Solubility Properties of Non-ionic Water-soluble Cellulose Ethers in Mixtures of Water and Alcohol *

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The behaviour of some non-ionic water-soluble cellulose ethers in mixtures of water and methanol, ethanol, n-propanol, isopropanol, tert-butanol or acetone was investigated by means of viscosity and turbidity measurements. A viscosity minimum and corresponding turbidity maximum were found for ethyl cellulose and ethyl-hydroxyethyl cellulose in some of the solvent mixtures. These effects are due to variations of the solubility of the cellulose ether. The well-known tendency of water and alcohol molecules to associate provides a possible explanation of the effect. The viscosity at 20° C of mixtures water-acetone, water-isopropanol and water-tert-butanol was determined.

Non-ionic cellulose ethers, soluble in water, are synthesized by introducing into the glucose residues of the cellulose chains moderate amounts of different substituents such as methyl, ethyl or hydroxyethyl groups, either one kind only or combined with each other. These cellulose ethers are insoluble in alcohols although they swell strongly. A peculiar phenomenon, which seemed to deserve further studies, was observed during experiments to investigate the solubility of ethyl-hydroxyethyl cellulose in water-alcohol mixtures. In some cases the solubility passes through a pronounced minimum with increasing alcohol content. The effect has been mentioned in a review article [1].

MATERIALS INVESTIGATED

Commercial cellulose ethers:

Methyl cellulose (Methocel [2] from Dow Chem. Corp., USA). .
Methyl-hydroxyethyl cellulose (Glutolin from Kalle und Co. AG., Germany).
Ethyl-hydroxyethyl cellulose (Modocoll [3] from Mo och Domsjö AB, Sweden).

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The physico-chemical properties of water-soluble ethyl-hydroxyethyl cellulose have been described by Jullander [4,5]. It should not be identified with ethyl-hydroxyethyl cellulose recently brought on the market by Hercules Powder Co under the name EHEC, and which is insoluble in water but soluble in a number of organic solvents [6,7].

Cellulose ethers made in the laboratory:

Ethyl cellulose was prepared from alkali cellulose through etherification with ethyl chloride. With increasing degree of substitution, the solubility of ethyl cellulose changes from solubility only in alkali over solubility in water to solubility in organic solvents. The available information as to the range of water solubility is scarce as well as confusing and a special investigation was made to settle this point [8]. Hydroxyethyl cellulose was obtained from alkali cellulose by etherification with ethylene oxide dissolved in ethyl chloride. If the temperature is kept sufficiently low, the ethyl chloride only acts as an inert diluent, cf. Sönnerskog [9].

Ethyl cellulose: the sample used was prepared in the same way as described in the investigation quoted. Raw material: sulphite cellulose from spruce, alpha content 89.7 % (CCA 7), cuprammonium viscosity (TAPPI) 22 cp, ethanol extract 0.48 %. Steeping lye 33.0 %, mercerization 45 min. at 24° C, press factor 2.58. Reaction time 210 min. at 100° C.

Hydroxyethyl cellulose: the same pulp as above was used as raw material. Steeping lye 18.7 %, mercerization 45 min. at 25° C, press factor 2.14. Ethylene oxide 2.75 moles per glucose unit of the cellulose, was dissolved in ethyl chloride, reaction 5 hours at 38°—43° C. The raw product obtained was neutralized with CO_2, and washed with 95 % ethanol acidified with acetic acid.

Some properties of the ethers are recorded in Table 1.

Table 1. Summary of properties of cellulose ethers.

Cellulose ether	Substituent	Degree of * substitution (DS)	Analytical methods Ref. No.	Viscosity ** cp
Methyl cellulose (Methocel 400)	Methyl	1.97	10	310
Methyl-hydroxyethyl cellulose (Glutolin Leim)	Methyl	1.11	11, 12	140
	Hydroxyethyl	0.14		
Ethyl-hydroxyethyl cellulose A (Modocoll M, batch No. 08822)	Ethyl	1.34	12, 13	65
	Hydroxyethyl	0.44		
Ethyl-hydroxyethyl cellulose B (Modocoll E 100, batch No. 34011)	Ethyl	0.74	12, 13	90
	Hydroxyethyl	0.65		
Ethyl cellulose	Ethyl	1.20	10	—
Hydroxyethyl cellulose	Hydroxyethyl	1.31	12	—

* Calculated on bone-dry and salt-free basis.
** Water solution at 20° C, 2 % airdry cellulose ether. Höppler viscometer, precision model.

EXPERIMENTS

Solutions of cellulose ethers in water are never molecularly dispersed to 100 %. Fragments of fibers and gel particles are always present to some extent.

Viscosity and turbidity are important physical characteristics of cellulose ether solutions and were therefore determined. A comparison of measurements in water/alcohol and water only can also be used to estimate the molecularly dispersed portion of the cellulose ether. It is here assumed that a decreased viscosity and increased turbidity indicate a decreased "solubility", *i.e.* a smaller portion of the material is molecularly dispersed. The reverse may not always be true. A notable example from the chemistry of cellulose derivatives is the viscosity increase during the ripening of viscose. The turbidity does not change in this process.

