

Neighbor Effects on the Group Contribution Method: Infinite Dilution Activity Coefficients of Binary Systems Containing Primary Amines and Alcohols

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Comparative ebulliometry was used to measure activity coefficients at infinite dilution for binary systems containing primary amines separately with alkanes and alcohols; alcohols with alkanes and alcohols; and diamines with alkanes, amines, and alcohols. Parameters for several Gibbs free energy models can be determined from these activity coefficients at infinite dilution, including new UNIFAC interaction parameters, which are presented here. Some conclusions are made regarding the reliability of the UNIFAC and modified-UNIFAC methods for predicting activity coefficients at infinite dilution for x -R₁-y/R₂ or x -R₁-y/R₂-x mixtures based on interaction parameters that have been determined from R₁-x/R₂ or R₁-x/R₂-y mixtures, where R₁ and R₂ indicate alkane chains and x and y are nonalkyl functional groups.

Introduction

Group contribution methods, such as UNIFAC (1), ASOG (2), and TOM (3), may be used for predicting activity coefficients and other thermodynamic properties of liquid mixtures when no experimental data are available. In this paper, we present new ebulliometric data and infinite dilution activity coefficients for binary mixtures containing amines and alcohols and then focus on the UNIFAC predictions for these systems. Interaction parameters for UNIFAC are generally found from thermodynamically consistent experimental vapor-liquid equilibrium data of binary systems containing molecules of no more than one nonalkyl functional group (i.e., R or R-x molecules, where R represents any number of alkyl functional groups and x is a single nonalkyl group). Interaction parameters for groups within the same main group are zero in UNIFAC and nonzero for unlike groups. For a multifunctional component in a multicomponent system, the key assumption in group contribution methods is that each functional group behaves the same way independent of the molecule in which it appears. Also, the infinite dilution region provides an especially severe test of the UNIFAC method because the combinatorial term used is known to give questionable predictions for infinite dilution activity coefficients, especially for mixtures of molecules of very different size (4, 5). This is one of the reasons that modified-UNIFAC methods have been developed. Other drawbacks of the UNIFAC method are reviewed elsewhere by Fredenslund and Rasmussen (4).

In the absence of complete experimental vapor-liquid equilibrium data, activity coefficients at infinite dilution can be used as a basis for modeling the vapor-liquid equilibrium phase behavior of mixtures (6). The relative experimental ease and rapid approach to equilibrium makes ebulliometry a preferred method for measuring activity coefficients at infinite dilution (7-9). The two parameters in local composition activity coefficient models such as Wilson, NRTL, or UNIQUAC can be determined directly from activity coefficients at infinite dilution. Also, infinite dilution activity coefficients are of direct use in the design of separation techniques for very dilute systems, such as the production of high-purity reagents and the removal of pollutants from the environment. Since activity coefficients at

infinite dilution represent the maximum deviation from ideal solution behavior for most binary systems, except mixtures that associate, parameters in a valid model determined from activity coefficients at infinite dilution can be used to accurately predict vapor-liquid equilibrium throughout the composition range.

Theory

The derivation of the equations for activity coefficients at infinite dilution from comparative ebulliometry is described elsewhere (6). At low pressures and isobaric experimental conditions, the equation for the activity coefficient at infinite dilution has been shown by Dohnal and Novotná (10) to be

$$\gamma_1^\infty = \frac{\epsilon_1 P_2^{\text{sat}}}{P_1^{\text{sat}}} \left[1 - \beta \frac{d \ln P_2^{\text{sat}}}{dT} \left(\frac{\partial T}{\partial x_1} \right)_{x \rightarrow 0} \right] \quad (1)$$

where

$$\epsilon_1 = \exp \left[\frac{(B_{11} - v_1^L)(P_2^{\text{sat}} - P_1^{\text{sat}}) + \delta_{12} P_2^{\text{sat}}}{RT} \right]$$

$$\beta = 1 + P_2^{\text{sat}} \left(\frac{B_{22} - v_2^L}{RT} \right)$$

$$\delta_{12} = 2B_{12} - B_{11} - B_{22}$$

where B_{ii} and B_{ij} are second virial coefficients for like and unlike species, respectively; P_i^{sat} is the pure component vapor pressure; and v_i^L is the liquid molar volume of component i . This equation contains no assumption regarding the liquid-phase ideality and uses the truncated virial equation of state to model the vapor phase. Experimental ebulliometric data are used to determine $(\partial T / \partial x_1)_{x \rightarrow 0}^{\text{sat}}$, the limiting slope at infinite dilution. The manner in which these equations have been used is described earlier (6).

UNIFAC and Modified-UNIFAC Models. In the UNIFAC model, the activity coefficient is divided into the combinatorial (denoted by the superscript C) and residual (denoted by superscript R) contributions:

$$\ln \gamma_1^\infty = \ln \gamma_1^{\text{C}\infty} + \ln \gamma_1^{\text{R}\infty} \quad (2)$$

The combinatorial term takes into account the differences in volume and surface area of the molecules, while the residual term accounts for energetic interactions. The combinatorial and residual parts of the infinite dilution activity coefficient with the UNIFAC model for a binary system are

$$\ln \gamma_i^{\text{C}\infty} = 1 - \frac{r_i}{r_j} + \ln \frac{r_i}{r_j} + \frac{z}{2} q_i \left(1 - \frac{r_i q_j}{r_j q_i} + \ln \frac{r_i q_j}{r_j q_i} \right) \quad (3)$$

where

$$z = 10, \quad r_i = \sum_k v_k^{(i)} R_k, \quad \text{and} \quad q_i = \sum_k v_k^{(i)} Q_k$$

and

$$\ln \gamma_i^{\text{R}\infty} = \sum_k v_k^{(i)} (\ln \Gamma_k - \ln \Gamma_k^{(i)}) \quad (4)$$

with

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

and

$$\theta_m = \frac{\nu_m^{(i)} Q_m}{\sum_k \nu_k^{(i)} Q_k} \quad \text{and} \quad \Psi_{nm} = \exp(-\alpha_{nm}/T)$$

Here, R_k and Q_k are the volume and area parameters of group k , the mole fractions x_i is equal to 0 and x_j is equal to 1 at infinite dilution, a_{nm} is a UNIFAC interaction parameter, \sum_m or \sum_n is a sum over all groups, \sum_k is the sum over all subgroups, and $\nu_k^{(i)}$ is the number of groups k in component i .

