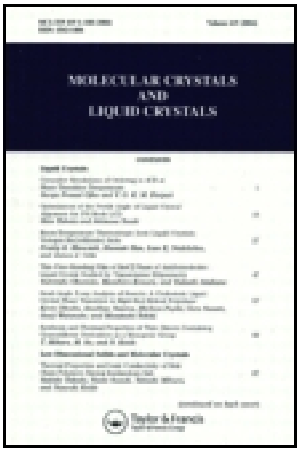

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

The Interactions of Methylated Ammonium Ions in Lyotropic Liquid Crystalline Solution

Alan S. Tracey [a] & Keith Radley [a]
[a] Department of Chemsitry, Simon Fraser University, Burnaby, British Columbia, Canada, V5A 1S6

Version of record first published: 20 Apr 2011.

To cite this article: Alan S. Tracey & Keith Radley (1986): The Interactions of Methylated Ammonium Ions in Lyotropic Liquid Crystalline Solution, Molecular Crystals and Liquid Crystals, 139:3-4, 241-251

To link to this article: http://dx.doi.org/10.1080/00268948608080130

Mol. Cryst. Liq. Cryst., 1986, Vol. 139, pp. 241–251
0026-8941/86/1394–0241/$20.00/0

The Interactions of Methylated Ammonium Ions in Lyotropic Liquid Crystalline Solution

ALAN S. TRACEY and KEITH RADLEY

Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

(*Received December 9, 1985; in final form March 6, 1986*)

The mono-, di- and trimethylammonium ions have been investigated in the lyotropic liquid crystalline system of potassium dodecanoate/alkyltrimethylammonium bromide. The results indicate that non-bonded forces deriving from the anisotropy of the medium contribute little to the alignment of these ions but that forces deriving from binding of the ions to the dodecanoate headgroups provide the major mechanism for the imposition of alignment. A three-site model of ion binding was found to be sufficient to describe the change in dipolar couplings as the micellar surface charge was varied. It was also found that anomolous changes in ratios of coupling constants were accounted for by the three site model of binding.

Keywords: lyotropic, mesophase, ion binding, ammonium, nematic

INTRODUCTION

The interaction of ions in surfactant solution is a subject of considerable interest in the areas of colloid and surface chemistry, the chemistry of amphiphilic liquid crystals and in biochemistry. The study of the behavior of ions has concentrated almost exclusively on alkali metal and halide ions[1–12] and, to a lesser extent, on various tetrahedral species.[13–14]

It has been shown that in the cholesteric mesophase prepared from potassium *N*-dodecanoyl-*l*-alaninate, where the amphiphile headgroup alignment can be monitored by way of dipolar couplings within the headgroup, quadrupole splittings maintain a direct proportionality with the dipolar splittings as the headgroup alignment is changed.[12] Such studies indicate that binding is the major mechanism for ion-amphiphile interactions and that non-bonding interactions are relatively unimportant. It is apparent that this conclusion can, to a limited extent, be checked by studying ions of symmetry much lower than that of the spherical or tetrahedral species. In this circumstance, forces deriving from the anisotropy of the medium may provide the major contribution to the alignment of ions. If not, it can be expected that the site binding model will be sufficient to describe the alignment of the ions.

A two- or, in some cases, a three-site model for ion binding has generally provided an explanation for the results of nuclear magnetic resonance (NMR) experiments investigating binding[1,6–8,10–12] of alkali metal and halide ions in amphiphilic systems containing a single amphiphile. In mixed systems containing both cationic and anionic detergents, a three-site model for binding has been used to describe the behavior of the quadrupole splittings as a function of total micellar charge for both monatomic ions[10–12] and polyatomic tetrahedral ions.[13]

The three sites of the three-site model correspond to: I) ions within the plane of the micellar interface and bound by more than one amphiphile; II) ions displaced from the plane of the interface and bound to a single amphiphile; III) ions moving freely in the aqueous region of the mesophase. It is to be noted that diffuse binding, that is to say ions bound by a potential which holds them near the interface rather than to a specific amphiphile, is not specifically considered in this model.

