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Thermodynamic study of (alkyl esters + α,ω-alkyl dihalides) I: H^E_m and V^E_m for 25 binary mixtures $\{xC_{u-1}H_{2u-1}CO_2C_2H_5 + (1-x)\alpha,\omega\text{-}ClCH_2(CH_2)_{v-2}CH_2Cl\}$, where $u = 1$ to 5, $\alpha = 1$ and $v = \omega = 2$ to 6

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Abstract

This article presents the experimental data of H^E_m and V^E_m, obtained at atmospheric pressure and at a temperature of 298.15 K, for a set of 25 binary mixtures composed of the first 5 ethyl alkanoates (methanoate to pentanoate) and five α,ω-dichloroalkanes (1,2-dichloroethane to 1,6-dichlorohexane). Quantitatively, and with only a few exceptions, small values are obtained for the excess properties and the results imply that specific interactions exist between both types of compounds, with exothermic process for most mixtures, but with the exception of some that contain ethyl methanoate and ethanoate. The change in enthalpies with increasing length of the dichloroalkane chain for the same ester is regular, and also the change in H^E_m with the acid portion of the ethyl ester. However, the change in excess volumes does not present such a regular variation. A behavioural structural model is established to explain the results of the excess properties. Experimental values of H^E_m and V^E_m were correlated, as a function of ester concentration, x with a new expression which uses the so-called active fraction as a variable and which, in turn, is a function of this concentration.

The application of two versions of the UNIFAC group contribution models produces no good estimations of H^E_m.

Keywords: Excess enthalpy; Excess volume; Ethyl esters; Dichloroalkane; UNIFAC

1. Introduction

This article is the first of a series of papers we intend to carry out on binary systems of aliphatic esters with alkyl dihalides. More specifically, we initially aim to compile sufficient information which permit us to study the behaviour of a set of binary mixtures that contain alkyl alkanoates and α,ω-dihaloalkanes (Cl, Br, I). The studies of these binary mixtures are of great theoretical interest owing to the probable existence of specific interactions between the molecules of the compounds involved, making it difficult to interpret the behaviour and application of theoretical models. Another objective is to study the so-called *proximity effect* between the halogen atoms in the α,ω-dihaloalkanes and its repercussion on excess thermodynamic quantities. As antecedents, our research team has published data in the literature on excess properties for binary mixtures of α,ω-dihaloalkanes + alkanes [1–3], and other authors have measured values for α,ω-dichloroalkanes + alkanes [4], or + alkanols [5], or + ketones [6,7]. Studies carried out in our laboratory with mixtures of ethyl esters with monochloroalkanes are also recorded in the literature [8,9]. However, for the systematization of these studies, experimental values are required and a preliminary analysis of primary systems,

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such as those corresponding to mixtures of α,ω-dihaloalkanes + alkanes [1–3], and esters + alkanes [10–12], requiring exhaustive work by our research team.

Therefore, the present work focuses on studies of binary mixtures of ethyl esters + α,ω-dichloroalkanes, providing data of H_m^E and V_m^E for a set of 25 binary mixtures, which will be used to complete contributions made in previous works and to verify the structural model proposed for other similar binary systems. Hence, the literature offers experimental data of H_m^E for some mixtures of alkyl esters + α,ω-dichloroalkanes [13,14], although there is no systematic study of a sufficient number of systems for their behaviour to be fully understood. In the cited papers, enthalpy data are explained on the basis of the CH_2Cl/COO interaction and the so-called *intramolecular proximity effect*. The behavioural change of the molecule of α,ω-dichloroalkane in solution was attributed to this effect because of the different proximity of the two Cl atoms [15–18]. For the present study, experimental data of H_m^E from a set of 12 mixtures, previously measured in our laboratory [19], will be used, showing here the measurements made for the other 13 systems. For this work, the V_m^Es were measured for the mixtures of the same set of 25 mixtures for which the actual literature does not give any values.

Finally, in this work on ester + dichloroalkane mixtures, we intend to verify the theoretical models considering two perspectives. On the one hand, to study the utility of an expression [11,12] for the treatment/correlation of experimental data which, in the longer time could be extended using other thermodynamic quantities for different conditions of temperature and pressure. On the other hand, we consider important to know in greater depth the nature of the inter/intramolecular interactions that affect the mixing process of these solutions, to be able to correctly apply these predictive models. Moreover, with the experimental data we can verify the validity of the UNIFAC group contribution model in two of its versions, that of Dang and Tassios [20], using the parameters obtained for the ester/chloride interaction by Ortega *et al.* [21] for mixtures of esters with monochloroalkanes, and that of Gmehling *et al.* [22].

2. Experimental

Both ethyl esters and dichloroalkanes used in this work presented the highest commercial purity provided by the manufacturers Fluka and Aldrich. Before use, all the products were exposed to a preliminary treatment, first being degasified in an ultrasound bath and then stored for several hours over a 0.3 nm molecular sieve from Fluka. The quality of all the pure compounds was verified by measuring several physical properties, such as the refractive index n_D and the density ρ, at the working temperature. The values obtained at a temperature of 298.15 K are compiled in table 1, where they

TABLE 1
Physical properties of pure substances measured at $T = 298.15$ and atmospheric pressure, where ρ and n_D denote the density and refractive index, respectively

Compound	Supplier	Mass fraction	$\rho/(kg \cdot m^{-3})$		n_D	
			Exp.	Lit.	Exp.	Lit.
$HCOOC_2H_5$	Aldrich	>0.970	914.17	915.30[a]	1.3580	1.3575[a]
				914.96[b]		1.3574[b]
$CH_3COOC_2H_5$	Fluka	>0.995	894.33	894.55[a]	1.3692	1.3698[a]
				894.24[c]		1.3700[c]
$CH_3(CH_2)COOC_2H_5$	Fluka	>0.990	884.02	884.00[a]	1.3815	1.3814[a]
				883.75[c]		1.3815[c]
$CH_3(CH_2)_2COOC_2H_5$	Fluka	>0.980	873.54	873.94[a]	1.3895	1.3900[c]
				873.56[c]		
$CH_3(CH_2)_3COOC_2H_5$	Aldrich	0.990	869.42	868.98[c]	1.3980	1.3980[c]
$ClCH_2CH_2Cl$	Fluka	>0.995	1245.65	1245.61[d]	1.4420	1.4422[e]
				1245.74[e]		
$ClCH_2(CH_2)CH_2Cl$	Aldrich	0.990	1178.34	1181.80[d]	1.4455	1.4460[d]
				1178.45[e]		1.4455[e]
$ClCH_2(CH_2)_2CH_2Cl$	Aldrich	0.990	1133.32	1135.30[d]	1.4520	1.4522[d]
				1133.06[e]		1.4524[e]
$ClCH_2(CH_2)_3CH_2Cl$	Aldrich	0.990	1095.27	1095.60[d]	1.4540	1.4541[d]
				1095.27[e]		1.4545[e]
$ClCH_2(CH_2)_4CH_2Cl$	Aldrich	0.980	1063.72	1064.48[f]	1.4555	1.4555[e]

[a] Ref. [23].
[b] Ref. [24].
[c] Ref. [25].
[d] Ref. [26].
[e] Ref. [2].
[f] Ref. [7].