

## GENERAL RESEARCH

# A Test of the Functional Dependence of $g^E(x)$ in Liquid-Liquid Equilibria Using Limiting Activity Coefficients

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This work presents a new approach for examining Gibbs energy expressions, which often fail when predicting derivative properties such as liquid-liquid equilibria (LLE). A differential boiling point technique is used to measure the limiting activity coefficients for several binary pairs. These binary data are then used to determine parameters in the UNIQUAC and NRTL equations. By use of these parameters, the LLE relationships for binary, ternary, and quaternary cases are predicted and compared to experimental data, to show the limitations of the present state of the art. This data set of derivative properties, LLE and  $\gamma^\infty$ , provides a basis for testing future  $g^E(x)$  models, which hopefully will characterize derivative properties of solutions better.

Although the excess Gibbs energy of nonionic solutions,  $g^E(x)$ , is vital in the calculation of phase equilibria for the design of separation equipment, our knowledge of the functionality of this important quantity is very limited. On the basis of VLE data, researchers have developed models for  $g^E(x)$  which have proved extremely useful in predicting vapor-liquid phase behavior for the design of distillation equipment. Nonetheless, the functionality of  $g^E(x)$  is quite insensitive to VLE data. The purpose of this paper is to demonstrate the need for a better understanding of  $g^E(x)$  and to present some data that would constitute more sensitive tests of potential new models.

Historically most phase equilibrium data have been VLE data, taken by traditional methods, either static or dynamic. Such data led to  $g^E(x)$  models, either enthalpy-based correlations such as the Margules and the Van Laar methods, or entropy-based correlations such as Wilson's equation, NRTL, and UNIQUAC. The entropic expressions yield in general a better fit of binary VLE data, and they permit an improved prediction of multicomponent VLE using binary data only. Such results have proven extremely useful in the design of various types of distillation equipment; however, the separation in distillation is due primarily to differences in vapor pressures and is relatively insensitive to liquid-phase nonidealities. Moreover, column design and performance are quite insensitive to the quality of the enthalpy predictions.

Liquid-liquid extraction, on the other hand, represents a separation technique based solely on differences in solution nonidealities and as such is quite unforgiving of inadequacies in the excess Gibbs energy expressions. Attempts have been made to predict multicomponent LLE from binary data using VLE data for the miscible pairs and mutual solubilities for the partially miscible pairs; such attempts sometimes work, but unpredictably may fail badly (Wittrig, 1977; Nicolaides and Eckert, 1978). In fact, it can be shown that LLE actually represent a second derivative of the Gibbs energy, and while the value of the integral Gibbs energy may be close enough for VLE cal-

culations, the derivatives, either enthalpy or LLE, are simply inadequate.

Significant progress on this problem has been made by showing first that derivative data yield far more information and by developing new experimental methods to measure them. The measurement and use of infinite dilution activity coefficients yields important derivative information and offers several distinct advantages:

- (1) One can construct the entire VLE curve quite accurately from the two limiting activity coefficients (Schreiber and Eckert, 1971).

- (2) The parameters found from the limiting activity coefficients give adequate representation of multicomponent VLE.

- (3) Several excellent techniques for estimating limiting activity coefficients exist such as ASOG (Pierotti et al., 1959), UNIFAC (Fredenslund et al., 1977a,b), and MOSCED (Thomas and Eckert, 1984).

- (4) New experimental methods exist that are both faster and more accurate than classical VLE techniques for the direct measurement of limiting activity coefficients including gas chromatography (Thomas et al., 1982b), gas stripping (Renon et al., 1977), headspace chromatography (Hussam and Carr, 1985), and differential ebulliometry (Thomas et al., 1982a; Scott, 1986).

In this study a series of totally miscible and partially miscible mixtures were studied by differential ebulliometry. The systems were chosen such that they would form type I ternary systems, such as would be important for liquid-liquid extraction processes, as well as a type II ternary and quaternary system. The four components so chosen were nitromethane, methylcyclohexane, furfural, and toluene. Limiting activity coefficients for the binary pairs were measured at 70 and 80 °C, and the LLE relationships were measured for binary pairs and for the ternary and quaternary cases at several temperatures.

