

Experimentation and thermodynamic representations of binaries containing compounds of low boiling points: Pentane and alkyl methanoates



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ABSTRACT

This work presents experimental mixing properties, h^E and v^E , at several temperatures and the isobaric vapor–liquid equilibria (*iso-p* VLE) at 101.32 kPa for four binaries containing pentane and four alkyl (methyl to butyl) methanoates. Particular conditions are established to work with these solutions with highly volatile compounds, especially for the case of methyl methanoate + pentane system, for which a continuous feeding device is designed and constructed for measuring the densities. The mixing processes of the compounds chosen give rise to high values for the excess properties and also for the activity coefficients, since in addition to the known effects that arise in the binaries ester + alkane, in this case the associative effects caused by the HCOO– group, which diminish with increasing methanoate chain length are also relevant. The change in temperature produces slopes of opposite signs for the mixing properties, being $(\partial v^E/\partial T)_p < 0$ and $(\partial h^E/\partial T)_p > 0$. The systems comprised of methyl and ethyl methanoate with pentane present azeotropes with coordinates $(x_{az}, T_{az}/K)$ situated at (0.558, 293.9) and (0.218, 306.5), respectively. The estimation of these coordinates and the *iso-p* VLE by the UNIFAC method are acceptable but do not give good predictions of the h^E even less so for the LLE of the methyl methanoate + pentane system. For this binary, experimental data of all the properties are correlated with a mathematical procedure described using two models, one developed by us, and an extended form of the NRTL model. The latter does not represent the LLE data but shows the properties of isobaric equilibria, with acceptable results, while the proposed model, in addition to representing the binodal curve, gives a good representation of the v^E and of these properties derived from excess Gibbs function.

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1. Introduction

In previous works, the mixing thermodynamic properties (v^E and h^E) were presented at several temperatures and also the isobaric vapor–liquid equilibria (*iso-p* VLE) for systems containing alkyl methanoate with hexane [1] and decane [2]. Another previous study [3] showed the associative influence of the HCOO– group in systems containing alkyl methanoate + alkanes and the contribution of this effect in the structural model proposed and in the estimation of properties by one of the versions of the UNIFAC method [4]. In the literature, there are few studies on VLE measurements [5–7] for systems with methanoates and alkanes, although in the same line further investigations have been conducted on the specific behavior of ester + alkane systems [8–10]. This work presents measurements of *iso-p* VLE and of other mixing properties

for the first four alkyl (methyl to butyl) methanoates with pentane, $\text{HCOOC}_u\text{H}_{2u+1}$ ($u = 1-4$) + C_5H_{12} , with the purpose of studying several aspects of these. These solutions are of special interest because of their peculiar behavior, mentioned briefly above, but also because of the difficulties of experimenting with formic acid derived esters.

Hence, studies of solutions containing pentane have certain experimental difficulties due to its low boiling point ($T_b^o = 309.22 \text{ K}$ [11]), resulting in the corresponding limitations for use. Moreover, the presence of alkyl methanoates as a second component further hinders the formation of these solutions, especially methyl methanoate, ($T_b^o = 304.90 \text{ K}$ [11]), as the experimentation presents some complications that should be known a priori. Although the UNIFAC group contribution method [12] is used in this work to estimate the phase equilibria and enthalpies of binary solutions, exceptionally a previous estimation has been made to verify the behavior of the most peculiar case, such as the mixture of methyl methanoate + pentane. The result is shown in Fig. 1, where the presence of an azeotrope is observed at the minimum

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B_{ii}	second virial coefficients for pure component i
B_{ij}	cross second virial coefficients for mixture $i - j$
c_i	weighting coefficients for property I , Eq. (19)
GA	genetic algorithm
G_{ij}	parameters of NRTL model, Eq. (A2)
g^E	excess molar Gibbs function (J mol^{-1})
g_{ij}^E	coefficients of Eqs. (21) and (26)
\hat{g}_{LLE}^E	excess molar Gibbs function (J mol^{-1}), for LLE
\hat{g}_{ij}^E	particular coefficients of Eq. (17) for LLE
h^E	excess molar enthalpy (J mol^{-1})
h_{ij}	coefficients of Eq. (6)
IL	ionic liquid
k_v	parameter of Eq. (2)
k_h	parameter of Eqs. (7)–(9)
k_g	parameter of Eq. (24)
N	number of experimental points
OF	objective function
p	pressure (kPa)
p_i^o	vapor pressure of component i
q_k	surface parameter of molecule k
R	gas constant ($\text{kJ kmol}^{-1} \text{K}^{-1}$)
r_k	volume parameter of molecule k
$s(m)$	standard deviation of a property m
T	temperature (K)
UCST	upper critical solution temperature (K)
v^E	excess molar volume ($\text{m}^3 \text{mol}^{-1}$)
v_{ij}	coefficients of Eq. (1)
x_i	molar fraction in the liquid phase for component i
y_i	molar fraction in the vapor phase for component i
Y	expression given by Eq. (23)
z_i	active fraction of component i .

