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A TEST OF THE EXCESS GIBBS FREE ENERGY MODELS IN TERNARY AND QUATERNARY LIQUID–LIQUID EQUILIBRIUM CALCULATIONS

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ABSTRACT

This work presents a comparative study on the ability of the NRTL and modified Wilson equations in predicting ternary and quaternary liquid–liquid equilibria. Parameters in these equations are determined from limiting activity coefficients for binary completely miscible pairs and mutual solubilities for partially miscible pairs. The modified Wilson equation works better than the NRTL equation for the multicomponent systems studied.

INTRODUCTION

Lafyatis et al. [1] studied a series of totally miscible and partially miscible mixtures by differential ebulliometry and determined parameters for the NRTL and UNIQUAC equations [2,3] from ebulliometric data only. The predicted tie-lines based on the binary parameters did not compare well with the experimental ternary and quaternary liquid–liquid equilibrium (LLE) data. Lafyatis et al. also stated that their method does not rely on mutual solubilities which have generally been used in the past for partially miscible pairs and which give parameters that are often poor. However, their derived parameters did not correctly reproduce mutual solubilities. For the binary partially miscible mixtures having moderate miscible regions studied by Lafyatis et al., the binary parameters should be obtained from experimental mutual solubilities instead of from infinite dilution activity coefficients, γ_i^∞.

This work presents a test of the functionality of the NRTL and modified Wilson equation [4] to ternary and quaternary LLE using binary data only.

SOLUTION MODELS

The binary and multicomponent forms of the activity coefficients for components are expressed according to two solution models.

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NRTL equation

$$\ln \gamma_1 = x_2^2\left[\frac{\tau_{21}G_{21}^2}{(x_1 + x_2G_{21})^2} + \frac{\tau_{12}G_{12}}{(x_2 + x_1G_{12})^2}\right] \tag{1}$$

$$\ln \gamma_2 = x_1^2\left[\frac{\tau_{12}G_{12}^2}{(x_2 + x_1G_{12})^2} + \frac{\tau_{21}G_{21}}{(x_1 + x_2G_{21})^2}\right] \tag{2}$$

with

$$\tau_{12} = a_{12}/T, \qquad \tau_{21} = a_{21}/T \tag{3}$$

$$G_{12} = \exp(-\alpha_{12}\tau_{12}), \qquad G_{21} = \exp(-\alpha_{21}\tau_{21}) \tag{4}$$

where the non-randomness parameters, α_{ij}, are set as 0.3 for all binary mixtures studied and a_{ij} are binary interaction energy parameters.

The activity coefficient of component i in a multicomponent mixture is given by

$$\ln \gamma_i = \frac{\sum_j^N \tau_{ji}G_{ji}x_j}{\sum_k^N G_{ki}x_k} + \sum_j^N \frac{x_jG_{ij}}{\sum_k^N G_{kj}x_k}\left(\tau_{ij} - \frac{\sum_l^N x_l\tau_{lj}G_{lj}}{\sum_k^N G_{kj}x_k}\right) \tag{5}$$

Modified Wilson equation

$$\begin{aligned}\ln \gamma_1 = {} & -\ln(x_1 + \alpha_{12}\Lambda_{12}x_2) + x_2\left(\frac{\alpha_{12}\Lambda_{12}}{x_1 + \alpha_{12}\Lambda_{12}x_2} - \frac{\alpha_{21}\Lambda_{21}}{\alpha_{21}\Lambda_{21}x_1 + x_2}\right)\\ & + \ln(x_1 + \alpha_{12}x_2) - x_2\left(\frac{\alpha_{12}}{x_1 + \alpha_{12}x_2} - \frac{\alpha_{21}}{\alpha_{21}x_1 + x_2}\right)\end{aligned} \tag{6}$$

$$\begin{aligned}\ln \gamma_2 = {} & -\ln(x_2 + \alpha_{21}\Lambda_{21}x_1) + x_1\left(\frac{\alpha_{12}\Lambda_{12}}{x_1 + \alpha_{12}\Lambda_{12}x_2} - \frac{\alpha_{21}\Lambda_{21}}{\alpha_{21}\Lambda_{21}x_1 + x_2}\right)\\ & + \ln(x_2 + \alpha_{21}x_1) - x_1\left(\frac{\alpha_{12}}{x_1 + \alpha_{12}x_2} - \frac{\alpha_{21}}{\alpha_{21}x_1 + x_2}\right)\end{aligned} \tag{7}$$

with

$$\Lambda_{12} = (V_2/V_1)\exp(-a_{12}/T), \qquad \Lambda_{21} = (V_1/V_2)\exp(-a_{21}/T) \tag{8}$$

where V_i is the molar liquid volume of pure component i. The adjustable parameters, α_{ij}, are unity for totally miscible mixtures and 1.1 for the partially miscible mixtures studied here. a_{ij} are binary interaction parameters.