The viscosity was measured at 20° C with a Brookfield viscometer (type LVF, usually spindle 1 at 30 and 60 rpm) on a system containing 1 wt.% of cellulose ether and 99 wt.% of a mixture of water and alcohol. Turbidity measurements were made on the same solutions by means of a method described earlier [4,14,15]. The results are expressed as % transmission, 100 % meaning that no measurable amount of light is scattered. The transmission values are not affected by light absorption.

The instrument was a Lumetron photoelectric colorimeter, Model 402-E (Photovolt Corp., New York, USA). Green filter (M 550); light path in cuvette 20 mm; displacement 12 cm.

A typical example of the effect obtained is shown in Fig. 1 where solutions of ethyl-hydroxyethyl cellulose A in mixtures of water and *n*-propanol were
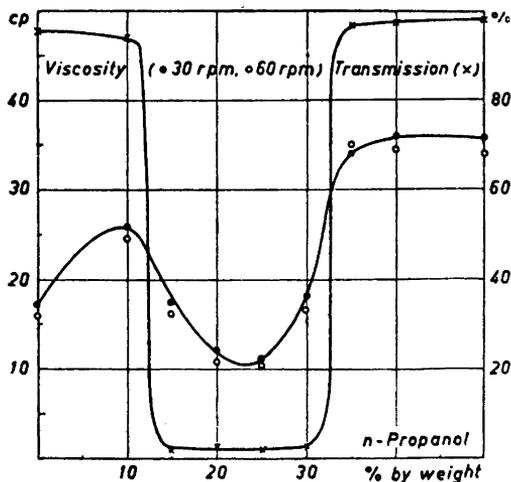

Fig. 1. Viscosity and transmission of solutions of 1 % ethyl-hydroxyethyl cellulose A in mixtures of water and n-propanol. Temp. 20° C.
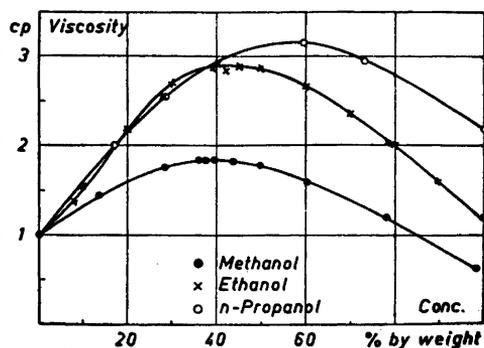
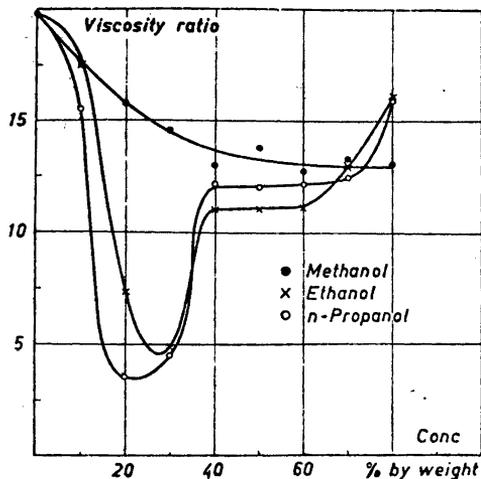Fig. 2. Viscosity of mixtures of water and methanol, ethanol or n-propanol. Temp. 20° C.

Fig. 3. Viscosity ratio of solutions of 1 %
ethyl-hydroxyethyl cellulose A in mixtures
of water and methanol, ethanol or n-pro-
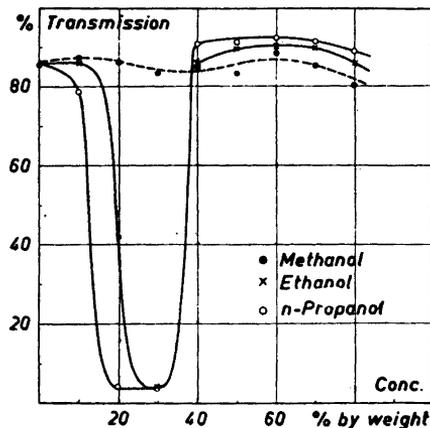panol. Temp. 20° C.

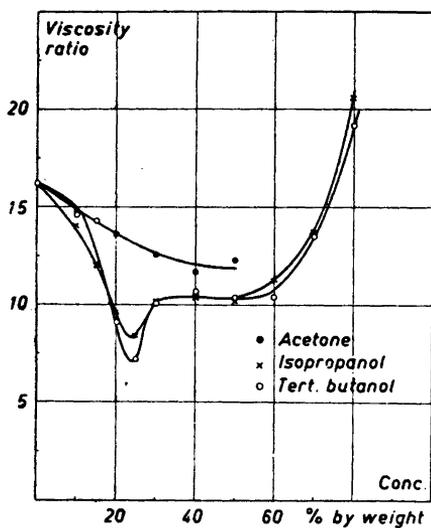Fig. 4. Transmission of same solutions as
in Fig. 3.

