ELSEVIER

Thermochimica Acta 286 (1996) 321–332

thermochimica
acta

Prediction of enthalpies of mixing and vapor–liquid equilibria for mixtures containing organic carbonates + *n*-alkanes using several versions of the UNIFAC model

J. García[a,*], E.R. López[a], J. Fernández[a], J.L. Legido[b]

[a] *Departamento de Física Aplicada, Facultade de Física, Universidade de Santiago, E-15706*
Santiago de Compostela, Galicia, Spain
[a] *Departamento de Física Aplicada, Facultade de Ciencias, Universidade de Vigo, E-36280 Vigo, Galicia, Spain*

Received 4 January 1996; accepted 29 February 1996

Abstract

Literature data on enthalpies of mixing and vapor–liquid equilibria of organic linear carbonates + *n*-alkanes mixtures examined on the basis of the UNIFAC model (in its original version as well as in those of Tassios et al., Larsen et al. and Gmehling et al.). For the four versions of the UNIFAC model, the interaction parameters for the carbonate group, O–CO–O, and the methyl and methylene groups, CH_3, CH_2, respectively, are reported. In the case of the Gmehling version, the geometrical parameters of the carbonate group are also determined. The best predictions are achieved with the Gmehling version, with mean deviations of 4.4% for the excess Gibbs energies and 2.3% for the excess enthalpies.

Keywords: Alkane; Diethyl carbonate; Dimethyl carbonate; Enthalpies; Gibbs energies; Mixtures; UNIFAC

---

1. Introduction

In spite of the applications of carbonic acid esters in the pharmaceutical industry, in agricultural and chemical products, as solvents of synthetic and natural resins, and of polymers, until 1987 no experimental thermodynamic data were reported for mixtures containing non-cyclic organic carbonates. From this time García et al. [1–3] reported excess enthalpies of diethyl carbonate + alkane and of dimethyl carbonate + hydrocarbons or tetrachloromethane. These papers were followed by others by Cocero and

---

* Corresponding author.

0040-6031/96/$15.00 © 1996 – Elsevier Science B.V. All rights reserved
PII: S0040-6031(96)02961-9

coworkers [4–6], in which VLE equilibria of this kind of mixture were published, and by González et al. [7], who measured LLE for dimethylcarbonate + some *n*-alkanes. Some of these thermodynamic data were treated by Kehiaian et al. [8] in the framework of the DISQUAC [9] model. In 1993, González et al. [10] redetermined new interchange coefficients for the linear organic carbonate–alkane interactions. Recently, Negadi et al. [11] reported molar excess Gibbs energies of dimethyl carbonate + heptane, which were not used by Kehiaian et al. to determine DISQUAC parameters.

No group contribution model other than DISQUAC was used to examine these experimental data. These models are interesting because they provides a basis for estimating properties of systems outside the set of investigated binaries. A single binary containing a specific pair of structural groups suffices to determine the corresponding group parameters. The parameters can be employed to estimate the properties of any other binary or multicomponent system containing the same structural groups. When applicable, this approach results in a considerable saving of experimental measurements, since the number of structural groups is much smaller than the number of molecular species.

One of our research lines [12,13] is the determination of the parameters of the UNIFAC group contribution model (original [14] and the versions of Tassios [15], Larsen [16] and Gmehling [17]). The purpose of this paper is to examine the properties of di-*n*-alkyl carbonates + *n*-alkanes with that model.

2. The theoretical model

The UNIFAC [14] contribution model is based on the UNIQUAC [18] equation. The original UNIFAC only predicts Gibbs excess energies and the Tassios version predicts excess molar enthalpies, whereas the Larsen et al. and the Gmehling et al. versions can be used to predict h^{E}, g^{E} and infinite dilution coefficients. We will now demonstrate the small differences between the Tassios, Larsen and Gmehling versions. The logarithm of the activity coefficients may be expressed as the sum of two contributions

$$\ln\gamma_i = \gamma_i^{\mathrm{comb}} + \ln\gamma_i^{\mathrm{res}} \tag{1}$$

where for the three versions

$$\ln\gamma_i^{\mathrm{res}} = \sum_{K=1}^{N} N_K^i(\ln\Gamma_K - \ln\Gamma_K^{(i)}) \tag{2}$$

where N_K^i is the number of group K for the molecule i

$$\ln\Gamma_K = Q_K\left[1 - \ln\left(\sum_m \theta_m\Psi_{mK}\right) - \sum_m\left(\frac{\theta_m\Psi_{mK}}{\sum_n \theta_n\Psi_{nK}}\right)\right] \tag{3}$$

Q_K is the surface of the group K and θ_m are the surface fractions

$$\Psi_{mn} = \exp\left[-\frac{\Delta U_{mn}}{RT}\right] = \exp\left[-\frac{a_{mn}}{T}\right] \tag{4}$$

In the original version, a_{mn} is assumed to be independent of the temperature.

