Thermochimica Acta, 131 (1988) 57–64
Elsevier Science Publishers B V , Amsterdam – Printed in The Netherlands

ISOBARIC EXPANSIVITIES OF THE BINARY MIXTURES $C_3H_7(OH) + C_nH_{2n+2}$ ($n = 11, 12$) BETWEEN 288.15 AND 318.15 K

J ORTEGA, J S MATOS and J A PEÑA

Cátedra de Termodinámica y Fisicoquímica de la Escuela Superior de Ingenieros Industriales de Las Palmas, Polytechnic University of Canarias, Canary Islands (Spain)

M I PAZ-ANDRADE, L PIAS and J FERNANDEZ

Departamento de Física Aplicada, Universidad de Santiago, Santiago de Compostela (Spain)

(Received 4 November 1987)

ABSTRACT

Densities and refractive indices of the binary mixtures of propan-1-ol with n-undecane and with n-dodecane at 288.15, 298.15, 308.15 and 318.15 K have been determined as a function of the concentration of the n-alkanol The results were employed in order to determine the mean thermal expansion coefficients, both of the pure compounds and of their mixtures by using, on the one hand, the basic expression $\alpha = -(\partial \ln \rho/\partial t)_p$ and, on the other, certain empirical expressions arising from the definitions of specific refraction given by Gladstone and Dale, Lorentz and Lorenz and Eykman The results obtained for α^E are also discussed

INTRODUCTION

Continuing in the same line as in earlier works (see refs list), the goal of the present investigation is the determination of the thermal expansion coefficients both of pure compounds and of their mixtures. The data reported in the literature normally give only values of α for pure compounds, representing the relative changes in density, calculated by means of $-(\Delta\rho/\rho)$ for each degree of temperature, and assuming that α remains constant in any thermal interval In previous works, empirical expressions were presented that allowed the value of α to be estimated with a certain degree of accuracy at each working temperature, when the refractive index n_D is known at that temperature and the slope of the function $n_D = \psi(t)$ The value of (dn_D/dt) usually remains constant for very wide intervals of temperature, ranging for the majority of organic liquids between -0.00035 and $-0.00055\,°C^{-1}$ The effectiveness of these equations has already been shown in refs 1 and 2 for a great variety of pure organic species, calculating values of α with errors below 7% in all cases relative to those obtained experimentally

There are several advantages in using this empirical route through n_{D} in order to calculate α, instead of resorting to the determination of densities The most important is, undoubtedly, the effect of temperature, a fundamental parameter in evaluating any thermal coefficient, since its influence on n_{D} is, for any one compound, smaller than that on ρ. On the other hand, and from an experimental point of view, n_{D} is generally simpler to determine than ρ It can be added that one of the factors that determine the refractive index is the packing degree of the molecules, this degree of arrangement bearing a major influence on the effects of the temperature on the normal refractive index.

Once the usefulness of these expressions was proven in pure organic compounds, their application was analysed in mixtures of organic liquids, this being one of the fields that have seen more developments in recent years

As in the case of pure substances, the thermal expansion coefficient of a mixture can be determined, at a certain concentration, by way of the function $\rho = \rho(t)$, since $\alpha = -(\partial \ln \rho)/\partial t)_{p,x}$ However, a greater contribution is made to the field of the properties of liquid mixtures if this calculation is made taking into account the addition of the partial contributions of the α_i of each component of the mixture To this end, the starting-point must be the basic expression that defines the molar volume of a mixture of i components, given by

$$V_{\mathrm{m}} = \sum x_i V_i^0 + V_{\mathrm{m}}^{\mathrm{E}} \qquad (1)$$

where V_i^0 and x_i correspond, respectively, to the molar volume and to the concentration of the pure compound i, and $V_{\mathrm{m}}^{\mathrm{E}}$ to the excess molar volume in the mixture Upon differentiating eqn. (1) with respect to the temperature and dividing by V_{m}, it is finally found that, at a certain composition x_i

$$\alpha = (1/V_{\mathrm{m}})\left[\sum x_i V_i^0 \alpha_i + \left(\partial V_{\mathrm{m}}^{\mathrm{E}}/\partial T\right)_{p,x_i}\right] \qquad (2)$$

α and α_i being, respectively, the expansivities of the mixtures and of the pure compounds it is composed of, at a certain temperature

