CELLULOSE CHEMISTRY AND TECHNOLOGY

PRETREATMENT OF CELLULOSIC SUBSTRATES WITH ACETATE- AND CHLORIDE-BASED IONIC LIQUIDS AND THEIR MIXTURES

IAKOV A. MASIUTIN, ALEXANDER V. GOLYSHKIN,
ARTEM A. LITVIN, ANDREI A. NOVIKOV, MIKHAIL S. KOTELEV, EVGENII V. IVANOV and
VLADIMIR A. VINOKUROV

Gubkin Russian State University of Oil and Gas (National Research University),
65, Leninsky Prospect, Moscow 119991, Russia
✉ *Corresponding author: Iakov A. Masiutin, yma1989@mail.ru*

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Cellulose has a complex structure that seriously hinders its processing. Ionic liquids (ILs) have the ability to dissolve cellulose, thus modifying its structure. A series of acetate- and formate-based ILs was synthesized from their chloride analogues and tested for dissolution of microcrystalline cellulose. Cellulose solubility in 1-butyl-3-methylimidazolium acetate [BMIm]Ac, 1-ethyl-3-methylimidazolium acetate [EMIM]Ac, 1-butyl-3-methylimidazolium chloride [BMIm]Cl, 1-ethyl-3-methylimidazolium chloride [EMIM]Cl and their mixtures was investigated. The optimal weight ratio of a chloride-based IL to an acetate-based IL was found to be 3:2. The solubilizing power of that mixture was maximal, while that of butyl-substituted ILs exceeds the solubilizing power of individual compounds. Despite having better solvent power, acetate-based ILs provide a lower decrease in cellulose crystallinity, as revealed by powder X-ray diffraction studies, in comparison with their chloride-based counterparts. The initial and pretreated cellulose substrates were also analyzed by scanning electron microscopy; the micrographs confirmed that substrate morphology changed profoundly after the pretreatment with ILs.

Keywords: lignocellulose, cellulose, pretreatment, ionic liquids, biofuel

INTRODUCTION

Biofuels are fuels of the next generation: they demonstrate excellent ecological characteristics and are based on renewable raw materials. Lignocellulosic feedstock is one of the main sources for their production. It is the most common type of biomass, consisting of three main components, namely cellulose, hemicelluloses and lignin.[1] Lignin and hemicelluloses prevent an easy access to cellulose, being its natural protective coating. The schematic structure of lignocellulose is shown in Figure 1a. Therefore, processing of an untreated lignocellulosic feedstock is economically unviable.[2] To significantly increase the efficiency of the production of biofuels from lignocellulose, it is necessary to remove the protective covering consisting of lignin and hemicellulose, and decrease the cellulose crystallinity.

One of the relatively new techniques of lignocellulosic biomass processing involves the application of ionic liquids.[3] Ionic liquids (ILs) are organic salts whose melting points are below 100 °C.[4] Their ability to dissolve cellulose was discovered quite recently, namely in 2002, by Rogers and Swatloski.[5] They established that chloride-based ILs have higher solvent power towards cellulose, compared to several other anions (bromide, rhodanide, tetrafluoroborate, hexafluorophosphate). Soaking wood chips in ILs facilitates the following grinding[6] and the usage of protic ILs, such as substituted imidazolium hydrosulfates, enables simultaneous dissolution and catalytic transformation of lignocellulose.[7,8] The usage of ILs also makes it possible to fractionate lignocellulose, since lignin and hemicelluloses remain in the solution after adding the counter-solvent, while quite pure cellulose is precipitated.[9–12] This subject has been reviewed by da Costa Lopes *et al.*,[13] and typical lignin extraction yields with acetate-based ILs range between 25 to 50%. Lignocellulose fractionation by protic ILs allows isolating lignins of different composition,[14] and the combination of IL pretreatment with supercritical CO_2 extraction leads to isolation of bioactive phenolic compounds.[15]

Despite plenty of studies devoted to cellulose dissolution in ILs, the mechanism of the process remains undefined.[16,17] It is certain, however, that the ability of the anion contained in the IL to form hydrogen bonding is crucial in the process. The anion diffusing into the intermolecular space of cellulose disrupts its intramolecular hydrogen bonds and forms intermolecular ones. Thereby, the cellulose dissolves in ILs.[18]

