X-ray Characterization of 12 Diuretics

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X-ray diffraction data for 12 diuretics have been obtained by the powder diffractometer technique. They include acetazolamide, althiazide, chlorthalidone, dichlorophenamide, ethacrynic acid, furosemide, hydrochlorothiazide, hydroflumethiazide, mersalyl acid, spironolactone, triamterene, and trichlormethiazide. The results obtained by using the McCreery and Byström-Asklund methods of sample loading were averaged and tabulated in terms of the lattice spacings and the relative line intensities.

Hannawalt and Rinn (*1*) introduced the powder diffraction technique for identifying polycrystalline materials. They described a system for classifying data based on values of d, the interplanar spacing, and I/I_1, the relative intensities of the lines, the strongest line being given a value of 100. The interplanar spacings and the relative intensities of the diffracted maxima can be used for qualitative and quantitative analysis of crystalline materials. Powder diffraction techniques are most commonly employed for determination of relatively pure crystalline materials. Small amounts of impurity, however, are not normally detectable by the X-ray diffraction method, and for reproducible results (concerning the relative intensities of the diffracted maxima) it is necessary to prepare samples where preferred orientation is reduced to a minimum (*2-4*).

On the other hand, characterization of pharmacologically active substances by X-ray powder diffraction data is a safe technique for the identification of drugs. In addition, different salts of the same compound or polymorphic forms are differentiated (*5*). In pharmaceutics this is particularly important because they may have different bulk properties such as suspendibility and rheology. The formulated products may also gain different bioavailability and shelf life.

The data presented in Tables I-XII have already been submitted to the Joint Committee on Powder Diffraction Standards (*7*). However, in the present work additional information is provided concerning mainly variations of line intensities in the patterns of the 12 diuretics.

Experimental Section

Diffraction patterns for 12 diuretics were recorded by the powder diffraction technique. Samples bought from Sigma Chemical Co. included acetazolamide ($C_4H_6N_4O_3S_2$), chlorthalidone ($C_{14}H_{11}ClN_2O_4S$), dichlorophenamide ($C_6H_6Cl_2N_2O_4S_2$), ethacrynic acid ($C_{13}H_{12}Cl_2O_4$), furosemide ($C_{12}H_{11}ClN_2O_5S$), hydrochlorothiazide ($C_7H_6ClN_3O_4S_2$), hydroflumethiazide ($C_8H_8F_3N_3O_4S_2$), mersalyl acid ($C_{13}H_{17}HgNO_6$), triamterene ($C_{12}H_{11}N_7$), and trichlormethiazide ($C_8H_8Cl_3N_3O_4S_2$) (*6*). The rest of the compounds, althiazide ($C_{11}H_{14}ClN_3O_4S_3$) and spironolactone ($C_{24}H_{32}O_4S$) (*6*), were kindly supplied by Searle epe, Kallithea, Athens, Greece. The proton and the carbon NMR spectra were in agreement with the molecular structures. The chemical formulas of the compound analyzed are presented in Figure 1.

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Table I. Values of Interplanar Spacings and Relative Intensities of Lines for Acetazolamide[a]

d/Å	I/I_0	d/Å	I/I_0	d/Å	I/I_0
8.934	*100*	*4.095*	*38*	2.698	5 (br)
8.547	7 (sh)	3.786	17	2.611	2
7.375	6	3.590	30	2.573	3
5.405	17	3.460	4	2.518	2
5.140	6	3.267	2	2.395	4
4.928	6	3.132	3	2.327	3 (br)
4.552	4	*3.033*	*38*	2.270	3
4.462	31	2.969	24	2.225	2
4.396	17 (sh)	2.835	16	2.180	2
4.260	12	2.770	2	2.125	2

[a] The three most intense lines are in italics. sh = shoulder attached to strong line. br = broad line.

Table II. Values of Interplanar Spacings and Relative Intensities for Lines for Altizide[a]

d/Å	I/I_0	d/Å	I/I_0	d/Å	I/I_0
14.14	*82*	3.926	55	2.694	17
10.164	41	3.818	24	2.626	2
8.672	50	3.786	12 (sh)	2.595	5 (br)
8.043	2	3.597	16	2.531	5 (br)
7.081	38	3.562	12 (sh)	2.548	6 (br)
5.455	17	3.460	5	2.462	2 (br)
5.356	15	3.424	10	2.446	4 (br)
5.111	5 (sh)	3.357	11	2.356	4 (br)
4.963	10 (br)	3.302	28	2.297	6 (br)
4.806	19 (sh)	3.240	13	2.222	2 (br)
4.796	*100*	3.164	25	2.154	2 (br)
4.322	22	3.121	16	2.137	2 (br)
4.250	19	3.053	6	2.067	3 (br)
4.210	*78*	2.876	4	2.010	2 (br)
4.162	68 (sh)	2.818	23	1.996	2 (br)
4.022	6	2.726	11 (sh)		

[a] The three most intense lines are in italics. sh = shoulder attached to strong line. br = broad line.