The modified-UNIFAC methods differ from the above in the expression used for the combinatorial term and in the expression for Ψ_{nm} of the residual term. Presently there are two different modified-UNIFAC methods. One is by Weidlich and Gmehling (5) in which the combinatorial activity coefficient at infinite dilution term in a binary mixture is

$$\ln \gamma_1^{C\infty} = 1 - \left(\frac{r_1}{r_2} \right)^{3/4} + \ln \left(\frac{r_1}{r_2} \right)^{3/4} - \frac{z}{2} q_1 \left(1 - \frac{r_1 q_2}{r_2 q_1} + \ln \frac{r_1 q_2}{r_2 q_1} \right) \quad (5)$$

and

$$\Psi_{nm} = \exp \left(- \frac{a_{nm,1} + a_{nm,2}T + a_{nm,3}T^2}{T} \right) \quad (6)$$

The second modified-UNIFAC method is that of Larsen et al. (11), in which

$$\ln \gamma_1^{C\infty} = 1 - \left(\frac{r_1}{r_2} \right)^{2/3} + \ln \left(\frac{r_1}{r_2} \right)^{2/3} \quad (7)$$

and

$$\Psi_{nm} = \exp \left(- \frac{a_{nm,1} + a_{nm,2}(T - T_0) + a_{nm,3} \left(T \ln \frac{T_0}{T} + T - T_0 \right)}{T} \right) \quad (8)$$

where T_0 is an arbitrary reference temperature, usually 298.15 K. Thus, in the modified-UNIFAC equations, the number of coefficients in the interaction parameters between two unlike groups is six, compared to two parameters in the original UNIFAC equation. The additional parameters are used for better predictions of the temperature dependence of the activity coefficients and the heat of mixing.

To find the two interaction parameters (Ψ_{nm} and Ψ_{mn}) between the unlike groups of interest from ebulliometric data, one solves the two simultaneous equations with the measured infinite dilution activity coefficients for the two unknown interaction parameters. If there are more than two different functional groups in the binary system under consideration, interaction parameters must be known from previous experiments or published data for all but two of the functional groups present.

Equipment and Procedure

The twin ebulliometers used have been described previously (6). The ebulliometers are connected through a common manifold to a high-accuracy Texas Instruments-Heise PPC159

precision pressure controller and measuring system. Pressure is controlled to ± 0.001 kPa and measured to ± 0.01 kPa absolute. The differences in boiling temperatures of the fluids in both ebulliometers are measured with differential platinum resistance thermometers. The differential and absolute temperatures are measured with accuracies of ± 0.002 and ± 0.010 °C, respectively. A schematic diagram of the entire apparatus and support equipment used here has also been given previously (6).

Aldrich chemicals with 99% or higher purity were purchased for all experiments. The alkanes were used as received. Butylamine, cyclohexylamine, butanol, pentanol, ethylenediamine, and 1,3-diaminopropane were purified in a reduced-pressure glass distillation column under a nitrogen atmosphere. Special care was taken to ensure that the distilled chemicals were exposed only to an atmosphere of dry nitrogen. After purification, all materials used had a purity of better than 99.9% as determined by gas chromatography. Pure-component vapor pressures were measured as a further test of purity, and these appear in Table I. The ebulliometers were cleaned with distilled water, rinsed with acetone, and subjected to total evacuation for at least 12 h before starting each measurement.

Pure-component vapor pressures were compared to those found in Boublík et al. (12) and from Reid et al. (13). Second virial coefficients, estimated by the method of Hayden and O'Connell (14), were used to account for the nonidealities of the vapor phase at low pressures.

Data Analysis and Results

Determination of the activity coefficients at infinite dilution from the experimental data is described in a previous paper (6). The major correction that must be made in the analysis of the experimental measurements is a result of the difference in composition between the gravimetrically prepared feed and the equilibrium liquid in the ebulliometer. This is taken into account by an evaporation or f factor. On the basis of our previous work, an f factor of 0.06 was used for the calculation of the activity coefficients at infinite dilution; the relative error in the f factor is about ± 0.01 . The significance of the errors in the experimental apparatus is reflected in the errors reported in the infinite dilution slopes and activity coefficients in Table II.

The experimental activity coefficients at infinite dilution are compared to the UNIFAC predictions in Tables III and IV. The UNIFAC equation of Fredenslund et al. (7) with the interaction parameters in Reid et al. (13) was used to find activity coefficients at infinite dilution. We also used the UNIFAC interaction parameters of Bastos, Soares, and Medina (15), which were obtained with use of both vapor-liquid equilibrium and γ^∞ data, with their modification of the original UNIFAC equation using the combinatorial term of eq 7 suggested by Larsen et al. (11). It should be pointed out that their interaction parameter set was compiled specifically for calculating infinite dilution activity coefficients. The modified-UNIFAC equation of Larsen et al. (11) was also used to determine activity coefficients at infinite dilution using the interaction parameters given in that reference. The modified-UNIFAC method of Weidlich and Gmehling (5) does not yet have parameters for the primary amine/alkyl interactions. However, parameters are reported for the OH/CH₂ interactions; the results for this modified-UNIFAC method are shown in Table IIIb. Due to the large volatility ($\nu_1/x_1 > 10$) of the solute in the alcohol/alkane system, a larger error is associated with the experimental activity coefficients at infinite dilution for these cases. In order to provide an additional test of the Weidlich-Gmehling modified-UNIFAC method, experimental activity coefficients at infinite dilution were obtained for the 1-butanol/1-propanol system that have less experimental error. However, the differences in the calculated activity coefficients at infinite dilution with the different UNIFAC

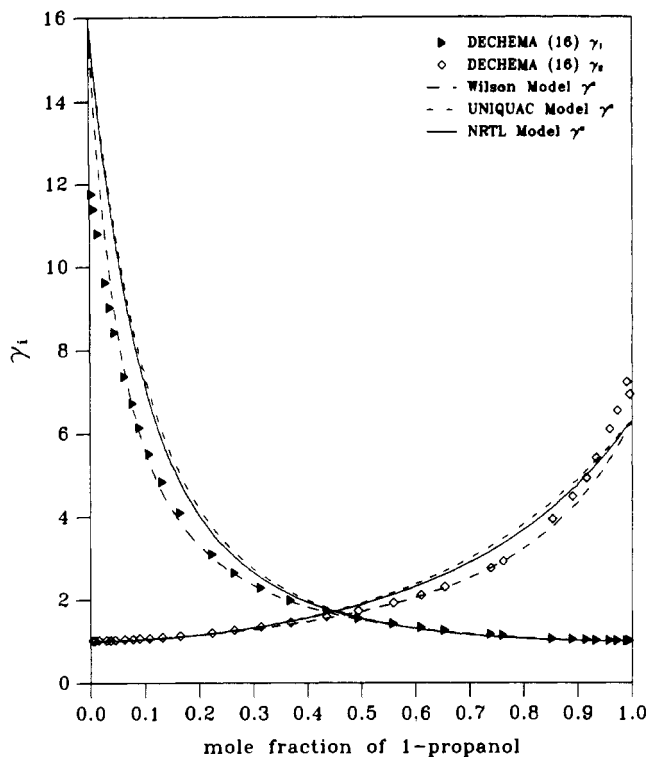


Figure 1. Comparison of predictions of three activity coefficient models with parameters fit to activity coefficients at infinite dilution with experimental vapor-liquid equilibrium data for 1-propanol (1)/*n*-heptane (2) at 60.0 °C of ref 16.

