

CORRELATION OF SOLUBILITIES OF VANILLINS IN DENSE CO₂, R23, R134a AND R236fa USING DIFFERENT EMPIRICAL DENSITY BASED MODELS

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The experimentally determined solubilities of vanillin, ethylvanillin, *o*-vanillin and *o*-ethylvanillin in compressed CO₂, R23, R134a and R236fa were correlated by four different empirical density based models. The solubility measurements were performed at temperatures 40°C and 60°C and over a pressure range between 1 and 25 MPa using a static-analytic method. The models, which differ in their linear expression between solubility and solvent's density, are named by their author as: Chrastil's model, Bartle's model, Kumar & Johnoston's model and Mendez Santiago & Teja's model.

The results showed that by using three temperature-independent parameters these models can be applied for satisfactory solubility predictions at different pressures and temperatures not only for CO₂ as solvent, but also for applied fluorinated hydrocarbons. An extensive comparison among the four models in terms of overall average absolute relative deviation (AARD%), regarding the type of model, type of solvent, chemical structure of solute..., was performed.

INTRODUCTION

Experimental determination of a solid's solubility in dense gasses and its correlation is necessary for the development of high pressure technologies using sub- or supercritical fluids. Models based on equations of state are rather complicated and require knowledge of data, which are sometimes difficult to obtain. Solubility of a substance in a dense gas can also be correlated by the density of solvent. Empirical equations contain three or more parameters that are obtained from a simple error minimization method of the objective function (deviation of calculated solubility data from experimental values). This kind of approach is rather simple, and relatively good agreements between correlated and experimentally determined data have been obtained in previous studies [1].

Furthermore, CO₂ is the most widely used solvent in experimental setups for solubility determinations, due to its wide usage in high pressure technologies. Thus, the correlation of solid's solubility in CO₂ has been widely covered by different equation of state and density based models. Solubility equilibrium data for binary systems of solids and refrigerants are very scarce and for being able to design a high pressure process using other viable solvents, it was necessary to experimentally determine such data. Application of alternative solvents, such as fluorinated hydrocarbons, in modelling solubility data with density based models is described in this work.

Equilibrium solubilities of vanillins in compressed CO₂ and fluorinated hydrocarbons were determined at temperatures 40°C and 60°C and over a pressure range between 1.1 and 26.0 MPa with a static-analytic method. Results showed that phase equilibria of vanillins in investigated compressed gasses are influenced by the type of alchoxy group (methoxy or ethoxy) and the position of OH group (ortho or para), bound to the aromatic ring of solute, as well as the molecular structure of the gas. Solubilities of *o*- vanillins in R23 and R236fa were higher in comparison with *p*- vanillins, whereas, in the case of R134a, the solubilities were influenced by the alchoxy group bound on aromatic ring: vanillin and *o*-vanillin with methoxy group

are more soluble than vanillins with ethoxy group (ethylvanillin and *o*-ethylvanillin). The highest solubility of all four vanillins was observed in R236fa [2, 3].

MATERIALS AND METHODS

Vanillin (99%, Cat.No. V110-4), *o*-vanillin (99%, Cat.No. 12,080-4), ethylvanillin (99%, Cat.No. 12,809-0) and *o*-ethylvanillin (97%, Cat.No. 16,098-9) were obtained from Aldrich (Seelze, D). Trifluoromethane (R23, 2.8), 1,1,1,2-tetrafluoroethane (R134a, 2.0) and 1,1,1,3,3,3-hexafluoropropane (R236fa, 2.0) were obtained from Linde (Linde plin d.o.o., Celje, SI).

The experimental determination of solubilities is described in our previously published works [2, 3].

