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STUDY OF INITIAL- AND TRANSITION-STATE SOLVATION IN THE SOLVOLYSIS OF *tert*-BUTYL HALIDES IN ALCOHOLS FROM INFINITE DILUTION ACTIVITY COEFFICIENTS

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The Gibbs energies of activation of the solvolytic reactions of *tert*-butyl halides (chloride, bromide and iodide) in eight mono-alcohols and eight di-alcohols were dissected into contributions from the initial state and transition state. The unified approach proposed by Abraham was applied and the various factors making up the overall solvent effect in both states were identified and compared. To perform this study, the Gibbs energies of transfer of the initial state were calculated using the infinite dilution activity coefficient values of the solutes in the solvents, γ^{∞}. These values were determined from the UNIFAC group-contribution method, with the modified Flory–Huggins equation in the combinatorial term and with group interaction parameters from the Parameter Table exclusively based on experimental γ^{∞} data reported in the literature. It is concluded that solvent polarizability and polarity–HBD acidity and cavity effects during the activated process are mainly due to transition-state contributions.

INTRODUCTION

During the past decade, the use of linear solvation energy relationships for analysing the physico-chemical processes involving *tert*-butyl halides has become commonplace.[1–6] It is now clear that the solvolytic reactions are dominated by several interaction mechanisms, namely the non-specific solvent–solute interactions due to the polarizability and polarity of the solvent, specific solvent hydrogen bond acidity interactions and disruption and reorganization of solvent–solvent interactions in order to accommodate the solute.[3,4]

In spite of the significant improvements achieved by the use of a rigorous multi-parameter approach on the understanding of reaction mechanisms, there is always a difficulty related to the fact that the Gibbs energy of activation, $\Delta^{\ddagger}G$, is a composite quantity, the difference between the Gibbs energy of the transition state and that of the initial state.

In another approach to the study of solvent effects, log k or $\Delta^{\ddagger}G$ is dissected into contributions from the initial state and the transition state and solvent influences are compared and analysed for both states. The first systematic studies using this method were performed by Winstein and Fainberg[7] and Arnett *et al.*[8] for the solvolysis of 2-chloro-2-methylpropane (t-BuCl) in several binary mixtures. Abraham[9] applied this procedure to the solvolysis of t-BuCl in nine pure solvents (three mono-alcohols) and later, some dissections were carried out using the Gibbs energy of activation for the decomposition of *tert*-butyl chloride and bromide in aliphatic aprotic and hydroxylic solvents (water and six mono-alcohols).[10,11]

For a more detailed analysis of the solvent effect of hydroxylic solvents on the solvolysis of *tert*-butyl halides, by means of the initial-state and transition-state contributions, more observed rate constant values, k, and Gibbs energies of transfer of the initial state, δG_i, from a reference solvent to other solvents are needed.

The aim of this work was to extend the study of the solvent influences on the Gibbs functions of transfer for the activation process, initial state and transition state

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of the solvolysis of *tert*-butyl halides (chloride, bromide and iodide) in 16 hydroxylic solvents (eight mono-alcohols and eight di-alcohols), for which k values are known with adequate precision.[4]

Values for δG_i can be calculated through the equation[9,10]

$$\delta G_i = RT \ln(\gamma_j^\infty / \gamma_r^\infty) \qquad (1)$$

where γ_j^∞ and γ_r^∞ are the infinite dilution activity coefficients of the solute in the solvent j and in a reference solvent r, respectively.

The infinite dilution activity coefficients for the different solutes presented in this work were calculated using a predictive method: the UNIFAC group-contribution model.[12,13] According to this model, the logarithm of the activity coefficient for a component is assumed to be the sum of two contributions: a combinatorial term, essentially due to differences in size and shape of the molecules in the mixture, and a residual term, essentially due to energy interactions.

The combinatorial activity coefficients were calculated using the modified Flory–Huggins equation in the Staverman–Guggenheim combinatorial expression, as proposed by Kikic *et al.*[14] The group interaction parameters from the γ^∞ Parameter Table[15] were used in the calculations carried out in this work.

