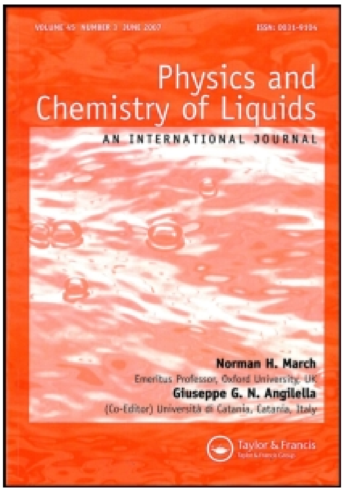

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Prediction of the enthalpy of vapourisation for anhydrides, formates, acetates, propionates, butyrates, esters, and ethers

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Prediction of the enthalpy of vapourisation for anhydrides, formates, acetates, propionates, butyrates, esters, and ethers

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Four analytical correlations based on the use of the corresponding states principle were used to calculate the enthalpy of vapourisation of fluids. Three of these correlations require as inputs the critical temperature and the acentric factor. The fourth requires a molecular Lennard–Jones parameter and the acentric factor. Results for 184 polar and non-polar fluids grouped into 9 families are compared with the values accepted by the Design Institute for Physical Property (DIPPR) project. Recommendations are given for the use of each model and for the choice of the adequate model for each family of fluids.

Keywords: enthalpy of vapourisation; correlations; pure fluids

1. Introduction

The enthalpy of vapourisation of a pure fluid is a very important thermodynamic property that is required in processes involving a liquid–vapour change of phase such as distillation, evaporation, drying, etc. Moreover, this property is sometimes used in the prediction or correlation of other thermodynamic properties. In the cases where experimental values are not known, empirical equations are used to predict them. Indeed, there are many empirical correlations that allow one to calculate the enthalpy of vapourisation of pure fluids [1–5]. Some of them include coefficients that must be calculated for each substance [6–11], or the value of the enthalpy at a given temperature [12–16]. Others are general analytical expressions based on the corresponding states principle, and then they only require certain properties of the fluid as input parameters [17–20], such as the critical temperature and the acentric factor, or molecular parameters [21,22]. These correlations do not require the calculation of specific coefficients for each substance, and thus can be regarded as predictive. The enthalpy of vapourisation may also be predicted by means of group contribution models [23–28], in which it is necessary to know the chemical groups in the molecule as well as its chemical structure.

In a recent article [29], we presented an overall comparison between the prediction given by four analytical models based on the corresponding states principle and the values accepted by the Design Institute for Physical Property (DIPPR) project for 1576

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substances [30–33]. Recommendations for the general use of those models were given. In the present work, we again make that comparison, but now in detail, for 183 fluids grouped into 9 families, and provide specific recommendations for the use of each model and for which model to choose for each family of fluids.

The models used are those proposed by Carruth and Kobayashi [17], Sivaraman *et al.* [18], and Morgan and Kobayashi [19] which use the critical temperature and the acentric factor as inputs, and that proposed by Faúndez *et al.* [21,22], which uses molecular parameters as input. We have checked these models for the particular cases of the vapourisation enthalpy at the standard and the boiling temperatures [34–36].

The present work completes those previous studies by considering the whole temperature range for the selected fluids.

2. Correlations

We shall here only consider those analytical expressions that are based on the application of the corresponding states principle, and that require neither specific adjustable coefficients for each substance nor the value of the enthalpy at a given temperature, but rather knowledge of some properties of the fluids. The simplest of these expressions is that proposed by Carruth and Kobayashi [17] which we shall call the 'CK' correlation,

$$\frac{\Delta H_{\mathrm{v}}}{RT_{\mathrm{c}}} = 7.08\left(1-\frac{T}{T_{\mathrm{a}}}\right)^{0.354} + 10.95\omega\left(1-\frac{T}{T_{\mathrm{c}}}\right)^{0.456}, \tag{1}$$

where T_{c} is the critical temperature, R the universal gas constant, and ω the acentric factor.

