of casting solvent was used and how they are dried. Therefore, the surface structure of a polymer blend is not a simple function of the surface free energy difference or the molecular interaction.

Figure 6 shows XPS results of (PMMA/SAN 30) ultrathin films with *ca.* 13 nm thick and thick films with 2 μm thick. Polymeric films with thickness less than about 2 Rg of the higher weight component, here PMMA (2 Rg= 14.6 nm), was defined as the ultrathin blend films.[8] Since polymeric chains at the interface, in general, are thermodynamically unstable, the molecular aggregation structure in the ultrathin film of binary polymer blend must be greatly different from that in the thick film. The surface structure of ultrathin film did not show any surface enrichment of PMMA, the lower surface free energy component in the blend. This result was agreed with that of (PMMA/PVAc) ultrathin films, that is, the mobility of chains in a blend film with this thickness is restricted due to its very narrow space.[8]

Conclusion

The surface structure of (PMMA/SAN) blends with various AN contents of SAN and in the carboxyl acid contents of PMMA was investigated on the basis of XPS, ATR-FT IR and AFM measurements. It was revealed that the degree of surface enrichment in phase mixed- and phase-separated systems is not a simple function of the surface free energy difference, entropy of mixing, or molecular interaction. The component enriched at the surface of a blend is strongly dependent on the difference of surface free energy between components in the blend whereas the degree of surface enrichment is dependent on several factors such as surface free energy difference, intermolecular interaction and sample preparation history. The carboxyl group in H-PMMA reduces the compatibility of (PMMA/SAN 30) blend due to the dilution of the repulsive force between S and AN unit.

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Rates of Conformational Change of 3,3-Dimethylpiperidine and Solvent Effects on Its Conformation When Coordinated to the Paramagnetic Undecatungstocobalto(II)silicate Anion Studied by ^{1}H NMR Spectroscopy

Jaewon Hyun and Hyunsoo So*

Department of Chemistry, Sogang University, Seoul 121-742, Korea
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^{1}H NMR spectra of 3,3-dimethylpiperidine (**1**) at −70 to 30 °C exhibit gradual change from slow to rapid exchange between two alternate chair forms. The exchange rate constant was determined as a function of temperature by simulating the line shape of the signal from the two methyl groups using the modified Bloch equations. The resulting free energy of activation is $\Delta G^* = 44.4 \pm 1.9$ kJ mol^{-1} at 298 K. The ^{1}H NMR spectrum of a D_2O or dimethylsulfoxide-d_6 (DMSO-d_6) solution containing **1** and $[SiW_{11}Co^{II}O_{39}]^{6-}$ exhibits separate signals for the free ligand and the complex, indicating that the ligand exchange is slow on the NMR time scale. In D_2O the piperidine ring is frozen as a chair form even at room temperature with the cobalt ion bonded to the axial position of the nitrogen atom. When DMSO-d_6 is added to the D_2O solution, the NMR spectral change suggests that a rapid exchange occurs between the chair form and another conformer. It is proposed that the conformation of **1** coordinated to $[SiW_{11}Co^{II}O_{39}]^{6-}$ in DMSO-d_6 is close to a twist form.

Introduction

Numerous NMR studies have been carried out on piperidine and its derivatives to elucidate their conformations. A recent book on piperidine devoted three chapters to conformational analysis and ^{1}H and ^{13}C NMR spectroscopies of

piperidine derivatives.[1] NMR spectra show that piperidine exists in solution as two chair conformers in rapid exchange at room temperature.[2] In addition, the equatorial and axial NH conformers are in rapid exchange, the equatorial/axial ratio being 7 : 3 at room temperature.[2] The ring inversion is frozen below −85 °C, the free energy of activation being 43.5 kJ/mol.[3,4] The nitrogen inversion is frozen at a much lower temperature.

