countered in the case of non-Newtonian fluids.

Figure 2 brings out the effects of the various parameters in Eq. 8. It is found that the Nusselt number decreases with increased pseudoplasticity, i.e., lower n. The effect of buoyancy in the present case is to assist forced convection and thereby increase the Nusselt number with a more profound effect for dilatant fluids, i.e., $n > 1.0$ than in the case of pseudoplastic fluids, i.e., $n < 1.0$. The increase in heat transfer rate is greater at higher Prandtl number. The effect of angle of inclination is evident from Figure 1 which shows that the Nusselt number decreases with increasing departure from the vertical. Due to lack of experimental work on laminar mixed convection to power law fluids, a comparison between the predictions of the present analysis and experimental data cannot be made at the present time.

NOTATION

$f(n)$ = function of n defined by Eq. 12
g = acceleration due to gravity
Gr_x = generalized local Grashof number defined by Eq. 6
K = consistency index for a power law fluid
n = flow behavior index for a power law fluid
$Nu_{x,F}$ = Nusselt number based on local distance x for forced convection heat transfer to power law fluids
$Nu_{x,M}$ = Nusselt number based on local distance x for mixed convection heat transfer to power law fluids and defined by Eq. 1
$Nu_{x,N}$ = Nusselt number based on local distance x for natural convection heat transfer to power law fluids
$Pr_{x,F}$ = generalized Prandtl number based on local distance x for forced convection heat transfer to power law fluids and defined by Eq. 10
$Pr_{x,N}$ = generalized Prandtl number based on local distance x for natural convection heat transfer to power law fluids and defined by Eq. 11
Re_x = generalized Reynolds number based on local distance x for forced convection to power law fluids and defined by Eq. 9
T = temperature of the fluid
T_w = temperature of the plate
T_∞ = temperature of the bulk of the fluid
U_∞ = free stream velocity for forced convection
u = velocity component along the x coordinate
v = velocity component along the y coordinate
x = distance along the plate from the leading edge
y = distance normal to the plate

Greek Letters

α = thermal diffusivity of the fluid
β = expansion coefficient of the fluid
γ = angle of inclination from the vertical
η_δ = dimensionless boundary layer thickness defined by Eq. 7
ρ = density of the fluid

LITERATURE CITED

Acrivos, A., M. J. Shah, and E. E. Peterson, "Momentum and Heat Transfer in Laminar Boundary-Layer Flows of Non-Newtonian Fluids Past External Surfaces," *AIChE J.* **6**, 312 (1960).

Chen, T. S., E. M. Sparrow, and A. Mucoglu, "Mixed Convection in Boundary Layer Flow on a Horizontal Plate," *ASME J. Heat Transfer*, **99**, 66 (1977).

Churchill, S. W., "A Comprehensive Correlating Equation for Laminar, Assisting, Forced and Free Convection," *AIChE J.*, **23**, 10 (1977).

Kubair, V. G., and D. C. Pei, "Combined Laminar Free and Forced Convection Heat Transfer to Non-Newtonian Fluids," *Int. J. Heat Mass Transfer*, **11**, 855 (1968).

Lin, H. T., and Y. P. Shih, "Combined Laminar Free and Forced Convection from a Vertical Plate to Power Law Fluids," *Chem. Eng. Commun.*, **7**, 327 (1980).

Mucoglu, A., and T. S. Chen, "Mixed Convection on Inclined Surfaces," *ASME J. Heat Transfer*, **101**, 422 (1979).

Oosthuisen, P. H., and R. Hart, "A Numerical Study of Laminar Combined Convective Flow over Flat Plates," *ASME J. Heat Transfer*, **95**, 60 (1973).

Ruckenstein, E., "Interpolating Equations between Two Limiting Cases for the Heat Transfer Coefficient," *AIChE J.*, **24**, 940 (1978).

Shenoy, A. V., "A Correlating Equation for Combined Laminar Forced and Free Convection Heat Transfer to Power-Law Fluids," *AIChE J.*, **26**, 505 (1980).

