The performance of UNIFAC and related group contribution models
Part I. Prediction of infinite dilution activity coefficients

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Abstract

Infinite dilution activity coefficients have been calculated for 24 systems including highly non-ideal and nearly non-ideal using original, modified UNIFAC and UNIFAC–FV models. The calculations are compared with experimental results. The performance of the models in predictions and the significance of free volume effects on solvent activities in solutions containing small compounds are discussed.

Keywords: Activity coefficient; Infinite dilution; UNIFAC; UNIFAC–FV

1. Introduction

Infinite dilution activity coefficients characterize the behaviour of a solute completely surrounded by solvent molecules. Values of limiting activity coefficients are important for the development of new thermodynamic models, but also for the choice of selective solvents for extractive rectification, extraction or absorption. In cases where experimental data is not available the UNIFAC (UNIQUAC functional group activity coefficients) model [1] may be very useful in predicting γ_i. The UNIFAC model defines

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functional groups, which make up the structures of compounds. Each functional group makes a unique contribution to the compound property. The interaction parameters obtained for a small number of groups using thermodynamically consistent data can be used for multicomponent systems.

In the UNIFAC model the activity coefficient is given in terms of a combinatorial part, γ_i^C, for entropy effects resulting from differences in molecular size and shape, and a residual part, γ_i^R, for energetic interactions between the functional groups in the mixture [2].

$$\ln \gamma_i = \ln \gamma_i^R + \ln \gamma_i^C \tag{1}$$

In the original UNIFAC model group interaction parameters have been assumed to be temperature-independent. Modifications of the UNIFAC model have been developed [3–5] for both the combinatorial and residual parts of the model. The modifications in the combinatorial part have been made for better evaluation of compounds with very different sizes. Temperature-dependent group interaction parameters introduced into the model enable better calculation of infinite dilution activity coefficients and enthalpies of mixing. For prediction of infinite dilution activity coefficients, γ_i^∞, the modified UNIFAC method by Weidlich and Gmehling [4] has been found superior to the modified UNIFAC by Larsen and coworkers [5,6].

The UNIFAC model, developed from the two-liquid lattice theory does not take into account changes in volume caused by mixing. This can be true for solutions with compounds of similar molar volume. When there is a significant difference in component sizes, a free volume contribution to the UNIFAC model is necessary. Oishi and Prausnitz [7] added a new contribution term besides the combinatorial, γ_i^C, and residual, γ_i^R, contributions to derive the following equation for γ_i:

$$\ln \gamma_i = \ln \gamma_i^R + \ln \gamma_i^C + \ln \gamma_i^{FV} \tag{2}$$

For better prediction of the solvent activities in polyalkanes, new efforts which try to combine the combinatorial and free volume contributions into a single term have been made [8,9]. This model is known as Entropic-FV:

$$\ln \gamma_i = \ln \gamma_i^R + \ln \gamma_i^{C-FV} \tag{3}$$

The models will be described in more detail in the text.

In this work, the original and modified UNIFAC [6] and UNIFAC–FV models are utilized to calculate γ_i^∞ of various solutions. The predictions are compared with experimental results found in the literature. The emphasis here will be on free-volume effects on solvent activities in solutions containing small compounds as solutes.

2. The original UNIFAC model

In the original UNIFAC model the combinatorial part is given by:

$$\ln \gamma_i^C = 1 - \phi_i + \ln \phi_i - \frac{z}{2} q_i \left(1 - \frac{\phi_i}{F_i} + \ln\left(\frac{\phi_i}{F_i}\right) \right) \tag{4}$$

$$\phi_i = \frac{r_i}{\sum_j r_j x_j}, \quad F_i = \frac{q_i}{\sum_j r_j x_j} \tag{5}$$

$$r_i = \sum v_k^{(i)} R_k, \quad q_i = \sum v_k^{(i)} Q_k \tag{6}$$

where x_i is the mole fraction of component i in the liquid phase and $v_k^{(i)}$ is the number of groups of type k in component i. R_k and Q_k are van der Waals group volume and surface area respectively, for group k, and z is the coordination number as defined in lattice theory and may have a value between 4 and 12 depending on the type of packing. For typical liquids z is 10.

The residual part of the activity coefficient is obtained from the relationships:

$$\ln \gamma_i^R = \sum_k v_k^{(i)}(\ln \Gamma_k - \ln \Gamma_k^{(i)}) \tag{7}$$

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

where the group area fraction, θ_m, and group mole fraction, X_m, are given by the equations:

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n}, \quad X_m = \frac{\sum_j v_m^{(j)} x_j}{\sum_j \sum_n v_n^{(j)} x_j} \tag{9}$$

The parameter ψ_{nm} contains the group interaction parameter, a_{nm} according to the equation:

$$\Psi_{nm} = \exp(-a_{nm}/T) \tag{10}$$

where m and n denote the main groups in the UNIFAC table.

3. The modified UNIFAC model

In the modified UNIFAC model [6], combinatorial part takes the form:

$$\ln \gamma_i^C = 1 - \phi_i' + \ln \phi_i' - \frac{z}{2} q_i \left(1 - \frac{\phi_i}{F_i} + \ln\left(\frac{\phi_i}{F_i}\right) \right) \tag{11}$$

$$\phi_i' = \frac{r_i^{3/4}}{\sum_j x_j r_j^{3/4}} \tag{12}$$

The residual part can be calculated using Eqs. (6)–(8), but the parameter ψ_{nm} with the new temperature-dependent energy interaction parameters a_{nm}, b_{nm} and c_{nm} between

groups n and m are introduced:

$$\Psi_{nm} = \exp\left(-\frac{a_{nm} + b_{nm}T + C_{nm}T^2}{T} \right)$$ (13)

4. The UNIFAC–FV model

In the UNIFAC–FV model by Oishi and Prausnitz [7] given by Eq. (2), the free volume part of activity coefficient is given by the equation:

$$\ln\gamma_i^{FV} = 3\,c_i \ln\left[\frac{\bar{v}_i^{1/3} - 1}{\bar{v}_m^{1/3} - 1} \right] - c_i \left[\left(\frac{\bar{v}_i}{\bar{v}_m} - 1 \right)\left(1 - \frac{1}{\bar{v}_i^{1/3}} \right)^{-1} \right]$$ (14)

Oishi and Prausnitz [7] developed this equation from Flory's equation of state [10] $3c_i$ is the external degrees of freedom and $\bar{v}_i$ is the reduced molar volume

$$\bar{v}_i = v_i/v_i^* = v_i/(15.17\,br_i)$$ (15)

where v_i is the molar volume, v_i^* is the hard core molar volume, b is the proportionality constant and r_i is given by Eq. (6). Molar volumes are calculated using Hankinson–Brobst–Thomson (HBT) technique [11].

