Analysis of the relationship between ternary mixtures and their binary sub-systems as represented by the UNIQUAC and NRTL models

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Abstract

The second derivative of the Gibbs free energy of mixing, G_{11}, was calculated for the binary mixtures water + alcohol and solvent + alcohol (alcohol is methanol or ethanol, solvent is *n*-amyl acetate, iso-amyl acetate, hexyl acetate or 1-octanol) using, for G, binary UNIQUAC and NRTL equations with interaction parameters obtained by fitting the corresponding ternary equations to liquid–liquid equilibrium data for the ternary systems water + alcohol + solvent. Apart from the usual result that the binary interaction parameters of the UNIQUAC and NRTL equations, and the corresponding thermodynamic descriptions of binaries in terms of G_{11}, depend heavily on the system from which they have been obtained (which should be borne in mind when using the binary parameters in calculations for multicomponent systems), the chief conclusion of this work is that the UNIQUAC and NRTL models do not imply any consistent relationship between the slopes of the ternary tie-lines and the characteristics of the G_{11} of the corresponding homogeneous binary mixtures.

Keywords: Gibbs energy; LLE; NRTL; UNIQUAC

1. Introduction

A liquid mixture is completely described thermodynamically if the molar Gibbs free energy of mixing, G^M, is given as a function of the composition of the mixture. G^M can be

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considered as the sum of two terms: the ideal contribution G^{M*}

$$G^{M*}/(RT) = \sum_{i=1}^{N} x_i \ln x_i \tag{1}$$

where N is the number of components in the mixture and x_i is the mole fraction of component i; and the excess contribution

$$G^{E}/(RT) = \sum_{i=1}^{N} x_i \ln \gamma_i \tag{2}$$

where γ_i is the activity coefficient of component i. Numerous models have been put forward for the composition dependence of G^E, two of the foremost being the UNIQUAC [1] and NRTL [2] equations. The chief distinguishing features of these two models are that they were both developed from thermodynamical considerations, and that both essentially involve only binary interaction parameters, even when applied to multicomponent mixtures.

If the assumption that ternary and higher-order interactions are negligible or irrelevant to the thermodynamic properties of liquid mixtures was strictly true, then knowledge of binary interaction parameters obtained from experimental data of binary mixtures would allow satisfactory prediction of the properties of multicomponent systems. Furthermore, binary interaction parameters obtained by fitting a UNIQUAC or NRTL model to experimental liquid–liquid equilibrium (LLE) data for ternary or higher-order mixtures would coincide with those obtained from data for binary mixtures. In practice, it is found that binary interaction parameters obtained from binary data generally do not allow satisfactory prediction of ternary properties, and that in general they do not coincide with binary interaction parameters obtained from ternary LLE data, which depend heavily on the identity of the third component of the ternary mixture. One way of highlighting the discrepancy is to calculate, for a single binary mixture, several sets of activity coefficients, each set being calculated using binary interaction parameters obtained by fitting the model to a different ternary system of which the binary forms part; in general there is considerable dispersion among the sets of activity coefficients thus obtained [3,4].

Largely on the basis of simulations carried out using the modified Wilson model of G^E, Novák et al. [3] put forward rough rules-of-thumb intended to allow qualitative prediction of the behaviour of ternary systems given knowledge of the mutual solubilities and non-idealities of the component binaries, non-ideality being discussed, for each binary, in terms of the shape and location of the function

$$G_{11} = \partial^2 [G^M/(RT)]/\partial x_1^2 = 1/x_1 x_2 + \partial^2 [G^E/(RT)]\partial x_1^2 \tag{3}$$

Certain results suggest that the NRTL model also leads to Novák et al.'s rules, at least in part; for example, the immiscible regions calculated for ternary systems using various sets of binary parameters obtained from binary data with different values of the NRTL non-randomness parameter, do not differ markedly provided each homogeneous binary remains fairly close to ideal, i.e. with a minimum value of $G_{11} > 2$ [5,6]. Again, the tie-lines of the ternary diagram slope down towards the side representing the less ideal homogeneous binary, i.e. the one with the lower minimum of G_{11}. Similar studies

cannot be carried out for the UNIQUAC equation, which unless its structural parameters are treated as optimizable, has only two adjustable parameters for each binary. An alternative procedure for investigation of these issues is available: fitting the model to LLE data for various ternary mixtures, and comparing the fitted binodal curves and predicted tie-lines with the variation in the calculated binary interaction parameters or the G_{11} calculated from these parameters. The same approach must be used with the NRTL equation if the non-randomness parameter is treated as a constant.