Table III. Values of Interplanar Spacings and Relative Intensities of Lines for Chlorthalidone[a]

d/Å	I/I_0	d/Å	I/I_0	d/Å	I/I_0
14.14	50	3.858	12 (sh)	2.743	15
8.014	7	3.778	35	2.714	17
7.284	*100*	3.714	37	2.574	9 (br)
6.692	40	3.470	22	2.518	3 (br)
5.840	11	3.339	32	2.464	2 (br)
5.556	7 (sh)	3.202	16	2.414	3 (br)
5.454	11	3.105	18	2.365	6 (br)
5.039	78	3.063	8	2.296	6 (br)
4.695	11	2.993	10	2.279	10 (br)
4.230	25	2.954	9 (sh)	2.219	5 (br)
4.143	60	2.917	19	2.178	4 (br)
4.095	*82*	2.812	11	2.103	4 (br)
3.943	24	2.767	16		

[a] The three most intense lines are in italics. sh = shoulder attached so strong line. br = broad line.

The X-ray powder diffractometer patterns were recorded by mounting ca. 1 g of ground sample in a window of an aluminium specimen holder and then exposing it to the X-ray beams for 40 min, Cu Kα radiation being used. It was essential, for the most satisfactory results, that the number of crystallites con-

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Table IV. Values of Interplanar Spacings and Relative Intensities of Lines for Dichlorophenamide[a]

d/Å	I/I_0	d/Å	I/I_0	d/Å	I/I_0
8.307	27	3.670	22	2.776	6 (br)
6.583	4	3.597	23 (br)	2.751	5 (br)
6.237	30	3.440	14	2.706	8 (br)
5.735	14	3.351	4	2.644	24
5.522	8	3.255	8 (sh)	2.596	4 (br)
5.356	25	3.210	30	2.436	10
4.564	19	3.164	34	2.350	9
4.407	24	3.105	8	2.268	18 (br)
4.307	*83*	3.059	13	2.225	9 (br)
4.171	*100*	3.028	20	2.213	20 (br)
4.125	50 (sh)	2.983	21	2.067	6 (br)
3.952	*83*	2.952	10 (sh)	2.040	4 (br)
3.867	52	2.871	52		

[a] The three most intense lines are in italics. sh = shoulder attached to strong line. br = broad line.

Table V. Values of Interplanar Spacings and Relative Intensities of Lines for Ethacrynic Acid[a]

d/Å	I/I_0	d/Å	I/I_0	d/Å	I/I_0
14.37	*100*	4.004	26	2.876	3 (br)
7.114	*35*	3.678	10 (sh)	2.814	4 (br)
6.657	8	3.626	22	2.780	3 (br)
5.885	12	*3.583*	*25*	2.702	4 (br)
5.810	5	3.562	18 (sh)	2.568	3 (br)
5.574	4	3.527	10 (sh)	2.408	2 (br)
5.293	4	3.414	5	2.380	4 (br)
4.733	8	3.342	12	2.347	3 (br)
4.552	5	3.263	8 (br)	2.279	2 (br)
4.353	2	3.110	2 (br)	2.227	2 (br)
4.271	2	2.993	2 (br)	2.094	3 (br)
4.040	10 (sh)	2.936	4 (br)	2.023	2 (br)

[a] The three most intense lines are in italics. sh = shoulder attached to strong line. br = broad line.

