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APPENDICES

APPENDIX A

CORRECTION FACTOR

Correction faction for GC with column Gaskuropack 54

Correction faction, $F = \frac{(A/W)_{COMPONENT}}{(A/W)_{STANDARD}}$ (A-1)

Given methyl *tert*-butyl ether (MTBE) is standard component (F=1)

REACTANTS	WEIGHT (W)	AREA (A)	CORRECTION FACTOR (F)
Water	3.936×10^{-7}	318420	1.5971
Ethanol (EtOH)	3.050×10^{-7}	215674	1.3959
tert-butyl alcohol (TBA)	3.060×10^{-7}	171234	1.1047
MTBE	3.155×10^{-7}	159814	1.0000
ETBE	3.100×10^{-7}	130855	0.8333

APPENDIX B

CALCULATION OF NUMBER OF MOLE

Number of mole of each component can calculate by using correction factors from Appendix A.

$$\text{Number of mole} = \frac{Area/(MWxF)_{component}}{\Sigma(Area)/(MWxF)_{component}} \text{ x Total mole} \qquad \text{(B-1)}$$

For example; Batch reactor

Reaction condition; temperature=323 K, speed level=660 rpm, catalyst weight=30 g, time=0 min, TBA_0=0.97 mol, $EtOH_0$=0.50 mol, H_2O_0=0.00 mol.

REACTANTS	AREA	MW	CORRECTION FACTOR(F)	NUMBER OF MOLE
Water	4995	18	1.5971	0.0312
Ethanol(EtOH)	177092	46	1.3959	0.4957
TBA	441439	74	1.1047	0.9703
ETBE	1358	102	0.8333	2.8709×10^{-3}

APPENDIX C

UNIFAC CALCULATION

The UNIQUAC equation treats $g \equiv G^E / RT$ as comprised of two additive parts, a *combinatorial* term g^C to account for molecular size and shape differences, and a *residual* term g^R to account for molecular interactions:

$$g = g^C + g^R \tag{C-1}$$

Function g^C contains pure-species parameters only, whereas function g^R incorporates two binary parameters for each pair of molecules. For a multicomponent system,

$$g^C = \sum x_i \ln \frac{\phi_i}{x_i} + 5 \sum q_i x_i \ln \frac{\theta_i}{\phi_i} \tag{C-2}$$

and

$$g^R = -\sum q_i x_i \ln(\sum \theta_j \tau_{ji}) \tag{C-3}$$

where

$$\phi_i = \frac{x_i r_i}{x_j r_j} \tag{C-4}$$

and

$$\theta_i = \frac{x_i q_i}{x_j q_j} \tag{C-5}$$

Subscript i identifies species, and j is a dummy index; all summations are over all species. Note that $\tau_{ji} \neq \tau_{ij}$; however, when $i = j$, then $\tau_{ij} = \tau_{ii} = 1$. In these equations r_i (a relative molecular volume) and q_i (a relative molecular surface area) are pure-species parameters. The influence of temperature on g enters through the interaction parameters τ_{ji} of Eq.(C-3), which are temperature dependent:

$$\tau_{ji} = \exp \frac{-(u_{ji} - u_{ii})}{RT} \tag{C-6}$$

Parameters for the UNIQUAC equation are therefore values of $(u_{ji} - u_{ii})$.

An expression for $\ln\gamma_i$ is applied to the UNIQUAC equation for g [Eqs.(C-1) through (C-3)]. The result is given by the following equations:

$$\ln\gamma_i = \ln\gamma_i^{C} + \ln\gamma_i^{R} \qquad \text{(C-7)}$$

$$\ln\gamma_i^{C} = 1 - J_i + \ln J_i - 5q_i\left(1 - \frac{J_i}{L_i} + \ln\frac{J_i}{L_i}\right) \qquad \text{(C-8)}$$