The multicomponent activity coefficient of component i is given by

$$\ln \gamma_i = -\ln\left(\sum_j^N x_j\alpha_{ij}\Lambda_{ij}\right) - \sum_k^N \frac{x_k\alpha_{ki}\Lambda_{ki}}{\sum_j^N x_j\alpha_{kj}\Lambda_{kj}} + \ln\left(\sum_j^N x_j\alpha_{ij}\right) + \sum_k^N \frac{x_k\alpha_{ki}}{\sum_j^N x_j\alpha_{kj}} \tag{9}$$

TABLE 1

Binary parameters obtained from infinite dilution activity coefficients and mutual solubilities

System (1–2)	Exptl. data [a]		Temp. (°C)	NRTL parameters			Modified Wilson parameters			
	γ_1^∞	γ_2^∞		a_{12} (K)	a_{21} (K)	α_{12}	a_{12} (K)	a_{21} (K)	α_{12}	α_{21}
Toluene–nitromethane	4.30	3.92	70	231.41	311.13	0.3	84.56	494.12	1.0	1.0
	4.13	3.69	80	216.84	320.10	0.3	82.56	488.62	1.0	1.0
Toluene–methylcyclohexane	1.33	1.38	70	124.21	−13.31	0.3	75.45	35.65	1.0	1.0
	1.30	1.36	80	145.87	−35.95	0.3	62.31	46.76	1.0	1.0
Toluene–furfural	2.75	3.64	70	368.43	79.99	0.3	45.60	420.50	1.0	1.0
Nitromethane–furfural	1.19	2.12	70	668.76	−312.75	0.3	−71.65	413.83	1.0	1.0
Methylcyclohexane–nitromethane	MS [b]		50	649.98	816.54	0.3	845.08	1220.40	1.1	1.1
			75	416.11	857.22	0.3	846.47	980.24	1.1	1.1
			90	417.13	768.92	0.3	722.01	980.23	1.1	1.1
Methylcyclohexane–furfural	MS [b]		50	614.04	512.40	0.3	606.17	997.08	1.1	1.1
			65	444.53	575.44	0.3	642.10	804.20	1.1	1.1

[a] Taken from Lafyatis et al. [1].

[b] Mutual solubilities.

