Correlation and prediction of excess enthalpies of ester + n-alkane systems using the UNIFAC model

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Abstract

The original UNIFAC model and two of its modifications have been fitted to binary molar excess enthalpy (H^E) data to correlate and predict binary excess enthalpy H^E in systems containing esters and n-alkanes.

The results show that the version of Rupp et al. (Ind. Eng. Chem. Process Des. Dev., 23 (1984) 391) and the UNIFAC model with tripled values of surface area parameters (UNIFAC(3Q)) are preferable to the original UNIFAC model. Both versions produce mean deviations of H^E better than 7% for all the systems containing methanoates, ethanoates, the other alkanoates and benzoates studied.

INTRODUCTION

During the past 18 years, different versions and modifications of the original UNIFAC model [1] have been created and investigated. It is clear that for good prediction of excess enthalpy H^E in binary and multi-component systems, interaction parameters between the main groups must be derived from the experimental molar excess enthalpy data.

The version of Tassios and coworkers [2–4] seems to be a very successful model for H^E calculations although the number of interaction parameters and the data base used for calculation have so far been insufficient.

We have investigated the influence of the surface area parameters (Q_s) on the value of the H^E correlation in many systems, using the original UNIFAC model, and have shown that in most cases the triple values of Q_s (these values are simultaneously tripled for all the groups) enable us to obtain good correlation [5, 6]. This version of UNIFAC, which is called UNIFAC(3Q), has been checked on systems containing aldehydes [7]. The matrix of the group interaction parameters used in UNIFAC(3Q) will be published soon [8].

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Ortega and his coworkers have systematically measured the excess enthalpy of systems containing methyl alkanoates, see, for example, refs. 9–15, and using all the reliable data for binary systems of alkyl alkanoates with n-alkanes, have determined new values for the ester–alkane interaction parameters for Rupp's version of the UNIFAC model [12]. The same model was successfully used to describe the interaction between alkyl methanoates (formates) and n-alkanes [16].

In this paper, the three versions of the UNIFAC model are compared to correlate and predict H^E values in binary systems containing esters (methanoates, ethanoates, other alkanoates and benzoates) and n-alkanes, using different main groups of esters.

RESULTS AND DISCUSSION

The experimental data needed for the calculations were taken from the literature (see Table 1). The Simplex method, adopting Nelder-Mead's procedure, described in detail by Fredenslund et al. (ref. 20, pp. 79–85) was used, taking for minimization the function

$$F = \sum_{i=1}^{k} \left(\frac{H_{exp}^E - H_{calc}^E}{H_{exp}^E} \right)_i^2 \tag{1}$$

where k is the overall number of experimental points.

The results of the investigation are presented in Table 2. The accuracy of the fit is here expressed by the mean percentage deviation $\delta\%$

$$\delta = \frac{1}{k} \sum_{i=1}^{k} \left| \frac{H_{exp}^E - H_{calc}^E}{H_{exp}^E} \right|_i \times 100 \tag{2}$$

For all aliphatic ester–n-alkane systems, Rupp's version and UNIFAC(3Q) are significantly better for correlating and predicting H^E values than the original UNIFAC model.

The data base used for non-ethanoates was similar to that of Ortega et al. [12], containing the same non-ethanoates, but data on ethanoates are less common. The interaction parameters found by Rupp's version are similar to those calculated earlier using the main group CCOO [12]. However, our results show that for the ester–alkane mixtures the small group COO can be successfully used for both methods, Rupp's version and UNIFAC(3Q). Using both the data on non-ethanoates and ethanoates (66 systems with 1193 values of H^E), the UNIFAC(3Q) gave better results for ethanoates described by the small COO group. (The total mean percentage deviation was 4.52%, with 4.47% for non-ethanoates and 6.82% for ethanoates.)

For good correlation and prediction of H^E values of ester/alkane systems, the ethanoates should be taken separately. In this case, the use of the main group CH_3COO gives the best results.

TABLE 1

Experimental data used for correlation and prediction of H^E in systems containing esters and n-alkanes

Systems	Number of sets	Ref.
(i) CORRELATION		
Non-ethanoates		
Methyl alkanoates + n-pentane	7	15
Methyl alkanoates + n-heptane	7	12
Methyl alkanoates + n-undecane	7	12
Methyl alkanoates + n-nonane	4	13
Methyl alkanoates + n-undecane	4	13
Methyl alkanoates + n-tridecane	8	14
Ethyl propanoate + n-alkanes	5	17
Propyl propanoate + n-alkanes	4	9
Propyl propanoate + n-alkanes	4	10
Ethanoates		
Methyl ethanoate + n-alkanes	2	12
Propyl ethanoate + n-alkanes	3	17
Butyl ethanoate + n-alkanes	3	17
Methanoates		
Ethyl methanoates + n-alkanes	5	11
Propyl methanoates + n-alkanes	2	16
Butyl methanoates + n-alkanes	2	16
Benzoates		
Methyl benzoates + n-alkanes	5	18
Ethyl benzoates + n-alkanes	4	18
Butyl benzoate + n-hexane	1	18
Ethyl benzoate + ethyl benzene	1	18
(ii) PREDICTION		
Non-ethanoates		
Methyl hexanoate + n-pentane	1	15
Methyl pentanoate + n-heptane	1	12
Methyl dodecanoate + n-nonane	1	13
Methyl octanoate + n-undecane	1	13
Methyl tetradecanoate + n-undecane	1	13
Methyl hexanoate + n-tridecane	1	14
Methyl dodecanoate + n-tridecane	1	14
Ethanoates		
Methyl ethanoate + n-pentane	1	15
Methanoates		
Propyl methanoate + n-octane	1	16
Butyl methanoate + n-heptane	1	16
Butyl methanoate + n-heptane	1	19
Benzoates		
Ethyl benzoate + toluene	1	18

