Supporting Information

Solution Structures of Lithium Enolates, Phenolates, Carboxylates, and Alkoxides in the Presence of *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine: A Prevalence of Cyclic Dimers

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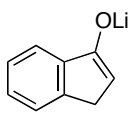
X_A = the mole fraction of enolate subunits **A**

X_B = the mole fraction of enolate subunits **B**

ϕ_n = a measure of the relative stability for an aggregate with *n* subunits of **A**

ϕ_{Nn} = a measure of the relative stability for an aggregate with *N* total subunits and with *n* subunits of **A**

RMS = the root mean square of the sum of the squares of the residuals



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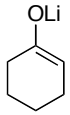

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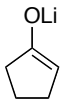

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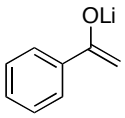

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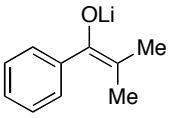

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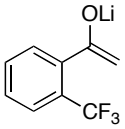

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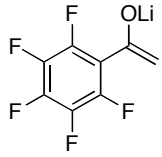

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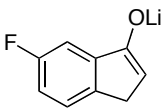

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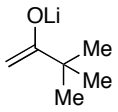

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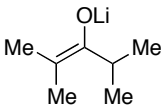

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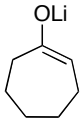

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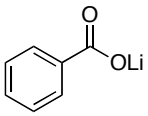

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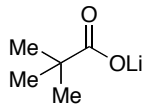

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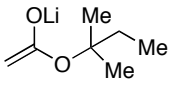

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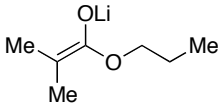

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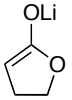

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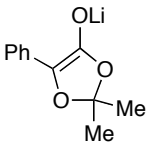

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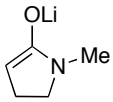

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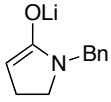

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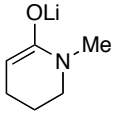

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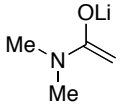

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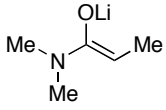

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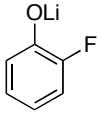

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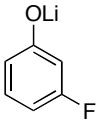

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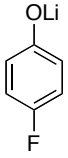

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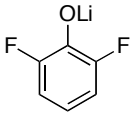

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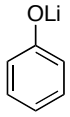

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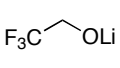

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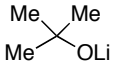

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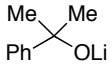

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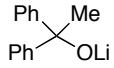

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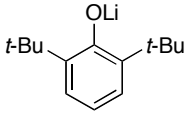

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I. Combinations of O-lithiated Species in TMEDA. S5

II. Job Plots.

For a full list of Job Plots and their corresponding page numbers, please refer to pages S5-S7.

III. Residual Plots.

a. Job plot of [^{6}Li]**1** and [^{6}Li]**7** fit to an ensemble of **A_2-AB-B** and **A_2-AB-B_4**. S44

b. Job plot of [^{6}Li]**1** and [^{6}Li]**13** fit to an ensemble of **A_2-AB-B** and **A_2-AB-B_4**. S45

c. Job plot of [^{6}Li]**34** and [^{6}Li]**1** fit to an ensemble of **A_2-AB-B** and **A_2-AB-B_4**. S46

IV. ^{13}C NMR Spectra.

a. ^{13}C NMR spectra of [^{6}Li]**13** in 0.24 M TMEDA/toluene showing free and bound TMEDA. S47

b. ^{13}C NMR spectra of [^{6}Li]**28** in 0.24 M TMEDA/toluene showing free and bound TMEDA. S48

c. ^{13}C NMR spectra of [^{6}Li]**15** in 0.24 M TMEDA/toluene showing free and bound TMEDA. S49

V. Alkoxides Studies.

a. [^{6}Li]**35** and [^{6}Li]**34** in 0.24 M TMEDA/toluene. S50

b. [^{6}Li]**34** and [^{6}Li]**36** in 0.24 M TMCDA/toluene. S51

c. [^{6}Li]**34** and [^{6}Li]**36** in neat toluene. S52

d. [^{6}Li]**34** and [^{6}Li]**36** in 0.24 M DMEA / toluene. S53

VI. Hindered Phenolate Studies.

a. Spectrum of [^{6}Li]**38** and [^{6}Li]**1**. S54

b. Spectrum of [^{6}Li]**38** and [^{6}Li]**36**. S54

I. Combinations of O-lithiated species in TMEDA.

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	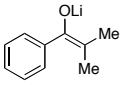	S9	Dimers	Yes
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	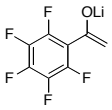	S11	Dimers	Yes
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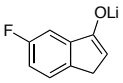
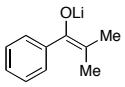
		S13	Dimers	Heteroaggregate Favored
		S14	Dimers	Yes
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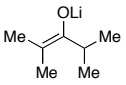
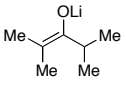
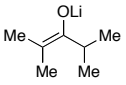
		S16	Dimers	Heteroaggregate Favored
		S17	Dimers	Yes
		S18	Dimers	Yes
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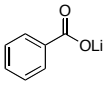
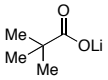
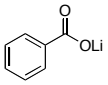
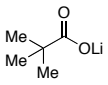
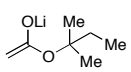
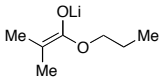
		S20	Dimers	Heteroaggregate Favored

		S21	Dimers	Heteroaggregate Favored
		S22	Dimers	Yes
		S23	Dimers	Yes
		S24	Dimers	Yes
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	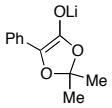	S26	Dimers	Yes
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		S28	Dimers	Yes
		S29	Dimers	Yes
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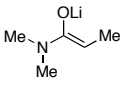
		S31	Dimers	Yes
		S32	Dimers	Yes
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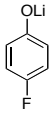
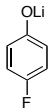
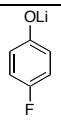
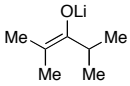
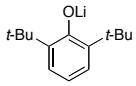
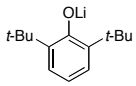
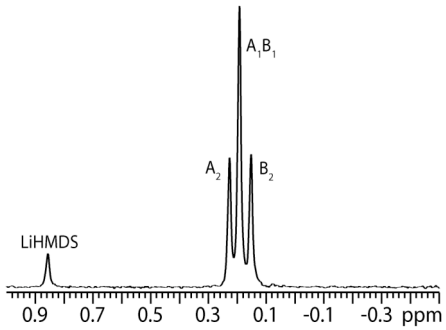
		S34	Dimers	Yes

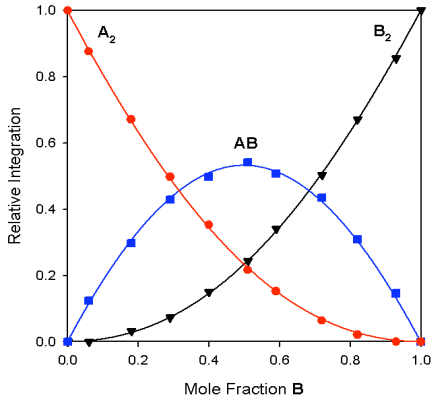
		S35	Dimers	Yes
		S36	Dimers	Heteroaggregate Favored
		S37	Dimers	Yes
		S38	Dimers	Yes
		S39	Dimers	Yes
		S40	**A** = Higher oligomer **B** = Dimer	Homoaggregate Favored
		S41	**A** = Higher oligomer **B** = Dimer	Homoaggregate Favored
		S42-43	Higher oligomers	Homoaggregate Slightly Favored
		S50	Higher oligomers	--
		S54	**A** = Monomer **B** =Dimer	--
		S54	**A** = Monomer **B** = Higher oligomer	--

II. Job Plots in TMEDA.

i.



ii.

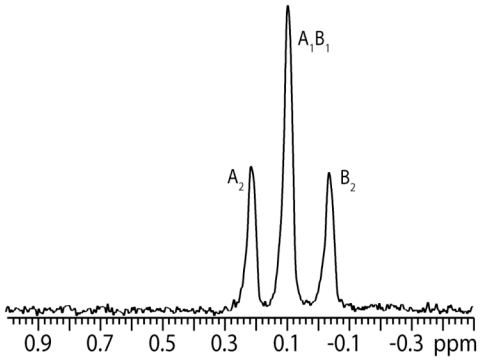


iii.

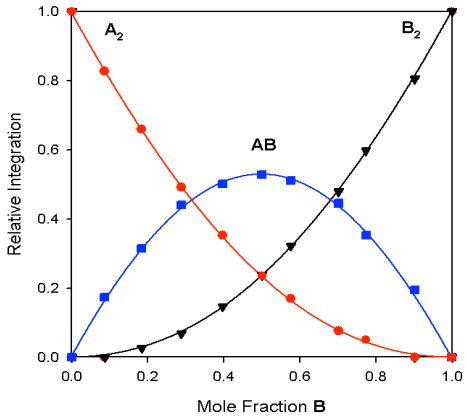
Calc. X_B	**A**$_2$	**A**$_1$**B**$_1$	**B**$_2$
0.00	1.00	0.00	0.00
0.06	0.88	0.12	0.00
0.18	0.67	0.30	0.03
0.29	0.50	0.43	0.07
0.40	0.35	0.50	0.15
0.51	0.22	0.54	0.24
0.59	0.15	0.51	0.34
0.72	0.06	0.43	0.50
0.82	0.02	0.31	0.67
0.93	0.00	0.15	0.85
1.00	0.00	0.00	1.00

i. ^{6}Li NMR spectrum of a 50:50 mixture of [^{6}Li]**1** (**A**) and [^{6}Li]**7** (**B**) in 0.24 M TMEDA/toluene at -50 °C. **ii.** Plot of the relative integration versus the mole fraction of **7** (**B**) for a mixture of [^{6}Li]**1** (**A**) and [^{6}Li]**7** (**B**) $\phi_0 = 0.88$; $\phi_1 = 1.00$; $\phi_2 = 0.88$; RMS = 0.006. **iii.** Relative integrations for aggregates in a mixture of **1** (**A**) and **7** (**B**) at various mole fractions of **A** and **B.**

i.



ii.

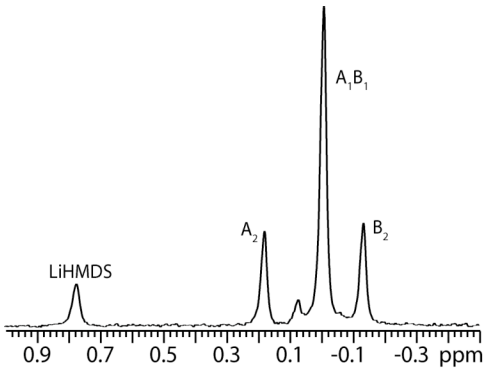


iii.

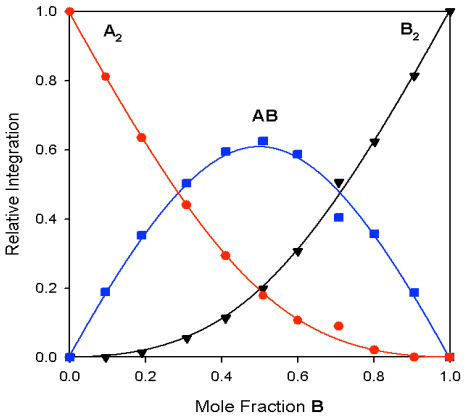
Calc. X_B	$\mathbf{A}_2$	$\mathbf{A}_1\mathbf{B}_1$	$\mathbf{B}_2$
0.00	1.00	0.00	0.00
0.09	0.81	0.19	0.00
0.18	0.63	0.35	0.01
0.29	0.44	0.50	0.06
0.40	0.29	0.59	0.11
0.50	0.18	0.63	0.20
0.58	0.11	0.59	0.31
0.70	0.09	0.40	0.51
0.77	0.02	0.36	0.62
0.90	0.00	0.19	0.81
1.00	0.00	0.00	1.00

i. ^{6}Li NMR spectrum of a 50:50 mixture of [^{6}Li]**1** (**A**) and [^{6}Li]**8** (**B**) in 0.24 M TMEDA/toluene at -90 °C. **ii.** Plot of the relative integration versus the mole fraction of **8** (**B**) for a mixture of [^{6}Li]**1** (**A**) and [^{6}Li]**8** (**B**) $\phi_0 = 0.89$; $\phi_1 = 1.00$; $\phi_2 = 0.89$; RMS = 0.01. **iii.** Relative integrations for aggregates in a mixture of **1** (**A**) and **8** (**B**) at various mole fractions of **A** and **B**.

i.



ii.

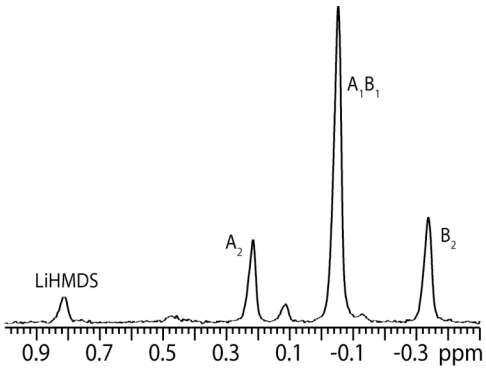


iii.

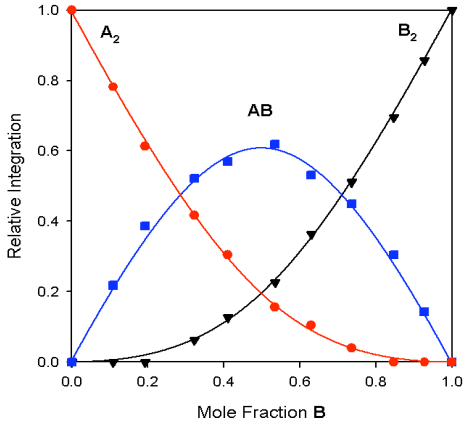
Calc. X_B	$\mathbf{A}_2$	$\mathbf{A}_1\mathbf{B}_1$	$\mathbf{B}_2$
0.00	1.00	0.00	0.00
0.10	0.81	0.19	0.00
0.19	0.63	0.35	0.01
0.31	0.44	0.50	0.06
0.41	0.29	0.59	0.11
0.51	0.18	0.63	0.20
0.60	0.11	0.59	0.31
0.71	0.09	0.40	0.51
0.80	0.02	0.36	0.62
0.91	0.00	0.19	0.81
1.00	0.00	0.00	1.00

i. ^{6}Li NMR spectrum of a 50:50 mixture of [^{6}Li]**1** (**A**) and [^{6}Li]**9** (**B**) in 0.24 M TMEDA/toluene at -90 °C. **ii.** Plot of the relative integration versus the mole fraction of **9** (**B**) for a mixture of [^{6}Li]**1** (**A**) and [^{6}Li]**9** (**B**) $\phi_0 = 0.64$; $\phi_1 = 1.00$; $\phi_2 = 0.64$; RMS = 0.02. **iii.** Relative integrations for aggregates in a mixture of **1** (**A**) and **9** (**B**) at various mole fractions of **A** and **B**.

i.



ii.

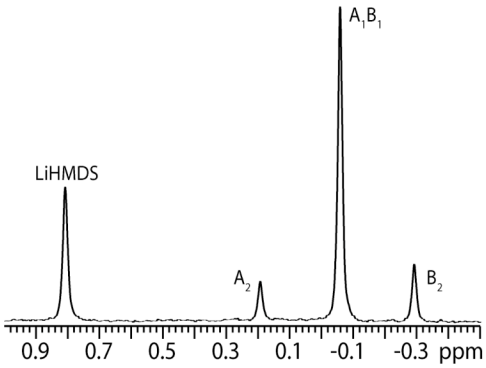


iii.