As a second aim of this work, the unified approach proposed by Abraham[11] was applied to the several Gibbs functions of transfer, making use of a three-parameter linear solvation-energy relationship,[3,4] in order to identify the dominant specific and non-specific solute–solvent–solvent interaction mechanisms in the initial state and the transition state.

RESULTS AND DISCUSSION

The Gibbs energies of activation presented in Table 1 were calculated from the rate constant data for the solvolytic reactions of *t*-BuCl, *t*-BuBr and *t*-BuI previously reported in a series of mono- and di-alcohols,[3,4] making use of the transition-state theory. From these values it is possible to effect a dissection of solvent influences on the solvolytic reactions into initial-state and transition-state contributions. In this context, infinite dilution activity coefficients play an important role.

Infinite dilution activity coefficients

The infinite dilution activity coefficients were calculated with the UNIVAC group-contribution model. This is a reliable and fast method for predicting liquid-phase activity coefficients in non-electrolyte, non-polymeric mixtures at low to moderate pressures and temperatures up to 425 K. The method was originally developed by Fredenslund *et al.*[12] The basic idea of the solution-of-groups method is to utilize existing phase equilibrium data for predicting phase equilibria of systems for which no data are available. The method entails the following: suitable reduction of experimentally obtained activity coefficient data to obtain parameters characterizing interactions between pairs of structural groups in non-electrolyte systems, and the use of these parameters to predict activity coefficients for other systems which have not been studied experimentally but contain the same functional groups. A 'group' is a convenient structural unit, such as CH_3, OH or CCl.[13] The molecules are built of groups.

Table 1. Gibbs energy of activation for the solvolytic reaction of *tert*-butyl halides at 25 °C (kJ mol^{-1})

		$\Delta^{\ddagger}G$		
No.	Solvent	*t*-BuCl	*t*-BuBr	*t*-BuI
1	Methanol	107·62	98·48	95·34
2	Ethanol	113·37	103·61	99·56
3	Propan-1-ol	114·86	104·07	100·76
4	Propan-2-ol	117·54	105·38	101·84
5	Butan-1-ol	115·94	105·04	101·27
6	Butan-2-ol	119·35	106·01	103·84
7	2-Methylpropan-1-ol	120·40	105·44	102·64
8	Pentan-1-ol	115·54	105·21	103·21
9	Ethane-1,2-diol	99·33	90·32	87·58
10	Propane-1,2-diol	104·47	96·02	93·34
11	Propane-1,3-diol	103·21	94·20	89·86
12	Butane-1,2-diol	108·07	99·10	96·76
13	Butane-1,3-diol	107·55	98·70	96·14
14	Butane-1,4-diol	107·21	97·39	94·77
15	Butane-2,3-diol	108·46	100·87	98·59
16	Pentane-1,5-diol	109·09	99·73	96·94

The logarithm of the activity coefficient is the sum of two contributions: a combinatorial ($\ln \gamma_i^C$), essentially due to differences in size and shape of the molecules in the mixture, and a residual ($\ln \gamma_i^R$), essentially due to energy interactions. The equations of the model are given in Table 2. The first term in the combinatorial expression is a Flory–Huggins term and the second term is a correction to the Flory–Huggins equation for the effect of molecular shape. The Flory–Huggins part of the Staverman–Guggenheim combinatorial can be modified, as shown in Table 2. The second part is unchanged.[14]

Three different types of tables, with group-interaction parameters, have been published: the VLE (vapour–liquid equilibrium) Parameter Table,[16–20] the LLE (liquid–liquid equilibrium) Parameter Table[21] and the γ^∞ (infinite dilution activity coefficients) Parameter Table,[15] depending on the type of experimental data used for the parameter estimation.