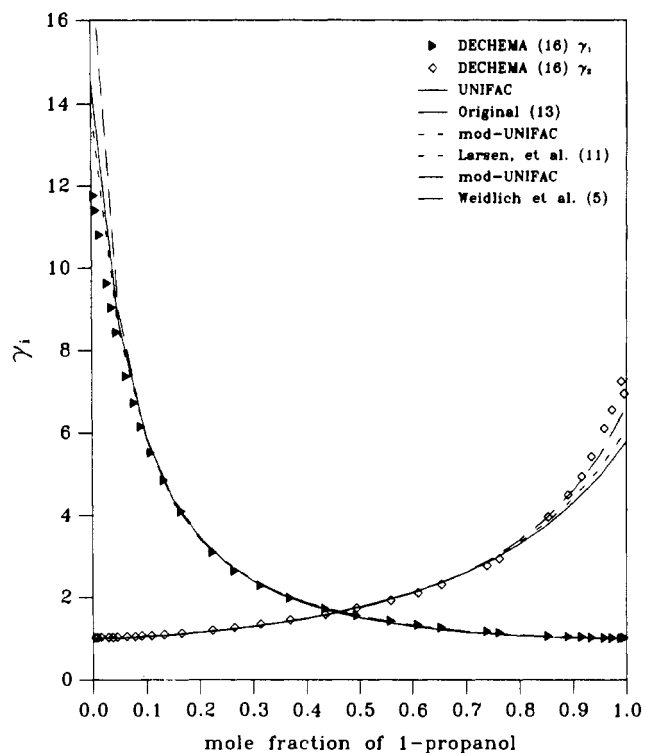


Figure 3. Comparison of predictions of three versions of the group contribution model, UNIFAC, with published parameters (5, 11, 13) with experimental vapor-liquid equilibrium data for 1-propanol (1)/*n*-heptane (2) at 60.0 °C of ref 16.

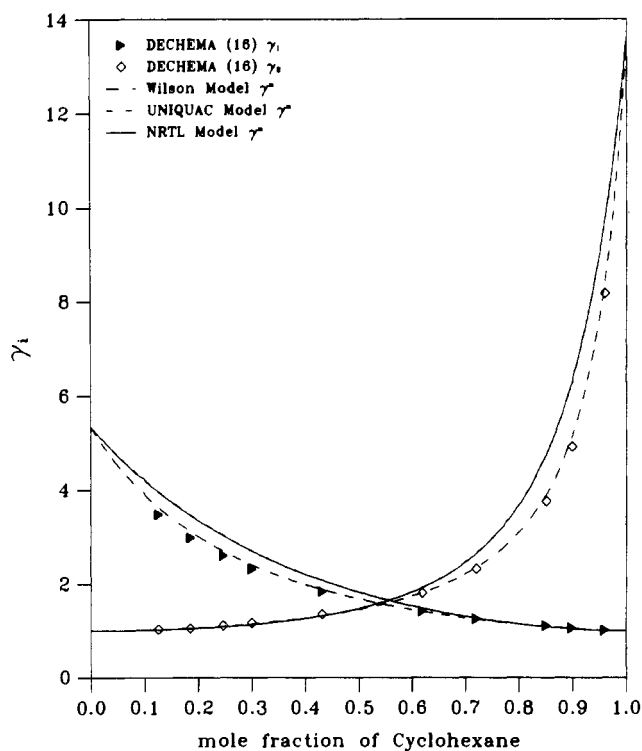


Figure 2. Comparison of predictions of three activity coefficient models with parameters fit to activity coefficients at infinite dilution with experimental vapor-liquid equilibrium data for cyclohexane (1)/2-propanol (2) at 60.0 °C of ref 16.

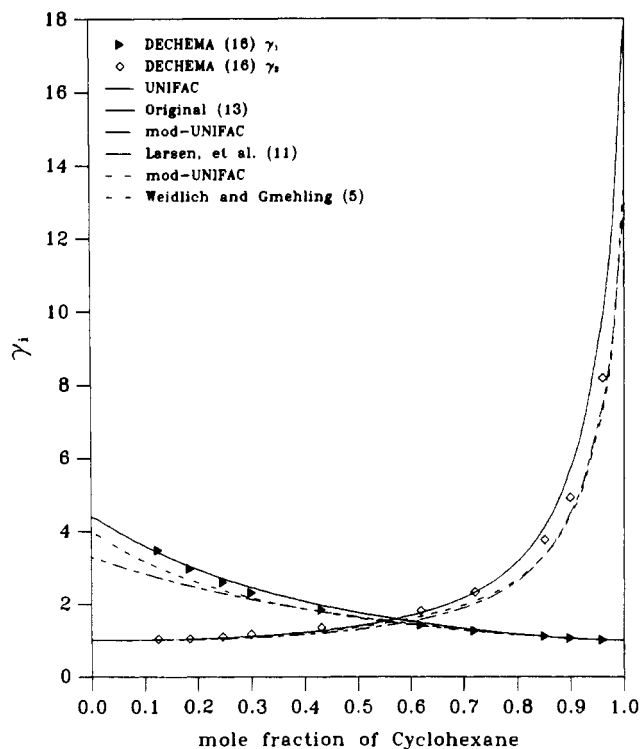


Figure 4. Comparison of predictions of three versions of the group contribution model, UNIFAC, with published parameters (5, 11, 13) with experimental vapor-liquid equilibrium data for cyclohexane (1)/2-propanol (2) at 60.0 °C of ref 16.

equations for this system provide little insight into the differences among the models since the molecules are similar in size and the OH/CH₂ interactions in both molecules cancel. Consequently, all of the UNIFAC methods gave equally good predictions of the experimental activity coefficients at infinite dilution for this almost ideal system.

