This equation can be further simplified to

$$T = \frac{1}{2}\exp\left(\frac{1}{\Delta}\right)\operatorname{erfc}\left(\frac{1}{2\Delta}\sqrt{\frac{1}{\eta t}} + \sqrt{\eta t}\right) + \frac{1}{2}\operatorname{erfc}\left(\frac{1}{2\Delta}\sqrt{\frac{1}{\eta t}} - \sqrt{\eta t}\right) \quad (36)$$

This is the solution of Lapidus and Amundson (1952).

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NOTATION

C = concentration in fluid, mol/m^3
C_o = inlet concentration in fluid, mol/m^3
D_L = longitudinal dispersion coefficient, m^2/s
D_S = diffusivity in solid phase, m^2/s
K = volume equilibrium constant, m^3/m^3
k_f = mass transfer coefficient, m/s
m = $\epsilon/(1-\epsilon)$
$\overset{\Delta}{q}$ = volume averaged concentration in particles, mol/m^3
q = internal concentration in particles, mol/m^3
q_s = $q_t(R,z,t)$, mol/m^3
R = particle diameter, m
R_F = $R/3k_f$, film resistance, s
r = radial distance from center of spherical particle, m
s = Laplace transform variable
t = time, s
T = C/C_o, dimensionless concentration in fluid
u = average linear flow velocity, m/s
x = variable of integration
z = distance in flow direction, m

Greek Letters

α_n = $n\pi/R, s^{-1}$
σ = $R\sqrt{\frac{s+\lambda}{D_s}}$
ϵ = porosity, m^3/m^3
λ = reaction rate constant, s^{-1}

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A Group Contribution Molecular Model of Liquids and Solutions

Part III: Groups and Interactions in Aromatics, Cycloparaffins, Ethers Amines, and Their Solutions

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Group contribution models permit predictions for a large number of molecular systems, provided that the properties of a small number of groups are known. According to the molecular model of group contributions developed by Nitta et al. (1977), properties of pure liquid paraffins, alcohols, ketones, and their solutions, including activity coefficients and heats of mixing, can be efficiently predicted based on four groups (Ch$_3$, CH$_2$, CO, OH) and their interactions. Chien et al. (1981) have recently shown that this model successfully describes water and aqueous solutions of nonelectrolytes. In this communication we report extension of the model by Nitta et al. (1977) to aromatics, cycloalkanes, di-alkylethers, primary amines, and their solutions. Parameter values are presented for five additional groups.

CORRECTION FOR ENTROPY EFFECT OF RING ELEMENTS

In applying the Nitta model to ring-containing molecules such as the aromatic and cycloalkane hydrocarbons, we have found it necessary to introduce a correction to their core volumes for use in the Flory-Huggins entropy formula

TABLE 1. PROPERTIES OF GROUPS AND THEIR INTERACTIONS

Group	Q	$V_0^*(\mathrm{cm}^3/\mathrm{mol})$	a(K)	c	b
CH_{ar}	3.13	7.98	33.28	0.174	0.328
$CH_{ar\text{-}al}$	0.95	5.54	33.28	−0.127	0.328
$CH_{2,r}$	4.84	9.76	21.20	0.165	0.167
O_e	1.90	4.10	55.10	0.128	
NH_2	5.50	10.76	0.01	0.218	

ϵ_{ij}(kJ/mol)	CH_3	CH_2	CH_{ar}	$CH_{ar\text{-}al}$	$CH_{2,r}$	O_e	NH_2	CO	OH
CH_{ar}	3.276	3.276	4.284	4.284				5.732	5.012
$CH_{ar\text{-}al}$	3.276	3.276	4.284	4.284				5.732	5.012
$CH_{2,r}$	2.572	2.572			2.674				
O_e	3.500	3.500				6.532			
NH_2	3.092	3.092					3.903		

