Proximity Effects on the Predictions of the UNIFAC Model: I. Ethers

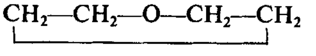
Huey S. Wu and Stanley I. Sandler
Department of Chemical Engineering
University of Delaware
Newark, DE 19716

Introduction

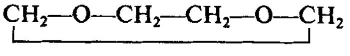
Group contribution methods have been used widely to predict liquid activity coefficients in the chemical industry. Of these, the UNIFAC model (Fredenslund et al., 1975 and 1977) is the best documented, and has been widely used as a tool for chemical process design and as part of molecular design strategy for the selection of extractive and azeotropic distillation solvents for separation processes. However, little attention has been given to the limitations of using group contribution models, although caution was expressed by Langmuir in 1925. Kehiaian (1983, 1987) pointed out that intramolecular effects are important factors frequently ignored in group contribution methods. In particular, the proximity effect is the change in the behavior of a group, and hence its interaction parameters with other groups, as a result of the presence of other groups on the same molecule. To be specific, consider two groups X and Y situated on the same molecule, as in $X—(CH_2)_n—Y$. A proximity effect is evident if the behavior of (or interaction parameters for) groups X and Y depends on n, the number of intervening methylene groups. If $X = Y$, this effect is called homoproximity effect; if $X \neq Y$, it is heteroproximity effect. A basic assumption underlying group contribution methods such as UNIFAC and ASOG is that proximity effects do not occur. Clearly this is an important limitation to the applicability of these group contribution models.

In this study we focus on a test of the homoproximity effect in the UNIFAC model by comparing its predictions with accurate vapor-liquid equilibrium (VLE) measurements. The compounds that we use in this test are the cyclic ethers

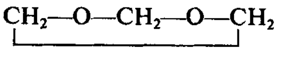
tetrahydrofuran (THF):



1,4-dioxane:



and 1,3-dioxolane:



In the UNIFAC model, tetrahydrofuran is considered to consist of 3 CH_2 and 1 FCH_2O groups, 1,4-dioxane consists of 2 CH_2 and 2 FCH_2O groups, while 1,3-dioxolane consists of 1 CH_2 and 2 FCH_2O groups. We compare the behavior of the two ether groups in 1,4-dioxane and 1,3-dioxolane with that of a single ether group in tetrahydrofuran. In particular, the activity coefficients of these three cyclic ether compounds determined from accurate vapor-liquid equilibrium measurements separately with hydrocarbons, water, and trichloromethane (chloroform) are compared with the UNIFAC predictions. The VLE data are for binary mixtures containing tetrahydrofuran (Wu and Sandler, 1988a; Paul, 1987), 1,4-dioxane (Gmehling et al., 1977), and 1,3-dioxolane (Wu and Sandler, 1988b).

We find that, while the predictions for these mixtures using the UNIFAC model with published parameters (Reid et al., 1987) are in reasonable agreement with the experimental results for the tetrahydrofuran system, the agreement with experiments becomes increasingly worse as we go to mixtures containing 1,4-dioxane and then to 1,3-dioxolane. This is what would be expected if the homoproximity effect was important.

Results

One goal of our work is to compare accurate experimental measurements with the group contribution predictions of the UNIFAC model. To do this in a concise way, we will use infinite dilution activity coefficients γ^∞ and excess Gibbs-free energies G^E for the mixtures of interest. Therefore, we have correlated the measured vapor-liquid equilibrium data with five well-known liquid activity coefficient models (the Margules, Van Laar, Wilson, NRTL, and UNIQUAC models) using the maximum likelihood parameter estimation method (discussed by Prausnitz et al., 1980), with a nonideal vapor-phase correction using second virial coefficients obtained from correlation (Hayden and O'Connell, 1975). The γ^∞ values derived from experimental data were extrapolated with the model which led to the best correlation of the VLE data. These values together with the predictions of the UNIFAC model appear in Table 1.

Correspondence concerning this paper should be addressed to S. I. Sandler.