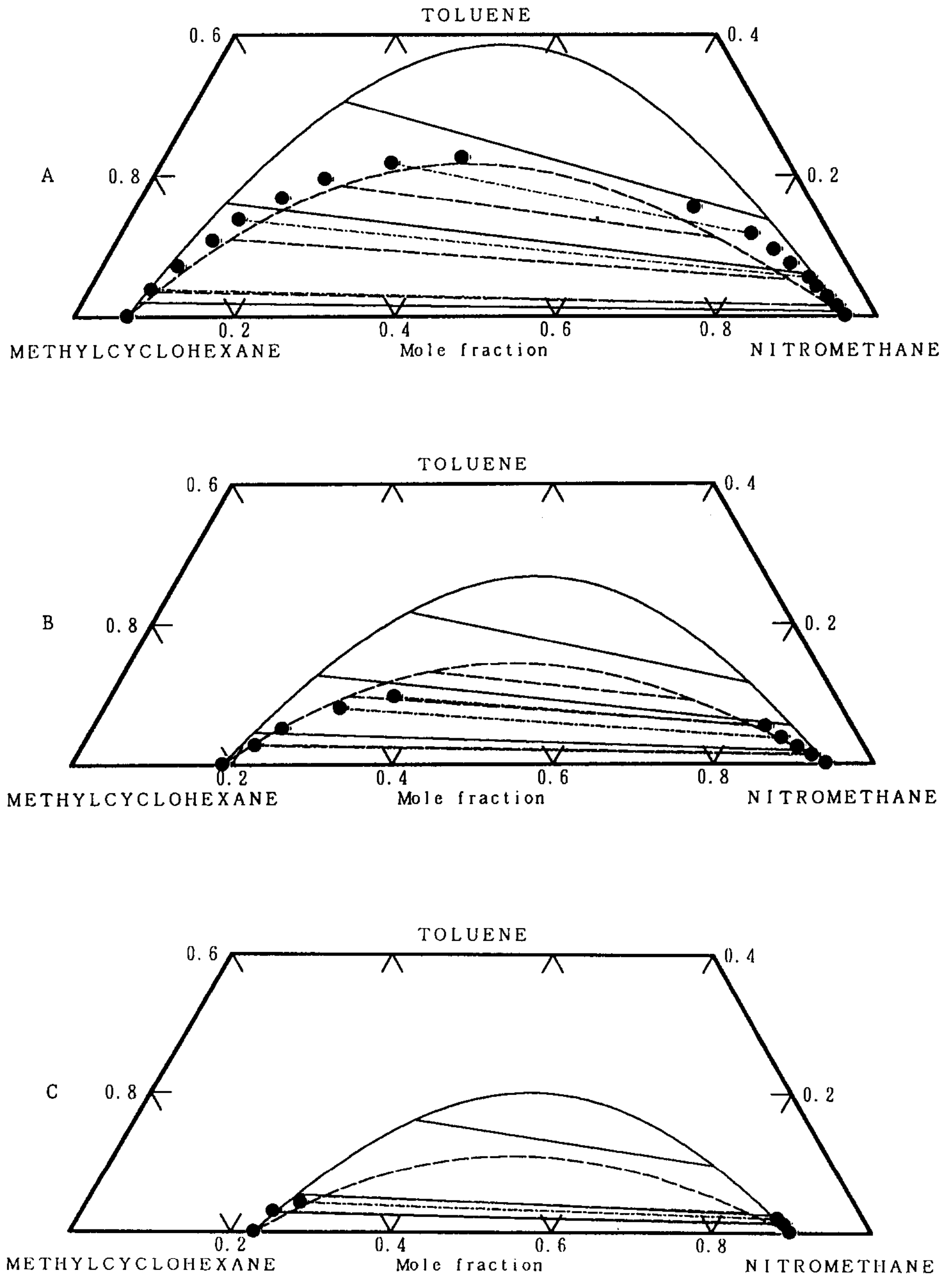

Fig. 1. Calculated and experimental liquid–liquid equilibria. Calculated: ———, NRTL; — — —, modified Wilson. Experimental tie-line data of Lafyatis et al. [1] (●·—·—·●): A, methylcyclohexane–toluene–nitromethane at 50 ° C; B, methylcyclohexane–toluene–nitromethane at 75 ° C; C, methylcyclohexane–toluene–nitromethane at 90 ° C; D, methylcyclohexane–toluene–furfural at 50 ° C; E, methylcyclohexane–toluene–furfural at 70 ° C; F, methylcyclohexane–furfural–nitromethane at 50 ° C.