Shenoy, A. V., and J. J. Ulbrecht, "Temperature Profiles for Laminar Natural Convection Flow of Dilute Polymer Solutions past an Isothermal Vertical Flat Plate," *Chem. Eng. Commun.*, **3**, 303 (1979).

Manuscript received October 5, 1982 and accepted March 4, 1983.

Vapor-Liquid-Liquid Equilibria using UNIFAC in Gasohol Dehydration Systems

I. A. FURZER

Department of Chemical Engineering
University of Sydney
NSW 2006, Australia

The UNIFAC group contribution method has been used to model the nonideal liquid behavior in the system water(1)–ethanol(2)–cyclohexane(3). The VLLE data for a given feed composition lies in a narrow temperature range. Outside of this range are neighboring LL and VL regions. Similar complex equilibria can be expected in gasohol dehydration systems using azeotropic distillation.

INTRODUCTION

The UNIFAC group contribution method developed by Fredenslund et al. (1975) has been widely used to calculate vapor-liquid equilibria (VLE) for systems with nonideal liquid phases. The UNIFAC tables have been steadily increased by Skjold-Jørgensen et al. (1979) and Gmehling et al. (1982). The UNIFAC-

TABLE 1. NUMBER IN EACH UNIFAC GROUP: WATER(1)–ETHANOL(2)–CYCLOHEXANE(3)

Group			Component		
Main Group	Subgroup		1	2	3
1	1	CH_3–	0	1	0
1	2	CH_2–	0	1	6
5	14	–OH	0	1	0
8	17	H_2O	1	0	0

TABLE 2. GROUP VOLUME AND SURFACE AREA PARAMETERS

Group			
Main Group	Subgroup	R_k	Q_k
1	1	0.9011	0.848
1	2	0.6744	0.540
5	14	1.0000	1.200
8	17	0.92	1.40

TABLE 3. UNIFAC INTERACTION PARAMETERS

Main Group	1	5	8
1	0.0	644.6	1300.0
5	328.2	0.0	28.73
8	342.4	−122.4	0.0

TABLE 4. ANTOINE CONSTANTS: WATER(1)–ETHANOL(2)–CYCLOHEXANE(3)

Component	A	B	C
1	7.95864	1,663.125	227.528
2	8.24739	1,670.409	232.959
3	6.85532	1,209.299	223.527

generated VLE data can be linked with mass balances for each component on each plate of a distillation column to give the composition profiles down the column. Furzer (1981) has used this method to study the effect of various third components on the separation of paraffinic-naphthenic hydrocarbon mixtures.

The use of the UNIFAC group contribution method for liquid–liquid equilibria (LLE) has been given by Sørensen et al. (1979a,b) and Magnussen et al. (1981). If has been found that parameters obtained solely from VLE data lead to an average deviation of 9.2 mol % for the prediction of LLE data. These deviations can be reduced to only 1.7 mol %, if a separate set of UNIFAC parameters, the MRF LLE UNIFAC parameters as given by Magnussen, Rasmussen and Fredenslund (1981), are used. When a three-phase system consisting of a vapor in equilibrium with two liquids is considered the vapor–liquid–liquid equilibria (VLLE) could be generated from either of these two tables. This internal inconsistency in the UNIFAC model is due to the difficulty of modelling highly nonlinear liquid systems. Further tests on the appropriate UNIFAC parameters could be made if sufficient experimental VLLE data were available. Before any VLLE data can be predicted from one of these UNIFAC tables, it is necessary to ensure that three phases exist at the temperature and pressure of the system. This requires the determination of the minimum in the Gibbs energy surface and this surface can be complex if the liquid–phase model is inadequate. A differential test on the Gibbs energy minima is made by evaluating the Gibbs energy at a neighboring differential composition point. If this energy is lower, an additional phase must be added and the process repeated until the global minimum is obtained. Under these conditions the system is stable. One difficulty in performing this calculation is that the predicted Gibbs energy surface is model-dependent. For example, Maurer and Prausnitz (1979) have studied the use of UNIQUAC on predicting VLLE systems, Gautam and Seider (1979) have