The values calculated by means of eqn (2) can be compared with those obtained from the densities Another parameter, the interpretation of which is not always clear but which is important in the field of mixtures, is the coefficient of excess thermal expansion α^{E} However, the second term of the member to the right of eqn (2) $(1/V_{\mathrm{m}})(\partial V_{\mathrm{m}}^{\mathrm{E}}/\partial T)_{p,x}$ is not consistent with the usual definition of a function of excess in order to show deviation from ideal behaviour. In this case

$$\alpha^{\mathrm{E}} = \alpha - \sum \phi_i \alpha_i \qquad (3)$$

$$\phi_i = x_i V_i^0 / \sum x_i V_i^0 \qquad (4)$$

being the fraction in volume of the components of the mixture Had eqn. (2)

been used, the excess coefficient α^E would be given by $\alpha^E = \alpha - \Sigma\phi'_i/\alpha_i$, where $\phi'_i = x_i V_i^0/V_m$ no longer corresponds to the usual definition (eqn (4)) of the fraction in volume, although it verifies $\Sigma\phi'_i + \phi^E = 1$ where $\phi^E = V_m^E/V_m$. According to Ewing et al. [3] ϕ'_i is the appropriate amount for these calculations although, in concept, the values of α^E thus obtained do not correspond to eqn (3). In previous works carried out on binary mixtures [4,5] the values of α^E obtained by way of eqn (3) do not differ greatly from those calculated by using the volumetric fraction ϕ'_i proposed by Ewing et al. [3].

EXPERIMENTAL AND RESULTS

The products used in this work were of high purity and were supplied by Fluka, the characteristics indicated by the manufacturer were as follows: propan-1-ol, puriss. p.a. > 99.5 mol%; n-undecane and n-dodecane, purum > 99.0 mol%. All the products were used without prior purification, however, before use they were degassed using ultrasound equipment and dried with a molecular sieve (type A4, by Fluka).

The refractive indices n_D were determined with an Abbe-type refractometer by Bausch & Lomb, the accuracy of which was of ±0.0001 units of n_D. At the working temperature 288.15, 298.15, 308.15 and 318.15 K the refractometer was calibrated with redistilled water, using the values of n_D taken from ref. 6.

Densities were measured by an Anton Paar model 60/602 digital densimeter with an accuracy of $\pm 1.5 \times 10^{-3}$ kg m^{-3}. For the case in hand the calibration and measuring technique used in the densimeter proved to be fundamental. Thus, the calibration procedure followed was that recommended by the authors in a previous work [7], where redistilled water and n-nonane were employed in order to determine the constants of the apparatus, the purpose of applying the above-mentioned calibration procedure was to unify the results obtained. The densimeter and the refractometer were installed parallel to each other, both being thermostated using a Heto Birdkerod ultrathermostat which controlled the temperature automatically within ±0.01 K. The values of n_D and ρ for the pure compounds used in this work are presented in Table 1.

The mixtures, in the entire range of concentrations, were prepared by weighing in hermetically sealed vials to avoid evaporation, with a Mettler H51AR balance with an accuracy of $\pm 10^{-5}$ g. The molar fractions of the n-alkanol were calculated with an error smaller than $\pm 2 \times 10^{-5}$.

In order to determine the thermal expansion coefficients, either by way of the densities or through eqn (2), the excess molar volumes were calculated for these mixtures, this parameter being frequently used in the interpretation of the volumetric behaviour of liquid mixtures. The determinations of the

TABLE 1

Values of ρ and n_D for pure compounds at various temperatures

	Temperature (K)			
	288 15	298 15	308 15	318 15
$C_3H_7(OH)$				
ρ (kg m^{-3})	808 37	799 65	791 48	783 21
	807 49 [6]	799 75 [6]	791 62 [8]	783 28 [8]
	807 71 [8]	799 75 [8]	791 3 [9]	783 0 [9]
n_D	1 3869	1 3831	1 3791	1 3750
		1 3837 [6]	1 3793 [2]	1 3752 [2]
		1 3832 [9]	1 3791 [9]	1 3750 [9]
$C_{11}H_{24}$				
ρ (kg m^{-3})	744 78	736 27	728 76	721 31
		736 55 [2]	728 79 [2]	721 40 [2]
		736 25 [10]		
n_D	1 4190	1 4150	1 4105	1 4062
		1 4150 [11]	1 4196 [2]	1 4061 [2]
		1 41507 [10]		
$C_{12}H_{26}$				
ρ (kg m^{-3})	753 75	745 34	737 96	730 67
		745 16 [2]	738 02 [2]	730 78 [2]
		745 32 [10]		
n_D	1 4237	1 4196	1 4155	1 4111
		1 4195 [2]	1 4155 [2]	1 4110 [2]
		1 4199 [10]		

