

# Studies in Swelling of Cotton. I. Neutral Salt Technique to Determine the True Swelling Parameters in Cadoxen

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## Synopsis

This paper describes the swelling of cotton fiber in cadoxen containing 4.6% cadmium (w/w) and 30% ethylenediamine (w/w). A special neutral salt technique is described involving the analysis of extract as well as mother liquor which enables the determination of mechanically held liquor and hence the values of true absorption. The percentage true weight swelling values are much lower than the percentage apparent weight swelling as measured by centrifuge technique. The effect of variation in material-to-liquor ratio on the true absorption of cadmium and ethylenediamine is also investigated.

## INTRODUCTION

Study of swelling is an important tool for investigating solvent-cellulose interaction. Cadoxen [solution of tris(ethylenediamine) cadmium dihydroxide in aqueous ethylenediamine] has recently received considerable attention as solvent and swelling agent for cellulose. Evans and Jeffries<sup>1</sup> have studied the swelling of cotton with cadoxen solutions of various compositions with respect to ethylenediamine (EDA) and cadmium (Cd). Varma and Bhatia<sup>2</sup> studied the relationship between amount of transverse swelling and Cd content in cadoxen and observed rapidly increasing swelling at low Cd content, followed by an almost linear portion and then a rapid swelling at high Cd contents. They have also reported that swelling in cadoxen under stretch improves orientation and mechanical properties of the fiber.<sup>3</sup> On treatment with crosslinking agents<sup>4</sup> or with bifunctional reactive dyes,<sup>5</sup> the extent of swelling or dissolution was found to be restricted. Evans and Jeffries<sup>6</sup> have suggested that this effect is not due to blocking of the hydroxyl groups by crosslinking agents but due to additional cohesion in the fiber introduced by the chemical crosslinks. Considerable restriction to swelling as observed by measurement of cadoxen retention value has been found to take place on dyeing of cotton with bifunctional reactive dyes, indicating possible formation of crosslinks.<sup>5</sup>

Evans and Jeffries<sup>1</sup> in their studies of swelling in cadoxen of varying Cd and EDA content have determined the absorption of Cd and EDA from analysis of the swollen sample after centrifuging without considering the amount

of mechanically held liquid in the interfibrillar voids and capillaries. They have observed that the concentration of absorbed Cd reaches a leveling-off value of one cadmium atom per anhydroglucose unit (a.g.u.). However, they have also stated that this ratio is likely to have no significance, since at least part of the absorbed Cd would be expected to be present in the swelling solution in the interfibrillar voids and capillaries. It has been shown by many workers that the amount of this mechanically held liquid is by no means negligible.<sup>7,8</sup>

The cellulose-cadoxen system on centrifuging at the end of the treatment period can be diagrammatically represented by Figure 1. Phase I consists of fiber along with chemically bound cadoxen, and phase II consists of mechanically held cadoxen in voids of the fiber. Phase III consists of external mother liquor. The strengths of the solution and other intensive properties in phases II and III are considered as continuous.

In order to precisely determine the composition of phase I involving the chemically bound cadoxen, it will be thus necessary to determine in some way the amount of phase II. This paper describes the swelling of cotton fiber in cadoxen solution at varying material-to-liquor ratios where the neutral salt technique is used to determine the amount of mechanically held liquor. The neutral salt technique is basically similar to the one used by earlier workers for studies of swelling in other agents.<sup>9-11</sup> However, a new method of calculation based on extract and mother liquor analysis for determining the various parameters of swelling has been developed by one of us.<sup>12</sup> Potassium iodide was found to be a suitable neutral salt for the present system; and after trials at different concentrations, 1.0% potassium iodide (w/v) was found to be optimum. At this concentration, the estimation of potassium iodide in the extract was sufficiently accurate, and the percentage apparent weight swelling values were not significantly different from the values obtained on swelling in cadoxen without potassium iodide. In the present system, potassium iodide behaves as an ideal neutral salt, as it has no effect on the chemically sorbed cadmium and EDA and it does not interact with cadoxen.<sup>12</sup>

## EXPERIMENTAL

### Materials

Scoured and bleached 20's (30 tex) single yarn from Indian cotton was used for the present study. The cadoxen solvent without free alkali was prepared and analyzed by a method described in an earlier paper.<sup>13</sup> Ten g/l. potassium iodide (w/v) was dissolved in the cadoxen solvent.

