netic probes on high-T_c superconductors.

Conclusions

The results show that the ESR line broadening of an adsorbed spin probe on the surface of an oxide superconductor due to vortex lattice emergence below T_c can be separated from Meissner effect flux exclusion and hence can lead to a valid determination of the magnetic field penetration depth. The spin probe on the surface of a superconductor, however, has to be deposited in a proper way and oriented perpendicularly to the external field.

The detection of vortex lattice melting in BiSrCaCuO is strong evidence that the ESR line broadening is due to the flux lattice that causes inhomogeneity of the magnetic field. Hence, the spin probe method can be used to determine the magnetic field penetration depth and the flux lattice melting temperature if it is significantly lower than T_c.

The results obtained for Ag-doped YBaCuO confirm the assumption that the magnetic field inhomogeneity caused by the vortex lattice is significantly weakened by the magnetic field penetrating through nonsuperconducting regions, in this case Ag. The values of λ_0 consequently increase with Ag content.

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Registry No. $YBa_2Cu_3O_x$, 107539-20-8; $B_{12}Sr_2CaCu_2O_x$, 114901-61-0; Ag, 7440-22-4.

Mass Spectrometric Searches for Gaseous Sodium Carbonates

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In connection with modeling of the chemistry of meteor-deposited sodium in the upper atmosphere, we have examined the mass spectra of several pertinent sodium-containing effusion sources for evidence of gaseous $NaHCO_3$, Na_2CO_3, or any other Na-C-O-H species. Although clear and unambiguous evidence for the presence of $Na_2CO_3(g)$ was obtained with various sources involving solid and liquid Na_2CO_3 and NaOH in the presence of gaseous CO_2, H_2O, and H_2, all searches for $NaHCO_3(g)$ were negative. An upper limit of about 29 ± 5 kcal mol^{-1} was estimated for the bond strength $D(NaOH–CO_2)$, based on the detection limit for $NaHCO_3$ and measured abundances of NaOH and CO_2. Preliminary thermodynamic quantities were derived for $Na_2CO_3(g)$. The results are discussed in terms of atmospheric chemistry models in the literature.

Introduction

Gaseous $NaHCO_3$ has been proposed[1] as a possible terminal reaction product for meteor-deposited sodium in the upper atmosphere and also as a potential source of "sudden sodium layers" in the E region of the ionosphere by means of the dissociative attachment process

$$NaHCO_3 + e \rightarrow Na + HCO_3^- \qquad (1)$$

which is expected to be efficient.[2] Beams of HCO_3^- have been generated by the interaction of O^- and OH^- with CO_2-H_2O mixtures,[3,4] but the electron affinity and related thermochemical properties have not been established experimentally. To our knowledge nothing is known about the gaseous species $NaHCO_3$.

The rate constants for the gaseous reaction NaOH + CO_2 + M, in which $NaHCO_3$ is the expected gaseous product, were reported,[5] but no evidence regarding product identity was presented. And for HCO_3^-, the geometrical structure parameters and binding energy of the gaseous ion were calculated from molecular theory,[6] but there has been no experimental confirmation. We are not aware of any other observations on gaseous bicarbonates.

To gain more information about these species, we have examined the mass spectra of vapors emitted from an effusion cell source containing Na_2CO_3 or NaOH in the presence of CO_2, H_2O, and H_2. Pressures of the added gases were increased to maximum permissible levels to optimize conditions for $NaHCO_3$ formation. The results of these experiments are described below.

Experimental Section

All parts of the tubular effusion cell source were fabricated from platinum. The main part of the cell was a 0.99-cm-i.d. thin-walled tube with an internal 0.32-cm diameter tube for gas addition; the tube cap contained a 0.11-cm diameter effusion orifice. A schematic of the cell and heater arrangement is shown in Figure 1. The Na_2CO_3 samples were contained in a Pt cup in the hot zone of the cell, as in a normal effusion experiment with gas addition. With NaOH, which has a higher vapor pressure, the sample was supported on a Pt screen below the heater zone. A ball of Pt wire placed in the sample region was effective at the higher temperatures in confining the molten samples by surface tension. Another ball of Pt wire placed near the exit orifice served as a baffle to increase gas-surface collisions and to promote equilibration. The reactive gases could be added singly or in premixed combinations.