In this work, for the combinatorial term we used the modified Flory–Huggins equation in the Staverman–Guggenheim expression,[14] and for the residual term we used group-interaction parameters from the γ^∞ table.[15] This allows us to predict γ^∞ with a much higher accuracy than that obtained with the original athermal Flory–Huggins equation and with the interaction parameters from either the VLE or the LLE Parameter Table.

The typical average error for the families of compounds involved in this work is less than 7·4% with γ^∞ parameters and around 11·7% with VLE parameters.[22]

Table 2. Equations for the UNIFAC group-contribution method

$$\ln \gamma_i = \ln \gamma_i^{\mathrm{C}} + \ln \gamma_i^{\mathrm{R}}$$

$$\ln \gamma_i^{\mathrm{C}} = [\ln(\omega_i/x_i) + 1 - \omega_i/x_i] - 5{\cdot}0 q_i [\ln(\phi_i/\theta_i) + 1 - \phi_i/\theta_i]$$

Original term: $$\omega_i = \phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \qquad j = 1, N$$

$$\theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \qquad j = 1, N$$

Modified Flory–Huggins term: $$\omega_i = \frac{x_i r_i^{2/3}}{\sum_j x_j r_j^{2/3}} \qquad j = 1, N$$

$$r_i = \sum_k \nu_{ki} R_k \qquad q_i = \sum_k \nu_{ki} Q_k \qquad k = 1, NG$$

$$\ln \gamma_i^{\mathrm{R}} = \sum_k \nu_{ki} (\ln \Gamma_k - \ln \Gamma_k^i)$$

$$\ln \Gamma_k = Q_k \left[1 - \ln\left(\sum_m \Theta_m \Psi_{mk} \right) - \sum_m \frac{\Theta_m \Psi_{km}}{\sum_n \Theta_n \Psi_{nm}} \right]$$

$$k = 1, NG; \; m, n = 1, NG$$

$$\Psi_{nm} = \exp(-a_{nm}/T) \qquad \Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \qquad X_m = \frac{\sum_j \nu_{mj} x_j}{\sum_j \sum_n \nu_{nj} x_j}$$

Definitions:

ω_i	modified molecular volume fraction
ϕ_i	molecular volume fraction
θ_i	molecular surface area fraction
x_i	liquid-phase mole fraction of component i
r_i	molecular volume of component i
q_i	surface area of component i
ν_{ki}	number of groups of kind k in molecule i
R_k	volume of group k
Q_k	surface area of group k
N	total number of components
NG	total number of functional groups
Γ_k	residual activity coefficient of group k in a solution
Γ_k^i	residual activity coefficient of group k in a reference solution containing only molecules of type i
a_{nm}	interaction parameter between group n and group m
Θ_m	group surface area fraction
X_m	group fraction

In this work we were not able to calculate the γ^∞ values for *t*-BuBr and *t*-BuI in methanol, because there are no available parameters between the groups bromide (Br) or iodide (I) and methanol (CH_3OH). Regarding the γ^∞ of the three solutes in ethane-1,2-diol, we used the interaction parameters for the group alcohol (OH), instead of considering this solvent as a single group, as usually advised.[15,17] This is because the relevant parameters for the diol group are not available.

Values of γ^∞ for the various solutes in the mentioned solvents are summarized in Table 3.

Transfer Gibbs energies

Table 4 gives the calculated Gibbs energies of transfer for the activation process, $\delta\Delta^{\ddagger}G$, the initial-state, δG_{i}, and the transition-state, δG_{t}, based on ethanol as the reference solvent. These values were obtained through equations (1) and (2). Equation (2) relates the three types of transfer Gibbs energies under study:

$$\delta G_{\mathrm{t}} = \delta G_{\mathrm{i}} + \Delta^{\ddagger}G_j - \Delta^{\ddagger}G_r = \delta G_{\mathrm{i}} + \delta\Delta^{\ddagger}G \qquad (2)$$