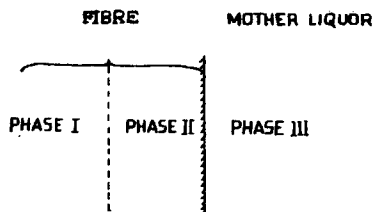


Fig. 1. Diagrammatic representation of cellulose-cadoxen system after centrifuging at end of treatment period.

### Determination of Extent of Swelling

A known volume of cadoxen solvent with neutral salt was added to a glass centrifuge tube and kept in the centrifuge chamber at the desired temperature (25°C). When the desired temperature was attained, a known weight of conditioned cotton yarn was immersed in it. After a 1-hr period of swelling at 25°C, the yarn sample along with the liquor was transferred to a G<sub>1</sub> sintered glass crucible kept suspended on the polyethylene centrifuge tube. The swollen sample was centrifuged at 1500 rpm (centrifugal force = 225 g) for 5 min using a Janetzki centrifuge Model K-23 at 25°C. The centrifuged sample was then transferred to a weighing bottle and immediately weighed. The percentage apparent weight swelling value was calculated on the basis of the dry weight of the fiber.

### Analysis of Centrifuged Sample

The centrifuged sample was transferred from the weighing bottle to a quickfit flask containing 100 ml distilled water and kept for a period of 24 hr. The extract was filtered, and the samples were washed several times with hot water until the washings gave no test for Cd and EDA. The extracts and washings were made to 250 ml; 10 ml of the diluted extract liquor solution was analyzed for EDA and Cd. EDA was estimated by titration with acid and Cd, by addition of excess of EDTA and back-titrating with zinc acetate.<sup>14</sup> Potassium iodide can be volumetrically estimated against potassium iodate under strong acidic conditions.<sup>15</sup> To 50 ml of the diluted cadoxen, 20 ml concentrated hydrochloric acid was added, the solution cooled, 10 ml chloroform incorporated in it, and the mixture titrated against potassium iodate with vigorous shaking until the red color in the chloroform layer vanished.

### Determination of Apparent Absorption of Cd and EDA by Analysis of Centrifuged Sample

If  $\gamma_{\text{Cd}}$  and  $\gamma_{\text{EDA}}$  be the readings of Cd and EDA in the extract, then

$$\frac{\text{atoms of Cd}}{\text{a.g.u.}} = \frac{162}{W} \times \gamma_{\text{Cd}} \times M_{\text{EDTA}} \times 0.025$$

and

$$\frac{\text{moles of EDA}}{\text{a.g.u.}} = \frac{162}{W} \times \gamma_{\text{EDA}} \times N_{\text{H}_2\text{SO}_4} \times 0.0125$$

where  $W$  is the weight of the sample and  $M_{\text{EDTA}}$  and  $N_{\text{H}_2\text{SO}_4}$  are the molality and normality of EDTA and H<sub>2</sub>SO<sub>4</sub> used as titrants.

### Analysis of the Mother Liquor

Ten ml of the mother liquor was diluted to 250 ml in a volumetric flask with distilled water. The analyses of EDA, Cd, and KI were carried out from this solution as described in the analysis of the centrifuged sample.

TABLE I  
Calculation of Apparent and True Weight Swelling

Ratio of cotton to solution	Apparent weight swelling A, %	Density of mother liquor	Reading of KI in extract liquor 0.0166N KIO <sub>3</sub> , ml	Volume of mechanically held liquid ml/100 g	Weight of mechanically held liquid, B g/100 g	Percentage true weight swelling A - B
2 g/30 ml	193	1.0612	4.66	161	171	22
1 g/30 ml	292	1.0629	3.60	250	266	26
0.5 g/30 ml	360	1.0643	2.24	311	331	29
0.5 g/50 ml	492	1.0673	3.04	422	450	42
0.5 g/100 ml	496	1.0673	3.06	426	454	42

## RESULTS AND DISCUSSION

### Determination of Apparent and True Weight Swelling

The extent of swelling is usually found from the increase in weight of the sample after impregnation in a swelling agent followed by centrifuging. However, the value obtained is only the apparent weight swelling value, as a part of the swelling agent in the swollen sample is held mechanically in the voidages (phase II) and its removal is difficult. The percentage apparent weight swelling values given in Table I were determined on the basis of the dry weight of the fiber.