Mass spectra were obtained with the magnetic-sector instrument and experimental technique described in previous publications.[7,8] As always, observed ion signals were checked for response to displacement of the neutral beam-defining slit to ascertain their effusion cell origin. The cell configuration is expected to yield an essentially equilibrium distribution of species. A pressure calibration based on the established vapor pressure of gold was combined with estimated ionization cross-section ratios to evaluate species partial pressures from measured ion intensities.

The Na_2CO_3 powder and NaOH pellet samples were reagent grade materials used without further purification. CO_2 and H_2 reagent gases were obtained from the Matheson Co., while lab-

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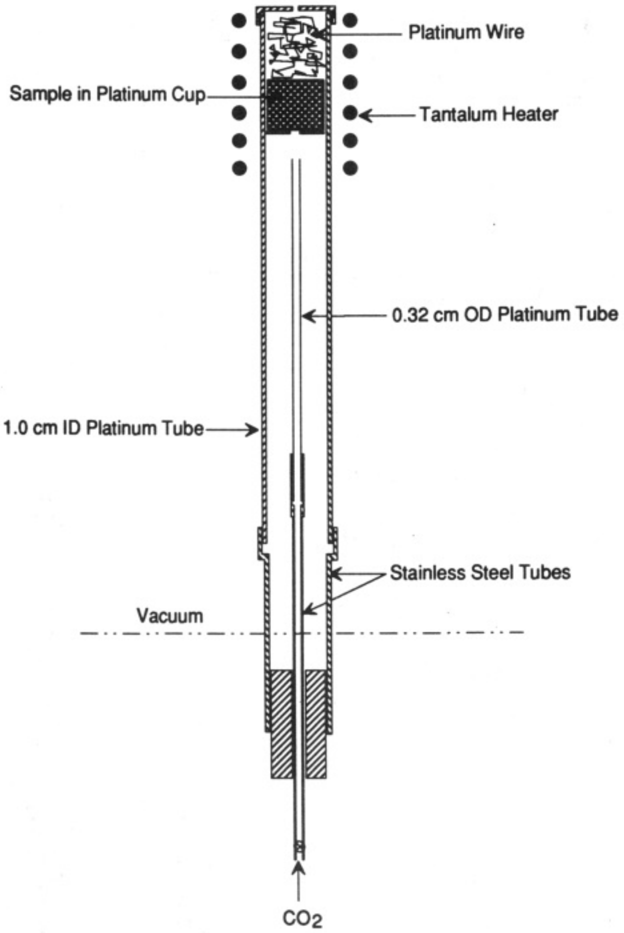

Figure 1. Schematic diagram of the platinum Kudsen cell arrangement.

oratory distilled water was used as the source of H_2O.

Results

A. Na_2CO_3 Reactions. Initial experiments on the vaporization of Na_2CO_3 in the absence of added gases showed emission of detectable quantities of gaseous Na, CO_2, and O_2 above 800 K, indicating the principal vaporization process to be

$$Na_2CO_3(s) = 2Na(g) + CO_2(g) + \tfrac{1}{2}O_2(g) \qquad (2)$$

Above 1050 K, smaller parent ion signals corresponding to the species Na_2CO_3, NaO, Na_2O, and an NaOH impurity that depleted with time were also observed. The threshold appearance potential of $Na_2CO_3^+$ was 7.5 ± 0.3 eV, while those of NaO^+ and Na_2O^+ agreed with values found previously in the sublimation of $Na_2O(s)$.[9] The $Na_2CO_3^+$ signal was easily detectable, varied reproducibly with temperature, and showed the characteristically sharp beam profile associated with effusion-beam species. A few $Na_2CO_3^+$ intensity measurements were made over the range 1065–1123 K for subsequent thermodynamic analysis.

The addition of CO_2, H_2O, and H_2, singly or together, up to pressures approaching the molecular flow limit of 10^{-4} atm yielded no significant changes in the mass spectrum other than the expected increase in the NaOH signal with H_2O and H_2. In particular, the $NaHCO_3^+$ mass position at m/e 84 was scanned carefully, but no signal above the background count rate of a few ions per second could be detected. Likewise, there was no evidence for any new fragment ions such as $NaCO_3^+$, $NaHCO_2^+$, or $NaCO_2^+$. $NaOH^+$ is a potential fragment from $NaHCO_3$, but an abundant parent ion contribution precludes that possibility.