Information concerning the number of amphiphile headgroups associated with an ion in a site I has been obtained through study of the mixed amphiphilic system potassium dodecanoate/alkyltrimethylammonium. Use of this system, which allows the surface charge or the micelles to be varied, provides a means of systematically creating and destroying binding sites. This allows some of the details of binding to be extracted.[10–13]

The mono-, di- and trimethylammonium ions provide a convenient system for studying such interactions. In the three-site model, the proton-proton dipolar couplings of the respective species are averaged values, dependent on the population of ions in a specific site and the dipolar coupling characteristic of that site. The observed dipolar coupling, D_{ij}, between nuclei i and j, is given by Eq. 1 when a three-site model of binding is assumed. The

$$D_{ij} = D_{ij}^{\mathrm{I}} X^{\mathrm{I}} + D_{ij}^{\mathrm{II}} X^{\mathrm{II}} + D_{ij}^{\mathrm{III}} X^{\mathrm{III}} \qquad (1)$$

superscript indicates the site occupied and X the mole fraction of ions in that site. In this model, the value of X is related to the number of binding amphiphiles in site I and the proportion of that amphiphile in the mixed detergent system as has been discussed for quadrupole splittings.[13] Equation 1 can be rewritten in terms which are a function of the number of liganding amphiphiles in site I and which in a rudimentary approximation reflects the tightness of ion binding. Equation 2 has been described in detail for quadrupole splittings[13] and is rewritten here for the case of dipolar couplings. In this equation,

$$
\begin{aligned}
&A\ 1 \geq x \geq (1 - 1/n)\\
&\quad D_{ij} = [A(D^{\mathrm{I}}_{ij}BC + D^{\mathrm{II}}_{ij}((1 - B)C + D))\\
&\qquad\qquad + D^{\mathrm{III}}_{ij}(xC_D(1 - A) + C_E)]/[xC_D + C_E]\\
&B\ (1 - 1/n) \geq x \geq 0\\
&\quad D_{ij} = [AD^{\mathrm{II}}_{ij}xC_D + D^{\mathrm{III}}_{ij}(xC_D(1 - A) + C_E)]/[xC_D + C_E]
\end{aligned}
\tag{2}
$$

$A = k_0 - k_1(1 - xC_D), B = k_2 - k_3n(1 - x), C = C_D(nx - (n - 1))$, $D = C_D(n - 1)(1 - x)$, C_E is the proportion of electrolyte relative to an amphiphile concentration (C_D) normalized to 1, n is the number of binding amphiphiles in site I, x is the mole fraction of binding amphiphile in total detergent while k_0, k_1, k_2 and k_3, in a crude approximation, are related to the efficiency of binding. k_0 and k_2 act much like scale factors and consequently are taken as being equal to 1. k_3 is related to the tightness of binding in site I compared to site II. k_1 provides a measure of the strength of ion binding relative to a free ion, site III. Values of k_1 and k_3 near 0 are indicative of tight binding, while large values indicate progressively weaker binding. Within the limits of the approximations leading to Eq. 2 a $k_1 = 1.0$ with $k_0 = 1.0$ means that at $x = 0.5$ one-half the available binding sites are occupied.

Equation 2 when written for quadrupole splittings, has been found to reproduce experimental results for various tetrahedral ions including NH_4^+ and $N(CH_3)_4^+$[13] and should be applicable to the mono-, di- and trimethylammonium ions if specific binding interactions are the predominant source of anisotropic motion of the ions. This equation should not be applicable if aligning forces derive predominately from the anisotropy of the medium. Furthermore, since these ions are highly hydrophilic this study, in essence, is restricted to an investigation of the anisotropic forces within the aqueous region of the mesophase.

EXPERIMENTAL

The liquid crystalline materials used for this study have been previously described and the procedure adopted here differs little from that description, except that the salts incorporated into the medium were methylammonium, dimethylammonium and trimethylammonium chloride instead of the more frequently used sodium chloride or sodium sulphate.[10–13] The compositions of the mesophases are given in Table I.