Table VI. Values of Interplanar Spacings and Relative Intensities of Lines for Furosemide[a]

d/Å	I/I_0	d/Å	I/I_0	d/Å	I/I_0
14.73	*48*	3.892	33	2.663	3 (br)
8.177	5	3.850	14 (sh)	2.622	4 (br)
7.375	16	3.818	12 (sh)	2.564	2 (br)
6.810	4	*3.597*	*100*	2.522	5 (br)
6.250	11	3.547	18 (sh)	2.455	4 (br)
5.200	4	3.404	12	2.362	6 (br)
5.082	8	3.243	8	2.309	5 (br)
4.900	24	3.119	22	2.233	4 (br)
4.720	28	3.058	12	2.171	4 (br)
4.695	26 (sh)	3.008	12 (br)	2.141	2 (br)
4.343	18	2.935	8	2.090	2 (br)
4.152	*45*	2.836	9 (br)		

[a] The three most intense lines are in italics. sh = shoulder attached to strong line. br = broad line.

Table VII. Values of Interplanar Spacings and Relative Intensities of Lines for Hydrochlorothiazide[a]

d/Å	I/I_0	d/Å	I/I_0	d/Å	I/I_0
9.408	3 (br)	3.453	13	2.508	10 (br)
6.937	7	3.408	5	2.453	8 (br)
6.326	2	3.339	2	2.404	9 (br)
5.389	*100*	3.198	19	2.298	10 (br)
4.783	43	3.145	10	2.249	2 (br)
4.683	*82*	3.105	32	2.219	2 (br)
4.281	*65*	2.903	5	2.161	7 (br)
4.171	43	2.747	5	2.127	2 (br)
4.095	7 (sh)	2.722	2	2.078	3 (br)
3.887	6	2.683	13		
3.633	40	2.627	8		

[a] The three most line intense lines are in italics. sh = shoulder attached to strong line. br = broad line.

tributing to each reflection was of the appropriate size and that the effect of the preferred orientation of the crystallites was held to a minimum. Since there is a close correlation between the method of packing and the preferred orientation, we checked whether the two basic methods of preparing the samples, the McCreery and Byström-Asklund methods (*8*), gave identical or reproducible results concerning the intensities of the lines. The calibration of the goniometer was checked using silicon as a standard.

Table VIII. Values of Interplanar Spacings and Relative Intensities of Lines for Hydroflumethiazide[a]

d/Å	I/I_0	d/Å	I/I_0	d/Å	I/I_0
6.970	4 (br)	3.597	4	2.718	3
5.539	8 (sh)	3.513	5 (sh)	2.603	2 (br)
5.438	*32*	3.477	11	2.543	2 (br)
4.914	3	3.372	4	2.507	2 (br)
4.683	21 (sh)	3.326	4	2.445	6
4.592	*100*	3.243	6 (br)	2.417	2 (br)
4.353	*22*	3.148	9	2.353	3
4.270	18	3.055	15	2.315	3
4.064	4	3.013	3	2.254	2
3.934	2	2.871	4	2.217	2
3.693	16	2.767	3	2.132	2

[a] The three most intense lines are in italics. sh = shoulder attached to strong line. br = broad line.

Table IX. Values of Interplanar Spacings and Relative Intensities of Lines for Mersalyl Acid[a]

d/Å	I/I_0	d/Å	I/I_0	d/Å	I/I_0
9.826	33	4.004	30 (sh)	2.827	10 (br)
8.863	*59*	3.948	37	2.767	12 (br)
8.506	29	3.754	22 (br)	2.667	12 (br)
7.225	*50*	3.693	40	2.578	7 (br)
6.394	24	3.562	24	2.550	8 (br)
5.887	*100*	3.408	44	2.508	3 (br)
5.680	49	3.261	12	2.442	5 (br)
5.539	27	3.203	34	2.398	2 (br)
5.315	5	3.069	4 (br)	2.292	3 (br)
4.901	14 (sh)	3.008	14 (br)	2.233	4 (br)
4.835	32	2.279	20	2.163	1 (br)
4.444	10	2.912	16	2.127	3 (br)

[a] The three most intense lines are in italics. sh = shoulder attached to strong line. br = broad line.

Table X. Values of Interplanar Spacings and Relative Intensities of Lines for Spironolactone[a]

d/Å	I/I_0	d/Å	I/I_0	d/Å	I/I_0
9.458	*90*	4.623	16	2.876	4 (br)
7.596	28	4.332	50	2.801	3 (br)
7.053	43	4.035	15	2.718	4 (br)
6.583	2	3.867	16	2.557	6 (br)
6.109	3 (br)	3.818	17	2.365	4 (br)
5.906	2 (br)	3.590	11 (br)	2.321	5 (br)
5.471	60	3.376	9 (br)	2.091	4 (br)
5.262	*88*	3.121	4 (br)	2.134	6 (br)
5.082	*100*	3.033	10 (br)		
4.770	34	2.979	13 (br)		

[a] The three most intense lines are in italics. sh = shoulder attached to strong line. br = broad line.

