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Multinuclear Relaxation and NMR Self-Diffusion Study of the Molecular Dynamics in Acetonitrile-Chloroform Liquid Mixtures

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The ^2H , ^{13}C , ^{14}N , and ^{35}Cl NMR relaxation times and ^2H NMR self-diffusion results are reported for acetonitrile and chloroform in pure liquids and in binary mixtures. The relaxation times provide the reorientational correlation times for different axes in the molecules. The diffusion data and the reorientational correlation times for the tumbling of the symmetry axes of the symmetric tops, studied as a function of the mixture viscosity, deviate from the hydrodynamic regime. The variation with the solution composition, however, can be explained by "chemical" arguments invoking intermolecular interactions decreasing in the series acetonitrile-acetonitrile, acetonitrile-chloroform, chloroform-chloroform. The correlation times derived from the relaxation data for the nuclei residing off the symmetry axis can be used to test the applicability of various models for the rotational motion in liquids. It is found that the spinning motion in acetonitrile is too rapid to be described by the small-step rotational diffusion, while chloroform is on the borderline of applicability of this model. The extended J -diffusion model can be used to correlate the composition dependence of the two reorientational correlation times for acetonitrile. However, the angular momentum correlation times obtained in this way disagree with the relaxation data for the carbon-13 nuclei in this molecule. The J -diffusion model also fails to describe the chloroform data.

Introduction

Nuclear spin relaxation measurements are an important source of information on molecular interactions and dynamics of pure liquids and solutions. The measurements become particularly attractive if several magnetic nuclei can be studied independently and if the molecular symmetry facilitates the analysis of the results. The symmetric top molecules acetonitrile and chloroform fulfill both of these criteria and have been studied extensively with the NMR relaxation methods. We report here a multinuclear relaxation study over the whole composition range of the mixtures of the two compounds in the deuterated form, an approach similar to that typically applied to the mixtures of water and organic solvents.¹⁻³ In this way one can study the motional behavior and interactions of the molecules and test the validity of dynamic models.

Molecular dynamics related data for acetonitrile were reviewed recently by Evans.⁴ The first nitrogen-14 relaxation study of acetonitrile was reported already in 1963 by Moniz and Gutowsky.⁵ A comprehensive set of ^{14}N and ^2D relaxation data for liquid trideuteroacetonitrile at various temperatures was reported by Bopp.⁶ Woessner and co-workers⁷ published a similar set of data, also including mixtures of CD_3CN and CH_3CN and proton measurements, and Bull and Jonas⁸ reported deuteron and nitrogen-14 results for CD_3CN as a function of pressure. Bull⁹ also studied acetonitrile- d_3 in an extended temperature interval covering both the liquid and the dense-gas range. von Goldammer and co-workers² studied nitrogen-14 relaxation in CH_3CN and deuteron relaxation in CD_3CN in pure liquids and in mixtures with water. Carbon-13 relaxation data for nondeuterated acetonitrile were reported by Lyerla et al.,¹⁰ by Leipert and co-workers,¹¹ and

by von Goldammer et al.,¹² while Heatley¹³ studied the proton relaxation of the carbon-13 satellites in the proton spectrum of CH_3CN . More recently, the molecular dynamics of acetonitrile in mixtures with carbon tetrachloride was studied with nitrogen-14 relaxation by Versmold¹⁴ and by Tiffon and co-workers.¹⁵ Among related papers on reorientational dynamics of acetonitrile, one should mention the Raman work by Griffiths¹⁶ and Gompf et al.,¹⁷ the Raman and Rayleigh scattering works by Patterson and Griffiths,¹⁸ Whittenburg and Wang,¹⁹ and Danninger and Zundel,²⁰ the vibrational dephasing paper by Yarwood et al.,²¹ and the molecular dynamics simulations by Lynden-Bell and co-workers.²²⁻²⁶

The current state of the art of the molecular dynamics of chloroform was reviewed by Evans.²⁷ The first chlorine-35 relaxation study of chloroform was reported by O'Reilly and Schacher already in 1963.²⁸ The combined deuteron and chlorine relaxation work was reported by Huntress²⁹ for different temperatures and for the neat deuteriochloroform as well as mixtures with benzene. The chlorine-35 relaxation in chloroform was later also studied by Hogenboom et al.³⁰ and by Forsén and co-work-

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ers.³¹ VanderHart³² reported a variable-pressure deuteron relaxation study of deuteriochloroform. Proton relaxation and translational diffusion in liquid chloroform were studied by Bender and Zeidler³³ and by Dinesh and Rogers.^{34,35} The proton-decoupled carbon-13 relaxation in chloroform was studied by Farrar, Shoup, and co-workers^{36,37} and by Dietrich et al.,³⁸ while Duplan et al.³⁹ and Rabii⁴⁰ reported investigations of the proton-coupled carbon relaxation. Related spectroscopic or light-scattering work was also reported by Jonas et al.,^{41,42} Laulicht and Meirman,⁴³ Patterson and Griffiths,¹⁸ van Konynenburg and Steele,⁴⁴ Alms et al.,⁴⁵ Gerschel,⁴⁶ and by Janik.⁴⁷

Binary mixtures of acetonitrile and chloroform have attracted attention of many authors. Murray and Schneider⁴⁸ studied the liquid-solid phase diagram. Kreglewski⁴⁹ and Handa, Jones, and Lorimer⁵⁰⁻⁵² reported measurements of thermodynamic excess functions. The conclusion from this work is that the association equilibria in the system are quite complicated. The association phenomena were already in the 1960s studied by proton NMR shift measurements at low chloroform concentrations by Berkeley and Hanna⁵³ and by Howard et al.,⁵⁴ similar work was also reported later by Lin and Tsay.⁵⁵ The NMR data were interpreted in terms of 1:1 complex formation, which may be an oversimplification. The 1:1 chloroform-acetonitrile complexes were also the subject of quantum chemical calculations by Remko and Polcin⁵⁶ and Figeys et al.⁵⁷ Lichter and Roberts⁵⁸ investigated the solvent effects on the chloroform carbon-13 chemical shifts, one of the solvents being acetonitrile. The dynamic properties in the acetonitrile-chloroform mixtures have been much less studied: proton relaxation measurements were reported by Woo,⁵⁹ while Moradi-Araghi and Schwartz⁶⁰ studied Raman line shapes for the chloroform lines.