Fig. 5. Viscosity ratio of solutions of 1 %
ethyl-hydroxyethyl cellulose A in mixtures
of water and acetone, isopropanol or tertiary
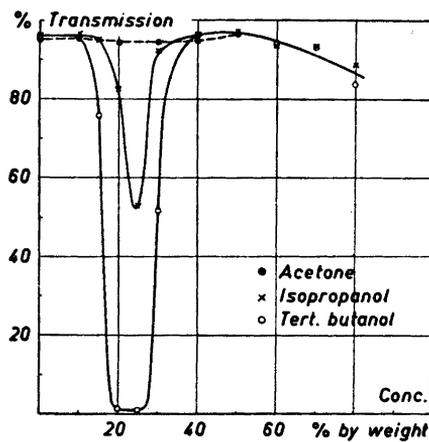butanol. Temp. 20° C.

Fig. 6. Transmission of same solutions as
in Fig. 5.

studied. The decrease in viscosity around the alcohol concentration 20 % by weight is counteracted by the well-known fact that the viscosity of mixtures of alcohol and water passes through a pronounced maximum when the composition is varied (Fig. 2). The values plotted were taken from the tables of Landolt-Börnstein [16]. It is therefore more correct to plot instead the viscosity ratio, η/η_0, against the solvent composition.

Fig. 1 shows that the structural viscosity, as expressed by the difference in readings of the Brookfield viscometer at 30 and 60 rpm resp., is moderate and of the same magnitude in water as in water-alcohol mixtures. Only occasionally does the difference exceed 10 %. The same was generally found in the measurements which are presented below but to avoid complicating the diagrams only measurements at 30 rpm are given. It is concluded, that in those cases where a viscosity maximum at 50—60 % alcohol concentration is found, this maximum is not due to gel formation.

Figs. 3 and 4 show viscosity ratio and transmission for solutions of ethylhydroxyethyl cellulose A within the concentration range 0—80 % of methanol, ethanol and n-propanol. The influence of the two remaining alcohols, which are completely miscible with water, was also investigated together with acetone (Figs. 5 and 6). No data for the viscosity of mixtures of water with isopropanol, tert-butanol or acetone usable for the calculation of viscosity ratios at 20° C were found in the literature. The viscosity of these mixtures was therefore measured with an Ostwald viscometer (Table 2 and Fig. 7).

Data for viscometers (No. 8 used for acetone, No. 14 used for isopropanol and tert-butanol):

	No. 8	No. 14
Volume of bulb:	1.25 ml	0.79 ml
Length of capillary:	9.9 cm	10.1 cm
Time for outflow of water, 20° C	133 sec	62 sec

Density determinations with precision areometer.

Table 2. Viscosity at 20° C of mixtures tertiary butanol-water, isopropanol-water and acetone-water.

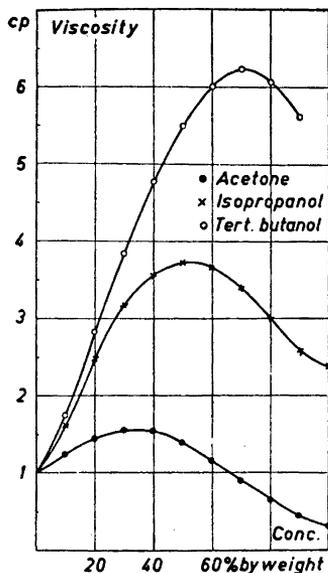| Organic solvent % by weight	Viscosity, cp		
	Butanol	i-Propanol	Acetone
0	1.00	1.00	1.00
10	1.75	1.62	1.24
20	2.84	2.49	1.45
30	3.85	3.18	1.56
40	4.78	3.57	1.54
50	5.50	3.73	1.40
60	6.01	3.67	1.17
70	6.23	3.41	0.91
80	6.07	3.02	0.65
90	5.62	2.58	0.45
100	—	2.38	0.31

Fig. 7. Viscosity of mixtures of water and acetone, isopropanol or tertiary butanol. Temp. 20° C.
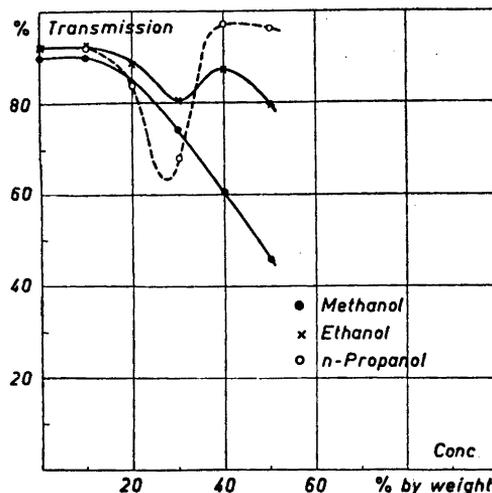
Fig. 8. Transmission of solutions of 1 % ethyl-hydroxyethyl cellulose B in mixtures of water and methanol, ethanol or n-propanol. Temp. 20° C.

The viscosity ratios obtained were corrected for the kinetic energy error, see Schulz [17]. The correction never exceeds 0.5 % except for the highest acetone concentrations.

Material: tertiary butanol (Eastman Kodak Co), *iso*propanol (purum) and acetone (puriss.) were all fractionated in a column with about 20 theoretical plates and the middle fractions collected. Boiling point interval $\leq 0.2°$ C. Density (with areometer): acetone 0.791; *iso*propanol 0.787.

From the diagrams presented so far it is found that mixtures of methanol and acetone with water do not show any effect at all. Mixtures of water with ethanol, *n*-propanol and *tert*-butanol give a strong effect, *iso*propanol a moderate effect.