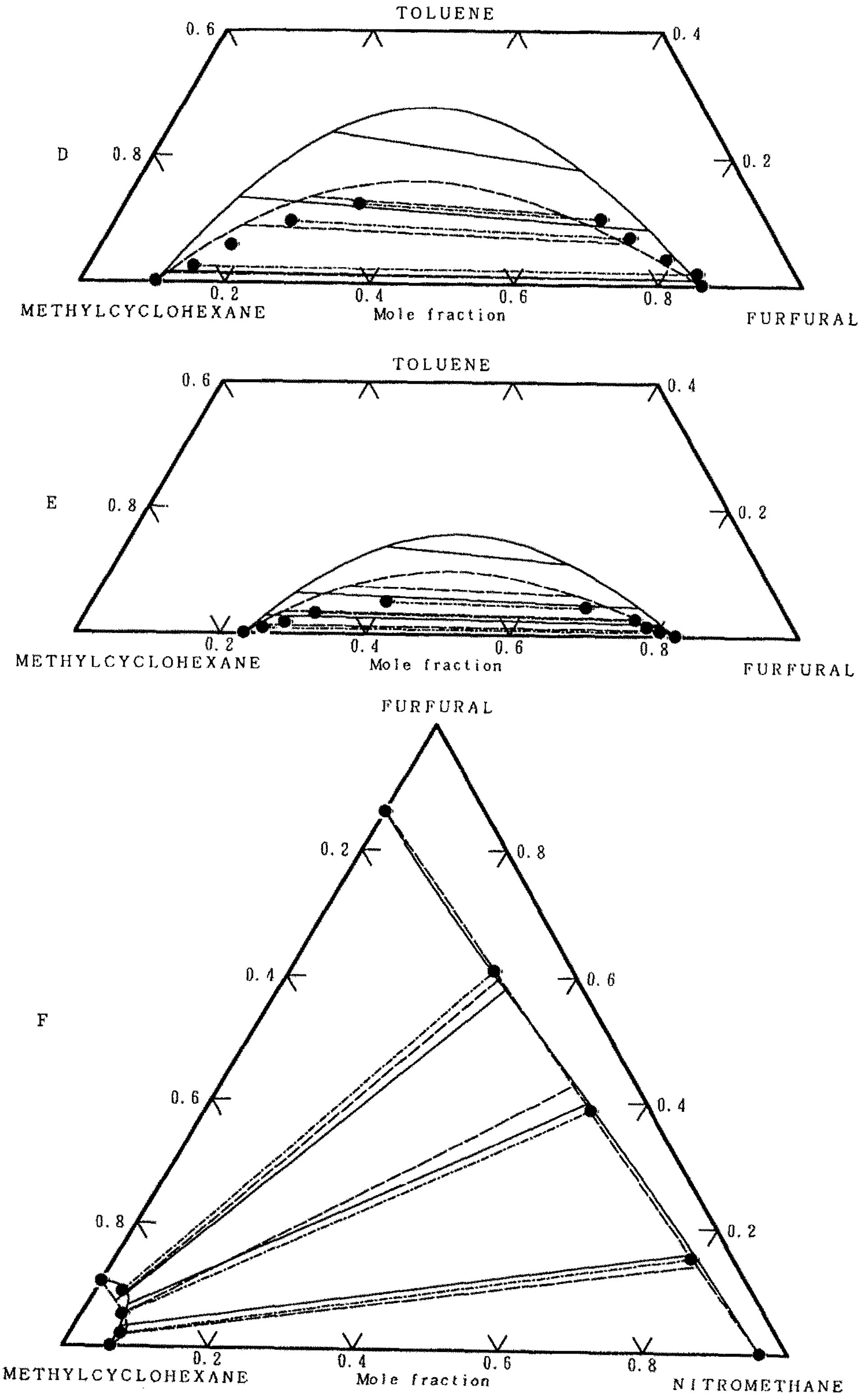

Fig. 1 (continued).

TABLE 2

Quaternary calculated results for the methylcyclohexane (1)–nitromethane (2)–furfural (3)–toluene (4) system at 50 °C [1]

Composition	Number of tie-lines used	Component 1-rich phase (mol%)				Component 1-poor phase (mol%)			
		NRTL		Modified Wilson		NRTL		Modified Wilson	
		AAM [a]	RMS [b]	AAM	RMS	AAM	RMS	AAM	RMS
δx_1	16	7.13	8.87	1.64	2.95	2.50	3.66	3.68	4.42
δx_2		5.25	7.60	1.31	2.51	1.80	3.13	3.24	4.09
δx_3		2.79	3.74	0.82	1.48	1.15	1.81	1.02	1.25
δx_4		0.92	1.51	0.36	0.55	0.42	0.70	0.61	0.79
δx_1	15 [c]			1.13	1.85			3.29	3.87
δx_2				0.77	0.84			2.82	3.44
δx_3				0.75	1.46			0.97	1.21
δx_4				0.26	0.33			0.53	0.67

[a] AAM, Absolute arithmetic mean deviation between the experimental and calculated liquid–liquid equilibrium compositions.

[b] RMS, Root-mean-square deviation.

[c] A tie-line for which the calculation did not show phase separation was rejected.

TABLE 3

Experimental quaternary tie-lines and predicted results obtained from the modified Wilson equation for the methylcyclohexane (1)–nitromethane (2)–furfural (3)–toluene (4) system at 50 °C