This was the approach adopted in this research, in which, in continuance of previous work [7], the UNIQUAC and NRTL equations were fitted to LLE data for two series of ternary mixtures (water + methanol + solvent and water + ethanol + solvent), and the binary interaction parameters thus obtained were used to calculate G_{11} curves for the homogeneous binaries. Our aims were to examine: (1) whether the UNIQUAC and NRTL equations, with binary interaction parameters obtained from ternary LLE data, afford G_{11} equations with the same minima and symmetry; (2) the effects (on G_{11}) of varying the NRTL non-randomness parameter and optimizing, for each specific ternary mixture, the UNIQUAC structural parameters; and (3) whether the G_{11} curves obtained comply with Novák et al.'s rule D, i.e. whether the tie-lines of the ternary diagram slope down towards the side representing the homogeneous binary with the lower minimum of G_{11}.

2. Methods

Correlation of ternary LLE data with the UNIQUAC and NRTL equations was carried out using a computer program written by Sørensen [8]. For each ternary mixture, three NRTL equations were fitted, one for each of the three most commonly used values of the non-randomness parameter (0.1, 0.2 and 0.3). Similarly, two UNIQUAC equations were fitted: one using "universal" values of the structural parameters r and q taken from the literature [9], and one using values of r and q obtained for each specific ternary system as part of the overall fitting process by minimization of deviation in composition and relative deviation in the solute distribution ratio ("system-specific" values, see Ref. [10] for more details). Table 1 lists the ternary systems considered and the corresponding pairs of homogeneous binary mixtures. All experimental data used were obtained at 25°C, and all calculations were carried out for this temperature.

3. Results

Table 2 lists the system-specific values r and q used in fitting the UNIQUAC equations, together with the usual universal values. Table 3 lists the sets of binary interaction parameters calculated for each system. Fig. 1 shows the LLE data and tie-lines for the systems studied, and Figs. 2 and 3 show the corresponding G_{11} curves calculated using, respectively, the *NRTL and UNIQUAC equations*.

3.1. Comparison of the UNIQUAC and NRTL versions of G_{11}

Figs. 2 and 3 show that the NRTL and UNIQUAC versions of G_{11} appear to differ randomly as regards their shape, their minima and the compositions at which the

Table 1
Ternary systems studied and the corresponding homogeneous binary mixtures

Ternary system			Binary sub-systems
Water(1) + ethanol(2) + n-amyl acetate(3)			Water + ethanol
(W)	(E)	(nAA)	Ethanol + n-amyl acetate
Water(1) + ethanol(2) + iso-amyl acetate(3)			Water + ethanol
(W)	(E)	(iAA)	Ethanol + iso-amyl acetate
Water(1) + ethanol(2) + hexyl acetate(3)			Water + ethanol
(W)	(E)	(HA)	Ethanol + hexyl acetate
Water(1) + ethanol(2) + 1-octanol(3)			Water + ethanol
(W)	(E)	(O)	Ethanol + 1-octanol
Water(1) + methanol(2) + n-amyl acetate(3)			Water + methanol
(W)	(M)	(nAA)	Methanol + n-amyl acetate
Water(1) + methanol(2) + iso-amyl acetate(3)			Water + methanol
(W)	(M)	(iAA)	Methanol + iso-amyl acetate
Water(1) + methanol(2) + hexyl acetate(3)			Water + methanol
(W)	(M)	(HA)	Methanol + hexyl acetate
Water(1) + methanol(2) + 1-octanol(3)			Water + methanol
(W)	(M)	(O)	Methanol + 1-octanol

minima occur. Most of these G_{11} curves are of type A, i.e. convex over the whole range of composition, but several of those for mixtures containing ethanol are of type B, i.e. there are composition ranges in which these curves are concave, though without maxima. The most marked example of the latter behavior is the G_{11} curve for ethanol + water calculated from the NRTL equation using a non-randomness value of 0.1 and binary interaction parameters obtained from the ternary system ethanol + water + n-amyl acetate.

For mixtures with ethanol, the use of system-specific structural parameters in the UNIQUAC equation afforded G_{11} curves that were slightly higher and more symmetric than those obtained using the universal structural parameters. No such consistent pattern is shown by the curves for the mixtures with methanol.