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TABLE I: Viscosities and Translational Diffusion Coefficients for Trideuterioacetonitrile-Deuteriochloroform Mixtures at 25 °C

acetonitrile, mol %	$\eta \times 10^3, ^a$ kg m ⁻¹ s ⁻¹	$D \times 10^9, \text{m}^2 \text{s}^{-1}$	
		acetonitrile	chloroform
100	0.34	4.04	
99.0	0.34		
95.8	0.35		
90.0	0.37		
84.7	0.39		
79.6	0.39		
69.2	0.43	3.28	2.68
50.1	0.50	2.88	2.42
30.4	0.53	2.68	2.34
22.0	0.54		
14.9	0.55	2.60	2.33
10.4	0.54	2.66	2.40
3.2	0.55	2.60	2.41
1.2	0.55		
0	0.54	2.45	

^a Measured in the mixture of nondeuterated acetonitrile and chloroform.

The main purpose of this paper is to investigate the effects of the intermolecular association phenomena in the acetonitrile-chloroform system on the microscopic dynamic properties in much greater detail. We report the nitrogen-14, deuteron, and chlorine-35 relaxation times for pure trideuterioacetonitrile, pure deuteriochloroform, and 13 mixtures of the two compounds at 25 and 50 °C. In addition, we report the translational diffusion constants at 25 °C (for some of the samples) and viscosity measurements for the corresponding mixtures of nondeuterated species. For some of the fully deuterated samples we also report and analyze the carbon-13 spin-lattice relaxation times at the two temperatures and at two magnetic fields. The experimental details are described in the next section, followed by the presentation and discussion of the results.

Experimental Work

Acetonitrile-*d*₃ was purchased from Merck, chloroform-*d* was from Stohler Isotope Chemicals, and both were used without further purification. The samples were prepared by weighing, degassed by several freeze-pump-thaw cycles, and sealed in 10-mm NMR tubes. Nondeuterated acetonitrile and chloroform for viscosity measurements were purchased from Merck. The chloroform was distilled twice before use in order to eliminate ethanol, which is used as a stabilizing agent. The viscosity measurements were performed at 25 °C on a Cannon-Fenske viscosimeter. The density values necessary for evaluation of the viscosities were determined at room temperature.

All the nitrogen-14, deuteron *T*₁, and chlorine-35 NMR experiments were performed at 9.4 T on a JEOL GX400 spectrometer. The carbon-13 spin-lattice relaxation times (*T*₁) were measured at 9.4 T on the GX400 spectrometer; some experiments were also performed at 2.35 T on a Varian XL-100 spectrometer. The deuteron pulsed-gradient spin-echo measurements of the self-diffusion coefficients⁶¹ were performed on JEOL FX100 NMR spectrometer operating at 2.35 T. The temperature was controlled by the standard variable-temperature equipment included in the instruments. The ¹⁴N, ³⁵Cl, and the high-field ¹³C experiments were carried out with deuteron lock. The low-field ¹³C experiments were performed with deuteron decoupling and external proton lock. The deuteron *T*₁ experiments at high field were performed without lock; the low-field deuteron spin-echo experiments employed the external ⁷Li lock. All the *T*₁ and *T*₂ values reported, with the exception of some carbon-13 measurements, are the averages of at least two measurements.

The carbon-13 and deuteron *T*₁ measurements were carried out by the fast inversion-recovery method combined with a three-parameter nonlinear fitting of line intensities.⁶² The standard

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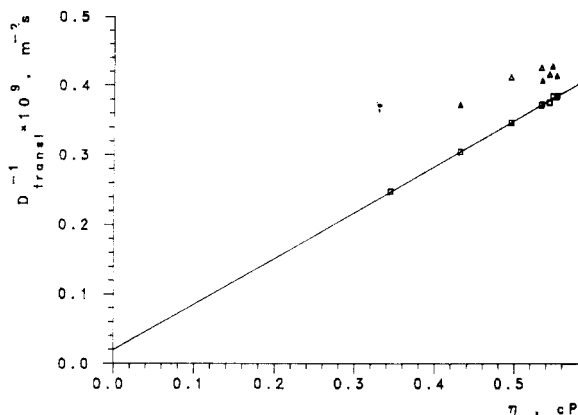


Figure 1. Inverse of the translational diffusion constant for acetonitrile- d_3 (\square) and chloroform- d (Δ) plotted against viscosity at 25 °C.

deviations of the fits for the deuterons were typically of the order of 1–3%, and the overall error was probably of the order of 5%. The overall error for the very long carbon-13 relaxation times was probably higher. The nitrogen-14 transverse relaxation times were determined from the line widths by means of the relation $T_2^{-1} = \pi \Delta \nu_{1/2}$ after transferring the original fids to a VAX 11/750 and employing the NMR1 computer program.⁶³ The estimated uncertainty in the line width measurements is of the order of 5–10%. The chlorine-35 fids were also transferred to the VAX 11/750 computer where a five-parameter (amplitude, frequency, phase, T_2 , dc offset) nonlinear curve fitting was made separately on the real and on the imaginary part of the fid.⁶⁴ The uncertainty is estimated to be the same as in the line width measurements, although the standard deviation within each fit actually became less than 5% after a number of initial points were discarded. We believe, however, that in a series of identical experiments for different samples even smaller variations than the experimental uncertainty are significant as they may reveal trends in the observed properties.

Results and Discussion

We choose to present and discuss the results starting with a macroscopic property—the viscosity—and continuing with the properties on the molecular level, the interpretation of which becomes increasingly complex and model dependent. Thus, translational diffusion coefficients are the first microscopic level property to be discussed, followed by the relaxation of the on-axis quadrupolar nuclei and the relaxation of the off-axis quadrupolar nuclei. The relaxation of carbon-13 is treated in the final part of this section.

