Vapor−Liquid Equilibria of the Systems Ethyl Ethanoate + 2-Methyl-2-butanol, 2-Methyl-1-propanol + 3-Methyl-1-butanol, and Cyclohexanol + Benzyl Alcohol at 101.32 KPa

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Isobaric vapor−liquid equilibrium (VLE) data have been measured for the binary systems ethyl ethanoate + 2-methyl-2-butanol, 2-methyl-1-propanol + 3-methyl-1-butanol, and cyclohexanol + benzyl alcohol at 101.32 kPa, using a dynamic method. None of these systems show an azeotrope, and all mixtures studied exhibit positive deviations from ideality. Consistency of the experimental results has been verified by point-to-point and area consistency tests. The results were correlated using a modified linear solvation energy relation (LSER) and various versions of UNIFAC and ASOG activity coefficient models. Details underlying some aspects of selection of an appropriate algorithm for fitting the data are discussed. Finally, the reliability of group contribution methods has been analyzed statistically on the basis of both the dimensionless group G^E/RT and γ_i, using a log-ratio objective function.

Introduction

The properties of a system containing substances capable of hydrogen-bond formation such as alcohols can be estimated using the concept of multiscale association (Prausnitz et al., 1980; Brandani and Evangelista, 1987), as well as applying a generalized solvatochromic approach combining the solvatochromic parameters of solvation energy of solution with the linear free energy principle, i.e., linear solvation energy relationship, LSER (Kamlet et al., 1988; Marcus, 1991).

The VLE results for the isomeric alcohol-containing associated solutions (Aucejo et al., 1994a,b; Resa et al., 1994; Dejoz et al., 1997) exhibit a strong deviation from ideality with a range that may be attributed to interactions leading to the formation of various associated aggregates. Along with a consideration of these factors, this article will deal with the vapor−liquid equilibria of ester + isomeric alcohol (I), C_4 isomeric alcohol + C_5 isomeric alcohol (II), especially a mixture of isomeric alcohols found in fusel oil, and cyclic alcohol + aromatic alcohol (III), respectively.

A project of extensive studies covering ester + isomeric alcohol mixtures has been fulfilled by Ortega and co-workers (González and Ortega, 1996). However, the isothermal VLE data for the 2-methyl-1-propanol + 3-methyl-1-butanol mixture was reported by Udovenko and Frid (1948).

In this study, attempts have been made to evaluate the properties of mixtures on the basis of group contribution methods using ASOG (Tochigi et al., 1990) and versions of the UNIFAC model (Fredenslund et al., 1977; Larsen et al., 1987; Gmehling et al., 1993), and a newly proposed approach, METLER (modified expansion terms for linear energy relation), which combines the modified solvatochromic parameters of LSER with the thermodynamic factors (of activity coefficients) derived from a particularly selected group contribution method (e.g., UNIFAC-Dortmund, Gmehling et al. (1993)) in a relation including expansion terms.

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Experimental Section

Chemicals. Chemicals were furnished from Fluka, except for ethyl ethanoate and 2-methyl-2-butanol supplied by Merck. The solvents were dried over anhydrous $CaSO_4$, available as Drierite. C_5-branched alcohols were redistilled with collection of the middle 65% volume. Ethyl ethanoate and cyclohexanol, both of analytical grade, as well as benzyl alcohol and 2-methyl-1-propanol were not subjected to further purification. Mass fractions of impurities of liquids detectable by GC (FI detector) were found to be <0.003 in ethyl acetate, cyclohexanol, 2-methyl-1-propanol, and 3-methyl-1-butanol, <0.005 in benzyl alcohol, and <0.0085 in 2-methyl-2-butanol, respectively. The pure substance densities measured to within an accuracy of ±0.0002 g/cm³ in a Westphal-Mohr buoyancy balance, as well as the refractive indices obtained from an Abbé-Hilger refractometer to within ±0.0003 precision, appear in Table 1.

Apparatus and Procedure. An all-glass dynamic recirculating vapor−liquid equilibrium apparatus developed by the Stansi Educational Division of Fischer Scientific Co. (Canada) and equipped with the digital Fischer manometer and thermometer were used in the equilibrium determinations. The still, described previously in detail elsewhere (Gültekin, 1989), is capable of handling pressures from 0.25 to 101.3 kPa and temperatures up to 523.15 K. The still allows good mixing and flowing of both vapor and liquid phases through an extended contact line, which guarantees an intense phase exchange and their separation once the equilibrium is reached. The equilibrium temperature was measured using a certificated (Fischer) mercury in glass thermometer within an accuracy of ±0.05 K. The temperature control of heating was achieved by a digital thermometer provided with a Pt-100 sensor. The total pressure of the system was controlled by an electronic manometer, as well as being checked from the boiling point of redistilled water in an ebulliometer. All VLE tests were run at (101.32 ± 0.03) kPa. The attainment of a constant temperature for about 1.5 h was the sign of equilibrium reached. However, the equilibrium conditions were cor-

Table 1. Physical Properties of Pure Compounds. Densities (ρ) and Refractive Indexes (n_D) at 298.15 K and Normal Boiling Points (T_b/K)

	T_b/K		n_D		ρ/(g cm^{-3})	
compound	obs.	lit.	obs.	lit.	obs.	lit.
ethyl ethanoate	350.20	350.21[a]	1.3709	1.3704[a]	0.8942	0.8940[a]
2-methyl-2-butanol	375.20	375.15[a]	1.4018	1.4024[a]	0.8057	0.8050[a]
2-methyl-1-propanol	381.05	381.02[a]	1.3947	1.3939[a]	0.7983	0.7978[a]
3-methyl-1-butanol	405.05	405.15[b,c]	1.4055	1.4052[a]	0.8071	0.8070[a]
cyclohexanol	434.20	434.25[b,c]	1.4633[e]	1.4629[d]	0.9412[e]	0.9416[d]
benzyl alcohol	478.50	478.60[b,c]	1.5364	1.5371[b]	1.0418	1.0413[b]

[a] TRC (1975). [b] Dean (1985). [c] Riddick et al. (1986). [d] Values at 303.15 K (Dean, 1985). [e] Observed at 303.15 K.