As stated earlier, phases II and III are continuous, and hence the density of the mother liquor will be the same as phase II and can be measured. From the amount of potassium iodide in the extract, the volume of the mechanically held liquid (held in phase II) by the material can be calculated by knowing the potassium iodide concentration in the mother liquor. The values of the true weight swelling (A-B) were calculated by subtracting the weights of the mechanically held liquid (B) in phase II from the apparent weight swelling (A) (Table I). The material-to-liquor ratio was varied from 1:15 to 1:200 by adjusting the volume and keeping the weight of the sample above 0.5 g for accuracy of the analysis. It is observed that the percentage apparent weight swelling value increases with increase in liquor-to-material ratio and reaches a constant value at  $l/m \geq 100/1$ .

The results clearly show that the extent of true weight swelling is only a small fraction of the apparent weight swelling. The true weight swelling values seem also to be affected by increasing the liquor-to-material ratio from 15:1 to 100:1, and further increase does not cause any change in values.

### Apparent Absorption of Cd and EDA by Analysis of Centrifuged Sample

The values of the apparent sorption of Cd and EDA calculated from the centrifuged sample analysis are given in Table II. It is observed that the apparent absorption values of Cd and EDA increase with the increase to liquor-to-material ratio and remain fairly constant at and above 100:1.

TABLE II  
Apparent Absorption of Cd and EDA from Centrifuged Sample

Ratio of cotton to solution	Reading of Cd, 0.05M EDTA, ml	Apparent absorption of Cd, atoms/a.g.u.	Reading of EDA, 0.52N H <sub>2</sub> SO <sub>4</sub> , ml	Apparent absorption of EDA, moles/a.g.u.
2 g/30 ml	2.14	0.215	3.28	1.75
1 g/30 ml	1.66	0.335	2.52	2.65
0.5 g/30 ml	0.98	0.400	1.54	3.25
0.5 g/50 ml	1.20	0.485	2.06	4.35
0.5 g/100 ml	1.22	0.495	2.08	4.40

TABLE III  
Absorption of Cd and EDA from Mother Liquor Analysis

Ratio of cotton to solution	Reading of KI, 0.0166N KIO <sub>3</sub> , ml	Correction factor <i>f</i>	Reading of Cd, 0.05M EDTA, ml	True absorption of Cd, atoms/a.g.u.	Reading of EDA, 0.052N H <sub>2</sub> SO <sub>4</sub> , ml	True absorption of EDA, moles/a.g.u.
0	14.34	—	3.52	—	8.25	—
2 g/30 ml	14.45	0.9923	3.16	0.12	8.08	0.37
1 g/30 ml	14.42	0.9944	3.26	0.17	8.14	0.49
0.5 g/30 ml	14.40	0.9958	3.38	0.19	8.20	0.54
0.5 g/50 ml	14.34	1.0000	3.42	0.20	8.25	—
0.5 g/100 ml	14.34	1.0000	—	—	8.25	—

These apparent values incorporate both phase I and phase II. To calculate the true absorption of the components, it is necessary to know the strength of the solutes in phase II and, as stated earlier, phase II and phase III (mother liquor) are continuous.

#### Absorption of Cd and EDA by Analysis of Mother Liquor

The change in concentration of a particular component in the mother liquor is due to (i) any preferential absorption by cellulose (resulting in decrease in titration reading) and (ii) any changes in total volume of cadoxen. The change in volume of cadoxen is partly due to the true absorption of liquid components by cellulose, as the truly sorbed liquid components become nonsolvents to neutral salt and cause increase in titration reading. In addition to this, the volume of cadoxen may also change because of moisture coming along with the conditioned fiber.