3.2. Prediction of tie-line slope

The slope of the tie-lines of the ternary mixture water + ethanol + n-amyl acetate was not correctly predicted by the G_{11} curves calculated using the binary parameters of any of the three NRTL equations or the two UNIQUAC equations that were fitted. The NRTL equation likewise failed to allow prediction of tie-line slope for water + ethanol + iso-amyl acetate and water + ethanol + hexyl acetate, and the UNIQUAC equation failed for water + ethanol + 1-octanol, water + methanol + n-amyl acetate and water + methanol + 1-octanol. However, both models correctly predicted the tie-line slope for water + methanol + iso-amyl acetate and water + methanol + hexyl acetate.

Table 2
Universal and system-specific UNIQUAC structural parameters employed

Ternary system	Component	Universal		System-specific	
		r	q	r	q
W + E + nAA	Water	0.92	1.40	1.104	1.120
	Ethanol	2.11	1.97	2.110	1.970
	n-amyl ac.	5.5018	4.736	5.5018	4.736
W + M + nAA	Water	0.92	1.40	0.92	1.680
	Methanol	1.4311	1.432	1.4311	1.432
	n-amyl ac.	5.5018	4.736	5.5018	4.736
W + E + iAA	Water	0.92	1.40	0.736	1.680
	Ethanol	2.11	1.97	2.110	1.970
	iso-amyl ac.	5.5018	4.732	5.5018	4.732
W + M + iAA	Water	0.92	1.40	0.552	1.400
	Methanol	1.4311	1.432	1.7171	1.432
	iso-amyl ac.	5.5018	4.732	5.5018	4.732
W + E + HA	Water	0.92	1.40	0.736	1.400
	Ethanol	2.11	1.97	2.110	1.970
	Hexyl ac.	6.1762	5.276	6.1762	5.276
W + M + HA	Water	0.92	1.40	0.736	0.840
	Methanol	1.4311	1.432	1.1448	1.718
	Hexyl ac.	6.1762	5.276	6.1762	5.276
W + E + O	Water	0.92	1.40	0.736	1.400
	Ethanol	2.11	1.97	1.266	1.970
	1-Octanol	6.6219	5.286	6.6219	5.826
W + M + O	Water	0.92	1.40	1.104	0.84
	Methanol	1.4311	1.97	1.4311	0.9592
	1-Octanol	6.6219	5.826	6.6219	5.826

3.3. Influence of the NRTL non-randomness and UNIQUAC structural parameters

The value of the non-randomness parameter hardly affected the G_{11} curves calculated from the NRTL equation for binaries containing ethanol, although it may be noted that the lowest values of G_{11} for these mixtures were always obtained with $\alpha = 0.3$ (except for the binaries of the ternary mixture containing octanol, for which the optimization procedure failed to converge for this value of the non-randomness). The differences between the curves obtained with $\alpha = 0.3$ and the others were more pronounced for the mixtures containing methanol, especially when the binary parameters had been obtained from ternary mixtures containing amyl acetate.

4. Discussion

The G_{11} curves obtained above, and the corresponding predictions of ternary tie-lines, depend in general on which model is used, and on the specific values of the

Table 3

NRTL and UNIQUAC binary interaction parameters calculated from the experimental ternary data

Ternary system	Binary sub-systems	i–j	a_{ij} (K)				
			NRTL			UNIQUAC	
			$\alpha = 0.1$	$\alpha = 0.2$	$\alpha = 0.3$	Universal r and q	Optimized r and q
W(1) + E(2) + nAA(3)	W + E	1–2	2227.0	994.54	436.30	−152.36	−337.98
		2–1	−1171.0	−435.99	116.63	−303.92	−220.07
	E + nAA	2–3	−827.02	−75.55	246.70	222.19	−92.46
		3–2	1469.7	375.56	254.34	−512.71	−423.43
W(1) + M(2) + nAA(3)	W + M	1–2	−1250.3	521.64	1262.1	−822.93	−696.89
		2–1	1394.6	−586.53	−121.92	477.95	−68.87
	M + nAA	2–3	25.90	634.19	633.38	−195.93	−230.93
		3–2	−104.74	−396.57	−1390.5	69.19	116.54
W(1) + E(2) + iAA(3)	W + E	1–2	76.925	159.01	560.45	127.44	8.11
		2–1	164.88	197.54	32.54	−357.97	−397.56
	E + iAA	2–3	−706.32	−342.25	202.96	74.81	496.06
		3–2	1207.4	812.01	314.89	−338.45	−275.12
W(1) + M(2) + iAA(3)	W + M	1–2	−1404.8	637.82	−890.73	959.91	−399.93
		2–1	1422.4	−663.37	−174.95	449.03	−473.07
	M + iAA	2–3	79.05	627.94	621.01	−118.90	−112.20
		3–2	−230.59	−362.77	−984.88	403.90	183.66
W(1) + E(2) + HA(3)	W + E	1–2	−136.45	836.55	474.30	510.0	−61.47
		2–1	206.52	−353.79	99.34	−356.23	−170.83
	E + HA	2–3	−745.39	52.02	351.55	98.27	−213.35
		3–2	1039.7	219.51	196.01	−171.93	408.06
W(1) + M(2) + HA(3)	W + M	1–2	−839.50	758.08	−233.52	800.25	−807.26
		2–1	678.59	−603.39	−59.35	−369.57	391.13
	M + HA	2–3	202.14	797.56	618.31	−61.03	−138.30
		3–2	−180.60	−322.41	−318.71	398.33	−228.06
W(1) + E(2) + O(3)	W + E	1–2	1724.1	1047.7	NC	−24.175	511.27
		2–1	−847.24	−334.67	NC	12.409	−176.22
	E + O	2–3	423.39	325.01	NC	536.07	−112.48
		3–2	−59.85	72.98	NC	−471.70	459.25
W(1) + M(2) + O(3)	W + M	1–2	851.03	NC	NC	−191.98	−323.64
		2–1	−418.70	NC	NC	−21.692	−253.98
	M + O	2–3	399.99	NC	NC	−267.94	−244.04
		3–2	20.68	NC	NC	445.46	40.314