Table 1. Comparison of Observed and UNIFAC-Predicted Infinite Dilution Activity Coefficients

System	Temp. (K)	γ_1^∞(obs)	γ_1^∞(cal)	Ref.
1,3-dioxolane(1)/cyclohexane(2)	313.15	4.54	11.15	(a)
cyclohexane(1)/1,3-dioxolane(2)	313.15	5.45	12.78	(a)
1,3-dioxolane(1)/cyclohexane(2)	333.15	3.75	9.93	(a)
cyclohexane(1)/1,3-dioxolane(2)	333.15	4.38	11.71	(a)
1,3-dioxolane(1)/heptane(2)	313.15	5.34	8.19	(a)
heptane(1)/1.3-dioxolane(2)	313.15	6.98	17.83	(a)
1,3-dioxolane(1)/heptane(2)	343.15	3.20	6.91	(a)
heptane(1)/1,3-dioxolane(2)	343.15	5.48	14.98	(a)
1,3-dioxolane(1)/water(2)	318.15	22.02	2.28	(a)
water(1)/1,3-dioxolane(2)	318.15	10.39	0.94	(a)
1,3-dioxolane(1)/water(2)	343.15	17.62	2.57	(a)
water(1)/1,3-dioxolane(2)	343.15	7.99	1.00	(a)
1,3-dioxolane(1)/ethanol(2)	313.15	3.90	2.62	(a)
ethanol(1)/1,3-dioxolane(2)	313.15	3.23	2.37	(a)
1,3-dioxolane(1)/ethanol(2)	338.15	2.89	2.39	(a)
ethanol(1)/1,3-dioxolane(2)	338.15	2.55	2.16	(a)
1,3-dioxolane(1)/chloroform(2)	308.15	0.40	0.24	(a)
chloroform(1)/1,3-dioxolane(2)	308.15	0.56	0.37	(a)
1,3-dioxolane(1)/chloroform(2)	323.15	0.46	0.27	(a)
chloroform(1)/1,3-dioxolane(2)	323.15	0.59	0.40	(a)
1,4-dioxane(1)/heptane(2)	353.15	2.69	5.18	(b)
heptane(1)/1,4-dioxant(2)	353.15	3.78	6.93	(b)
1,4-dioxane(1)/octane(2)	353.15	2.49	5.02	(b)
octane(1)/1,4-dioxane(2)	353.15	4.28	8.47	(b)
1,4-dioxane(1)/nonane(2)	353.15	2.20	4.84	(b)
nonane(1)/1,4-dioxane(2)	353.15	4.73	10.23	(b)
1,4-dioxane(1)/water(2)	308.15	6.64	5.17	(c)
water(1)/1,4-dioxane(2)	308.15	6.96	1.06	(c)
1,4-dioxane(1)/water(2)	323.15	7.05	5.58	(c)
water(1)/1,4-dioxane(2)	323.15	6.41	1.11	(c)
1,4-dioxane(1)/water(2)	343.15	7.27	5.99	(c)
water(1)/1,4-dioxane(2)	343.15	4.87	1.16	(c)
1,4-dioxane(1)/chloroform(2)	323.15	0.29	0.21	(d)
chloroform(1)/1,4-dioxane(2)	323.15	0.46	0.35	(d)
tetrahydrofuran(1)/cyclohexane(2)	313.15	1.81	1.88	(e)
cyclohexane(1)/tetrahydrofuran(2)	313.15	1.76	1.97	(e)
tetrahydrofuran(1)/cyclohexane(2)	333.15	1.70	1.81	(e)
cyclohexane(1)/tetrahydrofuran(2)	333.15	1.61	1.90	(e)
tetrahydrofuran(1)/hexane(2)	313.15	1.75	1.65	(e)
hexane(1)/tetrahydrofuran(2)	313.15	1.94	1.85	(e)
tetrahydrofuran(1)/hexane(2)	333.15	1.63	1.59	(e)
hexane(1)/tetrahydrofuran(2)	333.15	1.80	1.78	(e)
tetrahydrofuran(1)/water(2)	298.15	28.93	33.48	(f)
water(1)/tetrahydrofuran(2)	298.15	17.77	2.63	(f)
tetrahydrofuran(1)/water(2)	323.15	26.22	33.47	(g)
water(1)/tetrahydrofuran(2)	323.15	9.38	2.82	(g)
tetrahydrofuran(1)/water(2)	343.15	30.83	33.05	(g)
water(1)/tetrahydrofuran(2)	343.15	7.80	2.95	(g)
tetrahydrofuran(1)/chloroform(2)	303.15	0.17	0.35	(h)
chloroform(1)/tetrahydrofuran(2)	303.15	0.19	0.37	(h)
tetrahydrofuran(1)/chloroform(2)	313.15	0.20	0.37	(h)
chloroform(1)/tetrahydrofuran(2)	313.15	0.22	0.38	(h)
tetrahydrofuran(1)/chloroform(2)	323.15	0.22	0.38	(h)
chloroform(1)/tetrahydrofuran(2)	323.15	0.26	0.40	(h)