In the Tassios version, a_{mn} is given by

$$a_{mn} = \frac{z}{2} a'_{mn} \tag{5}$$

where z is a temperature function

$$z = 35.2 - 0.1272\,T + 0.00014\,T^2 \tag{6}$$

and a'_{mn} are the adjustable interaction parameters.
In the Larsen version, a_{mn} depends on the temperature as

$$a_{mn} = a_{mn,1} + a_{mn,2}(T - T_0) + a_{mn,3}(T \ln(T_0/T) + T - T_0) \tag{7}$$

For the Gmehling version, a_{mn} is expressed as a function of the temperature as

$$a_{mn} = a_{mn,1} + a_{mn,2}\,T + a_{mn,3}\,T^2 \tag{8}$$

In the original UNIFAC and Tassios version, the combinatorial term is given by the classical Guggenheim [19] approximation for athermal mixtures, whereas in the Larsen et al. version the modification of Kikic et al. [20] has been used. However, Gmehling et al. changed the original combinatorial part of the UNIFAC model, introducing an empirical 3/4-term

$$\ln \gamma_i^c = 1 - \Phi'_i + \ln \Phi'_i - 5q_i\left(1 - \frac{\Phi_i}{\theta_i} + \ln\left(\frac{\Phi_i}{\theta_i}\right)\right) \tag{9}$$

where q_i is the surface of the molecule i and the parameter Φ'_i can be calculated by using the relative Van der Waals volume R_k of the different groups

$$\Phi'_i = \frac{r_i^{3/4}}{\sum x_j r_j^{3/4}} \tag{10}$$

r_j being the Van der Waals volume of the molecule j.

3. Estimation of the geometrical and energetic parameters

As for the DISQUAC model, the organic carbonates were considered as being formed by a carbonate group O–CO–O, and methyl and methylene groups (with the same interaction parameters) for all versions. In order to improve the standard of the predictions in the case of the Tassios version, we also considered the carbonate group as C–O–CO–O– (with the subgroups CH_2–O–CO–O and CH_3–O–CO–O). The geometrical parameters Q_i and R_i were calculated using the Bondi [21] method for the original UNIFAC and the Tassios and Larsen versions. In the Gmehling version, these parameters are fitted to the experimental data. In consequence, for the methyl and methylene groups we have used the geometrical parameters determined by Gmehling et al. [17] and for the carbonate group these parameters were fitted to the data base in agreement with the usual procedure.

The employed data base contains the experimental values at $x = 0.2$, 0.5 and 0.8 for h^E and g^E (in the Larsen et al. and Gmehling et al. versions), for h^E (in the Tassios et al. version) and for g^E (in the original UNIFAC, of the systems indicated in Tables 1 and 2.

Table 1
Excess enthalpies of dialkyl carbonate + alkane (CH_3–$(CH_2)_{n-2}$–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}					Source of experimental data
	Exp.	Calc.				
		Gmehling	Larsen	TassiosI	TassiosII	
CH_3–O–CO–O–CH_3 +						
$n = 6$	1902	1833	1844	1612	1926	[2]
$n = 7$	1988	1959	1963	1750	2080	[2]
$n = 8$	2053	2072	2070	1875	2218	[2]
$n = 10$	2205	2264	2257	2096	2457	[2]
CH_3–CH_2–O–CO–O–CH_2–CH_3 +						
$n = 6$	1264	1249	1206	1259	1167	[1]
$n = 7$	1328	1350	1303	1374	1264	[1]
$n = 8$	1399	1441	1392	1480	1352	[1]
$n = 10$	1536	1598	1551	1668	1506	[1]
$n = 14$	1798	1843	1810	1971	1745	[1]

