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Characteristic parameters of the Tassios, Larsen and Gmehling versions of the UNIFAC model for enthalpies of mixing in organic anhydrides + N-alkanes mixtures

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Abstract

The characteristic parameters for the Tassios et al. (Ind. Eng. Chem. Process Des. Dev. 23 (1984) 391; 24 (1985) 701; 25 (1986) 22), Larsen et al. (Ind. Eng. Chem. Res. 26 (1987) 2274), and Gmehling et al. (Ibid. 32 (1993) 178) versions of UNIFAC model for organic anhydrides + n-alkane systems have been calculated. For the first time, published data on excess enthalpies have been used to estimate the interaction parameters between the anhydride group CO–O–CO and the methyl and methylene groups (CH_3 and CH_2), respectively. In the case of the Gmehling version, the geometrical parameters of the anhydride group are also determined. The mean deviations for the excess enthalpies were about 2% for all versions. We have also compared our results with those obtained by Kehiaian et al. (Fluid Phase Equilibria 69 (1991) 91) with the DISQUAC model. © 1998 Published by Elsevier Science B.V.

Keywords: Alkane; Butanoic anhydride; Heptanoic anhydride; Enthalpies; Mixtures; UNIFAC

1. Introduction

Alkanoic acid anhydride have interesting applications such as in the cellulose industry for the manufacture of lens and in the cosmetic and pharmaceutical industries. Inspite of that no experimental data were reported for mixtures containing organic anhydrides until 1988. At this time, García et al. [1,2] and Escarda et al. [3] published experimental excess enthalpies and excess volumes, respectively, of butanoic anhydride and heptanoic anhydride + alkane systems. Unfortunately, there are no experimental values of excess Gibbs energies and infinite dilution coefficients in the literature.

In previous papers, we have studied the ketone (–CO– group) + alkane [4], ester (–CO–O– group) + alkane [5] and carbonate (O–CO–O group) + alkane [6] systems, using the UNIFAC and Nitta-Chao group contribution models. The anhydride group (–CO–O–CO) is clearly the next step of this line of investigation. Furthermore, the interaction parameters between the anhydride group and the methyl and methylene groups have not been reported for any version of the UNIFAC model. Only, the group contribution DISQUAC model has been applied by Kehiaian et al. [7].

The aim of this work is to provide the parameters of the UNIFAC model (Tassios, Larsen and Gmehling versions), which characterize the the interaction between the anhydride and methylene groups. We shall use these parameters to analyze the excess enthalpies of the systems.

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2. The theoretical model

Group contribution models consider that the molecule is formed by a set of dissimilar functional groups, describing the mixing properties in terms of the interactions between the functional groups instead of the molecules. An interaction-parameter set is associated to each functional group pair. These parameters are determined by using the available experimental data, and can be used to predict the results for other mixtures containing the same groups. Therefore, with a limited parameter set, a great number of mixtures can be predicted. In order to compare the goodness of the models, we will proceed, in what follows, to state briefly the main differences among the versions of the UNIFAC model due to Tassios, Larsen and Gmehling.

2.1. Tassios version

Tassios group (Rupp et al. [8]; Stathis and Tassios [9]; Dang and Tassios [10]) modified the original UNIFAC model for the prediction of excess enthalpies. The main change was the introduction of new interaction parameters which are temperature independent, whereas the lattice coordination number depends on the temperature by the Skjold-Jorgensen [11] expression:

$$z = 35.2 - 0.1272T + 0.00014T^2 \tag{1}$$

This version assigns two parameters for each functional group pair.