The best two  $g^E(x)$  expressions currently available for LLE are the NRTL and UNIQUAC equations. In order to demonstrate the limitations of these methods, param-

eters for these equations were determined from ebulliometric data only. The predicted tie lines were then compared to the experimental LLE data. This work differs from previous attempts to use binary data to get multi-component LLE in three ways:

(1) The ebulliometric data are substantially more accurate and easier to measure than classical VLE, and they are always based upon a very precise representation of the limiting activity coefficient.

(2) This method does not rely on mutual solubilities, which have generally been used in the past for the partially miscible pairs and which give parameters that are often poor.

(3) This study presents a data base of value for evaluation of models that may be proposed in the future for the improved functionality of  $g^E(x)$ .

Previous solution theories have been constructed from Gibbs energy data alone. The more sensitive derivative data could permit a far better characterization of physical intermolecular interactions in solutions. The potential for practical applications is exciting; the new results could lead to predictability for a wide variety of separation processes from a limited amount of readily accessible data.

## Experimental Section

**(A) Ebulliometry.** Activity coefficients at infinite dilution were measured by differential ebulliometry, by the method of Scott (1986), incorporating high-speed stirring and an improved measuring head, which gave a temperature precision to  $10^{-4}$  °C.

In this procedure, two flasks containing pure solvent are brought to a boil with rapid agitation and allowed to reflux at the same pressure, held constant. The temperature above each boiler is measured continuously by a high-precision quartz thermometer encased in a thermowell. The pot and the thermowell are vacuum jacketed, and the cooling water in the condenser is at  $-20$  °C.

Small increments of solute are added to one flask, and the temperature changes are measured to  $\pm 0.0001$  °C. The mutual pressure over both flasks is adjusted to bring the test flask to its original temperature. The isothermal  $P$ - $x$  data are fit with various expressions to determine the best value of the limiting activity coefficient, as well as  $\gamma$  values at the finite concentrations.

Each of the six binary combinations was measured with two experiments to define the limiting activity coefficient at each end. Most systems were measured using a 500-mL test flask, but for systems of extremely high relative volatility (more than about 20) a 3000-mL pot was used to keep the relative amount of vapor and vapor condensate low. The solvents used in this study were all of greater than 99.9% purity, as analyzed by a gas chromatograph with FID detector. If moisture were present during a run, it could be identified because it would freeze onto the condenser during boilup. Such moisture could then be purged from the system at low pressures.

This procedure presents a much faster and more accurate technique for measuring  $\gamma^\infty$  than classical methods which rely on independent sampling and analysis of the liquid and vapor phases, as in a circulation still. With classical VLE measurement techniques, the limiting activity coefficient cannot be determined accurately, as one must extrapolate from outside the dilute region. Furthermore, VLE of partially miscible systems are very difficult to measure with classical methods.

**(B) Liquid-Liquid Equilibria.** The equilibrium cell used in this work consisted of a vertical glass cylinder with a volume of about 80 mL. The opening at the top of the cell was a 34/45 ground glass sleeve with a matching

Table I. Summary of Experimental Data

system	description	temp measd, °C
		(for $\gamma^\infty$ )
TOL/NTM	completely miscible	70; 80
TOL/MCH	completely miscible	70; 80
NTM/MCH	partially immiscible	70; 80
FUR/NTM	completely miscible	70
FUR/MCH	partially immiscible	70
FUR/TOL	completely miscible	70
		(for LLE)
TOL/FUR/NTM	completely miscible	
TOL/NTM/MCH	type I	50; 75; 90
TOL/FUR/MCH	type I	50; 65
FUR/MCH/NTM	type II	50
TOL/FUR/NTM/MCH	quaternary	50

ground glass top. The top had two serum-stoppered inlets with syringe needles inserted—one for sampling and the other an outlet to the atmosphere to allow for pressure changes in the cell. A magnetic stir bar was used for mixing the sample, and the cell was thermostated to  $\pm 0.01$  °C.