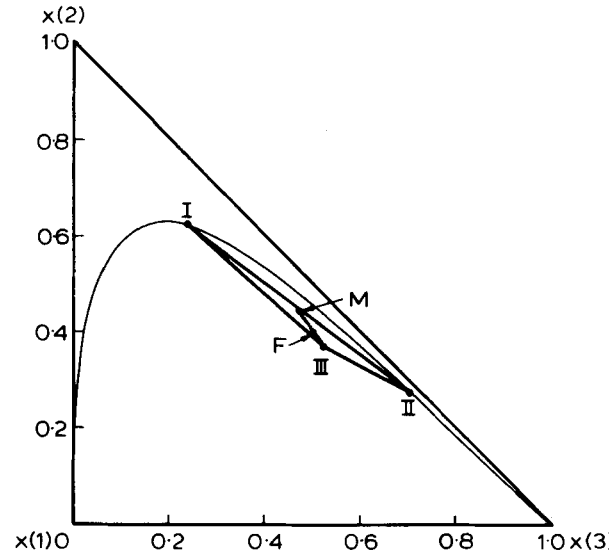

Figure 1. Water(1)–ethanol(2)–cyclohexane(3) UNIFAC VLLE Equilibria: LL Binodal Curve at T = 340 K; VLLE P = 101.325 kPa; phase (mol %), I = 18.67, II = 17.08, III = 64.24.

studied phase splitting, and Michelson (1980) has calculated phase envelopes.

The blending of gasoline with alcohol–water mixtures to produce gasohol requires a low water content to avoid the appearance of an aqueous phase rich in ethanol. Several methods have been suggested for the dehydration of alcohol–water mixtures that include adsorption, liquid–liquid extraction, and azeotropic distillation. The use of a third component such as benzene, cyclohexane, pentane or a naphtha cut has been suggested as the third component for azeotropic distillation. The original method to use benzene to produce absolute alcohol has been widely practiced and recently this material has been replaced by cyclohexane for toxicity reasons. Under many operating conditions it is possible to have three phases in equilibrium on a plate. It is necessary for the design of an azeotropic distillation column with cyclohexane to know the number of phases that exist on a plate before the normal mass balance and equilibrium equations can be solved.

UNIFAC GROUPS

A mixture of water(1)–ethanol(2)–cyclohexane(3) can be split into its UNIFAC LL groups. The ethanol (2) molecule can be subdivided into its UNIFAC LL groups as CH_3–, CH_2–, –OH. Cyclohexane(3) consists of six CH_2 groups, while water(1) is a special group by itself. The complete list of groups in a mixture of water(1)–ethanol(2)–cyclohexane(3) using the UNIFAC main group and subgroup numbers is given in Table 1. The UNIFAC group volume and surface area parameters are given for these groups in Table 2, while Table 3 contains the interaction parameters between the main groups.

The saturated vapor pressure of the three components can be correlated by the Antoine equation.

$$\log_{10} p^s = A - \frac{B}{C + T} \tag{1}$$

The Antoine constants for the three components are listed in Table 4.

VLLE EQUILIBRIA

A computer program LLECAL has been modified to obtain the binodal curve and the tie-lines for the system water(1)–ethanol(2) and cyclohexane(3). The operating instructions are given by Magnussen (1980). Figure 1 shows the binodal curve at 340 K with

TABLE 5. UNIFAC VLLE DATA: WATER(1)–ETHANOL(2)–CYCLOHEXANE(3)
P = 101.325 kPa
Feed $x(1) = 0.1$, $x(2) = 0.4$, $x(3) = 0.5$
(mole fraction)