^{1}H nuclear magnetic resonance (NMR) spectra were obtained at ambient temperature using a 400 MHz NMR spectrometer. Pulse widths of 55° were used while spectral widths and data set sizes were adjusted as required for the individual spectra. A Lorentz-Gauss lineshape transformation was routinely used when processing the spectra. NMR spectra were analyzed for the dipolar couplings using the instrument manufacturers software. In all analysis the indirect (J) coupling between the methyl group of the di- and trimethylammonium ions which is very small (~0.2 Hz) was ignored.

RESULTS AND DISCUSSION

The relative importance of the strengths of binding interactions and those deriving from the anisotropic forces of the liquid crystalline medium are important for understanding the properties of lyotropic mesophases. It has generally been recognized that highly symmetrical coions such as alkali metal or halide ions contained in lyotropic mesophases give rise to much smaller quadrupole splittings than when they exist in similar systems but as counterions.

Table I gives the mesophase composition and the values obtained for the dipolar splittings where the mole fraction of potassium dodecanoate is given relative to total detergent, potassium dodecanoate plus alkyltrimethylammonium bromide. The two trimethylammonium dipole splittings in the cationic mesophase are approximately 10% of the corresponding splitting in the dodecanoate system while the proportions are even less for the dimethyl- and methylammonium

TABLE I

Mesophase compositions and parameters measured for the methylated ammonium ions

Composition[a]						^{1}H NMR parameters[b]						
						$CH_3ND_3^+$	$(CH_3)_2ND_2^+$			$(CH_3)_3NH^+$		
X[c]	DDTMABr[d]	DTMABr[d]	KDD[d]	DeOH[d]	D_2O[e]	D_{11}	D_{11}	D_{12}	D_{12}/D_{11}	D_{11}	D_{12}	D_{12}/D_{11}
0.00	308		0	80	I	−7.0	−2.9	1.4	−0.47	−4.0	1.9	−0.48
0.10	277		24	65	I	−14.0	−5.6	2.6	−0.47	−6.5	2.7	−0.43
0.20	246		47	50	I	−18.0	−7.7	3.5	−0.46	−10.5	4.6	−0.45
0.30	216		71	30	I	−18.0	−11.7	5.5	−0.47	−18.1	8.3	−0.46
0.35	200		83	15	I	−7.4	−10.1	5.4	−0.53	−17.1	8.1	−0.48
0.40	185		95	5	I	10.5	−10.1	5.9	−0.58	−21.9	9.8	−0.45
0.45	169		107	0	I	42.0	−12.1	7.6	−0.63	−27.9	13.3	−0.48
0.50		140	119	10	I	82.0	−8.9	6.8	−0.77	−35.1	17.2	−0.49
0.52		134	124	8	II		−5.9	5.9	−0.99			
0.54		129	129	6	II		−3.0	3.9	−1.29			
0.56		123	134	4	II		1.1	4.0	3.70			
0.58		118	138	2	II		6.2	1.5	0.24			
0.60		112	143	0	I	275.0	10.5	−0.5	−0.05	−41.6	19.9	−0.48
0.65		98	155	1	II		29.1	−8.1	−0.28			
0.70		84	166	2	I	604.0	59.1	−19.7	−0.33	−35.9	17.2	−0.48
0.75	77		178	5	I	1010.0	107.2	−38.2	−0.35	−36.6	16.5	−0.45
0.80	62		190	15	I	1100.0	133.0	−50.2	−0.38	−12.4	5.4	−0.44
0.90	31		214	35	I	1270.0	170.9	−67.2	−0.39	25.0	−9.4	−0.37
1.00			238	65	I	1905.0	269.1	−109.5	−0.41	44.0	−19.1	−0.43

[a] Compositions are given as mg of component per sample.

[b] Splittings are given in Hz: D_{11}, dipolar coupling within methyl group; D_{12}, dipolar coupling between methyl groups. Signs of splittings are relative signs only and apply only within a series for a particular ion.