The negative ion spectrum was also scanned at the high flows of H_2O and CO_2 in order to check for the presence of HCO_3^-, which could result from dissociative electron attachment to $NaHCO_3$, reaction 1. However, no detectable HCO_3^- signal was observed under any of the experimental conditions. A moderate O^- signal with a maximum intensity at an electron energy of about 8 eV was observed, probably as a result of dissociative attachment to CO_2.[10]

In all, the search gave no evidence for the presence of $NaHCO_3$.

B. NaOH Reactions. In order to increase the partial pressure of NaOH and optimize the conditions for $NaHCO_3$ formation, the direct vaporization of NaOH in the presence of CO_2 was examined. At about 1150 K, partial pressures of NaOH and CO_2 approaching 10^{-4} atm were obtained. Again, however, no parent or fragment ion species associated with $NaHCO_3$ were detected under any conditions. A search of the negative ion spectrum gave no evidence for HCO_3^- or any related species, other than O^-.

With CO_2 addition, the parent ion $Na_2CO_3^+$ was detected readily at a level of about 10^5 smaller than $NaOH^+$ and CO_2^+, showing that the technique has ample sensitivity for detection of minor Na-containing species.

C. Preliminary Thermodynamic Analysis. Although the search for evidence of $NaHCO_3$ yielded only negative results, one can use the instrumental detection limit to set an upper bound on the $NaHCO_3$ partial pressure and use this information to derive a limiting value for the standard enthalpy of formation. NaOH and CO_2 partial pressures in the effusion source were evaluated from the measured parent ion intensities and were coupled with upper bound values for $NaHCO_3$ to estimate a lower limit to the equilibrium constant of the reaction

$$NaHCO_3(g) = NaOH(g) + CO_2(g) \qquad (3)$$

for subsequent thermodynamic analysis. The points selected were those with the highest partial pressures of NaOH and CO_2, since these conditions put the most stringent limits on the stability of $NaHCO_3$. A conservative estimate of the $NaHCO_3$ partial pressure was derived by increasing the minimum detectable $NaHCO_3^+$ signal limit (~1 ion/s) by a factor of 5, to allow for possible undetected fragmentation.

From two measurements at 1165 K, with NaOH, CO_2, and $NaHCO_3$ partial pressures of 3×10^{-5}, 7×10^{-5}, and $< 8 \times 10^{-11}$ atm, respectively, one calculates for reaction 3 an equilibrium constant $K° > 26$ atm. A third-law calculation with estimated thermal functions for $NaHCO_3$ and established functions for NaOH and CO_2 then yields the limiting enthalpy change $\Delta H°_{298}(3) < 29$ kcal mol^{-1}, with an estimated uncertainty of 5 kcal mol^{-1} based on a possible error of a factor of 5 in $K°$ and an uncertainty of 3 cal K^{-1} mol^{-1} in the Gibbs energy functions. The origins of the thermal functions used in the calculation are described in the Appendix. Note that $\Delta H°_{298}(3)$ is equivalent to the bond dissociation energy $D(NaOH–CO_2) < 29 \pm 5$ kcal mol^{-1}.

From measured intensities of the $Na_2CO_3^+$ signal, the equilibrium pressure of the sublimation process

$$Na_2CO_3(s) = Na_2CO_3(g) \qquad (4)$$

was estimated at seven temperatures over the range 1065–1123 K. Since the ion yield curve of Na_2O^+ indicated a probable fragmentation contribution from Na_2CO_3, a correction was applied to the $Na_2CO_3^+$ intensities to account for this effect in third-law calculations. Measurements were restricted to the region below the melting point of Na_2CO_3 to avoid difficulties created by creep of the liquid carbonate out of the sample container. The equilibrium pressures and derived thermodynamic data are given in Table I, leading to the average value for the enthalpy of sublimation of Na_2CO_3 at 298 K of 96.0 ± 3 kcal mol^{-1}. This value for $\Delta H°_{298}$(sub) and the established properties of the solid then yield the standard enthalpy of formation $\Delta_f H°_{298}(Na_2CO_3,g) = -174.2 \pm 3$ kcal mol^{-1}.