Table XI. Values of Interplanar Spacings and Relative Intensities of Lines for Triamterene[a]

d/Å	I/I_0	d/Å	I/I_0	d/Å	I/I_0
9.458	*100*	4.720	4	3.116	13 (br)
7.803	21	4.552	14	3.003	6
6.862	11	4.261	32 (sh)	2.862	8 (br)
6.026	26 (br)	*4.187*	*50*	2.734	4 (br)
5.829	8 (sh)	4.133	48 (sh)	2.374	3 (br)
5.421	17	3.892	7	2.281	4 (br)
5.293	16	3.548	9	2.171	3 (br)
4.975	14	*3.389*	*68*	2.036	3 (br)

[a] The three most intense lines are in italics. sh = shoulder attached to strong line. br = broad line.

Table XII. Values of Interplanar Spacings and Relative Intensities of Lines for Trichlormethiazide[a]

d/Å	I/I_0	d/Å	I/I_0	d/Å	I/I_0
8.889	12	4.124	40 (sh)	2.896	9 (br)
8.080	5	*4.037*	*100*	2.861	4 (br)
7.207	*25*	3.870	14	2.770	15
6.657	7	3.663	10	2.691	6 (br)
6.430	13	3.604	13	2.644	6 (br)
6.237	3	3.493	26	2.545	8 (br)
5.810	5	3.424	6 (br)	2.506	6 (br)
5.609	6	3.366	2 (br)	2.447	5 (br)
5.402	16	3.249	7 (br)	2.238	4 (br)
4.825	3	3.203	8 (br)	2.168	4 (br)
4.681	13	3.116	5 (br)	2.094	4 (br)
4.418	*62*	3.031	14		
4.252	14	2.969	14		

[a] The three most intense lines are in italics. sh = shoulder attached to strong line. br = broad line.

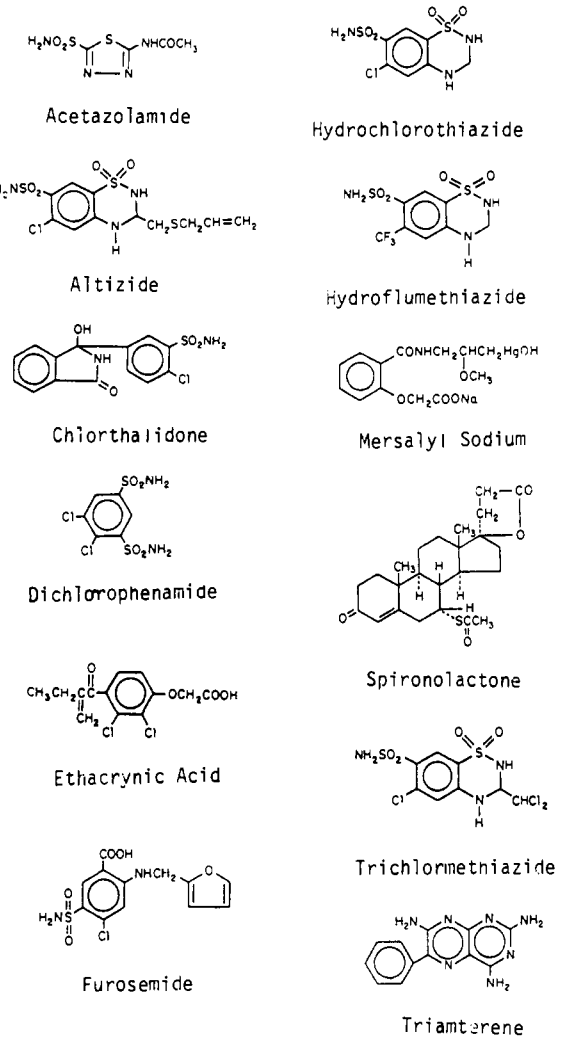

Figure 1. Chemical formulas of the 12 diuretics.

In the patterns obtained by the powder diffractometer, each centimenter was equal to 1° of 2θ on the chart paper output. The lattice spacing (*d*, Å) was calculated using the Bragg equation $d = 1.5418/2 \sin \theta$. Samples were scanned at 20 °C over the 2θ range 5–45° at 1°/min. The relative intensities (I/I_1) were measured simply in terms of peak height (I) above background, relative to peak height above background for the strongest line (I_1) in each pattern taken as 100.