[c] Mole fraction of potassium dodecanoate in total detergent.

[d] DDTMABr, dodecyltrimethylammonium bromide; DTMABr, decyltrimethylammonium bromide; KDD, potassium dodecanoate; DeOH, decanol.

[e] I: D_2O: 850 mg per sample of D_2O solution containing: trimethylammonium chloride, 0.5%; dimethylammonium chloride, 0.33%; methylammonium chloride, 0.17%.
II: D_2O: 850 mg per sample of D_2O solution containing 1% dimethylammonium chloride.

cations, being in the order of 1%. These observations indicate that specific binding interactions may provide the major contribution to the alignment of these ammonium ions. If such is true, it is possible that the site model for ion binding developed for the alkali metal,[10] halide[11] and tetrahedral ions[13] will describe the behavior of the dipolar couplings in the methylammonium, dimethylammonium and trimethylammonium ions of this study. These last ions have previously been studied in the decylsulphate mesophase system[15-17] and the procedure for analysis of the spectra follows that described. No effort to determine the absolute signs of the dipolar couplings of the ammonium ions in the dodecanoate mesophase studied here has been made, although they have been determined for the decylsulphate system.[15,16]

The analysis of the various dipolar coupling constants in terms of the three-site model for ion binding proceeds readily for all three ions. Figure 1 shows the experimental points and calculated curve from Eq. 2 for the methylammonium ion. The number of amphiphiles binding to this ion in site I is 2. Agreement between the experimental and calculated curves is quite good, however it must be noted that the experimental curve in terms of eq. 2 is ambiguous since it could also be reproduced quite well from consideration only of a two-site binding situation. In view of the results obtained for the other two ions in this series and for the ammonium ion,[13] this seems unlikely and the ambiguity must derive from a very small dipolar coupling

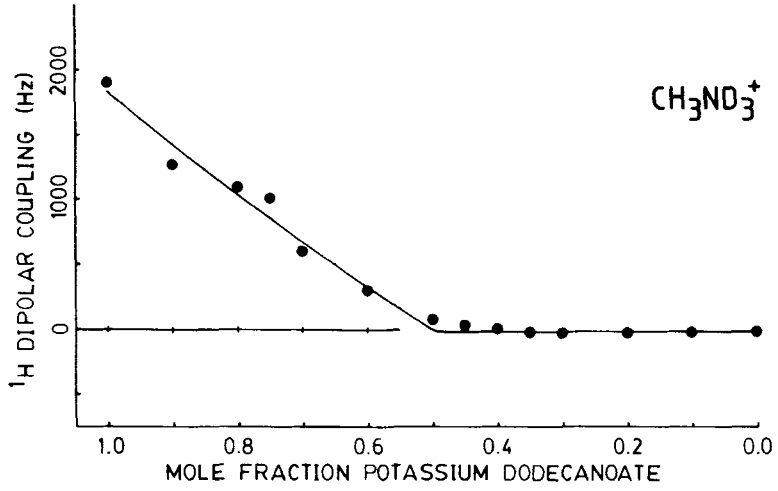

FIGURE 1 Calculated and observed curves obtained for the methylammonium ion as a function of the mole fraction of potassium dodecanoate in total detergent.

TABLE II

Characteristic dipolar couplings calculated for the various methylated ammonium ions in their binding sites

	Coupling constants (Hz)[a]							
Ammonium ion	D_{11}I	D_{11}II	D_{11}III	D_{12}I	D_{12}II	D_{12}III	k_1	k_3
Methylammonium	2024.0	−9.6	−7.0				0.53	0.32
Dimethylammonium	291.7	−23.6	−2.9	−116.9	16.9	1.4	0.90	0.47
Trimethylammonium	55.4	−97.8	−4.0	−24.8	47.4	1.9	1.18	0.85

[a] Signs of coupling constants for a particular ion are relative signs only: D_{11}, *HCH* dipolar coupling; D_{12}, CH_3NCH_3 dipolar coupling.

between the protons of the methyl group when the ion is in site II. This could occur if the preferred direction for alignment of the C—N bond is near 54.7° to the director for the micelles. The dipolar splittings characteristic of the three sites are given in Table II as are the relevant constants k_1 and k_3.