An independent value for $Na_2CO_3(g)$ can be derived from the gaseous equilibrium

$$Na_2O(g) + CO_2(g) = Na_2CO_3(g) \qquad (5)$$

with the results summarized in Table I. From the equilibrium

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TABLE I: Equilibrium Data and Derived Thermochemistry for Reactions Involving $Na_2CO_3(g)$

$Na_2CO_3(s) = Na_2CO_3(g)$

T, K	$P \times 10^{10}$, atm	ΔH°_{298}, kcal mol^{-1}	$\Delta_f H^\circ_{298}(Na_2CO_3,g)$, kcal mol^{-1}
1065	0.60	95.4	-174.9
1093	1.5	95.6	-174.7
1108	2.6	95.7	-174.6
1121	4.1	95.7	-174.6
1121	3.0	96.4	-173.9
1121	2.1	97.2	-173.1
1123	3.4	96.3	-174.0

$Na_2O(g) + CO_2(g) = Na_2CO_3(g)$

T, K	$K^\circ \times 10^5$, atm^{-1}	ΔH°_{298}, kcal mol^{-1}	$\Delta_f H^\circ_{298}(Na_2CO_{3,g})$, kcal mol^{-1}
1287	1.5	-75.7	-173.5
1298	1.0	-75.1	-173.1
1352	0.6	-76.7	-174.7

data for reaction 5, we derive $\Delta H^\circ_{298}(5) = -75.8 \pm 3$ kcal mol^{-1} and $\Delta_f H^\circ_{298}(Na_2CO_3,g) = -173.8 \pm 4$ kcal mol^{-1}, in good agreement with the value from the sublimation reaction. To our knowledge, there are no reported values for comparison.

We would not expect to observe any gaseous HCO_3 or H_2CO_3 under our experimental conditions, even with H_2 and CO_2 pressures near 10^{-4} atm. Assuming even a large exothermicity for the reaction

$$H_2O(g) + CO_2(g) = H_2CO_3(g) \qquad (6)$$

similar to that for H_2SO_4 formation from H_2O and SO_3, a third-law calculation with estimated thermal functions shows that H_2CO_3 would be several orders of magnitude below the detection limit. The same applies to HCO_3. Therefore, the results yield no useful information about H_2CO_3 or HCO_3.

Discussion

In view of the stability and ready detectability of $Na_2CO_3^+$ one would tend to expect similar stability for the parent ion $NaHCO_3^+$. Both neutrals are closed-shell species, probably (Na^+ CO_3^{2-} Na^+) and (Na^+ HCO_3^-), and loss of a single electron should lead to a stable parent ion, as found for the alkali sulfates, chromates, molybdates and nitrates.[11] In any event, the lack of a detectable parent or fragment ion is ascribed to the relatively low thermodynamic stability of $NaHCO_3(g)$ and the consequent low equilibrium partial pressure.

Interestingly enough, the limiting bond dissociation energy $D(NaOH-CO_2) < 29 \pm 5$ kcal mol^{-1} derived from this work is compatible with the value of 30 ± 5 kcal mol^{-1} adopted by Ager and Howard[5] from a consideration of several estimates for $D(OH^--CO_2)$. Although obviously not definitive, our results provide at least an upper bound on the stability of $NaHCO_3$ and indicate that the high estimates[4,6] for $D(OH^--CO_2)$ ranging from 56 to 88 kcal mol^{-1} may be in error. In the proposed stratospheric reaction scheme of Murad and Swider,[1] the reaction

$$NaOH + CO_2 + M \rightarrow NaHCO_3 + M$$

would have an exothermicity <29 kcal mol^{-1} or <1.2 eV. Although this exothermicity limit is felt to be reliable, it should be remembered that $NaHCO_3$ could be present at significant levels under the nonequilibrium conditions prevailing in the upper atmosphere and in some of the laboratory experiments.[5]

TABLE II: Estimated Molecular Constants of $NaHCO_3$ and Na_2CO_3

molecule	$I_xI_yI_z$, g^3 cm^6	σ	g°	ω_i, cm^{-1}
$NaHCO_3$	6×10^{-114}	1	1	1450, 1400, 1050, 880, 720, 700, 280, 240, 60, 3600, 600, 450
Na_2CO_3	4×10^{-113}	2	1	1450, 1050, 880, 720, 280 (2), 240 (2), 170, 1400, 700, 60

