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PHASE EQUILIBRIA BY EFFECTIVE UNIFAC GROUP-CONTRIBUTION METHOD

ISAMU NAGATA * and JITSUO KOYABU

Department of Chemical Engineering, Kanazawa University, 2-40-20 Kodatsuno, Kanazawa, Ishikawa 920 (Japan)

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ABSTRACT

A group-contribution method similar to the UNIFAC model is presented for the estimation of liquid phase activity coefficients. The method is based on an extension of the effective UNIQUAC equation, which represents well vapor—liquid equilibria of alcohol-saturated hydrocarbon mixtures with two parameters. Group-interaction parameters for 35 groups are obtained from experimental vapor—liquid equilibrium and solubility data. Activity coefficients in many binary and multicomponent mixtures may be estimated with good accuracy. Calculations are carried out for vapor—liquid, liquid—liquid, and solid—liquid equilibria. Both UNIFAC and effective UNIFAC seem to provide comparable results in most cases. The method, like the SIGMA of Vera, may be used for the prediction of both vapor—liquid equilibrium and excess enthalpy data for binary and ternary systems containing CH_2, CCOH, and CCl groups.

NOTATION

a_{mn}	group interaction parameter
A_{mn}	coefficient of group interaction parameter
B_{ij}	second virial coefficient for i—j interaction
B_{mn}	coefficient of group-interaction parameter
G_{ji}	effective UNIQUAC parameter defined by eqn. (5)
h^E	excess enthalpy
Δh_f	enthalpy of fusion
H_k	excess enthalpy of group k
$H_k^{(i)}$	excess enthalpy of group k in pure component i
P	total pressure
P_i^s	saturation pressure of pure component i
q_i	pure component area parameter of component i
Q_k	group area parameter for group k
r_i	pure component volume parameter of component i
R_k	group volume parameter for group k
R	gas constant

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* To whom correspondence should be addressed.

T	absolute temperature
T_m	melting temperature
u_{ji}	effective UNIQUAC binary interaction parameter
U_{mn}	energy parameter for m—n interaction
v_i^L	molar liquid volume of pure component i
x_i	liquid phase mole fraction of component i
X_k	group fraction for group k
y_i	vapor phase mole fraction of component i
Z	lattice coordination number, here equal to 10

Greek letters

γ_i	activity coefficient of component i
Γ_k	residual activity coefficient of group k
$\Gamma_k^{(i)}$	residual activity coefficient of group k in pure component i
ϕ_i	fugacity coefficient of component i
ϕ_i^s	fugacity coefficient of pure component i at its saturation pressure
Φ_i	segment fraction of component i
ν_{ki}	number of group of kind k in molecular species i
θ_i	area fraction of component i
θ_k	area fraction of group k
ψ_{mn}	effective UNIFAC parameter defined in eqn. (11)
η_{mn}	derivative with respect to temperature of ψ_{mn}

Subscripts

f	fusion
i, j	component
k	molecular group
m	melting in T_m; otherwise refers to molecular group
n	molecular group

Superscripts

C	combinatorial
L	liquid phase
R	residual
s	saturation pressure in P_i^s and ϕ_i^s; otherwise refers to solid phase
I, II	liquid phase

INTRODUCTION

The group-contribution concept has been used to estimate various physico-chemical properties of pure compounds such as densities, heat capacities, and critical constants and subsequently applied to calculate activity coeffients in liquid mixtures, because the desired experimental data are often not available in the literature. The most significant approaches on the latter subject are the ASOG (Analytical Solution of Groups) method [1—3] and the UNIFAC (UNIQUAC Functional Group Activity Coefficients) method [4—10]. The UNIFAC method, in principle, is similar to the ASOG method. The UNIFAC method is based on the UNIQUAC equation [11], which contains a combinatorial term due to differences in size and shape of the molecules in the mixtures and a residual part due to energy interaction. It has been shown that the UNIFAC method has three advantages over the ASOG method [5,10]: (1) UNIFAC has a well-defined molecular basis for establishing group sizes and shapes; (2) UNIFAC parameters are not strongly temperature-dependent for the temperature range studied; (3) UNIFAC parameters are available for many various functional groups. Skjold-Jørgensen et al. [9] have reported extensions and revisions of the UNIFAC parameter tables.

Nagata and Katoh [12] presented the effective UNIQUAC equation, which shows some advantages over the original UNIQUAC equation in representing phase equilibria for non-ideal mixtures. In this work, we report another group-contribution method based on the effective UNIQUAC equation in the calculations of vapor—liquid, liquid—liquid, and solid—liquid equilibria. The method has been tested for the prediction of vapor—liquid equilibria and excess enthalpy data for alkane, alcohol, and chloroalkane systems.

EFFECTIVE UNIFAC METHOD

The two-parameter effective UNIQUAC equation [12] in a multicomponent system is expressed by

$$\ln \gamma_i = \ln \gamma_i^C \text{ (combinatorial)} + \ln \gamma_i^R \text{ (residual)} \tag{1}$$

where

$$\ln \gamma_i^C = (\ln \Phi_i/x_i + 1 - \Phi_i/x_i) - (Z/2)\, q_i(\ln \Phi_i/\theta_i + 1 - \Phi_i/\theta_i) \tag{2}$$

$$\ln \gamma_i^R = 1 - \ln\Big(\sum_j x_j G_{ji}\Big) - \sum_k \left(\frac{x_k G_{ik}}{\sum_j x_j G_{jk}}\right) - \left(\ln\frac{\theta_i}{x_i} + 1 - \frac{\theta_i}{x_i}\right) \tag{3}$$

$$\Phi_i = r_i x_i \Big/ \sum_j r_j x_j\,, \qquad \theta_i = q_i x_i \Big/ \sum_j q_j x_j \tag{4}$$

$$G_{ji} = (q_j/q_i)\exp[-(u_{ji} - u_{ii})/RT] \tag{5}$$

In eqns. (1)—(5), x_i is the liquid phase mole fraction, Φ_i is the segment fraction, and θ_i is the area fraction. Pure component structural parameters r_i and q_i are the van der Waals molecular volumes and areas [11,13]. The coordination number Z is equal to 10. The combinatorial term $\ln \gamma_i^C$ contains only two composition variables: the average area fraction θ and the average segment fraction Φ. The two parameters per binary $(u_{ji} - u_{ii})$ and $(u_{ij} - u_{jj})$ are obtained from experimental phase equilibrium data. No ternary parameters are necessary for a multicomponent system.

The combinatorial term of the effective UNIFAC method is the same as in effective UNIQUAC. Parameters r_i and q_i are obtained by the sum of the group volume and area parameters given in Table 1 [4,5,9].

$$r_i = \sum_k \nu_{ki} R_k\,, \qquad q_i = \sum_k \nu_{ki} Q_k \tag{6}$$

TABLE 1

Group volume and surface-area parameters

Main group	Sub group	No	R_k	Q_k	Sample group assignment	
1 "CH_2"	CH_3	1	0.9011	0.848	Butane:	2 CH_3, 2 CH_2
	CH_2	2	0.6744	0.540		
	CH	3	0.4469	0.228	2-Methylpropane:	3 CH_3, 1 CH
	C	4	0.2195	0.000	2,2-Dimethylpropane:	4 CH_3, 1 C
2 "C = C"	CH_2 = CH	5	1.3454	1.176	1-Hexene:	1 CH_3, 3 CH_2, 1 CH_2 = CH
	CH = CH	6	1.1167	0.867	2-Hexene:	2 CH_3, 2 CH_2, 1 CH = CH
	CH = C	7	0.8886	0.676	2-Methyl-2-butene:	3 CH_3, 1 CH = C
	CH_2 = C	8	1.1173	0.988	2-Methyl-1-butene:	2 CH_3, 1 CH_2, 1 CH_2 = C
3 "ACH"	ACH	9	0.5313	0.400	Benzene:	6 ACH
	AC	10	0.3652	0.120	Styrene:	1 CH_2 = CH, 5 ACH, 1 AC
4 "$ACCH_2$"	$ACCH_3$	11	1.2663	0.968	Toluene:	5 ACH, 1 $ACCH_3$
	$ACCH_2$	12	1.0396	0.660	Ethylbenzene:	1 CH_3, 5 ACH, 1 $ACCH_2$
	ACCH	13	0.8121	0.348	Cumene:	2 CH_3, 5 ACH, 1 ACCH
5 "CCOH"	CH_2CH_2OH	14	1.8788	1.664	1-Propanol:	1 CH_3, 1 CH_2CH_2OH
	$CHOHCH_3$	15	1.8780	1.660	2-Butanol:	1 CH_3, 1 CH_2, 1 $CHOHCH_3$
	$CHOHCH_2$	16	1.6513	1.352	3-Octanol:	2 CH_3, 4 CH_2, 1 $CHOHCH_2$
	CH_3CH_2OH	17	2.1055	1.972	Ethanol:	1 CH_3CH_2OH
	$CHCH_2OH$	18	1.6513	1.352	2-Methyl-1-propanol:	2 CH_3, 1 $CHCH_2OH$
6	CH_3OH	19	1.4311	1.432	Methanol:	1 CH_3OH
7	H_2O	20	0.92	1.40	Water:	1 H_2O
8	ACOH	21	0.8952	0.680	Phenol:	5 ACH, 1 ACOH
9 "CH_2CO"	CH_3CO	22	1.6724	1.488	Ketone group is 2nd carbon; 2-Butanone:	1 CH_3, 1 CH_2, 1 CH_3CO
	CH_2CO	23	1.4457	1.180	Ketone group is any other carbon; 3-Pentanone:	2 CH_3, 1 CH_2, 1 CH_2CO
10	CHO	24	0.9980	0.940	Acetaldehyde:	1 CH_3, 1 CHO
11 "COOC"	CH_3COO	25	1.9031	1.728	Butyl acetate:	1 CH_3, 3 CH_2, 1 CH_3COO
	CH_2COO	26	1.6764	1.420	Butyl propanoate:	2 CH_3, 3 CH_2, 1 CH_2COO