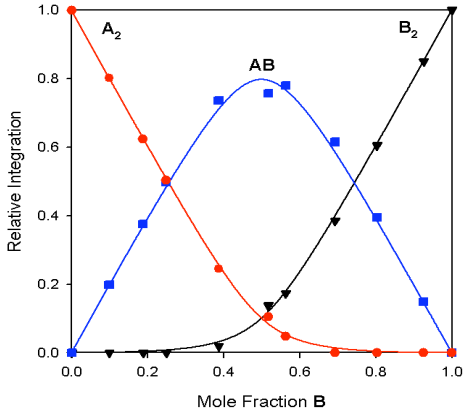
Calc. X_B	$\mathbf{A}_2$	$\mathbf{A}_1\mathbf{B}_1$	$\mathbf{B}_2$
0.00	1.00	0.00	0.00
0.11	0.78	0.22	0.00
0.19	0.61	0.39	0.00
0.32	0.42	0.52	0.06
0.41	0.30	0.57	0.13
0.54	0.16	0.62	0.23
0.63	0.10	0.53	0.36
0.74	0.04	0.45	0.51
0.85	0.00	0.31	0.70
0.93	0.00	0.14	0.86
1.00	0.00	0.00	1.00

i. ^{6}Li NMR spectrum of a 50:50 mixture of [^{6}Li]**1** (**A**) and [^{6}Li]**10** (**B**) in 0.24 M TMEDA/toluene at -90 °C. **ii.** Plot of the relative integration versus the mole fraction of **10** (**B**) for a mixture of [^{6}Li]**1** (**A**) and [^{6}Li]**10** (**B**) $\phi_0 = 0.64$; $\phi_1 = 1.00$; $\phi_2 = 0.64$; RMS = 0.01. **iii.** Relative integrations for aggregates in a mixture of **1** (**A**) and **10** (**B**) at various mole fractions of **A** and **B**.

i.



ii.

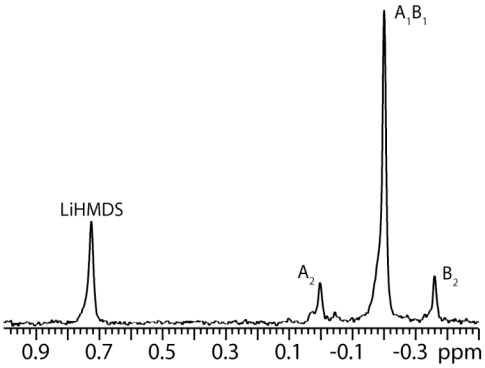


iii.

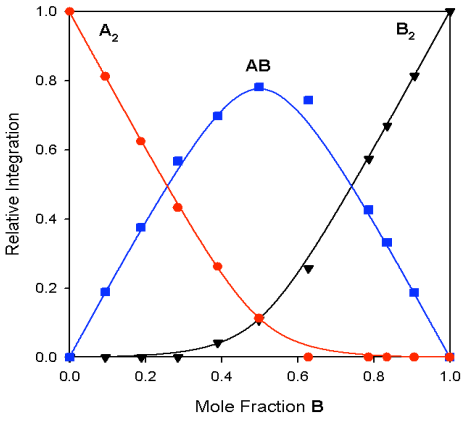
Calc. X_B	$\mathbf{A}_2$	$\mathbf{A}_1\mathbf{B}_1$	$\mathbf{B}_2$
0.00	1.00	0.00	0.00
0.10	0.80	0.20	0.00
0.19	0.62	0.38	0.00
0.25	0.50	0.50	0.00
0.39	0.25	0.74	0.02
0.52	0.11	0.76	0.14
0.56	0.05	0.78	0.17
0.69	0.00	0.62	0.39
0.80	0.00	0.40	0.61
0.93	0.00	0.15	0.85
1.00	0.00	0.00	1.00

i. ^{6}Li NMR spectrum of a 50:50 mixture of [^{6}Li]**1** (**A**) and [^{6}Li]**12** (**B**) in 0.24 M TMEDA/toluene at -90 °C. **ii.** Plot of the relative integration versus the mole fraction of **12** (**B**) for a mixture of [^{6}Li]**1** (**A**) and [^{6}Li]**12** (**B**) $\phi_0 = 0.76$; $\phi_1 = 3.00$; $\phi_2 = 0.76$; RMS = 0.01. **iii.** Relative integrations for aggregates in a mixture of **1** (**A**) and **12** (**B**) at various mole fractions of **A** and **B**.

i.



ii.

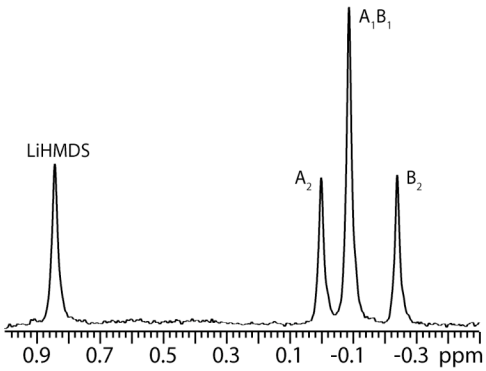


iii.

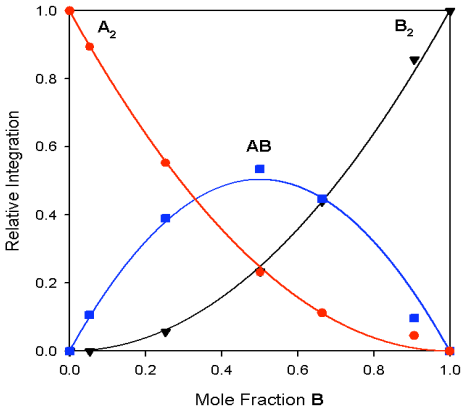
Calc. X_B	$\mathbf{A}_2$	$\mathbf{A}_1\mathbf{B}_1$	$\mathbf{B}_2$
0.00	1.00	0.00	0.00
0.09	0.81	0.19	0.00
0.19	0.62	0.38	0.00
0.28	0.43	0.57	0.00
0.39	0.26	0.70	0.04
0.50	0.11	0.78	0.11
0.63	0.00	0.74	0.26
0.79	0.00	0.43	0.57
0.84	0.00	0.33	0.67
0.91	0.00	0.19	0.81
1.00	0.00	0.00	1.00

i. ^{6}Li NMR spectrum of a 50:50 mixture of [^{6}Li]**11** (**A**) and [^{6}Li]**12** (**B**) in 0.24 M TMEDA/toluene at -90 °C. **ii.** Plot of the relative integration versus the mole fraction of **12** (**B**) for a mixture of [^{6}Li]**11** (**A**) and [^{6}Li]**12** (**B**) $\phi_0 = 0.87$; $\phi_1 = 3.00$; $\phi_2 = 0.87$; RMS = 0.07. **iii.** Relative integrations for aggregates in a mixture of **11** (**A**) and **12** (**B**) at various mole fractions of **A** and **B**.

i.



ii.

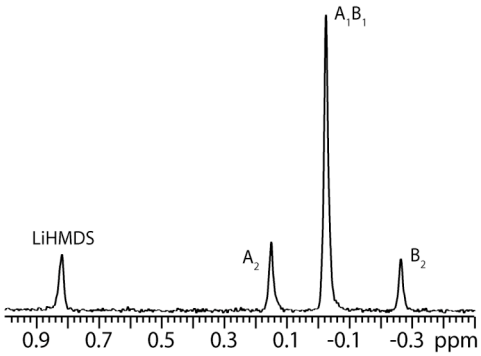


iii.

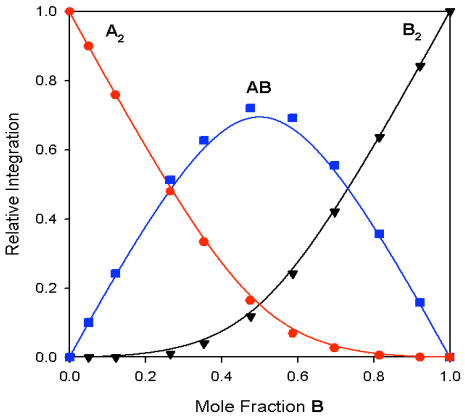
Calc. X_B	$\mathbf{A}_2$	$\mathbf{A}_1\mathbf{B}_1$	$\mathbf{B}_2$
0.00	1.00	0.00	0.00
0.05	0.89	0.11	0.00
0.25	0.55	0.39	0.06
0.50	0.23	0.54	0.23
0.66	0.11	0.45	0.44
0.91	0.05	0.10	0.86
1.00	0.00	0.00	1.00

i. ^{6}Li NMR spectrum of a 50:50 mixture of [^{6}Li]**8** (**A**) and [^{6}Li]**12** (**B**) in 0.24 M TMEDA/toluene at -90 °C. **ii.** Plot of the relative integration versus the mole fraction of **12** (**B**) for a mixture of [^{6}Li]**8** (**A**) and [^{6}Li]**12** (**B**) $\phi_0 = 0.93$; $\phi_1 = 1.00$; $\phi_2 = 0.93$; RMS = 0.02. **iii.** Relative integrations for aggregates in a mixture of **8** (**A**) and **12** (**B**) at various mole fractions of **A** and **B**.

i.



ii.

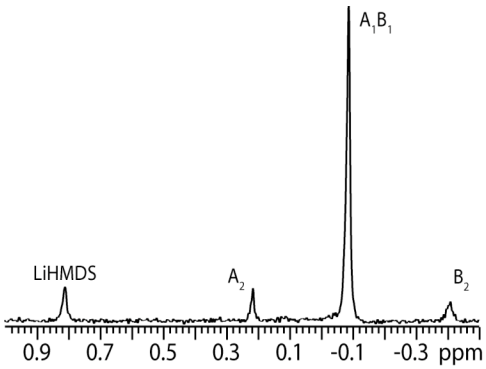


iii.

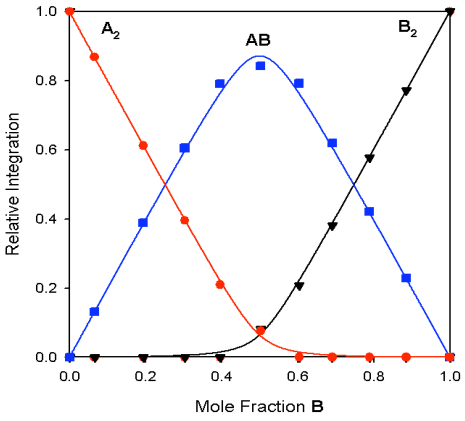
Calc. X_B	$\mathbf{A}_2$	$\mathbf{A}_1\mathbf{B}_1$	$\mathbf{B}_2$
0.00	1.00	0.00	0.00
0.05	0.90	0.10	0.00
0.12	0.76	0.24	0.00
0.27	0.48	0.51	0.01
0.35	0.33	0.63	0.04
0.48	0.16	0.72	0.12
0.59	0.07	0.69	0.24
0.70	0.03	0.55	0.42
0.82	0.01	0.36	0.64
0.92	0.00	0.16	0.84
1.00	0.00	0.00	1.00

i. ^{6}Li NMR spectrum of a 50:50 mixture of [^{6}Li]**7** (**A**) and [^{6}Li]**12** (**B**) in 0.24 M TMEDA/toluene at -90 °C. **ii.** Plot of the relative integration versus the mole fraction of **12** (**B**) for a mixture of [^{6}Li]**7** (**A**) and [^{6}Li]**12** (**B**) ϕ_0 = 1.32; ϕ_1 = 3.00; ϕ_2 = 1.32; RMS = 0.04. **iii.** Relative integrations for aggregates in a mixture of **7** (**A**) and **12** (**B**) at various mole fractions of **A** and **B**.

i.



ii.

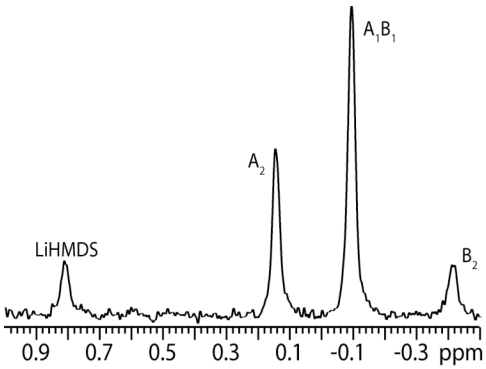


iii.

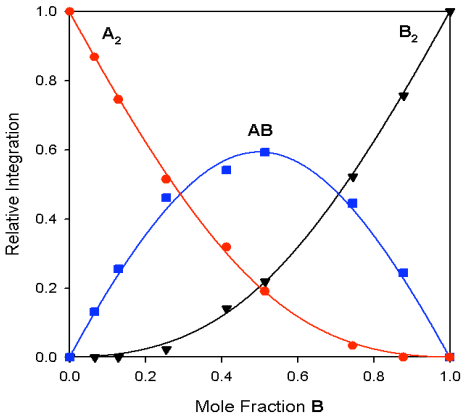
Calc. X_B	$\mathbf{A}_2$	$\mathbf{A}_1\mathbf{B}_1$	$\mathbf{B}_2$
0.00	1.00	0.00	0.00
0.07	0.87	0.13	0.00
0.20	0.61	0.39	0.00
0.30	0.40	0.61	0.00
0.40	0.21	0.79	0.00
0.50	0.08	0.84	0.08
0.60	0.00	0.79	0.21
0.69	0.00	0.62	0.38
0.79	0.00	0.42	0.58
0.89	0.00	0.23	0.77
1.00	0.00	0.00	1.00

i. ^{6}Li NMR spectrum of a 50:50 mixture of [^{6}Li]**1** (**A**) and [^{6}Li]**13** (**B**) in 0.24 M TMEDA/toluene at -90 °C. **ii.** Plot of the relative integration versus the mole fraction of **13** (**B**) for a mixture of [^{6}Li]**1** (**A**) and [^{6}Li]**13** (**B**) $\phi_0 = 0.74$; $\phi_1 = 5.00$; $\phi_2 = 0.74$; RMS = 0.01. **iii.** Relative integrations for aggregates in a mixture of **1** (**A**) and **13** (**B**) at various mole fractions of **A** and **B**.

i.



ii.

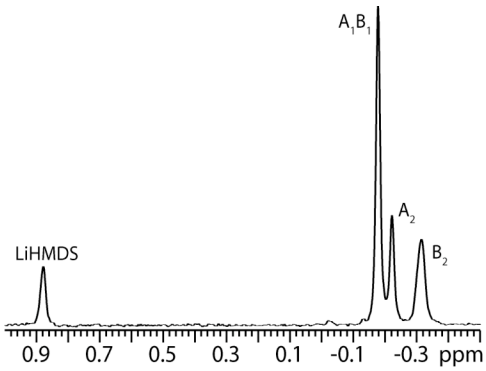


iii.

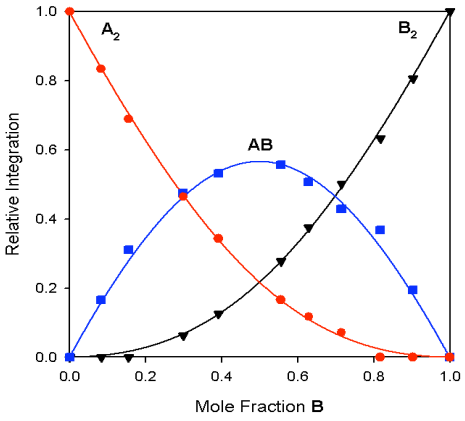
Calc. X_B	$\mathbf{A}_2$	$\mathbf{A}_1\mathbf{B}_1$	$\mathbf{B}_2$
0.00	1.00	0.00	0.00
0.07	0.87	0.13	0.00
0.13	0.75	0.26	0.00
0.25	0.52	0.46	0.02
0.41	0.32	0.54	0.14
0.51	0.19	0.59	0.22
0.75	0.03	0.45	0.52
0.88	0.00	0.24	0.76
1.00	0.00	0.00	1.00

i. ^{6}Li NMR spectrum of a 50:50 mixture of [^{6}Li]**7** (**A**) and [^{6}Li]**13** (**B**) in 0.24 M TMEDA/toluene at -90 °C. **ii.** Plot of the relative integration versus the mole fraction of **13** (**B**) for a mixture of [^{6}Li]**7** (**A**) and [^{6}Li]**13** (**B**) $\phi_0 = 0.69$; $\phi_1 = 1.00$; $\phi_2 = 0.69$; RMS = 0.01. **iii.** Relative integrations for aggregates in a mixture of **7** (**A**) and **13** (**B**) at various mole fractions of **A** and **B**.

i.



ii.

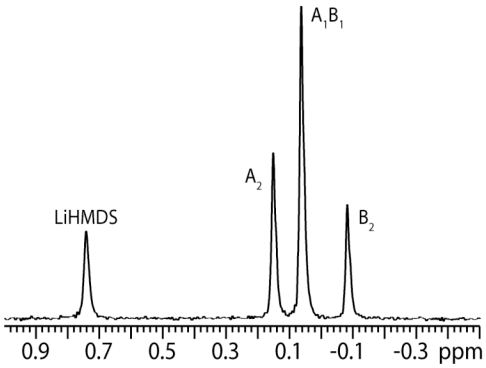


iii.

