Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2015.1102772

57 (2016) 19785–19793
September

Taylor & Francis
Taylor & Francis Group

Types of bulk liquid membrane and its membrane resistance in heavy metal removal and recovery from wastewater

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Received 9 March 2015; Accepted 23 September 2015

ABSTRACT

Bulk liquid membrane (BLM) is one of the simplest types of liquid membrane that shows superior membrane stability but inferior solute fluxes. The inferior solute fluxes of BLM are caused by its small interfacial area per unit volume, long transportation path, and high membrane resistance. The interfacial area and transportation path of BLM are influenced by its configurations, whereas the membrane resistance is governed by its membrane phase viscosity, stirring speed, and operating temperature. Hence, this paper aims to outline the different types of BLM and discuss the various factors affecting the membrane resistance of BLM in heavy metal removal and recovery from wastewater. Major challenges and future prospects toward the utilization of BLM as a prospective separation technique for large-scale industrial applications are also highlighted and discussed.

Keywords: Bulk liquid membrane; Heavy metal; Removal; Recovery; Membrane resistance

1. Introduction

Membrane has a long-standing history of selective separation for a target solute. If the molecular dimension of the target solute is different from other solutes, porous membranes like microfiltration, nanofiltration, ultrafiltration, and reverse osmosis, which comply to the pore flow model [1], can be used to achieve the separation. However, if the molecular dimension of the target solute is very close to other solutes, affinity membranes with selective recognition ability toward the target solute should be employed. An example of such a membrane is liquid membrane. It consists of two miscible liquids (source (S) and receiving (R) phases) which are separated by a third liquid (membrane (M) phase) that is immiscible with the preceding two liquids. Owing to the favorable thermodynamic conditions created at the S/M and M/R interfaces, the solute moves from the S, M, and finally to the R phase via a simple or facilitated transport [2]. The former is based on the solution–diffusion model [1], whereas the latter entails a selective and reversible reaction between the solute and a carrier (molecular recognition compound/functional moiety) borne by the M phase [2].

The idea of using liquid membrane to perform separation processes was probably initiated by Osterhout who studied the facilitated transport of ammonia across algae cell walls in 1935 [3]. However, development in this field had been slow until Ward and Robb reported the application of supported liquid membrane (SLM) in CO_2 gas separation in 1967 [4] and Li patented the emulsion liquid membrane (ELM) used for hydrocarbon separation and industrial desalination in 1968 [5]. The ongoing interest in liquid membrane arose from the endeavor to attain a larger solute flux across the membrane since the diffusion coefficients in liquids are higher by a few orders of magnitude than those in solid polymers [6]. In addition, a broad spectrum of extractants developed for the well-established solvent extraction process can be utilized as carriers for liquid membrane to achieve high fluxes and selectivity in various separation processes. Motivation toward utilizing liquid membrane is further strengthened by the fact that it can carry out the simultaneous removal and recovery of solutes in a single stage. This gives rise to a nonequilibrium mass transfer, that is, uphill transport, where a solute can move from low- to high-concentration solution counter to its concentration gradient and the ultimate separation is not limited to the equilibrium conditions. Today, the efficiency and economic advantages of liquid membrane have designated it as the optimal solution for selective separation, recovery, and preconcentration of solutes in a wide range of fields such as chemical and pharmaceutical industries, biotechnology, food processing, and environmental engineering [2]. Therefore, liquid membrane remains to be an attractive research area in spite of some technological challenges which presently restricts its large-scale industrial applications.

Depending on the configurations and contacts of S, M, and R phases, liquid membrane can generally be divided into three forms, namely, SLM, ELM, and bulk liquid membrane (BLM). SLM has the S and R phases separated by the M phase which is immobilized in the pores of a polymeric membrane, while ELM consists of double emulsions where small globules of M phase containing droplets of R phase are suspended or dispersed in the S phase. BLM, on the other hand, has the S and R phases separated by a solid impermeable barrier. Owing to their salient features, such as low solvent inventory of SLM and high fluxes of ELM [7], both SLM and ELM have drawn substantial interest from numerous researchers ever since their emergence as two distinct forms of liquid membrane. However, the poor membrane stability of SLM [8] and ELM [9] has always been the major technological predicament that seems to have no comprehensive solution. The former is caused by the inevitable washing out of solvents from the pores of polymeric membrane due to, among other things, lateral shear forces, progressive wetting, static pressure differential and osmotic pressure across the membrane [8], while the latter is mainly ascribed to the emulsion (membrane) formulation and preparation method [9]. Although the revolutionary advances in membrane contactors have led to a new evolution of liquid membrane that incorporates the advantages of SLM and/or ELM into membrane contactors (e.g. hollow fiber SLM, emulsion pertraction (also known as pseudoemulsion-based hollow-fiber strip dispersion) and hollow fiber renewal liquid membrane), the issue of membrane instability is still unresolved, particularly for a long-term operation, and further validation under various industrial conditions is necessary [2,10].

