889	1.4506	0.578 51	0.828 49	0.4042	1.4467
0.604 05	0.838 64	0.3928	1.4536	0.645 98	0.831 88	0.4019	1.4517
0.647 70	0.841 02	0.3925	1.4570	0.673 06	0.833 34	0.3962	1.4535
0.692 72	0.843 67	0.3811	1.4607	0.726 45	0.836 34	0.3841	1.4580
0.739 99	0.846 65	0.3609	1.4650	0.762 70	0.838 58	0.3622	1.4612
0.825 16	0.852 65	0.2950	1.4732	0.807 93	0.841 56	0.3270	1.4655
0.870 88	0.856 21	0.2475	1.4780	0.869 72	0.845 99	0.2648	1.4717
0.900 13	0.858 68	0.2063	1.4814	0.919 73	0.850 01	0.1908	1.4773
0.966 90	0.864 80	0.0950	1.4895	0.959 41	0.853 50	0.1174	1.4822

Table III. Parameters of Eq 6–8 and Standard Deviations for the Fit of V_m^e by Eq 8 at Various Temperatures

T, K	c_0	c_1	c_2	c_3	d_0	d_1	d_2	d_3	C	R	h	$\sigma(V_m^E)$
298.15	0.819 24	0.033 17	0.006 48	0.027 57	0.0002	0.0290	0.0013	0.0302	1.5990	1.650	1.02	0.0054
303.15	0.815 65	0.032 18	0.006 91	0.027 18	0.0002	0.0291	0.0008	0.0297	1.5701	1.660	1.00	0.0049
308.15	0.812 16	0.030 84	0.006 72	0.026 42	0.0001	0.0282	0.0031	0.0310	1.5045	1.664	0.96	0.0041
313.15	0.808 47	0.029 64	0.006 78	0.025 95	0.0002	0.0282	0.0007	0.0287	1.5575	1.676	0.97	0.0049

interval of temperatures considered in this work. The average values of density of the pure compounds (ρ_i) and those of the mixture (ρ), at each mole fraction, were considered. Thus eq 11 for a mixture can be written as

$$\alpha = \frac{\rho}{\sum(M_i x_i)} \left| \sum \frac{M_i}{\rho_i} x_i \alpha_i + \left(\frac{\partial V_m^E}{\partial T} \right)_{p,x} \right| \qquad (12)$$

α_i being, in the interval of temperature considered, the corresponding average expansivities of the pure compounds of the mixture, M_i the molar mass, and x_i the mole fraction of the i component. The values of α for the mixture calculated by eq 12 at every 0.1 unit of the molar fraction were contrasted with those obtained directly from the densities. The absolute concordance between both sets of values permitted us to use them in the following procedure.

Finally, the average values of α were calculated by using eq 3–5. These relationships give α values for each temperature if the corresponding values of n_D are substituted. Then from the sets of expansivity data can be determined an average value of α in the range of temperatures considered. So, a better comparison of the average values of α obtained can be carried out with those obtained from the densities or by using eq 12. The comparison appears graphically in the Figure 1

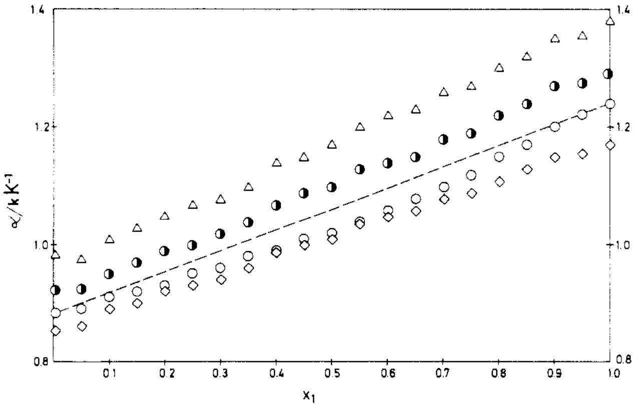

Figure 1. $\bar{\alpha}$ Values for the benzene (1) + 1-heptanol (2) mixture vs. the mole fraction of benzene: (○) average experimental values obtained from densities; (◑) average values estimated from eq 5; (▲) average values estimated from eq 3; (◇) average values estimated from eq 4.; (- - -) ideal solution.