A more sophisticated model is that proposed by Sivaraman et al. [18], which we shall call the 'SMK' correlation. This model uses two fluids as reference: benzene with $\omega^{(R1)}=0.21$, and carbazol ($C_{12}H_9N$) with $\omega^{(R2)}=0.46$. The analytical expression of the SMK correlation is

$$\frac{\Delta H_{\mathrm{v}}}{RT_{\mathrm{c}}} = \left(\frac{\Delta H_{\mathrm{v}}}{RT_{\mathrm{c}}}\right)^{(R1)} + \left(\frac{\omega-\omega^{(R1)}}{\omega^{(R2)}-\omega^{(R1)}}\right)\left[\left(\frac{\Delta H_{\mathrm{v}}}{RT_{\mathrm{c}}}\right)^{(R2)} - \left(\frac{\Delta H_{\mathrm{v}}}{RT_{\mathrm{c}}}\right)^{(R1)}\right], \tag{2}$$

where $(\Delta H_{\mathrm{v}}/RT_{\mathrm{c}})^{(R1)}$ corresponds to the enthalpy of vaporization of benzene,

$$\begin{aligned}\left(\frac{\Delta H_{\mathrm{v}}}{RT_{\mathrm{c}}}\right)^{(R1)} &= 6.537\left(1-\frac{T}{T_{\mathrm{c}}}\right)^{1/3} - 2.467\left(1-\frac{T}{T_{\mathrm{c}}}\right)^{5/6} \\ &\quad - 77.251\left(1-\frac{T}{T_{\mathrm{c}}}\right)^{1.208} + 59.634\left(1-\frac{T}{T_{\mathrm{c}}}\right) \\ &\quad + 36.009\left(1-\frac{T}{T_{\mathrm{c}}}\right)^{2} - 14.606\left(1-\frac{T}{T_{\mathrm{c}}}\right)^{3}\end{aligned} \tag{3}$$

and the second term includes the difference between the benzene and the carbazol enthalpies

$$\left(\frac{\Delta H_{\mathrm{v}}}{RT_{\mathrm{c}}}\right)^{(R2)}-\left(\frac{\Delta H_{\mathrm{v}}}{RT_{\mathrm{c}}}\right)^{(R1)}=-0.133\left(1-\frac{T}{T_{\mathrm{c}}}\right)^{1/3}-28.215\left(1-\frac{T}{T_{\mathrm{c}}}\right)^{5/6}-82.958\left(1-\frac{T}{T_{\mathrm{c}}}\right)^{1.208}+99.000\left(1-\frac{T}{T_{\mathrm{c}}}\right)+19.105\left(1-\frac{T}{T_{\mathrm{c}}}\right)^{2}-2.796\left(1-\frac{T}{T_{\mathrm{c}}}\right)^{3}, \tag{4}$$

with T_{c} and ω being the critical temperature and the acentric factor, respectively, of the substance whose enthalpy is to be determined.

Morgan and Kobayashi [19] proposed a model constructed by using data for alkanes and long-chain hydrocarbons. The correlation, which we shall call 'MK', is quadratic in the acentric factor:

$$\Delta H_{\mathrm{v}}=\Delta H_{\mathrm{v}}^{(0)}+\omega\Delta H_{\mathrm{v}}^{(1)}+\omega^{2}\Delta H_{\mathrm{v}}^{(2)}, \tag{5}$$

where each of the terms has the same analytical expression, that of Torquato and Stell [37]:

$$\frac{\Delta H_{\mathrm{v}}^{(j)}}{RT_{\mathrm{c}}}=b_1^{(j)}\left(1-\frac{T}{T_{\mathrm{c}}}\right)^{0.3333}+b_2^{(j)}\left(1-\frac{T}{T_{\mathrm{c}}}\right)^{0.8333}+b_3^{(j)}\left(1-\frac{T}{T_{\mathrm{c}}}\right)^{1.2083}+b_4^{(j)}\left(1-\frac{T}{T_{\mathrm{c}}}\right)+b_5^{(j)}\left(1-\frac{T}{T_{\mathrm{c}}}\right)^{2}+b_6^{(j)}\left(1-\frac{T}{T_{\mathrm{c}}}\right)^{3}. \tag{6}$$

The 18 coefficients, $b_i^{(j)}$ with $j=0,1,2$ and $i=1$–6, were obtained by a fitting procedure and are listed in Table 1 [19]. An absolute average deviation (AAD) of 2.21% was reported for the boiling enthalpy of 10-long n-alkanes (from C21 to C43). Extrapolations for other kind of fluids were not made.