NC, no convergence

non-randomness or structural parameters. The results for the NRTL equation tend to support previous literature in suggesting that the most recommendable value of the non-randomness parameter is 0.2.

The tie-line slope predictions made on the basis of Novák et al.'s rule D were hardly ever correct. The fact that they were correct more often for the systems with methanol than for those with ethanol may be due to the binary mixture water + methanol being
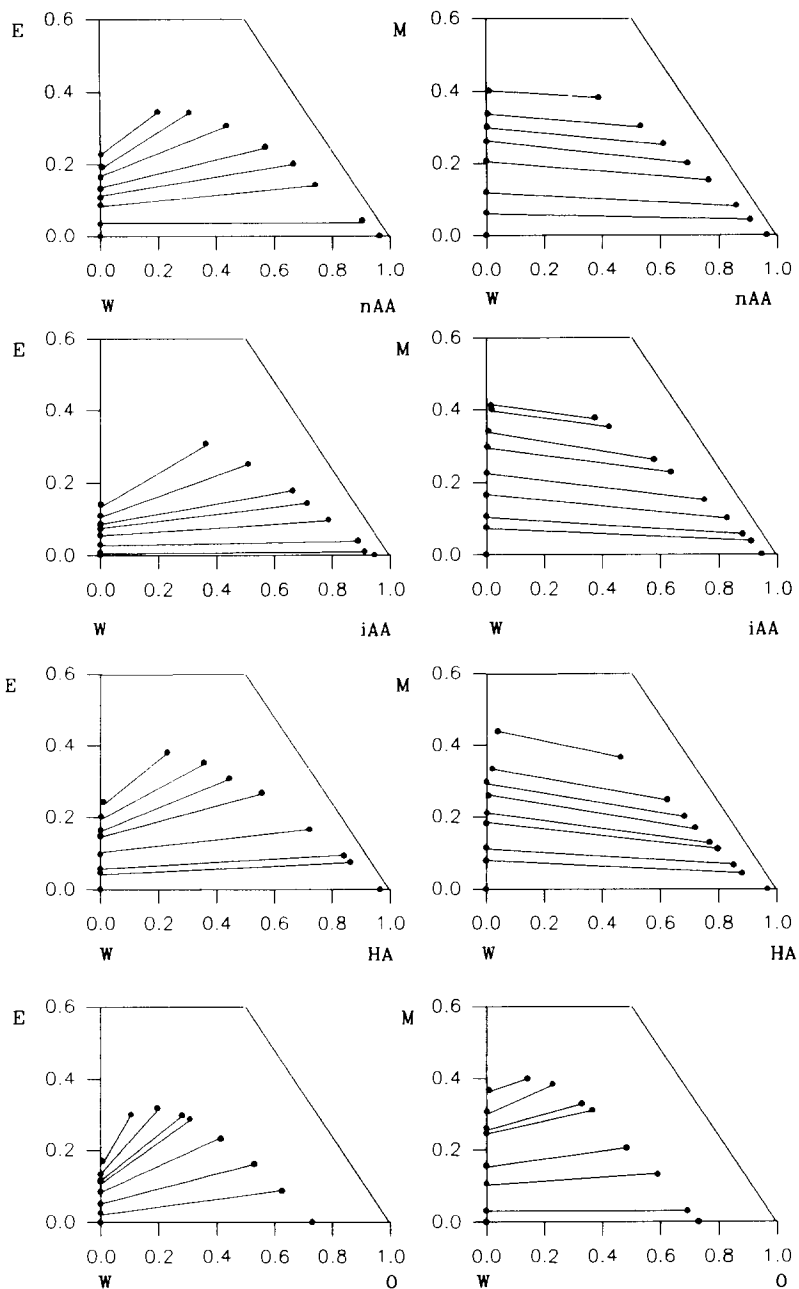
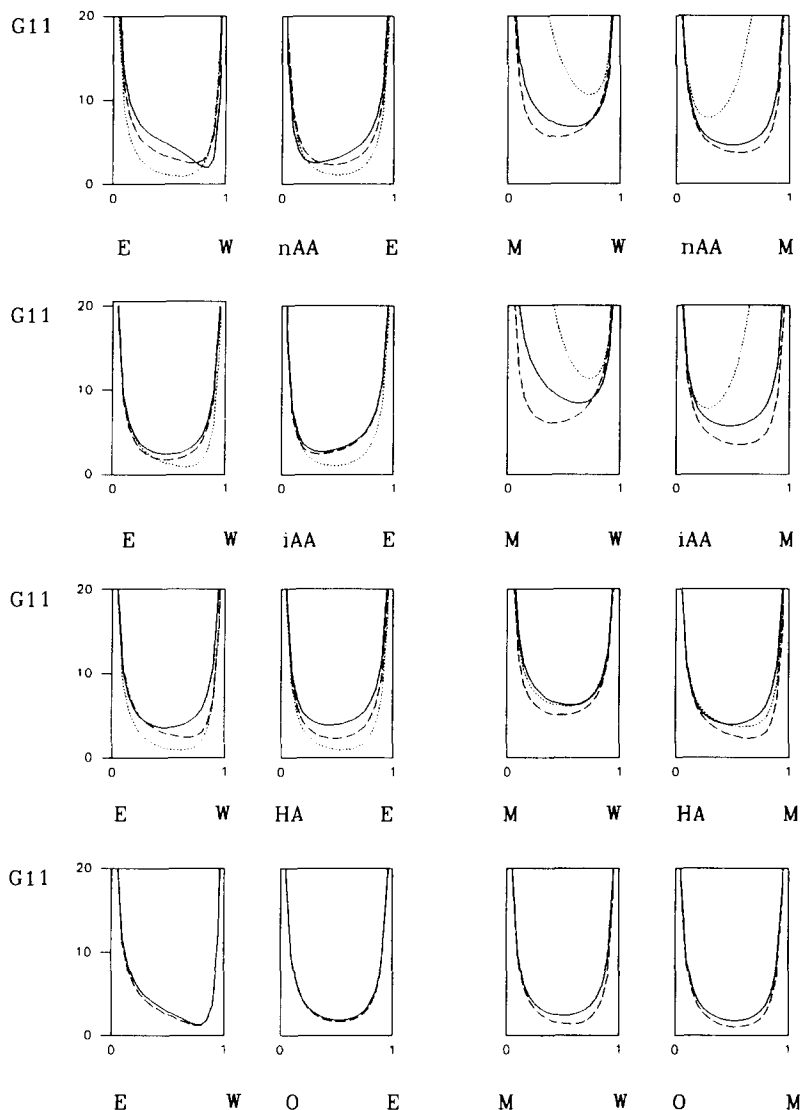Fig. 1. Experimental tie-lines of the ternary systems.

Fig. 2. G_{11} curves obtained for the homogeneous binary mixtures using NRTL equations fitted to the experimental data for the corresponding ternary mixture; $\alpha = 0.1$ (———), $\alpha = 0.2$ (– – –), $\alpha = 0.3$ (· · ·).

more ideal than water + ethanol and to the asymmetric mutual solubilities of the heterogeneous system (water is in all cases more soluble in the solvent than the solvent in water) having a greater effect on the interaction parameters calculated for water + ethanol than on those calculated for water + methanol.