Activity coefficients from experimental vapor-liquid equilibrium data (16) for two binary systems, 1-propanol with *n*-heptane and 2-propanol with cyclohexane at 60 °C, are plotted in Figures 1–6. In Figures 1 and 2, the activity coefficients derived from experimental composition versus activity coefficient data are compared to the Wilson, UNIQUAC, and NRTL

Table I. Vapor Pressure and Coefficients for Antoine Equation^a

component	T, °C	P ^{sat}		A	B	C	ref
		expt	lit.				
cyclohexane	40.0	24.618	24.623	6.151 59	1301.6960	233.4450	b
	70.0	72.755	72.720	5.975 61	1206.7310	223.2330	12
cyclooctane	80.0	10.672	10.695	5.787 20	1319.0756	197.1301	b
	100.0	22.288	22.336	5.986 70	1437.7510	210.0120	12
n-octane	60.0	10.486	10.481	6.137 91	1407.4911	215.0325	b
	80.0	23.296	23.329	6.043 94	1351.9380	209.1200	12
n-heptane	40.0	12.308	12.326	6.114 61	1316.1274	221.9507	b
	60.0	28.022	28.003	6.027 01	1267.5920	216.7960	12
	80.0	56.991	57.028				
n-nonane	80.0	9.682	9.694	6.383 97	1624.5175	220.9810	b
	100.0	21.031	21.033	6.062 80	1430.6300	201.8270	12
1-butylamine	40.0	24.987	24.952	6.258 21	1260.7694	219.4575	b
	70.0	79.925	79.956	6.263 50	1258.7450	218.6600	13
cyclohexylamine	60.0	7.539	7.486	6.114 94	1412.1758	209.6215	b
	80.0	17.338	17.409	5.873 04	1263.5930	192.7810	12
ethylenediamine	60.0	11.201	11.306	6.397 00	1401.4956	202.0802	b
	80.0	26.830	26.984	6.307 93	1344.5120	195.2540	12
1,3-diaminopropane	80.0	11.713		6.275 18	1405.1533	189.8839	b
	100.0	26.785					
1-propanol	60.0	20.277	20.261	7.209 19	1629.2341	216.0473	b
	80.0	50.810	50.838	6.869 10	1437.6860	198.4630	12
2-propanol	40.0	13.917	13.852	7.203 67	1543.3263	214.6685	b
	60.0	38.499	38.546	6.866 34	1360.1830	197.5930	12
1-butanol	60.0	7.929	8.071	6.362 00	1578.9800	220.9470	b
	80.0	17.206	17.245	6.766 66	1460.3090	189.2110	12
1-pentanol	80.0	9.382	9.376	6.526 50	1405.8184	173.2265	b
	100.0	23.961	23.998	6.315 59	1292.2730	161.8370	12
1-hexanol	90.0	7.148	7.023	6.524 58	1483.6410	171.7299	b
	110.0	18.130	17.978	6.201 07	1305.9840	153.9010	12
ethanolamine	90.0	4.015	3.901	6.087 69	1330.9115	152.6892	b
	110.0	10.500	10.340	6.541 75	1554.1491	171.1750	12

^a $\log_{10} P^{\text{sat}}$ (kPa) = $A - B/(T (^{\circ}\text{C}) + C)$. ^bDerived from our experimental vapor pressure data (>10 points).

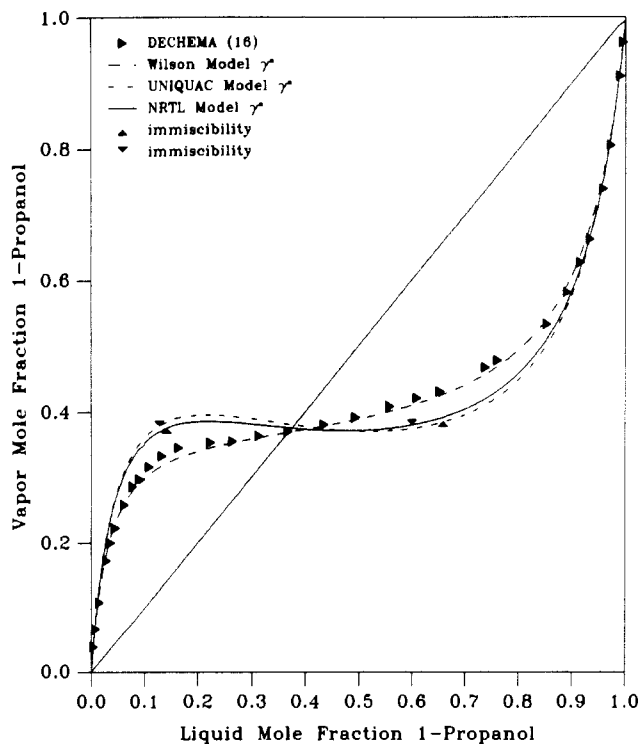


Figure 5. Comparison of predictions of three activity coefficient models with parameters fit to activity coefficients at infinite dilution with experimental vapor-liquid equilibrium data for 1-propanol (1)/n-heptane (2) at 60.0 °C of ref 16.

activity coefficient models whose parameters were found with only our experimental activity coefficients at infinite dilution. In Figures 3 and 4, the same vapor-liquid equilibrium data are compared to the original and the two modified-UNIFAC equations. The Wilson equation with parameters found with use of

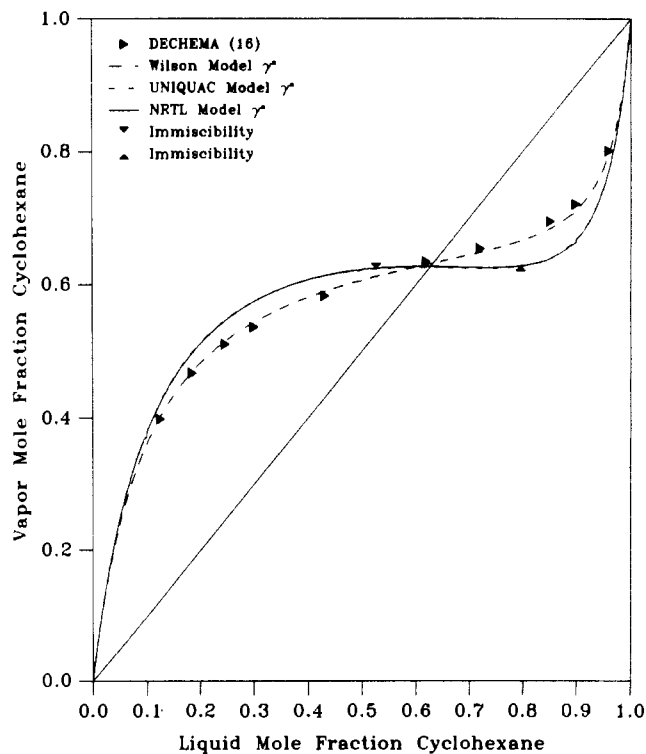


Figure 6. Comparison of predictions of three activity coefficient models with parameters fit to activity coefficients at infinite dilution with experimental vapor-liquid equilibrium data for cyclohexane (1)/2-propanol (2) at 60.0 °C of ref 16.