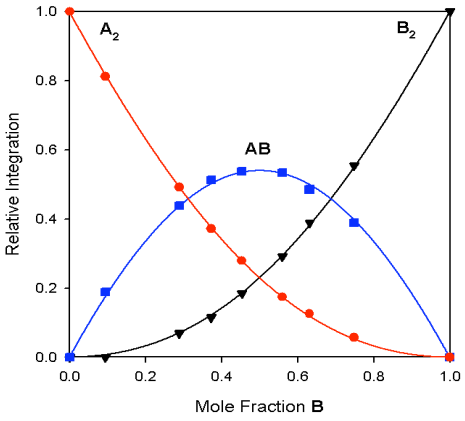
Calc. X_B	$\mathbf{A}_2$	$\mathbf{A}_1\mathbf{B}_1$	$\mathbf{B}_2$
0.00	1.00	0.00	0.00
0.08	0.83	0.17	0.00
0.16	0.69	0.31	0.00
0.30	0.46	0.47	0.06
0.39	0.34	0.53	0.13
0.56	0.17	0.56	0.28
0.63	0.12	0.51	0.38
0.72	0.07	0.43	0.50
0.82	0.00	0.37	0.63
0.90	0.00	0.19	0.81
1.00	0.00	0.00	1.00

i. ^{6}Li NMR spectrum of a 50:50 mixture of [^{6}Li]**12** (**A**) and [^{6}Li]**13** (**B**) in 0.24 M TMEDA/toluene at -90 °C. **ii.** Plot of the relative integration versus the mole fraction of **13** (**B**) for a mixture of [^{6}Li]**12** (**A**) and [^{6}Li]**13** (**B**) $\phi_0 = 0.77$; $\phi_1 = 1.00$; $\phi_2 = 0.77$; RMS = 0.01. **iii.** Relative integrations for aggregates in a mixture of **12** (**A**) and **13** (**B**) at various mole fractions of **A** and **B**.

i.



ii.

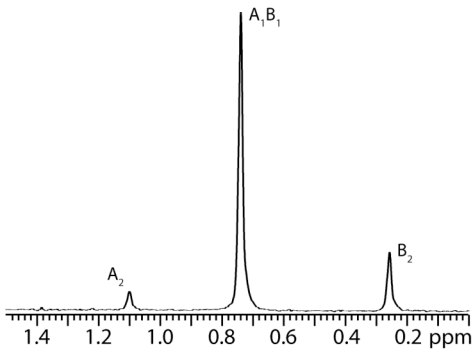


iii.

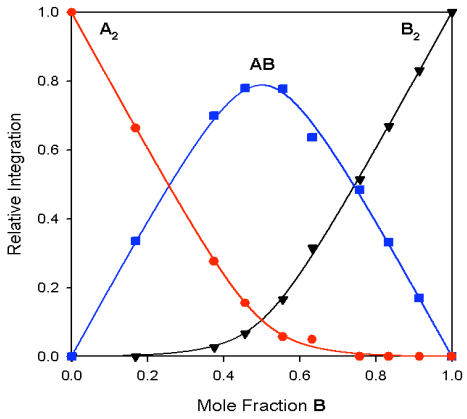
Calc. X_B	$\mathbf{A}_2$	$\mathbf{A}_1\mathbf{B}_1$	$\mathbf{B}_2$
0.00	1.00	0.00	0.00
0.09	0.81	0.19	0.00
0.29	0.49	0.44	0.07
0.37	0.37	0.51	0.12
0.45	0.28	0.54	0.18
0.56	0.17	0.53	0.29
0.63	0.13	0.49	0.39
0.75	0.06	0.39	0.55
1.00	0.00	0.00	1.00

i. ^{6}Li NMR spectrum of a 50:50 mixture of [^{6}Li]**1** (**A**) and [^{6}Li]**14** (**B**) in 0.24 M TMEDA/toluene at -90 °C. **ii.** Plot of the relative integration versus the mole fraction of **14** (**B**) for a mixture of [^{6}Li]**1** (**A**) and [^{6}Li]**14** (**B**) $\phi_0 = 0.85$; $\phi_1 = 1.00$; $\phi_2 = 0.85$; RMS = 0.01. **iii.** Relative integrations for aggregates in a mixture of **1** (**A**) and **14** (**B**) at various mole fractions of **A** and **B**.

i.



ii.

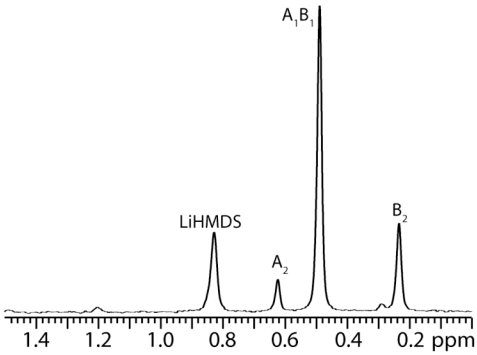


iii.

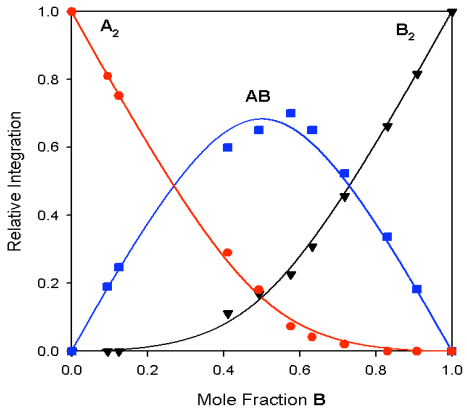
Calc. X_B	$\mathbf{A}_2$	$\mathbf{A}_1\mathbf{B}_1$	$\mathbf{B}_2$
0.00	1.00	0.00	0.00
0.17	0.66	0.34	0.00
0.38	0.28	0.70	0.03
0.46	0.16	0.78	0.07
0.56	0.06	0.78	0.17
0.63	0.05	0.64	0.32
0.76	0.00	0.49	0.52
0.83	0.00	0.33	0.67
0.92	0.00	0.17	0.83
1.00	0.00	0.00	1.00

i. ^{6}Li NMR spectrum of a 50:50 mixture of [^{6}Li]**15** (**A**) and [^{6}Li]**1** (**B**) in 0.24 M TMEDA/toluene at -78 °C. **ii.** Plot of the relative integration versus the mole fraction of **1** (**B**) for a mixture of [^{6}Li]**15** (**A**) and [^{6}Li]**1** (**B**) $\phi_0 = 0.81$; $\phi_1 = 3.00$; $\phi_2 = 0.81$; RMS = 0.01. **iii.** Relative integrations for aggregates in a mixture of **15** (**A**) and **1** (**B**) at various mole fractions of **A** and **B**.

i.



ii.

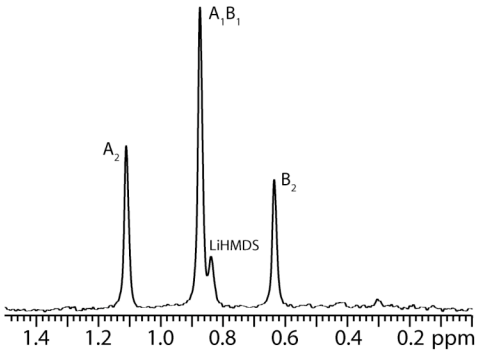


iii.

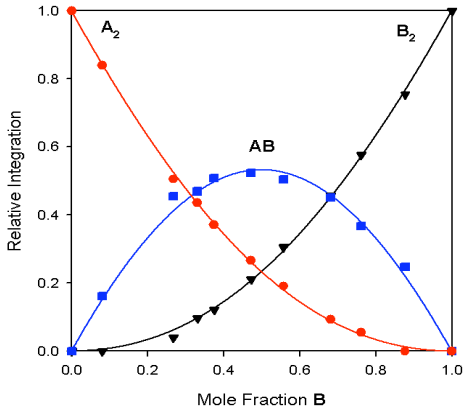
Calc. X_B	$\mathbf{A}_2$	$\mathbf{A}_1\mathbf{B}_1$	$\mathbf{B}_2$
0.00	1.00	0.00	0.00
0.10	0.81	0.19	0.00
0.12	0.75	0.25	0.00
0.41	0.29	0.60	0.11
0.49	0.18	0.65	0.17
0.58	0.07	0.70	0.23
0.63	0.04	0.65	0.31
0.72	0.02	0.52	0.46
0.83	0.00	0.34	0.66
0.91	0.00	0.18	0.82
1.00	0.00	0.00	1.00

i. ^{6}Li NMR spectrum of a 50:50 mixture of [^{6}Li]**16** (**A**) and [^{6}Li]**1** (**B**) in 0.24 M TMEDA/toluene at -90 °C. **ii.** Plot of the relative integration versus the mole fraction of **1** (**B**) for a mixture of [^{6}Li]**16** (**A**) and [^{6}Li]**1** (**B**) ϕ_0 = 1.34; ϕ_1 = 3.00; ϕ_2 = 1.34; RMS = 0.02. **iii.** Relative integrations for aggregates in a mixture of **16** (**A**) and **1** (**B**) at various mole fractions of **A** and **B**.

i.



ii.

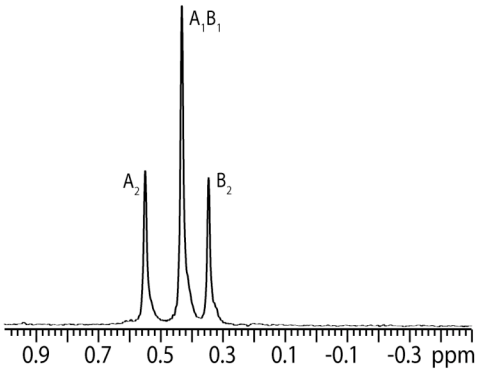


iii.

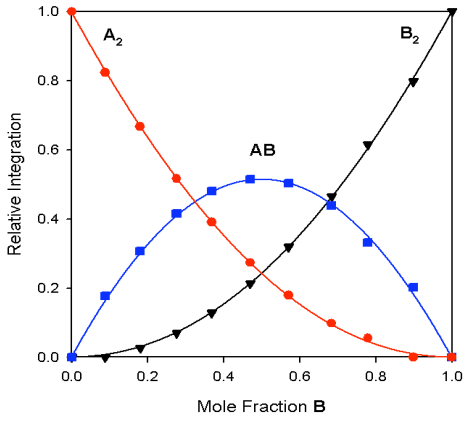
Calc. X_B	$\mathbf{A}_2$	$\mathbf{A}_1\mathbf{B}_1$	$\mathbf{B}_2$
0.00	1.00	0.00	0.00
0.08	0.84	0.16	0.00
0.27	0.51	0.46	0.04
0.33	0.44	0.47	0.10
0.38	0.37	0.51	0.12
0.47	0.27	0.52	0.21
0.56	0.19	0.50	0.31
0.68	0.09	0.45	0.46
0.76	0.06	0.37	0.58
0.88	0.00	0.25	0.75
1.00	0.00	0.00	1.00

i. ^{6}Li NMR spectrum of a 50:50 mixture of [^{6}Li]**15** (**A**) and [^{6}Li]**16** (**B**) in 0.24 M TMEDA/toluene at -78 °C. **ii.** Plot of the relative integration versus the mole fraction of **16** (**B**) for a mixture of [^{6}Li]**15** (**A**) and [^{6}Li]**16** (**B**) ϕ_0 = 0.88; ϕ_1 = 1.00; ϕ_2 = 0.88; RMS = 0.01. **iii.** Relative integrations for aggregates in a mixture of **15** (**A**) and **16** (**B**) at various mole fractions of **A** and **B**.

i.



ii.

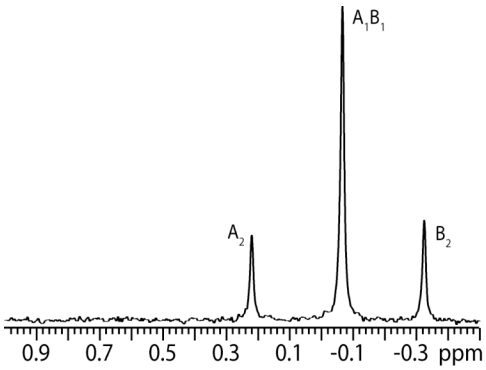


iii.

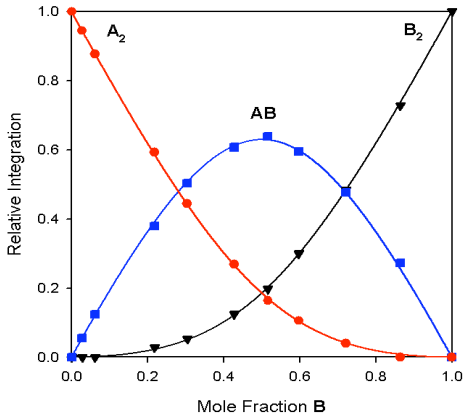
Calc. X_B	$\mathbf{A}_2$	$\mathbf{A}_1\mathbf{B}_1$	$\mathbf{B}_2$
0.00	1.00	0.00	0.00
0.09	0.82	0.18	0.00
0.18	0.67	0.31	0.03
0.28	0.52	0.42	0.07
0.37	0.39	0.48	0.13
0.47	0.27	0.51	0.21
0.57	0.18	0.50	0.32
0.68	0.10	0.44	0.46
0.78	0.06	0.33	0.61
0.90	0.00	0.20	0.80
1.00	0.00	0.00	1.00

II.r. i. ^{6}Li NMR spectrum of a 50:50 mixture of [^{6}Li]**1** (**A**) and [^{6}Li]**17** (**B**) in 3.0 M TMEDA/toluene/pentane and 0.11 M THF at -90 °C. **ii.** Plot of the relative integration versus the mole fraction of **17** (**B**) for a mixture of [^{6}Li]**1** (**A**) and [^{6}Li]**17** (**B**) $\phi_0 = 0.94$; $\phi_1 = 1.00$; $\phi_2 = 0.94$; RMS = 0.01. **iii.** Relative integrations for aggregates in a mixture of **1** (**A**) and **17** (**B**) at various mole fractions of **A** and **B**.

i.



ii.

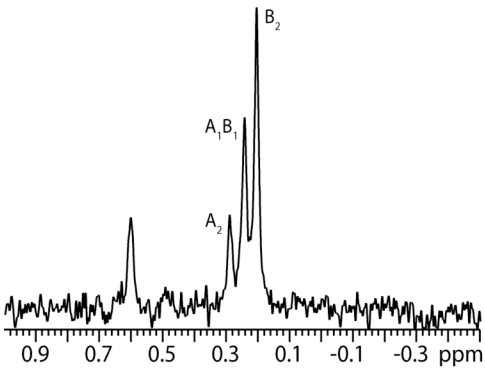


iii.

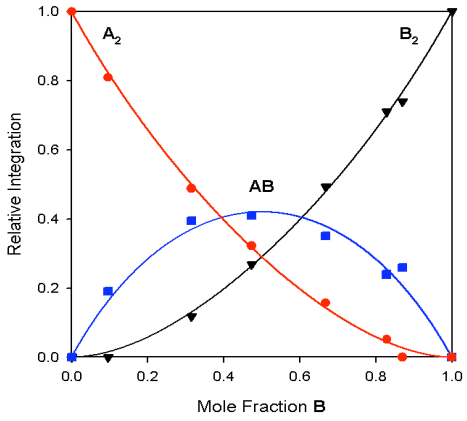
Calc. X_B	$\mathbf{A}_2$	$\mathbf{A}_1\mathbf{B}_1$	$\mathbf{B}_2$
0.00	1.00	0.00	0.00
0.03	0.94	0.06	0.00
0.06	0.88	0.12	0.00
0.22	0.59	0.38	0.03
0.30	0.44	0.50	0.05
0.43	0.27	0.61	0.12
0.52	0.16	0.64	0.20
0.60	0.11	0.60	0.30
0.72	0.04	0.48	0.48
0.86	0.00	0.27	0.73
1.00	0.00	0.00	1.00

i. ^{6}Li NMR spectrum of a 50:50 mixture of [^{6}Li]**1** (**A**) and [^{6}Li]**18** (**B**) in 0.24 M TMEDA/toluene at -90 °C. **ii.** Plot of the relative integration versus the mole fraction of **18** (**B**) for a mixture of [^{6}Li]**1** (**A**) and [^{6}Li]**18** (**B**) $\phi_0 = 0.59$; $\phi_1 = 1.00$; $\phi_2 = 0.59$; RMS = 0.005. **iii.** Relative integrations for aggregates in a mixture of **1** (**A**) and **18** (**B**) at various mole fractions of **A** and **B**.

i.



ii.

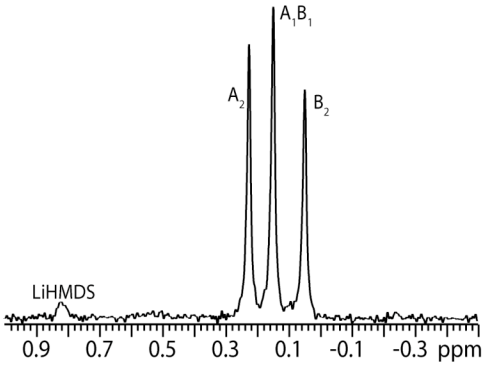


iii.