Table 2. Vapor−Liquid Equilibrium Data at 101.32 KPa. Boiling Temperature T, Liquid-Phase Mole Fraction x, Vapor-Phase Mole Fraction y, and Activity Coefficient γ

T/K	x_1	y_1	γ_1	γ_2	T/K	x_1	y_1	γ_1	γ_2
(a) Ethyl Ethanoate (1) + 2-Methyl-2-butanol (2)
350.450	0.9701	0.9781	1.0006	1.8661	363.200	0.3078	0.5375	1.1860	1.0226
350.660	0.9434	0.9680	1.0116	1.4276	364.630	0.2660	0.4830	1.1845	1.0219
350.940	0.9197	0.9616	1.0219	1.1933	366.660	0.2009	0.3942	1.2097	1.0207
351.200	0.8864	0.9462	1.0349	1.1688	367.950	0.1658	0.3384	1.2145	1.0191
351.700	0.8582	0.9341	1.0390	1.1232	368.260	0.1573	0.3245	1.2172	1.0186
352.400	0.8154	0.9140	1.0472	1.0934	369.730	0.1169	0.2547	1.2353	1.0177
353.450	0.7596	0.8841	1.0529	1.0834	370.930	0.0874	0.1980	1.2437	1.0158
354.900	0.6845	0.8402	1.0627	1.0725	371.120	0.0841	0.1918	1.2456	1.0133
356.150	0.6211	0.8016	1.0762	1.0542	372.240	0.0568	0.1351	1.2610	1.0127
357.850	0.5379	0.7441	1.0967	1.0418	373.040	0.0383	0.0945	1.2807	1.0116
359.650	0.4474	0.6740	1.1330	1.0342	373.470	0.0282	0.0734	1.3359	1.0094
361.420	0.3699	0.6046	1.1679	1.0274					
(b) 2-Methyl-1-propanol (1) + 3-Methyl-1-butanol (2)
381.100	0.9681	0.9807	1.0128	1.3643	389.470	0.4728	0.6701	1.0675	1.0364
381.300	0.9512	0.9723	1.0148	1.2702	391.050	0.4066	0.6074	1.0687	1.0359
381.900	0.9007	0.9484	1.0238	1.1367	392.750	0.3327	0.5315	1.0820	1.0355
382.200	0.8683	0.9321	1.0330	1.1151	394.700	0.2612	0.4452	1.0851	1.0352
382.650	0.8341	0.9144	1.0386	1.0972	396.070	0.2147	0.3823	1.0859	1.0347
382.750	0.8296	0.9128	1.0388	1.0841	397.670	0.1614	0.3039	1.0927	1.0343
383.850	0.7659	0.8754	1.0391	1.0822	398.750	0.1306	0.2547	1.0949	1.0301
383.950	0.7598	0.8727	1.0407	1.0735	400.150	0.0922	0.1891	1.1034	1.0246
384.950	0.7007	0.8358	1.0445	1.0708	401.250	0.0650	0.1387	1.1106	1.0190
386.030	0.6438	0.7995	1.0485	1.0559	402.280	0.0403	0.0902	1.1296	1.0139
386.120	0.6399	0.7973	1.0488	1.0524	402.650	0.0320	0.0738	1.1512	1.0111
386.900	0.6005	0.7701	1.0517	1.0457	403.000	0.0260	0.0615	1.1685	1.0067
387.770	0.5570	0.7384	1.0561	1.0397	403.250	0.0202	0.0501	1.2162	1.0048
387.870	0.5527	0.7352	1.0561	1.0385	403.800	0.0101	0.0267	1.2754	1.0011
(c) Cyclohexanol (1) + Benzyl Alcohol (2)
435.080	0.9651	0.9832	1.0038	1.6647	453.150	0.3169	0.6307	1.2342	1.0726
435.400	0.9435	0.9732	1.0074	1.6232	453.900	0.3052	0.6210	1.2394	1.0590
435.900	0.9103	0.9595	1.0155	1.5201	456.150	0.2667	0.5822	1.2610	1.0369
436.850	0.8422	0.9350	1.0423	1.3448	457.150	0.2499	0.5609	1.2667	1.0354
437.800	0.7886	0.9128	1.0593	1.3062	458.050	0.2358	0.5423	1.2712	1.0327
438.450	0.7425	0.8942	1.0831	1.2743	459.300	0.2154	0.5150	1.2842	1.0290
439.750	0.6893	0.8749	1.1027	1.1985	461.200	0.1883	0.4728	1.2918	1.0254
440.400	0.6604	0.8607	1.1130	1.1962	463.250	0.1610	0.4256	1.2991	1.0214
441.750	0.6139	0.8361	1.1227	1.1868	464.950	0.1383	0.3822	1.3082	1.0212
443.000	0.5762	0.8139	1.1272	1.1810	465.850	0.1279	0.3609	1.3098	1.0187
443.270	0.5695	0.8104	1.1277	1.1746	467.670	0.1091	0.3228	1.3204	1.0063
444.700	0.5297	0.7842	1.1310	1.1712	469.650	0.0862	0.2681	1.3307	1.0060
445.850	0.4895	0.7591	1.1507	1.1629	471.750	0.0627	0.2072	1.3530	1.0054
447.470	0.4498	0.7287	1.1542	1.1571	472.850	0.0515	0.1753	1.3622	1.0043
448.200	0.4309	0.7183	1.1662	1.1365	474.050	0.0391	0.1394	1.3920	1.0030
449.770	0.3909	0.6911	1.1899	1.1112	475.300	0.0270	0.1009	1.4225	1.0022
451.300	0.3556	0.6633	1.2094	1.0943					