Temp.	I (L)			II(L)			III (V)			Phase %		
k	$x(1)$	$x(2)$	$x(3)$	$x(1)$	$x(2)$	$x(3)$	$x(1)$	$x(2)$	$x(3)$	I	II	III
338.80	0.136	0.670	0.194	—	—	—	0.100	0.400	0.500	0.1	0.0	99.9
338.60	0.129	0.658	0.213	—	—	—	0.099	0.394	0.507	2.4	0.0	97.6
338.30	0.113	0.629	0.258	—	—	—	0.099	0.384	0.517	6.7	0.0	93.3
338.13	0.098	0.593	0.309	—	—	—	0.100	0.377	0.523	10.7	0.0	89.3
338.09	0.093	0.579	0.328	—	—	—	0.101	0.375	0.524	12.4	0.0	87.6
338.087	0.020	0.301	0.679	0.119	0.616	0.265	0.105	0.373	0.522	7.9	13.4	78.7
338.04	0.019	0.289	0.692	0.129	0.622	0.249	0.108	0.370	0.522	12.7	16.1	71.2
338.00	0.018	0.279	0.703	0.139	0.625	0.236	0.110	0.367	0.523	17.1	18.7	64.2
337.93	0.07	0.263	0.720	0.156	0.630	0.214	0.115	0.361	0.524	25.5	23.8	50.7
337.85	0.015	0.245	0.739	0.179	0.631	0.190	0.121	0.354	0.525	37.2	31.1	31.7
337.80	0.015	0.234	0.751	0.194	0.631	0.175	0.125	0.350	0.525	46.1	36.8	17.1
337.77	0.015	0.228	0.758	0.205	0.629	0.166	0.128	0.347	0.525	52.4	40.9	6.7
337.76	0.015	0.225	0.760	0.208	0.629	0.163	0.129	0.345	0.526	54.6	42.4	3.0
337.75	0.014	0.224	0.762	0.211	0.628	0.161	—	—	—	54.6	43.6	0.0
337.72	0.014	0.224	0.762	0.211	0.628	0.161	—	—	—	56.4	43.6	0.0
337.70	0.014	0.223	0.763	0.210	0.629	0.161	—	—	—	56.3	43.7	0.0
337.50	0.014	0.223	0.762	0.211	0.628	0.161	—	—	—	56.4	43.6	0.0

the pressure sufficiently high so that the system is below its bubble point temperature. The azeotrope for this system has a boiling point temperature of 335.8 K, which is lower than the boiling points of the three pure components. The binodal curve is not particularly sensitive to temperture and the curve at 340 K is typical of the boundary between one and two liquid phases that could exist in gasohol dehydration columns. The tie-lines for the system have large negative slopes and are directed to a region near the pure cyclohexane apex.

The same program has been used to obtain the VLLE data for the system at a pressure of 101.325 kPa. A feed stream containing $x(1) = 0.1$, $x(2) = 0.4$, and $x(3) = 0.5$ mol fraction has been flashed at various temperatures near 340 K. At 338 K three phases are present. There are two liquid phases (I and II) plus a vapor phase (III) in equilibrium, Figure 1. The tie-lines for this feed condition (F) and 338 K are shown by three lines linking the points I, II and III. The use of the lever rule to form point (M) from phases I and II and its combination with point III leads to the feed composition (F). The complete VLLE diagram for every feed condition and temperature would make such a figure very complex. The compositions of the liquid phases I and II are very close to the equilibrium values at 340 K at a higher pressure and lie almost on the binodal curve at 340 K. The line between the points I and II corresponds to a LL tie-line. In this example a flash distillation of the feed at 338 K results in 64.2 mol % of the feed being vaporized leaving two liquid phases (I and II) containing 18.67 and 17.08% of the feed, respectively.

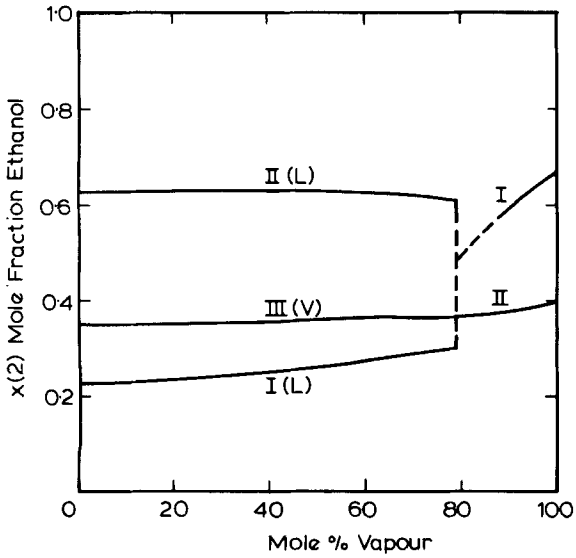

Figure 2. Water(1)–ethanol(2)–cyclohexane(3) UNIFAC flash distillation: mol % vaporized, P = 101.325 kPa; feed composition (mole fraction), $x(1) = 0.1$, $x(2) = 0.4$, $x(3) = 0.5$.