From the data in Table 4, it is difficult to conclude that, in general, $\delta\Delta^{\ddagger}G$ values in alcoholic solvents tend to be mainly associated with the corresponding functions of transfer for the initial state or the transition state. However, if mono- and di-alcohols are considered separately, we may say that, for solvent changes from ethanol, the solvation of the activated complex of the solvolytic reactions of *tert*-butyl halides in di-alcohols is much more important than the solvation of the

Table 3. Infinite dilution activity coefficients for *tert*-butyl halides in alcohols at 25 °C

		γ^∞		
No.	Solvent	*t*-BuCl	*t*-BuBr	*t*-BuI
1	Methanol	19·93	—	—
2	Ethanol	3·68	7·37	8·90
3	Propan-1-ol	2·64	4·67	5·70
4	Propan-2-ol	2·64	4·67	5·68
5	Butan-1-ol	2·13	3·47	4·27
6	Butan-2-ol	2·13	3·47	4·26
7	2-Methylpropan-1-ol	2·13	3·37	4·26
8	Pentan-1-ol	1·83	2·80	3·48
9	Ethane-1,2-diol	10·55	31·40	36·02
10	Propane-1,2-diol	6·31	15·82	18·37
11	Propane-1,3-diol	6·30	15·76	18·36
12	Butane-1,2-diol	4·43	9·82	11·55
13	Butane-1,3-diol	4·43	9·82	11·55
14	Butane-1,4-diol	4·42	9·80	11·55
15	Butane-2,3-diol	4·43	9·85	11·56
16	Pentane-1,5-diol	3·41	6·90	8·22

Table 4. Gibbs energy of transfer from ethanol to other solvents of *tert*-butyl halides solvolysis in alcohols at 25 °C (kJ mol^{-1})

	$\delta\Delta^{\ddagger}G$[a]			δG_i[b]			δG_t[c]		
No.[d]	*t*-BuCl	*t*-BuBr	*t*-BuI	*t*-BuCl	*t*-BuBr	*t*-BuI	*t*-BuCl	*t*-BuBr	*t*-BuI
1	−5·76	−5·14	−4·22	4·19	—	—	−1·57	—	—
2	0	0	0	0	0	0	0	0	0
3	1·48	0·46	1·20	−0·82	−1·13	−1·11	0·66	−0·67	0·09
4	4·17	1·77	2·28	−0·82	−1·13	−1·11	3·35	0·64	1·17
5	2·57	1·43	1·71	−1·35	−1·87	−1·82	1·22	−0·44	−0·11
6	5·88	2·40	4·28	−1·35	−1·87	−1·83	4·53	0·53	2·46
7	7·02	1·83	3·08	−1·35	−1·87	−1·83	5·67	−0·04	1·26
8	2·17	1·60	3·65	−1·73	−2·40	−2·33	0·44	−0·80	1·32
9	−14·04	−13·30	−11·99	2·61	3·59	3·46	−11·43	−9·71	−8·52
10	−8·90	−7·59	−6·22	1·34	1·89	1·80	−7·56	−5·70	−4·43
11	−10·16	−9·42	−9·70	1·34	1·88	1·79	−8·82	−7·53	−7·91
12	−5·67	−4·51	−2·80	0·46	0·71	0·64	−5·21	−3·80	−2·15
13	−5·82	−4·91	−3·42	0·46	0·71	0·64	−5·36	−4·20	−2·78
14	−6·16	−6·22	−4·79	0·46	0·71	0·64	−5·70	−5·52	−4·15
15	−4·91	−2·74	−0·97	0·46	0·72	0·65	−4·44	−2·02	−0·32
16	−4·28	−3·88	−2·26	−0·18	−0·16	−0·20	−4·46	−4·04	−2·46

[a] Transfer Gibbs energy of activation obtained from data in Ref. 4.
[b] Transfer Gibbs energy of initial state.
[c] Transfer Gibbs energy of transition state.
[d] Numbers of solvents as in Table 1.

substrate. This behaviour confirms previous suggestions[23] that the number of OH groups in the solvent molecule is an important factor in order to stabilize the transition state. In fact, δG_t for di-alcohols is always high and negative (as happens with $\delta\Delta^{\ddagger}G$). Conversely, δG_i is generally smaller and positive, no doubt owing to the weak hydrogen-bonding interactions between solvent and substrate (for pentane-1,5-diol, δG_i is negative for the three *tert*-butyl halides; however, the values are too small to allow any relevant conclusion).

