Solvent-resistant cellulose membranes for membrane gas-liquid contactors

T S Anokhina, V Ya Ignatenko, D S Bakhtin, S D Bazhenov and A V Volkov

A.V. Topchiev Institute of Petrochemical Synthesis RAS, 119991, Russia, Moscow, Leninsky pr., 29.

Abstract. In this paper, we analyzed the possibility of using cellulose membranes in gas-liquid contactors to separate CO2 from physical absorbents and stabilize gas condensate. It was shown that a solid cellulose film "cellophane" is not impermeable to hexane and tetraethylene glycol dimethyl ether due to the absence of pores. It also has been found that these solvents are not adsorbed in the membrane, and the cellulose does not swell therein. This lack of interaction of the investigated organic solvents with the natural polymer was explained in terms of Hansen's solubility parameters, which in the case of hexane and tetraethylene glycol dimethyl ether are more than twofold less than of Hansen's solubility of cellulose.

The impermeability and lack of interaction of the solvents under investigation with cellulose membranes makes them promising as membranes for gas-liquid contactors. But in order to realize the process it is necessary to create a membrane structure whose pore size not going to have hexane and tetraethylene glycol dimethyl ether penetration, but the permeance of CO2 and CH4 will be high.

1. Introduction

Recently, there have been actively developed approaches to intensify the process of releasing acid gases, first of all carbon dioxide, from gas streams (for example, flue gases, natural gas and synthesis gas) using membrane integrated systems that combine the absorption method with membrane method of separation [1-4]. For the purification of gas mixtures at elevated pressures, the most promising is the use of "physical" absorbents because of the ease of their regeneration, since selective dissolution of acidic components proceeds without chemical reactions [5]. Such a system is a gas-liquid membrane contactor in which a selective mass transfer of components occurs between two phases separated by a membrane. The selectivity of the separation process is determined, first of all, by the difference in the solubility of gases in the absorption liquid [6].

Another process in which the use of the membrane separation method can be very promising is the stabilization of the gas condensate. Gas condensate is a mixture of heavy hydrocarbons, sometimes called gas gasoline, released from gas before it is sent to gas trunklines. Unstable gas condensate has no qualified application, and there is such an application for individual hydrocarbons and stable gas condensate. To stabilize the gas condensate at present, 3 methods are used:

1. Stepwise weathering (separation, degassing);
2. Rectification in stabilization columns;
3. Combination of separation and rectification.
These methods have a number of disadvantages: reverse re-dissolution, incomplete separation of hydrocarbons, loss of light fractions of condensate, high consumption of thermal energy, which in turn increases the cost of the process.

The membrane separation method consists in the use of a gas-liquid membrane contactor in which a selective mass transfer of components occurs between two phases separated by a membrane. The prospects of using membrane contactors for gas purification processes are due to small mass-size characteristics, independent regulation of gas and liquid flows, absence of the need for vertical arrangement of the apparatus and its modularity. To separate CO₂ from the physical absorbents and stabilize the gas condensate, the membrane used in gas-liquid contactors must have chemical stability, be impermeable to organic media, and have a high permeability for the gases emitted [6, 7].

Therefore, cellulose (figure 1) can be a promising material for membranes in a gas-liquid membrane contactor. This polymer is one of the most common renewable, inexpensive and biodegradable organic materials and can be considered as an almost inexhaustible source of raw materials with increasing demand for environmentally friendly and biologically compatible products. Cellulose and its derivatives were among the first membrane materials to be used in industry [8]. For example, cellulose-based membranes are widely used for ultrafiltration processes [9] of nanofiltration [10, 11], pervaporation [12], and gas separation [13]. Gas separation membranes for cellulose show high permeabilities for individual gases and high selectivities for a pair of CO₂ and CH₄ [13], which also makes it promising for use as a membrane material in gas-liquid contactors.