The key physicochemical properties of ILs affecting the pretreatment of cellulosic substrates are their melting point and viscosity.[12,19] Both melting point and viscosity are significantly affected by the nature of the anion, although the cation has some influence as well.[20] Another important factor is the symmetry of the IL cation. The more symmetry has the cation, the higher is the melting point.[21] In spite of some common characteristics, ILs have quite different physicochemical properties, *e.g.* their melting points may vary from temperatures below -20 °C to 100 °C. It should be noted that ILs are acknowledged as "constructed solvents", since one can control their properties picking out one ion combination or another, while the potential number of possible structures is about 10^{12}.[22] Figure 1b shows the dependence of melting points on the composition of imidazolium-based ILs. The significant influence of the anion can be noted. The anion also influences the viscosity of the ILs. It decreases in the following order: $[Cl]^- > [PF_6]^- > [BF_4]^- > [Tf_2N]^-$.[12] Therefore, it is necessary to choose the appropriate IL structure for a specific task.

Classical synthesis of ILs is carried out in two stages. Firstly, one uses the Menshutkin reaction to obtain an IL with the required cation structure, containing the necessary heterocycle and substituents. Thereafter, one obtains the IL with the appropriate anion by the metathesis reaction. The Menshutkin reaction (often named quaternization reaction), is a reaction of nucleophilic substitution with S_N2 mechanism. During the reaction, tertiary amines and phosphines are converted to quaternary ammonium and phosphonium salts, respectively. The next stage, metathesis, constitutes a simple anion exchange reaction. It can be done in two main ways: either in a solution, resulting in precipitation of the insoluble compound (*e.g.* the IL itself) or using an anion-exchange resin. The ILs containing acetate, formate, nitrate, rhodanide and other anions are prepared *via* metathesis.[23]

Various ILs have different solvent power towards cellulose, and their cost differs significantly as well. In our previous study, we synthesized ILs *via* substituted imidazoles by the van Leusen reaction followed by quaternization.[24] Thus, we obtained 1-*tert*-butyl-3-benzylimidazolium chloride and 1-*tert*-butyl-3-methylimidazolium iodide. It was assumed that the synthesized ILs would have increased solvent power towards cellulose due to the high asymmetry of their cations, leading to lowered melting points, while a branched *tert*-butyl radical reduces the viscosity of the ILs. Nevertheless, the compounds obtained are unstable, oxidizing rapidly when exposed to air. Moreover, the compounds obtained are costly, since one of the components necessary for the van Leusen reaction, toluene sulfonylmethyl isocyanide, is very expensive.[25]

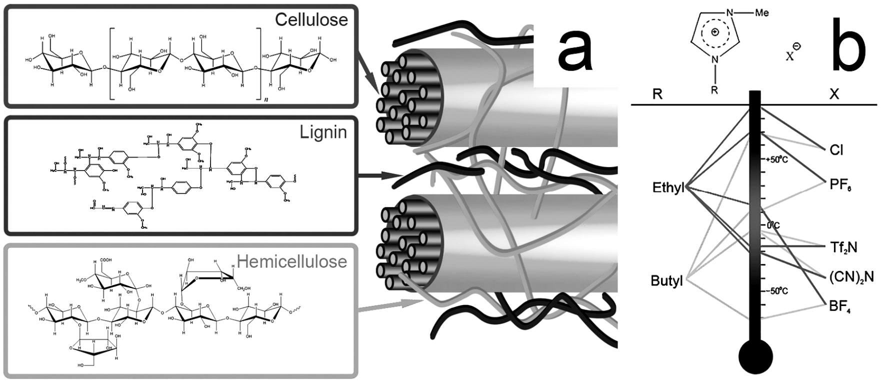

Figure 1: (a) Schematic representation of the lignocellulosic structure; (b) Melting points of selected imidazolium-based ILs depending on their ion composition

Therefore, their practical application is difficult, rendering us unable to use them for the intended purpose.

In this study, we aimed at evaluating the solubility of cellulose in some typical chloride-based ILs, as well as their mixtures with acetate-based ILs. These mixtures can be obtained from relatively low-cost chloride-based ILs by an incomplete ion exchange (metathesis) reaction.