5. The entropic–FV model

In the entropic–FV model given by Eq. (3), the combined combinatorial and free volume contribution, γ_i^{C-FV} is given by the relationship:

$$\ln\gamma_i^{C-FV} = \ln\frac{\phi_i^{FV}}{x_i} + 1 - \frac{\phi_i^{FV}}{x_i}$$ (16)

where ϕ_i^{FV} is the free volume contribution of component i:

$$\phi_i^{FV} = \frac{x_i v_{f_i}}{\sum_j x_j v_{f_j}} = \frac{x_i(v_i - v_i^*)}{\sum_j x_j(v_j - v_i^*)}$$ (17)

The free volume v_f, is defined as the difference between the molar volume, v and the hard core molar volume, v_i^*, as given in Eq. (15). This model, suggested by Kontogeorgis et al. [12], is the most successful method for phase-equilibrium calculations in polymer solutions. However, this model is not suitable for the prediction of infinite dilution activity coefficients where solute mole fraction, x_1 approaches zero.

6. Results and discussion

The calculated infinite dilution activity coefficients with original, modified UNIFAC and UNIFAC–FV models are compared with the experimental values found in the

literature in Table 1. For the original UNIFAC the parameter table by Hansen et al. [19] was used. Among the various systems studied are highly non-ideal (e.g. alcohol–alkane, alcohol–cycloalkane) and moderately non-ideal (e.g. ether–alkane, cyclic ether–alkane). The values of b and c_i in free volume calculations are either taken as constants with suggested values given in Table 2 or calculated from the following relationships given in Ref. [20]:

$$b = 3.91\,c0(c2^{4/3} - c1^{4/3})/(c2 - c1)^{0.58}(1 - c1\,c2)/(1 + c1\,c2)^{0.91} \tag{18}$$

$$c_i = c0^4(T/(T_{cr1}\,T_{cr2})^{0.5})^{(-c1c2^4)}/(c1c2) \tag{19}$$

$$c0 = (v_2 r_1)/(v_1 r_2) \tag{20}$$

$$c_k = 0.428 + 0.032(M_k - 2), \quad k = 1, 2 \tag{21}$$

where subscript k is 1 for the solute, and 2 for the solvent, T_{cr} is the critical temperature, M is the molecular weight, v is the molar volume, and r is the van der Waals volume given by Eq. (6). c_i values calculated with original UNIFAC and modified UNIFAC are different, because van der Waals group volume parameters R_i are different. Eqs. (18)–(21) when applied to systems containing water, cyclic ethers, alcohols, and chloroform with modified UNIFAC give erroneous c_i values in the range of 10–1000. For the isopropanol(1)–ethyl acetate (2) system, c_i values calculated from Eq. (19) with both original and modified UNIFAC were in the range of 27–52. This is consistent with Stelmachowski and Ledakowicz's [20] suggestion for using Eqs. (18)–(21) for alkanes only. Therefore, we propose using Eq. (22) with modified UNIFAC for systems where the solvent is either methanol, ethyl acetate or chloroform.

$$c_i = [c0^4(T/(T_{cr1}\,T_{cr2})^{0.5})^{(-c1c2^4)}/(c1c2)] - 10 \tag{22}$$

This equation was obtained intuitively rather than empirically, to reduce the deviations from experimental data. Using Eq. (22) for the systems tetrahydrofuran(1)–chloroform(2) and benzene(1)–methanol(2), gave better results in free volume calculations. When Eq. (22) was used for 1,4-dioxane(1)–alkane(2) systems the deviations from experimental data were reduced, but not significantly. For other systems the values of c_i and b are taken as in Table 2. The temperature dependence of c_i calculated from Eq. (19) for original UNIFAC and Eq. (22) for modified UNIFAC is shown in Figs 1 and 2. In general, c_i values calculated from both of the equations do not change very much with temperature. However, for benzene(1)–methanol(2) system (Fig. 1) c_i increases with temperature.

When the sizes of the solute and solvent are very different, especially in polymer solutions, the free volume effects become important. It has been stated by Fredenslund [2] that for mixtures of low-molecular-weight solvent systems, free volume differences can reach the same magnitude as in polymer solutions. Therefore, the infinite dilution activity coefficients are calculated with and without free volume effect, and the free volume contribution to infinite dilution activity coefficient, $\%FV_{eff}$, given in Table 1 is

Table 1
Experimental and calculated infinite dilution activity coefficients, $\%FV_{\text{eff}}$(Eq. (23)), $\%AE$(Eq. (24)