![Figure 1. The structural formula of cellulose.](image)

The existing limited number of systems of direct cellulose solvents: DMAA / LiCl [14], NMP / LiCl [15], DMSO / paraformaldehyde [16], N-methylmorpholine-N-oxide (MMO) [17] makes it difficult to create cellulose-based membranes. In addition, most of these systems are characterized by high cost, toxicity and difficulty in solvent recovery. Therefore, in recent years, more and more attention has been attracted to the method of dissolving cellulose with ionic liquids (IL), considered and more environmentally friendly. To reduce the time, temperature and cost of dissolution, also co-solvents are added to the IL. There are works in which dimethylsulfoxide (DMSO) [10] or acetone [18] was used as co-solvent to form nanofiltration membranes from cellulose solutions in IL as a cosolvent, which made it possible to substantially reduce the viscosity of the molding mixture. Thus, the aim of this work is to produce cellulose membranes from a mixture of IL 1-ethyl-3-methylimidazolium acetate [Emim] OAc with DMSO for gas-liquid contactors.

2. Experimental part

2.1. Materials

Commercial cellophane film with thickness of 31 μm produced according to GOST (State Standard) 7730-89 were investigated. Cellulose (degree of polymerization, 600; moisture content in cellulose, no more than 8% (under equilibrium conditions); alpha-cellulose content, 92%) produced at Baikalsk Pulp and Paper Mill (Russia) was used. The [Emim]OAc IL with a density of 1.27 g/cm³ (Sigma-Aldrich) was used to dissolve cellulose. The chemical formula of this IL is shown in figure 2. В качестве сорасторителя использовался DMSO (Sigma-Aldrich) anhydrous ≥ 99,9%. As organic liquids, tetraethylene glycol dimethyl ether (Sigma-Aldrich, 99%) simulating the industrial absorbent Genosorb (dimethyl ether of polyethylene glycols) and hexane (Chimmed, chemically pure grade) used as a model of liquid hydrocarbons. In the work the following gasses were used for membrane(s)
permeability tests: Carbon Dioxide (CO₂) (99.8% purity) produced by MGPZ, Russia Methane (CH₄) (99.99% purity) produced by MGPZ, Russia.

![Structural formula of [Emim]OAc.](image)

**Figure 2.** Structural formula of [Emim]OAc.

### 2.2. Investigation of the permeance of liquids through cellulose membranes

The permeability of liquids through cellulose membranes were studied in dead-end cells equipped with a magnetic stirrer at a transmembrane pressure from 10 to 30 atm. The entire setup was made of stainless steel; rubber rings resistant to the studied solvents were used as sealing gaskets. The active membrane area in the cells was 33.2 cm². Helium generated pressure in the cell.

### 2.3. Sorption and swelling of dense cellulose membranes

To measure the degree of swelling, a sample of dense cellulose membrane was placed in an aprotic solvent for 24 h, with the geometrical dimensions and thickness of the sample being preliminarily measured. After soaking the sample in the solvent, its geometrical dimensions and thickness were measured as well. The degree of cellulose swelling in liquids, SD, was determined according to equation (1):

$$ S_D = \frac{d_1d_2l-d_{10}d_{20}l_0}{d_{10}d_{20}l_0} \cdot 100\% $$

where \(d_{10}, d_{20}, d_1,\) and \(d_2\) are the geometrical dimensions of the sample and \(l_0\) and \(l\) is the values of the sample thickness. Subscript 0 index refers to the dry sample. To determine sorption (S), a sample with the preliminarily measured mass (\(m_0\)) was placed into a solvent of interest for 24 h. After soaking, the excess solvent was removed from the sample surface with filter paper, and the mass of the swollen sample (\(m\)) was measured. The value of sorption was calculated as follows:

$$ S = \frac{m-m_0}{m_0} $$

### 2.4. Contact angle measurement

Contact angle values were measured by via the conventional sessile drop technique using the LK-1 goniometer. For image capture and digital processing of the drops images, DropShape software was used providing Laplace-Young contact angle calculation. Measurement error was 2. Experiments were carried out at room temperature (23 ± 2).

Membrane surface energy value was determined according to the Owens-Wendt interfacial interaction model. The relation between surface energy and equilibrium contact angle of the liquid phase placed onto solid phase is derived from the Fowkes equation [19]:

$$ \gamma = (1 + \cos \theta) = 2(\gamma_d \gamma_s)^{1/2} + 2(\gamma_p \gamma_s)^{1/2} $$

where \(d\) and \(p\) subscripts relate to the dispersive and polar components of the liquid surface energy \(\gamma\) and the membrane surface energy \(\gamma_s\).