roborated by the reproducibility of the results of GC analysis of liquid samples syringed from two phases.

Analysis. Samples of 0.4 μL withdrawn from the liquid and condensed vapor phases were analyzed by gas chromatography on a Hewlett-Packard GC Analyzer, model 5890A, equipped with FI detector. A cross-linked methyl silicone capillary column, HP1-type 50 m $\times$ 0.2 mm $\times$ 0.5 μm in size was selected to separate organic compounds at tailorized oven programs available for each binary system studied. Nitrogen was used as a carried gas at a flow rate of 20 mL·min^{-2}. All injections were performed on the split 1/100 mode. Processing of results was achieved through HP 3365 Chemstation Software. The GC was calibrated with gravimetrically prepared (Sauter balance) standard solutions to convert the peak area to the mole-fraction composition. Mole fractions were accurate to better than ±0.004.

Results and Discussion

Table 2 presents the experimental $T-x_1-y_1$ vapor−liquid equilibrium values at (101.32 ± 0.02) kPa for the mixtures considered in this study and the activity coefficients, γ_i,

Table 3. The Constants of the Antoine Equation[d] for Pure Component Vapor Pressure

compound	A_i	B_i	C_i
ethyl ethanoate[a]	14.1231	2751.89	−60.68
2-methyl-2-butanol[a]	12.9962	1988.05	−137.85
2-methyl-1-propanol[b]	14.8562	2874.73	−100.30
3-methyl-1-butanol[b]	14.6977	3026.43	−104.10
cyclohexanol[c]	12.3884	2101.96	−164.02
benzyl alcohol[c]	14.5594	3759.18	−100.36

[a] TRC (1975). [b] Reid et al. (1987). [c] Dean (1985). [d] $\ln(P_i^o/\text{kPa}) = A_i - B_i/(C_i + T/\text{K})$ (Antoine equation).

for both the components in the liquid phase calculated using the following equation, in which the nonideality of the vapor phase is assumed

$$\phi_i P y_i = \gamma_i P_i^o x_i \phi_i^o \exp[v_i^L(P - P_i^o)/RT] \tag{1}$$

where x_i and y_i are the equilibrium liquid-phase and vapor-phase mole-fraction compositions, respectively, T/K is the boiling point of the mixture, and P is the total pressure. The pure component vapor pressures, P_i^o, were estimated through the Antoine equation using the constants A_i, B_i, and C_i given in Table 3. Variations in the molar volumes of saturated liquids, v_i^L, with temperature were determined by the method of Gunn and Yamada (1971). The fugacity coefficients, ϕ_i and ϕ_i^o, of component i in the mixture and pure vapor, respectively, were evaluated using the virial state equation truncated after the second term, namely:

$$\phi_i = \exp[(P/RT)(2\sum_j y_j B_{ij} - \sum\sum y_i y_j B_{ij})] \tag{2}$$

The second virial coefficients, B_{ii} and B_{ij}, for both the pure components and mixture, were estimated according to the method of Tsonopoulos (1974) using the parameters suggested by the author and critical properties of components given elsewhere (Reid et al., 1987; Riddick et al., 1986; TRC, 1975). However, the b parameters for isomeric alcohols were evaluated from the Tsonopoulos approach using the reduced dipole moment (μ_R) values:

$$b = 0.019\,08 + 0.000\,695\,7 \times \mu_R \tag{3}$$

The thermodynamic consistency of the data was evaluated in terms of the $L-W$ test method of Wisniak (1993) and the area tests of Redlich−Kister (1948) and Herington (1951), and the point-to-point test of Van Ness as described by Fredenslund et al. (1977) was applied yielding a third-order Legendre polynomial for the excess molar Gibbs energy, and assuming the excess enthalpy term turned out to be virtually negligible. All the mixtures proved to be consistent with respect to the last method for the average deviation of $|\Delta y| < 0.01$ established for the test, with the values after reduction found to be 0.0089 (ethyl acetate + 2-methyl-2-butanol), 0.0082 (2-methyl-1-propanol + 3-methyl-1-butanol), and 0.0094 (cyclohexanol + benzyl alcohol), respectively. All mixtures were inconsistent with the area test by Redlich Kister. The results of other tests are reported in Table 4. The consistency tests of various versions give reasonably different results. The 2-methyl-1-propanol + 3-methyl-1-butanol system presented negative consistency and the other two may be considered about the confidence limit in terms of the $L-W$ version, whereas the version of Herington yielded the negative result only for ethyl ethanoate + 2-methyl-2-butanol. The $L-W$ approach of Wisniak for both point-to-point and area