The ^{1}H NMR spectra of 2-, 3- and 4-methylpiperidine show that the piperidine ring is frozen even at room temperature as the chair form with the equatorial methyl group. The chair conformer with the axial methyl group has high energy because of two gauche interactions and repulsive interactions between the axial methyl group and the axial hydrogen atom(s).[5] Detailed assignments of the ^{1}H NMR peaks for these compounds were reported before.[6]

While studying ^{1}H NMR spectra of piperidine derivatives coordinated to the paramagnetic heteropolyanion, $[SiW_{11}Co^{II}O_{39}]^{6-}$ ($SiW_{11}Co$, **2**), we have noted that a detailed ^{1}H NMR study of 3,3-dimethylpiperidine (**1**) has not been reported. ^{13}C chemical shifts of **1** as a function of temperature were reported, and a chair-twist equilibrium was assumed.[7] However, we have found that the ^{1}H NMR spectra of **1** can be better interpreted in terms of two alternate chair conformers in equilibrium. This paper reports assignments of ^{1}H NMR peaks of **1** in dichloromethane-d_2, determination of the free energy of activation for the chair-chair conversion, and conformations of **1** coordinated to the paramagnetic $[SiW_{11}Co^{II}O_{39}]^{6-}$ anion in D_2O and DMSO-d_6.

Experimental

3,3-Dimethylpiperidine was used as obtained from Aldrich. Dichloromethane-d_2 solutions were prepared ~0.1 M in **1**. $K_6[SiW_{11}Co(H_2O)O_{39}]\cdot nH_2O$ was prepared according to the method of Simmons.[8] D_2O and DMSO-d_6 solutions were prepared ~0.02 M in each of **1** and $K_6[SiW_{11}Co(H_2O)O_{39}]\cdot nH_2O$.

^{1}H NMR spectra were obtained in the Fourier-transform mode with Varian Gemini-300 and -200 spectrometers equipped with broad band narrow-bore probes. NMR measurements were made at −70 to 30 °C. Sodium salt of 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid (TSP) or TMS was used as an internal reference.

The NMR spectra were simulated by using the computer program NMRSM[9] and also a program written by us. Two programs produced essentially the same results.

Results and Discussion

Free 3,3-Dimethylpiperidine. The ^{1}H NMR spectra of **1** at −70 to 20 °C are shown in Figure 1. The spectrum at −70 °C is typical of a fixed chair conformation of the piperidine ring. As the temperature is raised, the signals are broadened, then some signals merge, and finally the merged signals become sharp. Such temperature dependence is expected when the exchange rate between two different conformers increases with increasing temperature. The two methyl peaks appearing at 0.95-0.80 ppm at −70 °C become an exchange-narrowed peak at 20 °C, indicating that the axial and equatorial methyl groups are exchanged rapidly in the two conformers. Then the two conformers involved must be the two alternate chair forms. If a chair form and a twist form were involved, the two methyl peaks would not be merged even at high temperatures.

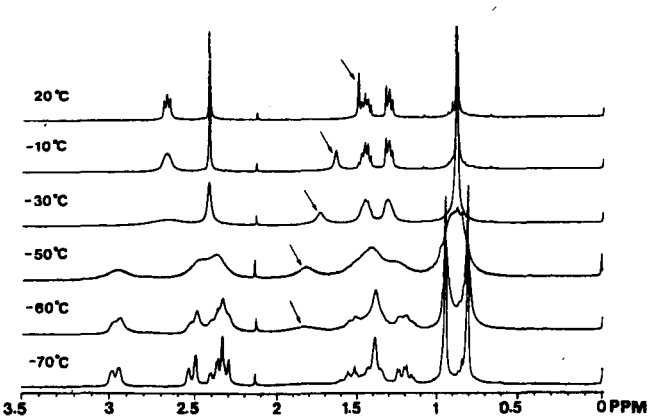


Figure 1. ^{1}H NMR spectra of 3,3-dimethylpiperidine in CD_2Cl_2 at −70 to 20 °C. The peaks designated by arrows originate from H_2O.