Hexane and dimethylether tetraethylene glycol were used to measure the contact angle.

### 2.5. Gas permeance measurements

Permeability coefficients were determined using gas chromatographic method. The steady stream of a penetrant gas under atmospheric pressure flew around up-stream part of the film, while down-stream part of it was flown around by gas carrier—helium or nitrogen (the latter in measurement of permeation rate of CO₂ and CH₄). The permeability coefficients were determined by measuring the
penetrant concentration in the gas carrier and the total flow of this mixture. Partial pressure of the penetrants was 1 atm in up-stream part of the cell and close to zero in the down-stream part. Temperature in the cell was 20–22 °C. The study of gas-transport properties according to time-lag method was performed using precision TimeLag GKSS setup, equipped with a pressure sensor Baratron with sensitivity to 10−7 bar (MKS Instruments) at 30 °C [20, 21].

2.6. Cellulose dissolution in an IL–DMSO mixture

Before dissolution, cellulose was placed in an oven at a temperature of 80°C for 16 h. The dried cellulose powder was mixed with DMSO and then with [Emim]OAc in an 1 : 1; after that, the weighing bottle was further sealed with paraffin wax. Cellulose dissolution was conducted under constant stirring at a temperature of 80°C and 100°C. Solutions with a cellulose content of 16 and 25 wt % were prepared. The solution preparation time was 24 and 72 h depending on the concentration of cellulose in the solution.

2.7. Cellulose membrane synthesis procedure

A freshly prepared solution was cooled to room temperature and then cast onto a continuous polyimide support; after that, a membrane was formed using an HLCL-1000 laminator (ChemInstruments, United States) by passing the resulting structure through the nip between the laminator rolls heated to a temperature of 80°C; the nip was calibrated to a predetermined thickness of 70 μm. Distilled water was used as the coagulation bath. The resulting composite cellulose membrane was washed in water and then air-dried.

3. Results and discussion

3.1. Investigation of the permeance of liquids through cellulose membranes

At the first stage of the work, the stability of commercial cellulose-based membranes (cellophane-cellulose continuous films obtained by the "viscose" method) in hexane and tetraethylene glycol dimethyl ether was analyzed. The permeance of these organic solvents via cellophane was also studied (table 1).

| Liquid | \(m_0^*\) | \(m_1^{**}\) | Permeance, \(\text{m}^2/\text{h} \text{bar}\) |
|--------|---------|---------|-----------------|
| Hexane | 0.1712  | 0.1712  | 0               |
| T. glycol dimethyl ether | 0.1730 | 0.1730 | 0               |

\*mass of the initial dry cellulose sample;
\**mass of the dried cellulose sample after aging in model liquids;

It can be seen from Table 1 that the weight of dry cellulosic samples after their storage for 24 hours in hexane and tetramethylene glycol dimethyl ether did not change compared to the initial weight, which indicates the chemical stability (insolubility) of cellulose in the organic liquids under study. Also, during the experiment in the dead-end filtration cell, the permeability of the liquids under study was equal to zero. This may be due to the fact that the cellophane films are solid, that is, they have no pores through which the liquid could move through the pore-flow model.

3.2. Sorption and swelling of dense cellulose membranes

In order to analyze the interaction of cellulose membranes with hexane and tetraethylene glycol dimethyl ether, the sorption of these liquids in the membrane material was measured, and the degree of cellulose swelling in them (table 2).

| Liquid | \(m_0^*\) | \(m_1^{**}\) | Permeance, \(\text{m}^2/\text{h} \text{bar}\) |
|--------|---------|---------|-----------------|
| Hexane | 0.1712  | 0.1712  | 0               |
| T. glycol dimethyl ether | 0.1730 | 0.1730 | 0               |

\*mass of the initial dry cellulose sample;
\**mass of the dried cellulose sample after aging in model liquids;

3.2. Sorption and swelling of dense cellulose membranes

In order to analyze the interaction of cellulose membranes with hexane and tetraethylene glycol dimethyl ether, the sorption of these liquids in the membrane material was measured, and the degree of cellulose swelling in them (table 2).
Liquids $\delta$, MPa$^{1/2}$ $S$, g/g $S_D$, %

| Hexane  | 14.9 | 0.042 | 0.4 |
| Tetraethylene glycol dimethyl ether | 17.9 | 0.015 | 0.5 |