Viscosities and self-diffusion coefficients for both components in the acetonitrile–chloroform mixtures at 25 °C are given in Table I. The viscosities of pure compounds agree well with the tabulated values.⁶⁵ The variation of the viscosity with the mixture composition resembles the binary system chloroform–acetone,^{65–67} which, likewise, exhibits a positive deviation from linearity. It has been suggested that this behavior is an indication of strong interactions between the unlike species.^{68–70}

The viscosity η and the diffusion coefficient D are, in the hydrodynamic limit, related to each other by the Stokes–Einstein equation⁷¹

$$D^{-1} = \frac{n\pi\eta r}{kT} \quad (1)$$

TABLE II: Molecular Constants for Trideuterioacetonitrile and Deuteriochloroform

parameter	trideuterioacetonitrile		deuteriochloroform	
	value	ref	value	ref
$r(\text{CD})$, pm	110.7	9, 72	107.3	72
$r(\text{CN})$, pm	115.7	9, 72		
$r(\text{CC})$, pm	145.8	9, 72		
$r(\text{CCl})$, pm			176.2	72
$\theta(\text{DCX})$, deg	109.6	9, 72	110.9	72
I_{\perp} , kg m ²	1.068×10^{-45}	9	2.640×10^{-45}	29
I_{\parallel} , kg m ²	1.092×10^{-46}	9	4.981×10^{-45}	29
QCC(² D), kHz	156	73, 74	155	74
QCC(¹⁴ N), MHz	4.224	74, 75		
QCC(³⁵ Cl), MHz			76.6	76
C_{∞} , kHz	-1.0 ± 0.1	94		
C_2 , kHz	-10.6 ± 0.5	94		

where r is the radius of the diffusing spherical particle and n is equal to 6 for the “sticking” and 4 for the “slipping” boundary condition. In Figure 1, we plot the inverse diffusion coefficients for both components of the acetonitrile–chloroform mixture against viscosity. The plot for acetonitrile is indeed linear with the zero viscosity intercept close to zero and the slope corresponding to the reasonable r value of the order of 2 Å. The plot for chloroform deviates clearly from eq 1.

The molecular constants for trideuterioacetonitrile and deuteriochloroform relevant for the analysis of the nuclear relaxation rates are collected in Table II. The relaxation rates for the quadrupolar nuclei with the nuclear spin quantum number I ($I = 1$ for ²H, ¹⁴N; $I = 3/2$ for ³⁵Cl), for a molecule reorienting isotropically and rapidly (extreme narrowing conditions), are given by⁷⁸

$$T_1^{-1} = T_2^{-1} = \frac{3\pi^2}{10} \left[\frac{2I+3}{I^2(2I-1)} \right] \left[1 + \frac{\epsilon^2}{3} \right] \left[\frac{e^2qQ}{h} \right]^2 \tau_c \quad (2)$$

e^2qQ/h is the quadrupole coupling constant (QCC), and ϵ the asymmetry parameter for the field gradient tensor. τ_c is the rotational correlation time for the second-rank spherical harmonics. If the motion is anisotropic, eq 2 can still be used (with τ_c denoting the correlation time for the reorientation of the principal axis of the field gradient tensor) provided that the field gradient is axially symmetric ($\epsilon = 0$). This correlation time can, for a symmetric top molecule, be expressed in terms of the more fundamental quantities, $\tau^{(2,m)}$ (defined as time integrals of normalized time autocorrelation functions for $l = 2$ and $m = 0, 1, 2$ spherical harmonics referred to the molecule–fixed axis system), by means of the following equation:^{22,79}

$$\tau_c = \frac{1}{4} (3 \cos^2 \theta - 1)^2 \tau^{(2,0)} + 3 \cos^2 \theta \sin^2 \theta \tau^{(2,1)} + \frac{3}{4} \sin^4 \theta \tau^{(2,2)} \quad (3)$$

θ is the angle between the principal axis under consideration and the symmetry axis of the symmetric top. Two further simplifications occur for the nuclei residing on the symmetry axis of a symmetric top molecule. First, the principal axis of the field

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TABLE III: Relaxation Rates at 25 °C for the Nuclei on the Symmetry Axes of the Symmetric Tops and the Derived Correlation Times

acetonitrile, mol %	acetonitrile		chloroform	
	$^{14}\text{N } T_2^{-1},$ s^{-1}	$\tau^{(2,0)},$ ps	$^2\text{D } T_1^{-1},$ s^{-1}	$\tau^{(2,0)},$ ps
100	270 ^a	1.02		
99.0	272	1.03	0.674	1.89
95.8	276	1.04	0.684	1.92
90.0	300	1.14	0.708	1.99
84.7	311	1.18	0.723	2.03
79.6	321	1.21	0.743	2.09
69.2	342	1.30	0.776	2.18
50.1	402	1.52	0.847	2.38
30.4	466	1.76	0.824	2.32
22.0	482	1.83	0.792	2.23
14.9	501	1.90	0.763	2.15
10.4	493	1.87	0.744	2.09
3.2	474	1.80	0.695	1.95
1.2	462	1.75	0.690	1.94
0			0.684 ^b	1.92

^a Literature values: 246 (CH_3CN);² 256 (room temperature);⁶ 228;⁷ 244 (23 °C).⁸ ^b Literature values: 0.741 (20 °C);²⁹ 0.71;³⁰ 0.680 (28 °C).³²

TABLE IV: Relaxation Rates at 50 °C for the Nuclei on the Symmetry Axes of the Symmetric Tops and the Derived Correlation Times

acetonitrile, mol %	acetonitrile		chloroform	
	$^{14}\text{N } T_2^{-1},$ s^{-1}	$\tau^{(2,0)},$ ps	$^2\text{D } T_1^{-1},$ s^{-1}	$\tau^{(2,0)},$ ps
100	217 ^a	0.82		
99.0	219	0.83		
95.8	223	0.84	0.552	1.55
90.0	241	0.91	0.562	1.58
84.7	249	0.94	0.575	1.62
79.6	257	0.97	0.587	1.65
69.2	269	1.02	0.610	1.71
50.1	309	1.17	0.654	1.84
30.4	355	1.34	0.645	1.81
22.0	368	1.39	0.629	1.77
14.9	384	1.45	0.602	1.69
10.4	378	1.43	0.599	1.68
3.2	368	1.40	0.571	1.61
1.2	359	1.36	0.565	1.59
0			0.568 ^b	1.60