Group Pair		σ_0(kJ/mol)	σ_1(kJ/mol)
CH_{ar}	CO	0.052	0.323
$CH_{ar\text{-}al}$	CO	0.052	0.323
CH_{ar}	H(of Alcohols)	1.851	2.027
$CH_{ar\text{-}al}$	H(of Alcohols)	1.851	2.027
O_e	O_e	6.540	8.763
NH_2	NH_2	2.301	4.950

$$ln\ \gamma_A = ln\frac{V_A^*}{V^*} + 1 - \frac{V_A^*}{V^*} \tag{1}$$

which is part of Nitta's Eq. 32. Core volume values that fit the liquid volumes lead to excessive entropy values for the ring-containing molecules. A ring element, being tightly bound, does not give rise to as much entropy as a nonring element of the same core volume. We introduce a core volume reduction factor $(1 - b)$ for a ring element for the calculation of its effective Flory-Huggins volume

$$V_{A\text{eff}}^* = \sum_i n_i^A V_i^* \,(1 - b_i) \tag{2}$$

$$V_{\text{eff}}^* = \sum_A x_A V_{A\text{eff}}^* \tag{3}$$

where n_i^A is the number of groups of i in a molecule A, and x_A is the mole fraction of A. For nonring groups $b = 0$; for ring groups $1 > b > 0$. The effective volumes of Eqs. 2 and 3 replace V_A^* and V^* in Eq. 1.

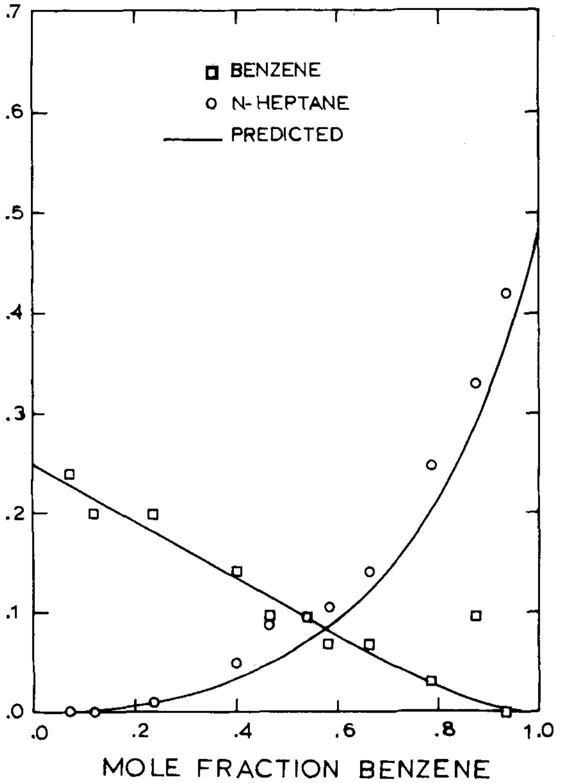

Figure 1. Activity coefficients in benzene + n-heptane at 348 K with data of Fu and Lu (1966).

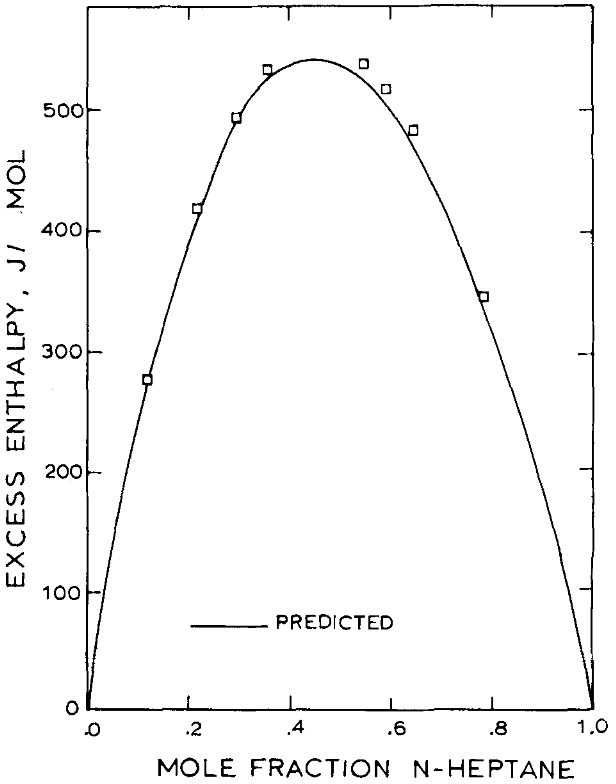

Figure 2. Excess enthalpy of n-heptane + toluene at 298 K with data by Lundberg (1964).