EXPERIMENTAL

Materials

1-Butyl-3-methylimidazolium chloride [BMIm]Cl, 1-ethyl-3-methylimidazolium chloride [EMIm]Cl, anion-exchange resin – Amberlite IRA-96® were purchased from Sigma-Aldrich. Ethanol (96% vol.) and formic acid were acquired from Chimmed (Russia).

Synthesis of ILs

1-Butyl-3-methylimidazolium acetate. [BMIm]Cl was dissolved in a water-ethanol (1:1) solution and eluted through a column packed with anion-exchange resin. For a complete displacement of 1-butyl-3-methylimidazolium acetate [BMIm]Ac from the column, it was washed additionally with a double volume of a pure eluent. The solvent was evaporated using a rotary evaporator, and the product was freeze-dried. The compound obtained was a fluid liquid at ambient temperature, with color ranging from light-yellow to light-orange and a freezing point lower than -20 °C. The yield was 98.0% (19.30 g).

NMR spectrum ^{1}H (DMSO-d_6), 400 MHz, 273 K, δ, ppm: 9.45 (1H, s, C_2-H), 7.80 and 7.70 (2H, 2d, C_4-HC_5-H), 4.18 (2H, t, N-CH_2-CH_2-CH_2-CH_3) 3.7 (3H, s, N-CH_3), 1.75 (3H, s, CH_3-COO^-), 1.75 (2H, m, N-CH_2-CH_2-CH_2-CH_3), 1.25 (2H, m, N-CH_2-CH_2-CH_2-CH_3), 0.9 (3H, t, N-CH_2-CH_2-CH_2-CH_3).

1-Ethyl-3-methylimidazolium acetate. [EMIm]Ac was synthesized in a similar manner as [BMIm]Ac, using [EMIm]Cl as a starting reagent. The product obtained was a fluid liquid at ambient temperature, with color ranging from light-yellow to light-orange, with a freezing point lower than -20 °C. The yield was 95.0% (16.00 g).

NMR spectrum ^{1}H (DMSO-d_6), 400 MHz, 273 K, δ, ppm: 9.84 (1H, s, C_2-H), 7.97 and 7.86 (2H, 2d, C_4-HC_5-H), 4.24 (3H, q, N-CH_2-CH_3), 3.88 (3H, s, N-CH_3), 1.64 (3H, s, CH_3-COO^-), 1.38 (3H, t, N-CH_2-CH_3).

1-Butyl-3-methylimidazolium formate. An anion-exchange resin was sequentially transformed to OH- and HCOO- forms. One should use a solution of formic acid in a water-ethanol mixture (1:1). Then it is necessary to elute 0.05 M solution of [BMIm]Cl. The product is eluted from the column with the same amount of pure solvent (1:1 water:ethanol mixture). The solvent is removed under aspirator vacuum by means of a rotary evaporator. The product is a fluid liquid at ambient temperature with color ranging from light-yellow to light-orange and a freezing point <-20 °C. The yield was 97.3% (18.30 g).

NMR spectrum ^{1}H (DMSO-d_6), 400 MHz, 273 K, δ, ppm: 9,45 (1H, s, C_2-H), 7.80 and 7.70 (2H, 2d, C_4-HC_5-H), 4.18 (2H, t, N-CH_2-CH_2-CH_2-CH_3) 3.7 (3H, s, N-CH_3), 1.65 (1H, s, $HCOO^-$), 1.75 (2H, m, N-CH_2-CH_2-CH_2-CH_3), 1.25 (2H, m, N-CH_2-CH_2-CH_2-CH_3), 0.9 (3H, t, N-CH_2-CH_2-CH_2-CH_3).

1-Ethyl-3-methylimidazolium formate. [EMIm]Fmt was obtained in a similar manner as [BMIm]Fmt, using [EMIm]Cl as a starting reagent. The product was a fluid light-yellow liquid at ambient temperature, with a freezing point <-20 °C. The yield was 98.3% (19.94 g).

NMR spectrum ^{1}H (DMSO-d_6), 400 MHz, 273 K, δ, ppm: 9.84 (1H, s, C_2-H), 7.97 and 7.86 (2H, 2d, C_4-H C_5-H), 4.24 (3H, q, N-CH_2-CH_3), 3.88 (3H, s, N-CH_3), 1.64 (1H, s, $HCOO^-$), 1.38 (3H, t, N-CH_2-CH_3).

