

Analytical Chemistry of Mowiol

To determine the individual products of the Mowiol range it is necessary to have a knowledge of certain simple methods of chemical and physical investigation.

1. Bulk density

The bulk density of Mowiol granules measured in accordance with DIN 53 468 is approx $0.4 - 0.6 \text{ g} \cdot \text{cm}^{-3}$ according to grade.

2. Volatile content

Mowiol is a technical product with a maximum volatile content of 5% (water and organic solvents).

Method of determination (based on DIN 53 189):

Approx 2g of Mowiol are weighed into a calibrated glass dish with a diameter of approx 5 cm and dried approximately 3 hours to constant weight at 105°C . After cooling in an exsiccator the Mowiol is reweighed and the percentage weight difference calculated.

3. Viscosity

According to DIN 51 550 the viscosity is a measure of the internal friction occurring in the displacement of two adjacent liquid layers.

Units:

The unit of *dynamic viscosity* (η) in the international system of units (SI) is $1 \text{ Pa} \cdot \text{s}$ (Pascal second).

The unit of *kinematic viscosity* (ν), (measured in an Ubbelohde viscometer), is $\text{cm}^2 \cdot \text{s}^{-1}$.

The relationship between dynamic viscosity and kinematic viscosity is as follows:

$$1 \text{ cm}^2 \cdot \text{s}^{-1} = \frac{0,1 \text{ Pa} \cdot \text{s}}{\text{Solution density}}$$

Method of determination:

The viscosity of Mowiol solutions is measured on *freshly made solutions* using a Höppler falling-ball viscometer (DIN 53 015) or an Ubbelohde viscometer (capillary viscometer, DIN 51 562 and DIN 53 012). It is international practice to state the viscosity of 4% aqueous polyvinyl alcohol solutions *at 20°C* . The volatile content of the polyvinyl alcohol has to be taken into account during production of the solution (see Section B 1.1.2). For production of the Mowiol solution see Chapter C.

The viscosity is determined immediately after dissolving and cooling to $20 \pm 0.1^\circ\text{C}$. The solutions must be free of air bubbles.

4. pH measurement

The pH is measured in a 4% aqueous solution using a pH electrode (for the standard commercial single rod measurement system see DIN 19 260, pH measurement, general terms, or DIN 19 261, pH measurement, terms for measuring methods).

5. Na_2O ash content

To determine the ash content, 4.5 – 5.0 g of a Mowiol sample is weighed into a nickel dish and burnt at approx. 700°C in a rapid asher. The residue is then treated for 1 h at 800°C in an oven. In a titration flask, 100 ml of hydrochloric acid = 0.015 mol/l is measured and then added to the hot nickel dish. After cooling, the nickel dish is removed and cleaned with de-ionized water. With a titroprocessor and a solution of sodium hydroxide the residue is titrated. In the same way, 100 ml of hydrochloric solution is titrated to determine a comparison value.

Evaluation

$$W_{\text{Na}_2\text{O-ash content}} = \frac{(V_{\text{B1}} - V_{\text{Sa}}) \cdot t_{\text{NaOH}} \cdot C_{\text{Tittr.Ag.}} \cdot M_{1/2 \text{ Na}_2\text{O}}}{M_{\text{Sa}} \cdot 10}$$

$$W_{\text{Na}_2\text{O-ash content}} = \text{mass of Na}_2\text{O-ash in \%}$$

$$V_{\text{B1}} = \text{consumption of NaOH-solution/ with blank sample}$$

$$V_{\text{Sa}} = \text{consumption of NaOH-solution/ with Mowiol sample}$$

$$t_{\text{NaOH}} = \text{titer of the solution of NaOH}$$

$$C_{\text{Tittr.Ag.}} = \text{concentration of the solution of NaOH (0.1 mol/l)}$$

$$M_{1/2 \text{ Na}_2\text{O}} = \text{half molar mass of Na}_2\text{O (31 g/mol)}$$

$$M_{\text{Sa}} = \text{weight of the sample in g}$$

$$10 = \text{calculation factor (l in ml and \%)}$$

6. Ester value

The term »ester value« (EV) connotes the number of mg KOH needed to neutralize the acid released from the ester by saponification in 1 g of substance.

Method of determination (based on DIN 53 401):

a. Partially hydrolysed grades:

Approximately 1 g Mowiol is weighed into a 250-ml round-bottomed flask and mixed with 70 ml distilled water and 30 ml neutralized alcohol, then heated with reflux until it dissolves. After cooling it is neutralized against phenol phthalein with 0.1 n KOH (see Section B 1.1.6).