and

$$\ln\gamma_i^{R} = q_i\left(1 - \ln s_i - \sum\theta_j \frac{\tau_{ij}}{s_j}\right) \qquad \text{(C-9)}$$

where in addition to Eqs. (C-5) and (C-6)

$$J_i = \frac{r_i}{\sum x_j r_j} \qquad \text{(C-10)}$$

$$L_i = \frac{q_i}{\sum x_j q_j} \qquad \text{(C-11)}$$

$$s_i = \sum\theta_l \tau_{li} \qquad \text{(C-12)}$$

Again subscript i identifies species, and j and l are dummy indices. All summations are over all species, and τ_{ij}=1 for i=j. Values for the parameters $(u_{ij} - u_{jj})$ are found by regression of binary VLE data, and are given by Gmehling et al.

The UNIFAC method for estimation of activity coefficient depends on the concept that a liquid mixture may be considered a solution of the structural units from which the molecules are formed lather than a solution of the molecules themselves. These structural units are called subgroups, and a few of them are listed in the second column of table C.1. A number, designated k, identifies each subgroup. The relative volume R_k and relative surface area Q_k are properties of the subgroups, and values are listed in column 4 and 5 of table C.1. Also shown (columns 6 and 7) are examples of the subgroup compositions of molecular species. When it is possible to construct a molecule from more than one set of subgroups, the set containing the least member of different subgroups id the correct set. The great advantage of the UNIFAC method is that a relatively small number of subgroups combine to form a very large number of molecules.

Activity coefficients depend not only on the subgroup properties R_k and Q_k, but also on interactions between subgroups. Here, similar subgroups are assigned to a main group, as shown in the first two columns of table C.1. The designations of main groups, such as "CH_2" , "ACH", etc., are descriptive only. All subgroups belonging to the same main group are considered identical with respect to group interactions. Therefore parameters characterizing group interactions are identified with pairs of main groups. Parameter value a_{mk} for a few such pairs are given in table C.2.

The UNIFAC method is base on the UNIQUAC equation, for which the activity coefficients are given by equation C-7. When applied to a solution of groups, Eqs. C-8 and C-9 are written:

$$\ln\gamma_i^{C} = 1 - J_i + \ln J_i - 5q_i\left(1 - \frac{J_i}{L_i} + \ln\frac{J_i}{L_i}\right) \qquad \text{(C-13)}$$

and

$$\ln\gamma_i^{R} = q_i\left[1 - \sum\left(\theta_k \frac{\beta_{ik}}{s_k} - e_{ki}\ln\frac{\beta_{ik}}{s_k}\right)\right] \qquad \text{(C-14)}$$

The quantities J_i and L_i are still given by Eqs. C-10 and C-11. In addition, the following definition apply:

$$r_i = \sum \nu_k^{(i)} R_k \qquad \text{(C-15)}$$

$$q_i = \sum \nu_k^{(i)} Q_k \qquad \text{(C-16)}$$

$$e_{ki} = \frac{\nu_k^{(i)} Q_k}{q_i} \qquad \text{(C-17)}$$

$$\beta_{ik} = \sum e_{mi}\tau_{mk} \qquad \text{(C-18)}$$

$$\theta_k = \frac{\sum x_i q_i e_{ki}}{\sum x_j q_j} \qquad \text{(C-19)}$$

$$s_k = \sum \theta_m \tau_{mk} \qquad \text{(C-20)}$$

$$\tau_{mk} = \exp\frac{-a_{mk}}{T} \qquad \text{(C-21)}$$

Subscript i identifies species, and j is a dummy index running over all species. Subscript k identifies subgroups, and m is a dummy index running over all subgroups. the quantity

$\nu_k^{(i)}$ is the number of subgroups of type k in a molecule of species i. Values of the subgroup parameters R_k and Q_k and of the group interaction parameters a_{mk} come from tabulation in the literature. Tables C.1 and C.2 show a few parameter values; the number designations of the compete table are remained.