12 "CH_2O"	CH_3O	27	1.1450	1.088	Dimethyl ether:	1 CH_3 1 CH_3O
	CH_2O	28	0.9183	0.780	Diethyl ether:	2 CH_3, 1 CH_2, 1 CH_2O
	CH-O	29	0.6908	0.468	Diisopropyl ether;	4 CH_3, 1 CH, 1 CH-O
	FCH_2O	30	0.9183	1.1	Tetrahydrofuran:	3 CH_2, 1 FCH_2O
13 "CNH_2"	CH_3NH_2	31	1.5959	1.544	Methylamine:	1 CH_3NH_2
	CH_2NH_2	32	1.3692	1.236	Propylamine:	1 CH_3, 1 CH_2, 1 CH_2NH_2
	$CHNH_2$	33	1.1417	0.924	Isopropylamine:	2 CH_3, 1 $CHNH_2$
14 "CNH"	CH_3NH	34	1.4337	1.244	Dimethylamine:	1 CH_3, 1 CH_3NH
	CH_2NH	35	1.2070	0.936	Diethylamine:	2 CH_3, 1 CH_2, 1 CH_2NH
	CHNH	36	0.9795	0.624	Diisopropylamine:	4 CH_3, 1 CH, 1 CHNH
15	$ACNH_2$	37	3.7165	2.816	Aniline:	1 $ACNH_2$
16 "CCN"	CH_3CN	38	1.8701	1.724	Acetonitrile:	1 CH_3CN
	CH_2CN	39	1.6434	1.416	Propionitrile:	1 CH_3, 1 CH_2CN
17 "COOH"	COOH	40	1.3013	1.224	Acetic acid:	1 CH_3, 1 COOH
	HCOOH	41	1.5280	1.532	Formic acid:	1 HCOOH
18 "CCl"	CH_2Cl	42	1.4654	1.264	1-Chlorobutane:	1 CH_3, 2 CH_2, 1 CH_2Cl
	CHCl	43	1.2380	0.952	2-Chloropropane:	2 CH_3, 1 CHCl
	CCl	44	1.0060	0.724	2-Chloro-2-methylpropane:	3 CH_3, 1 CCl
19 "CCl_2"	CH_2Cl_2	45	2.2564	1.988	Dichloromethane:	1 CH_2Cl_2
	$CHCl_2$	46	2.0606	1.684	1,1-Dichloroethane:	1 CH_3, 1 $CHCl_2$
	CCl_2	47	1.8016	1.448	2,2-Dichloropropane:	2 CH_3, 1 CCl_2
20 "CCl_3"	$CHCl_3$	48	2.8700	2.410	Chloroform:	1 $CHCl_3$
	CCl_3	49	2.6401	2.184	1,1,1,-Trichloroethane:	1 CH_3, 1 CCl_3
21	CCl_4	50	3.3900	2.910	Tetrachloromethane:	1 CCl_4
22	ACCl	51	1.1562	0.844	Chlorobenzene:	5 ACH, 1 ACCl
23 "CNO_2"	CH_3NO_2	52	2.0086	1.868	Nitromethane:	1 CH_3NO_2
	CH_2NO_2	53	1.7818	1.560	1-Nitropropane:	1 CH_3, 1 CH_2, 1 CH_2NO_2
	$CHNO_2$	54	1.5544	1.248	2-Nitropropane:	2 CH_3, 1 $CHNO_2$
24	$ACNO_2$	55	1.4199	1.104	Nitrobenzene:	5 ACH, 1 $ACNO_2$
25	CS_2	56	2.057	1.65	Carbon disulfide:	1 CS_2
26	CH_3N	57	1.1865	0.940	Trimethylamine:	2 CH_3, 1 CH_3N
"$(C)_3N$"	CH_2N	58	0.9597	0.932	Triethylamine:	3 CH_3, 2 CH_2, 1 CH_2N
27	HCOO	59	1.242	1.188	Ethyl formate:	1 CH_3, 1 CH_2, 1 HCOO
28	I	60	1.264	0.992	Iodoethane:	1 CH_3, 1 CH_2, 1 I
29	Br	61	0.9492	0.832	Bromomethane:	1 CH_3, 1 Br
					Bromobenzene:	5 ACH, 1 AC, 1 Br

TABLE 1 (continued)

Main group	Sub group	No	R_k	Q_k	Sample group assignment	
30	CH_3SH	62	1.877	1.676	Methanethiol	1 CH_3SH
31	Furfural	63	3.168	2.484	Furfural:	1 Furfural
32	C_5H_5N	64	2.9993	2.113	Pyridine:	1 C_5H_5N
"Pyridine"	C_5H_4N	65	2.8332	1.833	3-Methylpyridine:	1 CH_3, 1 C_5H_4N
	C_5H_3N	66	2.667	1.553	2,3-Dimethylpyridine	2 CH_3, 1 C_5H_3N
33 "DOH"	$(CH_2OH)_2$	67	2.4088	2.248	1,2-Ethanediol:	1 $(CH_2OH)_2$
34 "DMFA"	$HCON(CH_3)_2$	68	3.0856	2.736	Dimethylformamide:	1 $HCON(CH_3)_2$
35 "DMSO"	$(CH_3)_2SO$	69	2.8266	2.472	Dimethylsulfoxide:	1 $(CH_3)_2SO$

where ν_{ki} is the number of groups of type k in molecule i and is always an integer. ln γ_i^R is given by

$$\ln \gamma_i^R = \sum_k \nu_{ki}(\ln \Gamma_k - \ln \Gamma_k^{(i)}) - \left(\ln \frac{\theta_i}{x_i} + 1 - \frac{\theta_i}{x_i}\right) \tag{7}$$

where Γ_k is the group residual activity coefficient and $\Gamma_k^{(i)}$ is the residual activity coefficient of group k in a reference solution containing only molecules of type i. ln Γ_k and ln $\Gamma_k^{(i)}$ are calculated from the equation

$$\ln \Gamma_k = 1 - \ln\left(\sum_m X_m \Psi_{mk}\right) - \sum_m \left(\frac{X_m \Psi_{km}}{\sum_n X_n \Psi_{nm}}\right) \tag{8}$$

using the group fractions X_m in the mixture for ln Γ_k and the group fractions $X_m^{(i)}$ in pure component i for ln $\Gamma_k^{(i)}$. The mole fraction of group k in the mixture is given by

$$X_m = \sum_j \nu_{mj} x_j / \sum_j \sum_n \nu_{nj} x_j \tag{9}$$

For pure component i, eqn. (9) reduces to

$$X_m^{(i)} = \nu_{mi} / \sum_n \nu_{ni} \tag{10}$$

The group interaction parameter Ψ_{mn} is given by

$$\Psi_{mn} = (Q_m/Q_n) \exp[-(U_{mn} - U_{nn})/RT] = (Q_m/Q_n) \exp(-a_{mn}/T) \tag{11}$$

where U_{mn} is the energy of interaction between groups m and n. The group interaction parameters a_{mn} and a_{nm} ($a_{mn} \neq a_{nm}$) must be systematically evaluated from the existing literature concerning phase equilibrium data [14—16] as shown in Table 2.