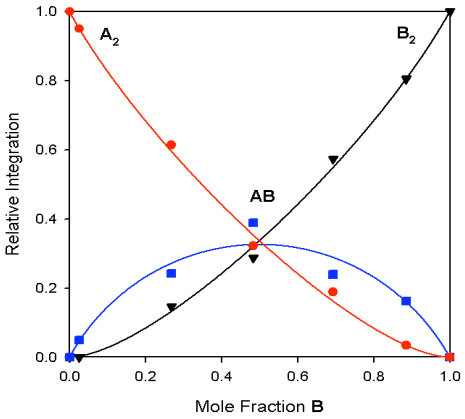
Calc. X_B	$\mathbf{A}_2$	$\mathbf{A}_1\mathbf{B}_1$	$\mathbf{B}_2$
0.00	1.00	0.00	0.00
0.10	0.81	0.19	0.00
0.32	0.49	0.40	0.12
0.47	0.32	0.41	0.27
0.67	0.16	0.35	0.49
0.83	0.05	0.24	0.71
0.87	0.00	0.26	0.74
1.00	0.00	0.00	1.00

i. ^{6}Li NMR spectrum of a 50:50 mixture of [^{6}Li]**19** (**A**) and [^{6}Li]**1** (**B**) in 0.24 M TMEDA/toluene at -90 °C. **ii.** Plot of the relative integration versus the mole fraction of **1** (**B**) for a mixture of [^{6}Li]**19** (**A**) and [^{6}Li]**1** (**B**) ϕ_0 = 1.38; ϕ_1 = 1.00; ϕ_2 = 1.38; RMS = 0.02. **iii.** Relative integrations for aggregates in a mixture of **19** (**A**) and **1** (**B**) at various mole fractions of **A** and **B**.

i.



ii.

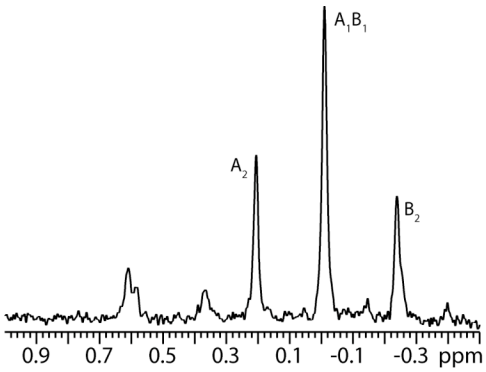


iii.

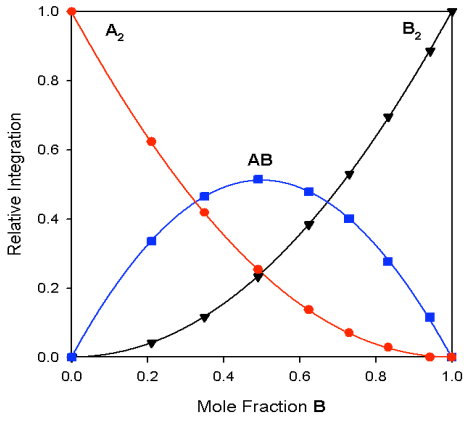
Calc. X_B	$\mathbf{A}_2$	$\mathbf{A}_1\mathbf{B}_1$	$\mathbf{B}_2$
0.00	1.00	0.00	0.00
0.03	0.95	0.05	0.00
0.27	0.61	0.24	0.15
0.48	0.32	0.39	0.29
0.69	0.19	0.24	0.57
0.89	0.03	0.16	0.81
1.00	0.00	0.00	1.00

i. ^{6}Li NMR spectrum of a 50:50 mixture of [^{6}Li]**1** (**A**) and [^{6}Li]**20** (**B**) in 0.24 M TMEDA/toluene at -90 °C. **ii.** Plot of the relative integration versus the mole fraction of **20** (**B**) for a mixture of [^{6}Li]**1** (**A**) and [^{6}Li]**20** (**B**) $\phi_0 = 0.83$; $\phi_1 = 1.00$; $\phi_2 = 0.83$; RMS = 0.03. **iii.** Relative integrations for aggregates in a mixture of **1** (**A**) and **20** (**B**) at various mole fractions of **A** and **B**.

i.



ii.

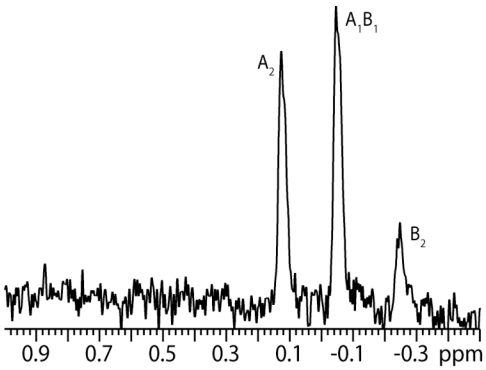


iii.

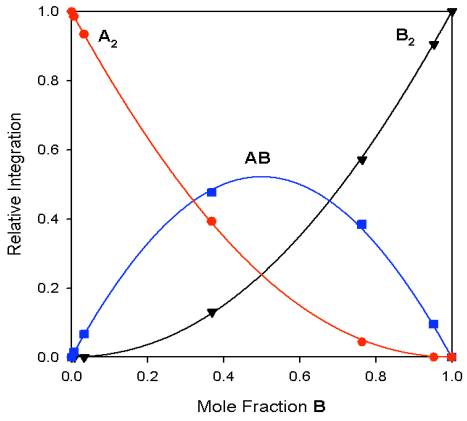
Calc. X_B	$\mathbf{A}_2$	$\mathbf{A}_1\mathbf{B}_1$	$\mathbf{B}_2$
0.00	1.00	0.00	0.00
0.00	1.00	0.00	0.00
0.00	1.00	0.00	0.00
0.21	0.62	0.34	0.04
0.35	0.42	0.47	0.12
0.49	0.25	0.51	0.23
0.62	0.14	0.48	0.38
0.73	0.07	0.40	0.53
0.83	0.03	0.28	0.70
0.94	0.00	0.12	0.89
1.00	0.00	0.00	1.00

i. ^{6}Li NMR spectrum of a 50:50 mixture of [^{6}Li]**1** (**A**) and [^{6}Li]**21** (**B**) in 0.24 M TMEDA/toluene at -90 °C. **ii.** Plot of the relative integration versus the mole fraction of **21** (**B**) for a mixture of [^{6}Li]**1** (**A**) and [^{6}Li]**21** (**B**) $\phi_0 = 0.95$; $\phi_1 = 1.00$; $\phi_2 = 0.95$; RMS = 0.002. **iii.** Relative integrations for aggregates in a mixture of **1** (**A**) and **21** (**B**) at various mole fractions of **A** and **B**.

i.



ii.

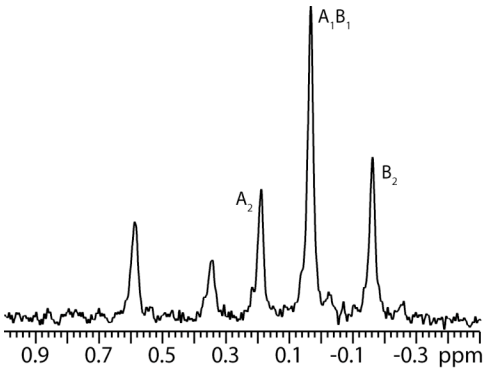


iii.

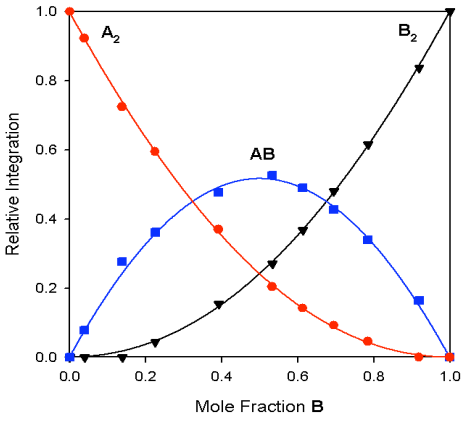
Calc. X_B	$\mathbf{A}_2$	$\mathbf{A}_1\mathbf{B}_1$	$\mathbf{B}_2$
0.00	1.00	0.00	0.00
0.01	0.99	0.02	0.00
0.03	0.93	0.07	0.00
0.37	0.39	0.48	0.13
0.76	0.04	0.38	0.57
0.95	0.00	0.10	0.91
1.00	0.00	0.00	1.00

i. ^{6}Li NMR spectrum of a 50:50 mixture of [^{6}Li]**7** (**A**) and [^{6}Li]**21** (**B**) in 0.24 M TMEDA/toluene at -90 °C. **ii.** Plot of the relative integration versus the mole fraction of **21** (**B**) for a mixture of [^{6}Li]**7** (**A**) and [^{6}Li]**21** (**B**) $\phi_0 = 0.92$; $\phi_1 = 1.00$; $\phi_2 = 0.92$; RMS = 0.004. **iii.** Relative integrations for aggregates in a mixture of **7** (**A**) and **21** (**B**) at various mole fractions of **A** and **B**.

i.



ii.

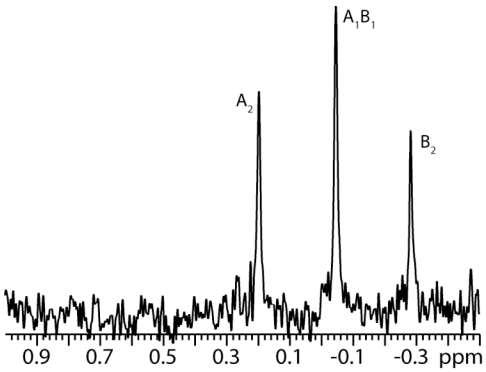


iii.

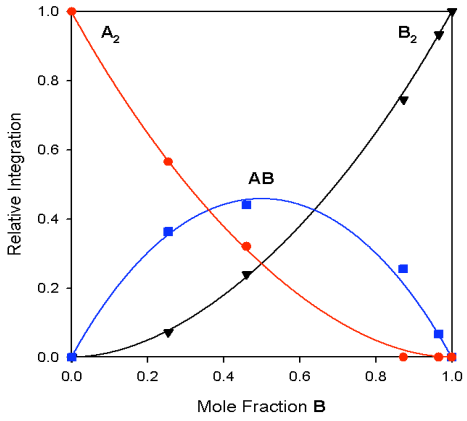
Calc. X_B	$\mathbf{A}_2$	$\mathbf{A}_1\mathbf{B}_1$	$\mathbf{B}_2$
0.00	1.00	0.00	0.00
0.04	0.92	0.08	0.00
0.14	0.72	0.28	0.00
0.23	0.60	0.36	0.04
0.39	0.37	0.48	0.15
0.53	0.20	0.53	0.27
0.61	0.14	0.49	0.37
0.69	0.09	0.43	0.48
0.79	0.05	0.34	0.62
0.92	0.00	0.16	0.84
1.00	0.00	0.00	1.00

i. ^{6}Li NMR spectrum of a 50:50 mixture of [^{6}Li]**1** (**A**) and [^{6}Li]**22** (**B**) in 0.24 M TMEDA/toluene at -90 °C. **ii.** Plot of the relative integration versus the mole fraction of **22** (**B**) for a mixture of [^{6}Li]**1** (**A**) and [^{6}Li]**22** (**B**) $\phi_0 = 0.94$; $\phi_1 = 1.00$; $\phi_2 = 0.94$; RMS = 0.01. **iii.** Relative integrations for aggregates in a mixture of **1** (**A**) and **22** (**B**) at various mole fractions of **A** and **B**.

i.



ii.

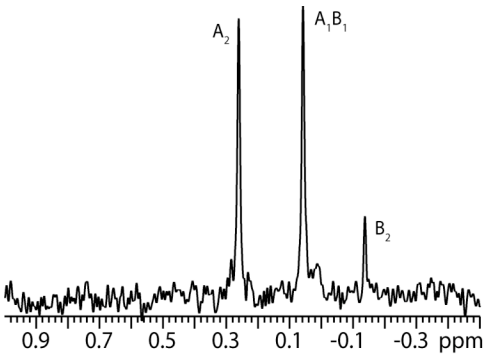


iii.

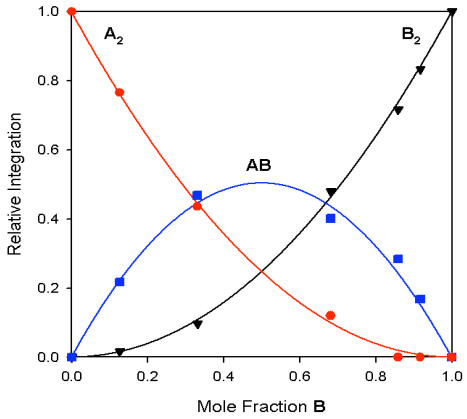
Calc. X_B	$\mathbf{A}_2$	$\mathbf{A}_1\mathbf{B}_1$	$\mathbf{B}_2$
0.00	1.00	0.00	0.00
0.25	0.57	0.36	0.07
0.46	0.32	0.44	0.24
0.87	0.00	0.26	0.75
0.97	0.00	0.07	0.93
1.00	0.00	0.00	1.00

i. ^{6}Li NMR spectrum of a 50:50 mixture of [^{6}Li]**1** (**A**) and [^{6}Li]**23** (**B**) in 0.24 M TMEDA/toluene at -90 °C. **ii.** Plot of the relative integration versus the mole fraction of **23** (**B**) for a mixture of [^{6}Li]**1** (**A**) and [^{6}Li]**23** (**B**) ϕ_0 = 1.18; ϕ_1 = 1.00; ϕ_2 = 1.18; RMS = 0.01. **iii.** Relative integrations for aggregates in a mixture of **1** (**A**) and **23** (**B**) at various mole fractions of **A** and **B**.

i.



ii.

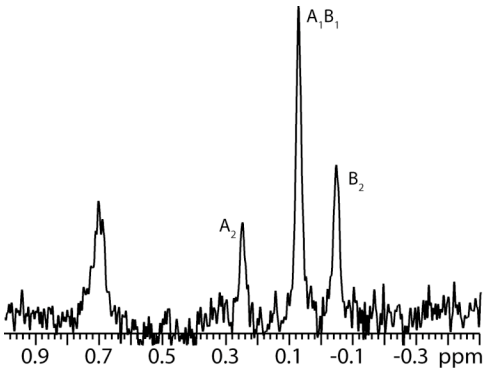


iii.

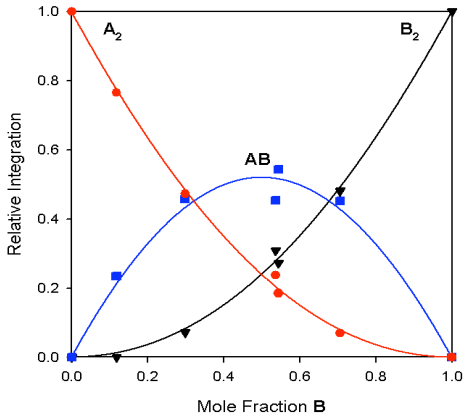
Calc. X_B	$\mathbf{A}_2$	$\mathbf{A}_1\mathbf{B}_1$	$\mathbf{B}_2$
0.00	1.00	0.00	0.00
0.13	0.77	0.22	0.02
0.33	0.44	0.47	0.10
0.68	0.12	0.40	0.48
0.86	0.00	0.28	0.72
0.92	0.00	0.17	0.83
1.00	0.00	0.00	1.00

i. ^{6}Li NMR spectrum of a 50:50 mixture of [^{6}Li]**1** (**A**) and [^{6}Li]**24** (**B**) in 0.24 M TMEDA/toluene at -60 °C. **ii.** Plot of the relative integration versus the mole fraction of **24** (**B**) for a mixture of [^{6}Li]**1** (**A**) and [^{6}Li]**24** (**B**) $\phi_0 = 0.98$; $\phi_1 = 1.00$; $\phi_2 = 0.98$; RMS = 0.01. **iii.** Relative integrations for aggregates in a mixture of **1** (**A**) and **24** (**B**) at various mole fractions of **A** and **B**.

i.



ii.

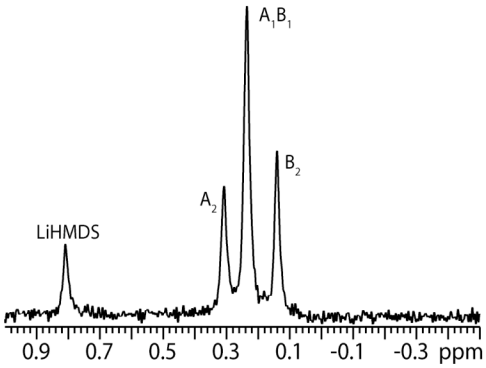


iii.