Table 2
Molar Gibbs excess energies g^E of dialkyl carbonate + alkane (CH_3–$(CH_2)_{n-2}$–CH_3) at equimolecular composition; comparison of experimental results with calculated values (Gmehling et al., Larsen et al. and Original UNIFAC)

System	T/K	g^E/J mol^{-1}				Source of experimental data
		Exp.	Calc.			
			Gmehling	Larsen	Original UNIFAC	
CH_3–O–CO–O–CH_3 +						
$n = 6$	298.15	1175	1187	1064	1078	[5]
$n = 7$	283.15	1241	1248	1116	1104	[11]
$n = 7$	293.15	1221	1214	1135	1121	[11]
$n = 7$	313.15	1180	1169	1166	1149	[11]
$n = 7$	323.15	1150	1153	1175	1162	[11]
$n = 8$	298.15	1189	1211	1180	1165	[5]
$n = 10$	298.15	1250	1224	1262	1210	[5]
CH_3–CH_2–O–CO–O–CH_2–CH_3 +						
$n = 6$	298.65	727	892	786	794	[4]
$n = 8$	298.65	821	918	899	903	[4]
$n = 12$	298.65	967	943	1043	1003	[4]

Table 3
Geometrical parameters (Q_i) and interaction parameters (a_{mn}) for organic carbonate + alkane for the original UNIFAC

Q_i	Subgroup	Main group	CH_2	O–CO–O
0.848	CH_3	CH_2	0	756.347
0.540	CH_2			
1.120	O–CO–O	O–CO–O	1907.897	0

No experimental data for γ^{∞} were found in the literature. The interaction parameters (Table 3) between carbonate and methylene groups for the three versions were determined using Marquardt's [22] optimization algorithm by minimizing the χ^2 objective function. In the Gmehling version, the geometrical parameters Q_i and R_i for the carbonate group were fitted together with the interaction parameters.

4. Results and discussion

The theoretical results are compared with the experimental values in Tables 1 and 2 in which two predictions using the Tassios version appear: Tassios I, obtained by using the group O–CO–O, and Tassios II, in which C–O–CO–O was used. The Larsen version gives better predictions for h^E, the overall mean deviations for the equimolecular mixtures for the Gmehling version is about 2.3% and for the Larsen version it is 1.8%, whereas for the Tassios version the prediction of excess enthalpies is about 7.6% when –O–CO–O– is used as the group definition of carbonate. The mean deviation decreases to 5.1% when the carbonate group is changed to C–O–CO–O.

The variation of h^E with the alkane length is well reproduced by all versions, as may be seen in Fig. 1. The Larsen and Gmehling versions give the best predictions, the variation of the theoretical h^E with the alkane length being slightly different from that found experimentally. Furthermore, the experimental excess enthalpies decrease as the carbonate length increases. This behaviour is well reproduced by all versions of the UNIFAC model.

In Figs. 2 and 3 we can see that the fitted and the theoretical curves are slightly skewed to the region rich in carbonate; consequently the symmetry of the h^E curves is well predicted by all versions. In the case of the Tassios version and when the employed data base contains only h^E for equimolecular compositions, the mean deviation are 7.7% and 3.2% when we use the carbonate group as O–CO–O and C–O–CO–O respectively. However, in this case the shape of the h^E–x curves is not well predicted by this model.

In the case of excess Gibbs energies, the mean deviations for equimolecular mixtures are 5.9%, 4.4% and 5.7% for the original UNIFAC and the Gmehling and Larsen versions, respectively. The equimolecular values of the experimental and the theoretical g^E values are plotted in Fig. 4. Taking into account the lack of data for longer