Chrastil's model is given by equation [4]:

$$\ln c = a_0 + a_1 \cdot \ln \rho + \frac{a_2}{T}, \quad (1)$$

where: c is the solubility of substance in dense gas (g/L), ρ density of the solvent (kg/m³), and a_0 , a_1 in a_2 parameters, which are calculated by fitting the correlated and experimental solubility data. Parameter a_1 is used for describing the heat of solvation. Total reaction heat, $\Delta_{\text{total}}H$ (heat of solvation, $\Delta_{\text{sol}}H$, plus heat of vaporization, $\Delta_{\text{vap}}H$) is equal:

$$\Delta_{\text{total}}H = -a_2 \cdot R \quad (2)$$

where R is the ideal gas constant.

Kumar and Johnston's model suggests a linear expression between $\ln y_2$ and solvent density, which is given by equation [5]:

$$\ln y_2 = b_0 + b_1 \cdot \rho + \frac{b_2}{T} \quad (3)$$

Similarly as a_2 , coefficient b_2 is related to total reaction heat:

$$\Delta_{\text{total}}H = -b_2 \cdot R \quad (4)$$

Bartle and others [6] suggested an empirical model, which describes the relationship between the solubility enhancement factor and solvent density. They introduced a reference pressure of 1 bar and reference density $\rho_{\text{ref}} = 700 \text{ kg/m}^3$. Bartle's model is given by equation:

$$\ln \frac{c \cdot p}{p_{\text{ref}}} = c_0 + c_1 \cdot (\rho - \rho_{\text{ref}}) + \frac{c_2}{T}, \quad (5)$$

where c (g/L) is the solubility of substance in dense gas. The coefficient c_2 is used for estimation of heat of vaporation of the solute:

$$\Delta_{\text{vap}}H = -c_2 \cdot R \quad (6)$$

Mendez-Santiago and Teja established an empirical model [7] as:

$$T \cdot \ln(y_2 \cdot p) = d_0 + d_1 \cdot \rho + d_2 \cdot T \quad (7)$$

RESULTS

The applied models assume that the solubility of a substance in a dense gas is a linear function of density, which is presented in Figure 1 for each investigated system. The plotted data are experimental solubility values, which are given in our previous works [2, 3].

Figure 2. represents the AARD values of experimental and correlated solubility values for each investigated system using different models. Total reaction heat, heat of vaporization as well as heat of solvation was calculated based on equations (2), (4) and (6) for each system. The results are given in Table 1. Average value of $\Delta_{\text{sol}}H$ was calculated from Charstil's and K-J's model, while $\Delta_{\text{vap}}H$ was calculated from Bartle's model. The total heat change for a chosen system, which was calculated based on two different models, differ in average 14 %. Highest $\Delta_{\text{sol}}H$ were obtained in systems with R236fa followed by R134a and CO₂ and R23. The $\Delta_{\text{sol}}H$ for all vanillins in CO₂ are in the order between 10 kJ/mol do 20 kJ/mol, where similar values are observed for pair of vanillin with methoxy group (V, oV) and ethoxy group (EV, oEV). In general, $\Delta_{\text{sol}}H$ are lower in systems with *o*-vanillins compared to systems with *p*-vanillins. Interestingly, obtained $\Delta_{\text{sol}}H$ values in systems with oEV – R134a and oEV – R236fa were negative, which more likely correspond to heat of condensation. These two systems were indeed difficult to observe since very high solubilities were visually observed during research in high pressure view cells. The mentioned systems should be further investigated.