infinite dilution activity coefficients modeled the experimental vapor-liquid equilibrium data most accurately. However, there is no way to determine, a priori, which model will predict the correct activity coefficient versus composition behavior for most

Table II. Measured Activity Coefficients at Infinite Dilution and Limiting Slope

component 1 in component 2	temp, °C	$(dT/dx_1)_P^\infty$	γ_1^∞	$(dT/dx_2)_P^\infty$	γ_2^∞
n-butylamine (1)/n-heptane (2)	50.0	-71.9 ± 1.9	1.950 ± 0.038	-1.2 ± 0.6	2.091 ± 0.045
	70.0	-76.3 ± 1.8	1.872 ± 0.032	1.2 ± 0.6	1.858 ± 0.038
n-butylamine (1)/cyclohexane (2)	40.0	-35.0 ± 1.0	2.331 ± 0.039	-20.6 ± 0.6	1.921 ± 0.028
	70.0	-31.6 ± 0.8	1.824 ± 0.022	-17.2 ± 0.6	1.728 ± 0.022
cyclohexylamine (1)/n-heptane (2)	60.0	11.8 ± 0.5	2.078 ± 0.075	-141.4 ± 6.8	1.962 ± 0.081
	80.0	14.3 ± 0.6	1.750 ± 0.062	-118.7 ± 4.8	1.769 ± 0.059
cyclohexylamine (1)/n-octane (2)	60.0	-6.7 ± 0.3	1.805 ± 0.020	-47.3 ± 1.5	2.206 ± 0.048
	80.0	-6.1 ± 0.3	1.646 ± 0.016	-39.9 ± 1.1	1.921 ± 0.031
n-heptane (1)/1-butanol (2)	80.0	-259.9 ± 18.3	5.132 ± 0.334	-79.4 ± 2.1	9.304 ± 0.176
	100.0	-211.5 ± 12.0	4.758 ± 0.240	-62.5 ± 1.3	5.616 ± 0.073
1-propanol (2)/1-butanol (2)	60.0	-28.8 ± 0.8	1.021 ± 0.017	12.3 ± 0.4	1.025 ± 0.054
	80.0	-28.6 ± 0.6	1.020 ± 0.013	13.6 ± 0.6	1.017 ± 0.059
n-pentanol (1)/cyclohexylamine (2)	80.0	13.9 ± 0.8	0.833 ± 0.059	10.0 ± 0.7	0.272 ± 0.019
	100.0	10.2 ± 0.6	0.988 ± 0.032	10.8 ± 0.8	0.355 ± 0.022
n-pentanol (1)/n-nonane (2)	80.0	-194.0 ± 10.4	9.321 ± 0.445	-70.7 ± 5.2	4.452 ± 0.256
	100.0	-150.2 ± 6.3	5.606 ± 0.198	-67.4 ± 4.2	4.474 ± 0.205
ethylenediamine (1)/n-heptane (2)	55.0	-139.3 ± 5.8	16.55 ± 0.58	-947.9 ± 113	18.36 ± 2.19
	70.0	-107.2 ± 3.4	10.69 ± 0.27	-787.2 ± 88.3	15.64 ± 1.70
ethylenediamine (1)/octane (2)	60.0	-213.0 ± 11.6	9.358 ± 0.461	-281.3 ± 25.3	15.26 ± 1.28
	80.0	-247.8 ± 13.7	8.753 ± 0.434	-188.5 ± 13.7	9.938 ± 0.636
ethylenediamine (1)/cyclohexylamine (2)	60.0	-53.2 ± 1.2	2.218 ± 0.036	-15.3 ± 1.3	2.599 ± 0.095
	80.0	-58.3 ± 1.3	2.130 ± 0.034	-24.6 ± 1.3	3.095 ± 0.084
ethylenediamine (1)/butanol (2)	80.0	16.8 ± 0.6	0.185 ± 0.023	17.1 ± 0.7	0.394 ± 0.037
	60.0	13.1 ± 0.7	0.204 ± 0.026	15.7 ± 0.7	0.387 ± 0.047
1,3-diaminepropane (1)/cyclooctane (2)	80.0	-184.0 ± 8.4	7.528 ± 0.303	-173.5 ± 9.4	9.639 ± 0.464
	100.0	-160.6 ± 6.3	5.401 ± 0.179	-144.3 ± 6.7	7.821 ± 0.309
1,3-diaminepropane (1)/cyclohexylamine (2)	80.0	-6.5 ± 0.3	1.855 ± 0.020	-37.5 ± 1.2	1.816 ± 0.036
	100.0	-7.0 ± 0.3	1.715 ± 0.013	-38.1 ± 1.1	1.798 ± 0.030
1,3-diaminopropane (1)/n-pentanol (2)	80.0	16.2 ± 0.7	0.147 ± 0.030	16.2 ± 0.7	0.350 ± 0.038
	100.0	14.1 ± 0.4	0.356 ± 0.017	18.0 ± 0.7	0.356 ± 0.028
ethanolamine (1)/1-hexanol (2)	90.0	4.5 ± 0.2	1.410 ± 0.021	-87.8 ± 4.3	3.147 ± 0.126
	110.0	4.4 ± 0.3	1.425 ± 0.020	-70.0 ± 2.8	2.438 ± 0.074

binary systems with only activity coefficients at infinite dilution data. In fact, the NRTL and UNIQUAC activity coefficient models with parameters estimated from our activity coefficients at infinite dilution predict liquid-liquid immiscibility (see Figures 5 and 6) for these two binary systems.