(a) Wu and Sandler (1988b)
(b) Valent (1976)
(c) Tassios and Winkle (1967)
(d) McGlashan (1958)
(e) Shnitko and Kogan (1968)
(f) Matous et al. (1972)
(g) Wu and Sandler (1988a)
(h) Paul (1987)

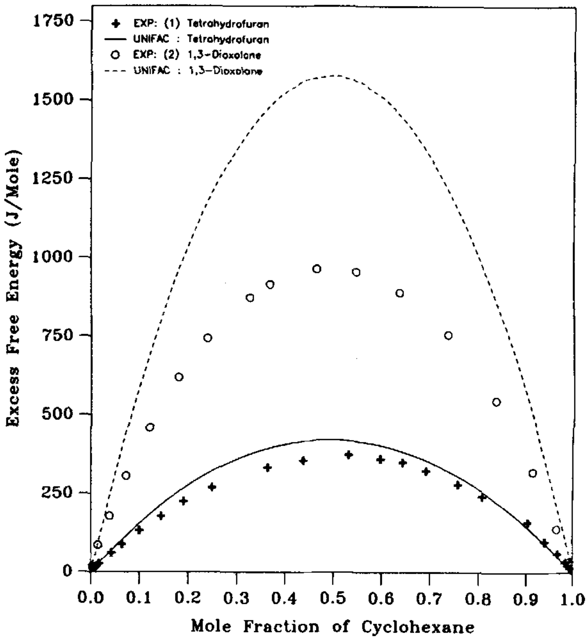


Figure 1. Comparison between measured G^E and prediction by the UNIFAC model for cyclohexane/THF and cyclohexane/1,3-dioxolane at 313.15 K.

The comparison between γ^∞(obs) and γ^∞(calc) shows good agreement for the tetrahydrofuran systems and increasingly poor agreement for the 1,4-dioxane and 1,3-dioxolane mixtures.

We then compared the excess Gibbs-free energies, G^E $(=RT\Sigma x_i \ln \gamma_i)$, for these mixtures over the whole composition range with the UNIFAC predictions. For binary mixtures of tetrahydrofuran with cyclic or straight chain hydrocarbons, the

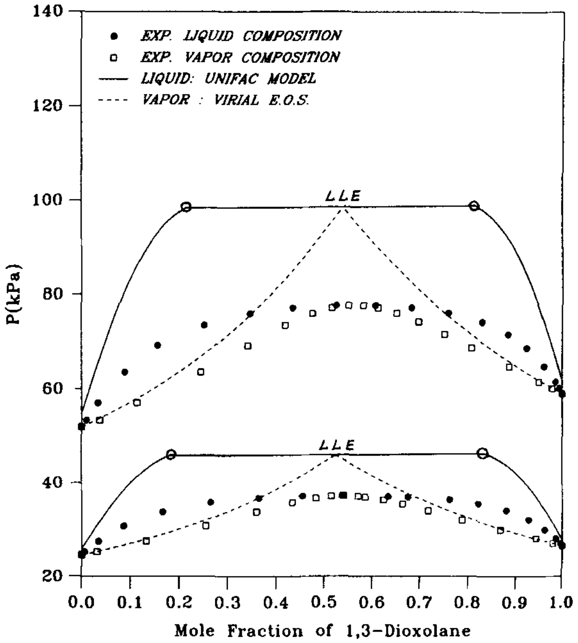


Figure 2. Comparison between measured VLE and prediction by the UNIFAC model for 1,3-dioxolane/cyclohexane at 313.15 & 333.15 K.

the predictions of the UNIFAC model. This is not surprising since the group interaction parameters were obtained mainly from VLE data for mixtures with only a single ether group in a molecule. However, for binary mixtures of 1,4-dioxane or 1,3-dioxolane with hydrocarbon systems, the UNIFAC model overpredicts G^E. The results are shown in Figures 1 and 2. Indeed, for the 1,3-dioxolane + cyclohexane mixture, the UNIFAC G^E derived from experiment are in reasonable agreement with model predicts a liquid-liquid equilibrium, while the experimental data show only vapor-liquid equilibrium.