When neutralization is complete, 50 ml 0.1 n KOH are added and the mixture is boiled for 1 hour with reflux. The excess caustic solution is back-titrated in the heat with 0.1 n HCl against phenol phthalein as indicator until the coloration fails to recur. A blank test is carried out at the same time.

b. Fully hydrolysed grades:

To avoid absorption of carbon dioxide from the air in the excess KOH, only 25 ml 0.1 n KOH are added to the Mowiol solution after neutralization and the solution is then heated for 30 min with reflux. The hot solution is mixed with 25 ml 0.1 n HCl and titrated against phenol phthalein with 0.1 n KOH after cooling. A blank test is carried out at the same time.

$$\text{Ester value (EV)} = \frac{(a-b) \cdot 5.61}{E}$$

a = consumption of ml 0.1 n KOH

b = consumption of ml 0.1 n KOH in the blank test

E = weighed quantity of Mowiol (dry)

7. Residual acetyl content

The residual acetyl content is calculated from the ester value as follows:

$$\text{EV} \cdot 0.0767 = \text{residual acetyl content (wt. \%)}$$

8. Degree of hydrolysis

The degree of hydrolysis (saponification) H indicates what percentage of the basic polyvinyl acetate molecule is »saponified« to polyvinyl alcohol. From the residual acetyl group content and thus the ester value EV, H is calculated by using the following formula:

$$\text{H in mol \%} = \frac{100 - 0.1535 \cdot \text{EV}}{100 - 0.0749 \cdot \text{EV}} \cdot 100$$

A degree of hydrolysis of 100% means, therefore, that the PVAL has no acetyl groups. *Table 2 and Figure 1* illustrate this non-linear relationship between the degree of hydrolysis and the ester value.

Table 2 Ester value (EV) in mg KOH/g and associated degree of hydrolysis (H) in mol %

EV	H	EV	H	EV	H	EV	H	EV	H	EV	H
0	100.0	50	95.9	100	91.5	150	86.7	200	81.5	250	75.8
1	99.9	51	95.8	101	91.4	151	86.6	201	81.4	251	75.7
2	99.8	52	95.8	102	91.3	152	86.5	202	81.3	252	75.6
3	99.8	53	95.7	103	91.2	153	86.4	203	81.2	253	75.7
4	99.7	54	95.6	104	91.1	154	86.3	204	81.1	254	75.4
5	99.6	55	95.5	105	91.1	155	86.2	205	81.0	255	75.3
6	99.5	56	95.4	106	91.0	156	86.1	206	80.9	256	75.1
7	99.4	57	95.3	107	90.9	157	86.0	207	80.8	257	75.0
8	99.4	58	95.2	108	90.8	158	85.9	208	80.7	258	74.9
9	99.3	59	95.2	109	90.7	159	85.8	209	80.5	259	74.8
10	99.2	60	95.1	110	90.6	160	85.7	210	80.4	260	74.6
11	99.1	61	95.0	111	90.5	161	85.6	211	80.3	261	74.5
12	99.0	62	94.9	112	90.4	162	85.5	212	80.2	262	74.4
13	99.0	63	94.8	113	90.3	163	85.4	213	80.1	263	74.3
14	98.9	64	94.7	114	90.2	164	85.3	214	80.0	264	74.2
15	98.8	65	94.6	115	90.1	165	85.2	215	79.9	265	74.0
16	98.7	66	94.5	116	90.0	166	85.1	216	79.8	266	73.9
17	98.6	67	94.5	117	89.9	167	85.0	217	79.7	267	73.8
18	98.6	69	94.4	118	89.8	168	84.9	218	79.5	268	73.7
19	98.5	69	94.3	119	89.7	169	84.8	219	79.4	269	73.6
20	98.4	70	94.2	120	89.6	170	84.7	220	79.3	270	73.4
21	98.3	71	94.1	121	89.6	171	84.6	221	79.2	271	73.3
22	98.2	72	94.0	122	89.5	172	84.5	222	79.1	272	73.2
23	98.2	73	93.9	123	89.4	173	84.4	223	79.0	273	73.1
24	98.1	74	93.8	124	89.3	174	84.3	224	78.9	274	72.9
25	98.0	75	93.8	125	89.2	175	84.2	225	78.8	275	72.8
26	97.9	76	93.7	126	89.1	176	84.1	226	78.6	276	72.7
27	97.8	77	93.6	127	89.0	177	84.0	227	78.5	277	72.6
28	97.8	78	93.5	128	88.9	178	83.9	228	78.4	278	72.4
29	97.7	79	93.4	129	88.8	179	83.8	229	78.3	279	72.3
30	97.6	80	93.3	130	88.7	180	83.7	230	78.2	280	72.2
31	97.5	81	93.2	131	88.6	181	83.6	231	78.1	281	72.1
32	97.4	82	93.1	132	88.5	182	83.5	232	78.0	282	71.9
33	97.3	83	93.1	133	88.4	183	83.4	233	77.8	283	71.8
34	97.3	84	93.0	134	88.3	184	83.2	234	77.7	284	71.7
35	97.2	85	92.9	135	88.2	185	83.1	235	77.6	285	71.6
36	97.1	86	92.8	136	88.1	186	83.0	236	77.5	286	71.4
37	97.0	87	92.7	137	88.0	187	82.9	237	77.4	287	71.3
38	96.9	88	92.6	138	87.9	188	82.8	238	77.3	288	71.2
39	96.8	89	92.5	139	87.8	189	82.7	239	77.1	289	71.0
40	96.8	90	92.4	140	87.7	190	82.6	240	77.0	290	70.9
41	96.7	91	92.3	141	87.6	191	82.5	241	76.9	291	70.8
42	96.6	92	92.2	142	87.5	192	82.4	242	76.8	292	70.7
43	96.5	93	92.2	143	87.4	193	82.3	243	76.7	293	70.5
44	96.4	94	92.1	144	87.3	194	82.2	244	76.6	294	70.4
45	96.3	95	92.0	145	87.2	195	82.1	245	76.4	295	70.3
46	96.3	96	91.9	146	87.1	196	82.0	246	76.3	296	70.1
47	96.2	97	91.8	147	87.0	197	81.9	247	76.2	297	70.0
48	96.1	98	91.7	148	86.9	198	81.7	248	76.1	298	69.9
49	96.0	99	91.6	149	86.8	199	81.6	249	76.0	299	69.7

