R & D NOTES

A Group Contribution Molecular Model of Liquids and Solutions Part IV: Group Pair Parameters for 15 Groups

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The group contribution molecular model of Nitta et al. (1977) describes molecular liquids and their solutions by means of the properties of the structural groups of these molecules. Since a large number of molecules are made up of a relatively few groups. Nitta's model, like other group contribution models, provides a means of making general predictions for large classes of molecular liquids and solutions. Unlike other group contribution models such as the ASOG and UNIFAC, Nitta's model also describes heat of mixing and density of the liquids in addition to activity coefficient.

Nitta et al. reported the properties of four groups: CH_3, CH_2, CO, and OH. Chien et al. (1981) added the interaction properties of water. Koukios et al. (1984) extended the model to aromatics, cycloparaffins, ethers, and amines. We report here the nitrile CN groups, and the CH and C groups; the two last groups are the branching elements of isomers. A total of 15 groups have been studied, and values of the parameters of all the groups and group pairs that have been determined are presented here for convenient reference. Table 1 presents the individual group properties. The attractive interaction of a group pair is described with up to three parameters. Table 2 presents the dispersive energies ϵ, Table 3 the base associative energies σ^0, and Table 4 the associative temperature parameter σ^1. New values are indicated with square brackets in the table entries. Unbracketed numbers represent previously reported values.

The method of determination of the group properties has been described previously (Nitta et al. 1977). The experimental data that were used to find the new group property values are described by Arnold (1980) and Eckart (1984), both of whom also give detailed comparisons of the model-fitting results with the experimental data used.

TABLE 1. INDIVIDUAL GROUP PARAMETERS

Formula	Description	V_o^* cm³/mol	a_K	b	c	Q
CH_3	Methyl	13.46	23.7	0.0	0.338	6.71
CH_2	Methylene	10.25	23.7	0.0	0.093	4.27
CH	Tertiary aliphatic carbon	[6.71]	[23.7]	[0.0]	[−0.1705]	[1.8]
C	Quaternary aliphatic carbon	[3.33]	[23.7]	[0.0]	[−0.347]	[0.0]
$CH_{2,r}$	Aliphatic ring element	9.76	21.2	0.167	0.165	4.84
CH_{ar}	Aromatic ring CH	7.98	33.28	0.328	0.0174	3.13
$C_{ar\text{-}al}$	Aromatic ring C bonded to a side chain	5.54	33.28	0.328	−0.127	0.95
CO	Carbonyl	11.6	11.2	0.0	0.147	5.06
O_e	Ethereal oxygen	4.10	55.1	0.0	0.128	1.90
CN	Nitrile	[14.2]	[14.5]	[0.0]	[0.428]	[6.93]
NH_2	Primary amine	10.76	0.01	0.0	0.218	5.50
O_{OH}	Oxygen in hydroxyl	8.01	39.6	0.0	0.245	3.62
H_{OH}	Hydrogen in hydroxyl	0.0	0.0	0.0	0.0	1.0
WOH	Water-Hydrogen bonds	10.48	55.0	0.0	0.353	4.00
CVT	Water cavities	0.0	0.0	0.0	0.0	2.06

TABLE 2. DISPERSIVE ENERGIES ε_{ij}, kJ/mol*

Group	CH_3	CH_2	CH	C	$CH_{2,r}$	CH_{ar}	$C_{ar\text{-}al}$	CO	O_e	CN	NH_2	O_{OH}	H_{OH}	WOH	CVT
CH_3	2.515														
CH_2	2.515	2.515													
CH	[1.937]	[1.912]	[0.293]												
C	[0.0]	[0.0]	[0.0]	[0.0]											
$CH_{2,r}$	2.572	2.572	[1.946]	[0.0]	2.674										
CH_{ar}	3.276	3.276	[2.464]	[0.0]	[3.401]	4.284									
$C_{ar\text{-}al}$	3.276	3.276	[2.464]	[0.0]	[3.401]	4.284	4.284								
CO	3.563	3.563	[2.393]	[0.0]	[3.607]	5.732	5.732	6.519							
O_e	3.500	3.500	[1.307]	[0.0]	[3.738]	[6.278]	[6.278]	[3.443]	6.532						
CN	3.582	3.582	[3.479]	[0.0]	—	[4.079]	[4.079]	[4.996]	—	[6.004]					
NH_2	3.092	3.092	—	[0.0]	—	[2.710]	[2.710]	—	—	—	3.903				
O_{OH}	3.738	3.738	[2.506]	[0.0]	[4.344]	5.012	5.012	6.703	[9.598]	[8.111]	[10.868]	6.887			
H_{OH}	3.738	3.738	[2.506]	[0.0]	[4.344]	5.012	5.012	6.703	[9.598]	[8.111]	[10.868]	6.887	6.887		
WOH	1.845	1.845	[0.249]	[0.0]	[1.540]	[4.321]	[4.321]	11.234	[6.514]	[9.092]	[10.999]	6.519	6.519	6.548	
CVT	3.309	3.309	[0.243]	[0.0]	[3.624]	[4.126]	[4.126]	7.343	[12.117]	[4.590]	[7.479]	6.498	16.673	5.736	3.765