where the thermal expansion coefficients vs. composition of benzene have been plotted. The distribution of the experimental α values gives a curvature due to the departure from the "ideal" behavior of the mixture, where $\alpha^{id} = x_1\alpha_1 + x_2\alpha_2$. However, the sets of α values estimated through eq 3-5 are distributed along a straight lines. Figure 1 also shows that eq 4, derived from Lorentz-Lorenz, presents the smallest deviation with the experimental values but only about the central zone of concentration, increasing for the extreme mole fractions, being greater when approaching the composition richest in benzene. On the other hand, eq 3, derived from Gladstone-Dale, offers greater differences with regard to the experimental values and its utilization is not recommended to estimate the α values and its utilization is not recommended to estimate the α values of this binary mixture. Equation 5, derived from Eykman, gives results whose mean error, with regard to the experimental values, is 6.4%, while the mean errors of eq 3 and 4 are 13.3% and 2.2%, respectively.

Registry No. Benzene, 71-43-2; 1-heptanol, 111-70-6.

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Excess Molar Volumes of Binary Mixtures of Butyl Formate with Normal Alcohols at 298.15 K

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Excess volumes at 298.15 K for binary mixtures of butyl formate with normal alcohols (C_1–C_{10}), determined from density measurements, are reported. The excess molar volumes were positive for *n*-alcohols with more carbon atoms than ethanol, sigmoidal for ethanol and negative for methanol. A suitable equation was used to fit the values of V_m^E.

Introduction

We have initiated an investigation to measure the thermodynamic properties of ester + alcohol binary mixtures. The present work reports the excess molar volumes of butyl formate + *n*-alcohols (from methanol to 1-decanol) at 298.15 K. As far as we know, there is no reference in the literature to previous experimental data of V_m^E for these mixtures and their behavior was found to be similar to that of other ester + alcohol systems. The excess molar volumes increase with the chain length of the alcohol except for methanol, the V_m^E values of which are negative, due to the arrangement of the small molecules of methanol with butyl formate. The values of V_m^E as a function of the molar fraction of the ester were fitted by applying a modified form of a smoothing equation already used by the author in previous papers (*1*, *2*).

Experimental Section

The butyl formate and all *n*-alcohols employed were supplied by Fluka. Their characteristics were as follows: methanol and ethanol (puriss >99.8 mol %), 1-propanol (puriss >99.5 mol %), 1-butanol (puriss >99.0 mol %), 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, and 1-decanol (puriss >99.0 mol %), 1-nonanol (purum >98.0 mol %). All these products were dried by using an Union Carbide Type 4A molecular sieve by Fluka, and the densities and refractive indices determined for the alcohols were in quite good agreement with those found in the literature (*3*-*5*). Two attempts to purify the butyl formate resulted in a degree of purity of about 98%, as determined by gas chromatography. Its physical properties differ slightly from those found in the literature (ρ = 887.64 kg·m^{-3}; 886.3, extrapolated from ref 3, and n_D = 1.3869, 1.3874 (*3*)).

The densities of the binary liquid mixtures were measured by an Anton Paar DMA-55 vibrating-tube densimeter with a reproducibility of ±0.01 kg·m^{-3}. The apparatus was calibrated at atmospheric pressure with redistilled and degasified water [ρ(298.15 K) = 997.04 kg·$^{-3}$] (*3*) and benzene [ρ(298. 15 K) = 873.68 kg·m^{-3}] whose density was confirmed 5 times by a precision pycnometer. The former is the average value from the five runs.

The measuring cell of the apparatus was thermostated with a Heto-Birkerod ultrathermostat with an accuracy of ±0.01 K. The imprecision in the determination of the mole fractions of the ester was estimated at $\pm 6 \times 10^{-5}$, and the mean error in the determinations of the excess molar volumes, V_m^E, was ±0.001 cm^3·mol^{-1}.

Results and Discussion

The values of V_m^E calculated from the densities of the pure liquids and their mixtures, are listed in Table I. A graphical comparison of the results for the 10 systems studied is given in Figure 1, where the excess molar volumes are plotted against the mole fraction of butyl formate.

In order to fit the experimental data of V_m^E as a function of the mole fraction, when they are distributed in a uniform manner and have the same sign, we have used the following equation in previous papers (*1*, *2*)

$$V_m^E = C[Z(1 - Z)]^b \tag{1}$$

where

$$Z = \frac{x}{x + R(1 - x)} \tag{2}$$

However, eq 1 cannot be used when the experimental points are distributed in a sigmoidal form. The form of eq 1 must

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