As opposed to SLM and ELM, BLM does not seem to have a problem with membrane stability as long as it has the agitation of S, M, and R phases under control. As the name implies, the bulky M phase of BLM eliminates the possibility of membrane rupture or fast carrier exhaustion, and thus it gives rise to its excellent membrane stability. Furthermore, BLM has the advantages of being simple and cheap to construct over other kinds of liquid membrane. The simplicity in the design, coupled with its characteristics such as constant interfacial area, constant hydrodynamic conditions and ease of manipulation, has rendered BLM a great laboratory tool for studying the kinetics, transport properties, and reaction mechanisms of various separation processes [11]. Nevertheless, this gain of BLM is invariably accompanied by a loss in the solute fluxes due to its small interfacial area per unit volume, long transportation path and high membrane resistance [7]. The small interfacial area tends to limit the complexation and decomplexation reactions between the solute and carrier molecules at the S/M and M/R interfaces [12], whereas the long transportation path and high membrane resistance are inclined to prolong the time to transport solute–carrier complexes from S/M to M/R interface. Collectively, these have resulted in low solute fluxes across BLM and put a limit on its large-scale industrial applications. In general, the size of interfacial area and length of transportation path are affected by the configurations of BLM, while the membrane resistance is determined by its M-phase viscosity, stirring speed, and operating temperature. With the aforementioned explanations, this review aims to summarize the different types of BLM reported in the recent literature and discuss the various factors affecting the membrane resistance of BLM in heavy metal removal and recovery from wastewater. Major challenges and future prospects toward the utilization of BLM as a prospective separation system for large-scale industrial applications are also highlighted and outlined.

2. Types of BLM

BLM can be designed with a wide variety of configurations which, in most cases, consists of two parts: a common part containing the M phase and a separate part where the S and R phases are either separated by a solid impermeable barrier or structurally separated without any barrier. The barrier is normally designed as a flat or cylindrical wall and placed in between the S and R phases. Some typical types of BLM with and without a solid impermeable barrier reported in the recent literature are given in Fig. 1. The former consists of the rectangular and cylindrical vessels, whereas the latter includes the H- and U-tube vessels. Some of these vessels have their common parts arranged at the top and separate parts at the bottom, while some of them have the opposite arrangement depending on the density of S, M, and R phases used. Most, if not all, of these phases are stirred at an appropriate intensity to avoid mixing between them. In general, the volume of M phase used is equal to or between those of S and R phases. For instance, Muthuraman et al. [13] and Akin et al. [14] used equal volumes of S, M, and R phases, that is S/M/R volume ratio of 1:1:1, in their BLM processes, while Koter et al. [15] and Candela et al. [16] applied S/M/R volume ratios of 4.2:2:1 and 10:2.5:1, respectively. Sometimes, the M phase with the highest volume among the phases is also used. For example, Minhas et al. [17] applied an S/M/R volume ratio of 1:1.5:1 in their BLM processes, whereas Dadali et al. [18] utilized an S/M/R volume ratio of 6.25:6.25:1. In any types of BLM shown in Fig. 1, the M phase is always in contact with the S and R phases and facilitates the mass transfer between them.