Cellulose pretreatment with IL mixtures

We have chosen Avicel microcrystalline cellulose (~50 μm, Sigma-Aldrich) as model substrate for the pretreatment. The experiments are planned to be continued with a natural substrate (pine sawdust). Synthesized acetate-based ILs ([BMIm]Cl and [EMIm]Cl) and a ready-made one ([BMIm]Cl – Sigma-Aldrich) were chosen as pretreating agents. Acetate-based ILs are preferable in comparison with formate-based ones, because of the higher thermal stability of the former compounds. However, formate-based ILs can be used as well.

For the pretreatment, the IL or IL mixture was dried under reduced pressure (≤10 mm Hg) in a round-bottom flask at 140 °C for 2 h. Then, the cellulosic substrate previously dried for 4 h at 80 °C was placed by several portions into a flask with the dry IL and heated for 4 h. Partial dissolution was observed. Then, to evaluate cellulose solubility, a homogeneous caramel-like portion of the solution was taken. A polar counter-solvent (*e.g.*, water or ethanol) was added to the portion, immediately resulting in precipitation of the cellulose gel. The gel was washed with water, then dried at 90 °C for 12 h and finally weighed. The IL was regenerated by the counter-solvent evaporation under reduced pressure.

XRD analysis of initial and pretreated cellulose substrates

XRD analysis was performed by means of a Bruker D2 Phaser diffractometer, using DIFFRAC.SUITE software. Scanning Mode: Cu Kα radiation, scanning angle interval (2Θ) – from 2° to 140°, time of accumulation of a reflection signal at a point – of 0.5 s, the accuracy of the diffraction peak determination –

±0.02 °Θ. To avoid errors when measuring the degree of crystallinity of the samples, they were scanned at different speeds, in triplicate. Experimental error was equal to ±1%.

The relative decrease in the degree of crystallinity was calculated as follows: (A - B)·100% / A, where A – degree of crystallinity of an initial sample, B – degree of crystallinity of a pretreated sample.

Scanning electronic microscopy (SEM) of initial and pretreated cellulose substrates

SEM micrographs of the initial and pretreated cellulose substrates were registered with a JIB-4501 multibeam system (Jeol, Japan). Samples were placed on aluminum SEM tables by a carbon sticky tape, dried under vacuum, and coated with a 20 nm layer of platinum in a JFC-1600 auto fine coater (Jeol, Japan). Samples were observed at 10 kV accelerating voltage with secondary electron detection.

RESULTS AND DISCUSSION

The results of the experiments are shown in Tables 1-3. From the obtained weight concentration of cellulose dissolved in ILs, one can conclude that the use of IL mixtures makes the process more efficient and allows achieving a higher concentration of cellulose than that observed using the individual compounds under the same conditions. For the butyl-substituted ILs, cellulose solubility in the solvent mixture is even higher than for individual compounds, while for the ethyl-substituted ILs cellulose solubility in [EMIm]Ac is higher than the maximal solubility in the solvent mixture. One should note that the solubilizing power of ethyl-substituted ILs is higher than that of butyl-substituted ILs. It can be explained by the shorter side chain of ethyl-substituted ILs, thus lowering the viscosities of those ILs and therefore promoting the dissolution of cellulose.

The use of mixtures of acetate-based and chloride-based ILs allows decreasing the diffusion resistance within the mixture and lowers the melting point of a mixed solvent (IL).[5,23,25] The application of such mixtures makes the process of cellulose dissolution more efficient, the reasons being the destruction of intra- and intermolecular hydrogen bonds of cellulose and the formation of new stronger intermolecular bonds between the cellulose and the chloride anions.

The use of IL mixtures increases cellulose concentration in the solution (Tables 1 and 2). This is important for their use in practice, as it allows increasing the raw material to solvent ratio. The ILs containing chloride anions decrease cellulose crystallinity quite efficiently, but the dissolution of cellulose is more complicated diffusionally because of their high viscosities, while acetate-based ILs have lower viscosities.[12] Therefore, lignocellulose pretreatment by IL mixtures is advantageous as it leads to highly concentrated solutions of cellulose in ILs.