As an alternative to the above, there has been proposed [21,22] a molecular model that consists of a polynomial expression whose input parameters are the Lennard-Jones parameter, ε, related to the intensity of the attractive intermolecular forces, and the acentric factor, ω, which is related to the shape of the molecules (its value increases for substances whose molecules have a shape that differs from the sphere assumed in the Lennard-Jones model). The analytical form of this model, which we shall denote the 'FMC' model, is a fourth-order polynomial in the temperature:

$$\Delta H_{\mathrm{v}}=\left(\frac{\varepsilon}{k}\right)R\left[\sum_{i=0}^{4}F_i\left(\frac{kT}{\varepsilon}\right)^{i}+\omega\sum_{i=5}^{8}F_i\left(\frac{kT}{\varepsilon}\right)^{i-5}+\omega^{2}\sum_{i=9}^{11}F_i\left(\frac{kT}{\varepsilon}\right)^{i-9}\right], \tag{7}$$

Table 1. Coefficients for the Morgan and Kobayashi model [19].

$b_i^{(j)}$	$i=1$	$i=2$	$i=3$	$i=4$	$i=5$	$i=6$
$j=0$	5.2804	12.8650	1.1710	−13.1160	0.4858	−1.0880
$j=1$	0.80022	273.23	465.08	−638.51	−145.12	74.049
$j=2$	7.2543	−346.45	−610.48	839.89	160.05	−50.711

where k is the Boltzmann constant, and the coefficients F_i, whose values are listed in Table 2 [21,22], are universal for non-polar fluids and were obtained by fitting the data provided by the DIPPR-1996 project [32] for 42 non-polar fluids over a wide range of temperatures, the absolute mean deviation being 0.8% and the maximum 2.8% [34]. The first summation of Equation (7) represents the value of the enthalpy of vapourisation of argon, the reference fluid, for which one takes $\omega = 0$. Equation (7) represents the only molecular model that has been proposed up to now. One of its drawbacks is that it does not explicitly include the convergence to zero at the critical point, so that there are certain limitations on the temperature range over which it can be applied, although extrapolations can be made in some cases.

In the present work, we study the validity of these models for the calculation of the enthalpy of vapourisation. The predicted values are compared with those accepted in the DIPPR database [33] for the nine families of fluids listed in Table 3.

Table 2. Coefficients of the Faúndez *et al.* molecular model [21,22], Equation (7).

i	F_i
0	−7.071434
1	68.842680
2	−118.404491
3	87.974558
4	−25.417920
5	−7.323657
6	96.873695
7	−124.019801
8	48.128476
9	−22.806287
10	67.410156
11	−33.826117

Table 3. Mean absolute percentage deviations (MAPD) of the values obtained with the models from the values provided by DIPPR [33] for several families of fluids.

Families	NF	ND	CK	SMK	MK	FMC
Anhydrides	9	263	**6.68**	7.76	9.65	9.61
Formates	15	437	*3.14*	**2.33**	*2.58*	*2.90*
Acetates	22	657	3.13	**2.02**	*2.55*	*2.27*
Propionates and butyrates	13	384	3.41	**1.68**	*2.00*	*2.49*
Other saturated aliphatic esters	21	520	*4.86*	**4.62**	5.73	*5.53*
Unsaturated aliphatic esters	23	624	*4.39*	**3.46**	*4.15*	*4.01*
Aromatic esters	29	813	4.82	**3.73**	*4.42*	*4.72*
Aliphatic ethers	31	1021	*2.08*	**1.82**	*2.16*	*2.31*
Other ethers/diethers	21	555	*3.94*	**3.15**	*3.91*	*3.67*

Notes: NF = number of fluids. CK = Carruth and Kobayashi [17], Equation (1); SMK = Sivaraman *et al.* [18], Equations (2)–(4); MK = Morgan and Kobayashi [19], Equations (5)–(6); FMC = Faúndez *et al.* [21], Equation (7). The lowest deviation in each family is given in **bold**. Deviations of up to 1% from the lowest one are given in *italics*.