Solute(1)–solvent(2)	$T/(K)$	Org. UNIFAC		Org. + FV		$\%FV_{\text{eff}}$	
		g1*	g2**	g1	g2	g1	g2
Methanol–cyclohexane	283.15	29.353	–	29.39	–	0.126	–
[13,14]	293.15	25.957	–	25.995	–	0.146	–
	308.15	21.910	15.215	21.951	15.243	0.188	0.182
	313.15	20.781	–	20.823	–	0.202	–
	318.15	19.743	14.761	19.786	14.792	0.219	0.212
	333.15	17.087	14.110	17.134	14.147	0.273	0.263
Methanol–Cyclopentane[14]	288.15	30.828	11.906	30.832	11.907	0.013	0.008
Pyridine–Water[13]	343.15	11.086	2.265	11.376	2.302	2.612	1.644
	363.15	12.681	2.373	13.015	2.412	2.633	1.656
	373.15	13.420	2.423	13.775	2.463	2.644	1.662
1,4-Dioxane–n-heptane[15]	353.15	2.304	6.927	2.327	6.945	1.017	0.258
1,4-Dioxane–n-octane[15]	353.15	5.017	8.470	5.032	8.479	0.294	0.097
1,4-Dioxane–n-nonane[15]	353.15	4.836	10.229	4.838	10.231	0.062	0.025
1,4-Dioxane–water[15]	308.15	5.174	1.062	5.308	1.083	2.580	2.007
	323.15	5.577	1.107	5.722	1.130	2.595	2.033
	343.15	5.996	1.162	6.152	1.186	2.616	2.071
1,4-Dioxane–chloroform[15]	323.15	0.205	0.351	0.206	0.351	0.229	0.083
Tetrahydrofuran–n-hexane[15]	313.15	1.650	1.849	1.659	1.851	0.556	0.135
	333.15	1.591	1.780	1.602	1.783	0.671	0.159
Tetrahydrofuran–Water[15]	298.15	33.479	2.634	34.340	2.693	2.572	2.218
	323.15	33.476	2.820	34.344	2.885	2.594	2.294
	343.15	33.053	2.947	33.917	3.016	2.612	2.363
Tetrahydrofuran–chloroform[15]	303.15	0.355	0.370	0.355	0.370	0.000	0.000
	313.15	0.368	0.384	0.369	0.384	0.003	0.000
	323.15	0.382	0.397	0.382	0.397	0.000	0.000
Tetrahydrofuran–cyclohexane[15]	313.15	1.877	1.965	1.881	1.967	0.201	0.084
	333.15	1.810	1.904	1.814	1.906	0.219	0.092
1–Butanol–Water[13]	343.15	44.005	3.965	45.049	4.031	2.372	1.682
	353.15	42.318	3.978	43.331	4.046	2.393	1.692
	363.15	40.775	3.986	41.760	4.054	2.415	1.701
	372.15	39.495	3.988	40.457	4.057	2.435	1.710
	383.15	38.054	3.986	38.990	4.055	2.461	1.721
Chloroform–Water[16]	293.15	911.49	–	934.79	–	2.56	–
	303.15	816.61	–	837.56	–	2.57	–
	308.15	774.64	–	794.55	–	2.57	–
	313.15	735.85	–	754.79	–	2.57	–
Methyl tertiary butyl ether–	303.15	1.55	1.51	1.51	1.55	0.00	0.00
2-Methylpentane[17]	323.15	1.50	1.47	1.50	1.48	0.00	0.68
Methyl tertiary butyl ether–	303.15	1.55	1.51	1.55	1.51	0.00	0.00
n-hexane[17]	323.15	1.50	1.47	1.50	1.47	0.00	0.00
Methyl tertiary butyl ether–	313.15	1.56	2.41	1.78	2.61	14.10	8.30
n-heptane[17]	323.15	1.52	2.33	1.74	2.52	14.47	8.15
Methyl tertiary butyl ether–	313.15	1.80	2.26	1.85	2.30	2.78	1.77
cyclohexane[17]	323.15	1.76	2.20	1.81	2.24	2.84	1.82
Methyl tertiary butyl ether–	313.15	1.93	2.14	1.99	2.18	3.11	1.87
cyclopentane[17]	323.15	1.89	2.09	1.94	2.13	2.65	1.91
Diisopropyl ether–	313.15	1.07	1.08	1.08	1.08	0.93	0.00
n-heptane[17]	333.15	1.07	1.07	1.07	1.07	0.00	0.00
Diisopropyl ether–cyclo	313.15	1.12	1.09	1.13	1.10	0.89	0.92
hexane[17]	333.15	1.12	1.09	1.12	1.09	0.00	0.00
Ethylene glycol/Water[18]	297.50	0.75	–	0.77	–	2.67	–
	308.20	0.79	–	0.81	–	2.53	–
	317.90	0.83	–	0.84	–	1.20	–
	328.20	0.86	–	0.88	–	2.33	–
	338.10	0.90	–	0.92	–	2.22	–
	348.10	0.93	–	0.95	–	2.15	–
Isopropanol–water[14]	288.15	20.84	3.20	21.32	3.25	2.30	1.56
Isopropanol–Ethyl acetate[14]	288.15	3.00	2.89	3.17	3.09	5.67	6.92

* g1-Activity coefficient of component 1 at infinite dilution.
** g2-Activity coefficient of component 2 at infinite dilution.