Table 1
Weight concentrations of cellulose in [BMIm]Cl-[BMIm]Ac mixtures

#	[BMIm]Cl, wt%	[BMIm]Ac, wt%	Cellulose (Avicel®) concentration, wt%
1	100	0	7.1
2	80	20	12.3
3	60	40	18.5
4	40	60	18.1
5	20	80	15.3
6	0	100	17.5

Table 2
Weight concentrations of cellulose in [EMIm]Cl-[EMIm]Ac mixtures

#	[EMIm]Cl, wt%	[EMIm]Ac, wt%	Cellulose (Avicel®) concentration, wt%
1	100	0	18.0
2	80	20	21.5
3	60	40	23.4
4	40	60	22.3
5	20	80	21.3
6	0	100	25.5

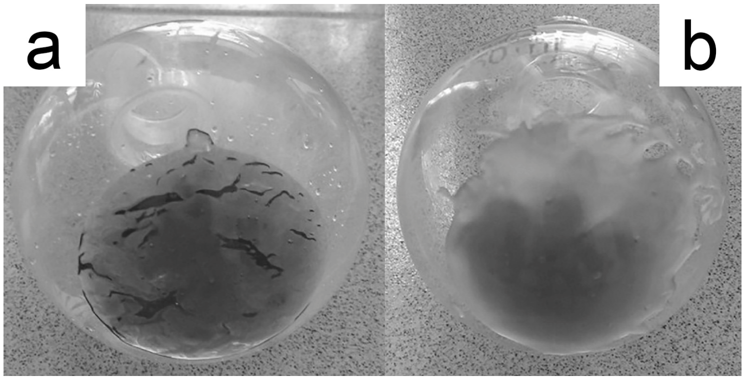

Figure 2: Cellulose solutions in IL mixtures [EMIm]Cl:[EMIm]Ac in ratios of (a) 3:2; and (b) 1:4

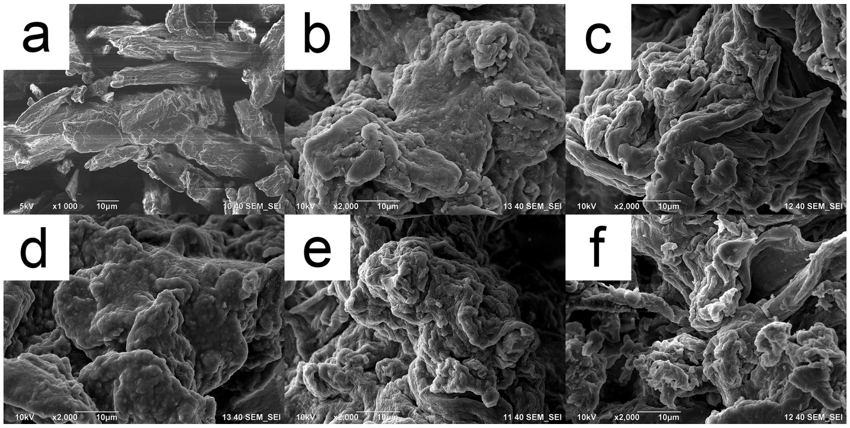

Figure 3: SEM images of cellulose without (a) and after pretreatment (b-f) in IL mixtures [EMIm]Cl:[EMIm]Ac with mass fractions of (b) 100:0%; (c) 20:80%; (d) 40:60%; (e) 60:40%; (f) 0:100%

Table 3
Results of XRD analysis of initial and pretreated cellulose (Avicel®) substrates

#	Mass fraction of [EMIm]Cl, %	Mass fraction of [EMIm]Ac, %	Degree of crystallinity, %	Relative decrease in crystallinity degree, %
1	Without pretreatment		37.2	-
2	100	0	15.8	57.5
3	80	20	22.0	40.9
4	60	40	23.2	37.6
5	40	60	23.4	37.1
6	20	80	30.3	18.5
7	0	100	22.2	40.3

Consequently, the application of ILs mixtures has a lot of advantages. In comparison with the individual ILs the dissolution rates in ILs mixtures are higher while the mixtures themselves have lowered melting points and viscosities. Moreover, it also allows simultaneous use of relatively cheaper chloride-based ILs that decrease cellulose crystallinity dramatically and acetate-based ILs that have better solubilizing ability and decrease the viscosity of the solvent system, favoring the cellulose dissolution. Surprisingly, using the mixture of ILs with 1:4 weight ratio of chloride-based IL to acetate-based leads to incomplete dissolution as can be seen in Figure 2c and minimal decrease in cellulose crystallinity (18.5%). Moreover, decrease of chloride-based IL content in an IL mixture has a negative impact on the process of pretreatment, unless using individual acetate-based IL. The cellulose precipitated from that solution has a lumpy, grained form, easily crumbling, whereas cellulose obtained from mixtures with higher content of the chloride-based IL has clearly visible homogeneous areas showing complete dissolution of the substrate. The cellulose pretreated by chloride-based ILs has the form of a semi-transparent, homogeneous gel after washing with water.