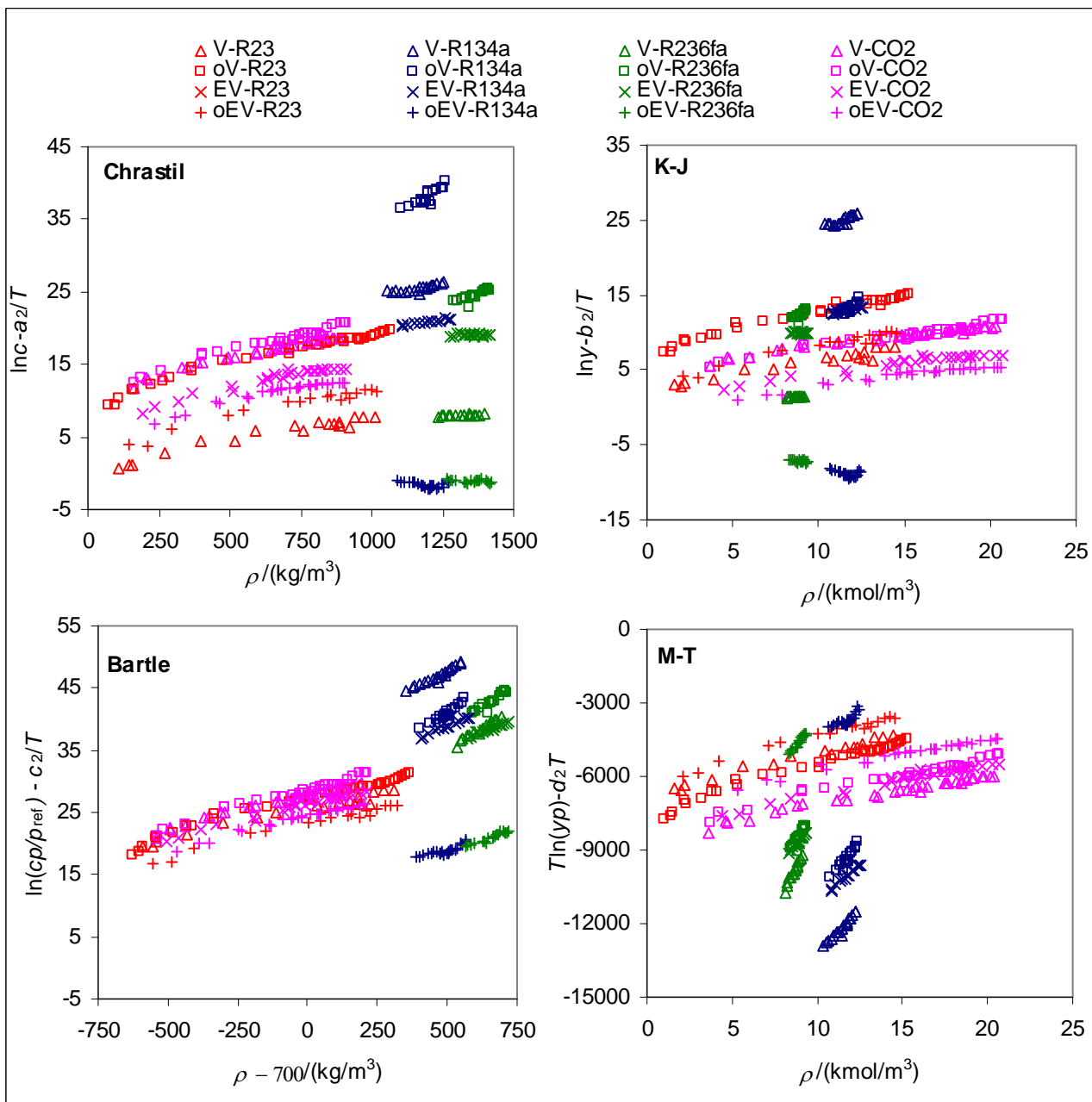


Figure 1: Comparison of different density based models for estimating the solubilities of vanillins in dense CO₂ and fluorinated hydrocarbons