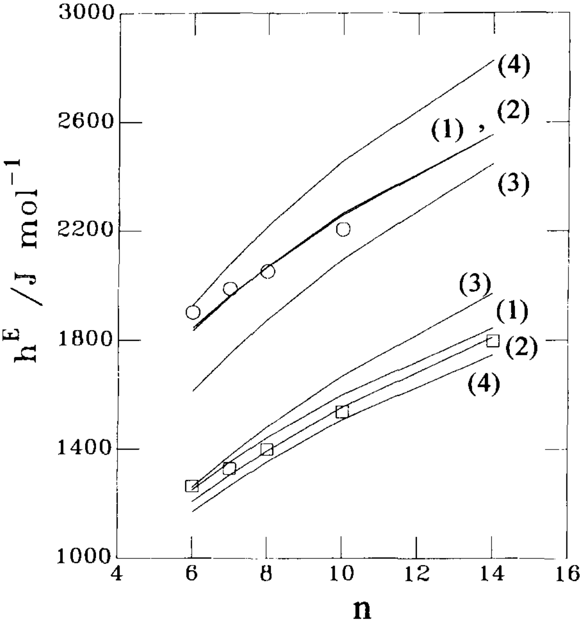

Fig. 1. Excess molar enthalpies, h^E ($x = 0.5$), of dialkyl carbonate + n-alkane against n, the number of carbon atoms of the alkane. Experimental points: ○, dimethyl carbonate; □, diethyl carbonate. Theoretical predictions: (1), Gmehling; (2), Larsen; (3), Tassios I; (4), Tassios II.

alkanes, the predictions of the trend of g^E with the alkane length seem to be fairly well represented.

In Fig. 5, the comparison between excess molar Gibbs energies determined from VLE data of Cocero et al. [5] and the theoretical predictions using the parameters determined in this work for the original UNIFAC, Larsen and Gmehling versions are plotted. The shape of the g^E vs. composition curves are well predicted. Both the experimental and theoretical curves are slightly skewed to the region rich in carbonate.

In the comparison with other group contribution models, so far only the interaction parameters for the carbonate and alkane groups for the DISQUAC model have been published. In 1991, Kehiaian et al. [8] determined these parameters for a data base which contains h^E and liquid–liquid equilibria for dimethyl and diethyl carbonates + alkane. Subsequently, Cocero et al. [5,6] measured the g^E of dimethyl and diethyl carbonate + alkane, but the g^E values of diethyl carbonate + alkane were not well predicted by these DISQUAC parameters. In order to improve the fit of the model, in 1993 González et al. [10] published revised interchange coefficients.

The predictions of the DISQUAC model for g^E are plotted for comparison in Fig. 4. The mean deviation for equimolecular mixtures using the original parameters is 2.8% for h^E and 6.4% for g^E. The mean deviation decreases to 2.6% for h^E and 2.3% for g^E when the

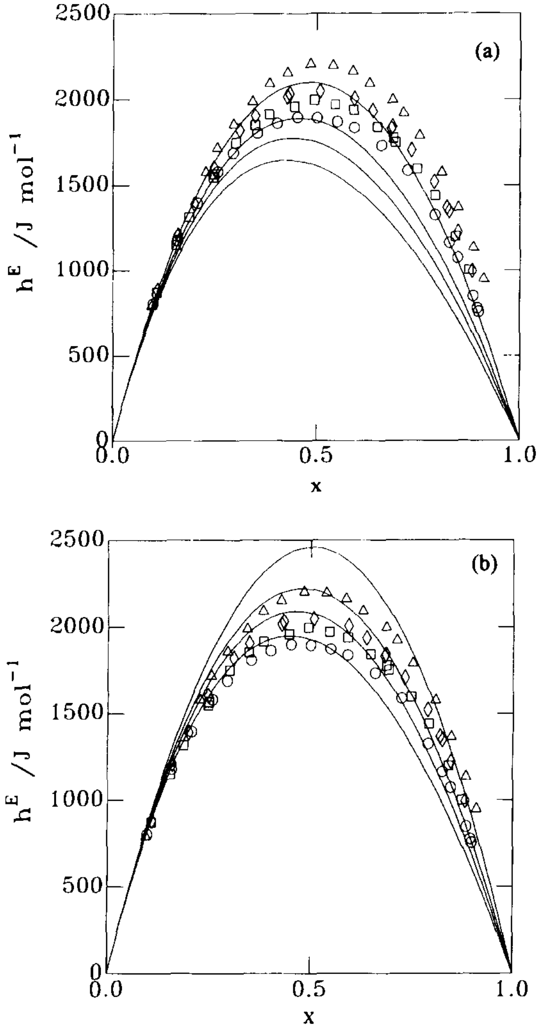

Fig. 2. Experimental excess molar enthalpies and theoretical predictions at 298.15 K of dimethyl carbonate + n-alkane against the mole fraction x of the linear carbonate. Theoretical predictions: (a), Tassios I; (b), Tassios II. Experimental points: ○, hexane; □, heptane; ◇, octane; △, decane.