TABLE III: Estimated Thermodynamic Functions of Gaseous Na_2CO_3. $H^\circ_{298} - H^\circ_0 = 4.651$ cal mol^{-1}

T, K	C_p, cal K^{-1} mol^{-1}	S°, cal K^{-1} mol^{-1}	$-(G^\circ_T - H^\circ_{298})/T$, cal K^{-1} mol^{-1}	$H^\circ_T - H^\circ_{298}$, cal mol^{-1}
298	21.450	81.901	81.901	0
300	21.499	82.034	81.901	40
400	23.841	88.554	82.774	2312
500	25.621	94.075	84.496	4789
600	26.945	98.869	86.501	7421
700	27.925	103.100	88.576	10167
800	28.657	106.879	90.632	12998
900	29.211	110.288	92.630	15892
1000	29.637	113.388	94.553	18835
1100	29.970	116.229	96.396	21816
1200	30.233	118.849	98.159	24827
1300	30.445	121.277	99.845	27861
1400	30.618	123.540	101.458	30915
1500	30.760	125.657	103.001	33984
1600	30.878	127.646	104.480	37066
1700	30.978	129.522	105.899	40159
1800	31.062	131.295	107.261	43261
1900	31.134	132.976	108.570	46371
2000	31.196	134.575	109.831	49488
2100	31.250	136.098	111.046	52610
2200	31.297	137.553	112.218	55737
2300	31.338	138.945	113.350	58869
2400	31.374	140.280	114.444	62005
2500	31.407	141.561	115.503	65144
2600	31.435	142.793	116.530	68286
2700	31.461	143.980	117.524	71431
2800	31.484	145.125	118.490	74578
2900	31.505	146.230	119.427	77728
3000	31.523	147.298	120.339	80879

TABLE IV: Estimated Thermodynamic Functions of Gaseous $NaHCO_3$. $H^\circ_{298} - H^\circ_0 = 3.941$ cal mol^{-1}

T, K	C_p, cal K^{-1} mol^{-1}	S°, cal K^{-1} mol^{-1}	$-(G^\circ_T - H^\circ_{298})/T$, cal K^{-1} mol^{-1}	$H^\circ_T - H^\circ_{298}$, cal mol^{-1}
298	18.474	74.679	74.679	0
300	18.530	74.793	74.679	34
400	21.192	80.506	75.440	2026
500	23.178	85.460	76.960	4250
600	24.646	89.822	78.747	6645
700	25.749	93.708	80.612	9167
800	26.599	97.204	82.471	11786
900	27.274	100.377	84.287	14481
1000	27.823	103.280	86.043	17237
1100	28.278	105.954	87.733	20042
1200	28.662	108.431	89.356	22890
1300	28.989	110.739	90.913	25773
1400	29.270	112.897	92.407	28686
1500	29.513	114.925	93.842	31625
1600	29.725	116.837	95.220	34588
1700	29.910	118.645	96.545	37570
1800	30.073	120.359	97.821	40569
1900	30.217	121.989	99.050	43583
2000	30.344	123.542	100.236	46612
2100	30.458	125.025	101.382	49652
2200	30.559	126.445	102.489	52703
2300	30.649	127.805	103.560	55763
2400	30.731	129.111	104.598	58832
2500	30.804	130.367	105.604	61909
2600	30.870	131.577	106.579	64993
2700	30.931	132.743	107.527	68083
2800	30.985	133.869	108.448	71179
2900	31.035	134.957	109.343	74280
3000	31.080	136.010	110.215	77386

The derived value for the enthalpy of sublimation of Na_2CO_3 at 298 K, 96.0 ± 3 kcal mol^{-1}, is significantly higher than tabulated[12] values for K_2CO_3 and Cs_2CO_3, 81.2 and 78.5 kcal mol^{-1}, respectively, both ±5 kcal mol^{-1}. It is also higher than the corresponding value[13] for Na_2SO_4, 87.0 kcal mol^{-1}.

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Since our search proved negative, we can say nothing about the thermochemistry of the negative ion HCO_3^- or about the energetics of reaction 1. The species $H_2CO_3(g)$ has recently been identified[14] as a product of the decomposition of $NH_4HCO_3(s)$ at 400 K, but as noted above, equilibrium calculations indicate that this species should be completely negligible under our experimental conditions.