Experiments on the sorption and degree of swelling of cellulose membranes have shown that there is no interaction between the liquid and the membrane material, since the sorption values are much less than 1, and the degree of swelling of the liquids does not exceed 0.5%. This lack of interaction can be explained in terms of Hansen's solubility parameters $14.9$ and $17.9$ MPa$^{1/2}$, respectively [22].

$$\delta = \sqrt{\delta_D + \delta_P + \delta_{HB}}$$ (3)

where $\delta_D, \delta_P, \delta_{HB}$ – dispersion, polar and the component associated with hydrogen bonds, respectively, which enter into Hansen's solubility parameter. The organic solvents under study are aprotic (they are not hydrogen donors or acceptors) due to the absence of hydroxyl groups and hydrogen bonds, so contributions to the Hansen solubility parameter of the polar and hydrogen bond components are small, and in the Hexane case they are zero. In contrast, there are hydroxyl groups in the cellulose structure, due to which hydrogen bonds are formed, the energy of which is 17 - 34 kJ / mol [23]. In this regard, Hansen's solubility parameter of cellulose is 38 MPa$^{1/2}$, which is more than twice the parameters of the solubility of hexane and tetraethylene glycol dimethyl ether. Such a difference in the solubility parameters leads to a small affinity between the cellulose and the solvents under investigation, hence, to the absence of sorption of them in the membrane material [17].

Since the sorption of the investigated solvents is much less than one, respectively, the liquid can not move through the cellulose membrane by the "sorption-diffusion" mechanism, and the absence of swelling of the membrane material in them does not lead to the pore opening effect, which could collapse during the drying process. All this results in zero permeability of hexane and tetraethylene glycol dimethyl ether through cellophane.

3.3. Contact angle measurement

Below are pictures of drops of model solvents on the surface of cellophane (figure 3). Hexane and tetraethylene glycol dimethyl ether have a low surface tension, so these solvents spread over the cellophane surface, so the contact angle between the liquid and the surface of the cellulose membrane is low and eventually tends to zero (the liquid is completely spreading). The values shown in the figure are averaged over five repetitions. Despite the fact that the liquid spreads over the surface, there is no interaction between the membrane material and the solvents, since their sorption is minimal, and the cellulose swelling steppe in these liquids is zero.

![Hexane](image1.png) ![Tetraethylene glycol dimethyl ether](image2.png)

*Figure 3.* Images of drops of model liquids on the surface of a cellulose membrane.
Despite the fact that the liquid spreads over the surface, as has already been determined the interaction between the membrane material and solvents does not occur.

3.4. Gas permeance measurements
In addition to the permeance of the liquids under study, the permeance of CO\textsubscript{2} and CH\textsubscript{4} gases through cellophane was analyzed. Experiments have shown that these gases are not permeable to these gases, which also confirms the absence of pores in the cellophane continuous film.

Thus, it can be concluded that cellulose membranes have a great potential for use in gas-liquid contactors, since they are not permeable to hexane and tetraethylene glycol dimethyl ether. But unfortunately, due to lack of pores, cellophane is also impermeable in gases. Therefore, in order to successfully realize the CO\textsubscript{2} release from physical absorbents and stabilize the gas condensate, it is necessary to create a membrane whose pores will be small for the passage of the molecules of the liquids under study, but this pore size will be sufficient to ensure that the gases have high permeance.

3.5. Cellulose membrane synthesis procedure
Cellulose membranes with a cellulose content of 16\% and 25\% were formed to carry out the separation of gases from hexane and tetraethylene glycol dimethyl ether and analyzed from the viewpoint of the permeability of said solvents. Unfortunately, experiments have shown that the membranes obtained are permeable according to organic solvents, which indicates the presence of pores in the structure that were formed during phase inversion. To obtain a denser membrane during phase inversion, it is necessary to slow the exchange of solvent and nonsolvent. This can be done by increasing the concentration even more, by changing the temperature of the nonsolvent, etc.