Further experiments were carried out with other cellulose ethers: ethyl-hydroxyethyl cellulose B (Fig. 8), methyl cellulose (Fig. 9), methyl-hydroxyethyl cellulose (Fig. 10). Samples of ethyl cellulose and hydroxyethyl cellulose were also investigated (Fig. 11).

The phenomenon is very sensitive to the chemical composition of the cellulose ether. Even the comparatively small difference between ethyl-hydroxyethyl cellulose A and B results in effects of quite different magnitude. The transmission minimum for ethanol in Fig. 8 seems to be real even if it is small, it has been observed repeatedly. Methyl cellulose and methyl-hydroxyethyl cellulose do not show any insolubility region. Fig. 11 is interesting. The decrease in transmission and viscosity for ethyl cellulose at very low alcohol concentrations is displaced towards higher values by hydroxyethyl groups.
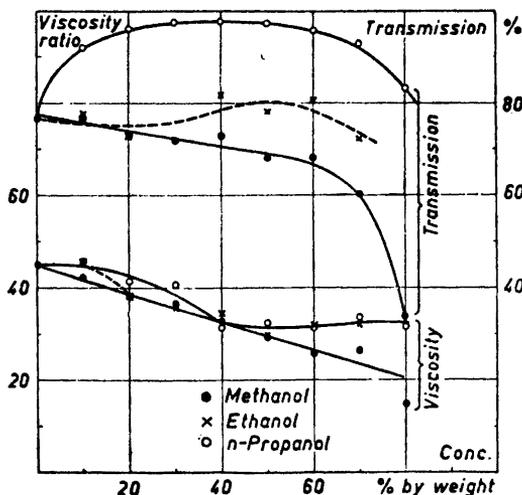
Fig. 9. Viscosity ratio and transmission of
1 % solutions of methyl cellulose in mixtures
of water and methanol, ethanol or n-pro-
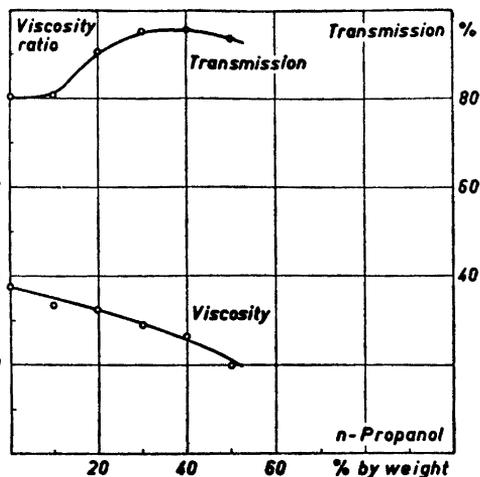panol. Temp. 20° C.

Fig. 10. Viscosity ratio and transmission
of 1 % solutions of methyl-hydroxyethyl
cellulose in mixtures of water and n-pro-
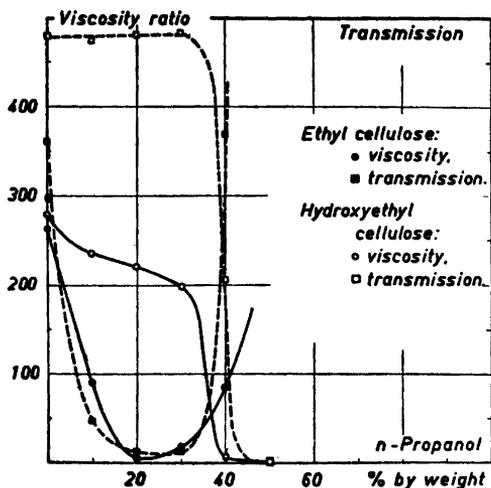panol. Temp. 20° C.

Fig. 11. Viscosity ratio and transmission of
1 % solutions of ethyl cellulose and hydroxy-
ethyl cellulose in mixtures of water and n-
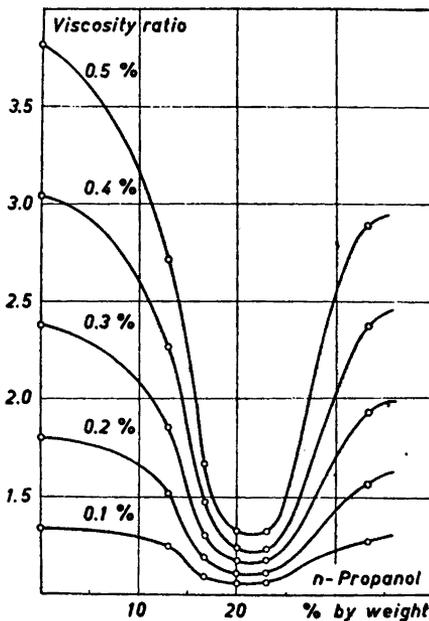propanol. Uemp. 20° C.

Fig. 12. Viscosity ratio of dilute solutions of
ethyl-hydroxyethyl cellulose A in mixtures of
water and n-propanol.