3. Results

Before making the comparison between the DIPPR accepted values and those predicted by the models, we carefully reviewed the DIPPR database. Thus, in our calculations we did not include two fluids for which fewer than five accepted data are available (ethyl propyl ether of the aliphatic ether family, and 1,2-diethoxyethane of the other ethers/diethers). Neither did we eventually take into account the fluid phthalan for which we found extremely high deviations for all the models studied.

Thus, the number of fluids studied was 184 grouped into 9 families. We calculated the absolute percentage deviation (PD) of the values obtained with each correlation from those accepted by the DIPPR project for each fluid at every temperature. We also calculated the AAD for each fluid (i.e. the mean of the PD for each fluid), and the mean absolute value of the PD (MAPD) for each family of fluids (i.e. by taking into account the number of available data for a family, not the number of fluids for each family). The results for each family are listed in Table 3.

The Lennard-Jones parameters for the FMC model (given by Equation (7)) were obtained following the method given by Cuadros *et al.* [38] using the values of the critical temperature and the acentric factor from the DIPPR database [33].

As can be seen in Table 3, very poor results were obtained for *anhydrides*, with the CK model giving the best overall results. In any case, for only three fluids (butyric anhydride, propionic anhydride, and acetic anhydride) did this model give AADs $\leq 4\%$. For the other fluids the enthalpies were overestimated, at least in the temperature range $T/T_c < 0.75$.

For *formates*, all the models gave MAPDs $<3.2\%$, with the SMK model being the best. The worst agreement in this family was for *n*-decyl formate where all the models except CK (with an AAD of 4.9%) gave deviations $>6.3\%$.

For *acetates*, the overall deviations were slightly lower than for the preceeding group. The SMK model again gave the best agreement. Allyl acetate was the exception in this family because all the models gave deviations $>4.9\%$ (with CK being the best).

For *propionates and butyrates*, the SMK, MK, and FMC models gave similar results, with MAPDs near 2%, whereas the CK model gave the poorest results. In the case of ethyl isobutyrate (Figure 1) all the models behaved similarly for $T/T_c > 0.62$, and except for the case of the FMC model which has a different shape (see the Appendix), overestimated the vapourisation enthalpy at lower temperatures.

For *other saturated aliphatic esters*, one can see from Table 3 that again the SMK model gave slightly better overall agreement than the others, with the CK model being very close to it. We can see in Figure 2 that there were some fluids for which high AADs are found for all the models, as was the case of ε-caprolactone, β-propiolactone, or diethyl oxalate. The rest of the data were very inhomogeneous, and we found that except for the FMC model, all the models gave the lowest MAPDs for at least five fluids. The best behaviour showed by the SMK model is due to not giving the worst AAD for any fluid.

There was the same inhomogeneity in the results for *unsaturated aliphatic esters* and *aromatic esters* in which the SMK model proved slightly better than the other models. There were some fluids such as 2-ethylhexyl acrylate, isopropyl acrylate, cetyl methacrylate, and diethyl maleate in the unsaturated aliphatic group, and dimethyl isophthalate, dimethyl terephthalate, 1,2-benzene dicarboxylic acid-heptyl-undecyl ester, 1,2-benzene dicarboxylic acid-heptyl-nonyl ester, and tri-*n*-heptyl trimellitate in the aromatic esters, for which all the models gave AADs $>5\%$. For the other fluids of these families, one could always find a model which gave AADs $<5\%$.

