Study of thermophysical properties of (iodobenzene + alkane) mixtures: from experimentation to molecular interpretation

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1. Introduction

Aromatic halogenated compounds are used in the manufacturing of Li batteries (Jiang et al. [1]), in medicinal chemistry as antidepressant or drugs to reduce cholesterol (Wilcken et al. [2]; Poleto et al. [3]), and in the pharmaceutical industry due to the halogen bonding that they can form (Müller et al [4]). They are found in urban air arising from fuel combustion emissions (Calvert et al. [5]). Thus, it is interesting to study their thermophysical behavior and get a deeper view into their molecular interactions. (Iodobenzene + n-alkane) systems (heptane, decane, dodecane, tetradecane) were investigated in this work in terms of densities (ρ), speeds of sound (c) and excess molar enthalpies (H_m^E) at a pressure (p) of 0.1 MPa and the whole composition range (see Section 2). ρ and c were measured in the temperature (T) range (288.15 to 308.15) K, whereas H_m^E were determined at T = 298.15 K. Common excess properties and T derivatives were calculated, correlated, and discussed (see Section 3).

2. Materials and methods

Chemicals. Pure liquids were used without further purification. Information about their source and purity is displayed in Table 1.

Table 1. Chemical formula, CAS number, source, and purity (in mole fraction, provided by the supplier) of pure compounds.

Chemical name	Chemical Formula	CAS Number	Source	Purification method	Purity
iodobenzene	C_6H_5I	591-50-4	Sigma-Aldrich	none	0.999
heptane	C_7H_{16}	142-82-5	Fluka	none	0.998
decane	$C_{10}H_{22}$	124-18-5	Sigma-Aldrich	none	0.995
dodecane	$C_{12}H_{26}$	112-40-3	Sigma-Aldrich	none	0.998
tetradecane	$C_{14}H_{30}$	629-59-4	Fluka	none	0.995

Experimental equipment. The concentration of the liquid mixtures, given as a mole fraction of iodobenzene (x_1), was calculated from mass measurements. The masses were determined by weighing using an analytical balance (MSU125P, Sartorius) and correcting for buoyancy effects, with a standard uncertainty of $5 \cdot 10^{-5}$ g. Pt-100 resistances, calibrated using the triple point of water and the melting point of Ga, were used to measure the T of the samples, with a standard uncertainty of 0.01 K. A densimeter and sound analyzer (DSA 5000, Anton Paar) was employed to determine ρ (by the vibrant U-tube method) and c (using ultrasonic pulses at 3 MHz center frequency) of the liquid samples with a temperature stability of 0.001 K. H_m^E (see equations (3) and (7)) were obtained by means of a standard Tian-Calvet microcalorimeter with a temperature stability of 0.01 K, using a self-designed, stainless steel mixing cell, and correcting the results from evaporation effects. More details about the techniques and the calibration and test of the equipment can be found elsewhere (Hevia et al. [6], Sanz et al. [7]).

Uncertainty. The following expanded uncertainties U (with a coverage factor 2, approximately 95 % confidence level) associated with our measurements, were estimated from repeatability considerations, including the uncertainty associated to calibration constants and/or reference values where appropriate, but not the purity of the source liquids. For the measurements reported in this work: $U(T)$ = 0.02 K, $U(p)$ = 10 kPa, $U(x_1)$ = 0.00008, $U(c)$ = 0.8 m·s^{-1}; the maximum value of $U(\rho)$ encountered in this work is 0.00008 g·cm^{-3} for pure iodobenzene. The expanded uncertainty of excess functions calculated from the measured values of ρ and c, estimated from repeatability considerations or by comparison with reference values of test systems, are: $U(H_m^E) = 0.015 \cdot H_m^E$; $U(V_m^E) = 0.010 \, |V_m^E|_{max} + 0.005$ cm^3·mol^{-1}, where $|V_m^E|_{max}$ stands for the maximum value of $|V_m^E|$ in the entire composition range of the mixture under study; $U(\kappa_S^E) = 0.015 \cdot \kappa_S^E$.