^a Literature value: 200 (60 °C).⁹ ^b Literature value: 0.538.³²

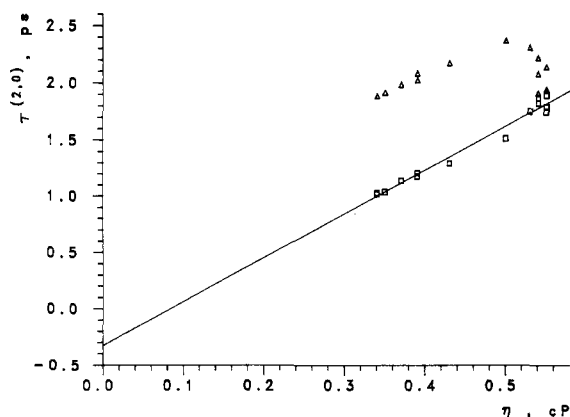
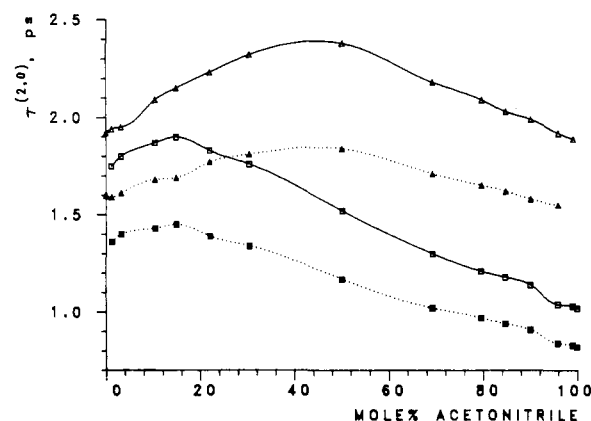
gradient coincides with the symmetry axis and only the first term in eq 3 is nonzero. Second, the asymmetry parameter in eq 2 vanishes by symmetry. Thus, if the QCC is known, the nuclear spin relaxation time measurements provide $\tau^{(2,0)}$ directly.

The relaxation rates at 25 °C for the nuclei on the symmetry axes of the two molecules are collected in Table III, and the corresponding data at 50 °C are found in Table IV. We note first that the data for neat liquids agree reasonably well with earlier experimental work. In order to analyze the experimental results, we assume that the QCC values are independent of the mixture composition and temperature and use the values given in Table II. Tables III and IV also contain the $\tau^{(2,0)}$ values computed from these QCC values.

The correlation times for neat liquids agree quite well with other estimates obtained by other spectroscopic methods.^{4,27} The magnitudes of the $\tau^{(2,0)}$ values in Tables III and IV can be compared to the free rotor correlation times by means of the χ -test of Wallach and Huntress.⁸⁰

$$\chi = \frac{5}{3} \tau^{(2,0)} [kT/I_{\perp}]^{1/2} \quad (4)$$

If $\chi \gg 1$, then the motion is in the small-step rotational diffusion limit. Using the I_{\perp} values of Table II, we obtain the χ values in the range of 3–6, which indicates that the tumbling motion of both molecules does not deviate much from the small-step diffusion picture. It can then be of interest to investigate whether the

**Figure 2.** Rotational correlation time $\tau^{(2,0)}$ for acetonitrile- d_3 (\square) and chloroform- d (Δ) plotted against viscosity at 25 °C.**Figure 3.** Rotational correlation time $\tau^{(2,0)}$ for acetonitrile- d_3 at 25 °C (\square) and 50 °C (\blacksquare) and for chloroform- d at 25 °C (Δ) and 50 °C (\blacktriangle) as a function of mixture composition.

variation of the $\tau^{(2,0)}$ values with the mixture composition can be related to viscosity. In the context of rotational motion it is usual to employ a modified analogue to eq 1, as discussed by Boeré and Kidd⁸¹ and Dote et al.⁸²

$$\tau_c = \frac{V_m f_{\text{stick}} C}{k} \frac{\eta}{T} + \tau_0 \quad (5)$$

τ_0 is the zero viscosity (or infinite temperature) intercept, V_m is the hydrodynamic volume of the reorienting molecule, and f_{stick} is the hydrodynamic friction coefficient dependent on the molecular shape. f_{stick} is equal to 1 for a sphere and can be obtained for more general shapes from the work of Perrin⁸³ and Woessner.⁸⁴ The dimensionless coefficient C is model dependent and takes into account the boundary conditions for the hydrodynamic description of the reorientational motion and possible deviations from such a description. For the "sticking" boundary condition, $C = 1$ and the C values for the slipping boundary condition were given for different molecular shapes by Hu and Zwanzig⁸⁵ and by Youngren and Acrivos.⁸⁶

The correlation times of Table III are plotted against viscosity in Figure 2. The plot for acetonitrile is reasonably linear with the slope of about $3.9 \times 10^{-9} \text{ kg}^{-1} \text{ ms}^2$. Assuming for this molecule the hydrodynamic volume of $47 \times 10^6 \text{ pm}^3$ and the axial ratio of 2.2:3,⁷⁴ one obtains $f_{\text{stick}} = 1.126$ and, from the slope of the straight line, $C = 0.30$. This value is somewhat higher than the slipping boundary value of 0.25.⁸⁵ The $\tau^{(2,0)}$ data for chloroform

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seem to follow the functional form of eq 5 only in the range of high acetonitrile concentrations.

It is in fact more enlightening to look at the $\tau^{(2,0)}$ data as a function of the mixture composition; cf. Figure 3. The region of high acetonitrile content corresponds to the linear part of the diagrams in Figure 2 or to the hydrodynamic regime. The chloroform-rich part of the diagram is the more interesting and challenging one. Below 15 mol % acetonitrile, the $\tau^{(2,0)}$ values for this molecule decrease slightly upon increasing dilution with chloroform. A similar variation of the nitrogen line width (and thus the acetonitrile correlation time $\tau^{(2,0)}$) was observed by Tiffon et al.¹⁵ in the dilute solutions of acetonitrile in carbon tetrachloride. The authors explained the increased mobility of acetonitrile upon dilution by the break up of the acetonitrile clusters. The same explanation probably holds for dilute solutions of acetonitrile in chloroform. The $\tau^{(2,0)}$ values for chloroform increase with increasing acetonitrile concentration up to the equimolar mixture. This was previously observed in the Raman study of Moradi-Araghi and Schwartz.⁶⁰ The authors explained the observation by proposing that the molecular reorientation of chloroform is slowed down by dipole-dipole "frictional" interactions with the highly polar acetonitrile molecules. While we judge their nomenclature (suggesting the dielectric friction mechanism⁸⁷⁻⁸⁹) as unfortunate, we agree with the notion of the molecular interactions between acetonitrile and chloroform retarding the reorientation of chloroform molecules. Since chloroform is also known to self-associate,²⁹ we believe that a consistent explanation of the $\tau^{(2,0)}$ data in Figure 3 can be obtained assuming all the species to interact with each other, with the strengths of the interactions decreasing in the series acetonitrile-acetonitrile, acetonitrile-chloroform, chloroform-chloroform. This interpretation is confirmed by the similar but somewhat flatter curve corresponding to the higher temperature in Figure 3. It also agrees with the thermodynamic analysis of Lorimer and Jones.⁵¹