values of V_m^E for each temperature from the densities were considered to have a mean error of $\pm 4 \times 10^{-4}$ cm^3 mol^{-1}, and were calculated by using eqn (1) placed as a function of the densities in order to write

$$V_m^E = \left(\sum x_i M_i\right)/\rho - \sum \left(x_i M_i/\rho_i\right) \tag{5}$$

TABLE 2

Parameters of eqn (6) at each working temperature

System	T (K)	C	k	h	$s(V_m^E)$ [a]
$C_3H_7(OH)+C_{11}H_{24}$	288 15	1 054	0 906	0 70	0 0033
	298 15	1 233	0 852	0 70	0 0029
	308 15	1 413	0 810	0 70	0 0036
	318 15	1 671	0 784	0 70	0 0032
$C_3H_7(OH)+C_{12}H_{26}$	288 15	1 099	0 936	0 70	0 0035
	298 15	1 255	0 872	0 70	0 0031
	308 15	1 452	0 832	0 70	0 0026
	318 15	1 679	0 794	0 70	0 0031

[a] $s(V_m^E)$ is the standard deviation of the excess molar volume

where ρ, ρ_i, x_i and M_i are, respectively, the density of the mixture and the density, molar fraction and molecular mass of compound i The excess molar volumes V_m^E were correlated as a function of the molar fraction of the alkanol, by using the potential equation employed in ref (4), where

$$V_m^E = C\{kx(1-x)/[x+k(1-x)]^2\}^h \tag{6}$$

The parameters obtained for each mixture appear in Table 2, together with the standard deviations at each of the working temperatures

DISCUSSION

In order to obtain the values of α, either by way of the densities or from the empirical formulas presented in ref 1, the experimental values obtained directly for n_D and were correlated, respectively, to a straight line

$$n_D = a + bt \tag{7}$$

and to an exponential function

$$\rho = A\ e^{Bt} \tag{8}$$

where B, with its sign changed, is the mean thermal expansion coefficient for the substance considered In this work we have lowered the interval of working temperatures to 298 15 K For this reason, in order to calculate the mean expansivities of the pure products, the experimental values shown in Table 1 have been jointly correlated with those reported in a previous article [2] The results were for propan-1-ol, $\bar{\alpha} = 0\ 00105$, 0 00105 [2], for n-undecane, $\bar{\alpha} = 0\ 00105$, 0 00103 [2], for n-dodecane, $\bar{\alpha} = 0\ 00102$, 0 00100 [2] The application of the empirical formulae already employed in other works [1,2] afforded the following results for propan-1-ol $\bar{\alpha}_{GD} = 0\ 00105$, $\bar{\alpha}_{LL} = 0\ 00094$, $\bar{\alpha}_E = 0\ 00100$, for n-undecane $\bar{\alpha}_{GD} = 0\ 00105$, $\bar{\alpha}_{LL} = 0\ 00092$, $\bar{\alpha}_E = 0\ 00100$, for n-dodecane $\bar{\alpha}_{GD} = 0\ 00101$, $\bar{\alpha}_{LL} = 0\ 00089$, $\bar{\alpha}_E = 0\ 00095$

As pointed out in the introduction, the mean expansivities of the binary mixtures at a certain concentration can be determined in two ways (a) from the densities, if $\rho = \rho(t)$ is known and (b) by applying eqn (2) In (a) it is first necessary to obtain suitable relationships of $\rho = \rho(x)$ and then, at a fixed x, to calculate the value of $\bar{\alpha}$ by using eqn (8) In this work a third grade equation was used, the values of each 0 05 units of the molar fraction between $x = 0$ and $x = 1$ being estimated The results obtained are plotted in Figs 1 and 2 for the systems $\{xC_3H_7(OH) + (1-x)C_nH_{2n+2}\ (n = 11, 12)\}$