Component 1-rich phase				Component 1-poor phase			
x_1	x_2	x_3	x_4	x_1	x_2	x_3	x_4
0.8460	0.0710	0.0600	0.0240 [a]	0.0870	0.5230	0.3770	0.0120 [a]
0.8520	0.0712	0.0536	0.0232 [b]	0.0983	0.5126	0.3760	0.0130 [b]
0.8200	0.0740	0.0600	0.0460	0.0920	0.5200	0.3630	0.0240
0.8127	0.0830	0.0598	0.0445	0.1109	0.5046	0.3587	0.0258
0.7480	0.0970	0.0750	0.0800	0.1050	0.5000	0.3500	0.0450
0.7456	0.1032	0.0731	0.0781	0.1359	0.4763	0.3394	0.0483
0.6780	0.1180	0.0930	0.1110	0.1230	0.4750	0.3340	0.0670
0.6736	0.1274	0.0905	0.1085	0.1673	0.4414	0.3189	0.0724
0.6330	0.1320	0.1050	0.1300	0.1340	0.4650	0.3200	0.0810
0.6243	0.1466	0.1028	0.1263	0.1907	0.4201	0.3003	0.0889
0.5770	0.1610	0.1200	0.1420	0.1510	0.4480	0.3060	0.0940
0.5807	0.1657	0.1143	0.1394	0.2131	0.4016	0.2821	0.1032
0.8800	0.0820	0.0210	0.0160	0.0600	0.7860	0.1480	0.0060
0.8770	0.0867	0.0214	0.0149	0.0645	0.7809	0.1476	0.0071
0.8350	0.0960	0.0250	0.0440	0.0600	0.7800	0.1420	0.0180
0.8410	0.1002	0.0235	0.0352	0.0778	0.7607	0.1408	0.0208
0.7770	0.1210	0.0290	0.0730	0.0730	0.7530	0.1420	0.0320
0.7753	0.1265	0.0290	0.0693	0.0950	0.7295	0.1387	0.0367
0.7310	0.1390	0.0330	0.0970	0.0810	0.7370	0.1370	0.0450
0.7260	0.1489	0.0330	0.0922	0.1117	0.7039	0.1329	0.0515
0.6450	0.1820	0.0400	0.1330	0.0940	0.7080	0.1310	0.0670
0.6412	0.1919	0.0406	0.1263	0.1448	0.6543	0.1226	0.0782
0.5360	0.2480	0.0530	0.1630	0.1210	0.6540	0.1270	0.0970
0.5323	0.2568	0.0542	0.1568	0.1988	0.5752	0.1129	0.1130
0.8110	0.0450	0.1070	0.0370	0.1180	0.2700	0.5900	0.0220
0.8311	0.0419	0.0905	0.0365	0.1349	0.2614	0.5805	0.0232
0.6980	0.0680	0.1510	0.0830	0.1420	0.2600	0.5440	0.0540
0.7396	0.0581	0.1189	0.0834	0.1728	0.2459	0.5242	0.0572
0.5950	0.0860	0.1980	0.1210	0.2000	0.2320	0.4810	0.0870
0.6469	0.0753	0.1557	0.1220	0.2187	0.2190	0.4713	0.0911
Root-mean-square deviations for 15 experimental points							
0.0185	0.0084	0.0146	0.0033	0.0387	0.0344	0.0121	0.0067

[a] Experimental data.

[b] Modified Wilson predictions.

CALCULATED RESULTS AND DISCUSSION

The binary interaction parameters, a_{12} and a_{21}, of the two equations, NRTL and modified Wilson, were obtained from γ_i^∞ for the totally miscible systems and from mutual solubilities for the partially miscible systems and are given in Table 1. The binary parameters determined from γ_i^∞ at 70 and 80 °C are not different from each other. Thus, two sets of the parameters, at 70 and 80 °C, give nearly the same calculated results. The ternary LLE predictions based on both equations are compared with the experimental data measured by Lafyatis et al. [1] in Fig. 1. The modified Wilson equation gives better predictions of ternary LLE than the NRTL equation, and similar results are obtained for the quaternary predictions of the methylcyclohexane–nitromethane–furfural–toluene system as shown in Table 2. The modified Wilson equation gives better predicted values for the methylcyclohexane-rich phase than for the nitromethane–furfural-rich phase. In contrast, the NRTL equation yields rather good predicted results for the nitromethane–furfural-rich phase. This is probably due to the functional dependence of each equation in the LLE calculations. Table 3 compares the experimental quaternary data with the calculated results obtained from the modified Wilson equation. To improve solution models that are able to treat ternary and quaternary LLE, it is necessary to incorporate ternary and quaternary parameters due to molecular interactions among three and four unlike molecules into the models. This work is in progress.

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LIST OF SYMBOLS

a_{12}, a_{21}	NRTL or modified Wilson binary interaction parameters
G_{ij}	NRTL coefficient as defined by $\exp(-\alpha_{ij}\tau_{ij})$
R	universal gas constant
T	absolute temperature
V_i	molar volume of pure liquid i

Greek letters

α_{12}, α_{21}	NRTL or modified Wilson binary parameters
γ_i	activity coefficient of component i
γ_i^{∞}	activity coefficient of component i at infinite dilution
Λ_{ij}	Wilson-like parameter defined by $(V_j/V_i)\exp(-a_{ij}/T)$
τ_{ij}	NRTL parameter defined by a_{ij}/T

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