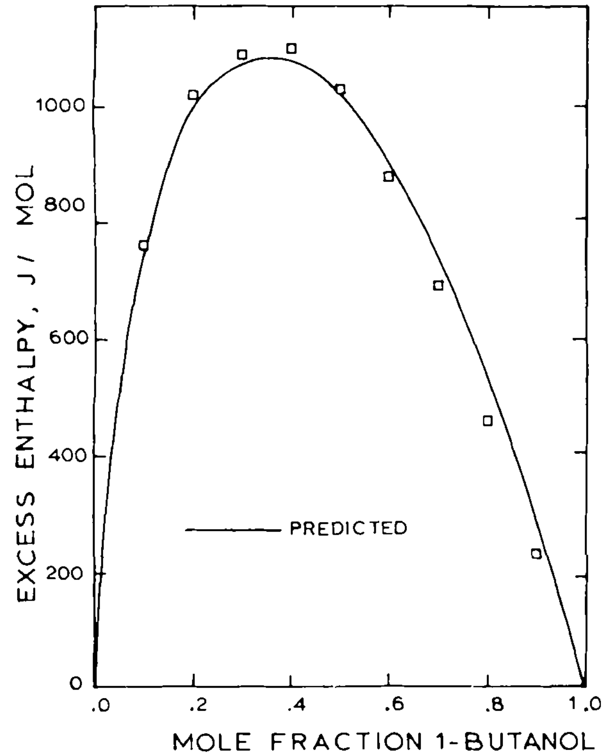

Figure 3. Excess enthalpy of 1-butanol + benzene at 298 K with data of Brown et al. (1969).

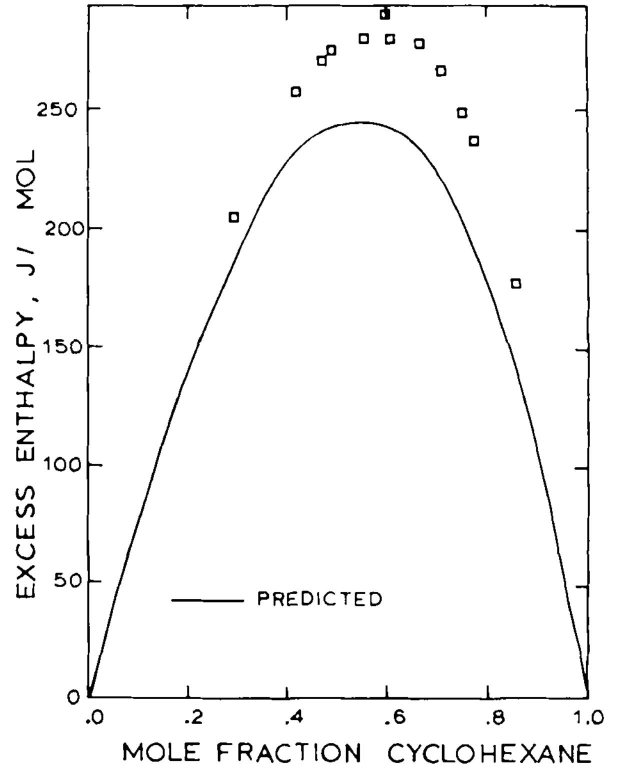

Figure 5. Excess enthalpy of cyclohexane + n-nonane at 298 K with data of Yang and Gómez-Ibanez (1976).