The two partially miscible components were charged to the equilibrium cell in approximately equal volumes, and the mixture was stirred for a minimum of 15 min. Then the stirring was stopped and the mixture allowed to separate into two phases for at least 15 min. Samples of each phase were taken and analyzed by gas chromatography. At least two GC analyses were made for each phase to ensure the precision of the analysis. Discrepancies between the mole fractions measured during the two analyses were often less than 0.002 and always less than 0.005. Since the miscibility gap is greater at room temperature than at the test temperatures, about 10% 2-butanone was added to each sample to prevent separation into two phases during the sampling procedure.

Next, the third component, which distributes itself between the two phases, was added to the equilibrium cell, stirred, and allowed to equilibrate before sampling. This process was repeated until enough of the third component was added so that only one phase was present.

A Varian Model 3300 gas chromatograph with a thermal conductivity detector was used with a Hewlett-Packard 3392A integrator for sample analysis. The components separated well on a 6-ft-long 0.1% AT-1000 on Graphpac column with temperature programming (120 °C for 0.05 min, followed by a 40 °C/min ramp to 180 °C and a final period at 180 °C). Calibration of the column was performed by injecting known amounts of the compound. Chromatographic analyses of the equilibrium phases were performed by injecting 0.5- $\mu$ L samples. The 2-butanone peaks were ignored.

## Results

A summary of the data measured for this work is presented in Table I. Differential ebulliometry was used to measure  $P$ - $x$  data for each of the binaries in both the dilute regions and the midcomposition range. The data were fit to a number of activity coefficient equations with the best fit used to give the  $\gamma_i$  versus  $x_i$  relationship, as well as the infinite dilution activity coefficient. The values of the limiting activity coefficients are given in Table II and should be considered to be independent of any specific expression for  $g^E(x)$ . The binary interaction parameters of UNIQUAC,  $\Delta u_{12}$  and  $\Delta u_{21}$ , were determined solely from the limiting activity coefficients and are given in Table III. Both limiting activity coefficients and finite concentration ebulliometric data for both halves of the concentration

**Table II. Limiting Activity Coefficients**

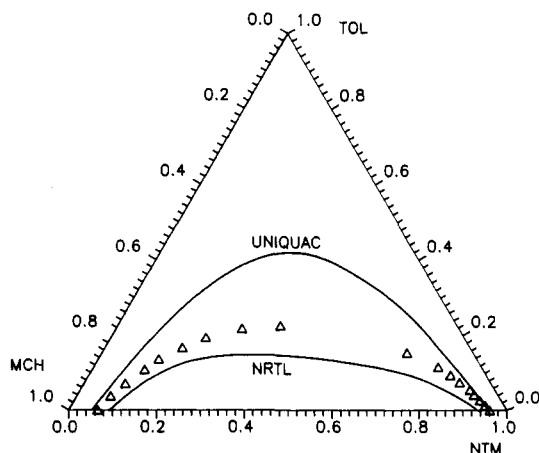
solvent	solute			
	TOL	NTM	MCH	FUR
At 70.0 °C				
TOL		3.92	1.38	3.64
NTM	4.30		28.0	2.12
MCH	1.33	22.6		14.0
FUR	2.75	1.19	13.5	
At 80.0 °C				
TOL		3.69	1.36	
NTM	4.13		24.9	
MCH	1.30	19.1		

**Table III. UNIQUAC Parameters from  $\gamma^\infty$  Values ( $\Delta u_{ij}$ , Calories/Mole)**

<i>j</i>	<i>i</i>			
	TOL	NTM	MCH	FUR
At 70 °C				
TOL	0.0	-62.2	103.1	-88.1
NTM	557.3	0.0	1107.4	-399.0
MCH	-39.0	103.1	0.0	48.4
FUR	452.8	728.8	697.9	0.0
At 80.0 °C				
TOL	0.0	-55.1	90.8	
NTM	541.3	0.0	1085.5	
MCH	-29.9	95.3	0.0	