BASIC PHASE EQUILIBRIUM EQUATIONS

We can summarize the following equations for three-phase equilibria [17].

Vapor—liquid equilibria under normal pressures are calculated by

$$\phi_i y_i P = x_i \gamma_i \phi_i^s P_i^s \exp[v_i^L (P - P_i^s)/RT] \tag{12}$$

where y_i is the vapor phase mole fraction, ϕ is the vapor phase fugacity coefficient, v_i^L is the molar liquid volume, P_i^s is the saturation pressure, and P is the total pressure.

The fugacity coefficients of pure components and components in a mixture are calculated from the second virial coefficients B_{ij}.

$$\ln \phi_i = (P/RT)\left(2 \sum_j y_j B_{ij} - \sum_i \sum_j y_i y_j B_{ij}\right) \tag{13}$$

The pure component and cross-virial coefficients are calculated from the correlation of Hayden and O'Connell [18].

TABLE 2

Effective UNIFAC group interaction parameters a_{mn}, K

		1 CH_2	2 C=C	3 ACH	4 $ACCH_2$	5 CCOH	6 CH_3OH	7 H_2O	8 ACOH	9 CH_2CO
1	CH_2	0	−211.6	126.7	176.2	963.6	1026.	1733.	1303.	487.9
2	C=C	2000.	0	660.8	4964.	10100.	1528.	5008.	357.6	386.7
3	ACH	−107.1	−269.3	0	107.7	552.5	721.9	1193.	966.6	119.8
4	$ACCH_2$	−87.66	−128.8	31.09	0	747.1	580.3	5319.	646.5	2887.
5	CCOH	134.7	1810.	249.6	79.89	0	247.1	407.4	−152.0	246.8
6	CH_3OH	94.54	201.8	170.4	81.55	−236.7	0	−150.6		112.2
7	H_2O	456.8	1156.	327.8	358.7	−214.3	255.1	0	−308.5	−305.5
8	ACOH	6091.	4462.	−56.41	−120.2	−649.4		7468.	0	
9	CH_2CO	243.0	389.6	239.8	4.681	48.56	89.10	674.5		0
10	CHO	473.4					961.3	656.0		24.82
11	COOC	298.4	−330.3	477.8	156.6	135.5	272.0	744.0	−9.114	292.9
12	CH_2O	66.80	125.6	158.7	1190.	−232.3	230.4	933.0		179.1
13	CNH_2	74.20	2335.	140.4		−330.2	−479.8	−545.9		
14	CNH	40.09	1145.	147.8	−17.29	−237.8	−533.2	−624.1		
15	$ACNH_2$	337.8	479.0	396.1	190.6	189.7	327.3	−101.1		−250.4
16	CCN	164.5	441.3	239.4	136.7	107.1	498.5	353.0		−5.491
17	COOH	240.9	3780.	187.6	220.8	−598.5	921.8	−433.9		−164.1
18	CCl	141.9	32.64	334.8	159.5	−81.00	691.2	1084.		77.34
19	CCl_2	154.1	216.4	705.1	424.0	713.9	789.8	5010.		53.88
20	CCl_3	222.8	320.9	511.1	167.9	647.3	783.5	5141.		91.44
21	CCl_4	470.6	594.0	630.8	404.0	931.6	1119.	8865.	1720.	421.6
22	ACCl	−151.8	−84.39	−74.73	−64.02	145.3	1307.	1471.		6052.
23	CNO_2	199.2	95.96	255.3	65.97		313.0	1431.		−118.2
24	$ACNO_2$	457.5		99.36				5716.		
25	CS_2	151.7	4.520	251.0	−153.2	1214.	977.7	2927.		442.9
26	$(C)_3N$	150.1	150.0	142.4		92.78	543.3	−792.9		
27	HCOO	329.1		252.4	2.197	133.5	209.4			130.2
28	I	−4.810		191.7		355.4				−166.1
29	Br	−69.69		−3.001	145.2	447.3				−206.7
30	CH_3SH	113.2		323.3			535.0			204.3
31	Furfural	271.6		529.3	403.5	4423.		344.1		423.4
32	Pyridine	180.7		280.4	281.8	−116.1	548.1	−332.4	−231.7	
33	DOH	473.8		429.6	5574	255.5			1798.	
34	DMFA	233.9		678.0	608.3	−27.84	353.6	−119.7		387.5
35	DMSO	320.0	668.4	304.3		−105.8	−59.19	−334.9		117.7

		10 CHO	11 COOC	12 CH_2O	13 CNH_2	14 CNH	15 $ACNH_2$	16 CCN	17 COOH	18 CCl
1	CH_2	476.6	364.9	193.6	407.3	302.6	517.1	927.8	727.6	67.58
2	C=C		391.8	300.7	297.8	277.7	717.9	931.6	20 080.	459.7
3	ACH		−245.7	−66.23	134.9	43.93	−5.894	101.9	566.4	−337.2
4	$ACCH_2$		602.9	−156.3		135.8	3847.	4874.	761.5	−124.7
5	CCOH		275.4	400.4	−107.5	−7.708	88.73	352.3	777.4	6073.
6	CH_3OH	−361.8	41.43	−61.09	44.35	87.55	−82.01	−6.257	−300.0	21.84
7	H_2O	−207.7	−356.4	−280.5	154.6	334.6	963.5	180.8	412.6	450.0
8	ACOH		−116.6							
9	CH_2CO	24.17	−190.1	−27.85			5421.	−20.10	290.5	−28.42
10	CHO	0								3009.
11	COOC		0	61.73		101.5		26.28	8.026	
12	CH_2O		69.60	0		−199.1		135.9	684.1	41.58
13	CNH_2				0	−33.52				
14	CNH		−23.17	939.7	118.2	0				
15	$ACNH_2$						0	−149.0		
16	CCN		20.65	60.55			476.0	0	861.8	
17	COOH		35.50	−305.3				−487.9	0	124.0
18	CCl	−72.09		354.3					623.5	0
19	CCl_2		−35.88	−141.5					273.5	61.79
20	CCl_3		65.74	−132.6				106.0		−2.826
21	CCl_4		248.6	−42.20		262.2	383.3	740.0	945.0	1299.
22	ACCl		−18.95		628.5	−15.66	1029.	7255.		
23	CNO_2			219.7				−125.4		
24	$ACNO_2$						−334.7			
25	CS_2		454.8	168.2				869.3		18.75
26	$(C)_3N$				−51.29			414.5		
27	HCOO		−18.87						−343.2	
28	I		41.60	797.6						
29	Br			−192.0						
30	CH_3SH			152.5	−45.09			186.0		−0.5514
31	Furfural		2.926							
32	Pyridine							306.2		
33	DOH			26.42			196.2			
34	DMFA			286.9						
35	DMSO		82.90	87.21			294.6			

TABLE 2 (continued)

		19 CCl_2	20 CCl_3	21 CCl_4	22 ACCl	23 CNO_2	24 $ACNO_2$	25 CS_2	26 $(C)_3N$	27 HCOO
1	CH_2	41.16	−31.00	−439.3	316.4	807.3	59.40	−53.53	−27.01	543.1
2	C=C	297.4	89.02	−430.3	4252.	1047.		185.4	413.6	
3	ACH	−722.7	−543.1	−627.9	350.8	153.9	424.2	−100.3	−134.0	177.0
4	$ACCH_2$	−31.37	207.2	−397.3	46.78	4121.		148.8		1293.
5	CCOH	−162.4	−115.0	117.1	285.1			300.1	−410.6	475.9
6	CH_3OH	−36.92	−137.3	125.5	38.77	241.3		465.7	−625.7	254.2
7	H_2O	1025.	1030.	1739.	525.5	119.2	−70.28	623.9	624.5	
8	ACOH			5136.						
9	CH_2CO	−163.4	−204.2	4522.	63.16	101.7		1108.		−75.00
10	CHO									
11	COOC	−51.66	−212.2	4685.	295.9			387.7		40.50
12	CH_2O	2441.	5264.	−91.82		−208.3		102.1		
13	CNH_2				−14.33				−38.07	
14	CNH			−48.11	157.1					
15	$ACNH_2$			195.0	171.4		417.7			
16	CCN		−1.076	125.9	152.5	148.5		576.8	−153.9	
17	COOH	2155.		6646.						691.6
18	CCl	−41.93	89.43	110.4				3523.		
19	CCl_2	0		42.50					−274.3	
20	CCl_3		0	−52.19				220.6	−401.1	155.6
21	CCl_4	98.95	107.1	0	833.2	834.7	1515.	147.2	−9.331	
22	ACCl			−653.9	0	8616.			1554.	
23	CNO_2			288.1	50.99	0				
24	$ACNO_2$			170.0			0			
25	CS_2		−62.20	−65.09				0		
26	$(C)_3N$	3016.	−302.3	382.0	−186.4				0	
27	HCOO		−57.81							0
28	I	51.06	32.56	−103.5		157.5		−169.4		
29	Br			3497.	136.5	201.8				
30	CH_3SH									355.7
31	Furfural		34.63	144.1						
32	Pyridine	−149.2	−294.4	−277.3						
33	DOH					1589.				
34	DMFA			−121.6						
35	DMSO	−219.5	−426.4	108.1						