Table 4. Results of Consistency Tests Applied to Binary Mixtures

	$L-W$ test		Herington test
	(point-to-point)	(area)	
system	dev_1 (%)[a]	dev_2 (%)[b]	$|D - J|$[c]
ethyl ethanoate/ 2-methyl-2-butanol	8.67	8.55	16.92
2-methyl-1-propanol/ 3-methyl-1-butanol	15.62	14.75	1.94
cyclohexanol/ benzyl alcohol	9.28	9.27	1.52

[a] $\text{dev}_1(\%) = (100/N)\sum_i|L_i - W_i|/(L_i + W_i)$, where L_i and W_i are the temperature and the excess Gibbs function dependent terms, respectively, defined by Wisniak (see Wisniak, 1993). [b] $\text{dev}_2(\%) = 100|L - W|/(L + W)$, where the integrals $L = \int_0^1 L_i\,dx_1$ and $W = \int_0^1 W_i\,dx_1$; dev $\leq 5\%$ is the criterion for consistency (Wisniak, 1993). [c] $D = 100|A - B|/(A + B)$; $J = 150|T_{\max} - T_{\min}|/T_{\min}$; A and B are the areas above and below the x-axis of the plot $\ln(\gamma_1/\gamma_2)$ vs x_1, respectively; $|D - J| < 10$ is the criterion for consistency (Herington, 1951).
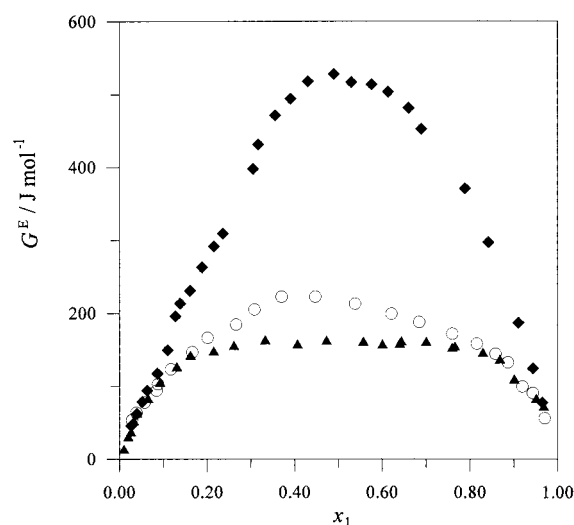

Figure 1. Variation of excess Gibbs energy, G^E, with liquid-phase composition. (○) ethyl ethanoate (1) + 2-methyl-2-butanol (2); (▲) 2-methyl-1-propanol (1) + 3-methyl-1-butanol (2); (◆) cyclohexanol (1) + benzyl alcohol (2).

tests was applied using the heat of vaporization of pure components given from TRC (TRC, 1975; Riddick et al., 1986).

All the mixtures studied exhibit positive deviations from ideality. Observed nonideal behavior is indicative from the magnitude of γ_i given in Table 2, as well as from the variation of excess Gibbs function, G^E, with composition as depicted in Figure 1. Referring to Figure 1, it will be observed that the largest deviation is found for the mixture cyclohexanol + benzyl alcohol ($G_{\max}^E \approx 540$ J·mol^{-1}), reflecting probably a strong dipole−dipole interaction of components through hydrogen bonding (dipole moments of both components, $\mu = 5.67 \times 10^{-12}$ C·m; Reid et al. (1987)) accompanying the multiple associating effects at the substituent and aromatic ring (aromatic π system) of benzyl alcohol; i.e., for aromatics with substituents that are strong π-electron donors to the aromatic ring, it is suggested the multiple hydrogen-bonding effects at the substituent and ring appear. In fact, the solvatochromic parameters of H-bond formation for benzyl alcohol are evaluated by summations of those for benzene and methanol (Table 5). The Gibbs function G^E for ethyl ethanoate + 2-methyl-2-butanol ($G_{\max}^E \approx 225$ J·mol^{-1}) and 2-methyl-1-propanol + 3-methyl-1-butanol ($G_{\max}^E \approx 160$ J·mol^{-1}) mixtures is re-

Table 5. Hildebrand Solubility Parameter (δ_H) and Solvatochromic Parameters of Compounds

compound	$\pi^{a,b}$	$\beta^{a,b}$	$\alpha^{a,b}$	$\delta_H^{c,d}$/MPa$^{0.5}$	$\delta^{a,b}$
ethyl ethanoate	0.55	0.45	0.00	18.61^c	0.0
2-methyl-2-butanol	0.40	0.57	0.32	25.06^e	0.0
2-methyl-1-propanol	0.40	0.45	0.33	21.48	0.0
3-methyl-1-butanol	0.40	0.45	0.33	25.06	0.0
cyclohexanol	0.45	0.51	0.31	23.32^c	0.0
benzyl alcohol	0.99	0.52	0.35	24.75^c	1.0

^{a} Kamlet et al. (1988). ^{b} Marcus (1991). ^{c} Barton (1975). ^{d} Riddick et al. (1986). ^{e} Calculated.

markably smaller, indicating that the weaker interactive forces appear in both systems with the interaction effect slightly predominant in the more polar ester + alcohol mixture ($\mu = 6.34 \times 10^{-12}$ C·m for both ethyl acetate and 2-methyl-2-butanol), as compared to the mixture of 2-methyl-1-propanol + 3-methyl-1-butanol (dipole moments, $\mu = 6.34 \times 10^{-12}$ C·m for 2-methyl-1-propanol and $\mu = 6.00 \times 10^{-12}$ C·m for 3-methyl-1-butanol).