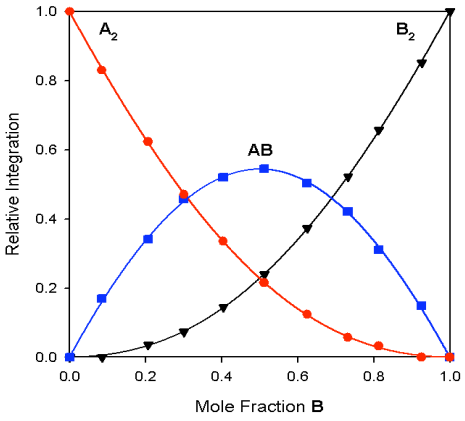
Calc. X_B	$\mathbf{A}_2$	$\mathbf{A}_1\mathbf{B}_1$	$\mathbf{B}_2$
0.00	1.00	0.00	0.00
0.12	0.77	0.24	0.00
0.30	0.47	0.46	0.07
0.54	0.24	0.45	0.31
0.54	0.19	0.54	0.27
0.71	0.07	0.45	0.48
1.00	0.00	0.00	1.00

i. ^{6}Li NMR spectrum of a 50:50 mixture of [^{6}Li]**1** (**A**) and [^{6}Li]**25** (**B**) in 0.24 M TMEDA/toluene at -70 °C. **ii.** Plot of the relative integration versus the mole fraction of **25** (**B**) for a mixture of [^{6}Li]**1** (**A**) and [^{6}Li]**25** (**B**) $\phi_0 = 0.92$; $\phi_1 = 1.00$; $\phi_2 = 0.92$; RMS = 0.02. **iii.** Relative integrations for aggregates in a mixture of **1** (**A**) and **25** (**B**) at various mole fractions of **A** and **B**.

i.



ii.

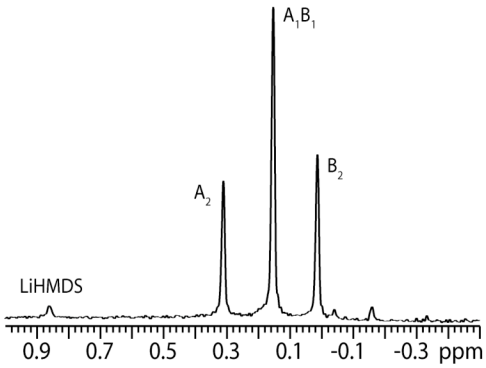


iii.

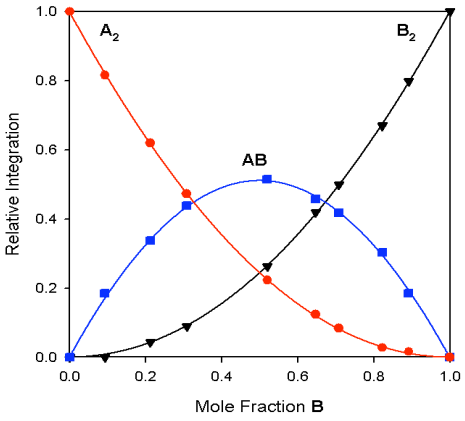
Calc. X_B	$\mathbf{A}_2$	$\mathbf{A}_1\mathbf{B}_1$	$\mathbf{B}_2$
0.00	1.00	0.00	0.00
0.09	0.83	0.15	0.00
0.21	0.62	0.31	0.04
0.30	0.47	0.42	0.07
0.40	0.34	0.50	0.14
0.51	0.22	0.55	0.24
0.63	0.12	0.52	0.37
0.73	0.06	0.46	0.52
0.81	0.03	0.34	0.66
0.93	0.00	0.17	0.85
1.00	0.00	0.00	1.00

i. ^{6}Li NMR spectrum of a 50:50 mixture of [^{6}Li]**26** (**A**) and [^{6}Li]**7** (**B**) in 0.24 M TMEDA/toluene at -90 °C. **ii.** Plot of the relative integration versus the mole fraction of **7** (**B**) for a mixture of [^{6}Li]**26** (**A**) and [^{6}Li]**7** (**B**) $\phi_0 = 0.84$; $\phi_1 = 1.00$; $\phi_2 = 0.84$; RMS = 0.004. **iii.** Relative integrations for aggregates in a mixture of **26** (**A**) and **7** (**B**) at various mole fractions of **A** and **B**.

i.



ii.

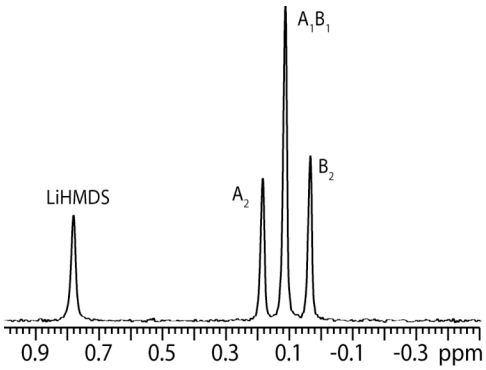


iii.

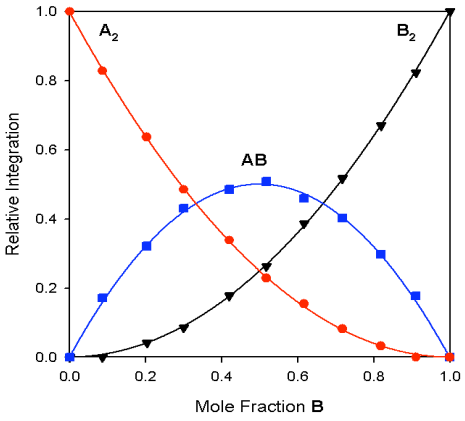
Calc. X_B	$\mathbf{A}_2$	$\mathbf{A}_1\mathbf{B}_1$	$\mathbf{B}_2$
0.00	1.00	0.00	0.00
0.09	0.82	0.19	0.00
0.21	0.62	0.34	0.04
0.31	0.47	0.44	0.09
0.52	0.22	0.51	0.26
0.65	0.12	0.46	0.42
0.71	0.08	0.42	0.50
0.82	0.03	0.30	0.67
0.89	0.02	0.19	0.80
1.00	0.00	0.00	1.00

i. ^{6}Li NMR spectrum of a 50:50 mixture of [^{6}Li]**26** (**A**) and [^{6}Li]**27** (**B**) in 0.24 M TMEDA/toluene at -90 °C. **ii.** Plot of the relative integration versus the mole fraction of **27** (**B**) for a mixture of [^{6}Li]**26** (**A**) and [^{6}Li]**27** (**B**) ϕ_0 = 0.96; ϕ_1 = 1.00; ϕ_2 = 0.96; RMS = 0.01. **iii.** Relative integrations for aggregates in a mixture of **26** (**A**) and **27** (**B**) at various mole fractions of **A** and **B**.

i.



ii.

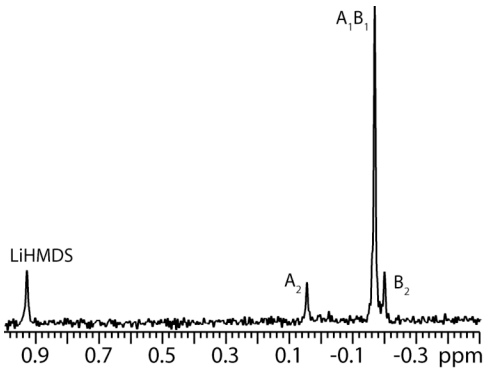


iii.

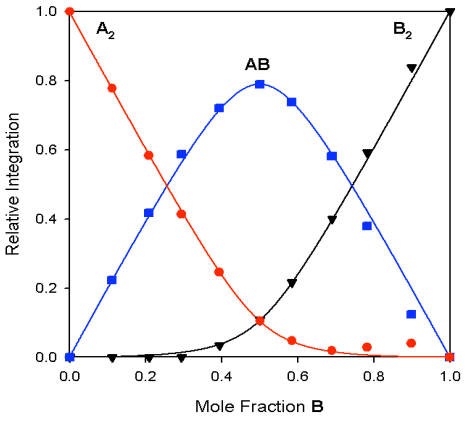
Calc. X_B	$\mathbf{A}_2$	$\mathbf{A}_1\mathbf{B}_1$	$\mathbf{B}_2$
0.00	1.00	0.00	0.00
0.09	0.83	0.17	0.00
0.20	0.64	0.32	0.04
0.30	0.49	0.43	0.09
0.42	0.34	0.49	0.18
0.52	0.23	0.51	0.26
0.62	0.15	0.46	0.39
0.72	0.08	0.40	0.52
0.82	0.03	0.30	0.67
0.91	0.00	0.18	0.82
1.00	0.00	0.00	1.00

i. ^{6}Li NMR spectrum of a 50:50 mixture of [^{6}Li]**1** (**A**) and [^{6}Li]**28** (**B**) in 0.24 M TMEDA/toluene at -90 °C. **ii.** Plot of the relative integration versus the mole fraction of **28** (**B**) for a mixture of [^{6}Li]**1** (**A**) and [^{6}Li]**28** (**B**) ϕ_0 = 1.00; ϕ_1 = 1.00; ϕ_2 = 1.00; RMS = 0.01. **iii.** Relative integrations for aggregates in a mixture of **1** (**A**) and **28** (**B**) at various mole fractions of **A** and **B**.

i.



ii.

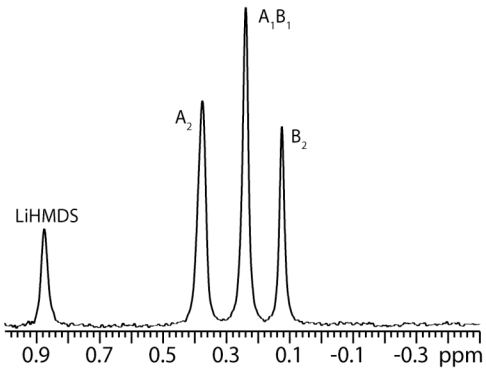


iii.

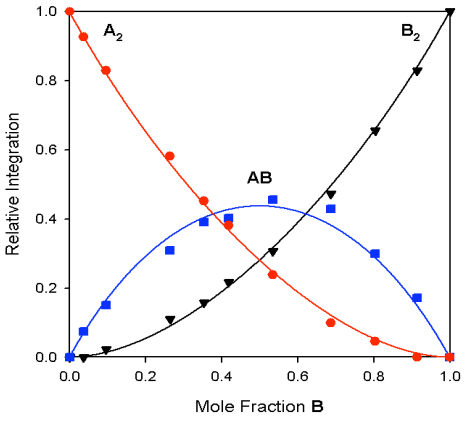
Calc. X_B	$\mathbf{A}_2$	$\mathbf{A}_1\mathbf{B}_1$	$\mathbf{B}_2$
0.00	1.00	0.00	0.00
0.11	0.78	0.22	0.00
0.21	0.58	0.42	0.00
0.29	0.41	0.59	0.00
0.39	0.25	0.72	0.03
0.50	0.11	0.79	0.11
0.59	0.05	0.74	0.22
0.69	0.02	0.58	0.40
0.78	0.03	0.38	0.59
0.90	0.04	0.12	0.84
1.00	0.00	0.00	1.00

i. ^{6}Li NMR spectrum of a 50:50 mixture of [^{6}Li]**28** (**A**) and [^{6}Li]**12** (**B**) in 0.24 M TMEDA/toluene at -50 °C. **ii.** Plot of the relative integration versus the mole fraction of **12** (**B**) for a mixture of [^{6}Li]**28** (**A**) and [^{6}Li]**12** (**B**) $\phi_0 = 0.80$; $\phi_1 = 3.00$; $\phi_2 = 0.80$; RMS = 0.02. **iii.** Relative integrations for aggregates in a mixture of **28** (**A**) and **12** (**B**) at various mole fractions of **A** and **B**.

i.



ii.

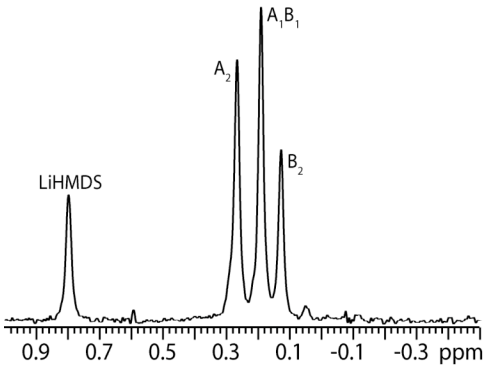


iii.

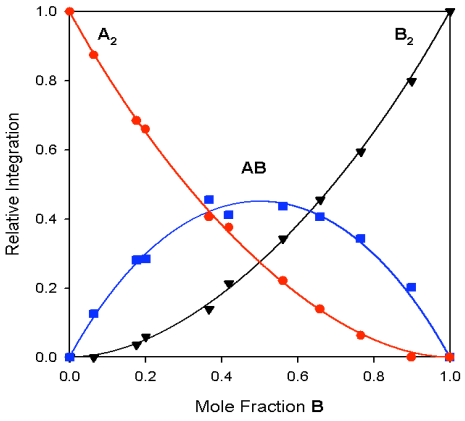
Calc. X_B	$\mathbf{A}_2$	$\mathbf{A}_1\mathbf{B}_1$	$\mathbf{B}_2$
0.00	1.00	0.00	0.00
0.04	0.93	0.07	0.00
0.10	0.83	0.15	0.02
0.26	0.58	0.31	0.11
0.35	0.45	0.39	0.16
0.42	0.38	0.40	0.22
0.53	0.24	0.46	0.31
0.69	0.10	0.43	0.47
0.80	0.05	0.30	0.66
0.91	0.00	0.17	0.83
1.00	0.00	0.00	1.00

i. ^{6}Li NMR spectrum of a 50:50 mixture of [^{6}Li]**26** (**A**) and [^{6}Li]**28** (**B**) in 0.24 M TMEDA/toluene at -90 °C. **ii.** Plot of the relative integration versus the mole fraction of **28** (**B**) for a mixture of [^{6}Li]**26** (**A**) and [^{6}Li]**28** (**B**) ϕ_0 = 1.29; ϕ_1 = 1.00; ϕ_2 = 1.29; RMS = 0.02. **iii.** Relative integrations for aggregates in a mixture of **26** (**A**) and **28** (**B**) at various mole fractions of **A** and **B**.

i.



ii.

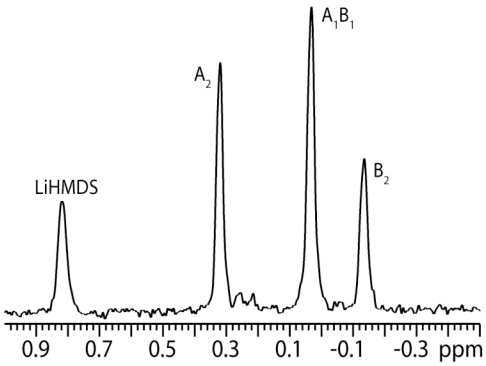


iii.

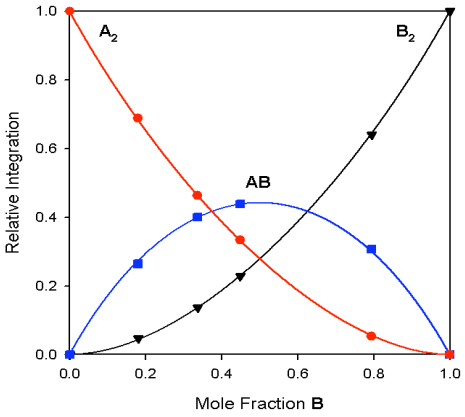
Calc. X_B	$\mathbf{A}_2$	$\mathbf{A}_1\mathbf{B}_1$	$\mathbf{B}_2$
0.00	1.00	0.00	0.00
0.06	0.87	0.13	0.00
0.18	0.68	0.28	0.04
0.20	0.66	0.28	0.06
0.37	0.41	0.46	0.14
0.42	0.38	0.41	0.21
0.56	0.22	0.44	0.34
0.66	0.14	0.41	0.46
0.77	0.06	0.34	0.60
0.60	0.00	0.20	0.80
1.00	0.00	0.00	1.00

i. ^{6}Li NMR spectrum of a 50:50 mixture of [^{6}Li]**30** (**A**) and [^{6}Li]**7** (**B**) in 0.24 M TMEDA/toluene at -90 °C. **ii.** Plot of the relative integration versus the mole fraction of **7** (**B**) for a mixture of [^{6}Li]**30** (**A**) and [^{6}Li]**7** (**B**) ϕ_0 = 1.22; ϕ_1 = 1.00; ϕ_2 = 1.22; RMS = 0.01. **iii.** Relative integrations for aggregates in a mixture of **30** (**A**) and **7** (**B**) at various mole fractions of **A** and **B**.

i.



ii.