The spectrum at 20 °C will be assigned first. The axial and equatorial protons bonded to the same carbon atom have the same average environment in the rapidly interconverting system. Since the α−protons are deshielded more than the other protons in 3- or 4-methylpiperidine,[6] the peaks at 2.67 and 2.42 ppm may be assigned to the α−protons. The singlet at 2.42 ppm is assigned to 2-H, for no significant spin-spin coupling is expected with the methyl groups at the position 3. The triplet at 2.67 ppm is then assigned to the 6-H protons, which are coupled with the 5-H protons. The spin-spin coupling constants for the two rapidly interconverting chair conformers can be obtained by averaging the values for the fixed chair forms. Analysis of the low-temperature spectrum produced one common value for each of J_{aa}, J_{ae}, and J_{ee} irrespective of the positions of the protons (see below).[10] The 6-H peak is expected to split into a doublet by $J_1=(J_{aa}+J_{ee})/2$ and again into doublets by $J_2=(J_{ae}+J_{ea})/2$. Since J_1 (6.5 Hz) and J_2 (4.5 Hz) are similar, the signal looks like a triplet. The triplet at 1.27 ppm is assigned to 4-H similarly as 6-H. The J values determined (J_1' =7.0 and J_2'=5.1 Hz) are slightly larger than the values determined from the 6-H signal. The quintet at 1.43 ppm is assigned to 5-H, for the peak is expected to split into a triplet by J_1 and J_1' and again into triplets by J_2 and J_2'. And finally the singlet at 0.85 ppm is assigned to the methyl groups.

The spectrum below −70 °C comes from a fixed piperidine ring. The fine structure is useful in assigning the signals. The coupling constant between geminal protons in the piperidine ring is ~13 Hz, and J_{aa}, J_{ae}, and J_{ee} are in the range of 8-13, 2-6, and 1-4 Hz, respectively.[11] The peak at 2.67 ppm at 20 °C splits into a doublet at 2.96 and a triplet at 2.37 ppm, which are assigned to 6-H_e and 6-H_a on the basis of their fine structures. This assignment is consistent with the well-established fact that an equatorial α−proton is deshielded more than an axial one.[12] The two doublets at 2.52 and 2.32 ppm, which merge into a singlet at 2.42 ppm at 20 °C, are assigned to 2-H_e and 2-H_a, respectively.

The quartet at 1.54 ppm and the triplet at 1.20 ppm are

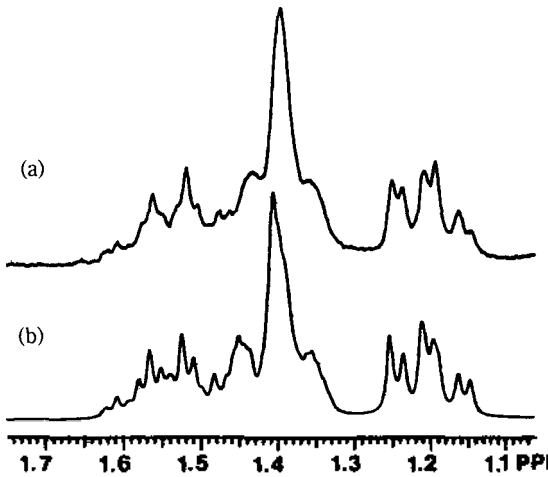


Figure 2. (a) Measured and (b) simulated spectra of 3,3-dimethylpiperidine in CD_2Cl_2 at 1.7-1.1 ppm.

assigned to 5-H_a and 4-H_a, respectively, based on their fine structures. Then the peaks centered at 1.40 ppm should be assigned to 4-H_e and 5-H_e. Since this portion of the spectrum is complicated, the measured and simulated spectra are shown in Figure 2. The resulting chemical shifts of 4-H_e and 5-H_e are 1.42 and 1.38 ppm, respectively. Finally the peaks at 0.95 and 0.80 ppm are assigned to the equatorial and axial methyl groups. The chemical shifts and the spin-spin coupling constants are given in Table 1.

The spin-spin coupling constants determined from the low-temperature spectrum are $J_{2e\text{-}2a}$=12.3, $J_{4e\text{-}4a}$=14.2, $J_{5e\text{-}5a}$=12.9, $J_{6e\text{-}6a}$=12.0, $^3J_{aa}$=12.9, and $^3J_{ae}$=4.3 Hz. An accurate value of $^3J_{ee}$ could not be determined. If $^3J_{ee}$ is assumed to be 1.1 Hz, $(J_{aa}+J_{ee})/2$=7.0 Hz is in agreement with J_1', but slightly larger than J_1. The average value of J_{ae} and J_{ea}, 4.3 Hz, is slightly smaller than J_2 and J_2'.