Figure 2 shows the experimental points and curves calculated for the trimethylammonium ion. Here, two curves are obtained since two sets of dipolar couplings are measured, the CH_3NCH_3 splitting be-

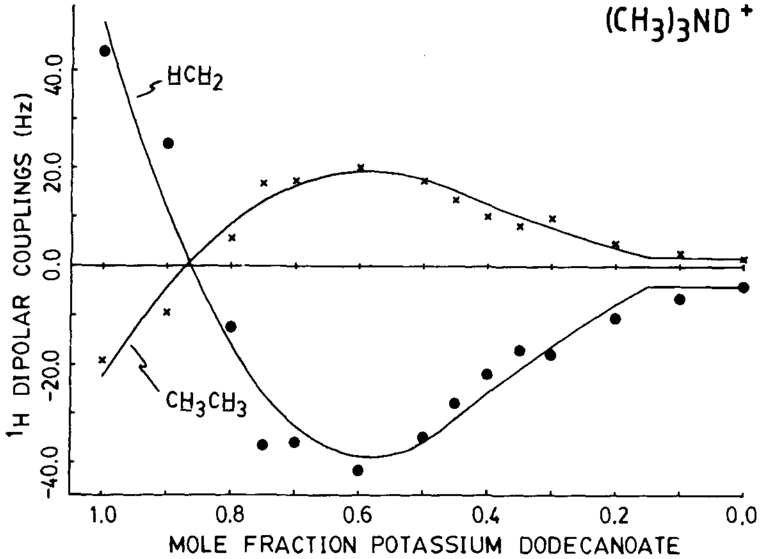

FIGURE 2 The calculated and observed curves for the two dipolar couplings of trimethylammonium ion obtained as a function of the mole fraction of potassium dodecanoate in total detergent.

tween methyls and the HCH_2 splittings within the individual methyl groups. Although these two curves are substantially different in appearance from that of the methylammonium ion, they also are fit well by Eq. 2 when it is assumed that the number of binding amphiphiles is 2. The values for k_1 and k_3 (Table II) of 1.15 and 0.98, respectively, are indicative of rather loose binding, as might be expected.

An attempt to ascertain whether the two dipolar couplings of the trimethylammonium ion went to zero simultaneously was made. One spectrum of total width of 6 Hz was obtained. This spectrum was consistent with both couplings going to zero at the same mole fraction of dodecanoate in total detergent. This could, however, simply be the result of a fortuitous proportion of amphiphiles since the two couplings need not simultaneously become zero. In the three-site model of binding utilized here, the zero derives from an average value of three order parameters, one for each site. Since the structure of the ion in site I may be different from the structure in site II or site III, the two couplings, which are structure related, need not simultaneously average to zero.[18]

Figure 3 shows the calculated and observed curves for the dimethylammonium ion. The results indicate that the number of carboxylates binding this ion is 2, as for the other ions. The characteristic dipolar