The relaxation rates of the nuclei residing off the symmetry axis of the symmetric top can also be interpreted by means of eq 2. However, further analysis is hampered by the lack of simplifications provided by the vanishing θ angle. For both molecules under consideration, there is only one θ angle for which τ_c can be obtained. Thus, the experiments do not allow for the independent determination of $\tau^{(2,1)}$ and $\tau^{(2,2)}$. Instead, it becomes necessary to introduce a dynamic model for the liquid that would contain a relation between the three correlation times $\tau^{(2,m)}$ ($m = 0, 1, 2$). The simplest such model is the rotational diffusion model of Shimizu⁹⁰ and Woessner.⁸⁴ In this model, the angular displacements are assumed to occur in small steps and the reorientation of a symmetric top can be described in terms of two rotational diffusion constants, D_{\perp} and D_{\parallel} . The correlation times in eq 2 are related to the two diffusion constants by the following simple relation:²²

$$(\tau^{(2,m)})^{-1} = (6 - m^2)D_{\perp} + m^2D_{\parallel} \quad (6)$$

Another model interrelating the three correlation times $\tau^{(2,m)}$ is the extended diffusion model of Gordon⁹¹ and McClung.⁹² In this model, the angular displacements of arbitrary size are allowed between molecular collisions. The collisions interrupt the rotation and randomize the magnitude and direction (J -diffusion) or only direction (M -diffusion) of the angular momentum. The correlation times $\tau^{(2,m)}$ depend on a single independent dynamic parameter, the average time between collisions or the angular momentum correlation time τ_J , and on the moments of inertia.

The relaxation rates for the off-axis nuclei, deuterons in tri-deuterioacetonitrile and chloride-35 in deuteriochloroform, are summarized in Tables V and VI. Also here, we can note a reasonable agreement with other relaxation rates reported for pure

TABLE V: Relaxation Rates at 25 °C for the Nuclei off the Symmetry Axes of the Symmetric Tops and the Corresponding Correlation Times

acetonitrile, mol %	acetonitrile		chloroform	
	$^2\text{D } T_1^{-1},$ s^{-1}	$\tau_c,$ ps	$^{35}\text{Cl } T_2^{-1} \times 10^{-3},$ s^{-1}	$\tau_c,$ ps
100	0.149 ^a	0.41		
99.0	0.150	0.42	35	1.52
95.8	0.151	0.42	36	1.56
90.0	0.154	0.43	37	1.59
84.7	0.155	0.43	37	1.62
79.6	0.158	0.44	38	1.65
69.2	0.162	0.45	39	1.69
50.1	0.171	0.47	41	1.76
30.4	0.176	0.49	41	1.75
22.0	0.177	0.49	40	1.73
14.9	0.175	0.48	40	1.73
10.4	0.173	0.48	39	1.67
3.2	0.177	0.49	38	1.62
1.2	0.175	0.49	37	1.61
0			37 ^b	1.59

^aLiterature value: 0.15;² 0.156 (room temperature);⁶ 0.152.⁷

^bLiterature value: 32 (20 °C).²⁹

TABLE VI: Relaxation Rates at 50 °C for the Nuclei off the Symmetry Axes of the Symmetric Tops and the Corresponding Correlation Times

acetonitrile, mol %	acetonitrile		chloroform	
	$^2\text{D } T_1^{-1},$ s^{-1}	$\tau_c,$ ps	$^{35}\text{Cl } T_2^{-1} \times 10^{-3},$ s^{-1}	$\tau_c,$ ps
100	0.129 ^a	0.36		
99.0	0.127	0.35		
95.8	0.128	0.36	29	1.26
90.0	0.130	0.36	30	1.29
84.7	0.131	0.36	30	1.32
79.6	0.133	0.37	31	1.34
69.2	0.136	0.38	32	1.36
50.1	0.142	0.40	32	1.40
30.4	0.146	0.41	33	1.41
22.0	0.146	0.40	32	1.39
14.9	0.143	0.40	32	1.39
10.4	0.143	0.40	32	1.38
3.2	0.145	0.40	31	1.33
1.2	0.156	0.43	31	1.32
0			30	1.31

^aLiterature value: 0.127.⁷

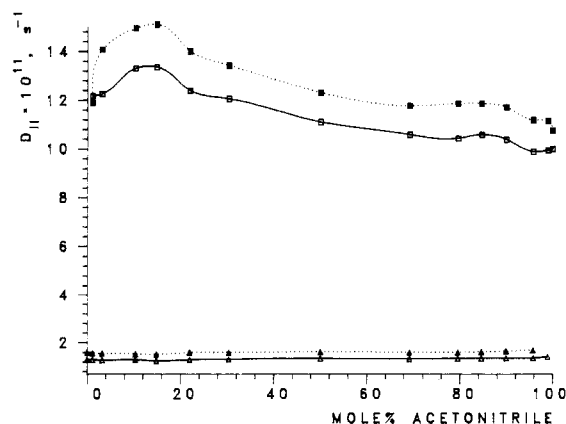


Figure 4. Rotational diffusion constant D_{\parallel} for acetonitrile- d_3 at 25 °C (\square) and 50 °C (\blacksquare) and for chloroform- d at 25 °C (\triangle) and 50 °C (\blacktriangle) as a function of mixture composition.

liquids. The tables also contain the effective correlation times obtained from the QCC values of Table II. The asymmetry parameters are neglected; for deuterons this is the usual procedure, while for chlorine in chloroform the neglect of ϵ is based on the results of ab initio calculations.⁹³