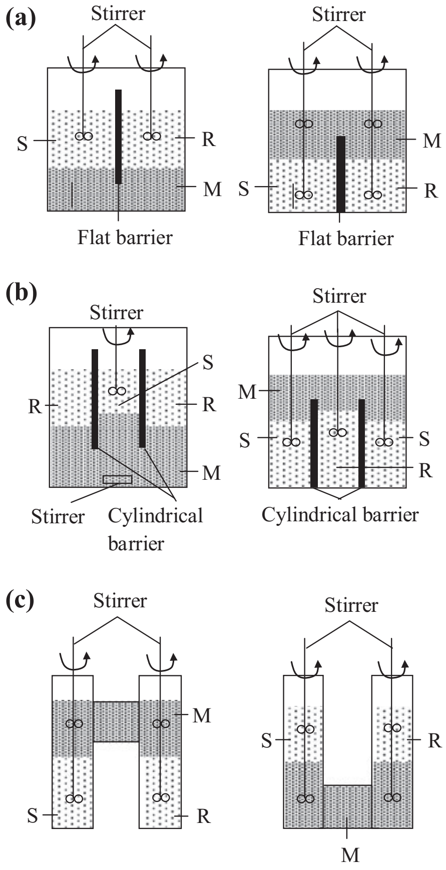

Fig. 1. BLM with and without a solid impermeable barrier: (a) rectangular vessel [12,19,20], (b) cylindrical vessel [21–28] and (c) H- and U-tube vessels [13,29–34].

3. Membrane resistance of BLM

In spite of the superior membrane stability of BLM as compared to other types of liquid membrane, BLM is not yet ready for industrial applications due to its high membrane resistance arising from the bulky M phase used. Consequently, the transportation of solutes across the M phase is impeded, and hence, this jeopardizes the overall performance of BLM. Various factors affecting this membrane resistance of BLM include, among other things, the M-phase viscosity, stirring speed, and operating temperature.

3.1. Effect of membrane phase viscosity

The materials used in formulating the M phase of BLM are mostly organic (carbon containing) solvents derived from petroleum resources which include the aliphatic, aromatic, chlorinated, and oxygenated solvents [7]. They form different components in the M phase as a carrier (<10% by volume), diluent (>85% by volume) or modifier (<5% by volume) [35]. The carrier functions as an active component that binds and transports solutes from one phase to another, while the diluent helps to manipulate the water content, and thus, this improves the hydrophobicity of the vicinity around the carrier molecules that would influence their transport efficiencies [36]. The modifier, on the other hand, improves the phase disengagement and overcomes any emulsion or third phase formation in the aqueous-organic system [7]. Examples of conventional organic solvents that have been used as carriers (organophosphorus compounds, amines, oximes, quinolines, and crown ethers), diluents (alkanes and cycloalkanes, chlorinated alkanes, acyclic and cyclic ketones, alcohols and aromatic compounds) and modifiers (alcohols and organophosphorus compounds) in formulating the M phase of BLM for wastewater treatment are well documented in the literature [7]. These solvents possess different viscosities due to the variations in their strengths of intermolecular forces and molecular shapes [37], which in turn bring about different degrees of membrane resistance in BLM. The viscous effect of these solvents is particularly significant in BLM relative to other types of liquid membrane due to its bulky M phase.

Table 1 shows the viscosities of some conventional organic solvents used to formulate the M phase of BLM in heavy metal removal and recovery processes. The viscosity of water as a reference liquid is also provided. In general, nonpolar solvents are less viscous (<1 mPa s) than polar solvents because of the zero or small dipole moments of their molecules. This leads to the formation of the weak van der Waals forces between solvent molecules instead of the strong intermolecular forces like dipole–dipole forces and hydrogen bonds [38]. Consequently, the solvent molecules can slide over each other more easily. However, van der Waals forces grow with the molecular size, and thus, long-chain nonpolar solvents like undecane, dodecane and kerosene are invariably quite viscous (>1 mPa s). For water, although its polarity allows it to form hydrogen bonds with the neighboring water molecules, it has a low viscosity due to its small molecular size. Therefore, by carefully choosing the right solvents in formulating the M phase of BLM, the membrane resistance of BLM can be reduced to the lowest possible level. The lower the membrane resistance of BLM, the faster a heavy metal can diffuse across the M phase, and the higher the kinetics of metal transport through BLM could be accomplished.