Appendix

Thermodynamic data for $Na_2CO_3(s)$, $H_2O(g)$, and $CO_2(g)$ were taken from the JANAF tables,[15] while values for NaOH(g) and $Na_2O(g)$ were taken from the compilation of Glushko et al.[12] Thermal functions for $NaHCO_3(g)$ and $Na_2CO_3(g)$ were calculated from molecular constants estimated as follows.

$Na_2CO_3(g)$. The moments of inertia were estimated from corresponding values in Na_2SO_4, K_2CO_3, and K_2SO_4,[12] while the fundamental frequencies were selected by analogy with those tabulated for K_2CO_3.[12]

$NaHCO_3(g)$. A planar structure was assumed, with structural parameters for the HCO_3 group as given by the calculations of Jonsson et al.;[6] the Na–O distance was taken to be 0.23 nm, with the Na located along an Na–C–O–H axis. The COONa frequencies were taken from those estimated above for Na_2CO_3, while those for the COH group were estimated by analogy with those of LiOH and NaOH.[12] The estimated frequencies associated with the overall HCO_3 group are consistent with the HCO_3^- fundamentals assigned from the infrared spectra of decomposed bicarbonate salts in alkali halide matrices.[16]

A summary of the estimated molecular constants of Na_2CO_3 and $NaHCO_3$ are listed in Table II in terms of the moments of inertia (I), fundamental frequencies (ω), rotational symmetry number (σ), and electronic ground state statistical weight (g). Tables of thermal functions calculated from these constants are given in Tables III and IV, based on a standard-state pressure of 1 atm. Uncertainties in the entropies and Gibbs energy functions are estimated to be on the order of 2 kcal K^{-1} mol^{-1} at 298 K and 3 cal K^{-1} mol^{-1} at 1000 K. For the sake of internal consistency, more significant figures are included than are warranted by the accuracy of the calculated functions.

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Registry No. Na_2CO_3, 497-19-8; NaOH, 1310-73-2; CO_2, 124-38-9; H_2O, 7732-18-5; H_2, 1333-74-0; $NaHCO_3$, 144-55-8; O, 7782-44-7; Na, 7440-23-5.

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Time-Resolved Fluorescence and Self-Diffusion Studies in Systems of a Cationic Surfactant and an Anionic Polyelectrolyte

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The interaction between the anionic polysaccharide hyaluronan (Hy) and the cationic surfactants decyl-(C_{10}TAB) and dodecyl-(C_{12}TAB) trimethylammonium bromide has been investigated by ^{1}H NMR self-diffusion measurements and by time-resolved fluorescence measurements with pyrene as the probe and dimethylbenzophenone as the quencher. The critical aggregation concentration (cac) was found to be slightly lower than the cmc and about half of the cmc, for C_{10}TAB and C_{12}TAB, respectively. The cac is furthermore seen to depend on the Hy concentration. The steady-state spectra for pyrene in surfactant solutions with and without Hy are almost identical, which indicates a structure of surfactant micelles in the presence of Hy. The fluorescence lifetime, τ_0, for pyrene is increased by the interaction between the surfactants and the polyelectrolyte, due to the ability of the polyelectrolyte to displace the bromide ions from the micellar surface. The increase is considerably larger for the longer surfactant. The τ_0 value furthermore depends on the quotient between Hy and surfactant in the sample. The fluorescence decay curves obtained in the presence of quencher are of the same type as for ordinary micelles, in the presence of Hy, and are well described by the model proposed by Infelta et al. The aggregation numbers for the micelles are relatively unaffected by the presence of Hy.

Introduction

The field of polymer–surfactant interactions in aqueous solution has been studied for more than 20 years, and several reviews have appeared.[1–4] More recently, an increasing interest has been directed toward the structure of polymer–surfactant aggregates which spontaneously are formed in many systems of this type, and a variety of methods have been used to examine polymer–surfactant systems. Among the most successful methods are small-angle neutron scattering (SANS) studies,[5,6] different nuclear magnetic resonance (NMR) methods,[7–9] and photophysical methods, such as fluorescence quenching techniques.[9–14] The general picture emerging from these studies is that the surfactant

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