Results and Discussion

Table I and Figures 2–13 show the data and the X-ray patterns obtained for the 12 diuretics in terms of the lattice spacings and the relative intensities of the lines. These, which characterize the 12 diuretics, are not described in full detail in the *Powder Diffraction File* (*7*). Some of them yield very characteristic patterns, whereas for others the intensity of lines

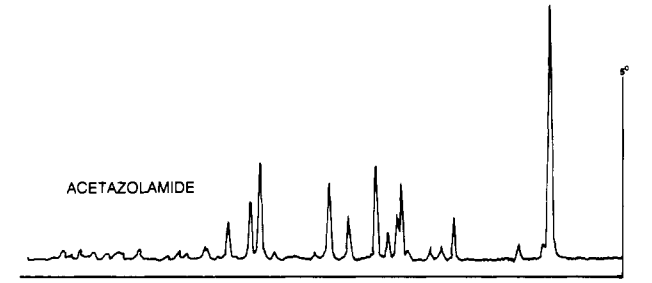

Figure 2. X-ray powder diffraction pattern of acetazolamide.

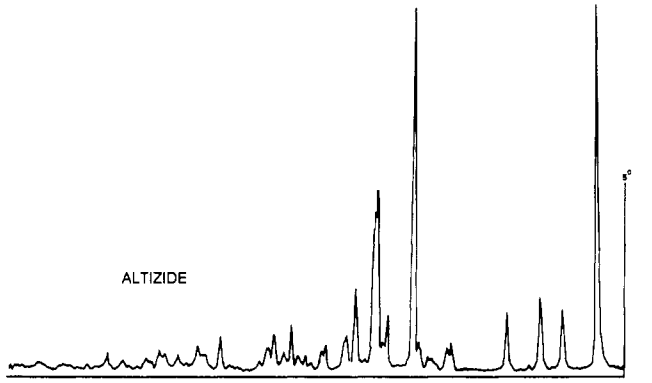

Figure 3. X-ray powder diffraction pattern of altizide.

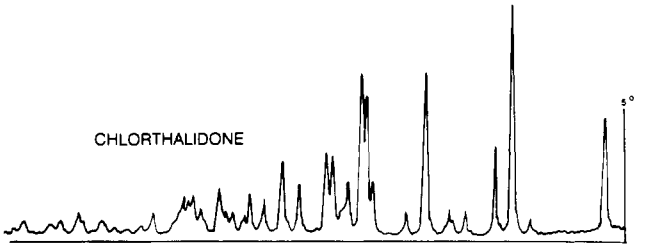

Figure 4. X-ray powder diffraction pattern of chlorthalidone.

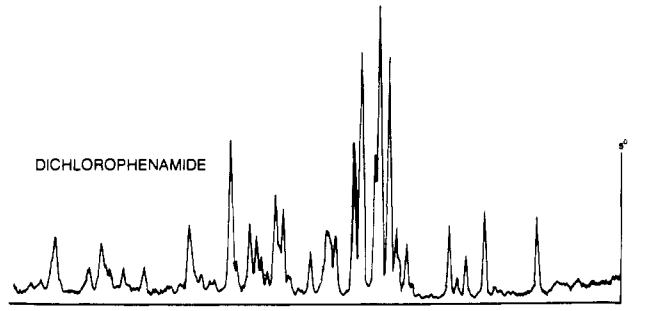

Figure 5. X-ray powder diffraction pattern of dichlorophenamide.

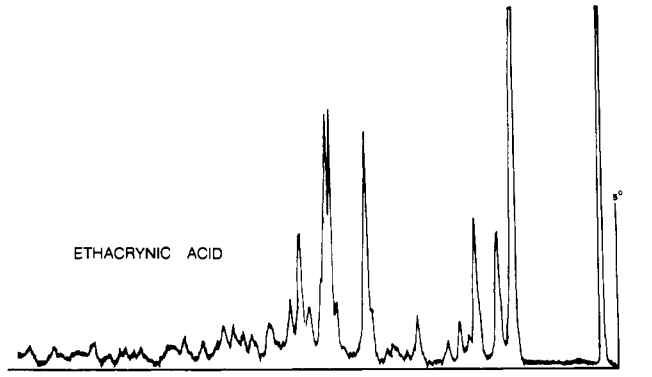

Figure 6. X-ray powder diffraction pattern of ethacrynic acid.