Next, for the binary mixture of tetrahydrofuran with water, the maximum predicted G^E is lower than, and skewed to the left of, that derived from experiment. In contrast, for the binary mixture of 1,4-dioxane with water, the predicted G^E are much less than the experimental values, and for 1,3-dioxolane with water the results are even worse as is evident in Figure 3. Comparing the VLE behavior of the system, as we do in Figure 4, we find that UNIFAC model predicts nearly ideal solution behavior for the 1,3-dioxolane + water mixture, while the experimental results show a strongly nonideal solution forming an azeotrope.

Finally, in binary mixtures of chloroform separately with tetrahydrofuran, with 1,4-dioxane, and with 1,3-dioxolane, there is a strong association between the ether group and the chloroform group because of hydrogen bonding. The G^E derived from experiment are compared with the predicted values in Figure 5. The value of G^E is negative for most associated mixtures, and a stronger association between two components results in more negative values of G^E. The UNIFAC model predicts the following association strength sequence for these three ether compounds: 1,4-dioxane > 1,3-dioxolane > tetrahydrofuran. However, the experimental results, in contradiction to this prediction, show the following association strength sequence: tetrahydrofuran > 1,4-dioxane > 1,3-dioxolane. This indicates that the single ether group in tetrahydrofuran is the strongest hydrogen acceptor, while each ether group in 1,3-dioxolane is the weakest. Thus, the homoproximity effect, that is, the chemical or electronic structure interference between the ether groups, is apparent in 1,4-dioxane and even more so in 1,3-dioxolane.

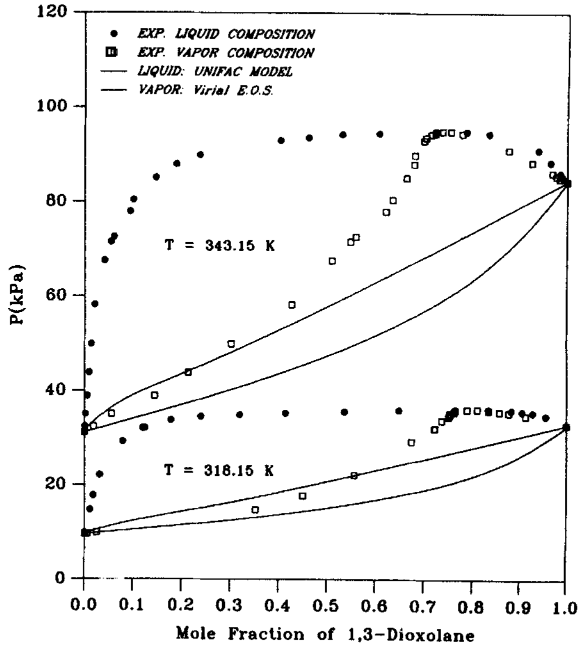


Figure 4. Comparison between measured VLE and prediction by the UNIFAC model for 1,3-dioxolane/water at 318.15 & 343.15 K.

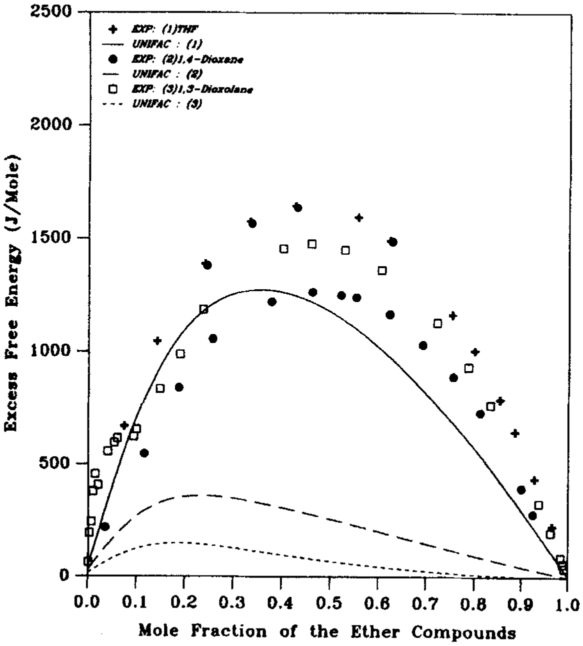


Figure 3. Comparison between measured G^E and prediction by the UNIFAC model for THF/water, 1,4-dioxane/water, and 1,3-dioxolane/water at 343.15 K.