TABLE 2

The group interaction parameters and mean percentage deviation ($\delta\%$) for excess molar enthalpies of ester + n-alkane systems and the correlation and prediction by the three UNIFAC models: the original UNIFAC [1], Rupp's version [2], and UNIFAC(3Q) [6, 8]

Esters	Main group G	Model	Correlation				Prediction		Total	
			Parameters CH$_2$/G	G/CH$_2$	Number of sets	$\delta\%$	Number of sets	$\delta\%$	Number of sets	$\delta\%$
Non-ethanoates + ethanoates	CCOO	UNIFAC	540.64	192.46	58	16.43	8	15.29	66	16.27
		Rupp's version	59.65	641.09	58	6.97	8	3.73	66	6.55
		UNIFAC(3Q)	265.63	−40.74	58	6.91	8	3.78	66	6.51
	COO	UNIFAC	655.99	174.94	58	25.44	8	23.88	66	25.24
		Rupp's version	72.41	38.92	58	6.13	8	5.29	66	6.02
		UNIFAC(3Q)	288.24	213.90	58	4.68	8	3.46	66	4.52
Non-ethanoates	CCOO	UNIFAC	541.36	185.51	50	16.26	7	13.36	57	15.89
		Rupp's version	57.87	100.20	50	4.41	7	2.73	57	4.20
		UNIFAC(3Q)	247.30	−8.12	50	4.62	7	2.90	57	4.40
	COO	UNIFAC	653.30	173.66	50	23.14	7	19.13	57	22.63
		Rupp's version	71.93	38.98	50	5.28	7	3.40	57	5.04
		UNIFAC(3Q)	290.62	287.61	50	4.45	7	2.72	57	4.23
Ethanoates	CH$_3$COO	UNIFAC	523.09	214.57	8	17.65	3	15.10	11	16.85
		Rupp's version	44.56	104.62	8	2.14	3	5.17	11	3.09
		UNIFAC(3Q)	160.80	47.42	8	2.50	3	5.37	11	3.40

Methanoates	HCOOCH$_2$	UNIFAC	231.39	311.81	9	2.97	3	4.00	12	3.22
		Rupp's version	14.00	15.60	9	2.58	3	2.39	12	2.53
		UNIFAC(3Q)	51.81	56.42	9	2.64	3	2.47	12	2.60
	HCOO	UNIFAC	629.96	190.26	9	46.51	3	40.92	12	45.15
		Rupp's version	77.42	43.51	9	2.66	3	3.09	12	2.76
		UNIFAC(3Q)	308.16	474.39	9	2.33	3	2.13	12	2.28
Benzoates	C$_6$H$_5$COO	UNIFAC	198.02	109.08	10	4.01	–	–	–	–
		Rupp's version	22.70	0.62	10	4.15	–	–	–	–
		UNIFAC(3Q)	97.59	–9.07	10	4.16	–	–	–	–
	COO(arom.) [a]	UNIFAC	385.85	294.98	11	3.68	–	–	–	–
		Rupp's version	45.01	–2.94	11	3.71	–	–	–	–
		UNIFAC(3Q)	132.08	75.65	11	4.02	–	–	–	–
	AC-COO [a]	UNIFAC	360.07	259.38	11	3.68	–	–	–	–
		Rupp's version	30.85	16.88	11	4.07	–	–	–	–
		UNIFAC(3Q)	176.48	–28.86	11	3.76	–	–	–	–

[a] The parameters for the COO(arom.) and AC-COO groups were determined together with the parameters AC/G and G/AC, using the following parameters for CH$_2$/AC and AC/CH$_2$: 93.20 and 70.99 for UNIFAC [21], 12.09 and 1.90 for Rupp's version [4], 36.47 and 13.35 for UNIFAC(3Q) [8].

For methanoate/alkane mixtures, both the main groups, $HCOOCH_2$ and HCOO, guarantee good correlation and prediction results, i.e. better than 3%. It is interesting that in the first case, the original UNIFAC also gave low values of deviation from experimental data (in our earlier work [8] we fell into the local minimum).

The excess enthalpy of benzoate–alkane systems can be correlated well by all three models, using a large group C_6H_5COO, or smaller groups COO(arom.), as well as AC-COO. In the latter case, it is impossible to calculate separately the interaction parameters between the small groups and CH_2 and, therefore, we determined simultaneously two pairs of parameters (CH_2/G, G/CH_2, AC/G, G/AC). To achieve more reliable results of correlation, the ethyl benzoate–ethyl benzene system was added to the ten benzoate–alkane systems. The excess enthalpy in the ethyl benzoate–toluene system is practically zero [18]. Using the determined values of the interaction parameters, the prediction of H^E for the last system actually gave low values. Evidently, the smaller groups can be preferred for the description of benzoates because they can also be used, for example, for phthalic acid esters. Unfortunately, experimental H^E data for phthalic acid ester–alkane mixtures are not available.

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