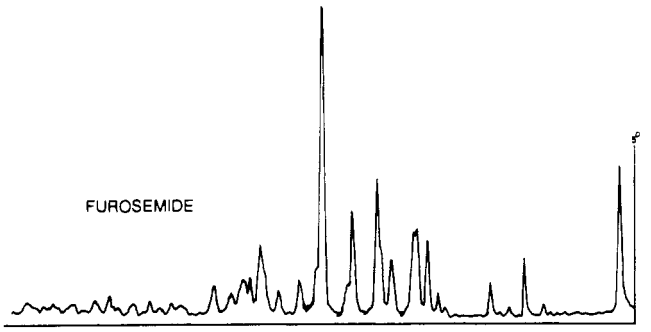

Figure 7. X-ray powder diffraction pattern of furosemide.

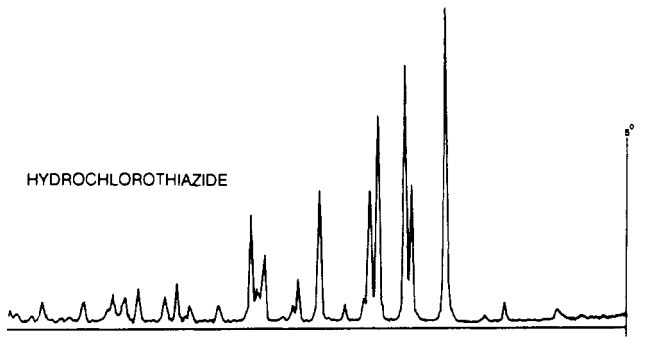

Figure 8. X-ray powder diffraction pattern of hydrochlorothiazide.

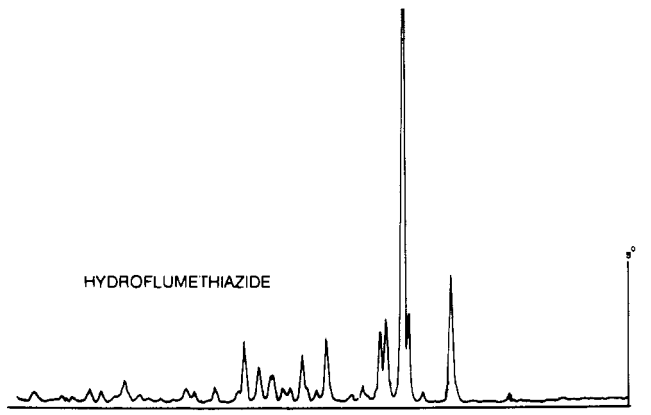

Figure 9. X-ray powder diffraction pattern of hydroflumethiazide.

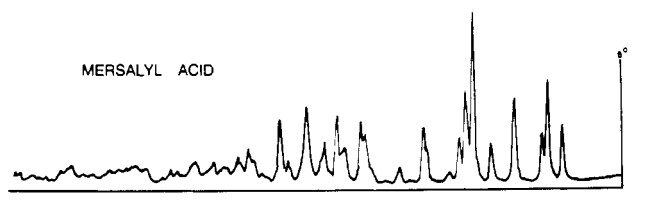

Figure 10. X-ray powder diffraction pattern of mersalyl acid.

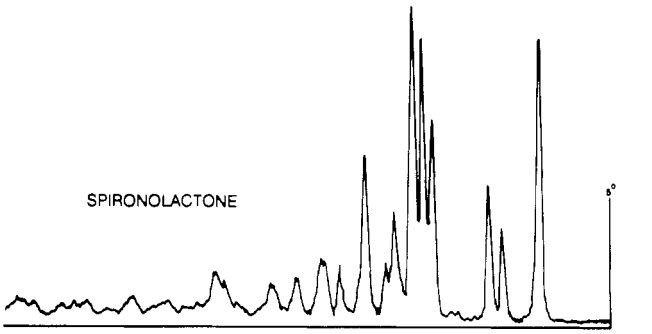

Figure 11. X-ray powder diffraction pattern of spironolactone.