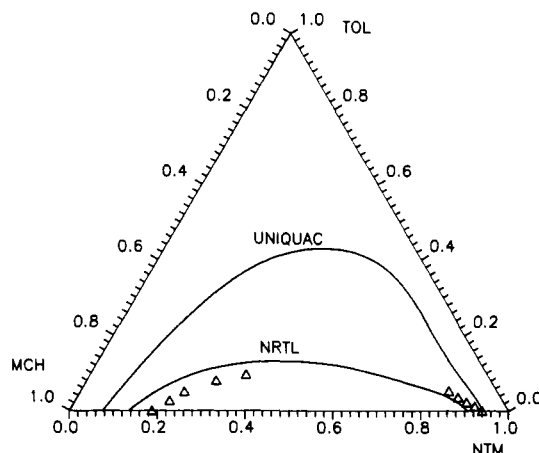
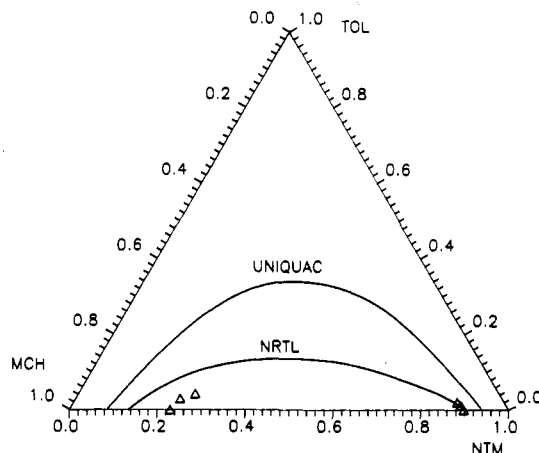
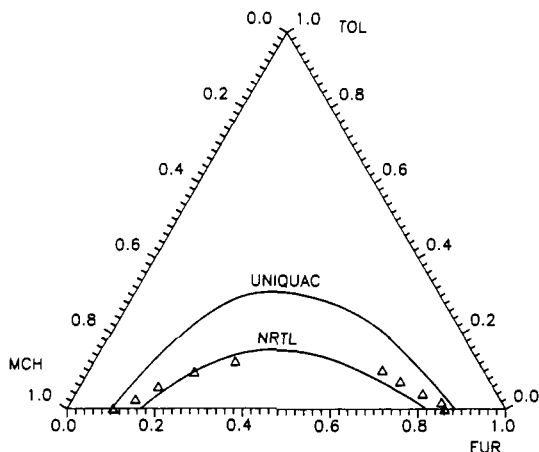
**Table IV. NRTL Parameters from Ebulliometric Data ( $\Delta g_{ij}$ , Calories/Mole)**

component		$\Delta g_{12}$	$\Delta g_{21}$	$\alpha_{12}$
1	2			
At 70.0 °C				
TOL	NTM	599.8	675.9	0.7189
TOL	MCH	283.7	-61.2	0.2739
NTM	MCH	1645.5	1493.2	0.3958
TOL	FUR	654.1	274.0	0.4739
NTM	FUR	484.0	33.5	2.4487
FUR	MCH	1159.2	1194.1	0.3796
At 80.0 °C				
NTM	MCH	1626.6	1429.3	0.4024
TOL	MCH	307.9	-88.3	0.2739
TOL	NTM	584.5	679.7	0.7410

**Figure 1.** 50 °C experimental data ( $\Delta$ ) and UNIQUAC and NRTL predictions using parameters from 70 °C ebulliometric data.

profile were combined and used to determine the three parameters of the NRTL equations,  $\Delta g_{12}$ ,  $\Delta g_{21}$ , and  $\alpha_{12}$  (see Table IV). The version of NRTL and UNIQUAC used as well as the pure-component UNIQUAC parameters are those given in Reid et al. (1987).

It would have been desirable to take ebulliometric data over a much wider temperature range. However we were limited at the upper end by the pressure limits of a glass

**Figure 2.** 75 °C experimental data ( $\Delta$ ) and UNIQUAC and NRTL predictions using parameters from 70 and 80 °C ebulliometric data.**Figure 3.** 90 °C experimental data ( $\Delta$ ) and UNIQUAC and NRTL predictions using parameters from 70 °C ebulliometric data.**Figure 4.** 50 °C experimental data ( $\Delta$ ) and UNIQUAC and NRTL predictions using parameters from 70 °C ebulliometric data.

apparatus and on the low side by the increased uncertainty caused by very high relative volatilities. For example, at 50 °C we estimate the relative volatility of methylcyclohexane in furfural as greater than 1000, which introduces significant errors into the  $\gamma^\infty$  measurement even when a very large (3000-mL) boiling pot is used (Scott, 1986).