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TABLE VII: Experimental ^{13}C Spin-Lattice Relaxation Rates (s^{-1}) for Trideuterioacetonitrile and Deuteriochloroform

acetonitrile, mol %	temp, $^{\circ}\text{C}$	acetonitrile, CD_3		acetonitrile, CN		chloroform	
		2.35 T	9.4 T	2.35 T	9.4 T	2.35 T	9.4 T
100	25	0.0204	0.0185	0.0154 ^a	0.0209		
	50	0.0282	0.0221		0.0235		
69.2	25	0.0226	0.0216	0.0141	0.0214		0.0058
	50	0.0249	0.0242	0.0161	0.0214		0.0068
50.1	25	0.0235	0.0235	0.0135	0.0226		0.0066
	50	0.0270	0.0258	0.0154	0.0227		0.0067
30.4	25	0.0256	0.0264	0.0128	0.0229		0.0063
	50		0.0288		0.0236		0.0070
0	25					0.0061	0.0062
	50						0.0080

^aLiterature values: ~ 0.018 ; $^{12} 0.017$ (CH_3CN , 2.11 T).¹¹

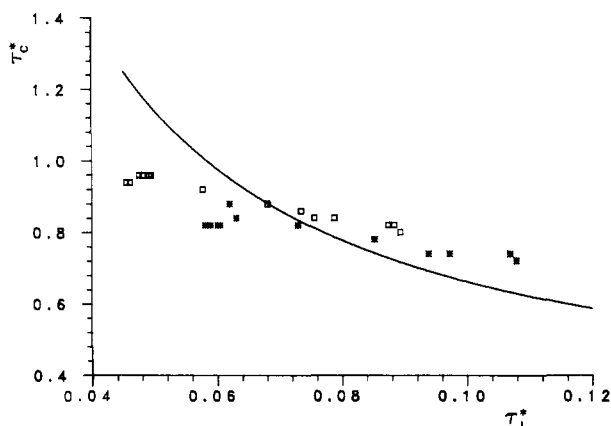


Figure 5. Reduced effective correlation time, τ_c^* , obtained from the deuteron relaxation for acetonitrile- d_3 at 25 $^{\circ}\text{C}$ (\square) and at 50 $^{\circ}\text{C}$ (\blacksquare) versus the reduced angular momentum correlation time, τ_J^* . The solid curve represents the J -diffusion model.

The effective correlation times of Tables V and VI can further be interpreted in terms of the rotational diffusion constants from the data in Tables III and IV for $\tau^{(2,0)}$ and eq 2 and 6. The rotational diffusion constants D_1 , obtained from the angles θ from Table II, are plotted against the composition in Figure 4. The first comment to be made regards the accuracy of the D_1 values; it is low since both the experimental errors in the two relaxation rates and the uncertainties in two QCCs squared propagate to the D_1 . In addition, the validity of the rotational small-step diffusion model on which eq 6 is based is questionable. The χ -test analogous to that of eq 4 (where the relation $\tau_c = (6D_1)^{-1}$ and the I_1 values of Table II are utilized) gives χ values of the order of unity or only slightly larger. This indicates that caution in using eq 6 indeed is required. We abstain therefore from further attempts to interpret Figure 4.

As the next step, we try to interpret the correlation times in Tables V and VI using the extended J -diffusion model. Bull⁹ reported a satisfactory interpretation of the variable-temperature nitrogen-14 and deuteron data for acetonitrile using that model. His conclusions, however, were criticized by Lassigne and Wells⁹⁴ and by Schwartz⁷⁷ on the basis of the carbon-13 experiments and by Böhm et al.²² on the basis of molecular dynamics simulations. We use here the same approach as Bull;⁹ i.e., we use the moments of inertia of Table II and vary the angular momentum correlation time τ_J until the experimental $\tau^{(2,0)}$ values of Tables III and IV are reproduced. These τ_J values are then used to compute $\tau^{(2,1)}$, $\tau^{(2,2)}$, and effective τ_c values (eq 3) corresponding to the correlation times of Tables V and VI. The results of this procedure are summarized in Figures 5 and 6, where the reduced rotational correlation times for the off-axis nuclei (the reduced τ_c is obtained by multiplying the ordinary correlation time by $(kT/I_J)^{1/2}$) are plotted against the reduced τ_J ; the solid curves result from the J -diffusion model. We can see that the agreement between the

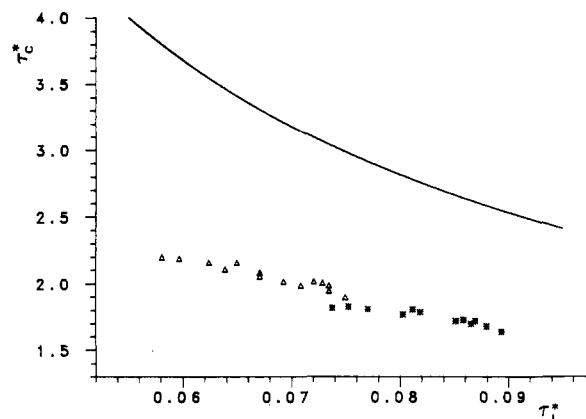


Figure 6. Reduced effective correlation time, τ_c^* , obtained from the chlorine-35 relaxation for chloroform- d at 25 $^{\circ}\text{C}$ (Δ) and at 50 $^{\circ}\text{C}$ (\blacksquare) versus the reduced angular momentum correlation time, τ_J^* . The solid curve represents the J -diffusion model.

solid curve and the points is reasonable for acetonitrile but not for chloroform. To our knowledge, it has never been claimed in the literature that the extended diffusion models could be used for chloroform.

Finally, we turn to the carbon-13 relaxation. The experimental spin-lattice relaxation rates for five of the samples are summarized in Table VII. The spin-lattice relaxation rate for this spin $-1/2$ nucleus is a sum of contributions from the dipole-dipole (DD), spin-rotation (SR), and chemical shift anisotropy (CSA) mechanisms:⁷¹

$$T_1^{-1} = T_{1\text{DD}}^{-1} + T_{1\text{SR}}^{-1} + T_{1\text{CSA}}^{-1} \quad (7)$$

Proton-bearing carbons usually relax predominantly by the dipole-dipole (DD) relaxation. In the deuterated molecules the efficiency of the DD relaxation is reduced due to the much lower magnetic moment of deuterons compared to protons. For the systems at hand, it is also possible to estimate the DD contributions from known interatomic distances (cf. Table II) and correlation times determined above by standard equations. The CSA contribution can easily be obtained from measurements at two different fields, from the fact that $T_{1\text{CSA}}^{-1}$ is proportional to the square of the magnetic field. The remainder is the spin-rotation contribution.