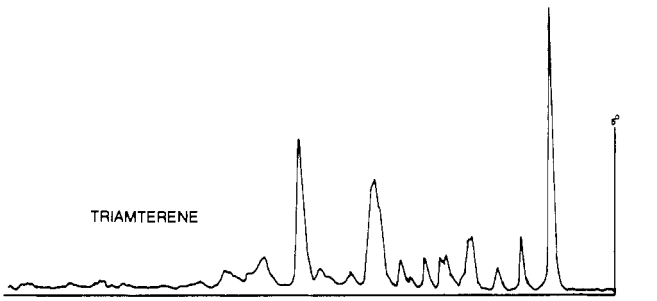

Figure 12. X-ray powder diffraction pattern of triamterene.

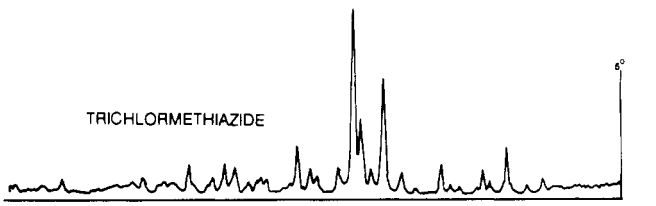

Figure 13. X-ray powder diffraction pattern of trichlormethiazide.

can vary with the method of loading the sample. In Table I, the values of the line intensities in some cases are an average of the same results obtained per compound by the two methods of preparing the crystalline material (*2–4*, *8*).

In chlorthalidone the three most intense lines are exposed at 7.284 Å (100), 4.095 Å (82), and 5.039 Å (78) and in hydrochlorothiazide at 5.389 Å (100), 4.683 Å (82), and 4.280 Å (65), correspondingly. It was observed that the intensity readings for each lattice spacing for both compounds varied with each sample preparation, and the maximum intensity values changed among themselves. Trichlormethiazide yields a very reproducible pattern, the only exception being the two most intense lines at 4.037 Å (100) and 4.418 Å (62), which may vary in intensity. That is, in some patterns the line at 4.418 Å can be much more intense than the other. The pattern of triamterene is very reproducible, but most of the lines are not sharp, and this is very characteristic of the pattern of the compound. In the case of altizide and acetazolamide, their polycrystalline powder suffers from preferred orientation effects and sharp lines are observed at low Bragg angles. This is why the samples have to be prepared carefully. Moreover, in acetazolamide, intense and characteristic lines are observed from 19.9° to 24.8° (lattice spacings (d) 4.462–3.590 Å) which seem unaffected by the method of packing, whereas for altizide the line at 21.10–21.35° (d = 4.210–4.162 Å) ends in two peaks of various intensities, according to the method of packing the sample. Dichlorophenamide reveals a characteristic series of intense lines from 19.45° to 23.00° (d = 4.564–3.867 Å) which are very reproducible. In hydroflumethiazide, the peak at 4.592 Å is sometimes extremely intense with a prominent shoulder at its base, whereas the intensity of the peak at 5.438 Å shows a variation in intensity which is connected with the method of packing. Furosemide, as a powder, is difficult to handle, which is why the Byström-Asklund method of loading the powder from the edge is the only approved technique of putting the sample into the window of an aluminum specimen holder. The pattern is relatively reproducible, but the broad line at about 4.720 Å usually splits into two peaks of various intensities. Ethacrynic acid usually shows only three lines which, compared with the rest of its patterns, are really intense (14.37, 7.114, and 3.583 Å). The line at 14.37 Å is sometimes observed as extremely intense, whereas the line at 3.583 Å splits into two peaks of different intensities. The pattern of mersalyl acid is very reproducible from 9° to 19.98° (d = 9.826–4.444 Å), as far as intensities are concerned. On the other hand, the d values of interplanar spacings 3.754, 3.693 Å and 4.004, 3.948 Å are double peaks of the same split line which usually show variation in intensity. Spironolactone's pattern is very

reproducible, and the most intense and characteristic lines occur from 9.35° to 20.5° (d = 9.458–4.332 Å). The rest of the lines show the usual line broadening of organic crystalline material.

In conclusion, the data presented show no fundamental discrepancies in the d spacings. Variations in intensities of the strongest line in the diffraction pattern have been explained. Moreover, by employing two different methods of loading the samples, preferred orientation effects were reduced to a minimum. Several runs of different sample loadings have shown that the results are both reproducible and reliable.

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Registry No. Acetazolamide, 59-66-5; althiazide, 5588-16-9; chlorthalidone, 77-36-1; dichlorophenamide, 120-97-8; ethacrynic acid, 58-54-8; furosemide, 54-31-9; hydrochlorothiazide, 58-93-5; hydroflumethiazide, 135-09-1; mersalyl acid, 486-67-9; spironolactone, 52-01-7; triamterene, 396-01-0; trichlormethiazide, 133-67-5.