Fitting the Data. The composition (y_1), the boiling temperature of mixture (T/K), and the ratio of activity coefficients data, all defined as *Pr*, were fitted using a log-basis equation consisting of two liquid phase−composition dependent parts, i.e., the part accounted for the properties at the composition limits (Pr_0), and the second one, considering the influence of an overall interaction in liquid phase and its nonideality, covered the expansion terms with respect to the thermodynamic factor (Γ_L), the Hildebrand solubility parameter (δ_H/(J·cm^{-3})$^{0.5}$), and the modified solvatochromic parameters π', α', and β'.

$$Pr = Pr_0 + \prod_i x_i \sum_k (C_{T,k}(\Gamma_L)^k + C_{H,k}(\delta'_H)^k + C_{\pi,k}(\pi')^k + $$
$$C_{\beta,k}(\beta')^k + C_{\alpha,k}(\alpha')^k) \quad (4)$$

where the modified terms are evaluated as

$$\delta'_H = \delta_{H,1}\delta_{H,m}/1000; \quad \pi' = (\pi_1 - 0.35\delta_1) \times \pi_m;$$
$$\beta' = \beta_1\beta_m; \quad \alpha' = \alpha_1\alpha_m \quad (5)$$

Estimates were performed assuming the degree of expansion $k = 1$. Index "1" designates the light component properties. The subscript "m" denotes the parameters related to the mixture in terms of x composition, assuming the additional parameter estimation rule:

$$\delta_{H,m} = \sum_i x_i\delta_{H,i}; \quad \pi_m = \sum_i x_i(\pi_i - 0.35\delta_i); \quad \beta_m = \sum_i x_i\beta_i;$$
$$\alpha_m = \sum_i x_i\alpha_i \quad (6)$$

δ_H is the Hildebrand solubility parameter. π and δ are the solvatochromic parameters that measure the component dipolarity/polarizability, i.e., the dipole−dipole and dipole−induced dipole interactions of component in mixture, respectively. The hydrogen-bonding terms, α and β, measure the H-bond-donating and H-bond-accepting abilities of component, respectively (Table 5). The thermodynamic factors, Γ_L^{ij}, for a system of n components are defined as follows (Taylor and Kooijman, 1991)

$$\Gamma_L^{ij} = \delta_{i,j} + x_i\frac{\partial(\ln \gamma_i)}{\partial x_j}|_{T,P,\Sigma} \quad (7)$$

where the symbol Σ (constrained condition) means that the differentiation with respect to x_j is to be carried out while

keeping all other mole fractions x_k ($k \neq j$, $k = 1, ..., n - 1$) constant except the nth, and $\delta_{i,j}$ is the Kronecker δ, 1 if $i = j$ and 0 if $i \neq j$. The mole fraction of species n must be eliminated using the fact that the x_i sum to unity, when the partial derivative of $\ln \gamma_i$ is evaluated. For a two-component system Γ_L is obtained from eq 7 as

$$\Gamma_L = 1 + x_1\frac{\partial(\ln \gamma_1)}{\partial x_1}|_\Sigma \quad (7a)$$

The constrained (by $x_1 + x_2 = 1$) partial derivative of $\ln \gamma_i$ needed in the evaluation of Γ_L is related to the unconstrained derivatives by

$$\frac{\partial(\ln \gamma_1)}{\partial x_1}|_\Sigma = \frac{\partial(\ln \gamma_1)}{\partial x_1}|_{x_2} - \frac{\partial(\ln \gamma_1)}{\partial x_2}|_{x_1} \quad (8)$$

The coefficients C were obtained by application of multivariable regression procedures of the *linpack* algorithm (Kuo, 1972; Himmelblau, 1989), using the parameters from Table 5, and the thermodynamic factors according to the Taylor and Kooijman (1991) approach for the unconstrained derivatives of activity coefficient (γ_1) applied to the UNIFAC models. Owing to the need for limiting the scope of this work, only the Γ_L values estimated from the UNIFAC-Dortmund model by the approach of Mori et al. (1996) with a slight modification will be thoroughly evaluated. The resulting C coefficients and corresponding properties (Pr − log mean) as well as a comparison with the observed performance using the root-mean-square deviation (σ) are presented in Table 6.

If it is assumed to proceed the UNIFAC-original (Fredenslund et al., 1977) algorithm, the following unconstrained γ_i derivatives in terms of the combinatorial part and a slightly modified approach of Mori for the residual one should be used

$$\frac{\partial(\ln \gamma_i^C)}{\partial x_j}|_{T,P,\bar{\Sigma}} = -V_j + 5q_i(V_j - F_j) + V_i(V_j\sum_j x_j l_j - l_j) \quad (9)$$

where

$$V_i = \frac{\Phi_i}{x_i} = \frac{r_i}{\sum_j r_j x_j}; \quad F_i = \frac{\theta_i}{x_i} = \frac{q_i}{\sum_j q_j x_j};$$
$$l_i = 5(r_i - q_i) - r_i + 1 \quad (9a)$$

$\bar{\Sigma}$ means the unconstrained γ_i derivatives when all the x_n ($n \neq j$) are kept constant, r_i and q_i are the UNIFAC parameters. The variation of Γ_L with composition is shown in Figure 2.