4. Conclusions
In this paper, we analyzed the possibility of using cellulose membranes in gas-liquid contactors to separate CO\textsubscript{2} from physical absorbents and stabilize gas condensate. It was shown that a solid cellulose film "cellophane" is not impermeable to hexane and tetraethylene glycol dimethyl ether due to the absence of pores. It also has been found that these solvents are not adsorbed in the membrane, and the cellulose does not swell therein. This lack of interaction of the investigated organic solvents with the natural polymer was explained in terms of Hansen's solubility parameters, which in the case of hexane and tetraethylene glycol dimethyl ether are more than twofold less than of Hansen's solubility of cellulose.

The impermeability and lack of interaction of the solvents under investigation with cellulose membranes makes them promising as membranes for gas-liquid contactors. But in order to realize the process it is necessary to create a membrane structure whose pore size not going to have hexane and tetraethylene glycol dimethyl ether penetration, but the permeance of CO\textsubscript{2} and CH\textsubscript{4} will be high.

Acknowledgments
The reported study was funded by RFBR according to the research project № 18-38-00702 mol_a

5. References
[1] Klaassen R, Feron P H M, Jansen A E 2005 Chem. Eng. Res. Des 83 234.
[2] Drioli E, Criscuoli A, Curcio E, 2006 Mem. Sci. and Tech. 11 1.
[3] Yeon S.H, Lee K.S, Sea B, Park Y.I, Lee K.H, 2005 J. Membr. Sci. 257 (1-2) 156.
[4] Bazhenov S, Bakhtin D, Volkov A 2018 J. Membr. Sci. Res. doi: 10.22079/jmsr.2018.82177.1179
[5] Kohl A L, Nielsen R B, Gas 1997 Gulf Professional Publishing 1395.
[6] Volkov A V, Tsarkov S E, Goetheer E L V, Volkov V V 2015 Petr. Chem. 55(9) 716.
[7] Volkov A, Yushkin A, Grekhov A, Shutova A, Bazhenov S, Tsarkov S, Khotimsky V, Vlugt T J H, Volkov V 2013 J. Membr. Sci. 440 98.
[8] Baker M.N, - American waterworks assoc – Denver. – 1948.
[9] Li H J, Cao T M, Qin J J, Jie X M, Wang T H, Liu J H, Yuan Q, 2006 J. Membr. Sci. 279 328.
[10] Anokhina T S, Pleshivtseva T S, Ignatenko V Ya, Antonov S V, Volkov A V, 2017 *Petr. Chem.* 57(6) 477.

[11] Anokhina T S, Yushkin A A, Volkov V V, Antonov S V, Volkov A V 2015 *Physics Procedia* 72 171.

[12] Mao Z, Cao Y, Jie X, Kang G, Zhou M, Yuan Q, 2010 *Sep. Purif. Technol.* 72 28.

[13] Wu J, Yuan Q, 2002 *J. Membr. Sci.* 204 185.

[14] Williamson S L, Armentrou R S, Porter R S, McCormick C L 1998 *Macromolecules* 31 8134.

[15] Masson J F, Manley R St J 1991 *Macromolecules* 24 6670.

[16] Bang Y H, Lee S, Park J B, Cho H H 1999 *J. Appl. Polym. Sci.* 73 2681.

[17] Anokhina T S, Yushkin A A, Makarov I S, Ignatenko V Ya, Kostyuk A V, Antonov S V, Volkov A V 2016 *Petr. Chem.* 56(11) 1085.

[18] Sukma F M, Çulfaz-Emecn P Z 2018 *J. Membr. Sci.* 545 329.

[19] Ovcharova A A, Vasilevsky V P, Borisov I I, Bazhenov S D, Volkov A V, Bildyukevich AV, Volkov V V 2017 *Separation and Purification Technology* 183 162.

[20] Borisov I I, Akmalov T R, Ivanov A O, Volkov V V, Finkelshtein Eu Sh, Bermeshev M V 2016 *Mendelev Commun.* 26 124.

[21] Chapala P, Bermeshev M, Starannikova L, Borisov I, Shantarovich V, Lakhtin V, Volkov V, Finkelshtein Eu 2016 *Macromol. Chem. Phys.* 1

[22] Hansen Solubility Parameters: A User’s Handbook. P. 345-483

[23] Klemm, D, 1998. Comprehensive Cellulose Chemistry. Wiley-VCH, Weinheim, New York