revised DISQUAC coefficients are used. In agreement with this, the obtained fit of the theoretical results is similar in the Gemhling and Larsen versions. When comparing the DISQUAC model with others, it must be borne in mind that the quasichemical coefficients determined by Kehiaian et al. [8] and González et al. [10] vary with the carbonate length. The number of interaction parameters calculated by these authors for linear carbonate + n-alkane is eight, whereas two, six and eight parameters are used for the

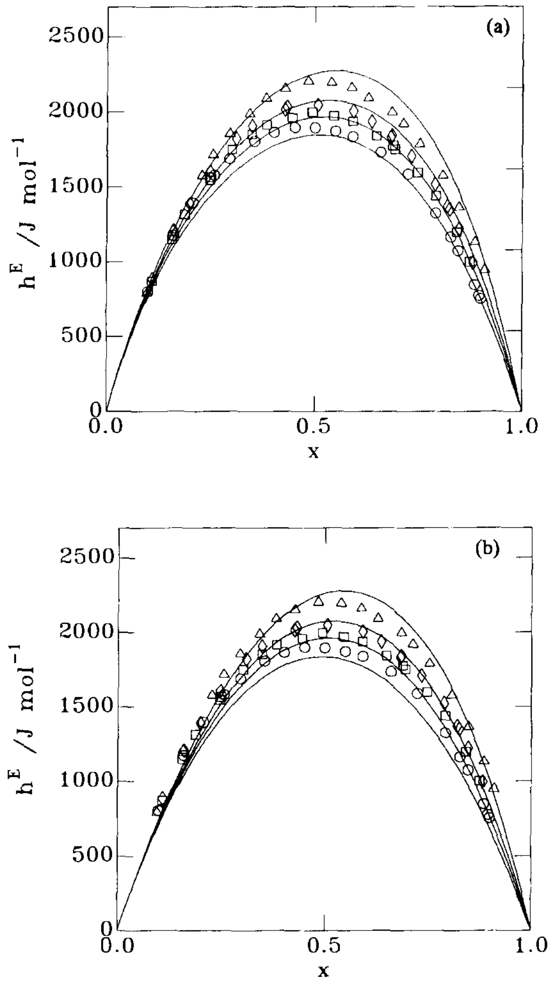

Fig. 3. Experimental excess molar enthalpies and theoretical predictions at 298.15 K of dimethyl carbonate + *n*-alkane against the mole fraction x of the linear carbonate. Theoretical predictions: (a), Larsen; (b), Gmehling. Experimental points: ○, hexane; □, heptane; ◇, octane; △, decane.

Tassios, Larsen and Gmehling versions respectively. Furthermore, for these models the parameters are independent of the carbonate length.

However, the DISQUAC model predicts reasonably well the liquid–liquid and solid–solid equilibria with the same set of parameters, and also the diminution of g^E with the temperature. In contrast, when the parameters determined in the present work for the Larsen version are used to calculate liquid–liquid equilibria and g^E temperature dependence, the predictions are poor. This fact could be due to the difficulty that the UNIFAC model (original and Larsen version) has in predicting the decrease in g^E when

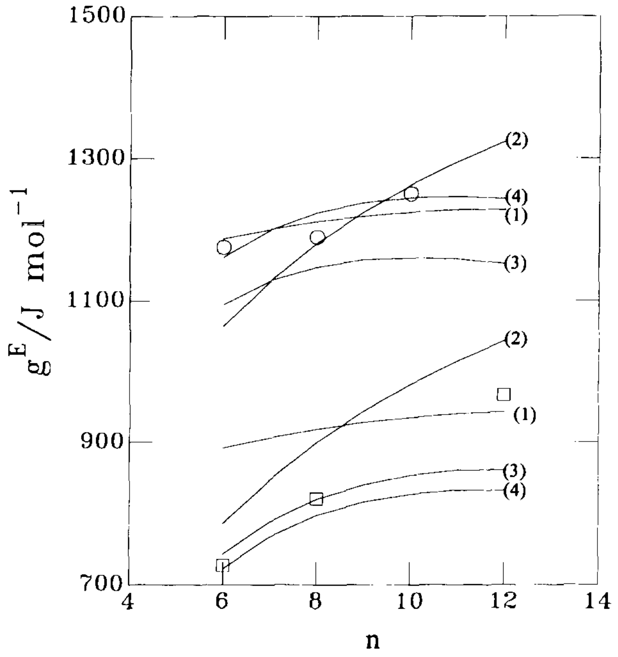

Fig. 4. Excess molar Gibbs energy g^E ($x = 0.5$) of dialkyl carbonate + n-alkane against n, the number of the carbon atoms of the alkane. Experimental points: ○, dimethyl carbonate; □, diethyl carbonate. Theoretical predictions: (1), Gmehling; (2), Larsen; (3), Kehiaian; (4), González.