The XRD method was chosen for confirming the changes in cellulose crystallinity. Due to the better results of cellulose dissolution in ethyl-substituted ILs, compared with that in butyl-substituted ILs, the former were investigated by XRD analysis. The maximum decrease in cellulose crystallinity was achieved when using [EMIm]Cl (57.5%) and [EMIm]Ac (40.3%). As for the mixtures of ethyl-substituted ILs, the best result was achieved by the mixture with 4:1 weight ratio of the chloride-based IL to the acetate-based IL (40.9%).

The results of scanning electronic microscopy (SEM) demonstrate deep changes in the morphology of the pretreated substrates. As it can be seen from the images (Fig. 3), the surface of the substrates pretreated by the chloride-based IL is more extended than that of the substrates pretreated by the acetate-based IL. This trend correlates with the observation that the decrease in cellulose crystallinity is higher for the substrates pretreated by the chloride-based ILs. Acetate-based ILs have been employed for the fractionation of lignocellulosic biomass and for decreasing the degree of crystallinity of the isolated cellulose.[26,27] Our results indicate that the developed procedures for biomass fractionation and cellulose isolation can be improved by using mixtures of acetate- and chloride-based ILs, instead of pure acetate-based ones.

The cost of ILs is a crucial factor, restraining their application for the pretreatment of lignocellulose.[28] It is well-known that ILs with different types of anions (acetate, formate *etc.*) are derivatives of the corresponding halide-based (Cl, Br, I) ILs.[29] Therefore, the price of the derived ILs is obviously higher, and the usage of mixtures containing chloride-based ILs is more economically feasible.

While mixtures of ILs with organic co-solvents[30] and mixtures of acetate-based and hydrosulfate-based ILs[31] have already been studied as powerful pretreatment agents for lignocellulose, the improvement of cellulose solubility in mixtures of acetate-based and chloride-based ILs is observed for the first time to the best of our knowledge. This effect was not observed when applying the mixture of chloride and dicyanamide ILs,[32] apparently because of the low solubilizing power of dicyanamide-based ILs.

The aim of substrate pretreatment is to achieve maximal decrease of cellulose crystallinity simultaneously with maximal solubility in the solvent or the solvent system. Thus, using the mixture of chloride-based IL to acetate-based IL with the 3:2 weight ratio provides the optimal values of the decrease of cellulose crystallinity (37.6%), solubilizing power of the solvent system (23.4%), and costs for IL employment (more than half of the mixture consists in a relatively inexpensive chloride-based IL).

CONCLUSION

Within the study, the efficacy of applying ionic liquid mixtures for pretreating cellulosic substrates was investigated. The precipitated cellulose samples after the pretreatment were studied by XRD and SEM analyses. Cellulose solubility in mixtures of butyl-substituted imidazolium ionic liquids exceeds that in any of the individual compounds, while cellulose solubility in mixtures of ethyl-substituted imidazolium ionic liquids is slightly lower than that in individual acetate-based ionic liquids. In contrast with individual acetate-based ILs, cellulose dissolution in mixtures of acetate-based and chloride-based ionic liquids leads to the formation of a homogeneous cellulose gel, along with a relatively high concentration of the substrate, thanks to the lower viscosity of the mixtures, thus avoiding the disadvantages of pretreatment by individual ionic liquids.

Considering the economic efficiency of applying ILs, using the mixture with the 3:2 weight ratio of chloride-based IL to acetate-based IL is the most beneficial choice due to the optimal values of the decrease of cellulose crystallinity (37.6%), solubilizing power of the solvent system (23.4%), and costs for IL employment (more than half of the mixture consists of a relatively inexpensive chloride-based IL).

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