		28 I	29 Br	30 CH_3 SH	31 Furfural	32 Pyridine	33 DOH	34 DMFA	35 DMSO
1	CH_2	422.6	360.8	164.1	779.9	357.2	181.8	657.1	1577.
2	C=C								1102.
3	ACH	−28.18	115.9	−284.9	−364.3	38.72	549.7	−644.9	252.9
4	$ACCH_2$		−86.31		477.0	−146.6	1122.	130.4	
5	CCOH	481.3	278.2		79.32	−14.51	−172.5	77.53	−210.4
6	CH_3OH			149.4		152.9		−465.6	−265.9
7	H_2O				230.7	932.0		125.8	−268.7
8	ACOH					−680.9	−866.8		
9	CH_2CO	482.2	292.4	−23.60	−267.6			−309.7	36.54
10	CHO								
11	COOC	164.0			14.79				194.1
12	CH_2O	−183.7	455.0	−141.4			4540.	−80.94	188.8
13	CNH_2			179.9					
14	CNH								
15	$ACNH_2$						384.0		−147.5
16	CCN			74.72		−139.7			
17	COOH								
18	CCl			41.37					
19	CCl_2	111.9				−50.75			166.3
20	CCl_3	128.4			−81.10	−15.32			171.3
21	CCl_4	430.6	309.2		369.7	451.8		837.6	710.7
22	ACCl		119.1						
23	CNO_2	241.4	76.47				782.7		
24	$ACNO_2$								
25	CS_2	358.1							
26	$(C)_3N$								
27	HCOO			41.15					
28	I	0							
29	Br		0						
30	CH_3SH			0			−41.99		
31	Furfural				0				
32	Pyridine					0			
33	DOH			142.3			0	−244.7	−406.1
34	DMFA						385.1	0	161.9
35	DMSO						81.65	−98.33	0

Liquid—liquid equilibrium compositions between two liquid phases (I and II) can be calculated by [19]

$$(x_i\gamma_i)^{\mathrm{I}} = (x_i\gamma_i)^{\mathrm{II}} \tag{14}$$

The solubility of a solid (component 2) in a liquid solvent (component 1) is calculated by eqn. (15) when there is no solubility of component 1.

$$f^{S}_{\mathrm{pure}\ 2} = \gamma_2 x_2 f^{L}_{\mathrm{pure}\ 2} \tag{15}$$

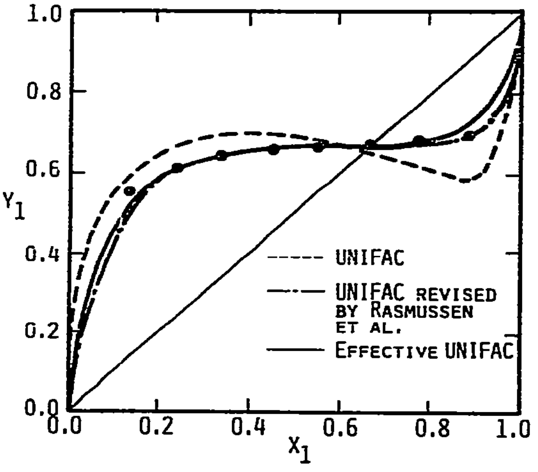
The ratio $(f^S/f^L)_{\mathrm{pure}\ 2}$ is given elsewhere [17] and its simplified form, which neglects terms containing specific heat difference between liquid and solid, is

$$\ln(f^S/f^L)_{\mathrm{pure}\ 2} = (\Delta h_{f.2}/RT)\ [T/T_{m.2} - 1] \tag{16}$$

where $\Delta h_{f.2}$ is the enthalpy of fusion, $T_{m.2}$ is the melting temperature of pure component 2 and T is the system temperature. The solubility x_2 can be calculated if the activity coefficient γ_2 is estimated by a group-contribution method. We must use the approximation $\gamma_2 = 1$ to obtain the ideal solubility.

RESULTS

The effective UNIFAC method can predict a better fit of vapor—liquid equilibria for alcohol-saturated hydrocarbon systems than the UNIFAC method as shown in Table 3. Figures 1 and 2 show typical examples to indi-



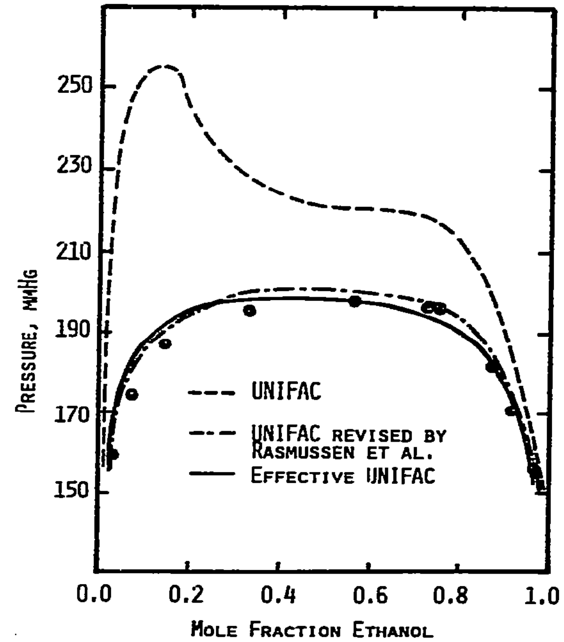


Fig. 1. Vapor—liquid equilibria for *n*-hexane (1)—ethanol (2) at 60°C. ●, Data from ref. 21.

Fig. 2. Vapor—liquid equilibria for ethanol—*n*-heptane at 40°C. ●, Data from ref. 22.

TABLE 3

Prediction of vapor—liquid equilibria for binary alcohol—hydrocarbon systems from group-contribution methods

System (component 1—component 2)	Temp. (°C)	No. of data points	Root-mean square deviation (× 1000)				Ref.
			Relative press.		Vapor mole fraction		
			I[a]	II[b]	I	II	
Methanol—*n*-hexane	60	23	75	37			20
Ethanol—*n*-hexane	60	8	153	45	56	18	21
Ethanol—*n*-heptane	40	10	225	19	89	24	22
Ethanol—*n*-octane	45	17	242	32	55	16	23
	55	19	259	35	60	21	23
	65	18	246	33	57	14	23
	75	19	256	36	70	18	23
Ethanol—isooctane	40	18	206	43	86	31	22
1-Propanol—*n*-hexane	45	5	26	57	11	9	24
1-Propanol—*n*-heptane	30	9	29	52			25
	60	13	28	53			25
1-Propanol—*n*-decane	90	11	104	42	10	7	22
1-Butanol—*n*-decane	100	19	33	35	18	18	26
2-Propanol—*n*-heptane	30	11	45	49			25
2-Propanol—isooctane	45	20	55	23	37	21	27

[a] I = UNIFAC.
[b] II = Effective UNIFAC.