Table 4
Geometrical parameters (Q_i) and interaction parameters (a'_{mn}) for organic carbonate + alkane for the Tassios model

Q_i	Subgroup	Main group	CH_2	O–CO–O	C–O–CO–O
0.848	CH_3				
		CH_2	0	105.1937	2.1343
0.540	CH_2				
1.120	O–CO–O	O–CO–O	39.0497	0	–
1.660	CH_3–O–CO–O				
		C–O–CO–O	59.1488	–	0
1.968	CH_2–O–CO–O				

the temperature increases, in the case of high g^E. We have also tried to fit only the g^E of the system dimethyl carbonate + heptane at four temperatures using several initializations, but no set of parameters was able to reproduce the experimental temperature dependence.

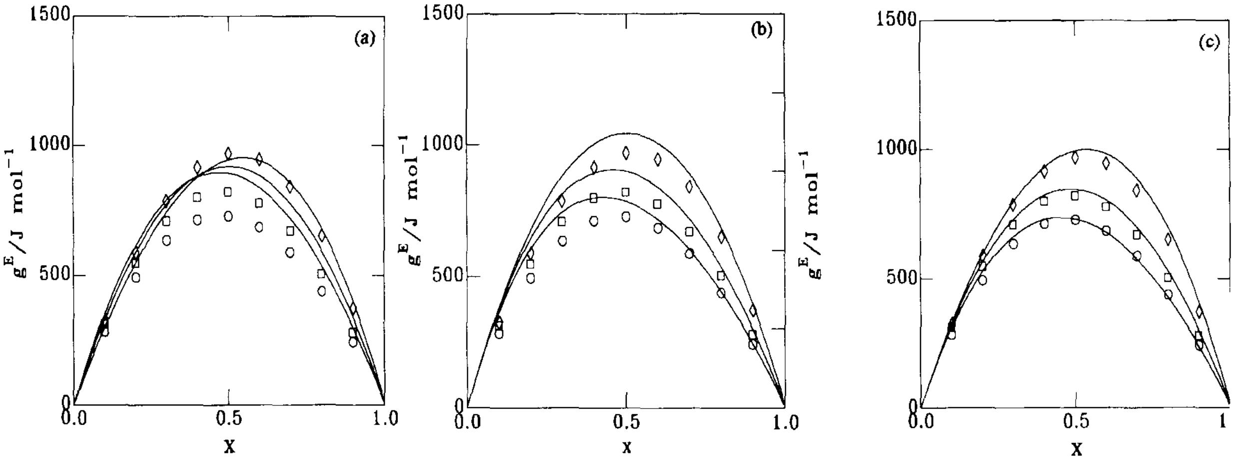

Fig. 5. Experimental excess molar Gibbs energy and theoretical predictions at 298.15 K of diethyl carbonate + *n*-alkane against the mole fraction *x* of the linear carbonate. Theoretical predictions: (a), Larsen; (b), Gmehling; (c), original UNIFAC. Experimental points: ○, hexane; □, octane; ◇, dodecane.

Table 5
Geometrical parameters (R_i) and interaction parameters ($a_{mn,i}$) for organic carbonate + alkane for the Larsen model

R_i	Subgroup	Main group	CH_2	O–CO–O
0.9011	CH_3		0	767.4093
		CH_2	0	0.1250
0.6744	CH_2		0	8.4611
			418.2082	0
1.2301	O–CO–O	O–CO–O	−38.6263	0
			−3998.7488	0

Table 6
Geometrical parameters (R_i) and (Q_i) and interaction parameters ($a_{mn,i}$) for organic carbonate + alkane for the Gmehling model

R_i	Q_i	Subgroup	Main group	CH_2	O–CO–O
0.6325	1.0608	CH_3		0	5788.9517
			CH_2	0	−35.1144
0.6325	0.7081	CH_2		0	0.0581
				1488.8469	0
2.0069	1.3890	O–CO–O	O–CO–O	−2.7981	0
				−0.0050	0

5. Conclusions

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

Quite recently, experimental h^E values of carbonate with cyclic ethers [23] or chloroalkanes [24] or ketones [25] have been published. The parameters determined in the present work would be useful in the determination of the interaction coefficients for the above systems. For all these systems, the UNIFAC parameters have not yet been reported. In the future, we will try to calculate these interaction coefficients.