As indicated in case (b), in order to apply eqn (2) the value of the slope $(\partial V_m^E/\partial T)_{p,x}$ must be found Once the $V_m^E = V_m^E(x)$ functions are defined, the V_m^Es are estimated at each 0 05 units of the molar fraction of propan-1-ol between $x = 0$ and $x = 1$ Finally, the slope of the said function is obtained

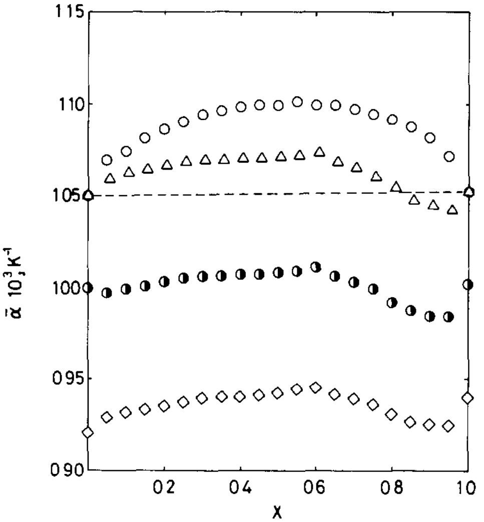

Fig 1 $\bar{\alpha}$-Values for $xC_3H_7(OH)+(1-x)C_{11}H_{24}$ (○) average values derived from densities, (△), α_{GD}, (○), $\bar{\alpha}_E$, (◇), $\bar{\alpha}_{LL}$

by using a linear equation of the type of eqn (7) The values of $\bar{\alpha}$ obtained by means of eqn (2) and those determined by way of the densities, as indicated in (a), present a great similarity, the maximum difference being

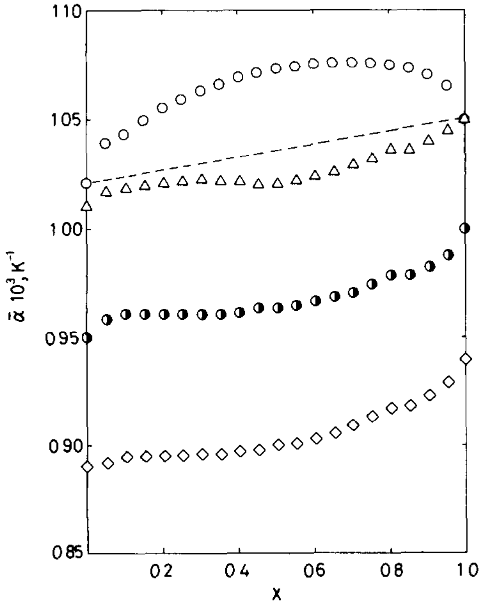

Fig 2 $\bar{\alpha}$-Values for $xC_3H_7(OH)+(1-x)C_{12}H_{26}$ (○) average values derived from densities, (△), $\bar{\alpha}_{GD}$, (○), $\bar{\alpha}_E$, (◇) α_{LL}

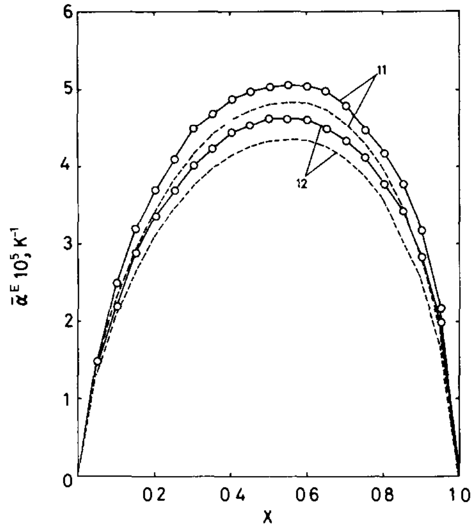

Fig 3 (o) Average excess expansivities, $\bar{\alpha}^E$ for $xC_3H_7(OH)+(1-x)C_nH_{2n+2}$ ($n=11, 12$) evaluated at every 0.05 units of x. The broken lines indicate the respective curves calculated by the Prigogine equation