Equations. If dispersion and absorption of the acoustic wave are negligible, the Newton-Laplace equation allows to determine the isentropic compressibility (κ_S) from experimental measurements of ρ and c:

$$\kappa_S = \frac{1}{\rho c^2} \tag{1}$$

The isothermal compressibility (κ_T) can be calculated through general thermodynamic relations involving κ_S, the molar isobaric heat capacity (C_{pm}), the molar volume (V_m) and the isobaric thermal expansion coefficient (α_p):

$$\kappa_T = \kappa_S + \frac{TV_{\mathrm{m}}\alpha_p^2}{C_{p\mathrm{m}}} \tag{2}$$

The values F^{id} of the thermodynamic properties of an ideal mixture at the same temperature and pressure as the real mixture are computed from the well-established formulae from Benson et al. [8]:

$$F^{\mathrm{id}} = x_1 F_1^* + x_2 F_2^* \qquad (F = V_{\mathrm{m}}, C_{p\mathrm{m}}, H_{\mathrm{m}}^{\mathrm{E}}) \tag{3}$$

$$F^{\mathrm{id}} = \phi_1 F_1^* + \phi_2 F_2^* \qquad (F = \alpha_p, \kappa_T) \tag{4}$$

where F_i^* is the value of the property F of pure component i, x_i represents the mole fraction of component i and $\phi_i = x_i V_{\mathrm{m},i}^* / V_{\mathrm{m}}^{\mathrm{id}}$ is the volume fraction of component i. Ideal values of κ_S and c are calculated using the equations (Benson et al. [8]):

$$\kappa_S^{\mathrm{id}} = \kappa_T^{\mathrm{id}} - \frac{TV_{\mathrm{m}}^{\mathrm{id}}\left(\alpha_p^{\mathrm{id}}\right)^2}{C_{p\mathrm{m}}^{\mathrm{id}}} \tag{5}$$

$$c^{\mathrm{id}} = \frac{1}{\left(\rho^{\mathrm{id}}\kappa_S^{\mathrm{id}}\right)^{1/2}} \tag{6}$$

being $\rho^{\mathrm{id}} = (x_1 M_{\mathrm{m},1}^* + x_2 M_{\mathrm{m},2}^*)/V_{\mathrm{m}}^{\mathrm{id}}$ and $M_{\mathrm{m},i}^*$ the molar mass of the i component.

Lastly, the excess quantities F^{E} are defined by:

$$F^{\mathrm{E}} = F - F^{\mathrm{id}} \tag{7}$$

Interactional effects in mixing are better evaluated by means of the excess molar internal energy at constant volume, $U_{\mathrm{m},V}^{\mathrm{E}}$ (Rowlinson et al. [9]):

$$U_{\mathrm{m},V}^{\mathrm{E}} = H_{\mathrm{m}}^{\mathrm{E}} - T\frac{\alpha_p}{\kappa_T}V_{\mathrm{m}}^{\mathrm{E}} \tag{8}$$

In equation (8), $T(\alpha_p/\kappa_T)V_{\mathrm{m}}^{\mathrm{E}}$ is called the equation-of-state term (EoS term) and is related to the volume variation during mixing.

3. Results and discussion

Experimental data on $V_{\mathrm{m}}^{\mathrm{E}}$, κ_S^{E} and $H_{\mathrm{m}}^{\mathrm{E}}$ of (iodobenzene + n-alkane) liquid mixtures were obtained at p = 0.1 MPa. $V_{\mathrm{m}}^{\mathrm{E}}$ and κ_S^{E} were measured at T = (288.15 to 308.15) K, while $H_{\mathrm{m}}^{\mathrm{E}}$ was measured at T = 298.15 K. These excess quantities are fitted to Redlich-Kister polynomials (Redlich et al. [10]):

$$F^{\mathrm{E}} = x_1(1 - x_1)\sum_{i=0}^{k-1} A_i(T)(2x_1 - 1)^i \qquad \left(F^{\mathrm{E}} = V_{\mathrm{m}}^{\mathrm{E}}, \kappa_S^{\mathrm{E}}, H_{\mathrm{m}}^{\mathrm{E}}\right) \tag{9}$$

First, $A_i(T)$ for each property and T were obtained by unweighted linear least-squares regressions to equation (9), taking an appropriate number (k) of $A_i(T)$ coefficients with guidance from F-tests of additional term (Bevington et al. [11]). For $F^{\mathrm{E}} \neq H_{\mathrm{m}}^{\mathrm{E}}$, the T dependence of $A_i(T)$ was assumed of the form:

$$A_i(T) = \sum_{j=0}^{m-1} A_{ij}\left(\frac{T}{\mathrm{K}}\right)^j \tag{10}$$

To ensure the consistency of the A_{ij} parameters, they were obtained from $A_i(T)$ values already determined. These were fitted by unweighted linear least squares regressions to equation (10), where the number (m) of necessary coefficients was chosen so that the T dependence of F^{E} was correctly represented. For each system, the total number of A_{ij} parameters necessary is between 2 and 4 for $V_{\mathrm{m}}^{\mathrm{E}}$ and between 6 and 8 for κ_S^{E}. From the mentioned correlations, other properties can be computed using their definitions and equations (1-6). $(\partial V_{\mathrm{m}}^{\mathrm{E}}/\partial T)_p$ has been computed by direct derivation of the correlation for $V_{\mathrm{m}}^{\mathrm{E}}$. κ_T cannot be evaluated exactly for the mixtures because of the lack of $C_{p\mathrm{m}}^{\mathrm{E}}$ data, so $U_{\mathrm{m},V}^{\mathrm{E}}$ has been evaluated assuming ideal values of $C_{p\mathrm{m}}$.