The changes in titration reading due to such volume changes can be corrected from changes in concentration of KI. If  $V_t$  and  $V_o$  be the initial and final volumes of cadoxen before and after interaction, then

$$V_t = V_o \frac{R_{KI,0}}{R_{KI,t}} = V_o \times f$$

where  $R_{KI,0}$  and  $R_{KI,t}$  are the initial and final readings of KI in the mother liquor, and  $f$  is the corresponding correction factor. After proper correction,

the changes in strength of a particular component are only due to the absorption of that component by cellulose. The values of  $f$  are given in Table III. Hence, the amount of truly sorbed Cd and EDA may be calculated from the mother liquor as shown below:

$$\frac{\text{atoms of Cd}}{\text{a.g.u.}} = \frac{162 \times V_0(R_{\text{Cd},0} - f \times R_{\text{Cd},t}) \times M_{\text{EDTA}} \times 0.0025}{W}$$

and

$$\frac{\text{moles of EDA}}{\text{a.g.u.}} = \frac{162 \times V_0(R_{\text{EDA},0} - f \times R_{\text{EDA},t}) \times N_{\text{H}_2\text{SO}_4} \times 0.00125}{W}$$

From the mother liquor analysis, it is observed (Table III) that at higher ratio of solution to cotton there is practically no change in the readings of KI from that in the original solvent, and hence no correction is required to calculate the true absorption value. The readings of EDA in the mother liquor are similar to that of the original solvent at a higher ratio of solution to cotton, but the readings of Cd differ only slightly from the original solvent. The absorption of Cd and EDA calculated after correction from the mother liquor analysis are given in Table III. At higher ratio of solution to cotton, these values cannot be calculated accurately only from the mother liquor analysis, as the difference in titration reading is too small to be determined accurately. At lower ratio of solution to cotton, the values can be calculated but go on increasing and appear to reach a value of true absorption of Cd of the order of 0.20 atoms/a.g.u. For lower ratio of solution to cotton, the value may not represent the equilibrium absorption of Cd for the starting composition of cadoxen, as the end concentration is different.

#### Determination of the Extent of Swelling by Simultaneous Analysis of Swollen Sample and Mother Liquor

The true sorption value for a particular component can be obtained as shown below:

true sorption = apparent sorption

– mechanically held amount of that component.

The apparent sorption values can be calculated from the analysis of extract samples as given earlier in Table II. The values of the mechanically held amount of the components are calculated by multiplying the volume of the mechanically held liquid (described earlier) by the strength of respective component in the mother liquor. The true absorption of Cd may be calculated as follows:

$$\frac{\text{atoms of Cd}}{\text{a.g.u.}} = \frac{162}{W} \left( \gamma_{\text{Cd}} \times M_{\text{EDTA}} \times 0.025 - \frac{\gamma_{\text{KI}}}{R_{\text{KI}}} \times \frac{V}{1000} \times R_{\text{Cd}} \times M_{\text{EDTA}} \times 2.5 \right)$$

and

TABLE IV  
True Absorption of Cd and EDA from Mother Liquor and Extract Analysis

Ratio of cotton to solution	True absorption of Cd, atoms/a.g.u.	True absorption of EDA, moles/a.g.u.	Ratio of moles EDA atoms Cd
2 g/30 ml	0.11	0.36	3.1
1.0 g/30 ml	0.17	0.52	3.0
0.5 g/30 ml	0.18	0.54	3.0
0.5 g/50 ml	0.20	0.60	3.0
0.5 g/100 ml	0.20	0.61	3.1

$$\frac{\text{moles of EDA}}{\text{a.g.u.}} = \frac{162}{W} \left( \gamma_{\text{Cd}} \times N_{\text{H}_2\text{SO}_4} \times 0.0125 - \frac{\gamma_{\text{KI}}}{R_{\text{KI}}} \times \frac{V}{1000} \times R_{\text{EDA}} \times N_{\text{H}_2\text{SO}_4} \times 1.25 \right)$$

where  $\gamma_{\text{KI}}$  and  $R_{\text{KI}}$  are the readings of KI in the extract and mother liquor, and  $V$  is the stock mother diluted for analysis.

The true absorption values of Cd and EDA calculated from the combined analysis of the extract and mother liquor are given in Table IV. It is observed that the true absorption of Cd and EDA increases and reaches a constant value at  $l/m \geq 100/1$ . It would, indeed, be ideal to take a very large liquor-to-material ratio and work in an infinite bath when the analysis of the swelling agent itself along with that of the extract will be quite adequate. However, considering the small total volume (50 ml) of the glass tube used for swelling and necessity to have sufficient weight of the material for analysis to obtain accurate results, the optimum conditions used for swelling were 0.5 g in 50 ml cadoxen, i.e.,  $m:l = 1:100$ . Under these conditions, analysis of the extract as well as the mother liquor would thus enable the determination of true weight swelling as well as true absorption of Cd and EDA. When the ratio of the true absorption of Cd and EDA is calculated, it is found that the ratio is about 3 in all cases.