Free Energy of Activation. Temperature-dependent line shapes of the signal from the methyl groups were simulated by using the modified Bloch equations,[13,14] and the transition probability, P, between the two conformers was determined as a function of temperature. According to the transition state theory the Arrhenius equation can be expressed as[15]

$$P = \frac{kT}{h} \exp(\Delta S^*/R) \exp(-\Delta H^*/RT)$$

Table 1. Chemical Shifts (in ppm) and Spin-Spin Coupling Parameters (in Hz) for 3,3-Dimethylpiperidine at − 70 °C

2-H_e	2.52 d* (12.3)
2-H_a	2.32 d (12.3)
4-H_e	1.42 d (14.2)
4-H_a	1.20 ddd (14.2, 12.9, 4.3)
5-H_e	1.38 d (12.9)
5-H_a	1.54 dtt* (12.9, 12.9, 4.3)
6-H_e	2.96 d (12.0)
6-H_a	2.37 ddd (12.0, 12.9, 4.3)
3-CH_3 (e)	0.95 s*
3-CH_3 (a)	0.80 s

*s, d, and t represent singlet, doublet, and triplet, respectively.

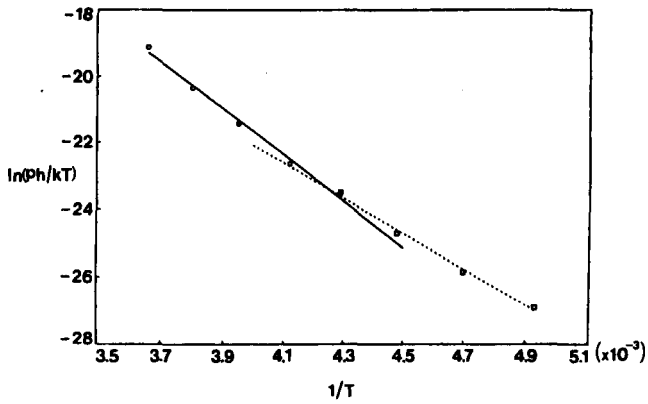


Figure 3. Least squares fit of ln(Ph/kT) as a function of 1/T. Two straight lines were obtained by using five experimental values at 0 to − 40 °C and four experimental values at − 40 to − 70 °C. Symbols represent values determined by simulating the line shape of the signal from the two methyl groups.

When ln(Ph/kT) is plotted as a function of 1/T (Figure 3), the experimental values fall on two straight lines instead of one. This may represent that more than one path contribute to the chair-chair interconversion. The activation parameters depend on the straight line chosen,[15] but the free energies of activation at room temperature are close enough to be expressed as 44.4±1.9 kJ mol^{-1}. This value is similar to that (43.5 kJ mol^{-1}) of piperidine.[3]

$SiW_{11}Co$ Complex. ^{1}H NMR spectra of **1** coordinated to **2** in D_2O, D_2O-DMSO-d_6, and DMSO-d_6 are shown in Figure 4. Separate peaks are observed for the free ligand and the complex, showing that the ligand exchange is slow on the NMR time scale. The peaks originating from the complex exhibit large isotropic shifts due to the unpaired electrons on the cobalt ion. Nine out of ten expected peaks are observed for the D_2O solution. Since the room-temperature spectrum of the free ligand exhibits well-resolved peaks from 2-, 4-, 5-, and 6-H protons, saturation transfer technique was used to identify these peaks. Then the peaks were assigned to the equatorial or axial protons by comparing with the spectra of related systems (see below).

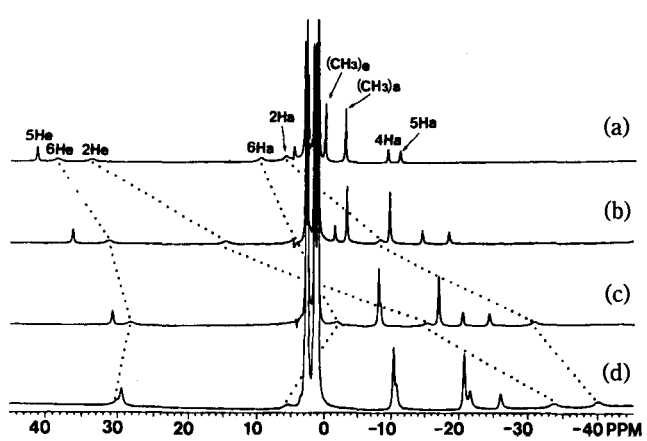


Figure 4. ^{1}H NMR spectra of (a) D_2O, (b) 40% (by volume) DMSO-d_6, (c) 80% DMSO-d_6, and (d) DMSO-d_6 solutions containing 3,3-dimethylpiperidine and $SiW_{11}Co$ in a 1 : 1 molar ratio. The peaks originating from the complex are labeled.