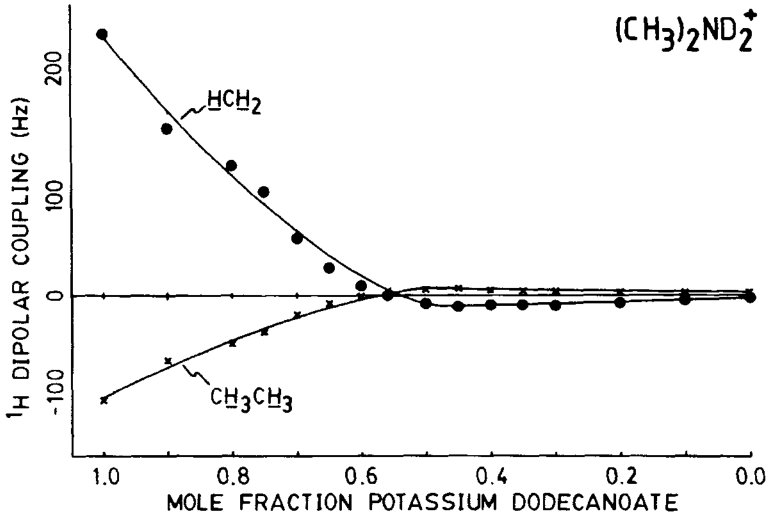

FIGURE 3 The observed and calculated dipolar couplings from the dimethylammonium ion are shown as a function of the mole fraction potassium dodecanoate in total detergent.

coupling constants for the various sites are given in Table II. The values for k_1 and k_3 are 0.90 and 0.47, respectively, and are intermediate between those for the methylammonium and trimethylammonium ions.

An interesting aspect of Figure 3 is that the two sets of dipolar couplings do not go through zero simultaneously. Questions of structural modification aside, this occurs because the order parameters giving rise to the dipole splitting are not fixed in proportion to each other as the ion moves from one site to another. This is clearly seen by taking the relevant ratios in Table II, from which $D^{\mathrm{I}}12/D^{\mathrm{I}}_{11} = -0.40$, $D^{\mathrm{II}}_{12}/D^{\mathrm{II}}_{11} = -0.72$ and $D^{\mathrm{III}}_{12}/D^{\mathrm{III}}_{11} = -0.48$. The observed dipolar couplings D_{11} and D_{12} vary, as described by Eq. 1, so that the observed ratio of couplings is constant only if the individual ratios for the various sites are identical. The points of Figure 4 shows how the ratio of observed dipolar splittings varies as the cationic to anionic surfactant proportions are changed. The behavior of this curve is consistent with a site model for ion binding. It is not consistent with a model which proposes that the dipolar coupling is modified by the term $1/2\,(3\cos^2\theta - 1)$, where θ is the angle between the major ordering axis and the normal to the bilayer. In this case, when $1/2(3\cos^2\theta - 1)$

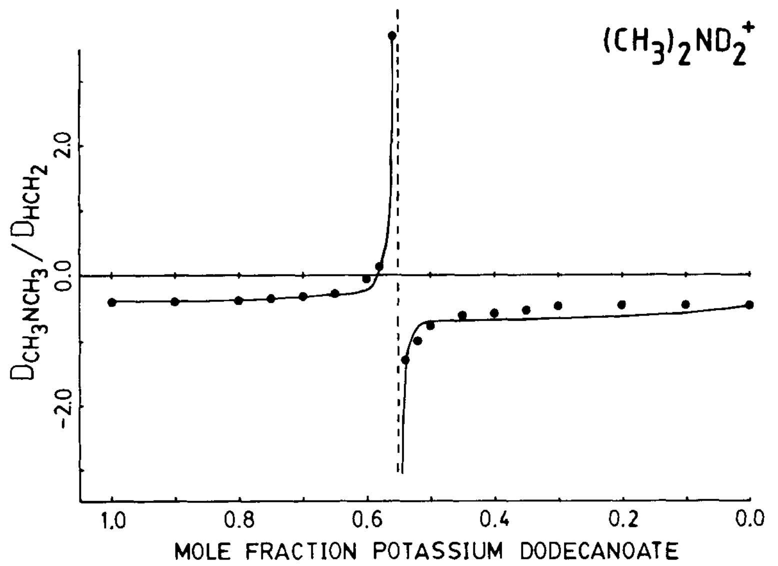

FIGURE 4 The experimental ratios of dipolar couplings from the dimethylammonium ion are shown as a function of the mole fraction potassium dodecanoate in total detergent as are the corresponding ratios calculated from the solid curves of Figure 3.