New UNIFAC interaction parameters can be found with our experimental data. Since some of the groups we studied appeared in different mixtures and at different temperatures, all mixtures were used in the UNIFAC parameter estimation scheme. The two optimal parameters were found with the Levenberg-Marquardt algorithm with a finite-difference approximation to the Jacobian. Then activity coefficients at infinite dilution were estimated through four variations of the UNIFAC equation and the appropriate UNIFAC interaction parameters: the original UNIFAC model (7) and the three modified versions (5, 11, 15). Table IV shows the percent deviation of the calculated and experimental activity coefficients at infinite dilution. In Table V, we report the three sets of temperature-independent interaction parameters (one set estimated from our experimental γ^∞ and two sets from the literature (13, 15)) used in the UNIFAC method. The modified-UNIFAC method has three parameters for each of the two temperature-dependent interaction parameters (see eq 6 and 8) as can be seen in the papers by Weidlich and Gmehling (5) and of Larsen, Rasmussen, and Fredenslund (11). Note that since Weidlich and Gmehling do not report interaction parameters for $\text{CHNH}_2/\text{CH}_2$, we can only compare experimental and calculated activity coefficients at infinite dilution using their modified-UNIFAC method for the alcohol/alkane and alcohol/alcohol systems.

The predictions of the standard UNIFAC method with parameters from Reid et al. (13) for the experimental activity coefficients at infinite dilution for binary systems containing butylamine and alkanes are quite good. This is not surprising since the interaction parameters were derived from vapor-liquid equilibrium data for similar mixtures at similar temperatures. However, this is not the case for the slightly more complex binary systems containing cyclohexylamine and alkanes. One reason for the poor performance of the original UNIFAC model

is that no adjustment is made depending on whether a ring structure or a straight-chain alkane is attached to the amine. However, if we use the modified-UNIFAC method of Larsen et al. (11), we obtain satisfactory predictions of the experimental activity coefficients at infinite dilution for cyclohexylamine and alkanes, which in part may be attributed to the different combinatorial term. None of the UNIFAC methods do well in predicting activity coefficients at infinite dilution for the systems of ethylenediamine and alkanes. However, for mixtures containing 1,3-diaminopropane and cyclooctane, the modified method of Larsen et al. is much better than the other UNIFAC methods in predicting our experimental activity coefficients at infinite dilution. One problem when considering ethylenediamine is that the proximity of the amine groups on the same molecule may affect their behavior, and this is not taken into account in any of the UNIFAC methods. Another difficulty in our comparison is that the high volatility of the solute in some systems due to the relatively large activity coefficient at infinite dilution (i.e., $\gamma_1^\infty > 15$) results in a larger experimental error (>10%) in the measured γ^∞ . Activity coefficients at infinite dilution were also measured for diamines with cyclohexylamine. The modified-UNIFAC method of Larsen et al. is also best for predicting the activity coefficients at infinite dilution of diamines with cyclohexylamine.

The interaction parameters given by Bastos et al. (15) for their version of the UNIFAC equation do not yield accurate estimates of the activity coefficients at infinite dilution for most of the systems we studied, and particularly for systems containing a diamine. A possible reason for this is that the interaction parameters in their model were derived from infinite dilution activity coefficients found by the gas liquid chromatography (GLC) method. This experimental method is used primarily with molecules of very different size and at relatively low temperatures (i.e., 25 °C) so that the stationary phase does not evaporate as fast as it would at higher temperatures. Thus, while Bastos et al. use the same combinatorial term as Larsen et al. to account for the large difference in molecular size, they obtain temperature-independent UNIFAC parameters that do

Table III. Comparison of Measured and UNIFAC Infinite Dilution Activity Coefficients

a						
component (1)/component (2)	temp, °C	γ_1^∞				
		exptl	a	b	c	
n-butylamine/cyclohexane	40.0	2.33 ± 0.04	2.32	1.82	2.32	
	70.0	1.82 ± 0.02	2.13	1.74	1.89	
cyclohexane/n-butylamine	40.0	1.92 ± 0.03	1.88	1.78	1.88	
	70.0	1.73 ± 0.02	1.80	1.70	1.68	
n-butylamine/n-heptane	50.0	1.95 ± 0.04	2.03	1.75	2.10	
	70.0	1.87 ± 0.03	1.92	1.69	1.85	
n-heptane/n-butylamine	50.0	2.09 ± 0.05	2.00	2.08	2.17	
	70.0	1.86 ± 0.04	1.92	2.01	1.97	
cyclohexylamine/n-heptane	60.0	2.08 ± 0.08	1.51	1.32	1.87	
	80.0	1.75 ± 0.06	1.47	1.30	1.68	
n-heptane/cyclohexylamine	60.0	1.96 ± 0.08	1.50	1.38	1.83	
	80.0	1.77 ± 0.06	1.46	1.36	1.69	
cyclohexylamine/n-octane	60.0	1.81 ± 0.02	1.47	1.31	1.85	
	80.0	1.65 ± 0.02	1.43	1.29	1.67	
n-octane/cyclohexylamine	60.0	2.21 ± 0.05	1.52	1.42	1.94	
	80.0	1.92 ± 0.03	1.48	1.40	1.78	
1-pentanol/cyclohexylamine	80.0	0.833 ± 0.059	0.877		0.611	
	100.0	0.988 ± 0.032	0.900		0.645	
cyclohexylamine/1-pentanol	80.0	0.272 ± 0.019	0.856		0.629	
	100.0	0.355 ± 0.022	0.884		0.666	

b						
component (1)/component (2)	temp, °C	γ_1^∞				
		exptl	a	b	c	d
1-propanol/heptane	60.0	16.0 ± 0.9	14.5	15.5	13.8	18.6
	80.0	8.95 ± 0.34	12.0	12.7	10.6	12.3
heptane/1-propanol	60.0	6.34 ± 0.32	5.78	5.41	6.05	7.65
	80.0	5.89 ± 0.27	5.53	5.18	5.47	6.83
2-propanol/cyclohexane	40.0	28.0 ± 1.9	22.0	20.2	18.4	31.7
	60.0	13.6 ± 0.7	17.7	16.1	14.3	20.0
cyclohexane/2-propanol	40.0	5.97 ± 0.34	4.72	3.69	4.09	2.34
	60.0	5.35 ± 0.21	4.57	3.58	3.89	2.18
1-butanol/heptane	80.0	9.30 ± 0.18	10.2	10.8	8.98	10.7
	100.0	5.62 ± 0.07	8.66	9.14	6.86	7.53
heptane/1-butanol	80.0	5.13 ± 0.33	4.12	3.93	4.03	4.85
	100.0	4.76 ± 0.24	3.96	3.79	3.60	4.33
n-pentanol/n-nonane	80.0	9.32 ± 0.45	8.54	9.19	7.60	8.58
	100.0	5.61 ± 0.20	7.29	7.78	5.88	6.10
n-nonane/pentanol	80.0	4.45 ± 0.26	4.27	4.15	4.18	4.69
	100.0	4.47 ± 0.21	4.08	3.97	3.72	4.17
1-propanol/1-butanol	60.0	1.021 ± 0.017	1.008	1.010	1.013	1.012
	80.0	1.020 ± 0.013	1.008	1.010	1.012	1.011
1-butanol/1-propanol	60.0	1.025 ± 0.054	1.009	1.012	1.016	1.015
	80.0	1.017 ± 0.057	1.009	1.012	1.014	1.013