Experimental values of $V_{\mathrm{m}}^{\mathrm{E}}$, κ_S^{E} and $H_{\mathrm{m}}^{\mathrm{E}}$ of (iodobenzene + n-alkane) liquid mixtures at p = 0.1 MPa and T = 298.15 K are depicted in Figures 1, 3 and 4, together with their corresponding Redlich-Kister regressions. Smoothed values of $(\partial V_{\mathrm{m}}^{\mathrm{E}}/\partial T)_p$ and $U_{\mathrm{m},V}^{\mathrm{E}}$ are plotted in Figures 2 and 5.
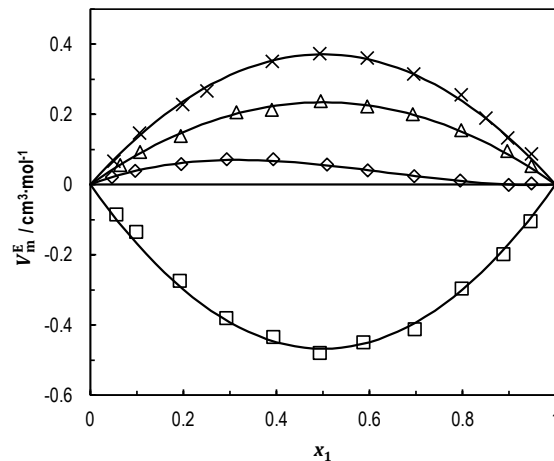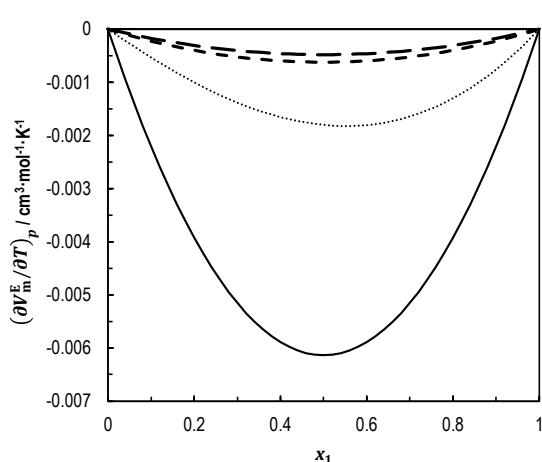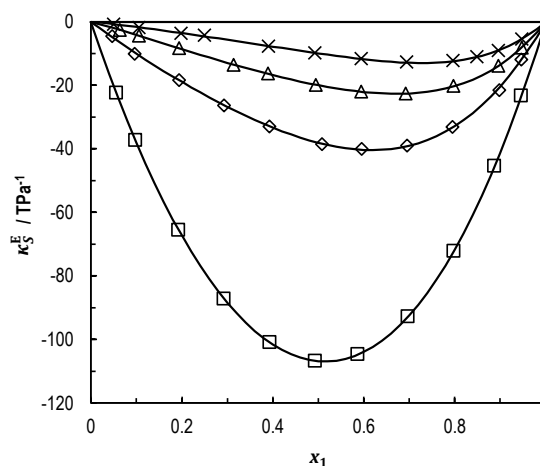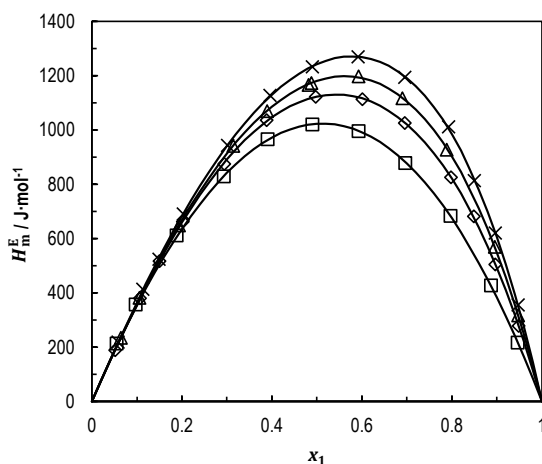