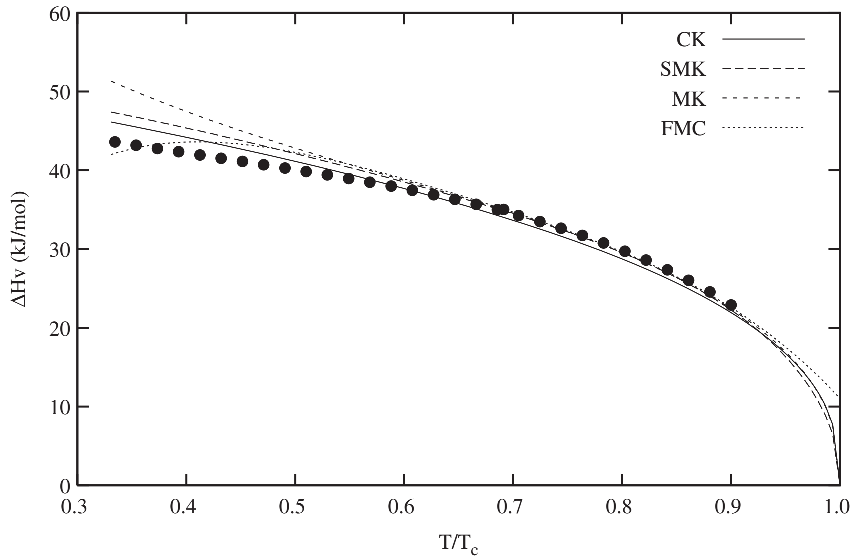

Figure 1. Vapourisation enthalpy of ethyl isobutyrate. Points are the accepted data of the DIPPR [33] database, and lines the predictions of the studied models.

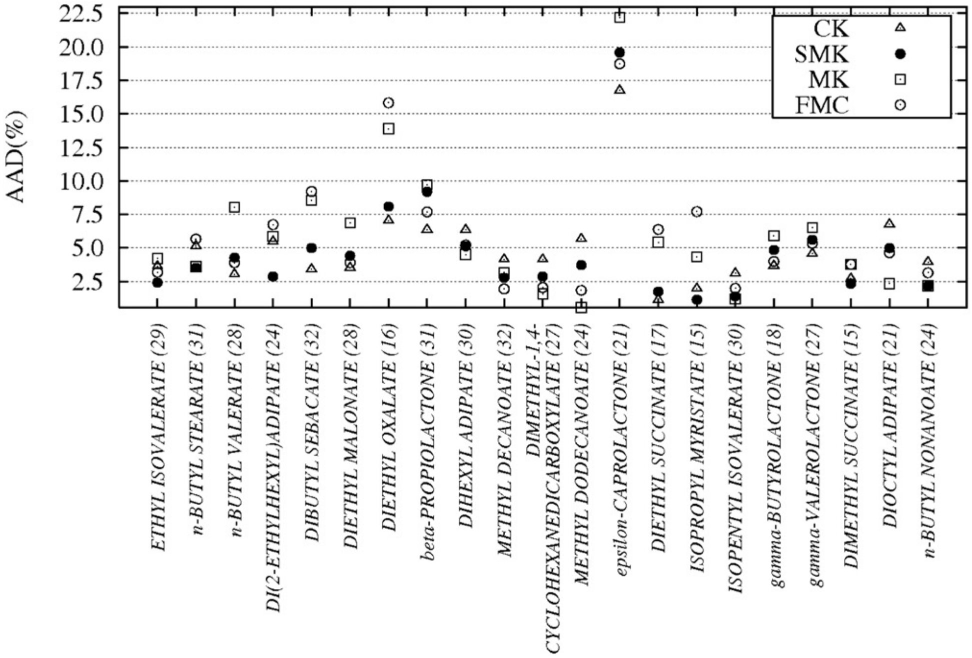

Figure 2. Average absolute deviations of the other saturated aliphatic esters family for the CK [17], SMK [18], MK [19], and FMC [21] models. The number of data points for each fluid is given in parentheses.