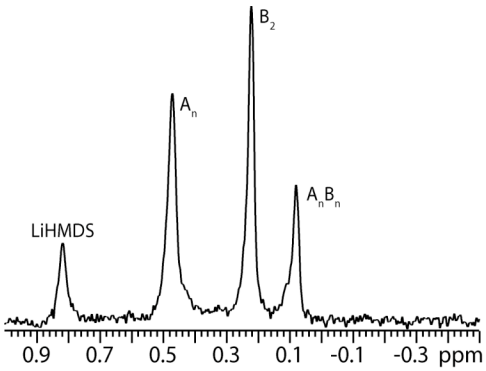


iii.

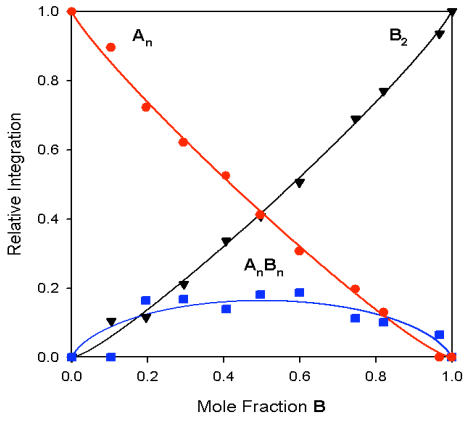
Calc. X_B	$\mathbf{A}_2$	$\mathbf{A}_1\mathbf{B}_1$	$\mathbf{B}_2$
0.00	1.00	0.00	0.00
0.18	0.69	0.31	0.05
0.34	0.46	0.44	0.14
0.45	0.33	0.40	0.23
0.79	0.05	0.26	0.64
1.00	0.00	0.00	1.00

i. ^{6}Li NMR spectrum of a 50:50 mixture of [^{6}Li]**29** (**A**) and [^{6}Li]**31** (**B**) in 0.24 M TMEDA/toluene at -90 °C. **ii.** Plot of the relative integration versus the mole fraction of **31** (**B**) for a mixture of [^{6}Li]**29** (**A**) and [^{6}Li]**31** (**B**) ϕ_0 = 1.26; ϕ_1 = 1.00; ϕ_2 = 1.26; RMS = 0.003. **iii.** Relative integrations for aggregates in a mixture of **29** (**A**) and **31** (**B**) at various mole fractions of **A** and **B**.

i.



ii.

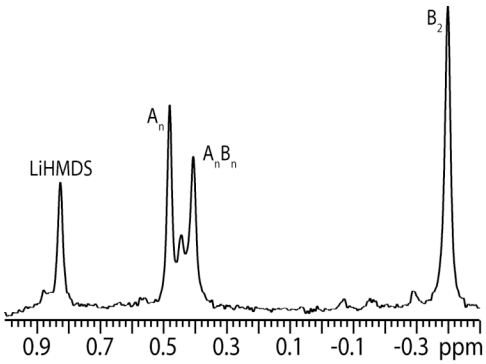


iii.

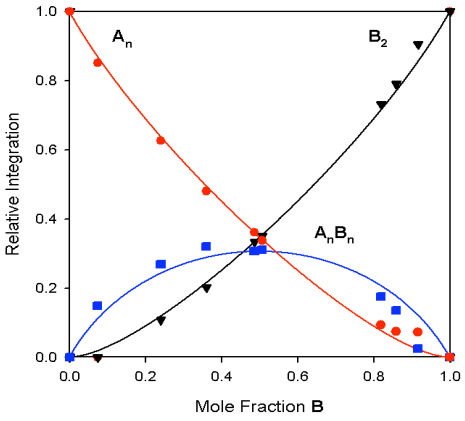
Calc. X_B	$\mathbf{A}_n$	$\mathbf{A}_n\mathbf{B}_n$	$\mathbf{B}_2$
0.00	1.00	0.00	0.00
0.10	0.90	0.00	0.10
0.20	0.72	0.16	0.12
0.30	0.62	0.17	0.21
0.41	0.53	0.14	0.34
0.50	0.41	0.18	0.41
0.60	0.31	0.19	0.51
0.75	0.20	0.11	0.69
0.82	0.13	0.10	0.77
0.98	0.00	0.07	0.94
1.00	0.00	0.00	1.00

i. ^{6}Li NMR spectrum of a 50:50 mixture of [^{6}Li]**34** (**A**) and [^{6}Li]**1** (**B**) in 0.24 M TMEDA/toluene at -90 °C. **ii.** Plot of the relative integration versus the mole fraction of **1** (**B**) for a mixture of [^{6}Li]**34** (**A**) and [^{6}Li]**1** (**B**) $\phi_0 = 5.11$; $\phi_1 = 1.00$; $\phi_2 = 5.11$; RMS = 0.02. **iii.** Relative integrations for aggregates in a mixture of **34** (**A**) and **1** (**B**) at various mole fractions of **A** and **B**.

i.



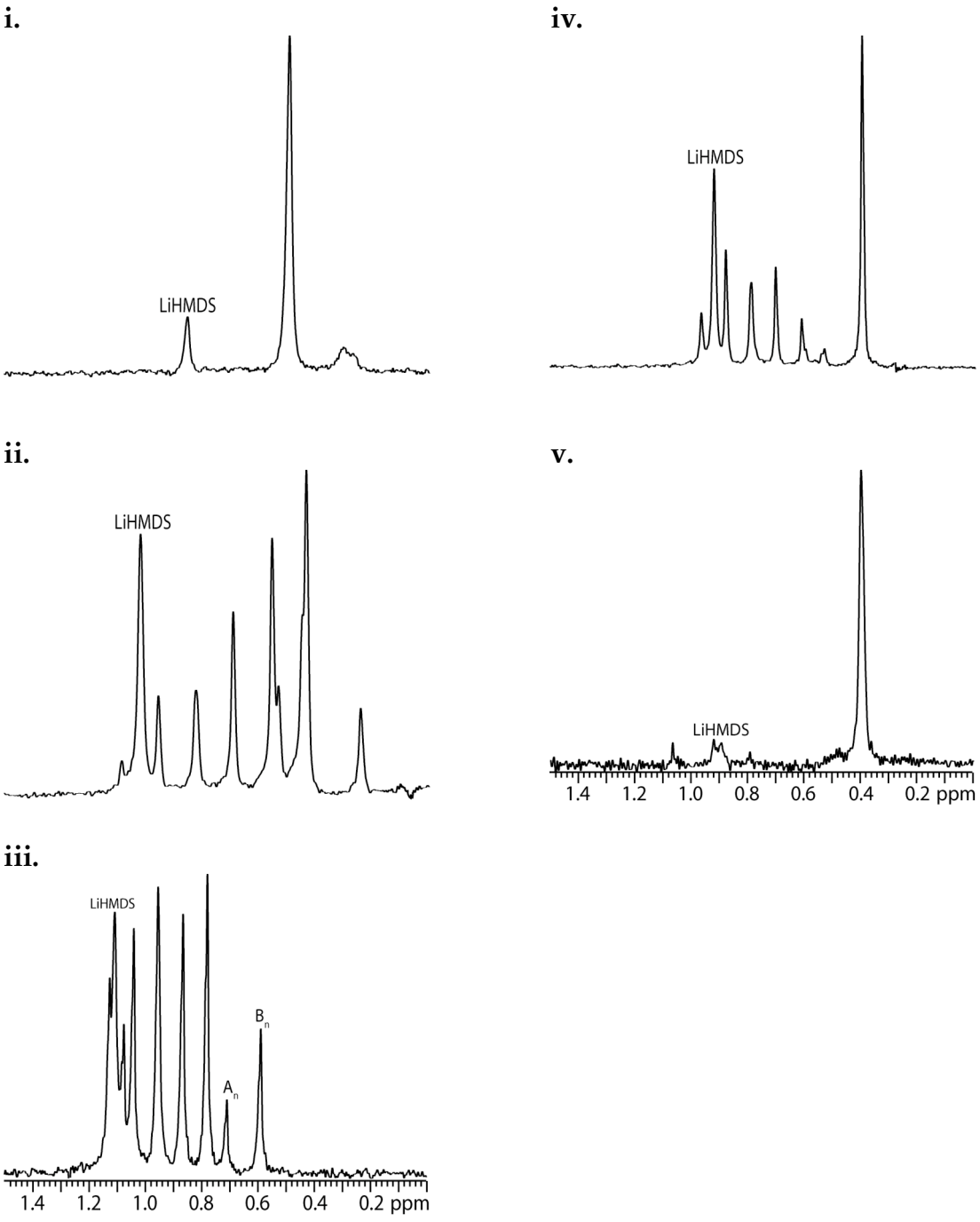
ii.



iii.

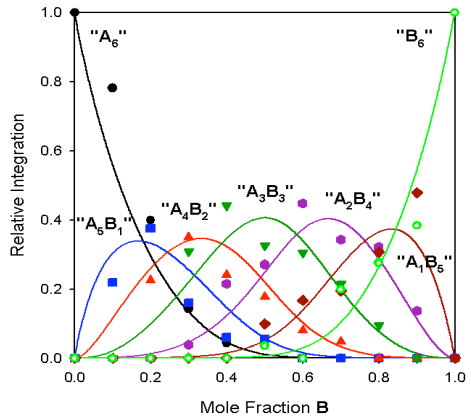
Calc. X_B	$\mathbf{A}_n$	$\mathbf{A}_n\mathbf{B}_n$	$\mathbf{B}_2$
0.00	1.00	0.00	0.00
0.07	0.85	0.15	0.00
0.24	0.63	0.27	0.11
0.36	0.48	0.32	0.20
0.49	0.36	0.31	0.33
0.51	0.34	0.31	0.35
0.82	0.09	0.18	0.73
0.86	0.07	0.14	0.79
0.92	0.07	0.02	0.91
1.00	0.00	0.00	1.00
1.00	0.00	0.00	1.00

i. ^{6}Li NMR spectrum of a 50:50 mixture of [^{6}Li]**34** (**A**) and [^{6}Li]**13** (**B**) in 0.24 M TMEDA/toluene at -90 °C. **ii.** Plot of the relative integration versus the mole fraction of **13** (**B**) for a mixture of [^{6}Li]**34** (**A**) and [^{6}Li]**13** (**B**) ϕ_0 = 2.27; ϕ_1 = 1.00; ϕ_2 = 2.27; RMS = 0.03. **iii.** Relative integrations for aggregates in a mixture of **34** (**A**) and **13** (**B**) at various mole fractions of **A** and **B**.

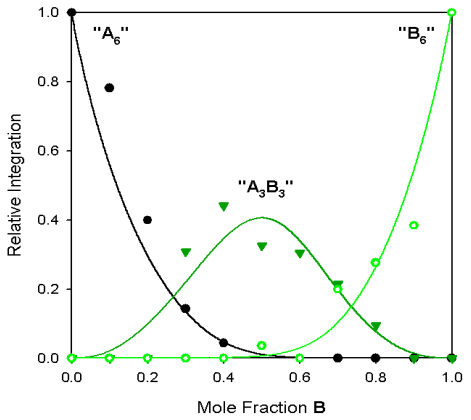


^{6}Li NMR spectra of [^{6}Li]**34** (**A**) and [^{6}Li]**36** (**B**) and 0.12 M [^{6}Li]LiHMDS in 0.24 M TMEDA/toluene at -30 °C. **i.** 0.10 M [^{6}Li]**34** (**A**) **ii.** 70:30 mixture of [^{6}Li]**34** (**A**) and [^{6}Li]**36** (**B**) **iii.** 50:50 mixture of [^{6}Li]**34** (**A**) and [^{6}Li]**36** (**B**) **iv.** 30:70 mixture of [^{6}Li]**34** (**A**) and [^{6}Li]**36** (**B**) **v.** 0.10 M [^{6}Li]**36** (**B**).

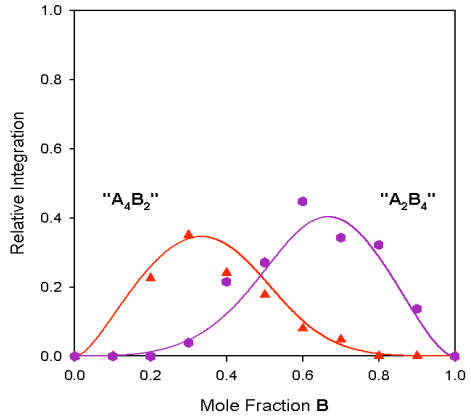
i.



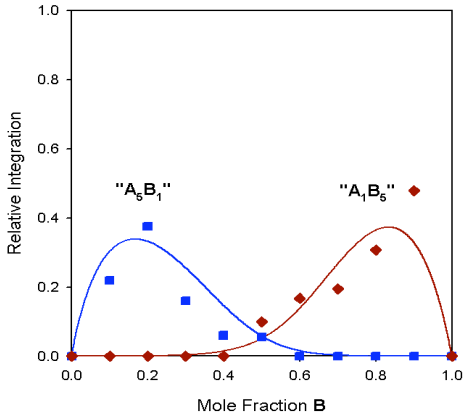
ii.



iii.



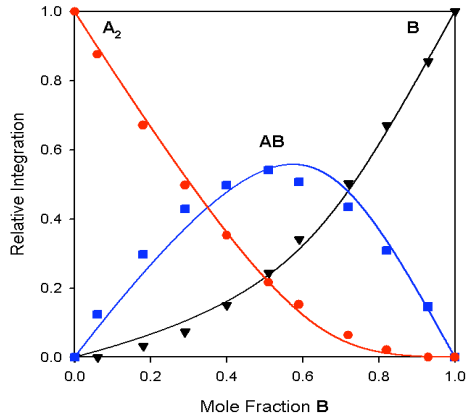
iv.



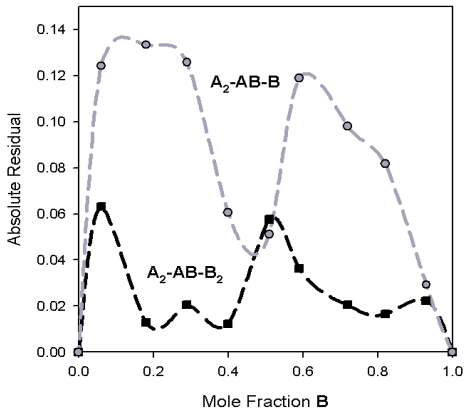
Plots of the relative integration versus mole fraction **36** (**B**) for an ensemble of [^{6}Li]**34** (**A**) and [^{6}Li]**36** (**B**) in 0.24 M TMEDA/toluene at -30 °C fit to a hexamer ensemble. Plot is shown together **(i)** and separately **(ii, iii, and iv)** for clarity. ϕ_{60} = 0.69; ϕ_{61} = 0.84; ϕ_{62} = 1.61; ϕ_{63} = 1.96; ϕ_{64} = 1.40; ϕ_{65} = 0.91; ϕ_{66} = 1.00; RMS = 0.05.

III. Residual Plots.

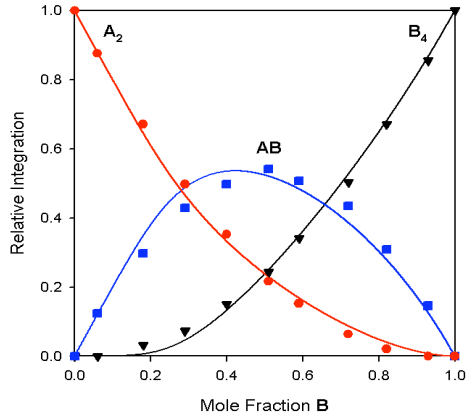
i.



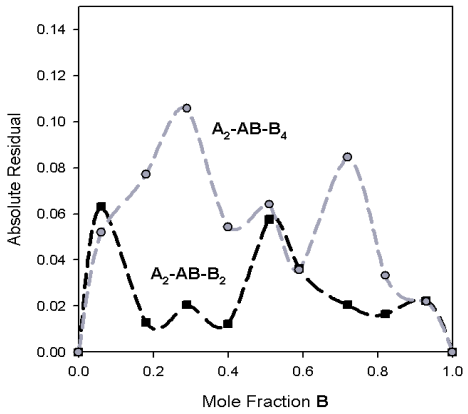
ii.



iii.