Prediction of VLE Using Group Contribution Models

The observed values of activity coefficients, γ_i, and vapor-phase composition, y_i, were compared with estimates using the group contribution methods ASOG (Tochigi et al., 1990), UNIFAC-original (Fredenslund et al., 1977) with the group interaction parameters from Gmehling et al. (1982), and modified versions of UNIFAC-Lyngby (Larsen et al., 1987) and UNIFAC-Dortmund (Gmehling et al., 1993), respectively. The OH/COO groups were used to represent alcohol/ester interaction in the ASOG model, while UNIFAC models contemplated the CH$_3$COO/OH interaction

Table 6. Coefficients C_i of Equation 4 and Root-Mean-Square Deviation σ Evaluated for Different Properties Pr

binary system[d]	C_Γ	C_H	C_π	C_β	C_α
$Pr = \ln(T/K)$; $Pr_0 = \sum_i x_i \ln(T_i)$; $\sigma(T/K)^a$					
ethyl ethanoate/2-methyl-2-butanol ($\sigma = 0.1564$)	-0.2618	-0.3176×10^{-5}	0.7829	0.5248×10^{-1}	0.0
2-methyl-1-propanol/3-methyl-1-butanol ($\sigma = 1.394$)	-9.9734	0.3697×10^{-3}	-8.8476	26.5710	55.0330
cyclohexanol/benzyl alcohol ($\sigma = 0.2082$)	-0.0789	-0.1615×10^{-4}	-0.8404	1.3753	-1.6814
$Pr = \ln(y_1/y_2)$; $Pr_0 = \ln((x_1/x_2)(1 + q))$; $q = (P_2^\circ/P_1^\circ)_{T_1}$; $\sigma(y_1)^b$					
ethyl ethanoate/2-methyl-2-butanol[e,1] ($\sigma = 0.0195$)	61.290	-0.2029×10^{-2}	-166.440	-66.726	0.0
2-methyl-1-propanol/3-methyl-1-butanol[e,2] ($\sigma = 0.0393$)	743.820	-0.2228×10^{-1}	629.620	-22.092×10^{2}	-36.458×10^{2}
cyclohexanol/benzyl alcohol[e,3] ($\sigma = 0.0241$)	127.510	0.1106×10^{-2}	227.520	-827.470	396.660
$Pr = \ln(\gamma_1/\gamma_2)$; $Pr_0 = x_2 \ln(\gamma_1^\infty) - x_1 \ln(\gamma_2^\infty)$; $\sigma(\gamma_1/\gamma_2)^c$					
ethyl ethanoate/2-methyl-2-butanol ($\sigma = 0.0827$)	7.8394	-0.2862×10^{-3}	-25.588	-2.2091	0.0
2-methyl-1-propanol/3-methyl-1-butanol ($\sigma = 0.1751$)	627.810	-0.1910×10^{-1}	532.860	-18.703×10^{2}	-30.864×10^{2}
cyclohexanol/benzyl alcohol ($\sigma = 0.0934$)	12.711	0.2564×10^{-3}	55.492	-134.010	89.794

[a] T_i is the normal boiling point of pure component i, K. [b] P_1° and P_2° are the vapor pressures of pure components estimated by the Antoine equation at the boiling point T_1, kPa. [c] γ_1^∞ and γ_2^∞ are activity coefficients at infinite dilution estimated by UNIFAC-Dortmund. [d] Binaries are presented as: component (1)/component (2). [e] For $Pr = y_1$ and $Pr_0 = x_1$ the coefficients defined for the systems are as follows: 1. $C_\Gamma = 1.556$; $C_H = -0.495 \times 10^{-4}$; $C_\pi = -9.035$; $C_\beta = 7.405$; ($\sigma(y) = 0.0029$); 2. $C_\Gamma = 268.85$; $C_H = -0.816 \times 10^{-2}$; $C_\pi = 228.69$; $C_\beta = -796.27$; $C_\alpha = -1324.3$; ($\sigma(y) = 0.071$); 3. $C_\Gamma = 7.981$; $C_H = -0.142 \times 10^{-3}$; $C_\pi = 29.804$; $C_\beta = -72.678$; $C_\alpha = 49.502$; ($\sigma(y) = 0.0035$).
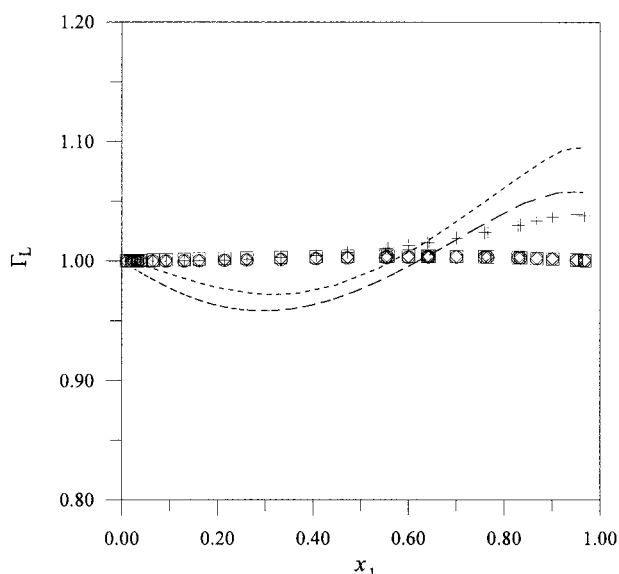