Table 5 provides a more comprehensive set of data for the equilibria in this system. At temperatures below 337.75 K, the bubble point temperature, only two liquid phases exist when the pressure is 101.325 kPa. When the feed has the composition given above, phase I contains 56.4 mol % of the feed and phase II, 43.6%.

Above 337.75 K to approximately 338.087 K is a region with two liquid phases and the system is a VLL system. In this temperature interval the mole percent vapor rises from 0 to 78.7%. The ethanol composition of the vapor phase is initially at $x(2) = 0.345$ at 337.76 K and rises to $x(2) = 0.373$ at 338.087 K. Above 338.09 K is a region with only one liquid phase and the system is a normal VL system. The ethanol composition of the liquid is intermediate between the compositions of phase I and II at a slightly lower temperature. The mole percent vapor has changed rapidly to 87.6% and increased to 99.9% at the dew point temperature of 338.80 K. The effect of flashing the feed on the ethanol content of the three phases is shown in Figure 2. The change from a VLLE system to a VLE system at higher mole percent vaporized represents some of the complexities that could be expected in gasohol dehydration systems.

DISCUSSION

The MRF LLE UNIFAC parameters have been used to predict the VLLE at temperatures near 338 K. This temperature is slightly higher than the recommended maximum temperature of 313 K. Further experimental work is required to establish the phase splitting characteristics as predicted by the UNIFAC model. The interaction parameters between the CH_2–Oh and H_2O groups in Table 3 are those recommended by Magnussen et al. (1981). These parameters give better mutual solubilities for the alcohols in water than the alkanes in water. Gasohol dehydration systems using cyclohexane for the azeotropic distillation can be expected to enter the VLLE region and the UNIFAC model is very useful in predicting the number of phase present and the phase compositions.

ACKNOWLEDGMENT

Many thanks to all the UNIFAC team of DTH Denmark. This project was supported by the Australian Research Grants Committee.

NOTATION

A = Antoine constant
B = Antoine constant
C = Antoine constant
p^s = saturated vapor pressure, mm Hg (kPa)
T = temperature, K
x = liquid composition, mole fraction

LITERATURE CITED

Fredenslund, Aa., R. L. Jones, and J. M. Prausnitz, "Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures," *AIChE J.*, **21**, 1086 (1975).
Furzer, I. A., "Azeotropic Distillation with UNIFAC," New Zealand, *Chemeca 81*, **9**, 219 (1981).
Gautam, R., and W. D. Seider, "Calculation of Phase and Chemical Equilibrium," Part II, *AIChE J.* **25**, 6 (1979).
Gmehling, J., P. Rasmussen, and Aa. Fredenslund, "Vapor-Liquid Equilibria by UNIFAC Group-Contribution," Revision and Extension II, *Ind. Eng. Chem. Process Des. Dev. 21*, 118 (1982).
Magnussen, T., "Manual for the Liquid-Liquid Equilibrium Program LLECAL," Inst. for Kemiteknik, Danmarks Tekniske Højskole, MAN 8001 (1980).
Magnussen, T., P. Rasmussen, and Aa. Fredenslund, "UNIFAC Parameter Table for Prediction of Liquid-Liquid Equilibria," *Ind. Eng. Chem. Process Des. Dev.*, **20**, 331 (1981).
Michelsen, M. L., "Calculation of Phase Envelopes and Critical Points for Multicomponent System," *Fluid Phase Equil.*, **4**, 1 (1980).
Maurer, G., and J. M. Prausnitz, "Thermodynamics of Multicomponent Liquid–Liquid–Vapor Equilibria for Distillation Column Design," *Inst. of Chem. Eng.*, **3**, 1.3/41 (1979).
Skjoid-Jørgensen, S., B. Kolbe, J. Gmehling, and P. Rasmussen, "Vapor–Liquid Equilibria by UNIFAC Group Contribution: Revision and Extension," *Ind. Eng. Chem. Process Des. Dev.*, **18**, 714 (1979).
Sørensen, J. M., T. Magnussen, P. Rasmussen, and Aa. Fredenslund, "Liquid–Liquid Equilibrium Date: Their Retrieval Correlation and Prediction," Part I, *Fluid Phase Equil.*, **2**, 297 (1979a).
Sørensen, J. M., T. Magnussen, P. Rasmussen, and Aa. Fredenslund, "Liquid–Liquid Equilibrium Date: Their Retrieval Correlation and Prediction," Part II, *Fluid Phase Equil.*, **3**, 47 (1979b).