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Dissociation Constants of Picric Acid in Mixtures of *N*,*N*-Dimethylformamide + Ethane-1,2-diol

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The acid dissociation constants of 2,4,6-trinitrophenol (picric acid) were determined in *N*,*N*-dimethylformamide and ethane-1,2-diol from −10 to +80 °C and in two *N*,*N*-dimethylformamide + ethane-1,2-diol mixtures from +20 to +80 °C using the conductometric method. The experimental conductivity data were analyzed by means of the Fuoss–Hsia equation, and the dissociation constants were fitted by the integrated Van't Hoff equation.

Introduction

In a series of papers (*1*) we have studied binary solvent systems and the acid–base properties that are characteristic of some solutes under certain conditions. In particular, we are interested in developing a model for predicting acid–base conductometric titration curves in nonaqueous media, such as monoprotic and diprotic acids, phenols, and aromatic nitroderivatives, either in binary mixtures or as mixtures with water.

This work is part of a systematic study of the influence of the solvents and the temperature on the dissociation constant of picric acid, chosen as a typical weak electrolyte (*2*, *3*). This work reports conductivity measurements and derived acid dissociation constants for picric acid in the *N*,*N*-dimethylformamide (1) + ethane-1,2-diol (2) solvent system, at 19 temperatures from −10 to +80 °C.

N,*N*-Dimethylformamide is regarded as a dipolar aprotic, protophilic, and a potentially basic solvent, while ethane-1,2-diol is regarded as a dipolar amphiprotic and a potentially acidic solvent. Measurements of dissociation constants of a weak acid in these solvents and their mixtures would provide a better understanding of solvent–cosolvent interactions, of the formation of stable adducts in solution, and of solute–solvent interactions.

N,*N*-Dimethylformamide and ethane-1,2-diol were chosen because they have very similar dielectric constants (ϵ_1 = 37.51 and ϵ_2 = 37.70 at 25 °C). By varying the composition of the binary mixtures, one would expect a gradual variation in the acid–base character of the solvent system, since *N*,*N*-dimethylformamide and ethane-1,2-diol are almost isodielectric over the temperature range studied.

Experimental Section

Materials. The 2,4,6-trinitrophenol (picric acid), supplied by BDH (purum ca. 95%), was twice purified by recrystallization from hot ethanol and diethyl ether (mp 122 °C; lit. 122–3 °C (*4*)). The purity of the final sample used (99.5%) was estimated by acid–base titrimetry by using standard 0.1 N sodium hydroxide solutions supplied by Aldrich. The solvents *N*,*N*-dimethylformamide and ethane-1,2-diol (containing both <0.10% by mass of water, as determined by Karl-Fischer titration) were Carlo Erba high-purity grade. The *N*,*N*-dimethylformamide was purified by passage through a neutral alumina column before use (final purity 99.6% gas cromatographically determined). The ethane-1,2-diol (purity 99.5% gas cromatographically checked) was used without further purification.

Apparatus. Conductances of the solutions were measured with an Amel Model 134 digital conductivity bridge operating in the $0.1 \times 10^{-6} \leq G/S \leq 0.3$ (scale-end) range, with a sensitivity of ≅1.0%, and using platinized platinum electrodes (cell constant 0.98 cm). Temperature control was provided by a Lauda K2R thermostatic bath maintained to ±0.02 °C. Viscosity measurements were performed using a Schott-Geräte AVS 400 viscosity measuring system, equipped with a series of Ubbelohde viscometers. The densities were determined with a digital density meter, Anton Paar Model DMA 60 equipped with a density measuring cell, Model DMA 602, with a sensitivity up to 0.000 001 g cm^{-3}. The dielectric constants were measured by the heterodyne beat method using a WTW-DM01 dipolmeter equipped with a stainless steel cylindrical cell, MFL3 ($21 < \epsilon < 90$), that was calibrated with ethanol (ϵ = 24.30 at 25 °C), methanol (ϵ = 32.63 at 25 °C), glycerol (ϵ = 42.50 at 25 °C), and water (ϵ = 80.37 at 20 °C) (*5*). A frequency of 2.0 MHz was used. Karl-Fischer titrations were performed for the water content of solvents with an automatic titration system

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