The Gibbs energies of transfer for the initial state of our reactions in mono-alcohols are negative except for methanol. This is in accordance with previous observations.[10] As stated before, the solvent effect of methanol on the Gibbs energy of the substrate *t*-BuCl is large[10] and this can be understood in terms of the structured molecular behaviour of this solvent. Values of δG_t in mono-alcohols tend to be positive, although several exceptions can be pointed out.

An analysis of substrate effects on the Gibbs energies of transfer (Table 4) shows a strong regularity of behaviour when di-alcohols are used as solvents: $\delta\Delta^{\ddagger}G$, δG_i and δG_t increase from *t*-BuCl to *t*-BuBr and from this substrate to *t*-BuI. Some discrepancies are of small magnitude and, probably, of the same order as the errors affecting the transfer energies.

A similar analysis involving mono-alcohols leads to a different conclusion: $\delta\Delta^{\ddagger}G$, δG_i and δG_t tend to decrease from the chloride to the bromide and to increase from the bromide to the iodide. We think that for di-alcohols the solvent structure and its particular interaction with the substrate and with the activated complex dominate over the polarity effect of these molecular species, measured by its dipole moment, μ [μ(*t*-BuCl) = 2·14 D, μ(*t*-BuBr) = 2·21 D and μ(*t*-BuI) = 2·20 D]. Conversely, for mono-alcohols the effect of the substrate and activated complex polarity have a marked influence on the solvent–solute interaction mechanisms.

The unified approach

Solvent effects on rate constants can be further analysed by combining the two main approaches, the dissection of solvent effects into contributions from the initial state and the transition state and the study of the same effects using empirical solvent parameters and multiple linear correlations. In this unified approach, proposed by Abraham,[11] the Gibbs energies of activation, for instance, are first separated into initial-state and transition-state values and then $\delta\Delta^{\ddagger}G$, δG_i and δG_t are analysed through a suitable correlation equation.

With respect to the solvolytic reactions and the solution processes of *tert*-butyl halides in hydroxylic solvents, we have shown before[3–6] that the application of equation (3) allows us to identify the dominant solute–solvent–solvent interactions:

$$X = a_0 + a_1 f(\varepsilon) + a_2 g(\eta) + a_3 E_T^N + a_4 C \qquad (3)$$

where X is a physico-chemical property dependent on the solvent, $f(\varepsilon) = (\varepsilon - 1)/(2\varepsilon + 1)$ is the Kirkwood function, $g(\eta) = (\eta^2 - 1)/(\eta^2 + 2)$, where η represents the refractive index, $E_{\mathrm{T}}^{\mathrm{N}}$ is the normalized Dimroth and Reichardt parameter and C is the cohesive energy density.

The results of the application of equation (3) to the transfer Gibbs energies of the activation process, initial state and transition state show that the a_1 coefficient has no statistical meaning. Details of the statistically preferred regression expressions:

$$X = a_0 + a_2 g(\eta) + a_3 E_{\mathrm{T}}^{\mathrm{N}} + a_4 C \qquad (4)$$

are given in Table 5. The values of the solvent parameters are listed in Table 2 in Ref. 4. The noncollinearity assumption between any two of the chosen parameters was tested previously and no relevant linear correlations were observed.[3]

The use of uniparametric relationships relating the transfer energies and one of the empirical parameters of solvent polarity shown in equation (3) has no relevant statistical meaning, except where the use of the $E_{\mathrm{T}}^{\mathrm{N}}$ variable is concerned. However, even in the most favourable plots (those involving the dependent variable δG_{i}), the final decision about the best fit, which was achieved by reference to the Ehrenson's criterion,[24] was always equation (4) at a confidence level $\geqslant 96{\cdot}3\%$.