Table C.1: UNIFAC-VLE subgroup parameters

Main group	Subgroup	k	R_k	Q_k	Examples of molecules and their constituent groups	
1 "CH_2"	CH_3	1	0.9011	0.848	n-Butane:	$2CH_3, 2CH_2$
	CH_2	2	0.6744	0.540	Isobutane:	$3CH_3, 1CH$
	CH	3	0.4469	0.228	2,2-Dimethyl	
	C	4	0.2195	0.000	propane:	$4CH_3, 1C$
3 "ACH" (AC = aromatic carbon)	ACH	10	0.5313	0.400	Benzene:	6ACH
4 "$ACCH_2$"	$ACCH_3$	12	1.2663	0.968	Toluene:	$5ACH, 1ACCH_3$
	$ACCH_2$	13	1.0396	0.660	Ethylbenzene:	$1CH_3, 5ACH, 1ACCH_2$
5 "OH"	OH	15	1.0000	1.200	Ethanol:	$1CH_3, 1CH_2, 1OH$
7 "H_2O"	H_2O	17	0.9200	1.400	Water:	$1H_2O$
9 "CH_2CO"	CH_3CO	19	1.6724	1.488	Acetone:	$1CH_3CO, 1CH_3$
	CH_2CO	20	1.4457	1.180	3-Pentanone:	$2CH_3, 1CH_2CO, 1CH_2$
13 "CH_2O"	CH_3O	25	1.1450	1.088	Dimethyl ether:	$1CH_3, 1CH_3O$
	CH_2O	26	0.9183	0.780	Diethyl ether:	$2CH_3, 1CH_2, 1CH_2O$
	CH−O	27	0.6908	0.468	Diisopropyl ether:	$4CH_3, 1CH, 1CH-O$
15 "CNH"	CH_3NH	32	1.4337	1.244	Dimethylamine:	$1CH_3, 1CH_3NH$
	CH_2NH	33	1.2070	0.936	Diethylamine:	$2CH_3, 1CH_2, 1CH_2NH$
	CHNH	34	0.9795	0.624	Diisopropylamine:	$4CH_3, 1CH, 1CHNH$
19 "CCN"	CH_3CN	41	1.8701	1.724	Acetonitrile:	$1CH_3CN$
	CH_2CN	42	1.6434	1.416	Propionitrile:	$1CH_3, 1CH_2CN$

[1]H. K. Hansen, P. Rasmussen, Aa. Fredenslund, M. Schiller, and J. Gmehling, *IEC Research*, vol. 30, pp. 2352-2355, 1991.

Table C.2: UNIFAC-VLE interaction parameters, a_{mk}, in kelvins

	1	3	4	5	7	9	13	15	19
1 CH_2	0.00	61.13	76.50	986.50	1.318.00	476.40	251.50	255.70	597.00
3 ACH	−11.12	0.00	167.00	636.10	903.80	25.77	32.14	122.80	212.50
4 $ACCH_2$	−69.70	−146.80	0.00	803.20	5,695.00	−52.10	213.10	−49.29	6.096.00
5 OH	156.40	89.60	25.82	0.00	353.50	84.00	28.06	42.70	6.712
7 H_2O	300.00	362.30	377.60	−229.10	0.00	−195.40	540.50	168.00	112.60
9 CH_2CO	26.76	140.10	365.80	164.50	472.50	0.00	−103.60	−174.20	481.70
13 CH_2O	83.36	52.13	65.69	237.70	−314.70	191.10	0.00	251.50	−18.51
15 CNH	65.33	−22.31	223.00	−150.00	−448.20	394.60	−56.08	0.00	147.10
19 CCN	24.82	−22.97	−138.40	185.40	242.80	−287.50	38.81	−108.50	0.00

[1]H. K. Hansen, P. Rasmussen, Aa. Fredenslund, M. Schiller, and J. Gmehling, *IEC Research*, vol. 30, pp. 2352–2355, 1991.

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