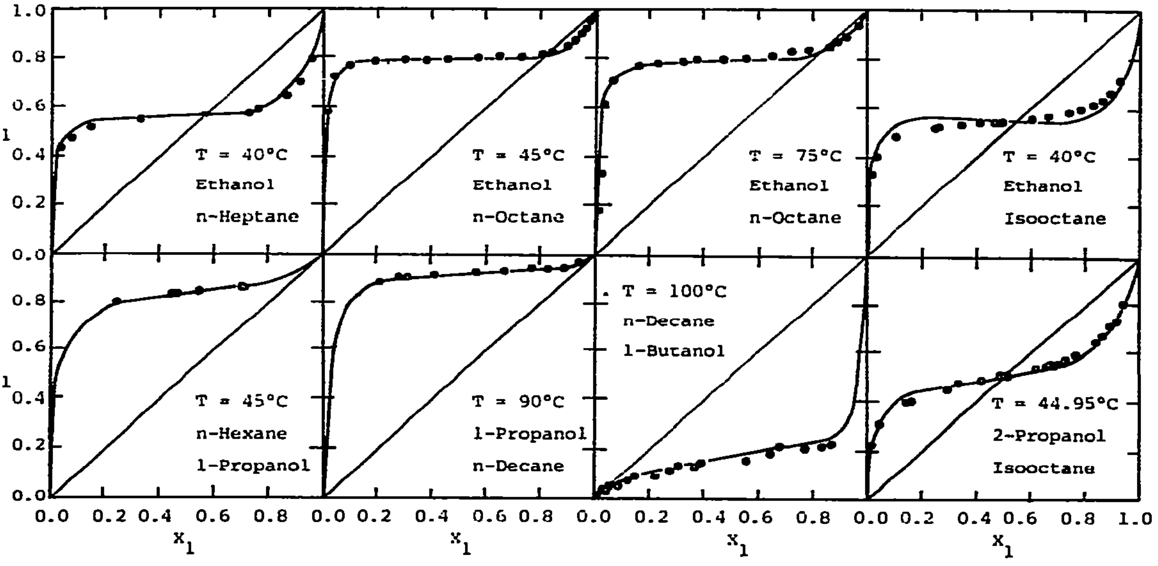


Fig. 3. Vapor—liquid equilibria for binary alcohol—hydrocarbon systems [22—24,26,27].

TABLE 4

Experimental and calculated activity coefficients for binary systems

System (component 1—component 2)	T (°C)	x_1	γ_1 (exptl.)	γ_1 (calcd.)	Ref.
Methanol—*n*-hexane	60	0.045	13.50	11.88	20
n-Hexane—methanol	60	0.0513	14.90	13.60	
Ethanol—*n*-octane	45	0.0206	16.36	16.30	23
n-Octane—ethanol	45	0.0985	6.679	6.223	
1-Propanol—benzene	45	0.0972	5.010	4.881	28
Benzene—1-propanol	45	0.0807	3.738	3.470	
Methanol—benzene	35	0.0242	11.08	11.34	29
Benzene—methanol	35	0.0803	4.977	5.204	
Methanol—toluene	70.25	0.130	4.574	4.454	30
Toluene—methanol	63.62	0.073	5.714	5.748	
n-Octane—phenol	132.41	0.250	2.789	2.731	31
Phenol—*n*-octane	125.59	0.014	8.730	8.730	
n-Heptane—1,4-dioxane	80	0.049	3.172	3.317	32
1,4-Dioxane—*n*-heptane	80	0.023	2.464	2.484	
1-Octene—1,4-dioxane	80	0.063	2.393	2.457	32
1,4-Dioxane—1-octene	80	0.120	1.742	1.828	
n-Pentane—acetone	45	0.105	3.500	3.577	33
Acetone—*n*-pentane	45	0.094	3.861	3.568	
1-Hexene—5-nonanone	60	0.	1.287	1.283	34
5-Nonanone—1-hexene	60	0.	1.633	1.564	
Benzene—dipropyl ether	70	0.0751	1.052	1.050	35
Dipropyl ether—benzene	70	0.0350	1.099	1.147	
Benzene—acetone	45	0.0916	1.409	1.327	36
Acetone—benzene	45	0.0470	1.531	1.474	
Toluene—acetone	45	0.1974	1.403	1.400	37
Acetone—toluene	45	0.0688	1.656	1.583	
Methyl acetate—cyclohexane	35	0.111	3.167	3.026	38
Cyclohexane—methyl acetate	35	0.079	3.641	3.409	
Methyl acetate—benzene	50	0.080	1.294	1.290	38
Benzene—methyl acetate	50	0.073	1.321	1.352	
Cyclohexane—propionaldehyde	45	0.0090	4.436	4.411	39
Propionaldehyde—cyclohexane	45	0.0093	3.624	3.599	
Hexylamine—*n*-hexane	60	0.123	1.546	1.504	40
n-Hexane—hexylamine	60	0.094	1.486	1.443	
Dimethylamine—*n*-hexane	20	0.0498	2.003	1.871	41
n-Hexane—dimethylamine	20	0.0440	2.469	2.468	
Aniline—methylcyclohexane	100	0.0976	4.318	5.430	42
Methylcyclohexane—aniline	100	0.0763	4.979	5.049	
n-Butylamine—benzene	70	0.0720	1.185	1.190	43
Benzene-*n*-butylamine	70	0.1135	1.130	1.127	
Acetonitrile—benzene	45	0.0940	2.300	2.130	44
Benzene—acetonitrile	45	0.0427	2.669	2.608	
Nitromethane—benzene	45	0.0445	2.968	2.763	45
Benzene—nitromethane	45	0.0399	3.072	2.897	
n-Hexane—chloroform	35	0.0991	1.622	1.691	46
Chloroform—*n*-hexane	35	0.1005	1.415	1.444	
Carbon disulfide—benzene	25	0.0581	1.343	1.325	47
Benzene—carbon disulfide	25	0.0211	1.700	1.637	
Water—benzene	25	0.0027	366.6	366.6	15
Benzene—water	25	0.0004	2427.	2430.	
Water—1-propanol	90	0.162	2.674	2.801	22

TABLE 4 (continued)

System (component 1—component 2)	T (°C)	x_1	γ_1 (exptl.)	γ_1 (calcd.)	Ref.
1-Propanol—water	90	0.111	4.663	4.753	
Water—2-propanol	45	0.1	2.985	3.135	48
2-Propanol—water	45	0.1	4.708	5.226	
Water—acetic acid	113.5	0.099	1.745	1.620	49
Acetic acid—water	100.1	0.015	2.860	2.911	
Water—acetonitrile	60	0.0529	5.231	5.698	50
Acetonitrile—water	60	0.0654	7.335	6.825	
Butyl acetate—phenol	176.6	0.1300	0.606	0.606	51
Phenol—butyl acetate	128.6	0.0500	0.558	0.543	
3-Pentanone—acetic acid	70	0.0314	1.434	1.517	52
Acetic acid—3-pentanone	70	0.0890	1.525	1.432	
Acetone—chloroform	62.06	0.0563	0.579	0.534	53
Chloroform—acetone	58.77	0.1609	0.662	0.650	
Chloroform—methanol	61.9	0.095	2.292	2.384	54
Methanol—chloroform	58.9	0.030	5.345	5.376	
Diethyl ether—methanol	55.78	0.0390	3.118	3.022	55
Methanol—diethyl ether	32.48	0.1716	2.413	2.475	
Methanol—water	93.5	0.040	2.093	2.011	56
Water—methanol	65.0	0.050	1.670	1.632	

cate the predictive ability of both methods. Figure 3 illustrates experimental and calculated vapor mole fractions for some alcohol—hydrocarbon systems. Table 4 presents typical experimental and calculated activity coefficients in the dilute regions for various binary systems, demonstrating that the effective UNIFAC method is able to represent a wide range of mixtures with few group parameters. Table 5 shows some of the predicted results for the chloroform—methanol—ethyl acetate system which exhibits positive and negative deviations from the Raoult law. Table 6 compares predictions obtained by the two methods for selected ternary systems. For the ethyl acetate—ethanol—water system, the effective UNIFAC method shows considerable improvement.

Prediction of liquid—liquid equilibria has been carried out for four ternary systems having a plait point. The data are obtained from Landolt—Börnstein [60]. The agreement between predicted and experimental solubility curves are quantitatively good for the water—propionic acid—*n*-octane and cyclohexane—ethanol—water systems at 25°C as shown in Figs. 4 and 5. However, the predictions agree qualitatively with experimental values for the toluene—acetic acid—water and water—2-propanol—chloroform systems at 25°C (Figs. 6 and 7). We may state that the prediction of liquid—liquid equilibria using group-contribution methods with parameters obtained from vapor—liquid equilibrium data will give results which agree qualitatively with experiment [5]. To predict liquid—liquid equilibria well by the present method, we should prepare a separate effective UNIFAC group interaction parameter table for liquid—liquid equilibria, which are derived from published binary and ternary liquid—liquid equilibrium data, and work on such a table is currently under way.