^a γ_1^∞ 's estimated from UNIFAC equation using parameters from Reid et al. (13). ^b γ_1^∞ 's estimated from UNIFAC equation using new parameters given by Bastos, Soares, and Medina (15). ^c γ_1^∞ 's estimated from modified-UNIFAC equation using parameters given by Larsen, Rasmussen, and Fredenslund (11). ^d γ_1^∞ 's estimated from modified-UNIFAC equation using parameters given by Weidlich and Gmehling (5).

not appear to extrapolate well to higher (or lower) temperatures (hence the use of the temperature-dependent parameters in the other modified-UNIFAC methods).

It would be interesting to measure activity coefficients at infinite dilution of binary systems with various primary diamines and several alcohol amines, where the nonalkyl groups were separated by an increasing alkane chain length to study the proximity effects. That is to measure the vapor-liquid equilibrium of $x-(\text{CH}_2)_n-y/\text{CH}_3-(\text{CH}_2)_n-\text{CH}_3$ or $y-(\text{CH}_2)_n-x/\text{CH}_3-(\text{CH}_2)_n-x$ where x and y are nonalkane groups (that are either the same or different) for the various values of n , the length of the alkane chain. However, because the vapor pressure of these multifunctional compounds, especially for $n > 2$, is very low at the temperatures which our equipment can be used, this is not possible.

Conclusions

Comparative ebulliometry was used to measure activity coefficients at infinite dilution for systems containing primary amines and normal alcohols. This method of measuring activity

coefficients at infinite dilution is accurate and less time consuming than vapor-liquid equilibrium measurements over the entire composition range. It is also shown that using model parameters derived from measured activity coefficients at infinite dilution, one can accurately predict vapor-liquid equilibrium over the whole composition range. Activity coefficients at infinite dilution can be used in engineering design and to estimate interaction parameters of the UNIFAC and other group contribution methods. However, we show here that the reliability of UNIFAC for predicting vapor-liquid equilibria of multicomponent systems containing a multifunctional component is questionable.

Except for the ethylenediamine/alkane systems, the modified-UNIFAC method of Larsen et al. predicted the measured infinite dilution activity coefficients reasonably well and better than any other UNIFAC method discussed here. For components that have only one functional group other than the alkane group, the original UNIFAC method provides reasonable estimates if the components in the system are similar in size and the temperature range is not too large. However, with more complex components (i.e., a component having two identical

Table IV. Infinite Dilution Activity Coefficients: Experimental vs UNIFAC

component (1)/component (2)	temp, °C	γ_1^∞			
		exptl	a	b	c
ethylenediamine/ <i>n</i> -heptane	55.0	16.6 ± 0.6	13.0	15.6	15.8
	70.0	10.7 ± 0.3	11.6	14.0	12.0
<i>n</i> -heptane/ethylenediamine	55.0	18.4 ± 2.2	11.5	138	23.6
	70.0	15.6 ± 1.7	10.9	113	20.1
ethylenediamine/ <i>n</i> -octane	60.0	9.36 ± 0.46	11.8	14.6	13.9
	80.0	8.75 ± 0.43	10.2	12.7	9.78
<i>n</i> -octane/ethylenediamine	60.0	15.3 ± 1.3	14.0	226	31.6
	80.0	9.94 ± 0.64	12.9	171	24.8
ethylenediamine/cyclohexylamine	60.0	2.22 ± 0.04	2.63	4.21	2.17
	80.0	2.13 ± 0.03	2.55	3.93	2.05
cyclohexylamine/ethylenediamine	60.0	2.60 ± 0.10	2.71	9.28	2.56
	80.0	3.10 ± 0.08	2.66	8.26	2.45
ethylenediamine/1-butanol	60.0	0.185 ± 0.023	0.245		0.233
	80.0	0.204 ± 0.026	0.268		0.360
1-butanol/ethylenediamine	60.0	0.394 ± 0.037	0.638		0.479
	80.0	0.387 ± 0.047	0.648		0.609
1,3-diaminopropane/cyclooctane	80.0	7.53 ± 0.30	9.19	8.49	7.63
	100.0	5.40 ± 0.18	8.10	7.65	5.75
cyclooctane/1,3-diaminopropane	80.0	9.64 ± 0.46	6.98	19.6	8.19
	100.0	7.82 ± 0.31	6.57	17.1	6.82
1,3-diaminopropane/cyclohexylamine	80.0	1.86 ± 0.02	2.13	2.65	1.65
	100.0	1.72 ± 0.01	2.08	2.54	1.58
cyclohexylamine/1,3-diaminopropane	80.0	1.82 ± 0.04	2.02	3.27	1.69
	100.0	1.79 ± 0.03	1.99	3.09	1.63
1,3-diaminopropane/1-pentanol	80.0	0.147 ± 0.030	0.262		0.360
	100.0	0.356 ± 0.017	0.286		0.503
1-pentanol/1,3-diaminopropane	80.0	0.350 ± 0.038	0.624		0.608
	100.0	0.356 ± 0.028	0.632		0.738
ethanolamine/1-hexanol	90.0	1.41 ± 0.02	1.28		1.69
	110.0	1.42 ± 0.02	1.30		1.67
1-hexanol/ethanolamine	90.0	3.15 ± 0.13	1.93		2.68
	110.0	2.44 ± 0.07	1.91		2.46

^a γ^∞ 's estimated from UNIFAC equation using parameters from ref 13. ^b γ^∞ 's estimated from UNIFAC equation using new parameters from ref 15. ^c γ^∞ 's estimated from modified-UNIFAC equation using parameters from ref 11.