Preparation of solutions:

(Figs. 3, 4 and 9.) Stock solutions in pure water were made by swelling 5 g cellulose ether with 145 g boiling water, adding water of 20° C as required and cooling the solution to 20° C. Organic solvent was then added and the solution left in a thermostat (20° C) at least over night. In the solutions with 80 % alcohol, less water had to be used. The solutions were neither frozen, filtered, nor centrifuged.

(Figs. 1, 5, 6, 8, 10, 11.) A 2 % stock solution of cellulose ether in water was prepared, frozen, thawed and then centrifuged — repeatedly if necessary — in order to get as clear solutions as possible. To the solution was then added water and organic solvent as required. The ethyl cellulose was dissolved in 2 % sodium hydroxide, the solution neutralized with hydrochloric acid and dialysed.

The composition of the solvent mixture is always expressed as parts by weight of alcohol per 100 parts of alcohol + water. The cellulose ether concentration is expressed as g/100 g solution.

All measurements hitherto described were made on solutions of 1 % concentration with respect to the cellulose ether content. It seemed to be of interest to study the effect also at lower concentrations in a typical case. The system ethyl-hydroxyethyl cellulose A in water — n-propanol was chosen for that purpose.

The effect is quite noticeable also at lower concentrations, as is seen from Fig. 12 where viscosity curves in the region 0—35 % n-propanol are drawn for cellulose ether concentrations from 0.5 % downwards. The result is another proof that the cellulose ether is molecularly dispersed on both sides of the minimum. If the high viscosity previously found in solutions rich in alcohol were due to some sort of gel structure, the latter would break down upon dilution.

Corresponding values of the limiting viscosity number, $[\eta]$, are given in Fig. 13. These values were determined by extrapolation of η_{sp}/c versus c as usual. Often but not always the curve had a tendency to an upward bend near zero concentration; examples are given in Fig. 14. Extrapolation of the
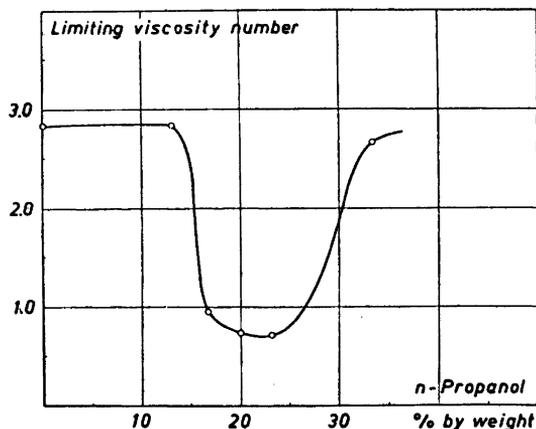

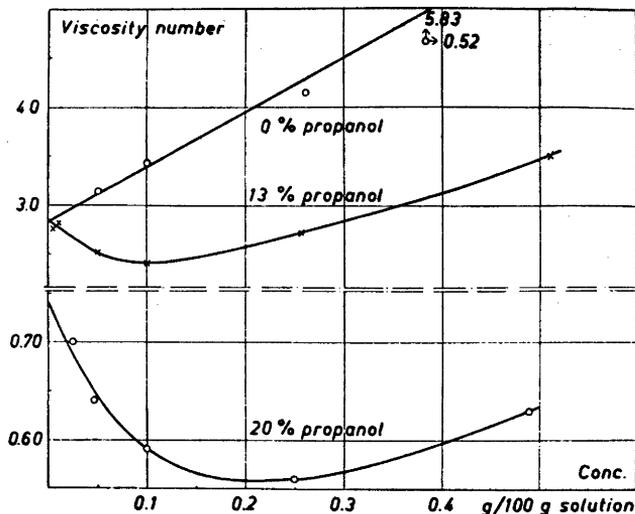*Fig. 13. Limiting viscosity number, [η], of ethyl-hydroxyethyl cellulose A in mixtures of water and n-propanol.*

Fig. 14. *Extrapolation of viscosity number, η_{sp}/c, of solutions of ethyl-hydroxyethyl cellulose A in mixtures of water and n-propanol.*

viscosity number without regard to this upward bend did not very much change the general form of the curve in Fig. 13. The position of the minimum remains unchanged.

A probable explanation of this unusual behaviour upon dilution of a polymer solution is dissociation of aggregates of molecules, with increased viscosity as a consequence. A related phenomenon has been reported by Steurer [18]. The reduced osmotic pressure of ethyl cellulose (51 % OC_2H_5) dissolved in toluene showed a tendency to increase at the lowest concentrations. Steurer explained this as being due to dissociation of aggregates of molecules.

Stock solutions of ethyl-hydroxyethyl cellulose A in pure water were prepared, frozen, thawed and centrifuged mainly as already described. The required amount of n-propanol was then added. The exact concentration of the strongest solution, around 0.5 %, was determined through evaporation of an aliquot portion and the necessary dilutions made from this solution. The viscosity was measured at 20° C in an Ostwald capillary viscometer: time of outflow for water 123 sec., volume of bulb 0.90 ml, length of capillary 99 mm, diam. of capillary 0.402 mm. Average gradient for water 765 cm³/sec.

The concentration is expressed as g/100 g solution, not g/100 ml solution. This was done in order to avoid possible confusion arising from the contraction of the liquid mixtures studied.