### SUMMARY AND CONCLUSIONS

Swelling of cotton has been studied in a cadoxen solvent containing 4.6% Cd (w/w) and  $30\% \pm 2\%$  EDA (w/w), as practically no dissolution of cellulose takes place during the period of swelling and the swelling is also of high order.<sup>16</sup> Apparent weight swelling values determined by weight increase are many times higher than the true weight swelling values, as shown by the large weight of the mechanically held liquor. For example, the apparent weight swelling value (492%) at  $l:m = 100:1$  is about 12 times higher than the true weight swelling (42%). These results conclusively show that, even after centrifuging, a substantial part of phase II remains entrapped and gives erroneous results about Cd and EDA sorption. The apparent and true weight swelling values increase with the increase in  $l:m$  ratio and reach a constant value at 100:1. This is due to the fact that, above this ratio, equilibrium absorption of cadoxen takes place corresponding to the cadoxen composition

studied. In the swollen sample analysis, it is found that the large excess of cadoxen is just physically entrapped in the voids and capillaries of the swollen fiber. Accurate estimation of this mechanically held liquid in the swollen fiber is possible by the use of the neutral salt method along with mother liquor analysis. The changes in strength of Cd and EDA in the mother liquor when corrected for the changes in volume by the neutral salt method give true absorption values of Cd and EDA. However, at higher liquor-to-material ratio, there is very little change in the concentration of Cd and EDA in the mother liquor, and true absorption values cannot be determined from the mother liquor analysis alone. When the true absorption values are calculated from the simultaneous analysis of extract and mother liquor, it is found that the value of Cd reaches 0.20 atoms/a.g.u. at  $l:m = 100:1$  and remains constant. The ratio of ethylenediamine to cadmium in all  $m:l$  ratios is about 3, which probably indicates some stoichiometric relation.

Using the neutral salt technique, detailed investigations have been carried out for determination of true absorption of Cd and EDA by standard cotton cellulose after swelling in cadoxen for various periods of treatment time and temperatures. A similar study has also been carried out using mercerized and other structurally modified cellulose to obtain information about the interaction between cellulose and cadoxen solvent during swelling. The effect of this swelling treatment on the fine structure of various cotton samples, as measured by physical and chemical methods of analysis, has been studied. The neutral salt technique has also been found to be useful for studying the swelling of cotton in other swelling agents, such as ethylenediamine and morpholine.

### References

1. G. M. Evans and R. Jeffries, *J. Appl. Polym. Sci.*, **14**, 633 (1970).
2. D. S. Varma and H. C. Bhatia, *Text. Res. J.*, **41**, 790 (1971).
3. D. S. Varma and H. C. Bhatia, *J. Appl. Polym. Sci.*, **14**, 655 (1970).
4. W. Schefer, *Text. Res. J.*, **41**, 927 (1971).
5. W. B. Achwal, Proceeding of 6th Symposium under the Centre of Advanced Study in Applied Chemistry held at Department of Chemical Technology, Bombay, 1971, p. 27.
6. G. M. Evans and R. Jeffries, *J. Appl. Polym. Sci.*, **14**, 655 (1970).
7. J. M. Preston, M. V. Nimkar, and S. P. Gundavda, *J. Text. Inst.*, **42**, T79 (1951).
8. B. Anderson and O. Samuelson, *Svensk Papperstid.*, **65**, 273 (1962).
9. O. Schwarzkopf, *Z. Elektrochem.*, **38**, 353 (1932).
10. G. Champetier, *Comp. Rend.*, **192**, 1593 (1931).
11. C. L. Boesen, *Cellulose Chem. Technol.*, **4**, 149 (1970).
12. S. M. Joshi, M.Sc. (Tech.) Thesis, University of Bombay, 1970.
13. W. B. Achwal and A. B. Gupta, *Angew. Makromol. Chem.*, **2**, 190 (1968).
14. H. Doering, *Das Papier*, **10**, 140 (1956).
15. A. Vogel, *A Textbook of Quantitative Inorganic Analysis*, Longman's Green and Co., London, 1961, p. 375.
16. W. B. Achwal and H. J. Gore, *J. Text. Assoc.*, **35**, 13 (1974).

Received June 23, 1975

Revised December 4, 1975