Mod. UNIFAC		Mod. +FV		%FV_{eff}		Measured		%AE (Org)		%AE(Mod)	
g1	g2	g1	g2	g1	g2	g1	g2	g1	g2	g1	g2
12.617	–	123.037	–	9.244	–	118.800	–	75.292	–	5.205	–
82.262	–	89.924	–	9.314	–	77.800	–	66.636	–	5.735	–
53.350	20.316	58.378	21.449	9.424	5.577	54.200	18.900	59.576	19.497	1.568	7.492
46.606	–	51.016	–	9.492	–	63.700	–	67.377	–	26.835	–
40.886	19.323	44.771	20.406	9.502	5.605	38.000	17.400	48.044	15.169	7.596	11.054
28.262	17.901	30.982	18.913	9.623	5.648	27.500	16.600	37.865	15.003	2.771	7.840
105.327	14.797	115.742	15.697	9.888	6.082	169.500	16.200	81.812	26.506	37.860	8.660
10.116	2.482	10.195	2.488	0.789	0.259	24.600	2.870	54.934	21.093	58.879	13.521
10.356	2.624	10.438	2.630	0.794	0.260	20.000	2.800	36.596	15.253	48.221	6.299
10.320	2.673	10.403	2.680	0.796	0.260	17.000	2.800	21.058	13.475	39.291	4.524
2.762	4.083	3.918	4.166	41.872	2.044	2.690	3.780	14.363	83.255	2.665	8.016
2.585	4.446	3.196	4.522	23.638	1.698	2.490	4.280	101.501	97.906	3.818	3.886
2.443	4.834	2.815	4.904	15.236	1.456	2.200	4.730	119.796	116.255	11.031	2.198
7.257	3.730	7.344	3.948	1.202	5.834	6.640	6.960	22.071	84.747	9.294	46.408
7.976	3.543	8.072	3.754	1.205	5.956	7.050	6.410	20.889	82.727	13.131	44.722
9.045	3.328	9.154	3.529	1.208	6.035	7.270	4.870	17.529	76.144	24.417	31.656
0.111	0.364	0.139	0.371	25.225	1.741	0.290	0.460	29.179	23.743	61.766	20.786
1.540	1.834	2.231	1.870	44.903	1.914	1.750	1.940	5.720	4.705	12.012	5.439
1.456	1.708	2.155	1.742	48.047	1.964	1.630	1.800	2.390	1.091	10.683	5.093
16.842	14.700	17.032	15.618	1.130	6.243	28.930	17.770	15.725	85.176	41.784	17.277
16.288	11.368	16.472	12.093	1.126	6.380	26.220	9.380	27.672	69.935	37.878	21.189
15.977	9.416	16.156	10.028	1.121	6.505	30.830	7.800	7.212	62.222	48.177	20.714
0.262	0.320	0.302	0.324	15.542	1.426	0.170	0.190	108.559	94.521	53.894	68.358
0.282	0.349	0.326	0.354	15.666	1.437	0.200	0.220	84.155	74.355	40.750	58.755
0.296	0.376	0.343	0.381	15.799	1.445	0.220	0.260	73.464	52.742	34.736	44.569
1.650	1.695	1.652	1.697	0.141	0.169	1.810	1.760	3.702	11.664	8.859	3.721
1.544	1.591	1.547	1.592	0.168	0.064	1.700	1.610	6.474	18.265	9.176	1.209
42.682	3.992	43.230	4.013	1.284	0.531	67.800	3.270	35.095	21.241	37.047	22.087
42.048	3.825	42.586	3.846	1.281	0.528	46.500	3.120	8.994	27.510	9.575	22.610
41.191	3.659	41.718	3.678	1.278	0.525	–	3.070	–	29.835	–	19.183
40.248	3.510	40.762	3.528	1.275	0.522	27.100	2.970	45.738	34.290	48.518	18.181
38.894	3.329	39.388	3.347	1.271	0.518	–	2.900	–	37.461	–	14.803
707.98	–	713.40	–	0.77	–	818.00	–	11.43	–	13.45	–
625.61	–	630.39	–	0.76	–	835.00	–	2.20	–	30.42	–
589.36	–	593.86	–	0.76	–	847.00	–	8.54	–	34.59	–
55.99	–	560.23	–	0.76	–	850.00	–	13.43	–	34.59	–
1.28	1.26	1.29	1.28	0.78	1.59	1.25	1.27	24.00	18.90	2.40	0.79
1.24	1.22	1.25	1.25	0.81	2.46	1.19	1.22	26.05	20.49	4.20	0.00
1.28	1.26	1.28	1.28	0.00	1.59	1.26	1.16	23.02	30.17	1.59	8.62
1.24	1.22	1.24	1.24	0.00	1.64	1.20	1.15	25.00	27.83	3.33	6.09
1.55	2.36	1.73	2.55	11.61	8.05	1.31	1.01	19.08	138.61	18.32	133.66
1.52	2.27	1.69	2.46	11.18	8.37	1.22	0.94	24.59	147.87	24.59	141.49
1.66	1.96	1.71	1.99	3.01	1.53	1.41	1.21	27.66	86.78	17.73	61.98
1.61	1.86	1.66	1.89	3.11	1.61	1.32	1.07	33.33	105.61	21.97	73.83
1.73	1.83	1.78	1.86	2.89	1.64	1.19	1.16	62.18	84.48	45.38	57.76
1.68	1.75	1.73	1.78	2.98	1.71	1.12	1.10	68.75	90.00	50.00	59.09
1.07	1.07	1.07	1.07	0.00	0.00	1.18	1.08	9.32	0.00	9.32	0.93
1.06	1.06	1.06	1.06	0.00	0.00	1.17	1.02	8.55	4.90	9.40	3.92
1.23	1.13	1.25	1.15	1.63	1.77	1.27	0.95	11.81	14.74	3.15	18.95
1.20	1.11	1.23	1.23	2.50	10.81	1.23	0.92	8.94	18.48	2.44	20.65
0.73	–	0.74	–	1.37	–	0.80	–	6.25	–	8.75	–
0.77	–	0.78	–	1.30	–	0.80	–	1.25	–	–	–
0.80	–	0.81	–	1.25	–	1.00	–	17.00	–	20.00	–
0.84	–	0.85	–	1.19	–	1.00	–	14.00	–	16.00	–
0.86	–	0.87	–	1.16	–	1.00	–	10.00	–	14.00	–
0.88	–	0.89	–	1.14	–	1.20	–	22.50	–	26.67	–
11.49	3.40	11.63	3.42	1.22	0.59	12.90	5.72	61.55	44.06	10.93	40.56
2.63	2.37	2.67	2.42	1.52	2.07	4.63	3.55	35.21	18.59	31.32	33.24

Table 2
The values of constants b and c_i

Systems	c_i	b	Ref.
With polymers	1.1	1.28	[7]
With polymers	2	1.28	[20]
With aliphatic hydrocarbons	1.1	–	[20]
Gases in alkanes and water	1	–	[20]
Gases in different organic solvents	1	–	[20]
Alkanes as solvent	–	1.32	[20]
Water as solvent	–	1.18	[20]
Different organic solvents	–	1.4	[20]
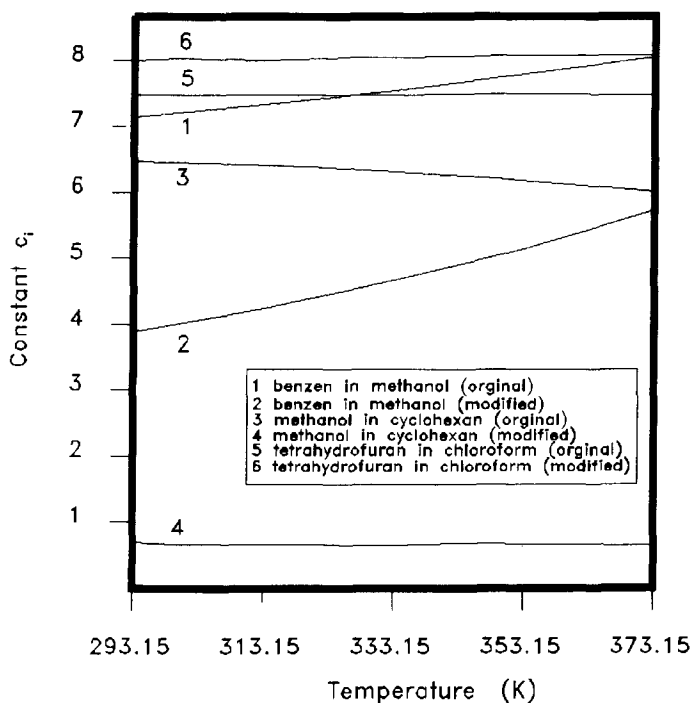
Fig. 1. Constant c_i as a function of temperature. 1, 3, 5: Eq. (20); 2, 4, 6: Eq. (22).