As was mentioned before, the effect is very sensitive to changes in composition of the cellulose ether. It was therefore of interest to see whether the chemical composition of the precipitate which is formed at the turbidity maximum differs from that of the ether still in solution. A 0.5 % solution of ethyl-hydroxyethyl cellulose A in 20 % of n-propanol was prepared as described above. It was allowed to stand at 20.0° C for three days; by that time 75 %

of the cellulose ether had precipitated. The phases were separated by means of decantation and centrifugation, evaporated and dried. The chemical analysis only showed a small difference between original cellulose ether, the soluble and the insoluble parts (Table 3). Limiting viscosity numbers determined on water solutions of the fractions showed large differences and evidently the main difference between the fractions is the chain length.

Table 3. Fractionation of 0.5 % solution of ethyl-hydroxyethyl cellulose A in 20 % n-propanol.

Analysis	Unfractionated material	Precipitate	Remaining in solution
Ethoxyl groups, DS	1.34	1.31	1.20
Hydroxyethyl groups, DS	0.44	0.35	0.45
Limiting viscosity number	2.83	3.07	0.90

DISCUSSION

The experimental results will be discussed from two view-points: similar phenomena earlier published and an effort to connect the observed effect with other physico-chemical properties of alcohol-water mixtures as a means of finding at least a qualitative explanation.

The effect described in this paper, should not be mistaken for the viscosity minimum often observed when a cellulose derivative is dissolved in a mixture of liquids, neither of which is itself a solvent for the derivative. A typical example is the dissolution of nitrocellulose in ethyl ether and ethyl alcohol, a pronounced minimum viscosity is found at approximately 50 % alcohol varying with the nitrogen content [19,20]. On both sides of this point the viscosity rises sharply, ending in semisolid gel-like structures.

Similar viscosity minima have also been observed in solutions of ethyl cellulose and benzyl cellulose [21,22]; *cf.* also the discussion by Mardles [23] of solvents for cellulose esters. When cellulose nitrate or cellulose acetate is dissolved in acetone and other solvents, the viscosity passes through a minimum upon addition of small amounts of water [20,24-27]. This addition is considered as improving the solubility.

A phenomenon more similar to the effect studied here is the salting-out of proteins in the presence of n-propanol which has been described by Jirgensons in several publications [28-32]. In some cases it was observed that the flocculation tendency of the protein upon addition of propanol first passed through a maximum and then through a minimum. Methanol did not show this effect and n-propanol had a stronger effect than ethanol. Also the investigation of Verstraete [33] on the solubility of saponin in water-alcohol should be mentioned. A minimum in solubility followed by a maximum (with increasing amount of organic solvent) was observed for methanol, ethanol, *iso*propanol and acetone but *not* for n-propanol. Bungenberg de Jong [34,35] found that when tannin or resorcinol is added in increasing amounts to solutions of agar or gelatin, the viscosity passes through a minimum and the turbidity simultaneously through a maximum.
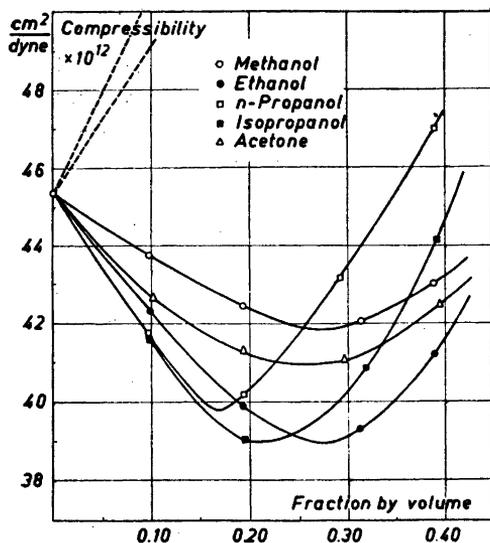
Fig. 15. Compressibility of mixtures alcohol-water and acetone-water as function of concentration of organic solvent. Temp. 20° C. Data from Jacobson (46). An ideal mixture gives a straight line within the sector indicated by the broken lines in the upper left corner.

It would be of interest to try to connect the observed solubility effects with the many abnormal physico-chemical properties of water-alcohol mixtures which are well-known in the literature; for a discussion see Kortüm [36]. They are interpreted as caused by the formation of more or less stable aggregates of water and alcohol molecules. Among the effects studied are the temperature coefficient of surface tension [37,38] and the diffusion [39-41]. Of greater interest are perhaps ultrasonic absorption and velocity, compressibility, contraction and viscosity.

The behaviour of water-alcohol mixtures in ultrasonic fields has been investigated by Burton [42] and Storey [43]; see also Refs. [44,45]. When the sound absorption is plotted against alcohol-water composition maxima are found, the magnitude of which increase strongly in the order ethanol, isopropanol, n-propanol, tert-butanol. No maximum was observed in mixtures of methanol and water.