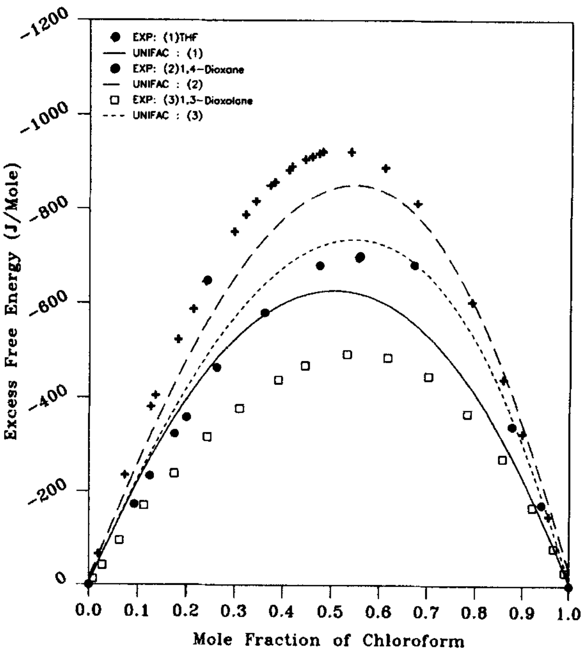


Figure 5. Comparison between measured G^E and prediction by the UNIFAC model for chloroform/THF, chloroform/1,4-dioxane, and chloroform/1,3-dioxolane at 323.15 K.

Thus, we see that the UNIFAC model can not accurately predict the VLE behavior for these three cyclic ether compounds separately with hydrocarbons, water, and chloroform. Therefore, we decided to determine separate UNIFAC interaction parameters for the ether groups in each of the three cyclic ethers considered here by correlating the VLE data with UNIFAC model. In this calculation, the absolute relative error between observed and predicted activity coefficients was minimized using the objective function

$$F(a_{12}, a_{21}): = \text{Minimize} \sum_{i=1}^{n} \left| \frac{\gamma_i^{obs} - \gamma_i^{calc}(a_{12}, a_{21})}{\gamma_i^{obs}} \right|$$

The optimal solution was found by means of an extended simplex method by Nelder and Mead (1965). Since the interaction parameters in UNIFAC (and most other two parameter) models are often highly intercorrelated, we plot error contours at both the 80% and 95% confidence levels of the objective function for each of the following group-group interactions, FCH_2O/CH_2, FCH_2O/H_2O, and $FCH_2O/CHCl_3$. If proximity effects were important, we would expect that the parameters for THF, which has a "free" cyclic ether group, and 1,3-dioxolane, which has only one methylene group between the two ether groups, to be at the two extremes, with the parameters for 1,4-dioxane lying somewhere between these two.

First, we plot, in Figure 6, the error contours for the objective function of FCH_2O/CH_2 group interaction based on the measured VLE of these three ether compounds with straight chain hydrocarbons (THF/hexane at 333.15 K; 1,4-dioxane/heptane at 353.15 K; 1,3-dioxolane/heptane at 343.15 K). We see from this figure that the optimal parameter values for the FCH_2O/CH_2 interaction of 1,3-dioxolane lies closest to the origin, while those for THF are farthest from the origin. Hence, the proximity effect between two cyclic ether groups in a molecule apparently weakens the FCH_2O/CH_2 group interaction. With the optimal interaction parameters for FCH_2O/CH_2 for these three ether compounds, we next determined the interaction parameters of FCH_2O/H_2O based on the VLE data of these three ether compounds with water all at 343.15 K. The error contours for the FCH_2O/H_2O interaction parameters in Figure 7 confirms our expectation that the proximity effect between two cyclic ether groups on a molecule weaken the FCH_2O/H_2O group interaction. Since the interaction parameters lie in a sequence with 1,3-dioxane closest to the origin and THF farthest from the origin. Finally, we determine the optimal $FCH_2O/CHCl_3$ group