2.2. Larsen version

This UNIFAC model version was developed by Larsen et al. [12] to predict with the same set of parameters, excess enthalpies, vapour–liquid equilibria (VLE) and liquid–liquid equilibria (LLE). In this version the combinatorial term is changed by the expression of Kikic et al. [13]:

$$(\ln \gamma_i)_{\text{comb}} = \ln\left(\frac{\omega_i}{x_i}\right) + 1 - \frac{\omega_i}{x_i} \tag{2}$$

ω_i being a new volume fraction introducing a 2/3-power term:

$$\omega_i = \frac{x_i r_i^{2/3}}{\sum_j x_j r_j^{2/3}} \tag{3}$$

Three coefficients are used to describe the temperature dependence of the interaction parameters:

$$a_{mn} = a_{mn,1} + a_{mn,2}(T - T_0) + a_{mn,3} \times \left(T \ln\frac{T_0}{T} + T - T_0\right) \tag{4}$$

Thus, three pairs of coefficients are assigned for each interaction between two functional groups.

2.3. Gmehling version

As in the previous version, the present one (Weidlich and Gmehling [14]; Gmehling et al. [15]) can be used to predict excess enthalpies, VLE and LLE. In this version, and empirical equation is adopted for the combinatorial term:

$$\ln \gamma_i^{\text{c}} = 1 - \Phi'_i + \ln \Phi'_i - \left(1 - \frac{\Phi_i}{\theta_i} + \ln\left(\frac{\Phi_i}{\theta_i}\right)\right) \tag{5}$$

where the parameter Φ'_i can be calculated by using the relative Van der Waals volume R_k of the different groups, r_j being the Van der Waals volume of the molecule j:

$$\Phi'_i = \frac{r_i^{3/4}}{\sum_j x_j r_j^{3/4}} \tag{6}$$

In this case, and a new expression for the temperature dependence of the interaction parameters is used:

$$a_{mn} = \frac{a_{mn,1} + a_{mn,2}T + a_{mn,3}T^2}{T} \tag{7}$$

The interaction parameter number associated with each pair of functional groups is 6, as in the Larsen version.

3. Estimation of the geometrical and energetic parameters

Following the DISQIAC model, the organic anhydrides were considered as being formed by a anhydride group CO–O–CO, and methlyl and methylene for all versions. The geometrical parameters Q_i and R_i for the anhydride group were calculated using the Bondi [16] method for the Tassios and Larsen versions. In the case of Gmehling version,

Table 1
Excess enthalpies of alkanoic acid anhydride + alkane (CH_3–$(CH_2)_{n\text{-}2}$–CH_3) at equimolecular composition and 298.15 K: comparison of experimental results with calculated values (Gmehling et al., Larsen et al. and Tassios et al.)

System	h^E (J mol^{-1})				
	Exp	Calc			Source of experimental data
		Gmehling	Larsen	Tassios	
CH_3–$(CH_2)_2$–CO–O–C–O–$(CH_2)_2$–$CH_3$$^+$					
n=6	1231	1182	1180	1175	[5]
n=7	1314	1288	1287	1283	[5]
n=8	1392	1383	1386	1382	[5]
n=10	1551	1558	1561	1558	[5]
n=12	1688	1712	1712	1710	[5]
n=14	1795	1851	1844	1842	[5]
CH_3–$(CH_2)_5$–CO–O–CO–$(CH_2)_5$–$CH_3$$^+$					
n=6	647	643	666	670	[6]
n=7	740	714	734	738	[6]
n=8	806	782	798	802	[6]
n=10	913	909	914	918	[6]
n=12	1031	1026	1017	1021	[6]
n=14	1137	1134	1109	1114	[6]

these parameters are fitted to the experimental data base in agreement with the usual procedure, whereas for the methyl and methylene groups we have used the geometrical parameters determined by Gmehling et al. [15].

The employed data base contains only the experimental values of h^E for the systems indicated in Table 1 for the three versions because no experimental data for g^E and γ^∞ were found in the literature. The interaction parameters (Tables 2–4) between anhydride and methylene groups for the three versions were determined using Marquardt's [17] optimization algorithm by minimizing the χ^2 objective function. In the Gmehling version the geometrical parameters Q_i and R_i for the anhydride group were fitted together with the interaction parameters.