Jacobson [46] studied the compressibility of alcohol-water mixtures. Part of his tabulated data are plotted in Fig. 15. The pure organic solvents have compressibilities between 83 and 99 × 10^{-12} cm²/dyne. The deviations from the ideal mixture are great in all cases, but the minima are more pronounced for ethanol and both propanols than for methanol and acetone. Position of the minima:

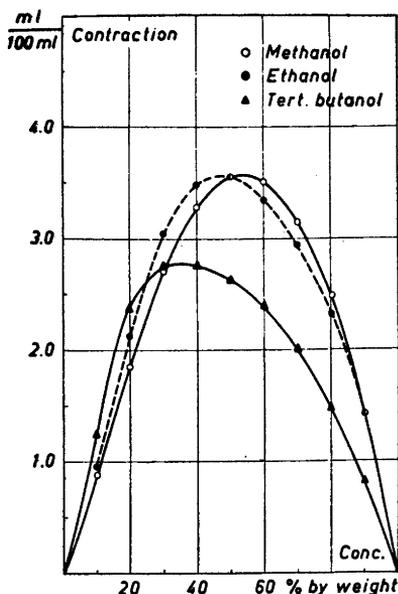|	Fraction by volume	% by weight
Ethanol	0.28	23
n-Propanol	0.17	14
Isopropanol	0.21	17

Fig. 16. Contraction of mixtures alcohol-water Temp. 20° C. Calculated from density data available in the literature.
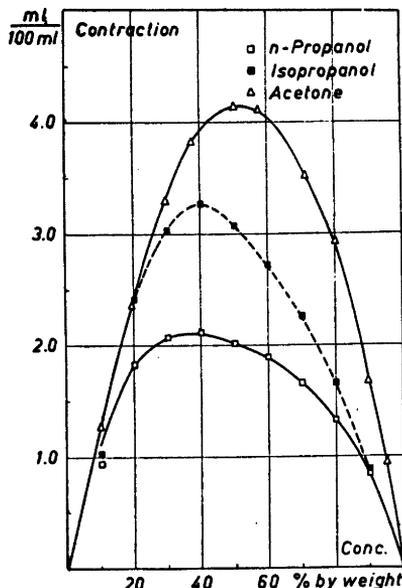
Fig. 17. See Fig. 16.

Contraction is a more direct measure of the association. Figs. 16 and 17 give the variation of contraction with the composition of the mixtures.

The contraction was calculated as recommended by Carr and Riddick [47], using what seemed to be the best available density data, taken from Ref. [48] (methanol, ethanol, n-propanol and isopropanol) and Ref. [49] (tert-butanol and acetone). The contraction is expressed as ml per 100 ml of constituents (not mixed). Values for n-propanol at 20° C were interpolated from available data for 15° and 30° C. The density of pure tertiary butanol in liquid state at 20° C was found to be 0.7850 through extrapolation. The melting point of the substance is 25.5° C.

Contrary to our expectations there is no correlation between the magnitude of the contraction and the effect studied in this paper. Acetone has the highest contraction and the curves for ethanol and methanol are close together. Position of maxima:

		corresponding to the approximate formula
Ethanol	47 %	C_2H_5OH, $3H_2O$
n-Propanol	37 %	C_3H_7OH, $6H_2O$
Isopropanol	41 %	C_3H_7OH, $5H_2O$
Tert-butanol	35 %	C_4H_9OH, $8H_2O$

The viscosity also passes through a maximum as has already been demonstrated (Figs. 2 and 7). Positions of the maximum deviation from a straight line relationship are:

Ethanol	42 %
n-Propanol	50 %
*Iso*propanol	45 %
Tert-butanol	60 %

Summing up, a partial correlation has been found between the solubility effects studied here, and the anomalous behaviour of water-alcohol mixtures with respect to sound absorption, compressibility, contraction and viscosity.

We believe that the following is a reasonable qualitative explanation. Water is a poor solvent for low substituted ethyl cellulose [8]. When therefore for instance propanol is added to a solution in pure water, the cellulose ether chains are easily dehydrated, and the solubility drops already at very low alcohol concentrations (Fig. 11). On the other hand the degree of substitution is too low to make the ether soluble in pure alcohol. Hydroxyethylation of cellulose makes the chains more hydrophilic and a higher alcohol concentration, 30—40 %, is needed to reach the precipitation point. In the case of ethyl-hydroxyethyl cellulose A in solutions with increasing alcohol content, the decrease in solubility at around 15 % alcohol is due to dehydration of the chains and, as expected, the precipitation point lies between those found for ethyl cellulose and for hydroxyethyl cellulose. When the alcohol concentration approaches contraction maximum, fairly strong propanol-water aggregates are formed. It must be assumed that aggregates with an average composition corresponding to the contraction maximum or slightly richer in alcohol, constitute an excellent solvent for ethyl-hydroxyethyl cellulose A. The aggregates can solvate both ethyl and hydroxyethyl groups at the same time on account of their composition. Steric effects could also play a part as obviously these »solvent molecules» are bulky and will keep the cellulose chains effectively apart. At high alcohol concentration finally, the hydroxyl groups are desolvated, and the chain can no longer remain in solution.

It is easy to understand that small changes in the composition of the ether have a large effect upon the solubility behaviour. Obviously a nice balance between ethyl groups and hydroxyl plus hydroxyethyl groups is needed to allow the alcohol-water aggregates to function properly as solvating agents. The aggregates formed between other alcohols and water may be more or less well suited for solvation of the cellulose ether and the strength of the association, as measured by contraction or some other physical property, gives no guarantee that the aggregates will have good solvating properties.