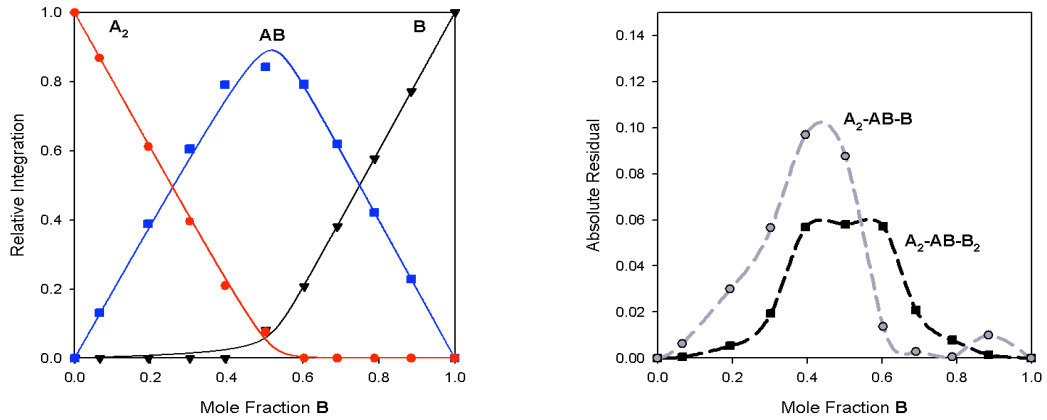


iv.

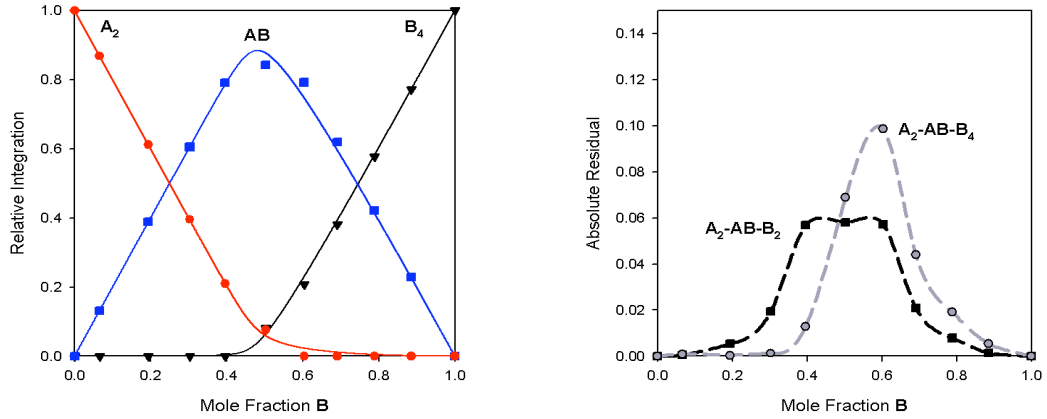


III.a. Plots of the relative integration versus mole fraction **7** (**B**) for an ensemble of [^{6}Li]**1** (**A**) and [^{6}Li]**7** (**B**) in 0.24 M TMEDA/toluene at -90 °C fit to an ensemble of **A_2-AB-B** and **A_2-AB-B_4**. **i.** Plot and fit of the relative integration versus the calculated mole fraction of **7 (B)** fit to **A_2-AB-B**; $\phi_{10} = 0.49$; $\phi_{11} = 0.00$; $\phi_{20} = 0.00$; $\phi_{21} = 1.04$; $\phi_{22} = 0.15$; RMS = 0.35. **ii.** Plot of the sum of the absolute residuals for **A_2-AB-B_2** and **A_2-AB-B** versus mole fraction of **7 (B)**. **iii.** Plot and fit of the relative integration versus the calculated mole fraction of **7 (B)** fit to **A_2-AB-B_4**; $\phi_{20} = 0.00$; $\phi_{21} = 0.53$; $\phi_{22} = 1.55$; $\phi_{40} = 0.91$; $\phi_{41} = \phi_{42} = \phi_{43} = \phi_{44} = 0.00$; RMS = 0.35. **iv.** Plot of the sum of the absolute residuals for **A_2-AB-B_2** and **A_2-AB-B_4** versus mole fraction of **7 (B)**.

i. **ii.**

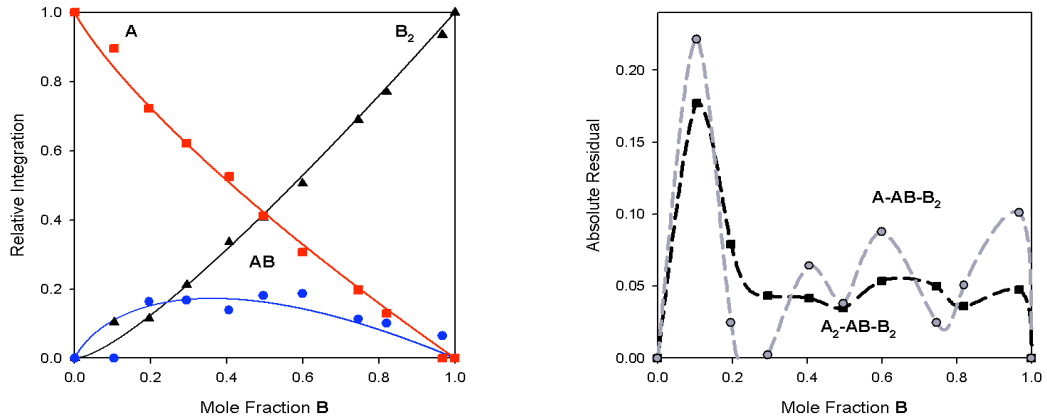


iii. **iv.**

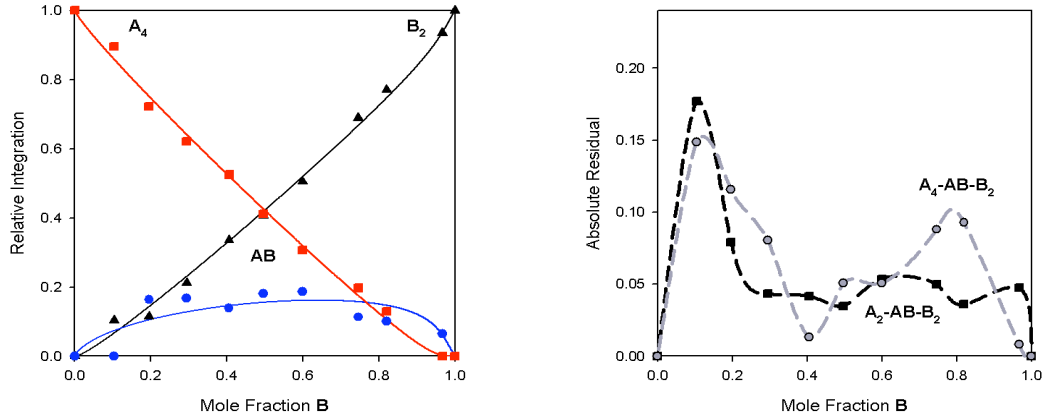


III.b. Plots of the relative integration versus mole fraction **13** (**B**) for an ensemble of [^{6}Li]**1** (**A**) and [^{6}Li]**13** (**B**) in 0.24 M TMEDA/toluene at -90 °C fit to an ensemble of **A_2-AB-B** and **A_2-AB-B_4**. **i.** Plot and fit of the relative integration versus the calculated mole fraction of **13 (B)** fit to **A_2-AB-B**; ϕ_{10} = 0.18; ϕ_{11} = 0.00; ϕ_{20} = 0.00; ϕ_{21} = 5.71; ϕ_{22} = 0.19; RMS = 0.02. **ii.** Plot of the sum of the absolute residuals for **A_2-AB-B_2** and **A_2-AB-B** versus mole fraction of **13 (B)**. **iii.** Plot and fit of the relative integration versus the calculated mole fraction of **13 (B)** fit to **A_2-AB-B_4**; ϕ_{20} = 0.00; ϕ_{21} = 1.54; ϕ_{22} = 0.54; ϕ_{40} = 1.14; ϕ_{41} = ϕ_{42} = ϕ_{43} = ϕ_{44} = 0.00; RMS = 0.01. **iv.** Plot of the sum of the absolute residuals for **A_2-AB-B_2** and **A_2-AB-B_4** versus mole fraction of **13 (B)**.

i. **ii.**



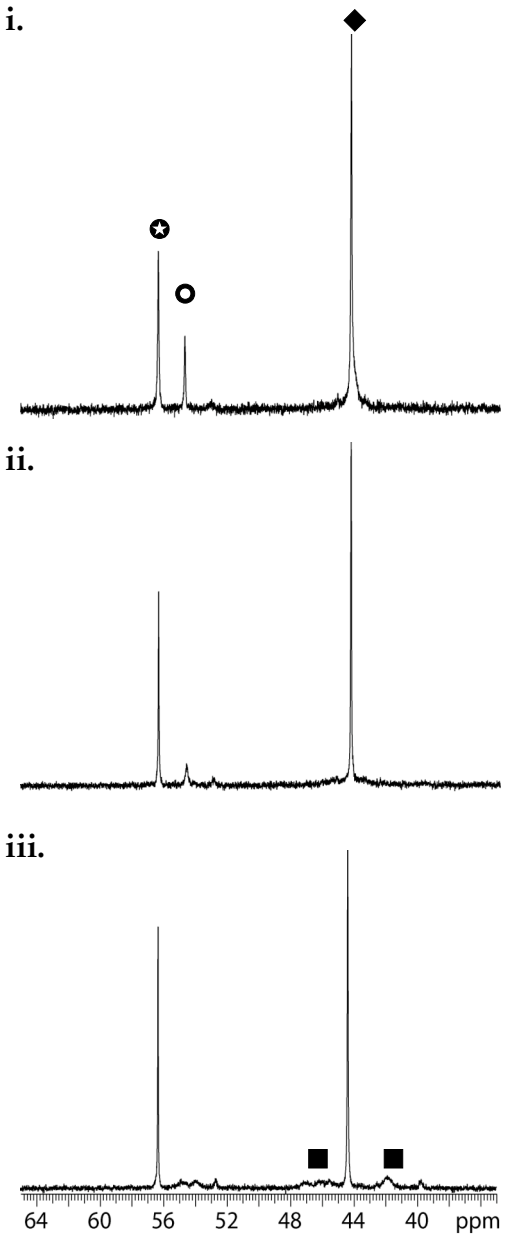
iii. **iv.**



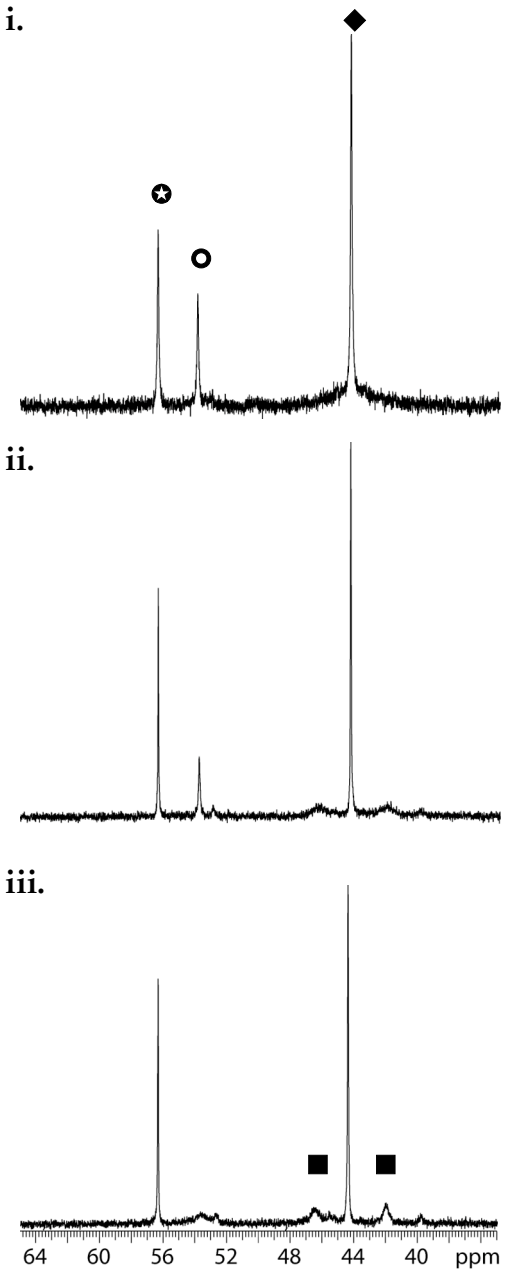
III.c. Plots of the relative integration versus mole fraction **1** (**B**) for an ensemble of [^{6}Li]**34** (**A**) and [^{6}Li]**1** (**B**) in 0.24 M TMEDA/toluene at -90 °C fit to an ensemble of **A_2-AB-B** and **A_2-AB-B_4**. **i.** Plot and fit of the relative integration versus the calculated mole fraction of **1 (B)** fit to **A_2-AB-B**; ϕ_{10} = 0.00; ϕ_{11} = 0.69; ϕ_{20} = 7.26; ϕ_{21} = 1.22; ϕ_{22} = 0.00; RMS = 0.03. **ii.** Plot of the sum of the absolute residuals for **A_2-AB-B_2** and **A_2-AB-B** versus mole fraction of **1 (B)**. **iii.** Plot and fit of the relative integration versus the calculated mole fraction of **1 (B)** fit to **A_2-AB-B_4**; ϕ_{20} = 1.54; ϕ_{21} = 0.19; ϕ_{22} = 0.00; ϕ_{40} = 0.00 = ϕ_{41} = ϕ_{42} = ϕ_{43}; ϕ_{44} = 5.34; RMS = 0.03. **iv.** Plot of the sum of the absolute residuals for **A_2-AB-B_2** and **A_2-AB-B_4** versus mole fraction of **1 (B)**.

As illlustrated by the plots, the fits are indistinguishable within error. Further investigation was necessary to characterize [^{6}Li]**34**.

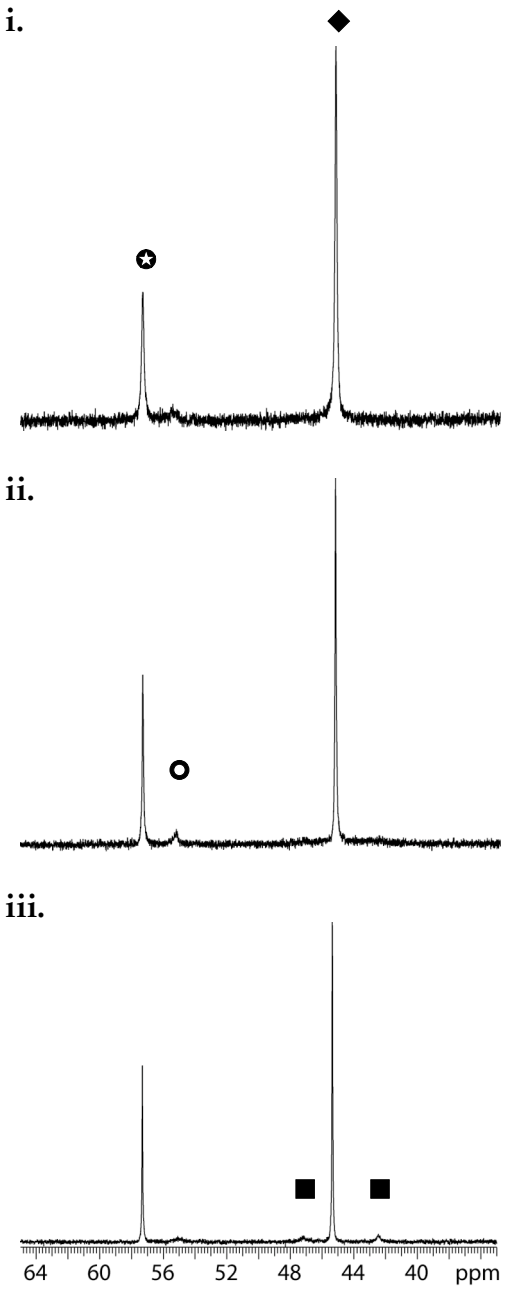
IV. ^{13}C NMR Spectra.