calculated according to the relationships:

$$\%FV_{eff,i} = \frac{\left(\gamma_{i,ORIG.UNIFAC\text{-}FV}^{\infty} - \gamma_{i,ORIG.UNIFAC}^{\infty}\right)}{\gamma_{i,ORIG.UNIFAC}^{\infty}} \times 100 \tag{23a}$$

$$\%FV_{eff,i} = \frac{\left(\gamma_{i,MOD.UNIFAC\text{-}FV}^{\infty} - \gamma_{i,MOD.UNIFAC}^{\infty}\right)}{\gamma_{i,MOD.UNIFAC}^{\infty}} \times 100 \tag{23b}$$
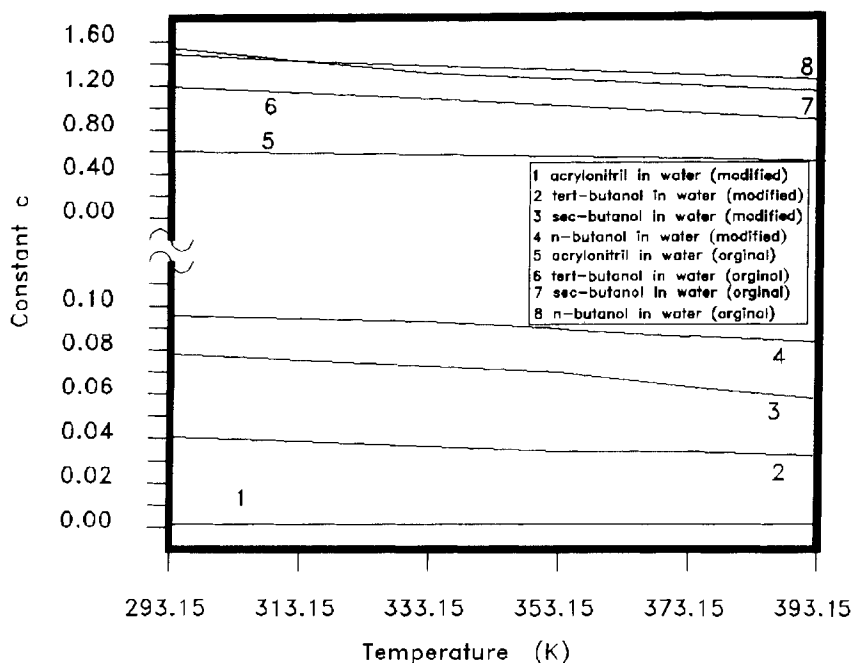
Fig. 2. Constant c_i as a function of temperature. 1,2,3,4: Eq. (22); 5,6,7,8: Eq. (20).

Free volume effects calculated with modified UNIFAC (Eq. (23b)) are, in general, greater than those calculated using original UNIFAC (Eq. (23a)), because calculated c_i values for the modified UNIFAC model are higher. The largest $\%FV_{eff}$ values are obtained for asymmetric, highly non-ideal (e.g. tetrahydrofuran(1)–water(2), n-butanol(1)–water(2), chloroform(1)–water(2), isopropanol(1)–water(2)) and asymmetric, moderately non-ideal (pyridine(1)–water(2), 1,4-dioxane(1)–water(2), ethylene glycol(1)–water(2)) systems where the solvent is water. For methyl tertiarybutyl ether–cycloalkane systems, $\%FV_{eff}$ values are as high as in water systems. The hydrogen bonding in these systems may be responsible for this effect.

Comparison of the predictions with experimental values found in the literature is made using the following absolute relative error, $\%AE$, definition:

$$\%AE = \frac{|\gamma_{i,exp}^{\infty} - \gamma_{i,cal}^{\infty}|}{\gamma_{i,exp}^{\infty}} \times 100 \qquad (24)$$

The values of $\%AE$ in Table 1 show that modified UNIFAC model predictions are better than original UNIFAC ones except for pyridine(1)–water(2), 1,4-dioxane(1)–water(2), 1,4-dioxane(1)–chloroform(2), tetrahydrofuran(1)–n-hexane(2), tetrahydrofuran(1)–water(2), tetrahydrofuran(1)–cyclohexane(2), n-butanol(1)–water(2) and chloroform(1)–water(2) systems. The new parameters for cyclic ethers, cyclic alkanes and tertiary and secondary alcohols have been introduced in the modified UNIFAC model [6]. The performance of the new parameters for primary, secondary and tertiary

butanol in water is shown in Figs. 3–5. In Fig. 3 the experimental results are compared with predictions for the system n-butanol(1)–water(2), the results do not agree with experimental data. The reason may be due to experimental errors or the poor representation of the parameters. The infinite dilution activity coefficients calculated with original UNIFAC are less than those calculated with modified UNIFAC until about 353.15 K for n-butanol and sec-butanol, but for tert-butanol predictions with modified UNIFAC are higher than those of original UNIFAC in the temperature range of 313.15–373.15 K. The order of decreasing infinite dilution activity coefficient is n-butanol, sec-butanol, tert-butanol. The same decreasing order is observed in deviations from Raoult's law. The free volume effect does not change with the position of the OH group in the butanol molecule in either model.

Fig. 6 shows comparison of experimental data with predictions for 1,4-dioxane in n-heptane, n-octane and n-nonane. The results from modified UNIFAC are much better for these systems. The free volume effects are the same for 1,4-dioxane in n-heptane, n-octane and n-nonane in original UNIFAC, whereas in modified UNIFAC the free volume effect decreases as carbon number in the solvent increases. This contradicts the fact that when changes between sizes of solvent and solute increase, the free volume effect also increases.