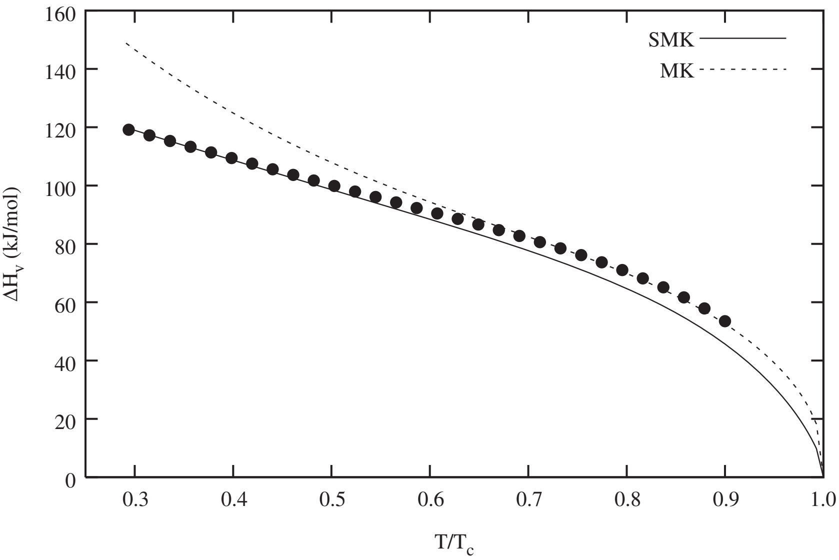

Figure 3. Accepted data [33] for di-*n*-hexyl phthalate and predictions of the SMK [18] and MK [19] models.

In any case, the SMK model would have to be used with caution at high temperatures, i.e. near the critical point, for some fluids for which the AADs were not small. We found that sometimes the SMK model agreed with the DIPPR data at low temperatures but not at high temperatures, while the contrary was the case for the MK model (Figure 3). At other times disagreement was only observed at low temperatures for both models.

The four models were similar in giving a good overall accuracy for *aliphatic ethers* and not so good for *other ethers and diethers*. For aliphatic ethers, the exceptions were di-*n*-pentyl ether for which all the models gave AADs >5% (the largest PDs being at lower temperatures), and di-*n*-octyl ether for which only the SMK model agreed with the data at low temperatures (but not at high temperatures), whereas the contrary was the case with the other models. For the rest of the fluids, there was always a model for which the AAD was <2.5%.

In the other ethers and diethers family, we found AADs >7% for diethylene glycol-di-*n*-butyl ether and tetraethylene glycol dimethyl ether with all the models studied. Also, most of the models failed to reproduce the shape of the data at low temperatures: for example, only the MK model reproduced the shape of the data at low temperatures for 1,2-epoxy-3-phenoxypropane (Figure 4).

4. Conclusions

In the present work, we studied the validity of four models (CK, SMK, MK, and FMC) for the prediction of the enthalpy of vapourisation, and compared them with the values in the DIPPR database for 184 fluids grouped into 9 families.

In general, the SMK model had the best overall results for all the families studied except the anhydrides where the CK model was better. The greatest disagreement between the predicted values and the accepted DIPPR data were found for those families for which

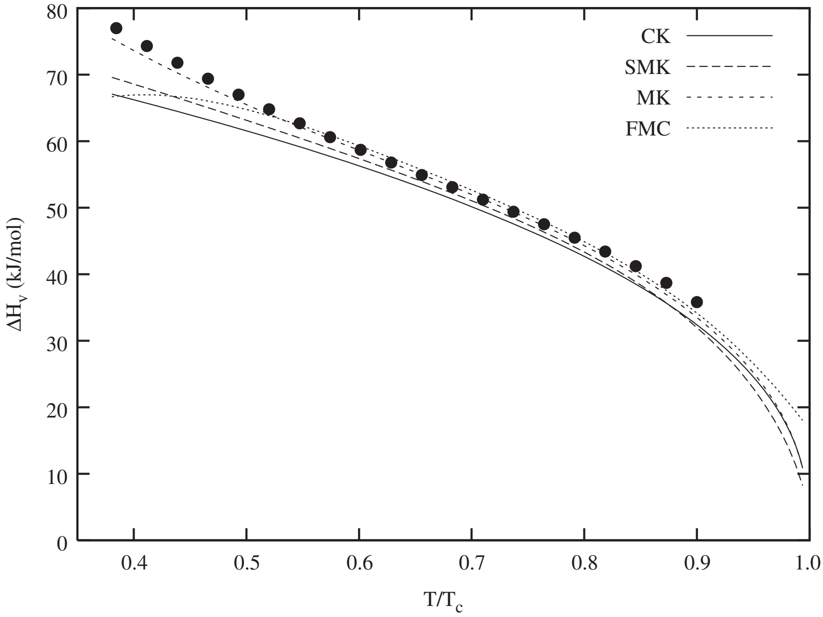

Figure 4. Accepted data [33] for 1,2-epoxy-3-phenoxypropane and predictions of the CK [17], SMK [18], MK [19], and FMC [21] models.

the dependence of the vapourisation enthalpy on the temperature is very inhomogeneous, changing greatly from one fluid to another even though the fluids are of the same kind. In particular, there was major disagreement for those fluids for which the data at low temperatures increased either sharply or very gradually (i.e. with a very high or a very low slope). In any case, we found that all the models would have to be used with caution at low temperatures. Most of the fluids for which the greatest deviations were found have been clearly identified in the text.