goes to zero at 54.7° both of the dipolar splittings should vanish. Since this clearly is not observed, strong support for a site model of binding is provided by these results. Furthermore, if the particular model of site binding employed here is a reasonable one then the ratio of dipolar couplings obtained from the curves of Figure 3 should reproduce the experimental ratios. The solid line of Figure 4 shows the calculated curve. It closely follows the experimental curve except that the discontinuity in the curve is slightly displaced from that of the calculated curve, from $x = 0.56$ to $x = 0.54$. In this diagram, the calculated curve is offset slightly so that the experimental points can be superimposed on it. The agreement is extremely good and provides further support for this three-site model of ion binding. The region of major discrepancy corresponds to the experimental values of D_{11} and D_{12} which are small in magnitude. No doubt better agreement between the experimental and calculated curves of Figure 4 would be obtained if the ratio of coupling constants was considered when fitting the two curves of Figure 3.

CONCLUSIONS

The good agreement between observed and calculated curves for this series of ammonium ions is strongly indicative that binding interactions provide the major contribution to the alignment of these species. The forces deriving from the anisotropy of the medium apparently are relatively insignificant in imposing alignment on such hydrophilic species. This however is probably not true for ionic species which are sufficiently hydrophobic to spend significant amounts of time inside the micelles. Ions, such as anilinium, have order parameters similar to those of the hydrocarbon chains of the surfactant moieties[19] and probably derive a major component of their alignment from interactions with the hydrocarbon chains. However, even here specific interactions between surfactant headgroup and counterion are still a significant source of aligning forces.

Acknowledgment

Thanks are gratefully extended to the Natural Sciences and Engineering Research Council of Canada for its support of this work.

References

1. K. Rendall, G. J. T. Tiddy and M. A. Trevethan, *J. Colloid Interface Sci.*, **98**, 565–571 (1984).
2. D. F. Evans, D. J. Mitchell and B. W. Ninham, *J. Phys. Chem.*, **88**, 6344–6348 (1984).
3. J. A. Beunen and E. Ruckenstein, *J. Colloid Interface Sci.*, **96**, 469–487 (1983).
4. A. Delville and P. Laszlo, *Biophys. Chem.*, **17**, 119–124 (1983).
5. D. F. Evans and B. W. Ninham, *J. Phys. Chem.*, **87**, 5025–5032 (1983).
6. O. Söderman, S. Engström and H. Wennerström, *J. Colloid Interface Sci.*, **78**, 110–117 (1980).
7. G. Lindblom, B. Lindman and G. J. T. Tiddy, *J. Am. Chem. Soc.*, **100**, 2299–2303 (1978).
8. N. Boden and S. A. Jones, *Israel J. Chem.*, **23**, 356–362 (1983).
9. J. F. Rathman and J. F. Scamehorn, *J. Phys. Chem.*, **88**, 5807–5816 (1984).
10. A. S. Tracey and T. L. Boivin, *J. Phys. Chem.*, **88**, 1017–1023 (1984).
11. A. S. Tracey, *Can. J. Chem.*, **62**, 2162–2167 (1984).
12. A. S. Tracey and K. Radley, *J. Phys. Chem.*, **88**, 6044–6048 (1984).
13. K. Radley and A. S. Tracey, *J. Phys. Chem.*, **89**, 2657–2661 (1985).
14. D. Bailey, A. D. Buckingham, F. Fujiwara and L. W. Reeves, *J. Mag. Res.*, **18**, 344–357 (1975).
15. L. W. Reeves and A. S. Tracey, *J. Amer. Chem. Soc.*, **96**, 1198–1205 (1974).
16. L. W. Reeves and A. S. Tracey, *J. Amer. Chem. Soc.*, **96**, 7176–7180 (1974).
17. L. W. Reeves and A. S. Tracey, *J. Amer. Chem. Soc.*, **97**, 5729–5735 (1975).
18. P. Diehl, M. Reinhold, A. S. Tracey and E. Wullschleger, *Mol. Phys.*, **30**, 1781–1793 (1975).
19. P. Diehl and A. S. Tracey, *Can. J. Chem.*, **53**, 2755–2762 (1975).