The relaxation rates for the trideuteriomethyl carbon in acetonitrile and for the carbon in chloroform (the relaxation times for chloroform are extremely long, and we were only able to perform a low-field measurement for the neat liquid at 25 $^{\circ}\text{C}$) show no significant field dependence, which means that the CSA mechanism is not operative. The nitrile carbon on the other hand has significantly higher relaxation rates at high field. In Table VIII we summarize the different contributions to the relaxation rates. The CSA relaxation rate follows closely the nitrogen-14 relaxation in acetonitrile, which is gratifying and results in a practically constant value of the chemical shift anisotropy ranging between 424 and 456 ppm (calculated from the correlation time obtained from ^{14}N data). This value can be compared with 307 ppm reported by Kennedy and McFarlane⁹⁵ and with 311 ± 30

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TABLE VIII: Different Contributions to ^{13}C Spin-Lattice Relaxation Rates (s^{-1}) in Acetonitrile- d_3 and Chloroform- d

acetonitrile, mol %	temp, $^{\circ}\text{C}$	acetonitrile, CD_3		acetonitrile, CN			chloroform	
		DD ^a	SR	DD ^b	CSA ^c	SR	DD ^d	SR
100	25	0.0038	0.0147 ^e	0.0002	0.0098	0.0109		
	50	0.0030	0.0191 ^f					
69.2	25	0.0048	0.0168	0.0003	0.0130	0.0081	0.0036	0.0022
	50	0.0038	0.0204	0.0002	0.0094	0.0118	0.0028	0.0040
50.1	25	0.0056	0.0179	0.0003	0.0162	0.0061	0.0039	0.0027
	50	0.0043	0.0215	0.0002	0.0130	0.0095	0.0030	0.0037
30.4	25	0.0065	0.0199	0.0004	0.0180	0.0045	0.0038	0.0025
	50	0.0049	0.0238				0.0030	0.0040
0	25						0.0031	0.0031
	50						0.0027	0.0053

^a Contribution from deuteron. ^b Contribution from nitrogen-14. ^c At 9.4 T. ^d Contribution from deuteron and three chlorine-35. ^e Literature value: 0.0209 (29 $^{\circ}\text{C}$). ^f Literature value: 0.020 (CH_3CN , 39 $^{\circ}\text{C}$).⁹⁴

TABLE IX: Derived Quantities Related to the Spin-Rotation Relaxation

acetonitrile, mol %	temp, $^{\circ}\text{C}$	acetonitrile, CD_3		aceto-nitrile, CN	chloroform	
		τ_J , ^a ps	τ_J , ^b ps	C_{eff}^2 , kHz^2	τ_J , ps	C_{eff}^2 , kHz^2
100	25	0.105	0.0455	3.33		
	50	0.126	0.0538			
69.2	25	0.120	0.0347	2.17	0.0716	0.307
	50	0.134	0.0417	2.60	0.0832	0.444
50.1	25	0.128	0.0294	1.53	0.0669	0.404
	50	0.141	0.0358	1.99	0.0789	0.433
30.4	25	0.142	0.0251	1.02	0.0680	0.368
	50	0.156	0.0309		0.0794	0.465
0	25				0.0789	0.393
	50				0.0884	0.553

^a From eq 9. ^b From $\tau^{(2,0)}$.

ppm given by Appleman and Dailey⁹⁶ from the measurements in nematic liquid crystal. There is even a better agreement with the $\Delta\sigma$ value of 460 ± 50 ppm reported by von Goldammer et al.¹² as estimated from ^{13}C and ^{14}N relaxation data and with $\Delta\sigma = 430$ ppm obtained by the same authors from the relationship between the ^{13}C spin-rotation coupling constant and the chemical shift. The analysis of the SR relaxation data is more complicated. We use here slightly different approaches for the three carbons. For the trideuteriomethyl carbon in acetonitrile, we follow the approach of Schwartz.⁷⁷ We express $T_{1\text{SR}}^{-1}$ using the extended diffusion equation of McClung in the limit of short τ_J .⁹²

$$T_{1\text{SR}}^{-1} = \left[\frac{2kT}{3\hbar^2} \right] (2\pi)^2 [(C_x^2 + C_y^2)I_x + C_z^2 I_z] \tau_J \quad (8)$$

The spin-rotation coupling tensor principal components $C_x = C_y$ and C_z in units of hertz are taken from Lassigne and Wells;⁹⁴ cf. Table II. These have been estimated from the average paramagnetic shielding of the ^{13}C by the method of Flygare⁹⁷ and Deverell.⁹⁸ The τ_J values obtained by means of eq 8 are summarized in Table IX together with the τ_J values extracted from the experimental $\tau^{(2,0)}$ data through the J -diffusion relation, as explained earlier. It can be seen that the angular momentum correlation times from eq 8 do not agree numerically with the corresponding values from the J -diffusion calculation; neither do they decrease with decreasing acetonitrile concentration. According to the extended diffusion theory, the same τ_J should govern the relaxation of the trideuteriomethyl and the nitrile carbons in acetonitrile. In order to confirm or dispute this point, we would need the spin-rotation interaction constants for the nitrile carbon. Such values have been proposed^{11,12,94} but are scattered. Instead, we choose to assume the validity of the extended diffusion assumption and use eq 8 to estimate an effective spin rotational interaction constant C_{eff}^2 such that setting $C_{\text{eff}}^2 = (2C_x^2 + C_z^2)/3$

and using the τ_J from the CD_3 group reproduces $T_{1\text{SR}}^{-1}$ for the nitrile carbon. Also these C_{eff}^2 values are shown in Table IX. There is a large variation in them, which indicates that the extended diffusion model does not describe the motion of acetonitrile successfully in the systems under consideration.