The predictions for the system tetrahydrofuran(1)–chloroform(2) are compared with experimental results in Fig. 7. The results from modified UNIFAC are also better for this system. The infinite dilution activity coefficient for tetrahydrofuran is higher than for 1,4-dioxane because of the stronger association in tetrahydrofuran. The reason may
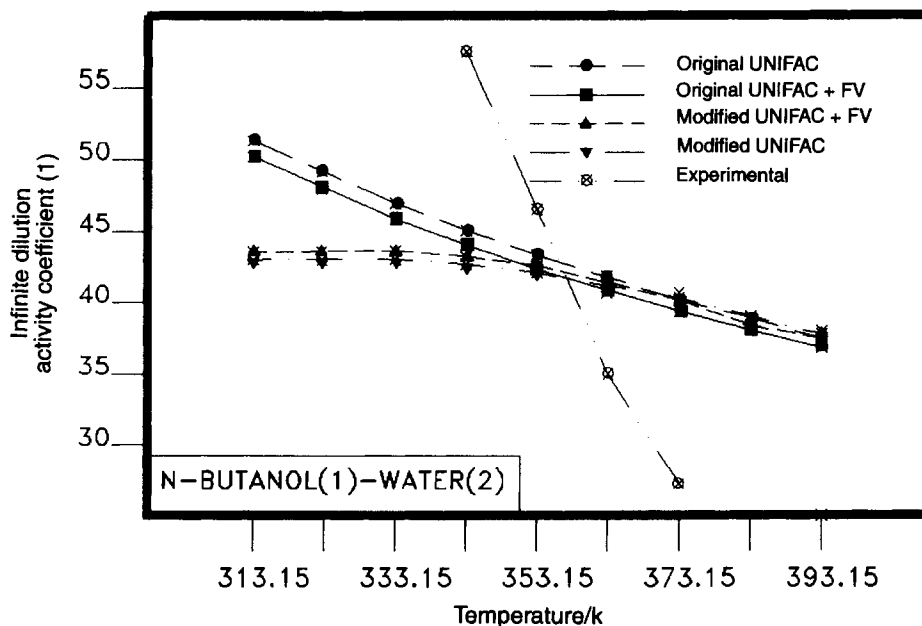

Fig. 3. Change of infinite dilution activity coefficient with temperature for n-butanol(1)–water(2).
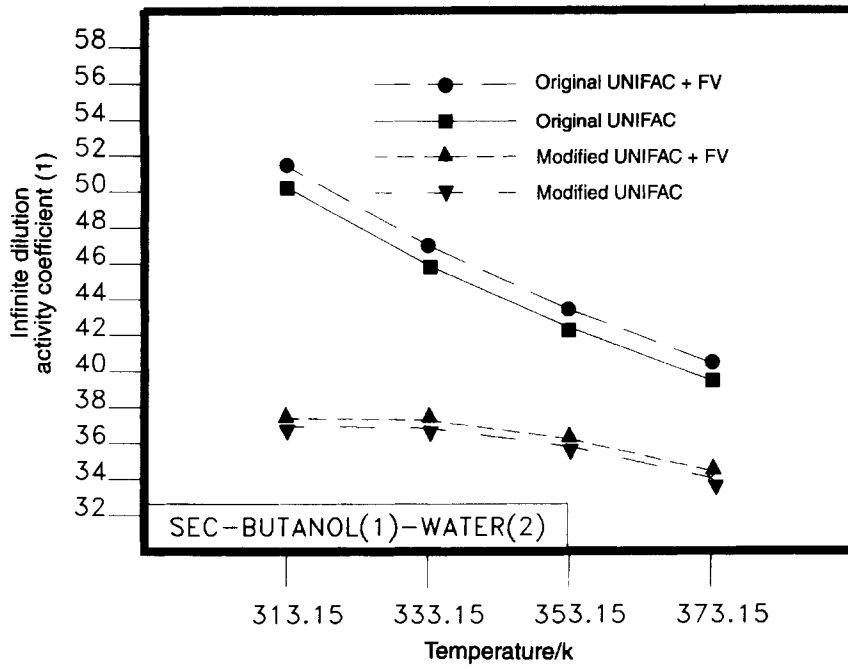
Fig. 4. Change of infinite dilution activity coefficient with temperature for *sec*-butanol(1)–water(2).
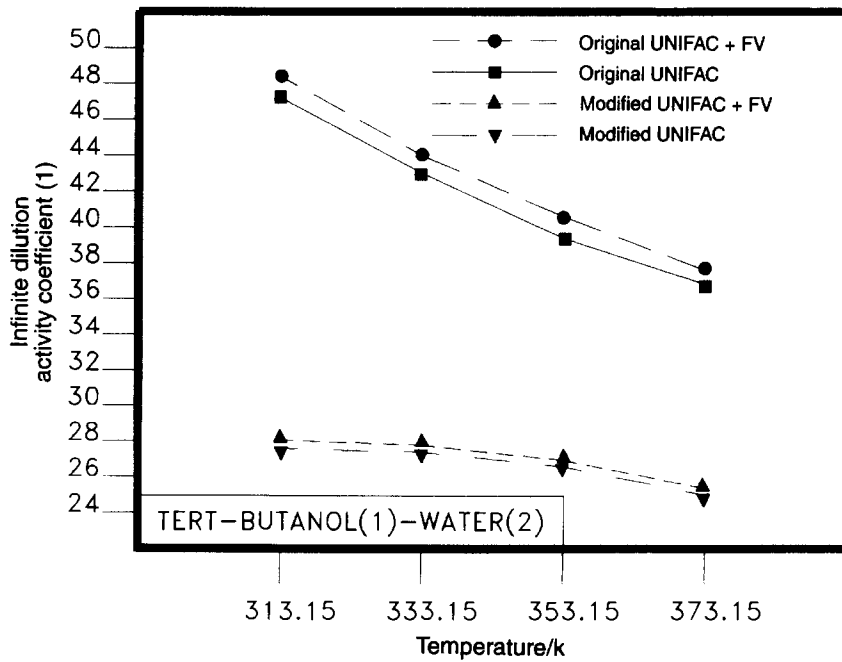