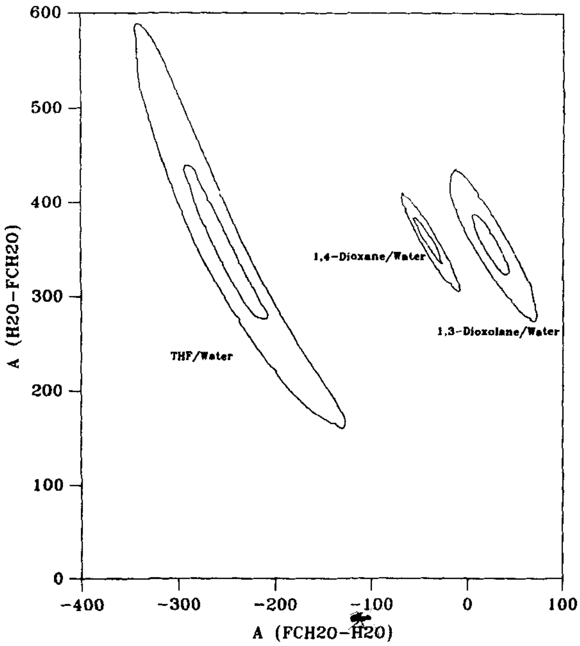


Figure 7. Error contours of the optimal UNIFAC interaction parameters for FCH$_2$O vs. CH$_2$.

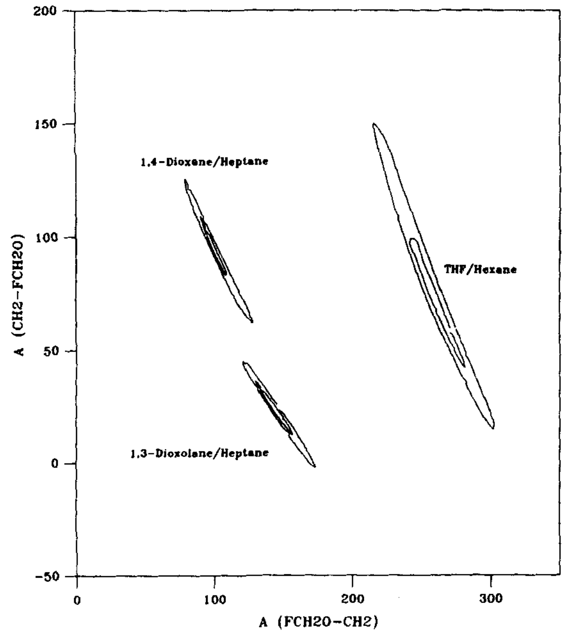


Figure 6. Error contours of the optimal UNIFAC interaction parameters for FCH$_2$O vs. CH$_2$.

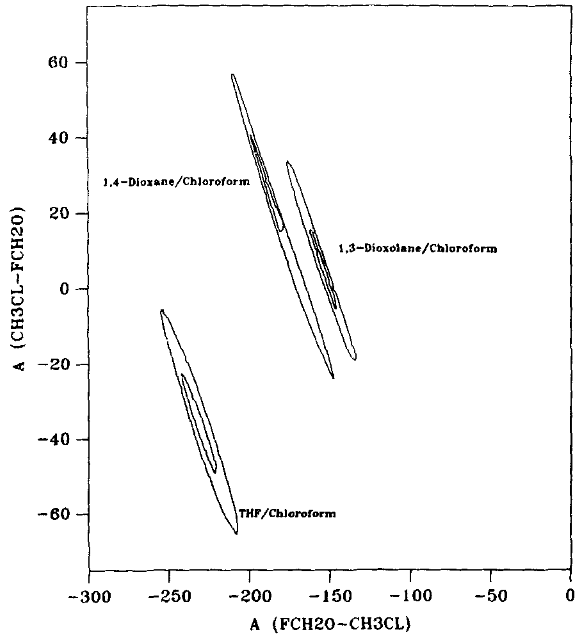


Figure 8. Error contours of the optimal UNIFAC interaction parameters for FCH$_2$O vs. CH$_3$Cl.

interaction parameters using the VLE data for these three ether compounds with chloroform, all at 323.15 K. We see in Figure 8, that the optimal $FCH_2O/CHCl_3$ interaction parameters lie in a sequence with that of 1,3-dioxolane closest to the origin while that of THF farthest from the origin, confirming the importance of the proximity effect in these ether compounds.