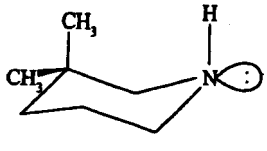
Table 2. Chemical Shifts (in ppm) for 3,3-dimethylpiperidine Coordinated to $SiW_{11}Co$

	D_2O solution	DMSO-d_6 solution
2-H_e	33.9	−33.8
2-H_a	5.9	−40.2
4-H_e	−	−11.0
4-H_a	−9.4	−21.8
5-H_e	41.4	29.5
5-H_a	11.1	−26.9
6-H_e	38.6	30.0
6-H_a	9.6	5.5
3-CH_3 (e)	0.0	−10.4
3-CH_3 (a)	−3.0	−20.8

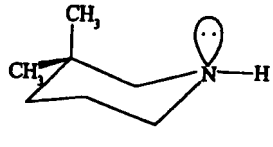
The lowest-field peak at 41.4 ppm in the D_2O spectrum, which comes from 5-H, is assigned to 5-H_e by comparing with the spectrum of 4-methylpiperidine coordinated to **2**.[17] The broad peak at 38.6 ppm in the D_2O spectrum, which originates from 6-H, is assigned to 6-H_e by comparing with the spectrum of 3-methylpiperidine coordinated to **2**.[17] The other peak at 9.6 ppm originating also from 6-H is assigned to 6-H_a. The two peaks at 33.9 and 5.9 ppm, which originate from 2-H, are similarly assigned to 2-H_e and 2-H_a, respectively. Assignments of the other peaks are shown in Figure 4 and Table 2.

Addition of DMSO-d_6 to the D_2O solution generally shifts the peaks upfield. Most remarkably 2-H_e and 2-H_a peaks are shifted by 68 and 46 ppm, respectively, when D_2O is replaced by DMSO-d_6. The gradual decrease of the chemical shifts with increasing concentration of DMSO-d_6 suggests that the chair form is in equilibrium with another conformer in D_2O-DMSO-d_6 solutions (see below).[18] Assignments for the DMSO spectrum are also given in Table 2.

Conformations of the Coordinated 3,3-Dimethylpiperidine. The NMR spectrum of **1** coordinated to **2** in D_2O exhibits separate peaks for equatorial and axial protons, indicating that the chair-chair interconversion does not occur even at room temperature. It is quite likely that the piperidine ring is frozen as a chair form, which is consistent with the observation that the chemical shifts of the two equatorial (or axial) α−protons are similar. The question arises whether the cobalt ion is bonded to the axial or equatorial position of the nitrogen atom. The chair conformer can exist in axial (A) and equatorial (E) forms.

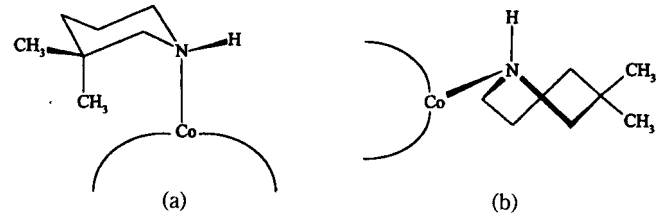


A conformer



E conformer

Since equatorial and axial α−protons in the A conformer are in equivalent steric positions with respect to the nitrogen lone pair,[19] they should exhibit the same isotropic shifts when the A conformer is coordinated to **2**. On the other hand, equatorial and axial α−protons are not equivalent in the E conformer. The fact that the peaks from the equatorial and axial α−protons in the D_2O spectrum are



(a) (b)

Figure 5. (a) The E form of the chair conformer and (b) the twist conformer coordinated to $SiW_{11}Co$.

separated by 28 ppm indicates that the coordinated piperidine exists as the E conformer (Figure 5).