Table 1
Viscosities of some conventional organic solvents used to formulate the M phase of BLM

Solvent type	Viscosity (mPa s)	Refs.
Nonpolar solvents		
Hexane	0.30 (25°C)	[39]
Heptane	0.376 (27°C)	[40]
Octane	0.51 (25°C)	[39]
Decane	0.86 (25°C)	[39]
Undecane	1.09 (100°C)	[39]
Dodecane	1.37 (25°C)	[39]
Cyclohexane	0.887 (25°C)	[38]
Kerosene	1.64 (27°C)	[40]
Dichloromethane	0.406 (25°C)	[38]
1,2-Dichloroethane	0.776 (25°C)	[38]
Chloroform	0.53 (27°C)	[40]
Carbon tetrachloride	0.97 (20°C)	[38]
Benzene	0.601 (27°C)	[40]
Toluene	0.55 (27°C)	[40]
Xylene	0.605 (25°C)	[38]
Polar solvents		
1-Heptanol	5.937 (25°C)	[38]
1-Octanol	7.598 (25°C)	[38]
1-Decanol	11.797 (25°C)	[38]
Cyclohexanone	2.02 (25°C)	[38]
Tributylphosphate	3.8 (20°C)	[38]
Tri-n-octylamine	8.325 (25°C)	[41]
Trioctylphosphine oxide	15 (55°C)	[38]
Di-2-ethylhexylphosphoric acid	21.22 (30°C)	[38]
Quinoline	3.36 (25°C)	[38]
Water[a]	0.89 (27°C)	[40]

[a] Reference liquid.

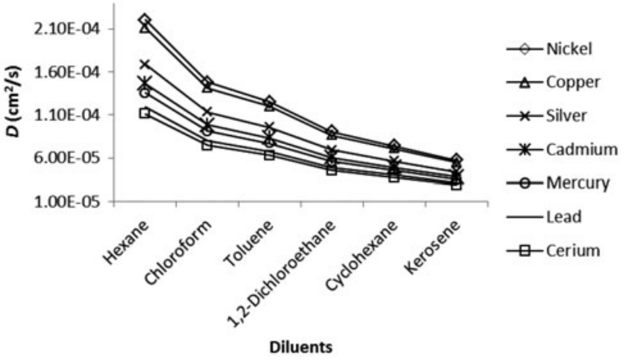

Fig. 2. *D* values of some heavy metals in various diluents predicted from the Wilke–Chang correlation [42].

Since diluent is the bulk component of an M phase, the rate at which a heavy metal diffuses across the M phase could be estimated by its diffusion coefficient (*D*) in the diluent. Fig. 2 shows the *D* values of some heavy metals in various diluents predicted from the Wilke–Chang correlation [42]. All heavy metals were presumably modified and converted into neutral species that possess little, or no, water of hydration. It was found that as the viscosity of diluents increases from hexane to kerosene (Table 1), the *D* values of different heavy metals in these diluents decrease accordingly. This implies that the more viscous the diluent, the slower the heavy metals could diffuse across it and the smaller the metal fluxes through BLM could be achieved. This assertion, as a matter of fact, has been verified by several researchers. For instance, Akin et al. [14], Minhas et al. [17], Saf et al. [22], Yilmaz et al. [23], and Alpaydin et al. [26] studied the effect of different diluents (carbon tetrachloride, chloroform and dichloromethane) on the kinetics of metal (chromium, mercury, palladium) transport through BLM. They jointly substantiated the significant rise in the maximum metal fluxes ($J_{\max}$) across BLM when the diluent of M phase was changed from the more viscous carbontetrachloride to the less viscous chloroform (237–1,115% increase in $J_{\max}$) or dichloromethane (467–3,600% increase in $J_{\max}$). This suggests that a slight reduction in the diluent viscosity of 40–60% could achieve a dramatic increase in $J_{\max}$ of up to 3,600%.

3.2. Effect of stirring speed

One of the solutions to overcome the viscous resistance in the M phase of BLM is by stirring. When the