Figure 2. Variation of thermodynamic factors, Γ_L, with composition. 2-Methyl-1-propanol + 3-methyl-1-butanol: +, ASOG; □, UNIFAC-original; ○, UNIFAC-Lyngby; ◇, UNIFAC-Dortmund. Ethyl ethanoate + 2-methyl-2-butanol (- - -) and cyclohexanol + benzyl alcohol (− −) UNIFAC-Dortmund.

groups available for all cases. Table 7 presents a quantitative assessment of the predictions achieved for each model with respect to the mean relative error ($\bar{e}$) and standard deviation (S) of the vapor-phase mole fraction (y_1). The convenience of existing models were also studied through a plot of the observed γ_i values against the estimates (Figures 3, 4, and 5).

Consequently, the UNIFAC-Dortmund model proved to be reasonably the most accurate, yielding a mean error of 4.5% for all the mixtures considered, as compared to 8%
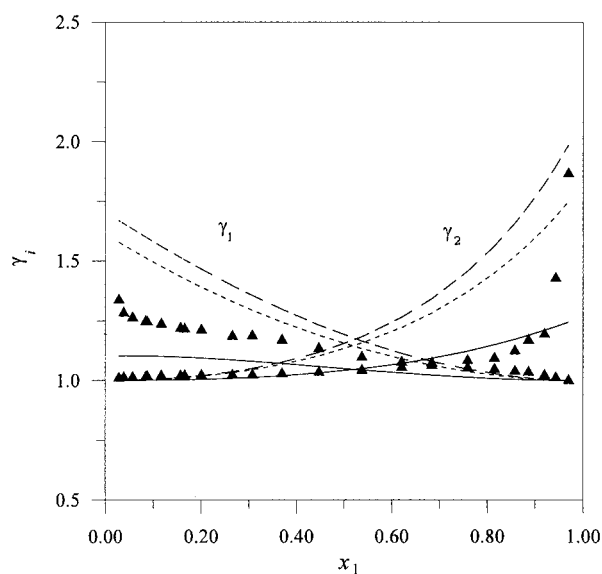

Figure 3. Comparison of activity coefficient models, ethyl ethanoate + 2-methyl-2-butanol: observed (▲); ASOG (- - -); UNIFAC-original (− −); UNIFAC-Dortmund (—).

for ASOG. The Lyngby model estimates do not track well the observed value at 19% error.

Model Reliability Analysis. The reliability of existing models was tested analytically by application of the following logarithmic ratio objective function (OF) proposed by Bolles and Fair (1982)

$$X = \ln(Y_{obs}/Y_{mod}) \tag{10}$$

where, X = OF of model reliability, Y_{obs} = observed value of performance (Giggs number, $G^E/RT = \sum_i x_i \ln \gamma_i$, or γ_j), Y_{mod} = model predicted (modeled) value.

Table 7. Comparison of Mean Errors $\bar{e}(y_1)^a$/% and Standard Deviations $S(y_1)$ Obtained in the Prediction of VLE Using Group Contribution Models

	ASOG		UNIFAC-original		UNIFAC-Lyngby		UNIFAC-Dortmund	
model	$\bar{e}$, %	$S(y_1)$	$\bar{e}$, %	$S(y_1)$	$\bar{e}$, %	$S(y_1)$	$\bar{e}$, %	$S(y_1)$
E-Et/2M-2B (system I)[b]	7.42	0.0253	9.76	0.0332	40.32	0.1270	4.27	0.0139
2M-1P/3M-1B (system II)[b]	3.79	0.0072	36.98	0.1604	3.79	0.0072	3.80	0.0072
CycH/B-A (system III)[b]	13.18	0.0568	4.24	0.0189	13.34	0.0618	5.56	0.0245

[a] $\bar{e}(y_1) = (100/N)\sum_{N=1}^{n}|(y_{1,exp} - y_{1,cal})/y_{1,exp}|$. [b] System I, ethyl ethanoate + 2-methyl-2-butanol; system II, 2-methyl-1-propanol + 3-methyl-1-butanol; system III, cyclohexanol + benzyl alcohol.
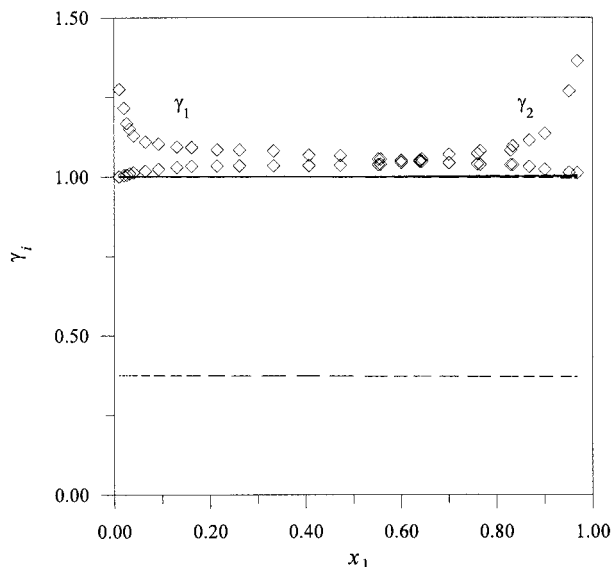
Figure 4. Comparison of activity coefficient models, 2-methyl-1-propanol + 3-methyl-1-butanol: observed ($\Diamond$); ASOG (- - -); UNIFAC-original (− −); UNIFAC-Lyngby (−··−); UNIFAC-Dortmund (−).
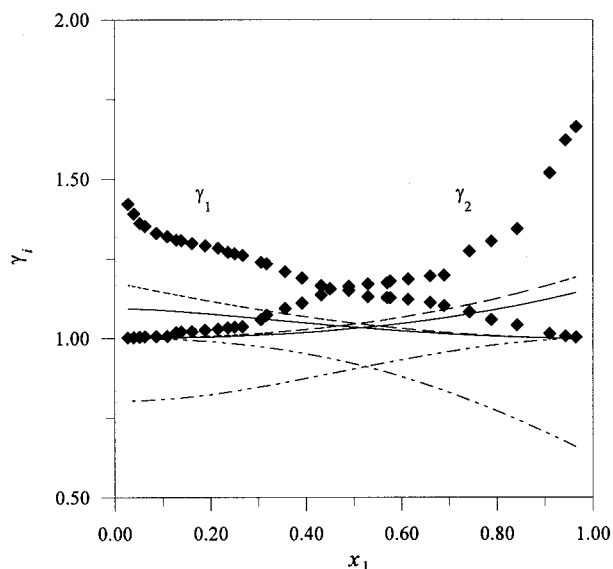