Fig.1. Excess molar volume, $V_{\mathrm{m}}^{\mathrm{E}}$, of (iodobenzene + n-alkane) liquid mixtures as a function of the iodobenzene mole fraction, x_1, at 298.15 K and 0.1 MPa: ($\square$) heptane, ($\diamond$) decane, ($\triangle$) dodecane, ($\times$) tetradecane. Solid lines are calculated with equations (9-10).
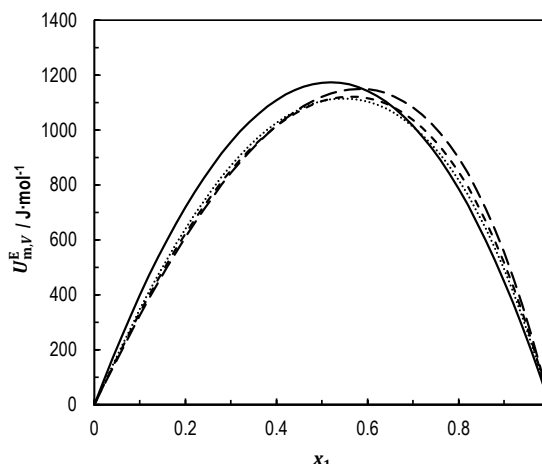
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Fig. 2. Smoothed curves of the temperature derivative of excess molar volumes, $(\partial V_{\mathrm{m}}^{\mathrm{E}}/\partial T)_p$, of (iodobenzene + n-alkane) liquid mixtures as a function of the iodobenzene mole fraction, x_1, at 298.15 K and 0.1 MPa: (solid line) heptane, (dotted line) decane, (short-dashed line) dodecane, (long-dashed line) tetradecane.

Fig. 3. Excess isentropic compressibility, κ_S^{E}, of (iodobenzene + n-alkane) liquid mixtures as a function of the iodobenzene mole fraction, x_1, at 298.15 K and 0.1 MPa: ($\square$) heptane, ($\lozenge$) decane, ($\triangle$) dodecane, ($\times$) tetradecane. Solid lines are calculated with equations (9-10).

Fig. 4. Excess molar enthalpy, $H_{\mathrm{m}}^{\mathrm{E}}$, of (iodobenzene + n-alkane) liquid mixtures as a function of the iodobenzene mole fraction, x_1, at 298.15 K and 0.1 MPa: ($\square$) heptane, ($\lozenge$) decane, ($\triangle$) dodecane, ($\times$) tetradecane. Solid lines are calculated with equations (9-10).

Fig. 5. Smoothed curves of the excess molar internal energy at constant volume, $U_{\mathrm{m},V}^{\mathrm{E}}$, of (iodobenzene + n-alkane) liquid mixtures as a function of the iodobenzene mole fraction, x_1, at 298.15 K and 0.1 MPa: (solid line) heptane, (dotted line) decane, (short-dashed line) dodecane, (long-dashed line) tetradecane.

Hereinafter, we will refer to values of the thermodynamic properties at 298.15 K and equimolar composition. We will denote by n the number of carbon atoms of the n-alkane.

$H_{\mathrm{m}}^{\mathrm{E}}$ values of (iodobenzene + n-alkane) liquid mixtures are large and positive, which can be ascribed to the rupture of interactions between molecules of the same species, especially iodobenzene-iodobenzene interactions, in the mixing process. A similar interpretation can be given to the negative κ_S^{E} values observed in the solutions. However, $V_{\mathrm{m}}^{\mathrm{E}}$ values, are either positive, but not very large, or negative. This kind of behavior of $H_{\mathrm{m}}^{\mathrm{E}}$ and $V_{\mathrm{m}}^{\mathrm{E}}$ indicates the presence of structural effects, such as those related to molecular size and shape and interstitial accommodation. In fact, structural effects are very important in these mixtures. Negative $(\partial V_{\mathrm{m}}^{\mathrm{E}}/\partial T)_p$, such as those encountered in this case, are also typical of systems where strong structural effects are present.