Greek letters

α	non-random parameter of NRTL model (Eq. (A2))
α_i	isobaric thermal expansion coefficient of component i (K^{-1})
ρ	density (kg m^{-3})
ϕ	fugacity coefficient
$\Delta g_{ij1}, \Delta g_{ij2}, \Delta g_{ij3}$	coefficients for NRTL model given by Eq. (A3)
γ_i	activity coefficient of component i
τ_{ij}	coefficients of NRTL equation.

temperature at intermediate compositions and $p = 101.32$ kPa, of $T_{az} = 294.3$ K (plane B), preventing the determination of mixing properties at this pressure over a wide range of compositions above the T_{az} . At the standard working temperature (298.15 K), the azeotropic pressure is estimated as 119 kPa, plane A. Although these predictions may not be very accurate, they can be used to establish special working conditions to measure the properties of the binary methyl methanoate + pentane. Hence, for this system values of v^E and h^E have only been obtained at $T = 291.15$ K and data of *iso-p* VLE, carrying out the experimentation in special working conditions. For the other three binaries alkyl (ethyl to butyl) methanoate + pentane, in addition to the *iso-p* VLE the v^E and h^E were determined at two temperatures 291.15 and 298.15 K. For this group the literature contains azeotropic data [13] for solutions with $u = 1, 2$ and studies of liquid–liquid equilibria (LLE) [14] for the binary with $u = 1$ at low pressure, whose curve is illustrated in Fig. 1, plane D.

Experimental data are correlated with a polynomial model on the excess Gibbs function of the form $g^E = g^E(p, T, x_i)$ [15,16]. A simultaneous correlation with different properties is carried out generating a multiobjective optimization procedure which

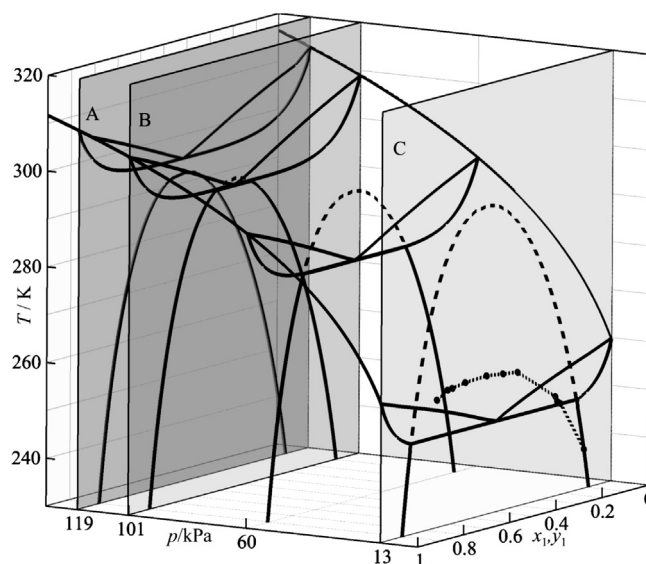


Fig. 1. Estimation by UNIFAC [12] of the curves of *iso-p* VLE (—) and *iso-p* LLE (---) for the binary methyl methanoate + pentane. (●) Experimental LLE points from Ref [14], at $p = 13$ kPa, plane C.

includes the residues of all of them. Hence, the procedure must be combined with another, more specific one, which also considers all the LLE data. The correlation procedure designed is also used to verify the capacity of a multiproperty fit for another model, NRTL [17], often used by chemical engineering researchers, which serves as a comparison. As mentioned, here we include the results obtained in the estimation of different properties of the systems containing methanoates using the UNIFAC group contribution model [12] that can be used to verify the predictive capacity of the method, when the set of parameters corresponding to the specific interaction $-\text{HCOO}/\text{CH}_2$ is used.

2. Experimental section

2.1. Materials

The products used were supplied by Sigma-Aldrich Co. and were all of the highest commercial purity. The quality of all the products was verified by a GC, model HP-6890N, with FID, giving slightly lower values of purity than those indicated by the manufacturer. Therefore, before use they were degasified with ultrasound and then stored over a 0.3 nm Fluka molecular sieve for several days to reduce the water contents. After this process, the purities were similar to, or higher than, those indicated by the manufacturer, see Table 1. However, the physical properties of all the compounds were also measured, such as the density ρ , and the refractive index n_D , both at $T = 298.15$ and 291.15 K; and the normal boiling point $T_{b,i}^o$. The values obtained for the four methanoates and pentane are shown in Table 2, where it can be appreciated that there are no significant differences between our values and those reported in the literature [1,11,18,19], less than 0.3% for all cases. The water used in the calibration apparatus was double-distilled and degasified in our laboratory.

2.2. Apparatus and procedures

The excess molar enthalpies h^E of the binaries were measured in a MS80D Calvet conduction calorimeter by Setaram, at temperatures of 291.15 and 298.15 K. The calorimetric system presents an excellent block thermal control accomplished only by heating. Hence, the workplace (with thermal, acoustic and electric

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