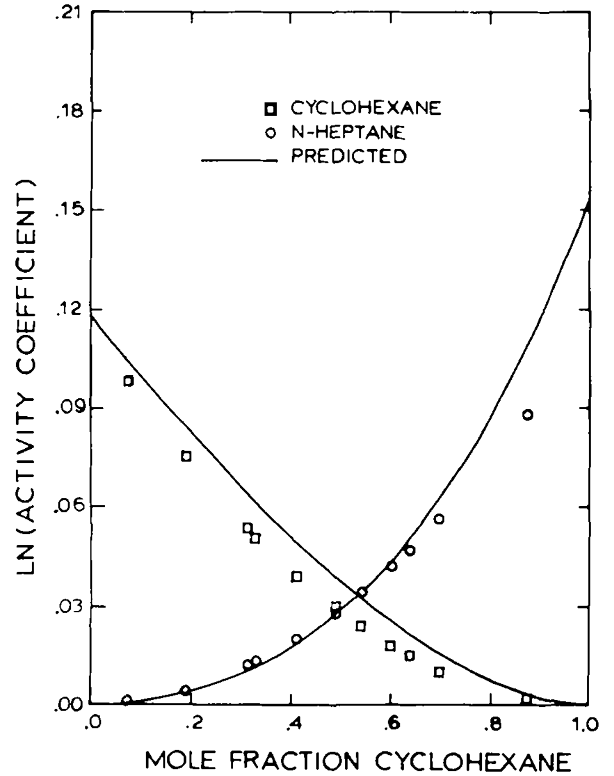

Figure 4. Activity coefficients in cyclohexane + n-heptane at 298 K with data by Young et al. (1977).

RESULTS AND DISCUSSION

Two groups in addition to those studied by Nitta et al are needed to describe systems containing alkylbenzenes, namely the aromatic CH, or CH_{ar}, and the aromatic-to-aliphatic branching C, or $C_{ar\text{-}al}$. We have determined the properties of these groups by fitting molar volumes and energies of vaporization of benzene, ethylbenzene and n-butyl-benzene, activity coefficients of n-hexane + benzene at 303 and 333 K, infinite dilution activity coefficients of benzene in n-hexadecane at 333 and 453 K and ethylbenzene in n-hexadecane at 393 K, and excess enthalpy of n-hexane + benzene at 298 K. The group parameters are listed in Table 1. The quantities given in the Table were explained in the article of Nitta et al. The energy parameters of the two aromatic groups are found to have equal values. Predicted results presented in Figures 1 and 2 show average deviations of less than 3% in activity coefficients and less than 40 J/mol in excess enthalpy. Pure compound properties, for those alkyl-benzenes not used in the fitting, are predicted with average deviations of less than 1%.

The energy parameters reflecting the interactions between the aromatic groups and CO were determined based on activity coefficients and heat of mixing of ethylbenzene + 2-butanone at 298 K. Interactions between the aromatic groups and OH were evaluated by fitting activity coefficients of ethanol + benzene at 348 K, ethanol + toluene at 248 K, and excess enthalpy of ethanol + toluene at 308 K. Predictions of mixture properties are in good agreement with experimental data (Chien, 1981). Figure 3 shows an example.

Cycloalkanes require the introduction of one additional group, CH_2 in ring, or $CH_{2,r}$. To determine the properties of this group we fitted the liquid molar volume and energy of vaporization of cyclohexane, activity coefficients in cyclohexane + n-hexadecane at 298 K, cyclohexane + n-dodecane at 298 K, n-octane + cyclohexane at 298 K, excess enthalpies of cyclohexane + n-hexane at 298 and 313 K, and cyclohexane + n-dodecane at 293 K. The parameters are listed in Table 1. An example of prediction for a system not used in the fitting procedure is presented in Figures 4 and 5. The deviations between calculated values and experimental data average less than 2% in activity coefficients and 100 J/mol in excess enthalpy. The properties of other cycloparaffins can be successfully calculated provided that the van der Waals volume and surface area are corrected according to Bondi (1968).