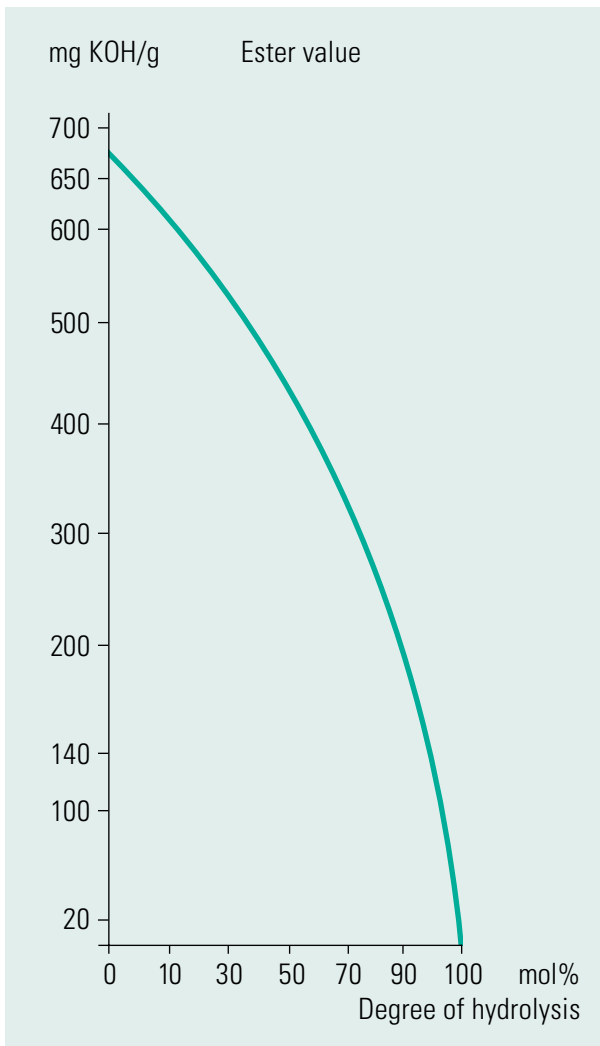


Figure 1 Relationship between degree of hydrolysis (mol %) and ester value (mg KOH/g)

9. Sieve analysis (to DIN 66 165)

To determine its particle size distribution, Mowiol is screened with a sieving machine on test sieves to DIN 4188. The residues left on the test sieves and the amount passing through the finest test sieve are determined by weighing.

Literature

- [1] B Kaesche-Krischer, H J Heinrich, Chem. Ing. Techn. 32, 598, 740 (1960)
[2] A S Dunn, R L Coley, B Duncalf, Soc. Chem. Ind., London 1968 (Monograph)