useful for studying retention processes in RPLC and can be utilized for obtaining optimum separations for a given sample with these stationary phases.

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Chemical Shifts in Carbon-13 Nuclear Magnetic Resonance Spectra of Aminopolycarboxylate Anions

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Prediction of chemical shifts based on emperical additive substituent parameters has been proved to be quite successful in ^{13}C-NMR. It was demonstrated in the pioneering work of Grant and Paul[1] that the chemical shift of a paraffinic carbon in a linear or branched hydrocarbon can be estimated by the emperical substituent rule. Lindeman and Adams[2] extended the work of Grant and Paul to estimate the chemical shifts of substituted alkanes by calculating the shift of the parent alkane and by adding the appropriate substituent parameters. Extensive studies for estimation of chemical shift have been made for compounds containing several functional groups such as alcohols,[3] amines,[4] carboxylates,[5] pyridines,[6] etc. But in our best knowledge the estimation of chemical shifts for more complicated compounds such as aminopolycarboxylic acids has not been reported.

In this paper we predict ^{13}C chemical shifts of 11 aminopolycarboxylate anions in aqueous solution which contain several functional groups (N, O, COO^-) using the emperical substituent parameters.

Table 1. Names and Abbreviations(in parantheses) of Aminopolycarboxylic Acids

Methyliminodiacetic acid(MIDA)
Ethyliminodiacetic acid(EtIDA)
Nitrilotriacetic acid(NTA)
Ethylenediaminetetraacetic acid(EDTA)
1,2-Propylenediaminetetraacetic acid(PDTA)
Diethylenetriaminepentaacetic acid(DTPA)
2-Hydroxyethylethylenediamintriacetic acid(HEDTA)
2-Hydroxyethyliminodiacetic acid(HEIDA)
Ethyletherdiaminetetraacetic acid(EEDTA)
Ethylenebis(oxyethylenenitrilo) tetraacetic acid(EGTA)
2-Hydroxy-1,3-propanediaminetetraacetic acid(HPDTA)

Experimental

The names and abbreviations of aminopolycarboxylic acids studied are listed in Table 1.

Sample solutions for NMR spectra were prepared by dissolving the weighed amounts of aminopolycarboxylic acid in 20% D_2O/80% H_2O to provide 0.5 M solution. The pH of the solution was adjusted with 50% NaOH or concentrated H_2SO_4 solution. Fully deprotonated forms were obtained by raising the pH value to two units above the highest *pKa* value.[7]

^{13}C NMR spectra were obtained at 25.2 MHz on a Varian XL-100 FT spectrometer at 40 ± 2 °C probe temperature. The experimental details for obtaining spectra are same as those given elsewhere.[8] For individual solutions spectral reproducibility was better than ±0.1 ppm.

Results and Discussion

The ^{13}C NMR spectra of 11 fully deprotonated aminopolycarboxylate anions were measured and ^{13}C chemical shifts of these compounds are summarized in Table 2.

Chemical shifts of carboxylate carbons can be predicted by Rabenstein equation (1)[5(b)]

$$\delta_{coo} = 182.09 + \Sigma n_i d_i \quad (1)$$

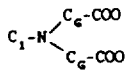
where d are additive parameters for given functional groups at specific numbers of bonds B from COO moiety and n_i is the number of functional groups. The d parameters are given in Table 3.

Chemical shifts of non-carboxylate carbons in aminopolycarboxylate can be predicted by two methods. The chemical

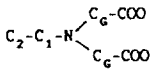
Table 2. Observed and Calculated(in parantheses) ^{13}C Chemical Shits(ppm) for Aminopolycarboxylate Anions

Compound[a]	C_{COO}	$C_{COO'}$	C_G	$C_{G'}$	C_α	C_β	C_γ	C_1	C_2
MIDA	180.25		62.41					43.29	
	(180.50)		(62.48)						(41.79)
EtIDA	180.77		59.33					49.43	12.32
	(180.92)		(59.79)					(48.36)	(12.61)
HEIDA	180.76		60.31					57.79	60.03
	(180.17)		(60.04)					(57.95)	(60.95)
NTA	180.67		60.00						
	(180.22)		(60.29)						
EDTA	181.00		60.16		53.18				
	(180.77)		(60.04)		(52.86)				
PDTA	180.57	181.06	60.44	56.55	59.19	55.10	15.82		
	(180.77)	(180.92)	(60.29)	(57.35)	(58.89)	(53.20)	(17.53)		
HEDTA	180.80	180.97	60.35	60.01	53.23	52.94	52.94	52.45	59.93
	(180.77)	(180.72)	(60.04)	(59.79)	(52.86)	(52.64)	(55.36)	(59.89)	
HPDTA	181.01		60.59		60.59	67.26			
	(180.17)		(59.99)		(59.91)	(67.80)			
DTDA	180.64	180.84	60.21	59.81	53.10	52.95			
	(180.77)	(181.32)	(60.04)	(59.79)	(52.86)	(53.63)			
EEDTA	180.67		59.93		54.67	69.13			
	(180.77)		(60.04)		(53.46)	(70.36)			
EGTA	180.55		59.33		54.36	69.38	70.43		
	(180.77)		(60.04)		(53.46)	(68.73)	(68.97)		