Figure 5. Comparison of activity coefficient models, cyclohexanol + benzyl alcohol: observed ($\blacklozenge$); UNIFAC-original (- - -); UNIFAC-Lyngby (−··−); UNIFAC-Dortmund (−).

In the design practice of distillation applying a new class rate-based algorithm, success (avoidance of failure) is assumed to be critical at only one end of the confidence band. Using the overall design factor (F_{od}), the model normalization factor ($F_m = \exp(\bar{X})$), and the safety factor ($F_s = \exp(tS)$) given by Bolles and Fair, the following expression for upper bound critical (activity coefficient) is obtained

$$\gamma_{desn} = e^{\bar{x}}e^{+tS}\gamma_{mod} = (F_m F_s)\gamma_{mod} = F_{od}\gamma_{mod} \qquad (11)$$

where γ_{desn} = design value, γ_{mod} = modeled value, $\bar{X} = \sum X_i/n$ = mean (bias) of the objective function, $\bar{X}_i$ = OF for the ith observation, n = number of observations; $S = [\sum(\bar{X} - X_i)^2/(n-1)]^{1/2}$ = standard deviation of OF (considering mean value for γ_i), and t = student's t for a certain degree of confidence.

The overall design factor, F_{od}, is the overall correction factor that must be applied to the model to achieve a

Table 8.

(a) Summary of Reliability of Group Contribution Models According to the Dimensionless Gibbs Number, G^E/RT

model	ASOG[a]	UNIFAC-original[b]	UNIFAC-Lyngby[c]	UNIFAC-Dortmund[d]
n (runs)	51	56	51	84
$\bar{X}$	2.1692	0.3003	1.5145	2.3600
S	0.3417	0.2002	0.4556	0.3314

(b) Comparison of Reliability of Existing Activity Coefficient Models Using the γ Variable in Objective Function

model	ASOG	UNIFAC-original	UNIFAC-Lyngby	UNIFAC-Dortmund
n (runs)[e]	84	84	84	84
$\bar{X}$	0.0683	0.1801	−0.0350	0.0774
S	0.1164	0.0873	0.2381	0.0716
F_s (95%)[f]	1.2118	1.1550	1.4811	1.1254
F_m	1.0707	1.1973	0.9656	1.0804
F_{od} (95%)[f]	1.2974	1.3829	1.4302	1.2159
Student's t	1.65	1.65	1.65	1.65

[a] Not available for cyclohexanol + benzyl alcohol. [b] Not available for 2-methyl-1-propanol + 3-methyl-1-propanol. [c] Not available for cyclohexanol + benzyl alcohol. [d] All systems available. [e] All systems considered. [f] For 95% confidence $t = 1.65$.

specified probability of success; i.e., F_{od} is the direct measure of the overdesign relative to the model. For a selected 95% probability of success (1 chance in 20 of failure), and an infinite number of degrees of freedom related to a 90% confidence band Student's $t = 1.645$ (Johnson and Leone, 1967).

The resulting statistical factors for both the Gibbs number and γ are presented in Table 8a,b. To avoid dealing with the negative values the evaluations with regard to the Gibbs number were restricted only by the mean and the standard deviation for the systems available, but disapprovingly not very convenient for analysis, since the experimental x data were executed in OF. These factors indicate the need to overdesign as the result of insufficient model reliability. For example, a safety factor of 1.125 for the UNIFAC-Dortmund model means that the vapor compositions in a distillation design algorithm estimated with this model must be, on the average, 12.5% larger than modeled value to achieve a reasonable (e.g., 95%) confidence of success in design.

Study of Table 8b reveals that the mean and the standard deviations of the design models are noticeably near, indicating a possible good agreement with a wide range of associated alcohol systems. Required overall design factors (F_{od}) for reasonable (95%) confidence of success range from a low of 1.216 for UNIFAC-Dortmund to a slightly high of 1.383 for the original version. The Lyngby version is questionably not acceptable at $F_{od} = 1.430$, indicating a possible inconsistency of selected interaction groups, or its parameters.

Acknowledgment

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