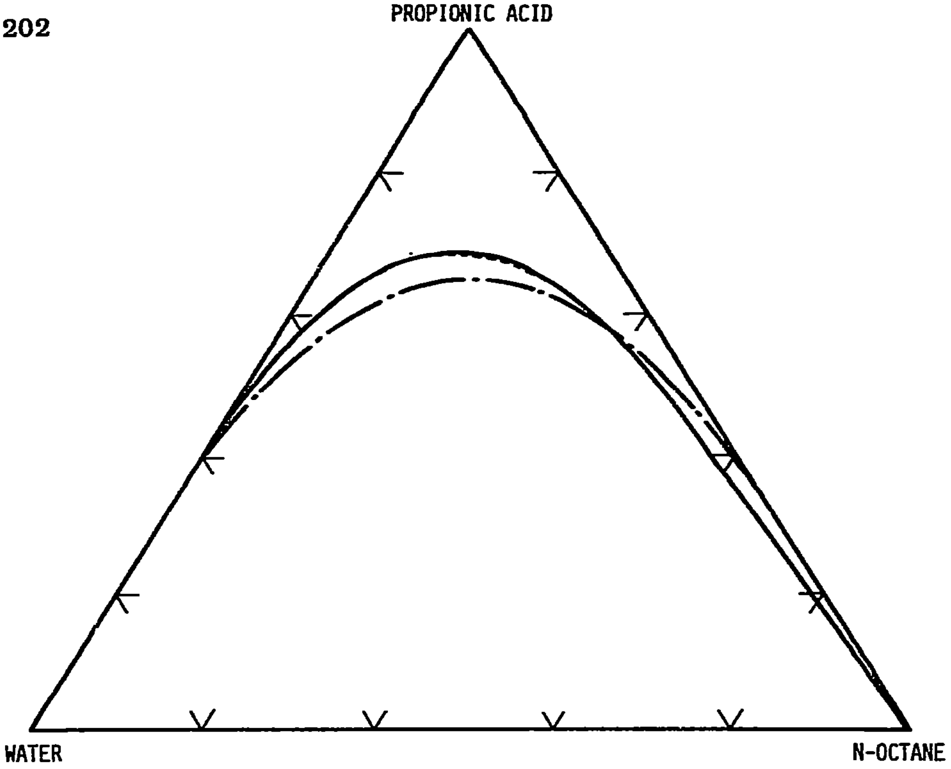


Fig. 4. Liquid—liquid equilibria for water—propionic acid—*n*-octane at 25°C [60]. — — —, Effective UNIFAC; · — · — ·, UNIFAC; ———, experimental.

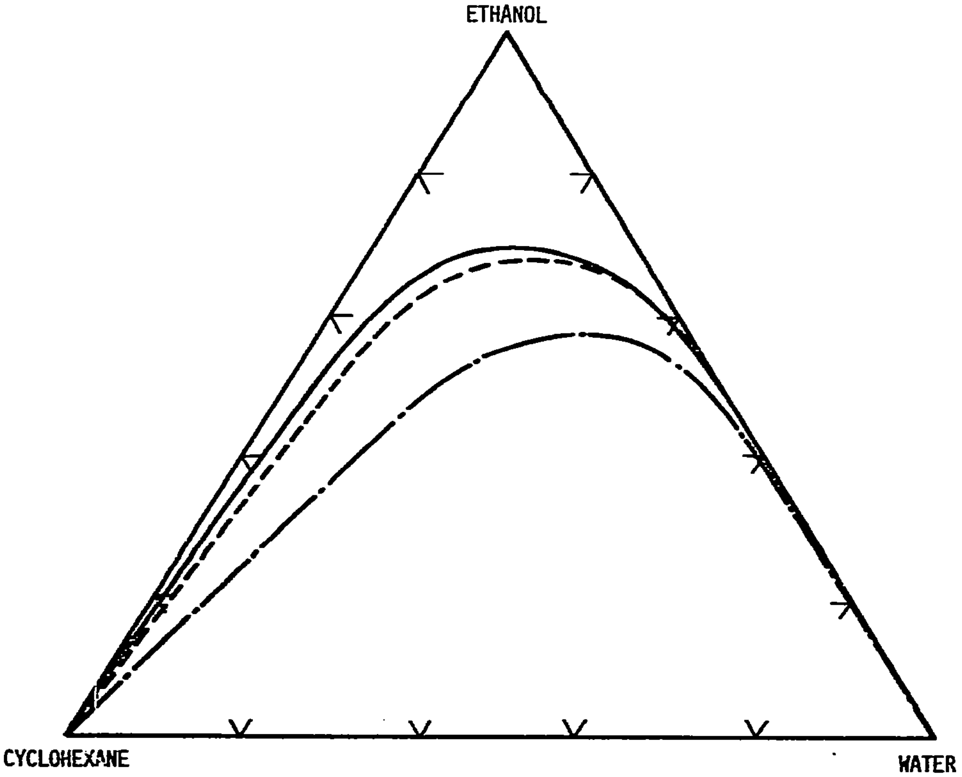


Fig. 5. Liquid—liquid equilibria for cyclohexane—ethanol—water at 25°C [60]. — — —, Effective UNIFAC, · — · — ·, UNIFAC; ———, experimental.

TABLE 5

Experimental and calculated activity coefficients for the chloroform(1)—methanol(2)—ethyl acetate(3) system at one atmosphere [54]

x_1	x_2	γ_1			γ_2			γ_3		
		Exptl.	I[a]	II[b]	Exptl.	I	II	Exptl.	I	II
0.122	0.539	1.01	1.14	1.13	1.28	1.27	1.25	1.27	1.28	1.27
0.115	0.179	0.637	0.695	0.686	1.94	2.10	2.05	1.02	1.01	1.01
0.120	0.637	1.24	1.36	1.34	1.15	1.18	1.16	1.39	1.43	1.40
0.345	0.465	1.24	1.26	1.24	1.42	1.39	1.38	0.812	0.989	0.971
0.454	0.325	1.12	1.11	1.09	1.70	1.76	1.73	0.774	0.812	0.811
0.597	0.077	0.896	0.904	0.895	3.10	3.51	3.39	0.673	0.733	0.734
0.058	0.634	1.11	1.26	1.24	1.16	1.16	1.15	1.44	1.48	1.45
0.653	0.082	0.939	0.938	0.931	3.19	3.57	3.43	0.573	0.672	0.673

[a] I = UNIFAC.

[b] II = Effective UNIFAC.

TABLE 6

Prediction of vapor—liquid equilibria for ternary systems from group-contribution methods

System	Temp. or press.	No. of data points	Root-mean square deviation (× 1000)				Ref.
			Relative press.		Vapor mole fraction		
			I[a]	II[b]	I	II	
Ethanol—					24	16	
2-butanone—	25°C	33	44	29	11	14	57
benzene					25	28	
Acetonitrile—					25	22	
benzene—	45°C	51	44	43	10	13	58
n-heptane					20	13	
Ethyl acetate—					111	22	
ethanol—	40°C	9	213	103	61	26	59
water					100	24	
Ethyl acetate					98	10	
ethanol—	70°C	9	215	43	60	18	59
water					82	15	
Chloroform—					11	11	
methanol—	1 atm	72	24	17	14	12	54
ethyl acetate					12	11	

[a] I = UNIFAC.
[b] II = Effective UNIFAC.

TABLE 7

Solubility of naphthalene, anthracene, and phenanthrene in solvents

Solvent	Temp. (°C)	Solubility (mole%)			Ref.
		I[a]	II[b]	Exptl.	
Naphthalene—methanol	40	4.8	6.7	4.4	65
Naphthalene—ethanol	40	5.4	10.1	7.3	62
Naphthalene—1-butanol	40	11.1	15.0	11.6	65
Naphthalene—acetone	40	35.8	37.0	37.8	65
Naphthalene—chloroform	40	47.0	43.0	47.3	66
Anthracene—acetone	20	0.25	0.91	0.31	67
Anthracene—chloroform	20	1.82	1.86	0.94	67
Anthracene—carbon tetrachloride	20	0.53	0.42	0.41	67
Anthracene—cyclohexane	20	0.31	0.29	0.12	67
Anthracene—methanol	20	0.03	0.12	0.02	67
Anthracene—aniline	20	0.27	0.30	0.35	67
Phenanthrene—acetone	20	9.7	14.0	14.5	68
Phenanthrene—chloroform	20	26.4	19.4	23.8	68
Phenanthrene—carbon tetrachloride	20	15.8	14.0	14.5	68
Phenanthrene—carbon disulfide	20	18.5	17.2	23.5	68

[a] I = UNIFAC.
[b] II = Effective UNIFAC.