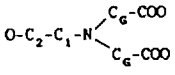
[a] Structural assignment:



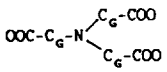
(MIDA)



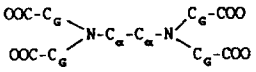
(EtIDA)



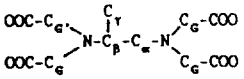
(HEIDA)



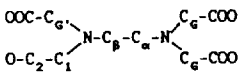
(NTA)



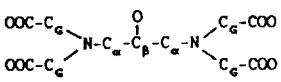
(EDTA)



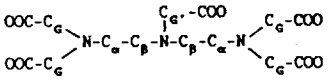
(PDTA)



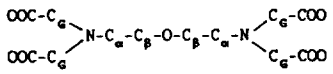
(MEDTA)



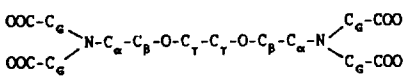
(HPDTA)



(DTDA)



(EEDTA)



(EGTA)

shifts of glycinate carbons can be calculated by the simple equation (2).

$$\delta_G = \delta_{alk} + 15.93 \qquad (2)$$

Table 3. Factors for Calculating ^{13}C-NMR Shifts of Carboxylate Carbons[a]

Factor	Group	B	Value
d_1	CH_3	3	−0.27
d_2	CH_3	4	0.15
d_3	CH_2	1	2.56
d_4	CO_2^-	4	−0.55
d_5[b]	NR_2	2	−3.33
d_6[b]	OH	5	−0.60

[a] From reference 5(b). [b] From this work.

A linear regression analysis was performed using the experimental chemical shifts of the 11 aminopolycarboxylated anions to obtain the equation (2). The chemical shifts of other carbons can be calculated from the substituent parameters which is proposed by Sarneski *et al.*[4(a)] First, the ^{13}C shifts of the appropriate alkanes are calculated by Lindeman and Adams equation (3)[2]

$$\delta_{alk} = B_s + n_2 A_{s2} + n_3 A_{s3} + n_4 A_{s4} + n_\gamma \gamma_s + n_\sigma \delta_s \qquad (3)$$

where s = No. of groups on C of interest, n_2 = No. of secondary α groups, n_3 = No. of tertiary α groups, n_4 = No. of quaternary α groups, n_γ = No. of γ groups, and n_σ = No. of δ groups. The parameters for alkane are given in Table 4. Second, the individual alkane shifts are multiplied by the nitrogen scaling factor (0.932); if the carbon of interest is α to the −OH or −OR moiety, the oxygen attenuation factor (0.83) is then applied. Finally the appropriate nitrogen and oxygen perturbations found in equations (4) through (8) are used to yield the calculated ^{13}C shift.[4(a)]

$$\delta_c = \delta_{alk} \times (0.932)^n + \Sigma N_i \ (n = \text{No. of nitrogen}) \qquad (4)$$

$$\delta_{ROH} = \delta_{RCH_3} \times 0.83 + 43.3 \ (\text{for } C_\alpha) \qquad (5)$$

$$\delta_{ROH} = \delta_{RCH_3} + 0.5 \ (\text{for } C_\beta) \qquad (6)$$

$$\delta_{ROH} = \delta_{RCH_3} - 1.7 \ (\text{for } C_\gamma) \qquad (7)$$

$$\delta_{ROR} = \delta_{RCH_2R} \times 0.83 + 46.87 \ (\text{for } C_\alpha) \qquad (8)$$

Ni is a constant which take into account the number of bonds(i) between the carbon and nitrogen and are found in Table 4. For dialkyl ether the equations (6) and (7) are applicable for C_β and C_γ but a slight modified equation (8) is applicable for C_α.

