

A new approach to the silica gel surface : characterization of different surface regions by ^{29}Si magic angle spinning NMR relaxation parameters and consequences for quantification of silica gels by NMR [Erratum to document cited in CA112(24):223903d]

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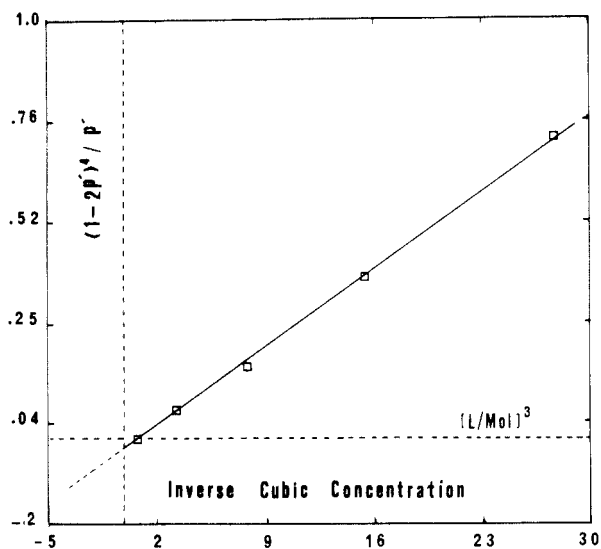


Figure 3. Dependence of mole fractions of complexed species, $(1 - 2P)^4/P'$, on the inverse cubic ligand concentration, $1/[E_0]^3$, for a 2:2 ratio of complexing of 12-crown-4/LiCl in methanol-*d*.

TABLE V: ^{13}C Dipole-Dipole Relaxation Time and Complex Formation Parameters of 12-Crown-4/LiCl in Methanol-*d* at 303 K

stoich ^a	T_{AE} ^b	K_e	$\log K_e$	$-\Delta G^\circ$	intercept ^d
1:1	1.340	0.575	-0.552	-0.332	-0.785
2:1	1.740	5.303	1.668	1.004	-0.009
1:2	1.400	3.787	1.331	0.801	-0.223
2:2	1.770	37.477	3.624	2.181	0.002
3:2	1.836	274.289	5.614	3.380	0.000
2:3	1.520	198.049	5.288	3.184	0.001
3:3	1.840	3093.500	8.037	4.839	-0.003
4:3	1.876	24027.000	10.087	6.072	-0.000

^aThe ratio of the ligand to the cation. ^bThe simulated relaxation time of fully complexed ligand. ^cThe free energy of complex formation in kcal/mol at 303 K. ^dThe intercept of Figures 1-3.

ion-ligand interactions. In fact, the increased degree for complexation, or aggregation, apparently caused relatively higher T_{AE} values for higher degree of the ligand and accordingly lower values for higher degree of cation, indicating the existence of a highly charged molecular liquid structure (Table V).

Figures 1-3 display the typical relationships for LiCl where the cation exchange rate is slow, even in a close packing system.

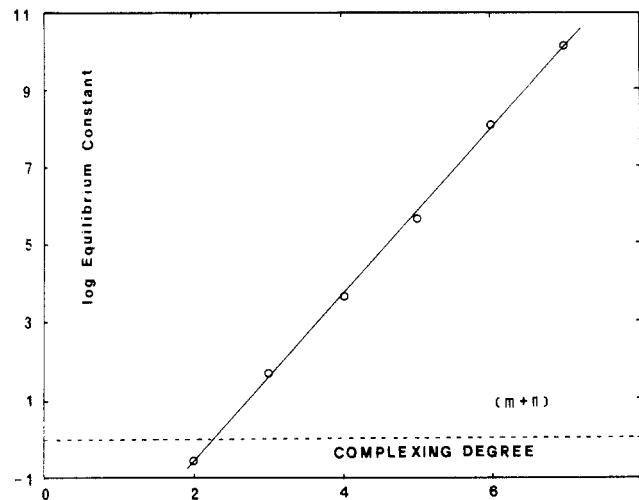


Figure 4. Dependence of log equilibrium constants on the sum of the complexing stoichiometries in 12-crown-4/LiCl solutions.

On the other hand, the y intercept of these plottings was expected to be close to zero for an increased ion/ligand chain; this was observed, providing another piece of evidence for the existence of a multiple degree of but not multistep complex formation. In all of the studies carried out in our laboratory, exactly the same results were observed.^{29,33} It could be concluded that the actual stoichiometry is different than usual, and the parent solvent (e.g., water or methanol) has a reasonable effect, depending on the cyclic ligand size and the conformation. In order to characterize the theory, utility and the practise of this topic, the 12-crown-4/Li⁺ complex is the most suitable structure. Specificity, several types of stoichiometries of such complexation are clearly displayed in Tables II, III, and IV and Figures 2 and 3. This type of interactions has been predicted before; however, a typical one was observed in the present study.

We should have also mention that, despite the small changes in relaxation time in the encapsulated structure, the $\log K_e$ values change dramatically while $(n + m)$ is increased (see Figure 4 and Table V). It is interesting to note that a linear relationship with the correlation factor of 0.999 was observed between the increased stoichiometry $(m + n = 2, 3, 4, \dots)$ and $\log K_e$ (therefore free energy) of complex formation, Figure 4.

(33) Erk, C. *J. Mol. Liq.*, in press.

ADDITIONS AND CORRECTIONS

1990, Volume 94

B. Pfeleiderer, K. Albert, E. Bayer, L. van de Ven, J. de Haan,* and C. Cramers: A New Approach to the Silica Gel Surface. Characterization of Different Surface Regions by ^{29}Si Magic Angle Spinning NMR Relaxation Parameters and Consequences for Quantification of Silica Gels by NMR.

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