To sum up, two general conclusions stem from this work. Firstly, we corroborate the usual result that the binary interaction parameters of the UNIQUAC and NRTL equations,
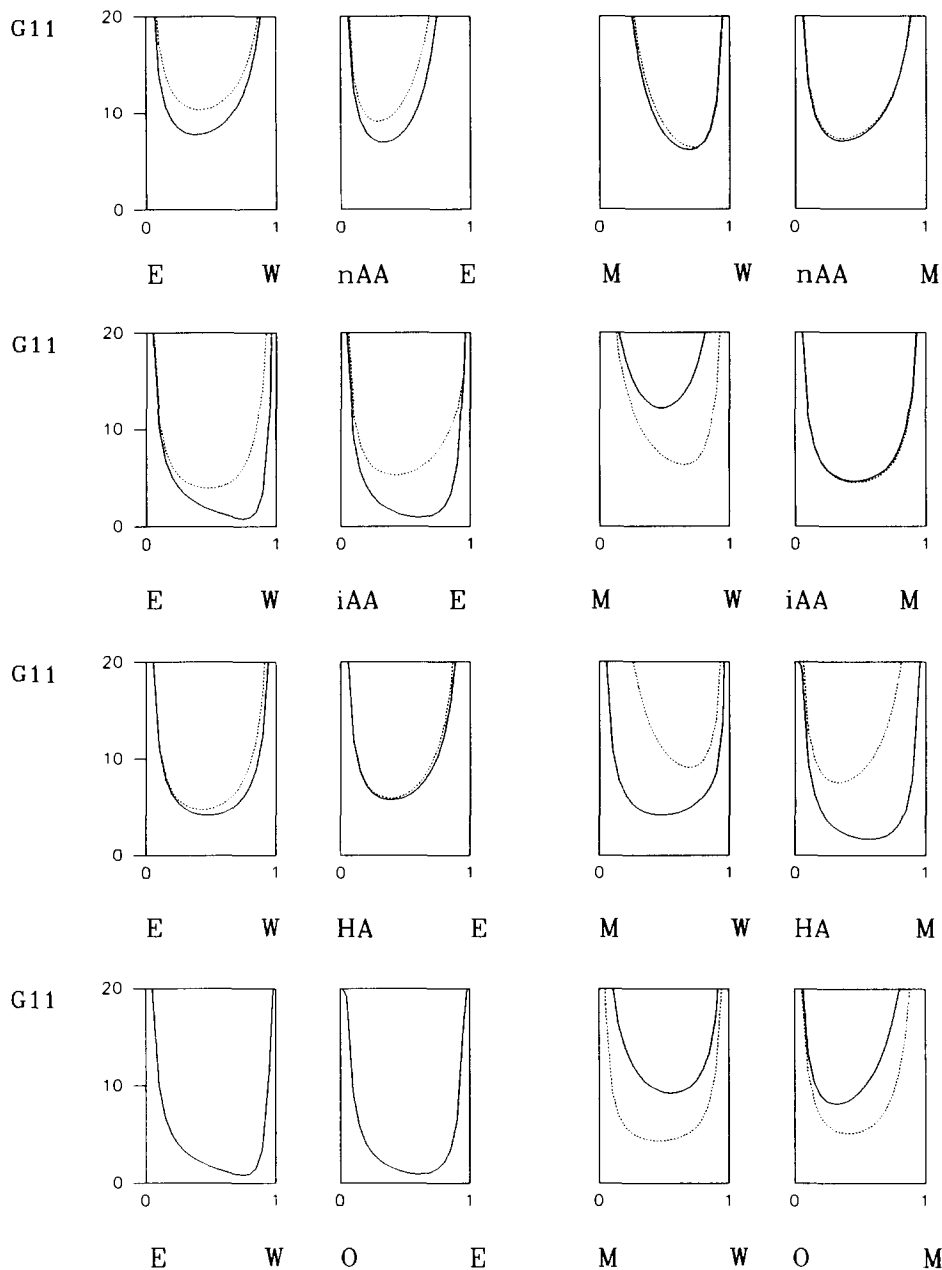
Fig. 3. G_{11} curves obtained for the homogeneous binary mixtures using UNIQUAC equations fitted to the experimental data for the corresponding ternary mixture: (——), using universal values for the structural parameters; (···), using system-specific values.

and the corresponding thermodynamic descriptions of binaries in terms of G_{11}, depend heavily on the system from which they have been obtained (which should be borne in mind when using the binary parameters in calculations for multicomponent systems). Secondly, we note that the UNIQUAC and NRTL models do not imply any consistent relationship between the slopes of ternary tie-lines and the characteristics of the G_{11} of the corresponding homogeneous binary mixtures.

Acknowledgement

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