Manuscript received October 5, 1982; revision received February 16, and accepted March 4, 1983.

Simulation of Pore Growth and Coalescence

JOW-LIH SU and D. D. PERLMUTTER

Department of Chemical Engineering
University of Pennsylvania
Philadelphia, PA 19104

The kinetics of gas-solid reactions are strongly affected by the growth and concomitant overlap of the pores that are the passages by which the gas has access to the reacting solid. Similarly the growth and coalescence of nuclei can play a major role in determining the rate of a solid-phase reaction. The geometric considerations are the same in both cases, differing only in whether the volumes and surfaces of interest are descriptive of filled spaces or voids. In either application, an approach is needed to relate actual changes in geometry to those that would have developed if the pores (or nuclei) had not overlapped. For this purpose Avrami (1940) developed a relationship between actual volume growth and the volume growth of a hypothetical nonoverlapped system:

$$dV = (1 - V)dV_E \tag{1}$$

Since $V \to 0$ as $V_E \to 0$, Eq. 1 can be integrated to give

$$V_E = -ln(1 - V) \tag{2}$$

If volume growth is uniform on all surfaces, Bhatia and Perlmutter (1980) have noted that a similar expression relates real and hypothetical surface areas:

$$S = S_E(1 - V) \tag{3}$$

Avrami's formulation has been instrumental in the development of a variety of useful kinetic models for solid phase reactions (Young, 1966; Tompkins, 1976) and for gas-solid systems (Bhatia and Perlmutter, 1980); however, there have been questions raised as to the range of applicability of Avrami's approximation. Noting that Eq. 2 only allows $V = 1$ as $V_E \to \infty$, Ruckenstein and Vavanellos (1975) and Gavalas (1980) expressed doubts as to whether Avrami's formulation could be precise at high levels of conversion. Bhatia and Perlmutter (1979) had other reservations for the low conversion range over which initial nuclei volumes might be significant but unaccounted for.

In the work reported in this communication, a computer simulation was used to model the growth and coalescence of pores in order to access the accuracy of Avrami's relationships. Following the computational techniques of Mohanty et al. (1982) for evaluating effects of irregular morphology in a porous medium, a sample space of 27,000 cubic building blocks was allowed to represent a reactive sample. The initial porosity was randomly distributed among the cubes, labeling each one as either full or empty. The empty cubes were allowed to grow one block at a time evenly in all directions, and to coalesce with their neighbors where overlap occurred. To keep the sample space representative of an infinite medium, symmetric growth was allowed to enter past a boundary of the space, whenever a cube grew past an opposite boundary. The process was allowed to continue until porosity reached 0.99. The simulation thus produced computed volumes and corresponding surfaces developed at each step of growth on both bases of interest here: 1) as predictions of actual behavior and 2) as hypothetical nonoverlapped configurations. A series of initial porosity values was used, ranging from 0.004 to 0.1. Values less than 0.004 were not used, lest the initial number of empty cubes be insufficient to assure a randomness within the sample space.

The computed results are presented in Figures 1 and 2, using