To determine the properties of the group O in ethers, or O_e, we

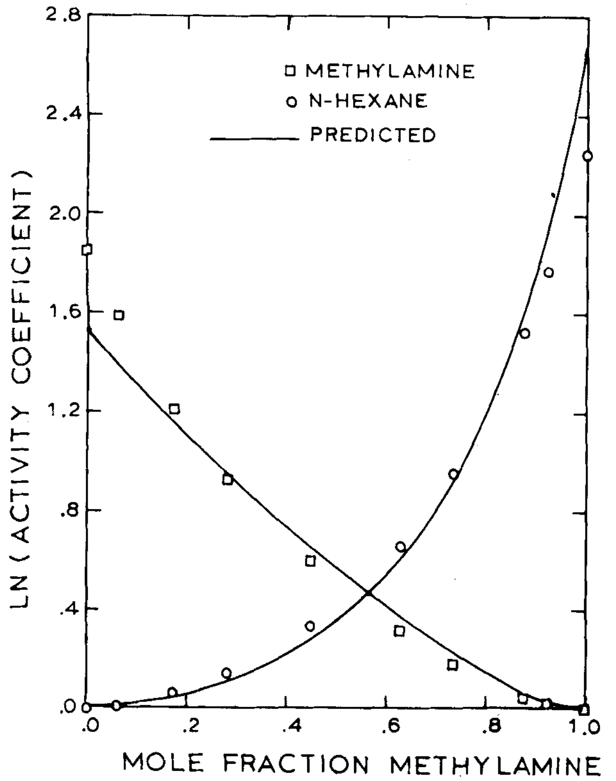

Figure 6. Activity coefficients of methylamine + n-hexane at 263 K with data by Wolff and Höpfner (1953).

fitted molar volumes and energies of vaporization of di-ethylether and di-n-propylether, and activity coefficients in ethane + di-ethylether at 298 K. The parameters are listed in Table 1. Average deviations are less than 1% for molar volume and 1.5 kJ/mol for energy of vaporization for systems not used in the parameter determination.

Primary amines require the introduction of NH_2. To determine the properties of this group that are listed in Table 1, we fitted molar volumes and energies of vaporization of ethylamine and n-butylamine, activity coefficients in n-hexane + hexylamine at 298 and 333 K, and heat of mixing of n-butylamine + n-heptone at 298 K. Predictions of pure compound and binary mixture properties not used in the optimization are in good agreement with experimental data. Deviations average less than 1% in molar volume, 3% in energy of vaporization for methylamine, n-propylamine, and n-hexylamine. Average deviation in activity coefficients shown in Figure 6 is less than 5%; average deviation in excess enthalpy shown in Figure 7 is less than 120 J/mol.

NOTATION

b_i = fractional reduction of effective core volume of group i for Flory-Huggins entropy calculations
n_i^A = number of groups of i in a molecule of A
V^* = core volume, cm^3/mol
V^*_{eff} = effective core volume for Flory-Huggins entropy calculation
x_A = mole fraction of A
γ_A = activity coefficient of molecule A

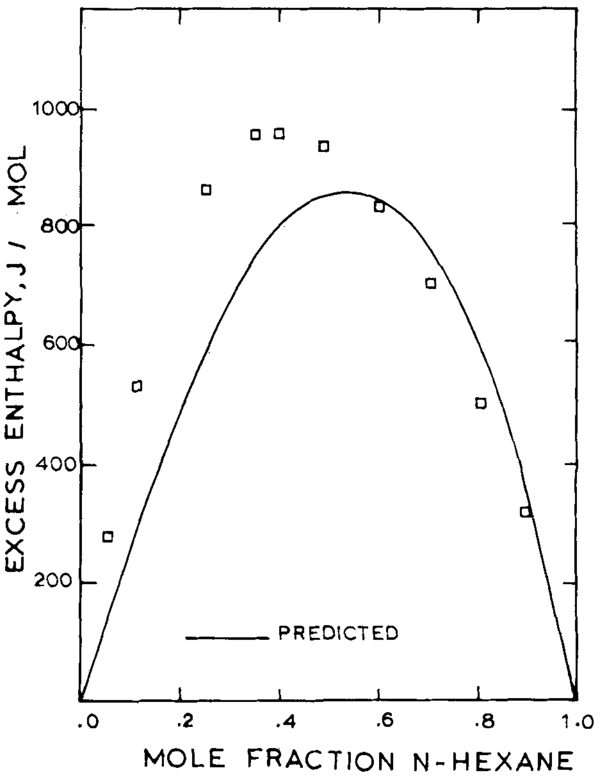

Figure 7. Excess enthalpy of n-hexane + n-hexylamine at 313 K with data of Kern et al. (1970).

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