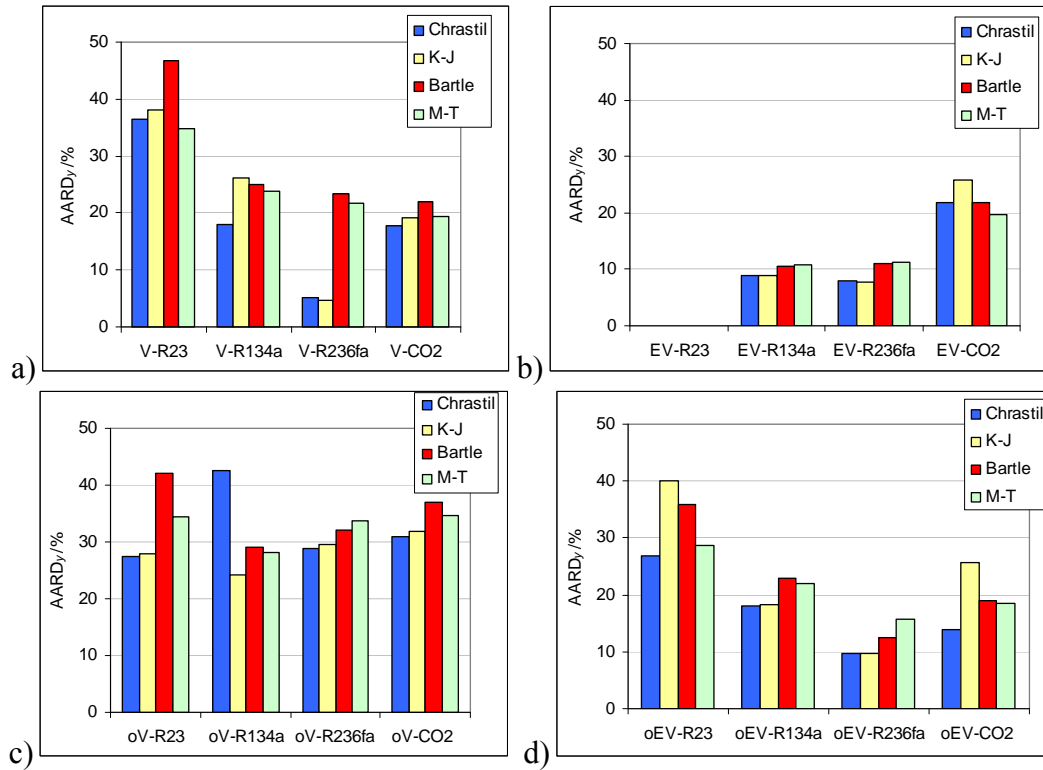


Figure 2: AARD values for deviation of correlated and experimental solubility values for different systems with: a) vanillin, b) ethvanillin, c) o-vanillin and d) o-ethylvanillin

Table 1: Heat values for systems of vanillins and dense gasses calculated from correlated parameters

Sistem	eq. (2)	eq.(4)	average	eq. (6)	$\Delta_{sol}H/(kJ/mol)$
	$\Delta_{total}H/(kJ/mol)$	$\Delta_{total}H/(kJ/mol)$	$\Delta_{total}H/(kJ/mol)$	$\Delta_{vap}H/(kJ/mol)$	
V-R23	14,68	35,24	24,96	55,22	30,26
V-R134a	40,68	77,00	58,84	103,83	44,98
V-R236fa	10,42	12,29	11,35	80,46	69,11
V-CO ₂	41,91	42,31	42,11	56,04	13,93
EV-R23	-	-	-	-	-
EV-R134a	47,45	46,87	47,16	82,19	35,03
EV-R236fa	36,91	32,35	34,63	75,54	40,91
EV-CO ₂	28,72	30,45	29,58	49,90	20,32
oV-R23	36,09	44,65	40,37	51,51	11,13
oV-R134a	89,62	43,07	66,35	83,82	17,48
oV-R236fa	49,26	36,93	43,10	85,01	41,92
oV-CO ₂	39,77	37,45	38,61	52,89	14,28
oEV-R23	15,87	32,62	24,25	40,49	16,24
oEV-R134a	-12,84	-12,00	-12,42	28,95	41,37
oEV-R236fa	-19,02	-15,17	-17,10	26,65	43,75
oEV-CO ₂	20,16	22,76	21,46	41,28	19,82

CONCLUSION

In general, best agreements between experimental and correlated solubility data of vanilins in CO₂ and fluorinated hydrocarbons were obtained with Chrastil's model.

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