Table 2
Geometrical parameters (Q_i) and interaction parameters (a_{mn}) for alkanoic acid anhydride + alkane for the Tassios version

Q_i	Subgroup	Main group	CH_2	CO–O–CO
0.848	CH_3			
		CH_2	0	61.067
0.540	CH_2			
2.000	CO–O–CO	CO–O–CO	41.537	0

Table 3
Geometrical parameters (R_i, $(z/2)Q_i$) and interaction parameters ($a_{mn,i}$) for alkanoic acid anhydride + alkane for the Larsen version

R_i	$(z/2)Q_i$	Subgroup	Main group	CH_2	CO–O–CO
0.9011	0.848	CH_3		0	308.862
			CH_2	0	−1.261
0.6744	0.540	CH_2		0	887.806
				645.021	0
1.7865	2.000	CO–O–CO	CO–O–CO	−23.956	0
				−100.000	0

Table 4
Geometrical parameters (R_i, Q_i) and interaction parameters ($a_{mn,i}$) for alkanoic acid anhydride + alkane for the Gmehling version

R_i	Q_i	Subgroup	Main group	CH_2	CO–O–CO
0.6325	1.0608	CH_3		0	622.7292
0.6325			CH_2	0	2.0803
0.6325	0.7081	CH_2		0	−0.0018
				4378.9526	0
2.6555	1.7497	CO–O–CO	CO–O–CO	−3.6782	0
				−0.0335	0

4. Results and discussion

The theoretical results are compared with the experimental values in Table 1. The overall mean deviations for the equimolecular mixtures between the experimental h^E and the theoretical predictions using the three versions are about 2%.

In Fig. 1 we can see that the experimental points and the theoretical curves for the Tassios, Larsen and Gmehling versions are slightly skewed to the region poor in anhydride. Consequently, the symmetry of the h^E curves is well predicted by all versions.

The variation of h^E with the alkane length is described consistently by all versions of UNIFAC model, as may be seen in Fig. 2. Furthermore, the experimental excess enthalpies decrease as the anhydride length increases. This behaviour is well reproduced by the three versions.

In the comparison with other group contribution models, so far only the interaction parameters for the anhydride and methylene groups for the DISQUAC model have been published. In 1991, Kehiaian et al. [7] determined these parameters for a data base which contains h^E of butyric or heptanoic anhydrides + n-alkanes (hexane through tetradecane) and liquid–liquid equilibria of acetic anhydride + heptane systems. The mean deviation at equimolecular mixtures for h^E is the same for the three versions of UNIFAC (2%). The predictions of the DISQUAC model for h^E also are plotted for comparison in Fig. 2.

When comparing DISQUAC model with others, it must be borne in mind that the quasichemical coeffi-

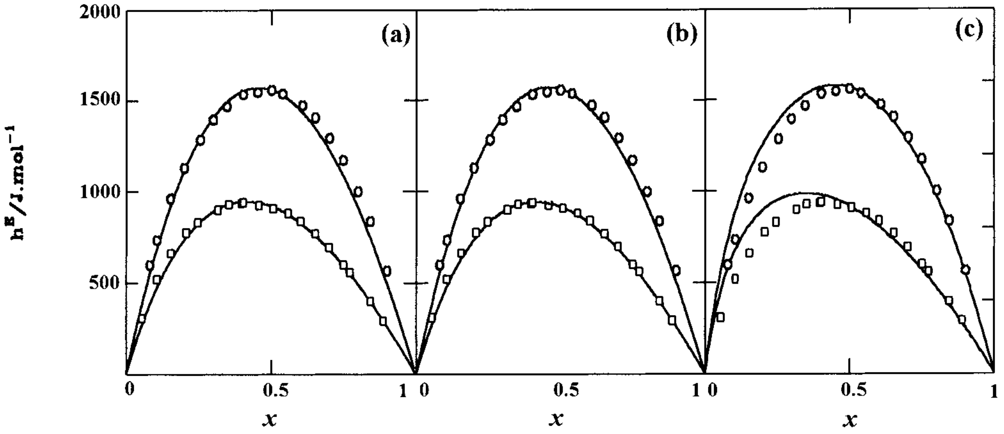

Fig. 1. Experimental excess molar enthalpies and theoretical predictions at 298.15 K of alkanoic acid anhydride+decane against the mole fraction x of the organic anhydride.Experimental points: ○ butanoic anhydride [5]; □ heptanoic anhydride [6]; ——— Theoretical predictions: (a) Tassios; (b) Larsen; (c) Gmehling.