The LLE relationships were measured as indicated in Table I. Data were measured at a number of temperatures in order to investigate the temperature dependence in the UNIQUAC and NRTL models. Table V gives the binary mutual solubilities of the two partially miscible pairs and compares them to the UNIQUAC and NRTL predictions,

**Table V. Binary Mutual Solubilities**

temp, °C	measured				NRTL prediction				UNIQUAC prediction			
	MCH	FUR	MCH	FUR	MCH	FUR	MCH	FUR	MCH	FUR	MCH	FUR
Methylcyclohexane/Furfural <sup>a</sup>												
50	0.139	0.861	0.895	0.105	0.180	0.820	0.832	0.168	0.114	0.886	0.899	0.101
65	0.172	0.828	0.767	0.233	0.212	0.788	0.801	0.199	0.129	0.871	0.879	0.121
70	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	0.223	0.777	0.789	0.211	0.134	0.866	0.872	0.128
temp, °C	measured				NRTL prediction				UNIQUAC prediction			
	MCH	NTM	MCH	NTM	MCH	NTM	MCH	NTM	MCH	NTM	MCH	NTM
Methylcyclohexane/Nitromethane <sup>c</sup>												
50	0.934	0.066	0.039	0.961	0.908	0.092	0.064	0.936	0.947	0.053	0.046	0.954
70	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	0.888	0.112	0.080	0.920	0.932	0.068	0.053	0.947
75	0.812	0.188	0.060	0.941	0.883	0.117	0.084	0.916	0.928	0.072	0.054	0.946
75 <sup>d</sup>	0.812	0.188	0.060	0.941	0.863	0.137	0.092	0.908	0.924	0.076	0.056	0.943
80 <sup>e</sup>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	0.846	0.154	0.099	0.901	0.915	0.085	0.062	0.938
90	0.771	0.229	0.102	0.898	0.866	0.134	0.098	0.902	0.914	0.086	0.060	0.940

<sup>a</sup>All predictions are from using parameters determined from 70 °C ebulliometry data. <sup>b</sup>Not measured. <sup>c</sup>All predictions are from parameters determined from 70 °C ebulliometry data except *d* and *e*. <sup>d</sup>Prediction is from average of binary interaction parameters from 70 and 80 °C ebulliometry data. <sup>e</sup>Prediction is from parameters determined from 80 °C ebulliometry data.

**Table VI. LLE Data: Methylcyclohexane/Nitromethane/Toluene**

upper phase mole fraction			lower phase mole fraction		
MCH	NTM	TOL	MCH	NTM	TOL
At 50.0 °C					
0.934	0.066	0.000	0.039	0.961	0.000
0.885	0.077	0.038	0.043	0.944	0.013
0.835	0.094	0.071	0.048	0.926	0.026
0.774	0.119	0.108	0.054	0.905	0.041
0.726	0.137	0.137	0.057	0.889	0.054
0.657	0.176	0.167	0.070	0.856	0.074
0.590	0.216	0.194	0.081	0.825	0.094
0.496	0.287	0.217	0.098	0.786	0.116
0.405	0.370	0.225	0.150	0.696	0.154
At 75.0 °C					
0.812	0.188	0.000	0.060	0.940	0.000
0.758	0.215	0.027	0.071	0.917	0.012
0.712	0.237	0.051	0.084	0.893	0.023
0.625	0.295	0.080	0.097	0.867	0.036
0.549	0.355	0.096	0.109	0.838	0.053
At 90.0 °C					
0.771	0.229	0.000	0.102	0.898	0.000
0.733	0.238	0.029	0.103	0.885	0.012
0.692	0.266	0.042	0.107	0.873	0.020