Fig. 5. Change of infinite dilution activity coefficient with temperature for *tert*-butanol(1)–water(2).
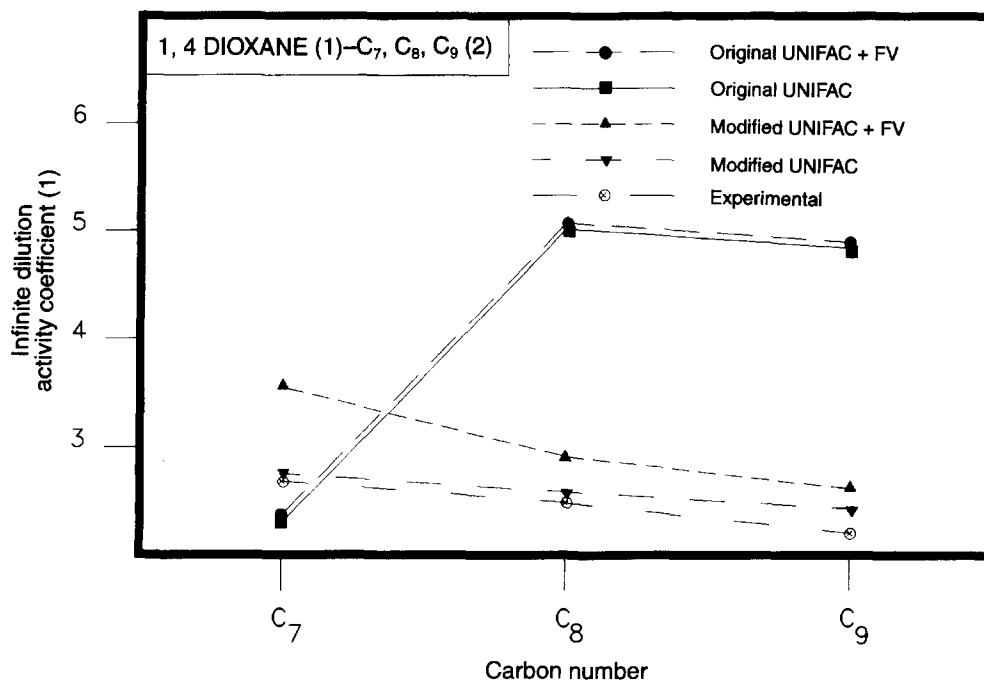
Fig. 6. Comparison of predicted and experimental infinite dilution activity coefficient of 1,4-dioxane in n-heptane, n-octane and n-nonane at 353.15 K.

be because the single ether group is the strongest hydrogen acceptor, compared with 1,4-dioxane which has two ether groups [15]. c_i values calculated from the new equation proposed in this work, give better results in free volume calculations. This is also observed for benzene(1)–methanol(2), as seen in Fig. 8.

For the system acrylonitrile(1)–water(2), the predictions of the original and modified models are close (Fig. 9). The free volume effects calculated with the original UNIFAC are higher than those from the modified UNIFAC, in contrast with other systems studied in this work.

For strongly non-ideal systems, which include the alcohol–alkane mixtures, e.g. the methanol(1)–cyclohexane(2) system, the predictive performance of modified UNIFAC is better than that of original UNIFAC (Fig. 10). This shows that the new parameters proposed by Gmehling et al. [6] for cycloalkanes in modified UNIFAC work very well for this system.

7. Conclusions

Infinite dilution activity coefficients for 24 systems, including highly non-ideal and moderately non-ideal systems are calculated with original UNIFAC, modified UNIFAC, and UNIFAC–FV models. Modified UNIFAC predictions are better than
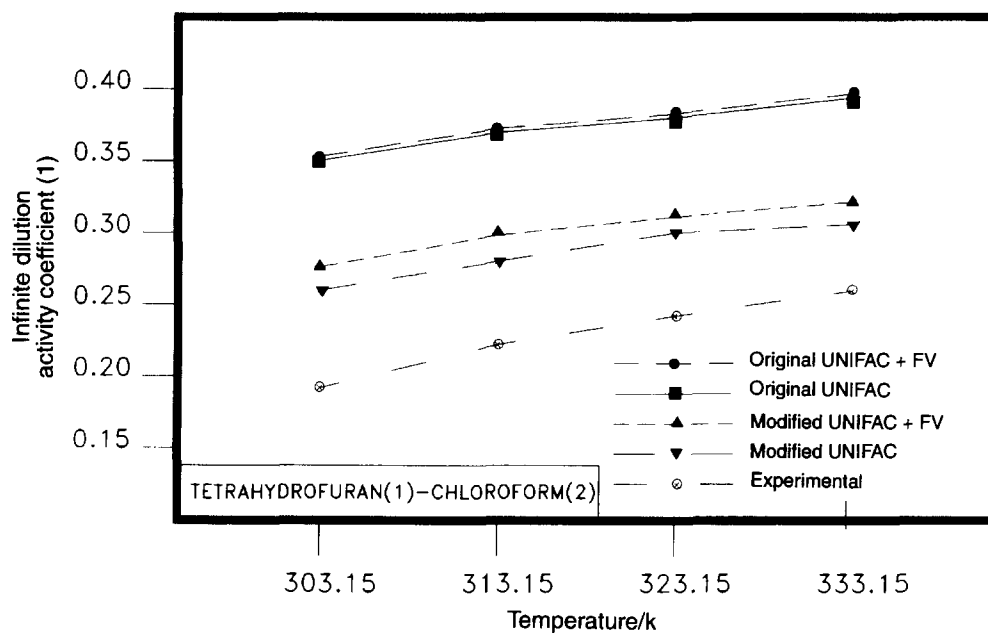
Fig. 7. Change of infinite dilution activity coefficient with temperature for tetrahydrofuran(1)–chloroform(2).
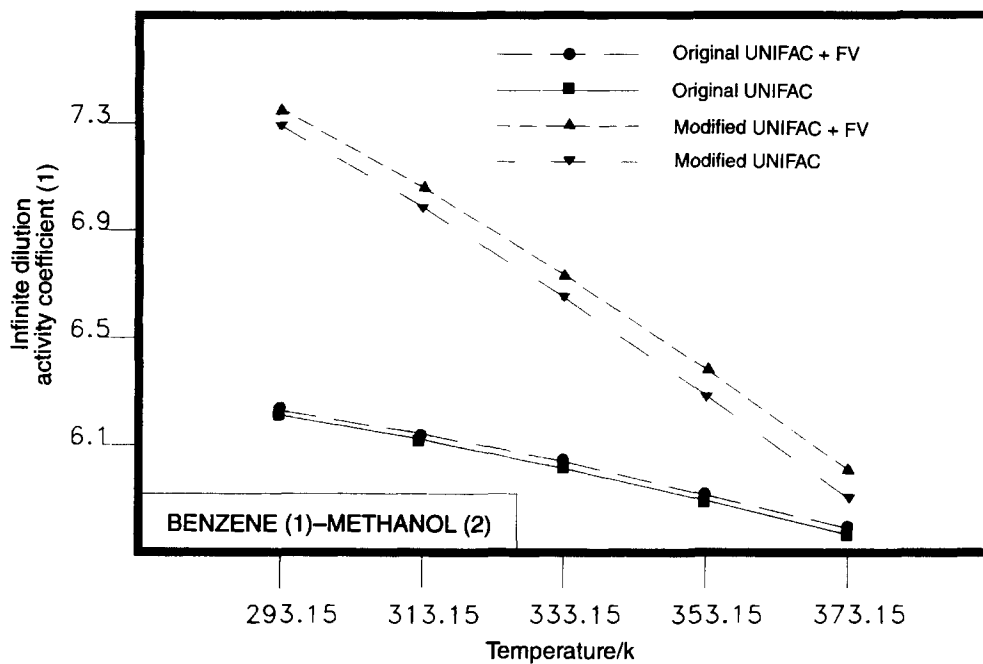