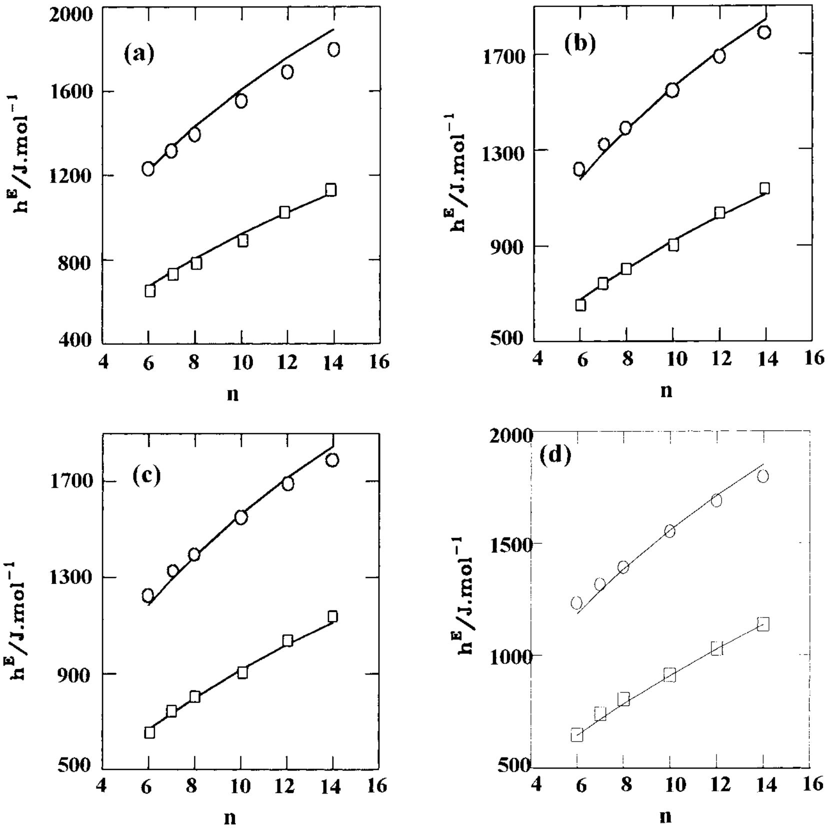

Fig. 2. Excess molar enthalpies, h^E (x=0.5), of alkanoic acid anhydride + n-alkane against n, the number of carbon atoms of the alkane. Experimental points: ○ butanoic anhydride [5]; □ heptanoic anhydride [6]; ——— Theoretical predictions: (a) DISQUAC; (b) Tassios; (c) Larsen; (d) Gmehling.

cients determined by Kehiaian et al. [7] vary with the anhydride length. The number of interaction parameters calculated by these authors for alkanoic acid anhydride + n-alkane is eight, whereas two, six and eight parameters are used for the Tassios, Larsen and Gmehling versions, respectively. Furthermore, for these last versions the parameters are independent of the anhydride length.

However, we must note that the DISQUAC model reproduces with reasonable agreement the experimental miscibility gap of acetic anhydride + heptane with the same set of parameters. In contrast, when the parameters determined in the present work for Larsen and Gmehling versions are used to calculate liquid–liquid equilibria, the predictions are very poor.

5. Conclusions

We have determined for the first time the interaction parameters between anhydride and methylene groups for the different versions of UNIFAC model (Tassios et al., Larsen et al. and Gmehling et al.). In the case of the Gmehling version, the geometrical parameters of the anhydride group are also reported. The h^E values of systems containing an alkanoic acid anhydride and an n-alkane are fairly well represented by all the tested versions of the UNIFAC model.

Finally, these interaction parameters could need revision when g^E and γ^{∞} data become available. Additional accurate measurements especially of these properties would be of great interest.

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