A comparison of correlations A–F with G–J and K–N (Table 5) shows conclusively that all the various factors making up the overall solvent effect [polarizability, dipolarity–HBD acidity and disruption–reorganization, measured by $g(\eta)$, $E_{\mathrm{T}}^{\mathrm{N}}$ and C, respectively] which dominate the activation process are mainly due to transition-state contributions. In fact, the coefficients affecting each dependent variable in the $\delta\Delta^{\ddagger}G$ and δG_{t} correlations show the same sign and are almost of the same order of magnitude. Conversely, the coefficients a_0–a_4 for $\delta\Delta^{\ddagger}G$ and δG_{i} correlations always show opposite numerical signs. A previous study on *t*-BuCl solvolysis, although in a different set of solvents, led to similar conclusions.[11] However, we must point out that this global analysis makes the conclusions about the particular, and sometimes opposite, effects of mono- and di-alcohols observed in this work ambiguous.

CONCLUSIONS

Solvent effects on the Gibbs energies of transfer from ethanol for the initial state and transition state of the solvolysis of *tert*-butyl halides in mono- and di-alcohols were analysed in terms of the contributions to the transfer Gibbs energy of the activated process. It was shown that the solvation of the activated complex in di-alcohols is more important than that in mono-alcohols and is dominant when compared with the solvation of the substrate. We must point out that in these media there is evidence that the *tert*-butyl halides undergo $\mathrm{S_N}$I solvolysis, which means that no significant changes in the nature of the transition state should be expected.

Substrate effects on the Gibbs energies of transfer were also analysed and discussed in terms of the dipole moment of the *tert*-butyl halide molecules and the solvent structure.

Considering the application of the unified approach to the several Gibbs energies of transfer, we were able to perform a meaningful multiple regression analysis. The application of this approach shows that, in general, the solute–solvent interactions, on account of the polarizability and polarity–HBD acidity properties of the solvent, and the solvent–solvent interactions, on account of the cavity effect, during the activated process are mainly due to transition-state effects.

Table 5. Correlations of Gibbs energy of transfer from ethanol to other solvents at 25 °C (kJ mol^{-1})

$$X = a_0 + a_2 g(\eta) + a_3 E_{T}^{\mathrm{N}} + a_4 \times 10^{-3} C$$

X	Substrate	Correlation	a_0	a_2	a_3	a_4	r[a]	σ[b]	N[c]
$\delta\Delta^{\ddagger}G$	*t*-BuCl	A	62·116	−100·20	−55·602	−5·6595	0·982	1·28	16
		B	62·802	−105·08	−54·564	−5·8519	0·982	1·33	15
	t-BuBr	C	45·452	−89·823	−28·002	−12·200	0·976	1·13	16
		D	46·409	−96·637	−26·551	−12·469	0·976	1·17	15
	t-BuI	E	43·979	−74·696	−28·927	−13·031	0·974	1·20	16
		F	38·471	−57·587	−24·306	−16·109	0·969	1·36	15
δG_{i}	*t*-BuCl	G	−5·0993	−23·110	14·866	2·0878	0·943	0·59	16
		H	−9·1493	5·7297	8·7289	3·2257	0·951	0·43	15
	t-BuBr	I	−13·100	9·7849	12·211	4·3344	0·951	0·60	15
	t-BuI	J	−12·472	8·4608	11·821	4·2232	0·951	0·57	15
δG_{t}	*t*-BuCl	K	57·013	−123·30	−40·728	−3·5768	0·980	1·11	16
		L	53·646	−99·323	−45·830	−2·6308	0·982	1·10	15
	t-BuBr	M	33·313	−86·886	−14·338	−8·1301	0·967	0·92	15
	t-BuI	N	28·623	−45·652	−21·479	−8·0097	0·958	1·07	15

[a] Correlation coefficient.