Conclusion

In this communication we have illustrated the importance of the proximity effect in group contribution methods by considering three ether compounds. We believe the same failure of present group contribution methods may occur with other compounds containing more than one strong functional group in a molecule. One way around this problem, while still keeping the present group contribution structure, is to define larger functional groups providing a more detailed account of molecular structure. However, as more groups are defined, more experimental data are needed, and the advantage of using the group contribution model is lost. Another alternative, suggested by the results reported here, is to experimentally find optimal interaction parameters for two extreme cases, one in which proximity effects are not important and another in which they are very important, such as the ether groups in tetrahydrofuran and 1,3-dioxolane. The parameter values for other cases could then be obtained by some interpolation procedure. Clearly, a more complicated group contribution model will be needed to include the effect of intramolecular group proximity effects on intermolecular interactions. Therefore, we conclude that homoproximity effects are important corrections to current group contribution models and that the applicability of the UNIFAC model to compounds having more than one non-hydrocarbon group is open to question.

Acknowledgment

The authors are grateful to Professor H. Kehiaian for helpful comments. The research reported here was supported, in part, by the National Science Foundation Grant CBT-8612285 to the University of Delaware.

Notation

G^E = excess Gibbs free energy
R = molar gas constant
T = temperature (K)
X, Y = functional group
a_{12}, a_{21} = interaction parameters of UNIFAC model

Greek letters

γ_i = activity coefficient of component i
γ_i^{obs} = measured activity coefficient of component i
γ_i^{calc} = calculated activity coefficient of component i by UNIFAC model
γ^∞ = infinity dilution activity coefficient

Literature Cited

Boublik, T., V. Fried, and E. Hala, *The Vapor Pressures of Pure Substances,* 2nd ed., Elsevier, Amsterdam (1984).

Eng, R., and S. I. Sandler, "Vapor-Liquid Equilibrium for Three Aldehyde/Hydrocarbon Mixtures," *J. Chem. Eng. Data,* **29,** 156 (1984).

Fredenslund, A., R. L. Jones, and J. M. Prausnitz, "Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures," *AIChE J.,* **21,** 1086 (1975).

Fredenslund, A., J. Gmehling, and P. Rasmussen, *Vapor-Liquid Equilibrium Using UNIFAC,* Elsevier, Amsterdam (1977).

Gmehling, J., U. Onken, and W. Arlt, "Vapor-Liquid Equilibrium Data Collection," *DECHEMA Chemistry Data Ser.,* Vol. 1 (12 parts), Frankfurt (1977).

Hayden, J. G., and J. P. O'Connell, "A Generalized Method for Predicting Second Virial Coefficients," *Ind. Chem. Process Res. Dev.,* **14,** 209 (1975).

Kehiaian, H. V., "Group Contribution Methods For Liquid Mixtures: A Critical Review," *Fluid Phase Equilibria,* **13,** 243 (1983).

———, personal communication (1987).

Langmuir, I., "The Distribution and Orientation of Molecules," *Third Colloid Symp. Monograph,* Chemical Catalog Company, New York (1925).

Nelder, J. A., and R. Mead, *Comp. J.,* **7,** 308 (1965).

Paul, I., Ph.D. Thesis, Technical University of Berlin (1987).

Prausnitz, J. M., T. F. Anderson, E. A. Grens, C. A. Eckert, R. Hsieh, and J. P. O'Connell. *Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria,* Prentice-Hall (1980).

Reddick, J. A., W. B. Bunger, and T. K. Sakano. *Organic Solvents, Physical Properties and Methods of Purification: II. Techniques of Chemistry* (1986).

Reid, R. C., J. M. Prausnitz, and B. E. Poling, *The Properties of Gases & Liquids,* 4th ed., McGraw-Hill, New York (1986).

Wu, H. S., and S. I. Sandler, "Vapor-Liquid Equilibrium of Tetrahydrofuran Systems," *J. Chem. Eng. Data,* **33,** 157 (1988).

Wu, H. S., and S. I. Sandler, "Vapor-Liquid Equilibrium of 1,3-dioxolane Systems," *J. Chem. Eng. Data,* submitted (1988).

Manuscript received Feb. 25, 1988 and revision received June 20, 1988.