**Table VII. LLE Data: Methylcyclohexane/Furfural/Toluene**

upper phase mole fraction			lower phase mole fraction		
MCH	FUR	TOL	MCH	FUR	TOL
At 50.0 °C					
0.895	0.105	0.000	0.139	0.861	0.000
0.831	0.144	0.025	0.137	0.845	0.018
0.762	0.179	0.059	0.168	0.791	0.041
0.661	0.242	0.097	0.203	0.723	0.074
0.553	0.322	0.125	0.229	0.668	0.103
At 65.0 °C					
0.767	0.233	0.000	0.172	0.828	0.000
0.737	0.255	0.008	0.190	0.804	0.006
0.703	0.280	0.017	0.205	0.782	0.013
0.653	0.315	0.032	0.215	0.760	0.025
0.546	0.404	0.050	0.273	0.684	0.043

using the parameters determined as mentioned above. The program used was an adaptation of the LLE programs given in Prausnitz et al. (1980). Tables VI–VIII present the experimental LL tie lines for the three ternary systems investigated. The experimental data are compared to the UNIQUAC and NRTL predictions in Figures 1–6. Finally, the experimental quaternary data are presented in

**Table VIII. LLE Data: Methylcyclohexane/Furfural/Nitromethane**

upper phase mole fraction			lower phase mole fraction		
MCH	NTM	FUR	MCH	NTM	FUR
At 50.0 °C					
0.934	0.066	0.000	0.039	0.961	0.000
0.895	0.000	0.105	0.139	0.000	0.861
0.893	0.056	0.051	0.084	0.529	0.386
0.910	0.070	0.020	0.059	0.789	0.152
0.874	0.037	0.089	0.111	0.280	0.609

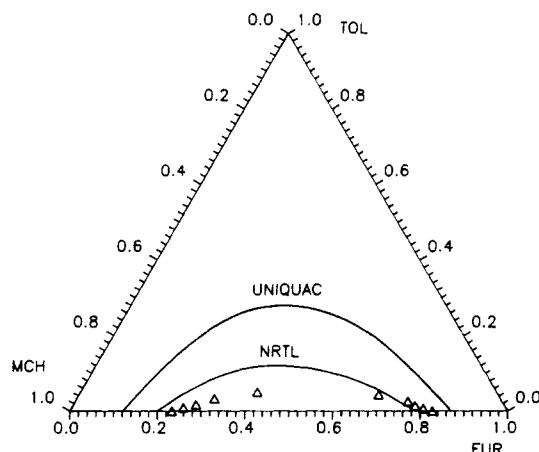
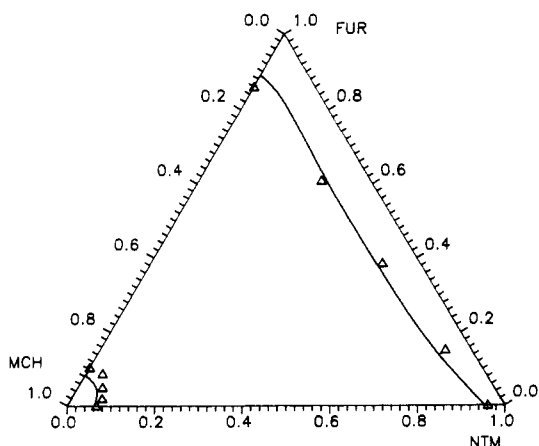
**Figure 5.** 65 °C experimental data (Δ) and UNIQUAC and NRTL predictions using parameters from 70 °C ebulliometric data.**Figure 6.** 50 °C experimental data (Δ) and UNIQUAC prediction using parameters from 70 °C ebulliometric data.

Table IX. Experimental Quaternary LLE Data and UNIQUAC Prediction Using 70 °C Limiting Activity Coefficient Data<sup>a</sup>