IV.**a**. ^{13}C NMR spectra of [^{6}Li]**13** 0.24 M TMEDA/toluene at **i.** -100 °C; **ii.** -80 °C; **iii.** -70 °C. (■) bound $\underline{C}H_3$-N-; (◆) free $\underline{C}H_3$-N-; (O) bound -$\underline{C}H_2$-; (✪) free -$\underline{C}H_2$-

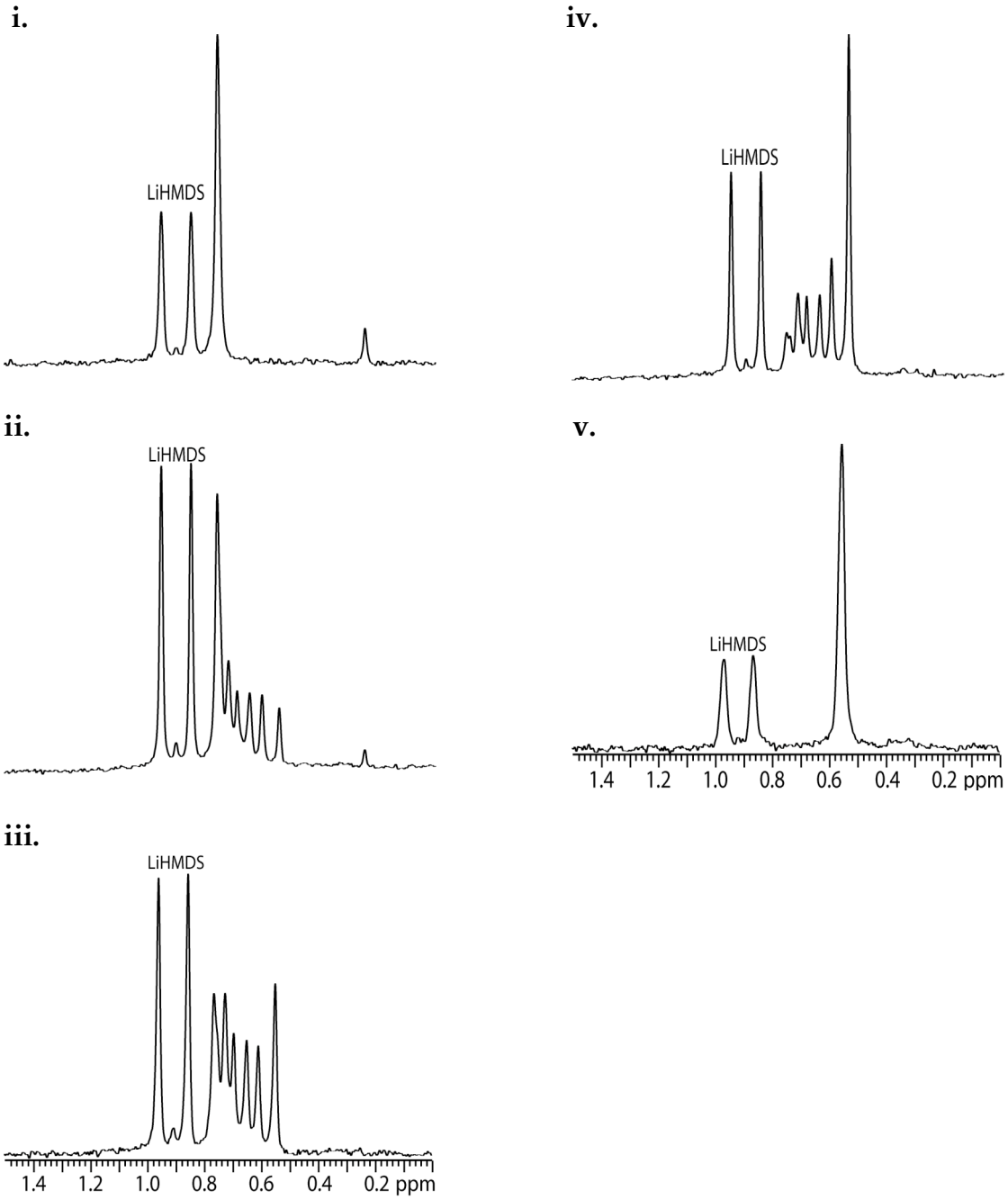


IV.**b**. ^{13}C NMR spectra of [^{6}Li]**28** 0.24 M TMEDA / toluene at **i.** -100 °C; **ii.** -80 °C; **iii.** -70 °C. (■) bound $\underline{C}H_3$-N-; (◆) free $\underline{C}H_3$-N-; (**O**) bound -$\underline{C}H_2$-; (✪) free -$\underline{C}H_2$-

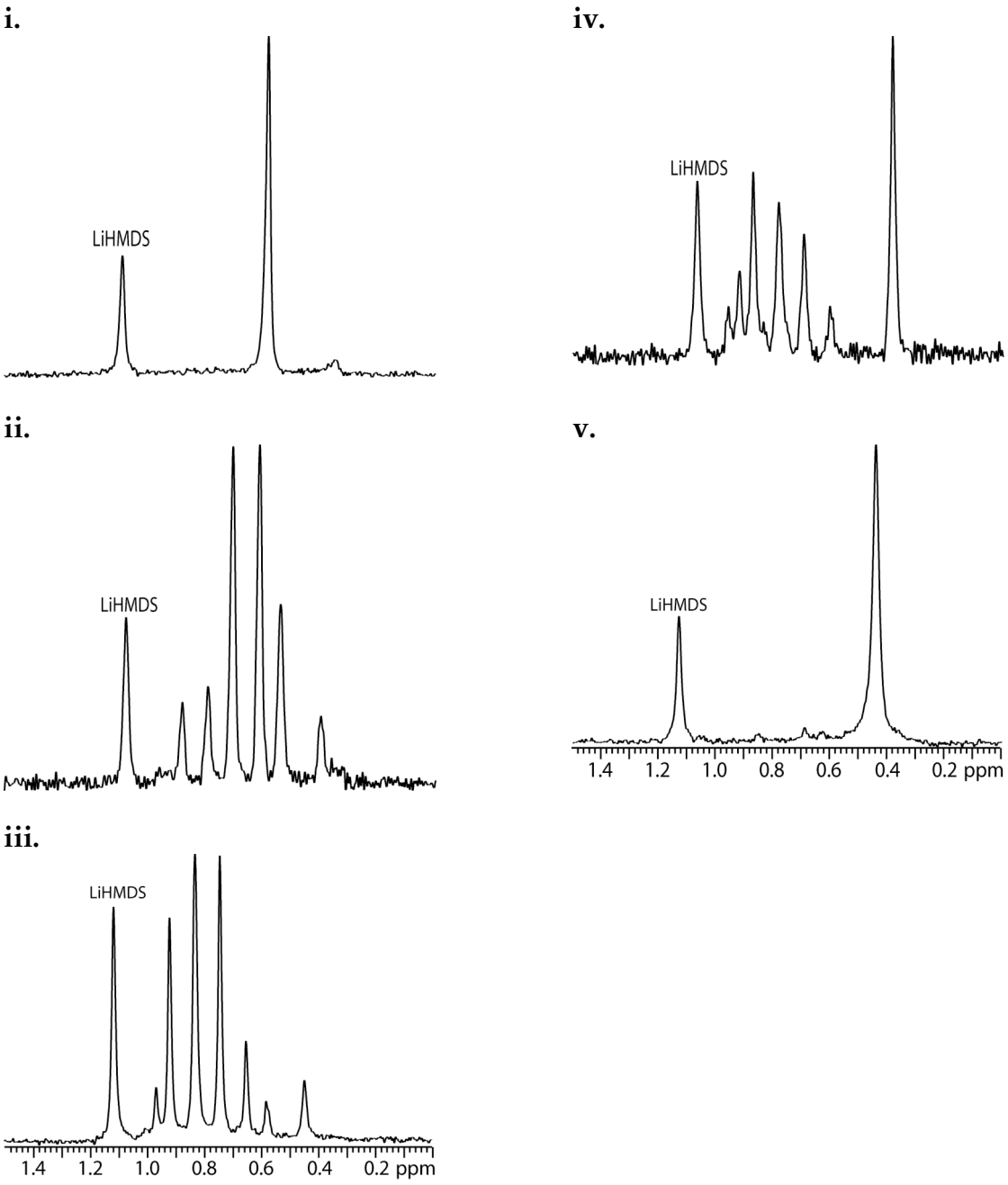


IV.**c**. ^{13}C NMR spectra of [^{6}Li]**15** 0.24 M TMEDA/toluene at **i.** -100 °C; **ii.** -80 °C; **iii.** -70 °C. (■) bound $\underline{C}H_3$-N-; (◆) free $\underline{C}H_3$-N-; (O) bound -$\underline{C}H_2$-; (✪) free -$\underline{C}H_2$-

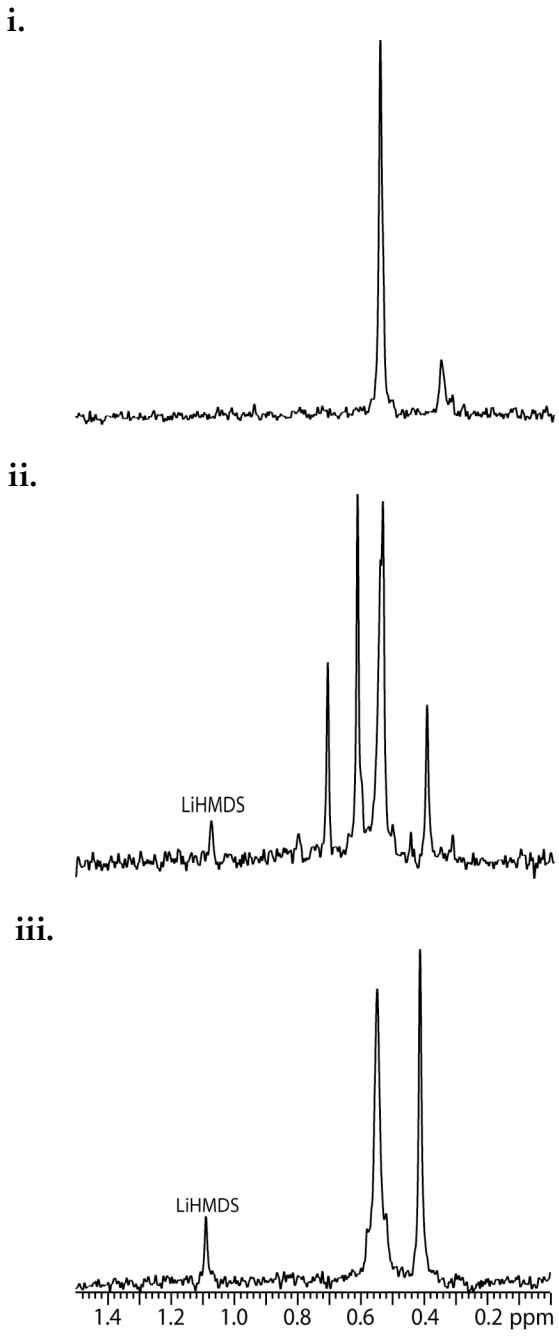
V. Alkoxide Studies.



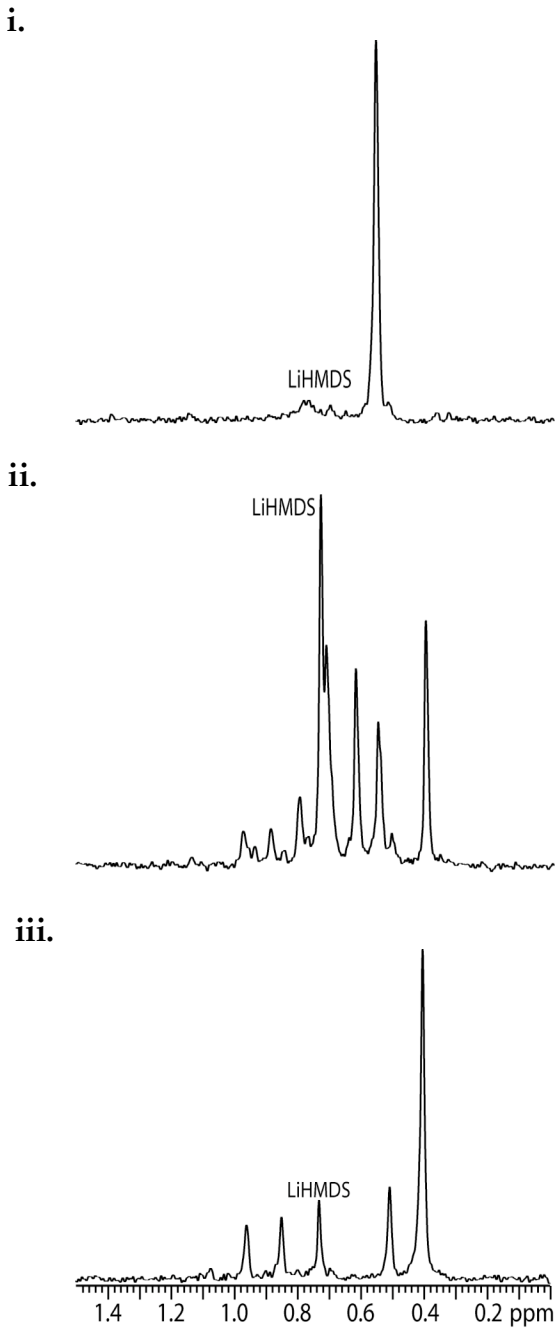
V.a. ^{6}Li NMR spectra of [^{6}Li]**35** (**A**) and [^{6}Li]**34** (**B**) and 0.12 M [^{6}Li, ^{15}N]LiHMDS in 0.24 M TMEDA/toluene at -70 °C. **i.** 0.10 M [^{6}Li]**35** (**A**) **ii.** 70:30 mixture of [^{6}Li]**35** (**A**) and [^{6}Li]**34** (**B**) **iii.** 50:50 mixture of [^{6}Li]**35** (**A**) and [^{6}Li]**34** (**B**) **iv.** 30:70 mixture of [^{6}Li]**35** (**A**) and [^{6}Li]**34** (**B**) **v.** 0.10 M [^{6}Li]**34** (**B**).



V.b. ^{6}Li NMR spectra of [^{6}Li]**34** (**A**) and [^{6}Li]**36** (**B**) in 0.24 M TMCDA/toluene at -30 °C. **i.** 0.10 M [^{6}Li]**34** (**A**) **ii.** 70:30 mixture of [^{6}Li]**34** (**A**) and [^{6}Li]**36** (**B**) **iii.** 50:50 mixture of [^{6}Li]**34** (**A**) and [^{6}Li]**36** (**B**) **iv.** 30:70 mixture of [^{6}Li]**34** (**A**) and [^{6}Li]**36** (**B**) **v.** 0.10 M [^{6}Li]**36** (**B**).

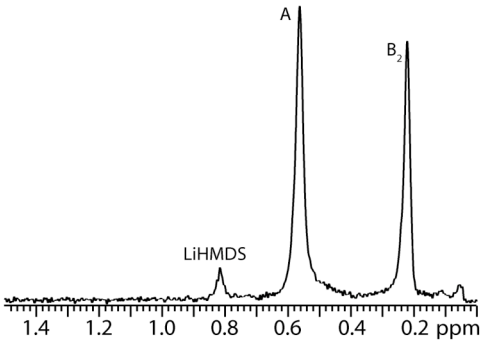


V.c. ^{6}Li NMR spectra of [^{6}Li]**34** (**A**) and [^{6}Li]**36** (**B**) in neat toluene at -30 °C. **i.** 0.10 M [^{6}Li]**34** (**A**) **ii.** 50:50 mixture of [^{6}Li]**34** (**A**) and [^{6}Li]**36** (**B**) **iii.** 0.10 M [^{6}Li]**36** (**B**).

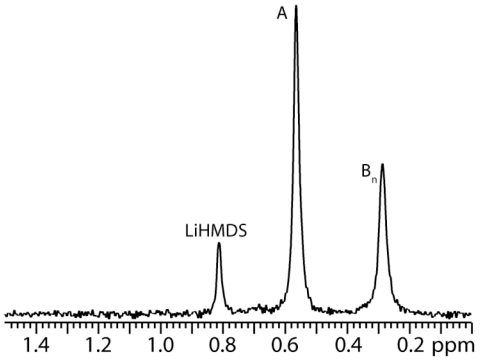


V.d. ^{6}Li NMR spectra of [^{6}Li]**34** (**A**) and [^{6}Li]**36** (**B**) in 0.24 M DMEA/toluene at -30 °C. **i.** 0.10 M [^{6}Li]**34** (**A**) **ii.** 50:50 mixture of [^{6}Li]**34** (**A**) and [^{6}Li]**36** (**B**) **iii.** 0.10 M [^{6}Li]**36** (**B**).

VI. Hindered Phenolate Studies.



VI.a. ^{6}Li NMR spectrum of a 50:50 mixture of [^{6}Li]**38** (**A**) and [^{6}Li]**1** (**B**) in 0.24 M TMEDA/toluene at -90 °C.



VI.b. ^{6}Li NMR spectrum of a 50:50 mixture of [^{6}Li]**38** (**A**) and [^{6}Li]**36** (**B**) in 0.24 M TMEDA/toluene at -90 °C.