M phase is stirred, the thickness of its boundary layer, and thus its viscous resistance, is minimized and its hydrodynamics is improved. The solute transport in the M phase becomes dominated by convection which has a much faster mass transfer rate than that of molecular diffusion when the M phase is unstirred. In a stirred M phase, the solutes are subjected to fluid forces arising from stirring and are physically carried from one position to another by the random motion of small lumps of fluid [43]. Intuitively, the greater the stirring speed, the larger the fluid velocity and the higher the rate of solute transport through BLM. In fact, this had been verified by numerous researchers [14,17,23,24,26,44] who found that the rise in stirring speed of M phase from 33 to 250% was able to increase $J_{\max}$ from 5 to 202% for the transport of various heavy metals (chromium, mercury, palladium) through BLM. The smaller increase in $J_{\max}$ with stirring speed relative to that with the M-phase viscosity (as discussed earlier in Section 3.1) implies that the latter is a more significant factor in affecting the membrane resistance of BLM. The maximum speed to which the M phase can be stirred is, however, limited by the hydrodynamic stability of the aqueous organic interfaces, that is, S/M and M/R interfaces, in BLM and it varies from one type of BLM to another. For example, Muthuraman et al. [13] observed the deformation of S/M and M/R interfaces and some mixing of S and R phases at a stirring speed of 350 rpm in a H-tube type of BLM with S:M:R volume ratio of 1:1:1. However, the similar observation was reported at a much lower stirring speed of approximately 90 rpm in another study by Minhas et al. [17] who used a U-tube type of BLM with S/M/R volume ratio of 1:1.5:1.

3.3. Effect of operating temperature

Another way to reduce the viscous resistance in the M phase of BLM is by increasing its operating temperature. As the operating temperature increases, the cohesive force between the solvent molecules decreases and the kinetic energy of the solvent molecules increases. This causes a reduction in the fluid shear stress and, as a result, the solvent molecules become more mobile and this reduces the viscous resistance of the M phase. Subsequently, a solute could diffuse across the M phase at a much faster rate with increasing temperature and this is consistent with both the Stokes–Einstein equation and Wilke–Chang correlation [42]. It had been shown experimentally by several researchers [17,23,26,44] that the increase in operating temperature from 2 to 5% led to an upsurge in $J_{\max}$ from 8 to 85% for the transport of various heavy metals (chromium, mercury) through BLM. Obviously, the increase in $J_{\max}$ with operating temperature is much larger than that with stirring speed but it is still smaller than that with the M-phase viscosity. This suggests that the order of decreasing significance of various factors with respect to their influence on the membrane resistance of BLM is M-phase viscosity > operating temperature > stirring speed. This could, however, be further verified by using a full or fractional factorial design [45]. The same group of researchers had also determined the activation energy of metal removal and recovery processes through BLM from the Arrhenius equation by using the rate constants obtained at different temperatures. The activation energy of metal removal process was found to range from 5.77 to 29.13 kJ/mol, whereas that of metal recovery process from 7.99 to 28.92 kJ/mol. Since all the values of activation energy obtained were less than 41.86 kJ/mol [44], they collectively concluded that both the metal removal and recovery processes in BLM were diffusion-controlled but not chemical reaction-controlled.

4. Major challenges and future prospects

Over the past few decades, the widespread enthusiasm for preserving the environment and its limited natural resources has been one of the most challenging topics, and it has drawn considerable public attention to the removal and recovery of contaminated resources. The removal and recovery of heavy metals from wastewater, in particular, has gained massive interest amongst researchers owing to the toxicity and recycling value of heavy metals. Although various techniques such as chemical precipitation, coagulation–flocculation, ion exchange, membrane filtration, adsorption, flotation and electrochemical process [46] have been developed to treat metal-containing wastewater, there is little emphasis on the recovery of the removed heavy metals. Even if the recovery is available, it is normally carried out in a separate unit by elution with suitable reagents [47] and this incurs additional cost. Liquid membrane, in this context, outshines other separation techniques since it is capable to remove and recover heavy metals simultaneously in a single unit. Other salient features of liquid membrane include nonequilibrium mass transfer, high selectivity, high recovery and low-energy consumption [2]. Accordingly, numerous studies have been documented on the application of liquid membrane, for instance BLM, in the removal and recovery of various heavy metals such as chromium [15,26,48], cadmium [15,18,49], copper [24,25,32], zinc [18,25,28], nickel [25], cobalt [31], mercury [17], palladium [14,50], platinum [50], silver [27], and uranium [16,51] from wastewater.

