

Thermodynamic properties of (an ester + an alkane). XVII. Experimental H_m^E and V_m^E values for (an alkyl propanoate + an alkane) at 318.15 K

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Abstract

In this article, we record the experimental values of H_m^E and V_m^E , obtained at a temperature of $T = 318.15$ K and atmospheric pressure for a set of 30 binary mixtures comprised of five alkyl propanoates (methyl to pentyl) with six odd alkanes (heptane to heptadecane). The net values obtained for these properties are the result of different effects of the selected compounds on the mixing process. These effects and the variation with temperature are studied. The H_m^E are positive in all cases and increase with the saturated hydrocarbon chain and diminish with the alkanolic portion of the ester. The variation in V_m^E is similar to that occurring in the H_m^E . For the data correlation, a new form of polynomial equation is used in which the variable is the so-called active fraction which, in turn, is a function of the concentration of the mixture, giving acceptable estimations for simultaneous correlations between the values of Gibbs function obtained in the isobaric (liquid + vapour) equilibria and the enthalpies of the mixture, for some of the mixtures studied. The results are explained with the molecular model proposed for (ester + alkane) mixtures. Finally, the application of two versions of the UNIFAC groups contribution method to estimate enthalpies of the mixtures does not give satisfactory results, although the modified UNIFAC gives somewhat better results.

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1. Introduction

This article is one more of the series belonging to a research project on the general behaviour of (ester + alkane) binary systems. Here, among other factors, variations in some properties of the mixture with temperature are analysed in order to interpret correctly the mixing process and to proceed to formulating the model. In previous works [1–7], mixing quantities enthalpies H_m^E and volumes V_m^E have been determined

at $T = 298.15$ K for binary systems of propanoates (methyl to pentyl) with several alkanes. Also, in the literature (vapour + liquid) equilibria (VLE) have been found for mixtures of (methyl propanoate + heptane) [8] and (propyl propanoate + heptane or nonane) [9]. In this line, in a previous work a similar study was carried out with systems containing different alkyl ethanoates [10]. For all (ester + alkane) mixtures studied to date the behaviour can be standardised, in that the mixing processes presents endothermic effects, where H_m^E is negatively correlated with the increasing number of ester carbons, for the acid part R_1 or the alkanolic part R_2 in R_1COOR_2 . Regarding the second component, the C_nH_{2n+2} hydrocarbon, the H_m^E increase with n .

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A similar change also occurs in V_m^E . In the previously mentioned work [10], it was established for binary mixtures with alkyl ethanoates that $(\partial H_m^E/\partial T)_{p,x} > 0$ and $(\partial V_m^E/\partial T)_{p,x} > 0$.

For this work, values of H_m^E and V_m^E have been experimentally determined for a set of 30 binary mixtures of alkyl propanoates (methyl to pentyl) with odd alkanes (heptane to heptadecane), measured at 318.15 K. It is important to establish the influence of temperature since this permits different structural aspects to be defined and the results obtained in other conditions to be corroborated as well as the hypothesis of the structural behavioural model already proposed [10]. In the empirical sphere, the data can be used to study the value of a new simple polynomial expression to correlate thermodynamic properties, which is expressed in relation to the so-called *active fraction* with temperature-dependent coefficients. With this expression [11], isobaric VLE and H_m^E data can be simultaneously correlated and in this work VLE data from the literature are used and other values determined experimentally for this work.

Finally, another aspect to take into consideration in this work is that measurements made at a temperature of 318.15 K can be used to verify the value of some group contribution models [12,13] at a different temperature than that used in most cases to obtain acceptable parameters for the (ester + alkane) interaction.

2. Experimental

Alkyl esters and alkanes used for this work were acquired from either Aldrich or Fluka, depending on the commercial purity of these products offered by each manufacturer. Before use, all compounds were degasified with ultrasound for several hours and then passed through a molecular sieve of 0.3 nm Fluka to eliminate any traces of moisture. Compounds were characterised by verifying the purity of each of them with a GC model HP9860 equipped with FID, giving similar values to those specified by the manufacturer. Also, the refractive indices n_D and densities ρ , of the pure compounds were

experimentally determined at a temperature of 318.15 K. Table 1 gives the values found for alkyl propanoates since the values measured for the hydrocarbons were almost the same as those presented in a previous work [10]. Since there are few data in the literature corresponding to the experimental values of alkyl propanoates at a temperature of 318.15 K, those shown for purposes of comparison in table 1 were mostly obtained by interpolation.

Direct measurements of enthalpies H_m^E and values of the excess molar volumes V_m^E obtained, the latter from density measurements, were made at a constant temperature of (318.15 ± 0.01) K using, respectively, a Calvet microcalorimeter, model MS80D, of Setaram and a digital densimeter of Anton Paar, model DMA60/602.

The calorimeter was also calibrated electrically at a temperature of 318.15 K and with a Joule effect, reproducing a similar thermogram to that of the mixing processes with an estimated error for enthalpies of $\pm 1 \cdot 10^{-1} \cdot H_m^E$, while that of the concentrations was $\pm 2 \cdot 10^{-4}$. The apparatus was checked by taking measurements at the same temperature of 318.15 K, of the binary mixture of (ethanol + nonane), and comparing these values with those recorded in the literature [16], giving differences lower than 1%.

The densimeter was calibrated as described in a previous work [10], using four substances of known density at a temperature of $T = (318.15 \pm 0.01)$ K, such as water, nonane, cyclohexane and 2,2,4-trimethylpentane, see [17]. Apparatus constants were obtained for each pair of substances and the average value of these gave final values for the set of four substances. For this work, the densities of the pure products and of the 30 binary mixtures were measured $\{\text{CH}_3\text{CH}_2\text{CO}_2\text{C}_v\text{H}_{2v+1} (v = 1 \text{ to } 5) + \text{C}_n\text{H}_{2n+2} (n = 7, 9, \dots, 17)\}$ at 318.15 K and the V_m^E values were calculated at a known concentration; the error in the calculations of molar fractions of the ester was $\pm 5 \cdot 10^{-5}$ and for V_m^E was $\pm 2 \cdot 10^{-9} \text{ m}^3 \cdot \text{mol}^{-1}$.

Finally, the method used to determine (vapour + liquid) equilibria, the accuracy of the data and a detailed description of the experimental apparatus have been clearly described in previous works by our group [8,9].

TABLE 1

Physical properties of pure substances measured at $T = 318.15$ K and atmospheric pressure, where ρ and n_D denote the density and refractive index, respectively

Compound	Supplier	Mass fraction	$\frac{\rho_{\text{expt}}}{\text{kg} \cdot \text{m}^{-3}}$	$\frac{\rho_{\text{lit.}}}{\text{kg} \cdot \text{m}^{-3}}$	$n_{D,\text{expt}}$	$n_{D,\text{lit.}}$
Methyl propanoate	Fluka	0.99	884.60	883.70 ^a	1.3641	
Ethyl propanoate	Fluka	0.99	860.98	860.53 ^a 860.94 ^b	1.3711	1.3712 ^b
Propyl propanoate	Fluka	0.98	854.57	856.48 ^a	1.3809	
Butyl propanoate	Aldrich	0.99	851.33	851.99 ^a	1.3895	
Pentyl propanoate	Aldrich	0.99	848.98	849.07 ^a		

^a Values obtained from Ref. [14] are interpolated.

^b Ref. [15].

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