For example, the ^{13}C chemical shifts of fully deprotonated EDTA can be predicted as follows:

$$\delta_G = B_2 + n_3 A_{23} + n_\gamma \gamma_2 + n_\sigma \delta_2 + 15.93$$
$$= (15.34 + 2 \times 16.70 - 2 \times 2.69 + 3 \times 0.25) + 15.93$$
$$= 60.04$$

$$\delta_\alpha = (B_2 + n_2 A_{22} + n_\gamma \gamma_2 + n_\sigma \delta_2)\ (0.932)^n + N_\alpha + N_\beta$$
$$= (15.34 + 9.75 - 4 \times 2.69 + 6 \times 0.25) \times (0.932)^2$$
$$+ 22.58 + 2.02 = 52.86$$

Table 4. Emperical Parameters for ^{13}C Chemical Shifts of Alkanes[a] and Amines[b]

S	B_S	A_{S2}	A_{S3}	A_{S4}	γ_S	δ_S	N_i
1	6.80	9.56	17.83	25.48	-2.99	0.49	$N=22.58$
2	15.34	9.75	16.70	21.43	-2.69	0.25	$N=2.02$
3	23.46	6.60	11.14	14.70	-2.07		$N=0.20$
4	27.77	2.26	3.96	7.35	0.68		$N=1.63$

[a]From reference 2. [b]From reference 4(a).

$$\delta_{COO} = 182.09 + d_3 + d_4 + d_5$$
$$= 182.09 + 2.56 - 0.55 - 3.33$$
$$= 180.77$$

The experimental values of δ_G, δ_a, and δ_{COO} are 60.16, 53.18 and 181.00 ppm, respectively.

The standard deviations between the shifts calculated by this approach and those determined experimentally for aminopolycarboxylate anions are 0.29 ppm for the carboxylate carbons, 0.40 ppm for the glycinate carbons, and 1.13 ppm for other carbons. We found the good agreement for carboxylate and glycinate carbons but less agreement for other carbons. The larger difference between calculated and experimental values might be originated from the conformational and/or electronic differences between compounds whose data are used as models for the parameterization.

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A New Method of Density Measurement

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Density is defined as a ratio of the sample mass to the volume occupied by that mass. In case of fine powderous or fine porous solid material, it is essential to eliminate a fake volume contributed from fine pores and internal voids in measuring the volume to obtain an accurate density. For this purpose, in the conventional method[1-4] the gas which fills these pores and internal voids is displaced with a wetting liquid such as water and the mass difference thereupon is measured to determine the gas phase volume inside the sample. In most of the experiment, however, a considerable amount of gas, dispersed as fine bubbles in the sample, can not be displaced completely by the liquid, thereby resulting in a negative deviation in the measured density.

In this brief note, a method of measuring an accurate density of powderous or porous substances is reported. In this new method, the void volume is measured with an inert gas using the BET adsorption apparatus.

Experimental

Meterial. Argon gas of 5 N purity is used as the displacing fluid and ambient gas in the BET apparatus. The powder sample is the perovskite-type mixed oxides ($LaNiO_3$, $La_{0.98}Sr_{0.02}NiO_3$, $La_{0.96}Sr_{0.04}NiO_3$, $LaFeO_3$, $La_{0.9}Sr_{0.1}FeO_3$), which are synthesized by the citrate precipitate method[5] from the component metal nitrates in this laboratory and sieved out between 230 and 270 meshes.

Apparatus and Measurement. The BET adsorption apparatus used in this work is a gravimetric one, which has been described in a previous paper[6]. The sensitivity of the microbalance was determined to be 2.23 μg/mV.

Description of the Method

A buoyancy effect is used to measure the volume of the sample with the microbalance in the BET system. Buoyancy effect results from the volume difference between the sample bucket and the counterbalancing magnet of the microbalance. The magnitude of the effect is expected to increase with the pressure of the gas inside the system according to the Archimedes' principle;

$$W = \frac{MP}{RT}\Delta V,$$

where W is a difference of the buoyant force of the bucket and magnet, arising from their volume difference ΔV, and all other symbols have their usual physical meanings. The buoyancy difference W is read off from the counterbalancing currents flowing through the solenoid surrounding the magnet, and then plotted against the gas pressure. From the slope of this plot ΔV can be obtained.

The value of ΔV determined in this way includes two contributions: one from the sample and the other from the unequal volume between the two arms of the balance itself. In order to calibrate for the latter effect, the experiments are carried out with the sample bucket loaded successively with 5 tiny glass bulbs of known volume. One of these calibration