*Values determined in this work denoted by brackets

TABLE 3. BASE ASSOCIATIVE ENERGIES σ°_{ij}, kJ/mol

Group	CH_3	CH_2	CH	C	$CH_{2,r}$	CH_{ar}	$C_{ar\text{-}al}$	CO	O_e	CN	NH_2	O_{OH}	H_{OH}	WOH	CVT
CH_3	0.0														
CH_2	0.0	0.0													
CH	[0.0]	[0.0]	[0.0]												
C	[0.0]	[0.0]	[0.0]	[0.0]											
$CH_{2,r}$	0.0	0.0	[0.0]	0.0	0.0										
CH_{ar}	0.0	0.0	[0.0]	0.0	[0.0]	0.0									
$C_{ar\text{-}al}$	0.0	0.0	[0.0]	0.0	[0.0]	0.0	0.0								
CO	0.0	0.0	0.0	0.0	[0.0]	0.052	0.052	2.929							
O_e	0.0	0.0	[0.0]	0.0	[0.0]	[0.0]	[0.0]	[6.702]	6.540						
CN	0.0	0.0	[0.0]	0.0	—	[0.929]	[0.929]	[3.403]	—	[2.510]					
NH_2	0.0	0.0	—	0.0	—	[1.412]	[1.412]	—	—	—	2.301				
O_{OH}	0.0	0.0	0.0	0.0	[0.0]	0.0	0.0	0.0	[0.0]	[0.0]	[0.0]	0.0			
H_{OH}	0.0	0.0	0.0	0.0	[0.0]	1.851	1.851	12.761	[12.732]	[9.921]	[5.871]	12.552	0.0		
WOH	0.0	0.0	[0.0]	0.0	[0.0]	[0.010]	[0.010]	0.678	[6.160]	[3.028]	[0.002]	4.937	12.570	7.627	
CVT	0.0	0.0	[0.0]	0.0	[0.0]	[0.0]	[0.0]	0.0	[0.0]	[0.0]	[0.0]	0.0	0.0	0.0	0.0

*Values determined in this work denoted by brackets

TABLE 4. ASSOCIATIIVE TEMPERATURE PARAMETER σ'_{ij}, kJ/mol*

Group	CH_3	CH_2	CH	C	$CH_{2,r}$	CH_{ar}	$C_{ar\text{-}al}$	CO	O_e	CN	NH_2	O_{OH}	H_{OH}	WOH	CVT
CH_3	0.0														
CH_2	0.0	0.0													
CH	[0.0]	[0.0]	[0.0]												
C	[0.0]	[0.0]	[0.0]	[0.0]											
$CH_{2,r}$	0.0	0.0	[0.0]	0.0	0.0										
CH_{ar}	0.0	0.0	[0.0]	0.0	[0.0]	0.0									
$C_{ar\text{-}al}$	0.0	0.0	[0.0]	0.0	[0.0]	0.0	0.0								
CO	0.0	0.0	0.0	0.0	[0.0;	0.323	0.323	2.929							
O_e	0.0	0.0	[0.0]	0.0	[0.0]	[0.0]	[0.0]	[6.577]	8.763						
CN	0.0	0.0	[0.0]	0.0	—	[1.266]	[1.266]	[0.024]	—	[3.828]					
NH_2	0.0	0.0	—	0.0	—	[2.537]	[2.537]	—	—	—	4.950				
O_{OH}	0.0	0.0	0.0	0.0	[0.0]	0.0	0.0	0.0	[0.0]	[0.0]	[0.0]	0.0			
H_{OH}	0.0	0.0	0.0	0.0	[0.0]	2.027	2.027	16.192	[36.610]	[11.017]	[24.902]	17.154	0.0		
WOH	0.0	0.0	[0.0]	0.0	[0.0]	[2.594]	[2.594]	1.878	[12.272]	[22.608]	[2.103]	9.920	17.384	15.084	
CVT	0.0	0.0	[0.0]	0.0	[0.0]	[0.0]	[0.0]	0.0	[0.0]	[0.0]	[0.0]	0.0	0.0	0.0	0.0

*Values determined in this work denoted by brackets

LITERATURE CITED

Arnold, D. W., "A Group Contribution Model for Liquids and Their Mixtures with Experimental Determination of Infinite Dilution Activity Coefficients," Ph.D. Dis., Purdue Univ. (1980).

Chien, C. H., R. A. Greenkorn, and K .C. Chao, "A Group Contribution Molecular Model of Liquids and Solutions. II: Groups and Their Interactions in Water and Aqueous Solutions of Paraffins, Ketones, and Alcohols," *AIChE J.*, **27**, 303 (1981).

Eckart, D. E., "Implementation of a Group Contribution Thermodynamic Model," M.S. Thesis, Purdue Univ. (1984).

Koukios, E. G., et al., "A Group Contribution Molecular Model of Liquids and Solutions. III: Groups and Interactions in Aromatics, Cycloparaffins, Ethers, Amines, and Their Solutions," *AIChE J.*, **30**, 662 (1984).

Nitta, T., et al., "A Group Contribution Molecular Model of Liquids and Solutions," *AIChE J.*, **23**, 144 (1977).

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