Table V. Infinite Dilution Activity Coefficients: Experimental vs UNIFAC^c

component (1)/ component (2)	% dev in γ_1^∞	% dev in γ_2^∞	a_{12}	a_{21}	ref
UNIFAC Parameters: $a_{12} = a_{\text{CNH}_2/\text{CH}_2}$ and $a_{21} = a_{\text{CH}_2/\text{CNH}_2}$					
<i>n</i> -butylamine/alkane	4.61	3.31	18.03	349.81	a
	5.99	3.42	-30.48	391.50	b
	11.48	4.25	217.06	216.12	c
	3.35	3.69			d
cyclohexylamine/ alkane	4.68	4.49	884.05	427.51	a
	18.89	23.73	-30.48	391.50	b
	27.86	28.86	217.06	216.12	c
	4.30	7.72			d
ethylenediamine/ alkane	12.82	24.38	-15.50	363.15	a
	17.96	26.57	-30.48	391.50	b
	27.18	906.5	217.06	216.12	c
	19.30	78.30			d
1,3-diaminopropane/ alkane	12.32	5.91	59.55	283.91	a
	36.03	21.81	-30.48	391.05	b
	27.14	110.8	217.06	216.12	c
	3.92	13.92			d
cyclohexylamine/ diamine	10.92	7.93	-72.39	431.30	a
	9.84	18.53	-30.48	391.50	b
	143.96	66.17	217.06	216.12	c
	9.62	6.29			d
UNIFAC Parameters: $a_{12} = a_{\text{OH}/\text{CH}_2}$ and $a_{21} = a_{\text{CH}_2/\text{OH}}$					
1° alcohol/alkane	17.13	5.80	1754.9	921.38	a
	19.91	10.20	156.50	986.50	b
1° alcohol/alcohol	21.22	16.16	173.32	1024.5	c
	12.14	14.07			d
	18.17	18.51			e

^aParameters estimated for UNIFAC equation using experimental γ^∞ 's. ^bParameters for UNIFAC equation from ref 13. ^cParameters for UNIFAC equation from ref 15. ^dParameters from modified-UNIFAC equation (11). ^eParameters from modified-UNIFAC equation (5). ^fSome new parameters based on experimental γ^∞ 's.

nonalkane functional groups or a ring instead of a straight chain), the standard UNIFAC method does not perform as well. Table V shows how well several of the UNIFAC methods do for a number of systems containing alkane, alcohol, and primary amine groups. The UNIFAC interaction parameters found from the measured activity coefficients at infinite dilution have no significance other than they provide a best fit to the experimental data. In some cases, quite different parameter sets, in the different UNIFAC models, provide comparable fits of the data.

The main conclusion is that the group contribution method is very valuable for predicting thermodynamic properties of mixtures for which experimental data do not exist. However, it is also important to realize the limitations of the method, especially when dealing with complex components and components that have more than one nonalkyl functional group. Some of these problems were demonstrated in this communication.

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List of Symbols

a_{nm}	UNIFAC interaction parameter of groups <i>m</i> and <i>n</i>
$a_{nm,i}$	coefficients of the temperature-dependent UNIFAC parameter
<i>A, B, C</i>	coefficients of the Antoine vapor pressure equation
B_{ii}, B_{ij}	second virial coefficients
<i>f</i>	evaporation factor
<i>P</i>	absolute pressure
P_i^{sat}	saturation vapor pressure of component <i>i</i>
r_i, q_i	UNIQUAC volume and area parameter for component <i>i</i>

R_k, Q_k	UNIFAC volume and area parameter for group k
R	gas constant
R_i	alkyl chain
T	absolute temperature in Kelvin
T_0	reference temperature, usually 298.15 K
v_i^l	liquid molar volume of component i
x, y	nonalkyl UNIFAC groups on a molecule
x_i, y_i	equilibrium liquid- and vapor-phase mole fraction of component i

Greek Letters

δ_{12}	$=2B_{12} - B_{11} - B_{22}$
γ_i^∞	activity coefficient at infinite dilution of component i
ϵ_i^∞	vapor-phase correction
$\nu_k^{(l)}$	coefficient of group k in component i
θ_m	area fraction of group m in a mixture of components
Ψ_{nm}	$=\exp(-a_{nm}/T)$

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Solubility of Nonpolar Gases in Halogenated Compounds. 3. Solubility of Helium, Neon, Argon, Krypton, and Xenon in Chlorocyclohexane and Bromocyclohexane at 263.15–303.15 K and 101.32-kPa Partial Pressure of Gas

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Solubility measurements of noble gases in chlorocyclohexane and bromocyclohexane in the temperature range 263.15–303.15 K and 101.32-kPa partial pressure of gas are reported. Thermodynamic functions for the solution process (Gibbs energy, enthalpy, and entropies) are evaluated. With the Pierotti method, Lennard-Jones 6,12 pair potential parameters for these solvents were determined. For this purpose, we also used the solubilities of ten other nonpolar gases in the same solvents, measured by us, the results of which also appeared in this journal.

Introduction

This study is a continuation of our work on gas solubilities in halogenated solvents (1, 2). We report the solubilities of He, Ne, Ar, Kr, and Xe at 263.15–303.15 K and 101.32-kPa partial pressure of gas in chlorocyclohexane and bromocyclohexane solvents and their thermodynamics properties. In previous papers, we reported the solubilities of the nonpolar gases (H_2 , D_2 , N_2 , O_2 , CH_4 , C_2H_4 , C_2H_6 , CF_4 , SF_6 , and CO_2) in the same solvents, with the same temperature interval and partial molar pressure of gases.

We are interested in the influence of the halogen atom (Cl, Br) of the solvent molecule on the solubility of gases. For this purpose, we compare these results with the experimental solubilities of nonpolar gases in cyclohexane (3). Likewise,

through a theoretical treatment, it is possible to estimate pair potential parameters for solvent molecules with use of the scaled particle theory (SPT) (4). The Pierotti method is an application of SPT to the solubility of gases in liquids; Morel-Desrosiers (5) showed that it is coherent to use it for determining the intermolecular potential distance and energy parameters, particularly if they are going to be used to predict the solubility of gases.

We have calculated these parameters by application of the Pierotti method (4, 6) to the solubility of 15 nonpolar gases in chlorocyclohexane and bromocyclohexane, and from them, we have calculated the solubility of gases in these solvents with the objective of comparing the theoretical and experimental results.

Experimental Section

The method used for the solubility measurements was identical with that described earlier (1, 2, 7). The solvents were chlorocyclohexane (Merck) and bromocyclohexane (Fluka); their purity, >98.5%, was checked by GLC and refraction measurements (1, 2). The gases used were He (99.995%), Ar (99.9990%), Kr (99.95%), and Xe (99.995%), all of them SEO (Sociedad Española del Oxígeno S.A.), and Ne (99.9%) (Baker).

The mole fraction of the dissolved gases is estimated from both the volume change at constant pressure of saturated gas in the burets and the mass of liquid in the solution vessel, determined by weighing. We assume that the solvent mole fraction in the gas phase is that corresponding to the vapor pressure.