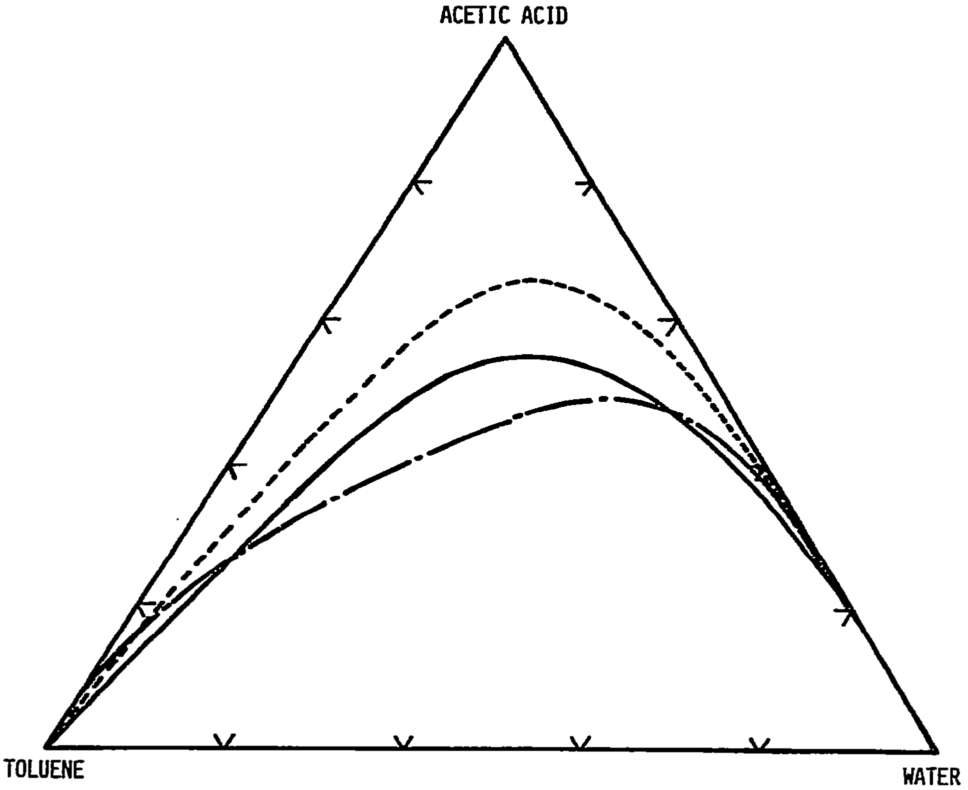


Fig. 6. Liquid—liquid equilibria for toluene—acetic acid—water at 25°C [60]. — — —, Effective UNIFAC; · — · — ·, UNIFAC; ——— experimental.

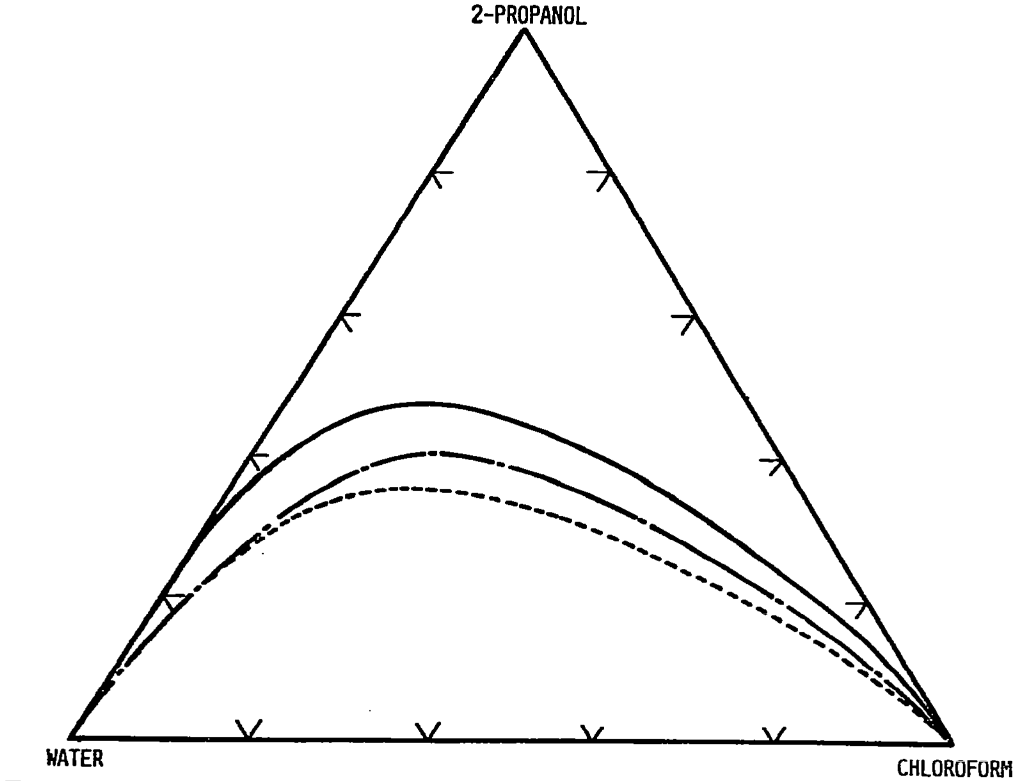


Fig. 7. Liquid—liquid equilibria for water—2-propanol—chloroform at 25°C [60]. — — —, Effective UNIFAC; · — · — ·, UNIFAC; ———, experimental.

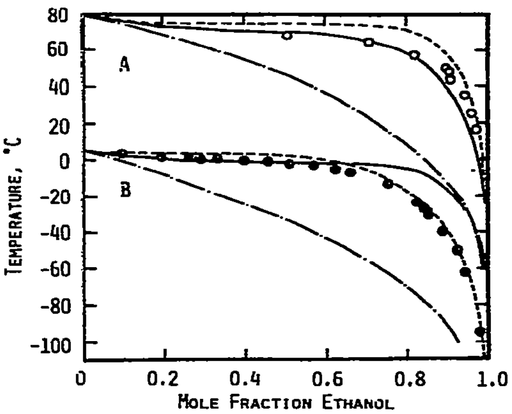
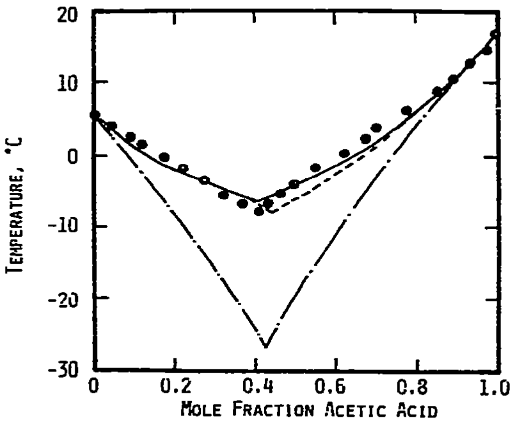


Fig. 8. Solid—liquid equilibria. Experimental: (A) ethanol—naphthalene, ○, Sunier [62]; (B) ethanol—benzene, ●, Viala [63]. Calculated: ———, effective UNIFAC; - - - - - -, UNIFAC; · — · — ·, ideal.