upper phase mole fraction				lower phase mole fraction			
MCH	NTM	FUR	TOL	MCH	NTM	FUR	TOL
At 50.0 °C							
0.893	0.056	0.051	0.000	0.084	0.529	0.386	0.000
0.904	0.048	0.048	0.000	0.110	0.515	0.375	0.000
0.846	0.071	0.060	0.024	0.087	0.523	0.377	0.012
0.875	0.052	0.050	0.023	0.114	0.508	0.364	0.014
0.820	0.074	0.060	0.046	0.092	0.520	0.363	0.024
0.848	0.056	0.051	0.045	0.117	0.506	0.351	0.026
0.748	0.097	0.075	0.080	0.105	0.500	0.350	0.045
0.801	0.063	0.056	0.080	0.125	0.488	0.339	0.048
0.678	0.118	0.093	0.111	0.123	0.475	0.334	0.067
0.755	0.070	0.061	0.114	0.133	0.468	0.329	0.070
0.633	0.132	0.105	0.130	0.134	0.465	0.320	0.081
0.725	0.076	0.065	0.134	0.138	0.458	0.319	0.085
0.577	0.161	0.120	0.142	0.151	0.448	0.306	0.094
0.702	0.081	0.067	0.150	0.143	0.451	0.309	0.097
0.175	0.415	0.287	0.124	0.175	0.415	0.287	0.124
0.653	0.091	0.074	0.182	0.154	0.429	0.296	0.121
0.910	0.070	0.020	0.000	0.059	0.789	0.152	0.000
0.924	0.056	0.020	0.000	0.079	0.774	0.147	0.000
0.880	0.082	0.021	0.016	0.060	0.786	0.148	0.006
0.906	0.059	0.020	0.015	0.080	0.770	0.142	0.008
0.835	0.096	0.025	0.044	0.060	0.780	0.142	0.018
0.873	0.064	0.021	0.042	0.083	0.759	0.137	0.021
0.777	0.121	0.029	0.073	0.073	0.753	0.142	0.032
0.836	0.070	0.022	0.072	0.087	0.739	0.137	0.037
0.731	0.139	0.033	0.097	0.081	0.737	0.137	0.045
0.804	0.076	0.023	0.097	0.091	0.725	0.134	0.050
0.645	0.182	0.040	0.133	0.094	0.708	0.131	0.067
0.752	0.086	0.025	0.137	0.097	0.701	0.129	0.073
0.536	0.248	0.053	0.163	0.121	0.654	0.127	0.097
0.694	0.099	0.028	0.179	0.105	0.667	0.128	0.100
0.379	0.373	0.074	0.173	0.191	0.563	0.110	0.137
0.640	0.114	0.031	0.215	0.113	0.640	0.122	0.125
0.267	0.477	0.094	0.162	0.267	0.477	0.094	0.162
0.622	0.119	0.032	0.227	0.116	0.629	0.120	0.134
0.874	0.037	0.089	0.000	0.111	0.280	0.609	0.000
0.896	0.029	0.075	0.000	0.118	0.278	0.604	0.000
0.811	0.045	0.107	0.037	0.118	0.270	0.590	0.022
0.848	0.033	0.081	0.038	0.124	0.269	0.585	0.022
0.698	0.068	0.151	0.083	0.142	0.260	0.544	0.054
0.782	0.039	0.091	0.087	0.134	0.262	0.550	0.054
0.595	0.086	0.198	0.121	0.200	0.232	0.481	0.087
0.720	0.045	0.104	0.131	0.145	0.244	0.528	0.083
0.275	0.190	0.412	0.123	0.275	0.190	0.412	0.123
b	b	b	b	b	b	b	b

<sup>a</sup> In each group of two rows, the first line is experimental data and the second line is UNIQUAC predictions. <sup>b</sup> Composition was too close to the plait point—program did not converge.

Table IX and are compared to the UNIQUAC prediction. The UNIQUAC tie-line end points are the prediction based on the overall composition at which the corresponding experimental values were measured.

## Discussion

For the methylcyclohexane/nitromethane/toluene system, the best prediction of the experimental data should occur with the 75 °C data. The UNIQUAC and NRTL parameters used were the averages of the parameters determined from 70 and 80 °C ebulliometric data. As evident in Figure 2, the NRTL prediction, requiring three parameters for each binary, comes much closer than UNIQUAC, which only used two parameters for each binary—obtained solely from the limiting activity coefficients. The UNIQUAC equation greatly overpredicts the two-phase region. Figures 1 and 3 give an indication of the accuracy of the temperature dependence incorporated in the two models. The temperature dependence of NRTL is too weak. At

50 °C, NRTL underpredicts the two-phase region, while at 90 °C it overpredicts, particularly on the methylcyclohexane-rich end. The only observation about the UNIQUAC temperature dependence is that it is qualitatively correct—as the temperature increases, solubility increases.

The same relationships are evident in the methylcyclohexane/furfural/toluene system (Figures 4 and 5). UNIQUAC greatly overpredicted the two-phase region, while NRTL came much closer, yet its temperature dependence is again too weak.