It should be noted that regardless of the size of the alcohol, the minimum solubility is found at around the same *weight* composition (25 % alcohol) and not *molar* composition of the solvent mixture.

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REFERENCES

1. Jullander, I. *Svensk Kem. Tidskr.* **65** (1953) 223.
2. "*Methocel*", Dow Chem. Co., Midland, Mich., USA, Copyright 1949.
3. "*Modocoll, water-soluble cellulose ethers as thickeners, emulsifiers and binders*", Mo och Domsjö AB, Örnsköldsvik, Sweden 1952.
4. Jullander, I. *Svensk Papperstidn.* **55** (1952) 197.
5. Jullander, I. *Ibid.* **56** (1953) 443.
6. U. S. pat. 2.610.180.
7. Cohen, S. G., Haas, H. C., Farney, L. and Valle, C. *Ind. Eng. Chem.* **45** (1953) 200.
8. Jullander, I. *Acta Chem. Scand.* **9** (1955) 1291.
9. Sönnerskog, S. *Some ethers of cellulose and starch*, Diss. Stockholm 1952.
10. Vieböck, F. and Schwappach, A. *Ber.* **63** (1930) 2818.
11. Pregl, F. and Roth, H. *Die quantitative organische Mikroanalyse*, 4th Ed., Berlin 1935, p. 223.
12. Morgan, P. W. *Ind. Eng. Chem., Anal. Ed.* **18** (1946) 500.
13. Lemieux, R. U. and Purves, C. B. *Can. J. Research*, Sect. B, **25** (1947) 485.
14. Jullander, I. *Acta chem. Scand.* **3** (1949) 1309.
15. Jullander, I. and Brune, K. *Ibid* **4** (1950) 870.
16. Landolt-Börnstein, *Physikalisch-chemische Tabellen*, Hauptwerk p. 140; I. Ergän-zungsband p. 84; II. Ergänzungsband p. 106; 5th Ed. Berlin 1923—1931.
17. Schulz, G. V. *Z. Elektrochem.* **43** (1937) 479.
18. Steurer, E. *Z. physik. Chem.* A **190** (1942) 1.
19. Gibson, W. H. and McCall, R. *J. Soc. Chem. Ind. London* **39** (1920) 172T.
20. Highfield, A. *Trans. Faraday Soc.* **22** (1926) 57.
21. Kauppi, T. A. and Bass, S. L. *Ind. Eng. Chem.* **30** (1938) 74.
22. Moll, W. L. H. and Fuller, G. W. *Kolloid-Z.* **80** (1937) 320.
23. Mardles, E. W. J. *J. Soc. Chem. Ind. London* **42** (1923) 127T.
24. Masson, I. and McCall, R. *J. Chem. Soc.*, Transactions, **117** (1920) 819.
25. Barr, G. and Bircumshaw, L. L. *Kolloid-Z.* **28** (1921) 223.
26. Rocha, H.-J. *Kolloidchem. Beih.* **30** (1929—30) 230.
27. Suida, H. *Cellulosechemie* **12** (1931) 310.
28. Jirgensons, B. *Kolloid-Z.* **41** (1927) 331.
29. Jirgensons, B. *Ibid* **44** (1928) 76.
30. Jirgensons, B. *Ibid* **46** (1928) 114.
31. Jirgensons, B. *J. Colloid Sci.* **1** (1946) 539.
32. Jirgensons, B. *Makromol. Chem.* **10** (1953) 78.
33. Verstraete, E. O. K. *Kolloid-Z.* **104** (1943) 96.
34. Bungenberg de Jong, H. G. *Rec. trav. chim.* **46** (1927) 727.
35. Bungenberg de Jong, H. G. *Ibid* **48** (1929) 494.
36. Kortüm, G. *Z. physik. Chem.* B **38** (1937) 1.
37. Teitel'baum, B. Y. *Doklady Akad. Nauk S.S.S.R.* **71** (1950) 705; *Chem. Abstracts* **44** (1950) 6251.
38. Teitel'baum, B. Y., Ganelina, S. G. and Gortalova, T. A. *Zhur. Fiz. Khim.* **25** (1951) 1043; *Chem. Abstracts* **46** (1952) 6470.
39. Franke, G. *Ann. Physik* [5] **14** (1932) 675.
40. Lemonde, H. *Compt. rend.* **202** (1936) 468, 731.
41. Taylor, H. S. and Taylor, H. A. *Elementary Physical Chemistry*, 3rd Ed. New York 1942, p. 461.
42. Burton, C. J. *J. Acoust. Soc. Amer.* **20** (1948) 186.
43. Storey, L. R. O. *Proc. Phys. Soc. London*, Sect. B, **65** (1952) 943.
44. Parshad, R. *Indian J. Phys.* **15** (1941) 323.
45. Willis, F. H. *J. Acoust. Soc. Amer.* **19** (1947) 242.
46. Jacobson, B. *Arkiv Kemi* **2** (1950) 177.
47. Carr, C. and Riddick, J. A. *Ind. Eng. Chem.* **43** (1951) 692.
48. *International Critical Tables*, Vol. III, p. 115—121, New York 1928.
49. Landolt-Börnstein, *Physikalisch-chemische Tabellen*, Hauptwerk p. 454, I. Ergän-zungsband p. 214; 5th Ed., Berlin 1923—1927.