Although good results can be obtained for some particular fluids, none of the models can be used with good overall accuracy (MAPDs $<3.5\%$) for anhydrides, other saturated aliphatic esters, or aromatic esters.

For five out of the nine families, all the selected models were found to reproduce the data with MAPDs $\leq 4\%$. In any case, these models would have to be used with caution for some particular fluids and/or some particular temperature ranges. For these families, the overall results were similar for the different models, being the degree of improvement of one model with respect to another for the same family not very high. There were, however, some clear exceptions.

With respect to the models, CK and FMC had poorer overall accuracy than SMK and MK. In particular, while we found the FMC model giving good overall agreement with the data at intermediate temperatures: it showed an overall lack of accuracy at very low and very high temperatures.

With respect to the choice between the MK and the SMK models, the following conclusions could be drawn. First, for some fluids the SMK model agrees with the data only at low temperatures, whereas MK does so only at high temperatures. Second, in general the MK model must be used with caution at low temperatures because it predicts excessively high values for some fluids; similarly, the SMK model must be used with caution at high temperatures. Third, for most of the other families we recommend the use of the SMK model because of its simplicity and similar or slightly better overall agreement with the DIPPR data.

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Appendix

One can see in Figure 1 that the shape of the FMC model is different from that of the others. This is due to its different analytical form which leads to negative values at lower temperatures. That is, taking $T = 0$ in Equation (7) one has

$$\begin{aligned}\Delta H_\mathrm{v} &= \left(\frac{\varepsilon}{k}\right) R(-7.071434 - 7.323657\omega - 22.806287\omega^2)\\ &= -22.806287\left(\frac{\varepsilon}{k}\right) R(\omega + 0.16056099)^2,\end{aligned} \tag{8}$$

which is negative for all ω. For higher temperatures, the term $F_4(kT/\varepsilon)^4$ dominates and leads to negative values at high temperatures (this behaviour can be seen in Figure 5). Taking into account that intermediate temperatures give positive values, the FMC equation presents maxima that can be seen in the experimental range in some fluids, as in the case of ethyl isobutyrate (Figure 1).

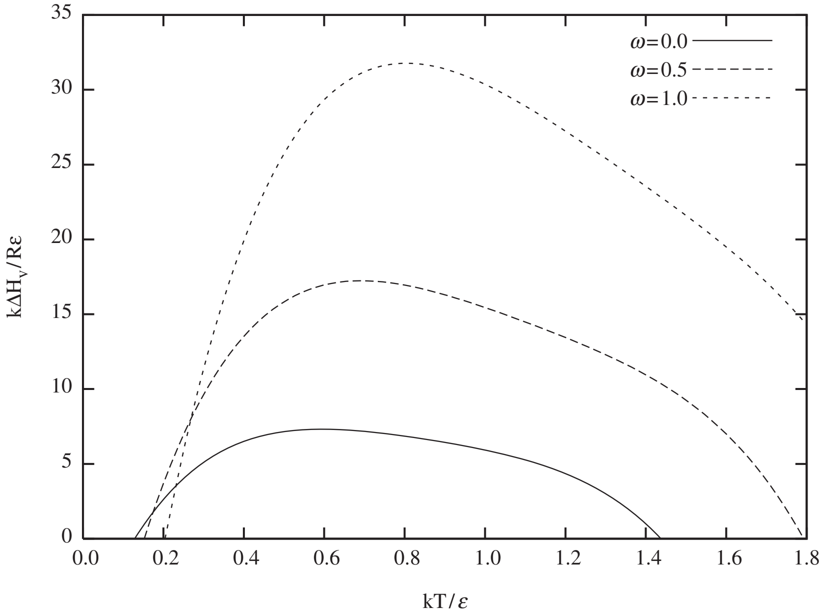

Figure 5. Behaviour of the FMC model for different acentric factors. One observes the maximum and the negative values for lower and higher temperatures.