Even though BLM seems to be very promising and can apparently remove and recover heavy metals effectively from wastewater, most of the BLM processes are demonstrated on laboratory-scale and large-scale application of BLM is still under research. Undoubtedly, a distinct downside of BLM is its low metal fluxes which are attributed to its small interfacial area per unit volume, long transportation path and high membrane resistance as described earlier. Moreover, the conventional organic solvents that are used to prepare the M phase of BLM (Table 1) are mostly derived from petroleum resources which are invariably toxic and non-biodegradable. Consequently, they are difficult to handle and often result in ecological hazard to the aquatic systems in the case of solvent loss. Of late, attempts to replace these toxic solvents with green solvents such as ionic liquid [52] and vegetable oil [12,53,54] in formulating the M phase of BLM have been reported by several researchers. Although their removal and recovery efficiencies are compatible with their petroleum-based counterparts [11], their high viscosity attributes would jeopardize their transport kinetics if care is not taken to reduce their viscous effects via stirring and/or operating at elevated temperatures [11,52]. Between ionic liquid and vegetable oil, the former has the advantage of being tunable molecularly which could modify its physical properties including viscosity [55,56]. Nevertheless, ionic liquid can be inordinately expensive since it is a specialty chemical that is custom-manufactured in small quantities for specific applications [57]. Vegetable oil, on the other hand, is produced abundantly as a food commodity and hence is much cheaper than ionic liquid. Being a food commodity, vegetable oil is widely acknowledged to be nontoxic and safe to consume. The green credentials of ionic liquid, however, have recently sparked a debate amongst researchers following the growing evidence of its potential environmental hazards and toxicity to living organisms including human beings [58–60].

Amidst these challenges, much more dedicated work and further exploration are indispensable to maximize the metal fluxes across BLM so as to improve its performance and competency as a separation technique. For instance, a new evolution in the design of BLM which incorporates the favorable features of spiral wound and hollow fiber types SLM [61] and/or those of emulsion globules of ELM [9] that tend to provide high interfacial area to volume ratios could be initiated. Moreover, additional driving forces for achieving maximum metal fluxes such as electrical potential difference [62], ultrasonic [63] and magnetic [64] forces could also be introduced across BLM. Not only would these forces help to move metal ions from one phase to another, but they would also reduce the solvent viscosity [65,66]. This makes the application of low cost and environmentally benign, but viscous, solvents like waste vegetable oil [7] as the M phase of BLM possible. It could also contribute to the global green technology initiatives [67]. While most of the BLM reported in the literature are operated in batch mode, attempts to develop a continuous BLM system which favors large-scale industrial applications should be made. Concomitant with the widespread heavy metal pollution and the ever increasing heavy metal demand across various industries, liquid membrane technology is forecasted to be a prospective substitute for the conventional multiunit metal removal and recovery technologies as more and more researchers are presently unveiling the great benefits of this powerful technology.

5. Conclusion

The ability to remove and recover heavy metals simultaneously in a single unit is one of the salient features of liquid membrane which makes it stand out from the other separation techniques that usually remove and recover heavy metals separately in multiple units. Among the different types of liquid membrane, BLM is the simplest type that exhibits excellent membrane stability owing to its bulky membrane phase that eliminates the possibility of membrane rupture or fast carrier exhaustion. However, BLM tends to show relatively low fluxes due to its small interfacial area per unit volume, long transportation path and high membrane resistance. The former two is related to the configurations of BLM, while the latter is influenced by its membrane phase viscosity, stirring speed and operating temperature. BLM is usually designed with (rectangular and cylindrical vessels) or without (H- and U-tube vessels) a solid impermeable barrier which possesses a small interfacial area per unit volume and a long transportation path. The small interfacial area restricts the complexation and decomplexation reactions between solutes and carrier molecules, whereas the long transportation path prolongs the time to transport solutes across BLM. The order of decreasing significance of various factors with respect to their influence on the membrane resistance of BLM is membrane phase viscosity > operating temperature > stirring speed. It was found that membrane phase with small viscosity, high operating temperature and stirring speed would reduce the membrane resistance of BLM and thus maximize the metal fluxes across BLM. Hitherto, the limited large-scale industrial application of BLM in the removal and recovery of heavy metals from wastewater confirms the many challenges that have to be overcome before a great progress in this technology could be envisaged in the future.

Acknowledgements

The author would like to acknowledge the research grant provided by the Ministry of Higher Education of Malaysia under the Research Acculturation Grant Scheme (Project reference number: RAGS/2013/UITM/TK05/11; Project code: 600-RMI/RAGS 5/3 (80/2013)).

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