For the methylcyclohexane/nitromethane/furfural system (type II) the UNIQUAC prediction is quite good (Figure 6). This is not surprising because the prediction is a function largely of how well the mutual solubilities of the two partially miscible pairs are predicted. As seen in Figures 1 and 4, UNIQUAC predicts the mutual solubilities quite well, but this may be due to cancellation of errors.

The fourth ternary, nitromethane/toluene/furfural, is totally miscible.

For the quaternary system, UNIQUAC makes a reasonable prediction for the nitromethane/furfural-rich phase, with mole fractions usually within  $\pm 0.02$  of the experimental values. In the methylcyclohexane-rich phase, much larger differences in mole fractions are present, probably due to the limitations of the predictive method. Also, at the single-phase composition values, UNIQUAC still predicts a separation into two phases.

## Conclusions

Current Gibbs energy models are inadequate in extending experimental VLE data to the prediction of LLE data. This work has presented a technique to measure VLE, and more importantly  $\gamma^\infty$ , of partially miscible systems for application to LLE. Present  $g^E$  expressions were shown to fail in attempting to predict the LLE relationships from VLE data. The continuing measurement of derivative data will lead to better understanding of solution behavior and to improved  $g^E$  models that will better be able to characterize LLE behavior.

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## Nomenclature

FUR = furfural

MCH = methylcyclohexane

NTM = nitromethane

TOL = toluene

$\Delta g_{12}$  = NRTL binary interaction parameter, cal/mol

$\Delta u_{12}$  = UNIQUAC binary interaction parameter, cal/mol

## Greek Letters

$\alpha_{12}$  = NRTL binary parameter

$\gamma^\infty$  = activity coefficient at infinite dilution

**Registry No.** Toluene, 108-88-3; nitromethane, 75-52-5; methylcyclohexane, 108-87-2; furfural, 98-01-1.

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# Experiments and Model for the Oscillatory Oxidation of Benzaldehyde

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The oxidation of benzaldehyde is investigated experimentally in a gas-liquid stirred cell reactor into which both gas and liquid phases are added continuously. The gas-liquid interfacial area is known, and the mass-transfer coefficient can be controlled. Regions of steady-state and oscillatory behavior are studied as a function of two system parameters, the liquid residence time and the liquid-side mass-transfer coefficient for oxygen absorption. An eight-variable mathematical model of the oxidation reaction is used to investigate stability and oscillations in the system. The mathematical simulation results were found to agree qualitatively with those found experimentally throughout most of the two-parameter space. A simpler three-variable model is then developed and shown to predict behavior similar to that of the more complicated model over most of the range of parameters.

Many chemical oscillators, such as the well-known Belousov-Zhabotinskii (Belousov, 1959; Zhabotinskii, 1964) and Bray-Liebhafsky (Bray, 1921; Liebhafsky, 1931a,b) reactions, occur in homogeneous liquid-phase systems. However, chemical systems involving gas-liquid reactions can also exhibit multiple steady states and oscillations.

Multiplicity and stability of gas-liquid reactors have been investigated numerically by a number of authors. In these studies, the gaseous component is absorbed into the liquid in which a simple exothermic reaction occurs. Schmitz and Amundson (1963) showed that multiple-steady-state and oscillatory behavior can exist in gas-liquid systems. In later studies, overall material and energy balances demonstrated that multiple steady states are possible in both adiabatic (Hoffman et al., 1975; Raghuram and Shah, 1977) and nonadiabatic (Huang and Varma,

1981a; Raghuram et al., 1979) reactors. Ding et al. (1974) have shown experimentally that two stable steady states can occur in the adiabatic chlorination of *n*-decane. Huang and Varma (1981b) have determined numerically that oscillatory behavior is possible—but not highly probable—in nonadiabatic reactors in which a fast pseudo-first-order reaction occurs in the liquid. Hancock and Kenney (1977) have reported oscillations in the formation of methyl chloride from hydrochloric acid and methanol in a two-phase reactor in which the reactants enter and the products leave in the gas phase, but reaction occurs in the liquid phase. In this case, the oscillatory behavior resulted mainly from a complex interaction between the product vapor pressure and the reactant partial pressure.

Oscillations in some more recently discovered gas-liquid systems are caused by positive feedback in the reaction