found to be less than 0.5%. With a view to avoiding the systematic accumulation of errors in these calculations, the entire process was treated in a microcomputer, mean values finally being obtained for the excess expansivities, $\bar{\alpha}^E$, calculated every 0.05 units of the molar fraction of the n-alkanol. These amounts for both the systems studied are plotted in Fig. 3, the points obtained at each value of x having been joined by a solid line. These values have been determined using eqn (3), differences ranging between 5 and 10% being observed when the fraction in volume ϕ_i' defined by Ewing et al [3] is employed. The broken lines in Fig. 3 correspond to the determination of the values of $\bar{\alpha}^E$ by means of the Prigogine relationship [12]

$$\alpha^E = V^{-1}\left(\partial V_m^E/\partial T\right)_{p,x} - \alpha_0 V_m^E/V_0 \qquad (9)$$

where $\alpha_0 = \Sigma\phi_i\alpha_i$ and $V_0 = \Sigma V_i^0 x_i$. Equation (9) allows α^E to be determined at each temperature, however, for comparison purposes, it was decided to obtain mean values $\bar{\alpha}^E$ by also using average values of the other factors involved. The maximum difference existing between the values determined using eqn (9) and those obtained using eqn (3) is 10%, a percentage which almost totally corresponds to the values of the second term of the member to the right of eqn (9). This equation suggests the sign of $\bar{\alpha}^E$ better than eqn. (3), and its importance as a function of the $(\partial V_m^E/\partial T)_{p,x}$ slope, since the empty spaces increase (as do therefore the values of V_m^E), it being concluded that if $(\partial V_m^E/\partial T) > 0$, then $\alpha^E > 0$

For the reasons given in the introduction, we were also interested in comparing the results obtained for $\bar{\alpha}$ with those calculated by means of the empirical equations appearing in ref 1 A graphical comparison is presented in Figs 1 and 2 First, it is worthwhile to point out the significant deviation of $\bar{\alpha}_{\mathrm{exp}}$ with regard to the straight line $\bar{\alpha}_1 x + \bar{\alpha}_2(1 - x)$, both for the system propan-1-ol + n-undecane and for propan-1-ol + n-dodecane Initially, it seems logical that the only comparable results are those calculated by means of the equation obtained by differentiation from that of Gladstone and Dale because, ultimately, for each equation the data oscillate over the straight line joining the end points $\bar{\alpha}_1$ and $\bar{\alpha}_2$, and for this case practically coincide with those obtained experimentally, however, they differ considerably in the calculation of the values of $\bar{\alpha}^{\mathrm{E}}$ obtained by way of this equation, in as much as the $\bar{\alpha}^{\mathrm{E}}$ values are negative The mean errors of the values of $\bar{\alpha}$ calculated using the empirical equations, with regard to those obtained from the density correlations (or eqn (2)) are, respectively, for propan-1-ol + n-undecane and propan-1-ol + n-dodecane, 2 2 and 3 5% for $\bar{\alpha}_{\mathrm{GD}}$, 8 7 and 9% with $\bar{\alpha}_{\mathrm{E}}$, 13 8 and 15% with $\bar{\alpha}_{\mathrm{LL}}$

REFERENCES

1 J Ortega, Lat Am J Chem Eng Appl Chem , 14 (1984) 89
2 J Ortega and J S Matos, Mat Chem Phys , 15 (1986) 415
3 M B Ewing, K N Marsh and R H Stokes, J Chem Thermodyn , 4 (1972) 637
4 J Ortega, J Chem Eng Data, 30 (1985) 462
5 J Ortega and M I Paz-Andrade, J Chem Eng Data, 31 (1986) 231
6 J H Riddick and H B Bunger, Organic Solvents, 3rd edn , Wiley-Interscience, New York, 1970
7 J Ortega, J S Matos, M I Paz-Andrade and E Jimenez, J Chem Thermodyn , 17 (1985) 1127
8 R C Wilhoit and B J Zwolinski, J Phys Chem Ref Data, 1973, Vol II, Suppl 1
9 J Ortega, J Chem Eng Data, 27 (1982) 312
10 H S Nutting, Physical Properties of Chemical Compounds-II, Vol 22, American Chemical Society, Washington, DC, 1959
11 J Timmermans, Physico-Chemical Constants of Pure Organic Compounds, Vol 2, Elsevier, Amsterdam, 1965
12 I Prigogine, The Molecular Theory of Solutions, North-Holland, Amsterdam, 1957