Both $V_{\mathrm{m}}^{\mathrm{E}}$ and $(\partial V_{\mathrm{m}}^{\mathrm{E}}/\partial T)_p$ increase when n increases, suggesting that the positive contribution to $V_{\mathrm{m}}^{\mathrm{E}}$ from the breaking of iodobenzene-iodobenzene interactions by the n-alkane (which is expected to be high given the large and positive $U_{\mathrm{m},V}^{\mathrm{E}}$ values of these mixtures) gains importance against the negative contribution from structural effects as the length of the n-alkane increases. Accordingly, as n increases, the EOS term in $H_{\mathrm{m}}^{\mathrm{E}}$ increases, being negative for the heptane mixture (–149 J·mol⁻¹) and becoming positive for decane (18 J·mol⁻¹), dodecane (77 J·mol⁻¹) and tetradecane (122 J·mol⁻¹). The large difference between $\alpha_p^*/10^{-3}$ K⁻¹ values of iodobenzene (0.8372) and shorter n-alkanes, like heptane (1.248) or decane (1.040), suggests that the mentioned structural effects are, at least in part, due to free volume effects. Similar features are observed on (chlorobenzene + n-alkane) and (bromobenzene + n-alkane) mixtures (González et al. [12]), (González et al. [13]).

To analyze the interactional effects isolated from volume variation effects, we note that $U_{\mathrm{m},V}^{\mathrm{E}}$ values of (iodobenzene + n-alkane) mixtures are large and positive, revealing a dominant contribution from the rupture of interactions between molecules of the same component along mixing. An interesting feature of the systems under study is the presence of a minimum of $U_{\mathrm{m},V}^{\mathrm{E}}(n)$, that is, of $U_{\mathrm{m},V}^{\mathrm{E}}$ as a function of n (Figure 6). This behavior seems to have the same origin as that of (chlorobenzene + n-alkane) and (bromobenzene + n-alkane) mixtures, for which $U_{\mathrm{m},V}^{\mathrm{E}}(n)$ is a decreasing function (González et al. [13]). In fact, the analysis of excess molar isochoric heat capacities of the later systems reveals two effects: (i) larger n-alkanes break a lower number of interactions between molecules of the halogenated benzene, which implies a less positive contribution to $U_{\mathrm{m},V}^{\mathrm{E}}$; and (ii) the halogenated compound breaks the short-range orientational order existing in longer n-alkanes, with a more positive contribution to $U_{\mathrm{m},V}^{\mathrm{E}}$. The higher relevance of one effect or the other for different n values may explain the trend of $U_{\mathrm{m},V}^{\mathrm{E}}(n)$ for the three homologous (halogenated benzene + n-alkane) series just considered.
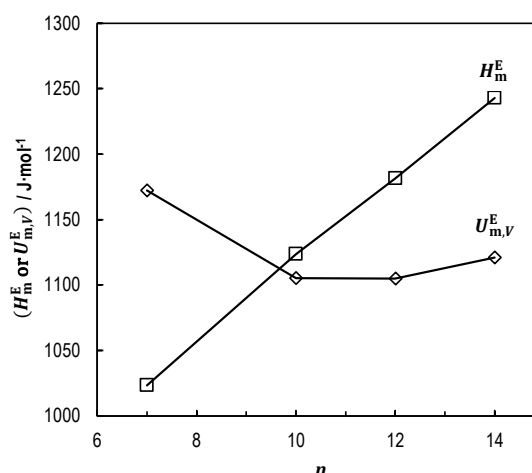

Fig.6. Excess molar enthalpy, $H_{\mathrm{m}}^{\mathrm{E}}$ ($\square$), and excess molar internal energy at constant volume, $U_{\mathrm{m},V}^{\mathrm{E}}$ ($\diamond$), of (iodobenzene + n-alkane) liquid mixtures as a function of the number of carbon atoms of the n-alkane, n, at equimolar composition, 298.15 K and 0.1 MPa.

4. Conclusions

Mixtures containing iodobenzene and n-alkanes have been investigated in terms of thermodynamic properties from new experimental data obtained in this work. $H_{\mathrm{m}}^{\mathrm{E}}$ and $U_{\mathrm{m},V}^{\mathrm{E}}$ are large and positive, pointing out to the predominance of the rupture of interactions of like molecules for this property. The mixtures are characterized by strong structural effects, as indicated by positive $H_{\mathrm{m}}^{\mathrm{E}}$ and $U_{\mathrm{m},V}^{\mathrm{E}}$ together with negative or small and positive $V_{\mathrm{m}}^{\mathrm{E}}$, and by negative $(\partial V_{\mathrm{m}}^{\mathrm{E}}/\partial T)_{p}$. $U_{\mathrm{m},V}^{\mathrm{E}}$ decreases with increasing n and then increases again, a trend that has been also observed in (chlorobenzene + n-alkane) and (bromobenzene + n-alkane) mixtures. It is proposed that this behavior is the result of a more positive contribution to $U_{\mathrm{m},V}^{\mathrm{E}}$ due to the breaking of the short-range orientational order existing in longer n-alkanes by the halogenated compound.

5. Acknowledgements

6. References

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