In solid-solubility calculations, enthalpies of fusion and melting temperatures for the solids studied in this work are taken from the literature [15,61]. Figure 8 shows temperature—composition diagrams for the ethanol—naphthalene and ethanol—benzene systems. In the ethanol—naphthalene system, effective UNIFAC gives calculated results closer to experimental data than UNIFAC [64]. However, for the ethanol—benzene system,



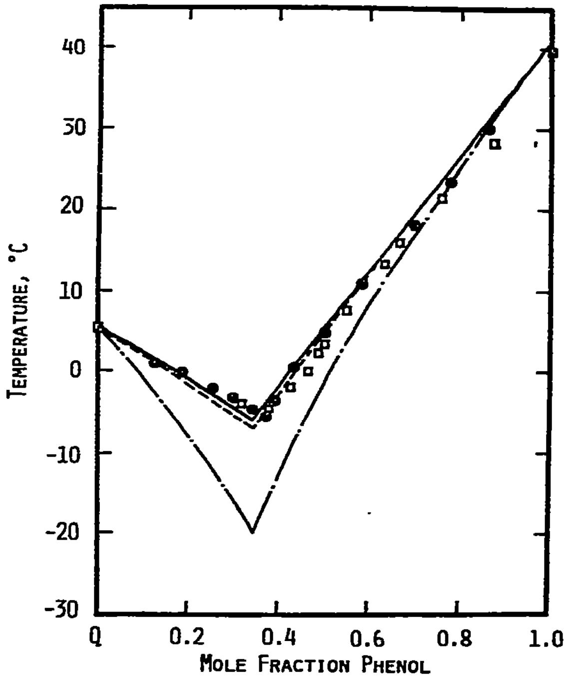


Fig. 9. Solid—liquid equilibria for acetic acid—benzene. ●, Experimental data of Tan et al. [69]. Calculated: ———, effective UNIFAC; - - - - - -, UNIFAC; · — · — ·, ideal.

Fig. 10. Solid—liquid equilibria for benzene—phenol. Experimental: ●, Tsakalotos and Guye [70]; □, Hatcher and Skirrow [71]. Calculated: ———, effective UNIFAC; - - - - - -, UNIFAC; · — · — ·, ideal.

TABLE 8

Calculated and experimental eutectics in binary systems

System (component 1—component 2)	Mole% of component I			Temp. (°C)		
	I[a]	II[b]	Exptl. [60]	I	II	Exptl. [60]
Acetone—diethyl ether	32.0	34.0	24.0	—123	—123	—126
Acetone—ethanol	24.4	22.4	21.0	—124	—122	—119
Benzene—1,2-dichloroethane	31.6	30.6	32.0	—55	—56	—55
Benzene—phenol	65.4	65.8	62.5	—7	—6	—6
Benzene—1,4-dioxane	56.9	57.4	56.5	—26	—25	—26
Benzene—acetonitrile	12.6	3.4	5.0	—49	—45	—51
Benzene—cyclohexane	26.6	28.0	26.5	—48	—50	—44
Benzene—nitrobenzene	51.7	49.4	50.0	—27	—23	—26
Phenol—naphthalene	83.7	81.1	83.8	30	27	29
Acetic acid—benzene	44.6	40.9	40.9	—8	—7	—8
Acetic acid—cyclohexane	7.4	9.8	7.4	—6	—8	—1

[a] I = UNIFAC.
[b] II = Effective UNIFAC.

UNIFAC works much better. Table 7 presents solubilities for naphthalene, anthracene, and phenanthrene in different solvents. Figures 9 and 10 show two eutectic systems where UNIFAC and effective UNIFAC predict the experimental eutectic composition and eutectic temperature well. Calculated and experimental eutectic compositions and eutectic temperatures are listed for 11 binary systems in Table 8. Both methods give generally good agreement with experiment.

SIMULTANEOUS CORRELATION OF VAPOR—LIQUID EQUILIBRIA AND EXCESS ENTHALPY DATA

In the estimation of excess enthalpies with group-contribution methods, it has been found that a set of group parameters required for reproducing experimental excess enthalpy data are different from that used for activity coefficients [72,73]. Two recent investigations [74,75] were attempted to find a unique set of parameters which are able to reproduce activity coefficients and excess enthalpies simultaneously. Skjold-Jørgensen et al. [74] presented the modified UNIFAC model suited for the representation of mixtures containing non-associating components. Ashraf and Vera [75] tested SIGMA (Simplified Group Method Analysis) for the prediction of both data for alkane, alcohol, and chloroalkane systems. In this section, we will compare the ability of the effective UNIFAC method with that of SIGMA in the simultaneous representation of these two thermodynamic properties.

The Gibbs—Helmholtz equation provides the thermodynamic relation between excess enthalpy and activity coefficients.

$$-h^E/RT^2 = \sum_i x_i \, \partial \ln \gamma_i / \partial T \tag{17}$$

The basic equation of the effective UNIFAC may be given by

$$h^{E} = \sum_{i} x_{i} \sum_{k} \nu_{ki}(H_{k} - H_{k}^{(i)}) \tag{18}$$

with

$$\frac{H_{k}}{RT^{2}} = -\frac{\partial \ln \Gamma_{k}}{\partial T} = \sum_{m} X_{m}\eta_{mk}/\sum_{m} X_{m}\psi_{mk} + \sum_{m} \left(X_{m}\eta_{km}/\sum_{n} X_{n}\psi_{nm}\right)$$
$$- \sum_{m} \left[X_{m}\psi_{km}\left(\sum_{n} X_{n}\eta_{nm}\right)\Big/\left(\sum_{n} X_{n}\psi_{nm}\right)^{2}\right] \tag{19}$$

where

$$\eta_{nm} = \partial \psi_{nm}/\partial T \tag{20}$$

The group parameters a_{mn} are considered to be temperature-dependent.

$$a_{mn} = A_{mn}T + B_{mn} \tag{21}$$

Then

$$\eta_{mn} = \psi_{mn}B_{mn}/T^{2} \tag{22}$$

Table 9 lists the coefficients A_{mn} and B_{mn}, which were obtained according to the procedure described by Ashraf and Vera [75]. Root-mean square relative deviations (percent) between experimental and calculated pressures and excess enthalpies for the reference systems studied in this work are given in Table 10 together with the values obtained using SIGMA coefficients. Excess enthalpies and total pressures for ternary systems including all three groups, CH_2, CCOH, and CCl, are predicted and compared with literature values and the values by SIGMA in Table 11. It may be stated that the results obtained by effective UNIFAC are comparable with those by SIGMA for the systems tested here.

In conclusion, the practical utility of effective UNIFAC has been demonstrated. Omissions in the group-parameter table show where new reliable experimental data are necessary. The effective UNIFAC method will be revised as new phase equilibrium data become available. Further modifications of the present group-contribution method will contain the modified combinatorial expression suggested by Kikic et al. [81].

TABLE 9

Effective UNIFAC coefficients evaluated for prediction of both activity coefficients and excess enthalpies

m/n	a_{mn} at 25°C	A_{mn}	B_{mn} (K)
CH_2/CCOH	1081.0	−1.292	1466.0
CCOH/CH_2	143.7	0.135	103.4
CH_2/CCl	278.1	−0.746	500.6
CCl/CH_2	27.77	0.061	9.400
CCOH/CCl	167.6	−0.022	174.2
CCl/CCOH	641:1	−2.315	133.1

TABLE 10

Predicted results of vapor—liquid equilibria and excess enthalpies for binary systems

System	T (°C)	Data type	No. of data points	Root-mean square relative deviation (%)		Ref.
				SIGMA	Effective UNIFAC	
n-Heptane—1-propanol	25	V[a]	11	2.8	4.5	76
n-Heptane—1-propanol	30	V	9	2.9	2.6	77
n-Hexane—ethanol	55	V	17	4.5	3.8	78
n-Heptane—ethanol	40	V	10	8.2	6.6	22
n-Heptane—1-chlorobutane	25	V	11	0.6	0.5	76
1-Propanol—1-chlorobutane	25	V	15	1.5	1.1	76
n-Heptane—1-butanol	30	H[b]	11	8.5	6.6	77
n-Hexane—1-octanol	25	H	10		9.7	79
n-Hexane—2-chlorobutane	25	H	19	2.8	1.0	80
n-Octane—2-chlorobutane	25	H	19	1.4	1.9	80
1-Heptanol—1-chlorobutane	25	H	19	5.1	3.2	80
1-Octanol—1-chlorobutane	25	H	19	5.0	2.6	80

[a] V = vapor—liquid equilibria and deviation means pressure.

[b] H = excess enthalpy.

TABLE 11

Predicted results of vapor—liquid equilibria and excess enthalpies for ternary systems at at 25°C

System	Data type	No. of data points	Root-mean square relative deviation (%)		Ref.
			SIGMA	Effective UNIFAC	
n-Hexane(1)—1-octanol(2)—1-chlorobutane(3)					79
$(x_2/x_3) = 0.993$	H[a]	10	3.5	7.4	
$(x_1/x_3) = 1.000$	H	10	8.0	5.3	
$(x_1/x_2) = 1.007$	H	10	4.5	7.6	
n-Heptane—1-propanol—1-chlorobutane	V[b]	44	2.6	2.1	76

[a] H = excess enthalpy.

[b] V = vapor—liquid equilibria and deviation means pressure.

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