Fig. 8. Change of infinite dilution activity coefficient with temperature for benzene(1)–methanol(2).
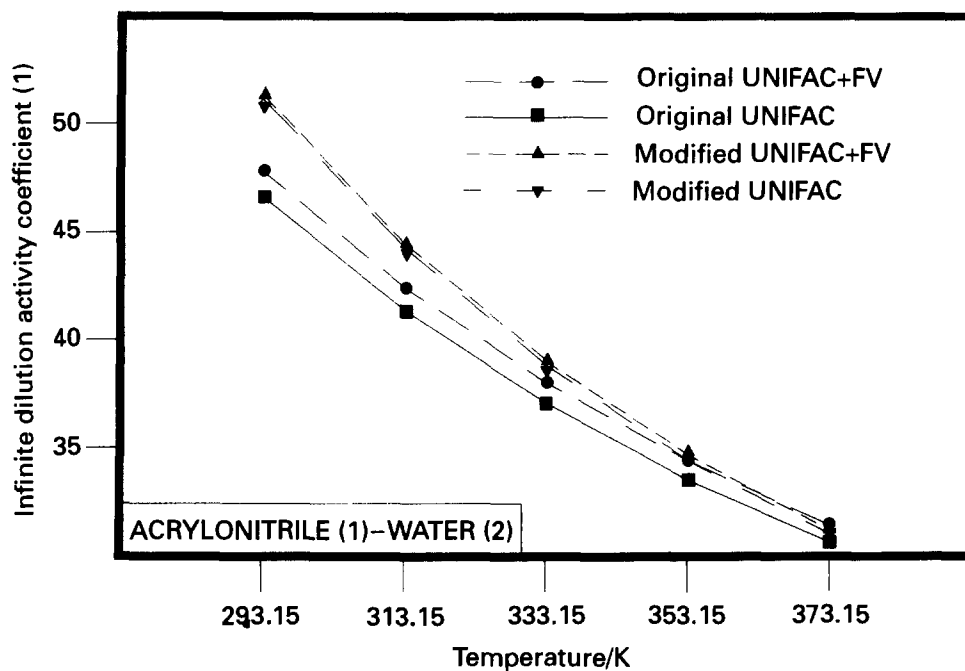
Fig. 9. Change of infinite dilution activity coefficient with temperature for acrylonitrile(1)–water(2).
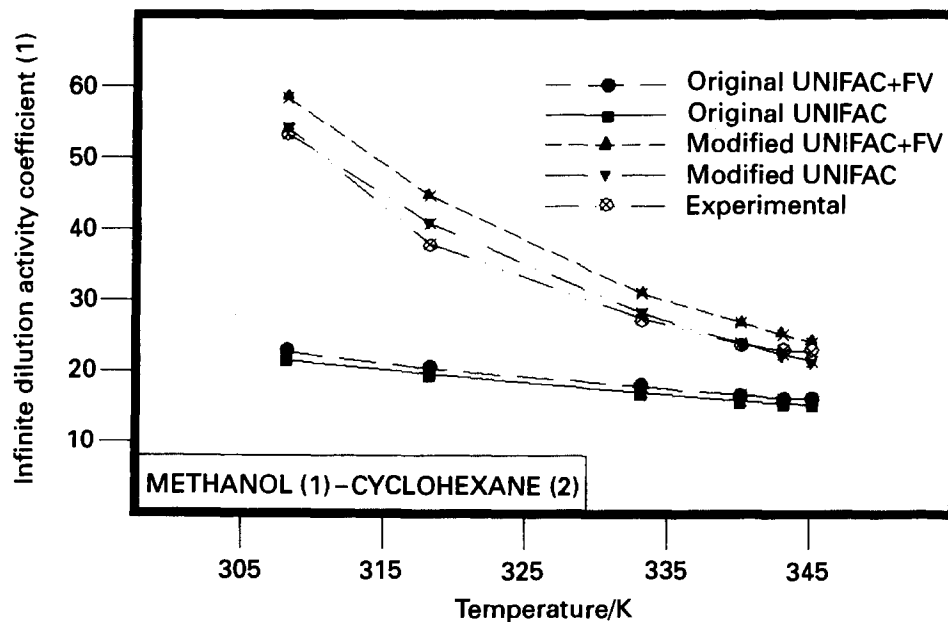

Fig. 10. Change of infinite dilution activity coefficient with temperature for methanol(1)–cyclohexane(2).

those of the original UNIFAC for most of the systems studied. Including the free volume effect in inifinite dilution activity coefficient, especially for asymmetric systems where solvent is water, gives better results. In free volume calculations care should be taken to use the right c_i and b constants. The equation for c_i proposed in this work predicts the free volume effect better with modified UNIFAC when the solvent is either chloroform, ethyl acetate or methanol.

Acknowledgements

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