It is quite surprising that the coordinated **1** has the E conformer, although it is slightly more stable than the A conformer for free piperidine.[20] The A conformer, if coordinated to **2**, would be directed away from **2**, while the E conformer, especially its axial methyl group, comes close to the surface of **2**. The A conformer would be preferred, if there were a repulsive interaction between the methyl group and the surface of **2**. However, the following observations suggest that there is an attractive interaction between them. The piperidine ring of **1** coordinated to **2** in D_2O is frozen even at room temperature, while the free ligand undergoes rapid inversion. On the other hand, piperidine coordinated to **2** is in rapid equilibrium between two chair conformers.[21] It is probable that the axial methyl group in **1** forms a weak hydrogen bond with a bridging oxygen atom in **2**.[22]

When D_2O is replaced by DMSO-d_6, 6-H peaks are shifted upfield by less than 10 ppm, but 2-H peaks are shifted upfield by 48 and 69 ppm. In the DMSO-d_6 spectrum 2-H_e and 2-H_a peaks are separated by less than 7 ppm, while 6-H_e and 6-H_a peaks are separated by more than 30 ppm. These observations, suggesting that 2-H_e and 2-H_a are in similar steric positions with respect to the Co-N bond and that 6-H_e and 6-H_a are not, cannot be explained in terms of either the E or A form of the chair conformer. The chemical shifts can be similar for 2-H_e and 2-H_a and quite different for 6-H_e and 6-H_a, only when the ligand is in a boat or a twist conformer. For free piperidine the boat form corresponds to a transition state and the twist form to a potential energy minimum.[23] So it is more likely that the ligand has a twist form in DMSO-d_6 (Figure 5).

The question arises why **1** coordinated to **2** has different conformations in D_2O and DMSO-d_6. We speculate that the hydrophobic side of the piperidine ring in D_2O moves away from the solvent toward the surface of $SiW_{11}Co$. It is probable that a weak hydrogen bond between the axial methyl group and a bridging oxygen atom in $SiW_{11}Co$ stabilizes the E form of the chair conformer. On the other hand, the piperidine ring in DMSO-d_6 may be more stable when surrounded by the solvent molecules. Now the axial methyl group destabilizes the chair form causing conversion to the twist form, in which the two methyl groups can be accommodated in the axis position.

The isotropic NMR shifts in a paramagnetic system contain contact and pseudocontact contributions. Since the pseudocontact shifts arise from through-space dipolar interactions between the electronic and nuclear moments,[24] they can provide detailed information about the conformation of the ligand. Unfortunately, it has not been possible to separate the isotropic shifts into contact and pseudocontact

contributions for our system. More work is needed to extract detailed conformational information from our NMR data.

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17. Our unpublished results. (2-H_e+6-H_e), 6-H_a, 2-H_a, and 4-H_a peaks are resolved for free 3-methylpiperidine, and 2-H_e, 2-H_a, 3-H_e, and 3-H_a peaks are resolved for free 4-methylpiperidine. Thus, the corresponding peaks in the spectra of the $SiW_{11}Co$ complexes can be identified by saturation transfer technique.
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Approximate Nonrandom Two-Fluid Lattice-Hole Theory. General Derivation and Description of Pure Fluids

Ki-Pung Yoo*, Hun Yong Shin, and Chul Soo Lee†

Department of Chemical Engineering, Sogang University, Seoul 121-742, Korea
†Department of Chemical Engineering, Korea University, Seoul 136-701, Korea
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An approximate molecular theory of classical fluids based on the nonrandom lattice statistical-mechanical theory is presented. To obtain configurational Helmholtz free energy and equation of state (EOS), the lattice-hole theory of the Guggenheim combinatorics is approximated by introducing the nonrandom two-fluid theory. The approximate nature in the derivation makes the model possible to unify the classical lattice-hole theory and to describe correctly the configurational properties of real fluids including macromolecules. The theory requires only two molecular parameters for a pure fluid. Results obtained to date have demonstrated that the model correlates quantitatively the first- and second-order thermodynamic properties of real fluids. The basic simplicity of the model can readily be generalized to multicomponent systems. The model is especially relevant to (multi) phase equilibria of systems containing molecularly complex species.

Introduction

Knowledge of phase equilibria is essential for the understanding of various phenomena occurring in nature and industrial processes. Investigation of these equilibria, especially in multicomponent systems, is of importance in numerous branches of science and engineering. In principle a single volumetric equation of state (EOS) is sufficient for des-