[b] Standard deviation of the fit.

[c] Number of points used in the regression analysis.

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REFERENCES

1. M. H. Abraham, R. M. Doherty, M. J. Kamlet, J. M. Harris and R. W. Taft, *J. Chem. Soc., Perkin Trans. 2* 913 (1987).
2. M. H. Abraham, P. L. Grellier, J.-L. M. Abboud, R. M. Doherty and R. W. Taft, *Can. J. Chem.* **66**, 2673 (1988).
3. R. M. C. Gonçalves, A. M. N. Simões and L. M. P. C. Albuquerque, *J. Chem. Soc., Perkin Trans. 2* 1379 (1990).
4. R. M. C. Gonçalves, A. M. N. Simões and L. M. P. C. Albuquerque, *J. Chem. Soc., Perkin Trans. 2* 825 (1991).
5. R. M. C. Gonçalves, A. M. N. Simões, R. A. S. E. Leitão and L. M. P. C. Albuquerque, *J. Chem. Res.* (*S*) 330 (1992); (*M*) 2701 (1992).
6. R. M. C. Gonçalves, L. M. P. C. Albuquerque, F. E. L. Martins, A. M. N. Simões and J. J. Moura Ramos, *J. Phys. Org. Chem.* **5**, 93 (1992).
7. S. Winstein and A. H. Fainberg, *J. Am. Chem. Soc.* **79**, 5937 (1957).
8. E. M. Arnett, W. G. Bentrude, J. J. Burke and P. McC. Duggleby, *J. Am. Chem. Soc.* **87**, 1541, 2048 (1965).
9. M. H. Abraham, *J. Chem. Soc. B* 299 (1971).
10. M. H. Abraham, *J. Chem. Soc., Perkin Trans. 2* 1343 (1972).
11. M. H. Abraham, *Pure Appl. Chem.* **57**, 1055 (1985).
12. Aa. Fredenslund, R. Jones and J. M. Prausnitz, *AIChE J.* **21**, 1086 (1975).
13. Aa. Fredenslund, J. Gmehling and P. Rasmussen, *Vapor–Liquid Equilibria Using UNIFAC*, Elsevier, Amsterdam (1977).
14. I. Kikic, P. Alessi, P. Rasmussen and Aa. Fredenslund, *Can. J. Chem. Eng.* **58**, 253 (1980).
15. J. C. Bastos, M. E. Soares and A. G. Medina, *Ind. Eng. Chem. Res.* **27**, 1269 (1988).
16. S. Skjold-Jørgensen, B. Kolbe, J. Gmehling and P. Rasmussen, *Ind. Eng. Chem., Process Des. Dev.* **18**, 714 (1979).
17. J. Gmehling, P. Rasmussen and Aa. Fredenslund, *Ind. Eng. Chem., Process Des. Dev.* **21**, 118 (1982).
18. E. A. Macedo, U. Weidlich, J. Gmehling and P. Rasmussen, *Ind. Eng. Chem., Process Des. Dev.* **22**, 676 (1983).
19. D. Tiegs, J. Gmehling, P. Rasmussen and Aa. Fredenslund, *Ind. Eng. Chem. Res.* **26**, 159 (1987).
20. H. K. Hansen, P. Rasmussen, Aa. Fredenslund, M. Schiller and J. Gmehling, *Ind. Eng. Chem. Res.* **30**, 2352 (1991).
21. T. Magnussen, P. Rasmussen and Aa. Fredenslund, *Ind. Eng. Chem., Process Des. Dev.* **20**, 331 (1981).
22. J. C. Bastos, PhD Thesis, University of Porto (1987).
23. R. M. C. Gonçalves, A. M. N. Simões, L. M. P. C. Albuquerque and S. J. Formosinho, *J. Chem. Soc., Perkin Trans. 2* 931 (1991).
24. E. Ehrenson, *J. Org. Chem.* **44**, 1793 (1979).