For chloroform, which deviates less from a spherical top, we use an even simpler approach, analogous to that applied earlier to chlorosilanes.⁹⁹ Thus, we estimate τ_J using the simple and approximate relation proposed by Hubbard,¹⁰⁰ valid for spherical tops in the small-step diffusion limit

$$\tau_J = \frac{I_{\text{eff}}}{6kT\tau_{\text{eff}}} \quad (9)$$

where I_{eff} is the moment of inertia and τ_{eff} is the only rotational correlation time required for a spherical top. We set $I_{\text{eff}} = (I_{\parallel} + 2I_{\perp})/3$ and $\tau_{\text{eff}} = (\tau^{(2,0)} + \tau_c)/2$ where $\tau^{(2,0)}$ are taken from Tables III and IV and τ_c from Tables V and VI. The resulting τ_J are listed in Table IX. Finally, the isotropic equivalent of eq 8 is used to evaluate C_{eff}^2 , which are also displayed in Table IX. The values of the spin rotational constants thus obtained are fairly constant, which indicates that the use of the Hubbard small-step diffusion model is a reasonable choice in the case of chloroform. The average of $|C_{\text{eff}}|$ is 0.65 ± 0.06 kHz; deviations reflect experimental uncertainties and anisotropy in the diffusional motion. Appleman and Dailey¹⁰¹ have performed an analysis of the complete shielding tensors in similar molecules and published a value of -0.59 ± 0.02 kHz as the spin rotational constant for CHCl_3 derived from the chemical shift; this value is very close to ours.

Conclusions

The multinuclear diffusion and relaxation approach to the molecular dynamics in simple liquid mixtures provides a wealth of information and, at the same time, a demanding test of the interpreting ability of dynamic models. The translational diffusion coefficients and the rotational correlation times for the tumbling motion of each component in the binary liquid system trideuterioacetonitrile-deuteriochloroform follow similar patterns as a function of the mixture composition and/or viscosity. However, the tumbling motion, which seems to be in the small-step rotational diffusion regime, appears somewhat more sensitive to the intermolecular interactions. The translational diffusion and tumbling data are consistent with the intermolecular forces between two acetonitrile molecules being stronger than those between acetonitrile and chloroform, and those forces being in turn stronger than those between two chloroform molecules.

The spinning motion of both molecules is poorly described by the small-step diffusion model. The extended J -diffusion model works reasonably well as a tool for relating the tumbling and spinning motion of acetonitrile, while the same approach is not satisfactory in the case of chloroform. Carbon-13 relaxation contains a large contribution from the spin-rotation mechanism.

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The interpretation of spin-rotation data is complicated, and we are not able to get an entirely consistent J -diffusion description of both the quadrupolar and the spin-rotation relaxation processes in acetonitrile.

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Affinity Partitioning in Two-Phase Aqueous Polymer Systems: A Simple Model for the Distribution of the Polymer-Ligand Tail Segments near the Surface of a Particle

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A simple lattice model to investigate the binding of polymer-ligands to particles in aqueous polymer solutions has been developed. Calculations from the model indicate that a significant number of the polymer-tail segments of the polymer-ligand are near the particle surface, where the phase polymer concentration is generally lower than that in the bulk. Consequently, theories that relate the effect of polymer-ligands on particle partitioning behavior to the polymer-ligand distribution between the bulk phases may be inaccurate. Calculations from the model also agree with the data of Cordes et al. for the binding strength of polymer-ligands to particles in aqueous polymer solution.

Introduction

Since the discovery by Albertsson in the 1950s that biomaterials partition unevenly in two-phase aqueous polymer systems,¹ researchers have been trying to develop methods to improve the selectivity of this technique for biomaterial separations. Several papers in the 1960s and 1970s described methods for enhancing the partitioning of specific biomaterials by modifying the phase-forming polymers; these efforts developed into the so-called "affinity partitioning" techniques, in which moieties that preferentially interact with the biomaterial are covalently bound to the ends of a fraction of one of the phase-forming polymers.²

Two particular affinity partitioning methods have predominated: hydrophobic ligand partitioning and site-specific ligand partitioning. The first method entails attachment of hydrophobic groups onto a phase polymer. With poly(ethylene oxide) [PEO], for instance, this means esterifying one or both of the hydroxyl end groups of the PEO with a fatty acid to produce a PEO ester containing at least one hydrophobic end group.³⁻⁹ The number of methylene groups in the ester determines the hydrophobicity of the chain ends and, therefore, the strength of the hydrophobic interaction of the PEO ester with the targeted biomaterials. This method has been used for the selective separation of blood serum proteins and other particles^{3,4,6,7,9,11} and also to examine the surface composition of proteins.^{5,8,12}

The second method^{2,13-20} is similar to the first, except that an

affinity ligand that binds to a specific receptor site on the biomaterial is covalently bound to the phase polymer. The use of polymer-ligands has been reported to significantly enhance the partitioning of some proteins, sometimes by as much as several orders of magnitude.⁷ Although affinity partitioning techniques hold great promise both as a method for investigating the surface of biomaterials and as a way of improving biomaterial separation in two-phase systems, very little is understood about the physics of the relevant interactions.

Flanagan and Barondes² have offered a general thermodynamic model to explain biomaterial partitioning in the presence of polymer-ligands. Assuming that all binding sites on the surface of the biomaterial are independent (i.e., the binding of a polymer-ligand at one site on the biomaterial does not affect the binding of another polymer-ligand at a second site on the same particle) and equal (i.e., the binding strengths of ligands at all sites on the biomaterial are equal), they derived the result

$$\Delta \log K_{\max} = n(\log K_{\text{polymer-ligand}} + \log [(K_a)_{\text{upper}}/(K_a)_{\text{lower}}]) \quad (1)$$

Here the subscripts "upper" and "lower" are labels used to distinguish between the two phases, $\Delta \log K_{\max}$ is the difference between the maximum biomaterial partition coefficient in the presence of polymer-ligand (the biomaterial binding sites are assumed to be saturated) and the biomaterial partition coefficient in the absence of polymer-ligand (defined as $K = [\text{protein}]_{\text{upper}}/[\text{protein}]_{\text{lower}}$), n is the number of binding sites on the biomaterial available to the ligand, $K_{\text{polymer-ligand}}$ is the partition coefficient for the unbound polymer-ligand, and $(K_a)_{\text{upper}}$ and $(K_a)_{\text{lower}}$ are the association, or binding, constants for the polymer-ligand/biomaterial complex in the upper and lower phases, respectively. If the association constants in the two phases are constant or equal, a plot of $\Delta \log K_{\max}$ versus $\log K_{\text{polymer-ligand}}$ (produced, for example, by changing the phase compositions) should yield a straight line of slope n . In general, however, such a plot is not obtained.^{9,20}

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