Acknowledgments

The authors gratefully acknowledge financial support of Xunta de Galicia (XUGA 20605B93) and of DGICYT-Spain (PB94-1083-CO3-O2).

References

[1] I. Garcia, J.C. Cobos, J.A. González and C. Casanova, Int. DATA Ser. Sel. Data Mixtures Ser. A (1987) 164.

[2] I. Garcia, J.C. Cobos, J.A. González and C. Casanova, Int. DATA Ser. Sel. Data Mixtures Ser. A (1987) 245.

[3] I. Garcia, J.C. Cobos, J.A. González and C. Casanova and M.J. Cocero, J. Chem. Eng. Data, 33 (1988) 423.

[4] M.J. Cocero, J.A. González, I. Garcia, J.C. Cobos and F. Mato, Int. DATA Ser. Sel. Data Mixtures Ser. A, (1991) 112.

[5] M.J. Cocero, I. Garcia, J.A. González and J.C. Cobos, Fluid Phase Equilibria, 68 (1991) 151.

[6] M.J. Cocero, J.A. González, I. Garcia and J.C. Cobos, Int. DATA Ser. Sel. Data Mixtures Ser. A (1991) 158.

[7] J.A. González, I. Garcia, J.C. Cobos and C. Casanova, J. Chem. Eng. Data, 36 (1991) 162.

[8] H.V. Kehiaian, J.A. González, I. Garcia, J.C. Cobos, C. Casanova and M.J. Cocero, Fluid Phase Equilibria, 64 (1991) 1.

[9] H.V. Kehiaian, Pure Appl. Chem., 57 (1985) 15.

[10] J.A. González, I. Garcia, de la Fuente, J.C. Cobos, C. Casanova and H.V. Kehiaian, Thermochim. Acta, 217 (1993) 57.

[11] L. Negadi, A. Blondel, I. Mokbel, A. Ait-Kaci and J. Jose, Int. DATA Ser. Sel. Data Mixtures Ser. A 21(3) (1993) 169.

[12] J.M. Pico, C.P. Menaut, J. Fernández, J.L. Legido and M.I. Paz Andrade, J. Solut. Chem., 20 (1991) 115.

[13] J. Ortega, J.L. Legido, J. Fernández, L. Pías and M.I. Paz Andrade, Ber. Bunsen-Ges. Phys. Chem., 95 (1991) 128.

[14] A. Fredenslund, R.L. Jones and J.M. Prausnitz, AIchE. J., 21 (1975) 1086.

[15] W. Rupp. S. Hetzel, I. Ojini and D. Tassios, Ind. Eng. Chem. Process. Des. Dev., 23 (1984) 391.

[16] B.L. Larsen, P. Rasmussen and A. Fredenslund, Ind. Eng. Chem. Res., 26 (1987) 2274.

[17] L. Gmehling, J. Li and M. Schiller, Ind. Eng. Chem. Res., 26 (1993) 178.

[18] D.S. Abrams and J.M. Prausnitz, AIChE. J., 21 (1975) 16.

[19] E.A. Guggenheim, Mixtures, Clarendon Press, Oxford, London, 1952.

[20] I. Kikic, P. Alessi, P. Rasmussen and A. Fredeenslund, Can. J. Chem. Eng. Data, 58 (1980) 253.

[21] A. Bondi, J. Chem. Phys., 68 (1964) 441.

[22] D.W. Marquardt, J. Soc. Ind. Appl. Math., 11 (1963) 431.

[23] F. Comelli and R. Francesconi, J. Chem. Eng. Data, 40 (1995) 28.

[24] F. Comelli and R. Francesconi, J. Chem. Eng. Data, 40 (1995) 509.

[25] F. Comelli and R. Francesconi, J. Chem. Eng. Data, 40 (1995) 805.