On the Relationship between the Permeability Parameters of Gases and Vapors of C_1-C_4 Aliphatic Alcohols in Hydrophobic Polymeric Membranes

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Abstract: A correlation approach for the evaluation of permeability, diffusion and solubility coefficients of lower aliphatic alcohols in polymeric membranes using basic parameters of gas transfer is proposed in this work. Previously published results of experimental study of water, ethanol and n-butanol vapors transfer in hydrophobic membranes based on glassy polymers as well as obtained new experimental data on vapor permeability of methanol, n-propanol and gases were critically reviewed. An attempt to demonstrate correlation of selective gas and vapor transfer parameters of membranes is made in the present study. The establishment of correlation of permeability of gases and C_1-C_4 aliphatic alcohols vapors in hydrophobic polymeric membranes allows to use available methods and data of gas transfer characteristics of membrane materials and membranes for estimation of the vapor separation properties, *e.g.*, modern Data Base for gas permeability parameters of polymers can be used for evaluation of the membrane separation potential in relation to lower aliphatic alcohols. The hydrophobic polymers were selected in order to avoid specific interactions between alcohols and polymer (such as strong induction, dipole-dipole interactions and H-bond creation). Results include a preliminary estimation of diffusion coefficients of water and C_1-C_4 alcohols vapors on the basis of correlation analysis that was previously proposed for the estimation of gas transport parameters. The proposed approach allows to explain the observed characteristics of the mentioned vapors permeability in polymeric membranes and to show new relations of gases and vapors transfer in membranes. It seems that obtained results will be useful for the development of vapor-phase membrane methods of organic substances separation.

Keywords: Membrane vapor separation, Lower aliphatic alcohols, Gas separation polymeric membranes.

INTRODUCTION

Currently, much attention is paid to the processes of recovery and concentration of C_1-C_4 alcohols, namely, bioalcohols which are often produced in the form of diluted water-alcohol mixtures. One of the most important tasks in the area of bioalcohols production is their recovery directly during fermentation that simultaneously solves the problem of biological processes inhibition and increases productivity and yield. Gas stripping and pervaporation are the most suitable methods for this task since their application does not affect significantly the operation of bioreactor. The main activities in the field of pervaporation demonstrate energy-efficient separation of diluted water-alcohol mixtures by nonporous polymeric membranes due to the selective transfer of components by the solution-diffusion mechanism [1-12], concentration of alcohol occurs in permeate.

Recent views on the membrane vapor permeation (MVP) phenomena as the fundamental aspects as the application potential [13,14] demonstrate the importance and perspective development of inorganic and polymeric membranes for separation processes of gaseous mixtures containing condensable components. Nevertheless, historically the polymeric membranes were the first ones applied to pervaporation and vapor permeation processes. Both processes are operating under the gradient of the partial vapor pressure which in case of pervaporation is close to the saturation pressure.

To understand the practical potential of MVP the particular attention is put on fundamental aspects of separation: (1) the contribution of liquid/vapor phase transition and (2) vapor selective properties of hydrophobic membranes. Contribution (1) is based on knowledge of vapor-liquid equilibrium. Contribution (2) can be evaluated by correlation with gas transfer parameters of polymeric membranes.

However, despite the effectiveness of pervaporation separation, the application of this method for alcohols recovery from real fermentation broth is quite difficult due to fouling of membrane modules by the biomedium, as well as sorption in membrane selective layer of various low-volatile organic components presenting in fermentation mixtures that leads to significant losses of the process separation characteristics. Vapor-phase membrane separation is proposed as alternative method for the recovery of

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bioalcohols [15]. This method is based on combination of stripping of the initial solution by a carrier gas and further membrane separation of the resulting vapor-gas mixture. Membrane vapor-phase method allows to apply as alcohol-selective (organophilic) as water-selective membranes for separation and concentration of alcohols from dilute aqueous solutions without the need of evaporation of bulk water [16]. This is possible due to the fact that diluted alcohol-water systems demonstrate significant positive deviation from Raoult's law (equilibrium alcohol content in the vapor phase is significantly higher than that in the original liquid phase). Thus, alcohol vapors concentration in the vapor phase becomes comparable with water vapors concentration, therefore, alcohol concentration over the membrane by water vapors removing with water-selective membrane would also be beneficial. Sufficiently large number of papers since the 80s of the last century are devoted to investigation of pervaporation properties of polymeric membranes (*e.g.*, [1, 6, 7, 11, 12]), these papers have accumulated knowledge in the field of application of membranes in pervaporation. However, this area of research still stands separately and does not demonstrate linkages with selective gas transfer in non-porous polymeric media, despite the fact that transport of vapors also occurs by solution-diffusion mechanism. Large amount of data was obtained for non-porous polymeric gas separation membranes and membrane materials and several approaches have been proposed for the general evaluation and selection of membrane materials for target practical gas separation applications [17-24]. The establishment of correlation of permeability of gases and C₁-C₄ aliphatic alcohols vapors in hydrophobic polymeric membranes will allow to use available methods and data of gas transfer characteristics of membrane materials and membranes in the area of vapor separation. It means that modern Data Base [24] for gas permeability parameters of polymers can be used for evaluation of the membrane separation potential in relation to lower aliphatic alcohols.

An attempt to demonstrate correlation of selective gas and vapor transfer parameters of membranes is made in the present study. For this purpose hydrophobic polymeric membranes with known (or experimentally measured) permeability are selected as objects of study. In addition, the analysis of water and alcohols vapors transfer by solution-diffusion mechanism (as for gases) involves the assessment of both kinetic component of selective transport (diffusion coefficient D) and the thermodynamic component (solubility coefficient S), which are well known for gases [*e.g.*, 16, 22].

The results include a preliminary estimation of diffusion coefficients of water and C₁-C₄ alcohols vapors on the basis of correlation analysis, which was previously proposed for the transport of gases [22]. The proposed approach allows to explain the observed characteristics of studied vapors permeability in polymeric membranes. It seems that the obtained results will be useful for the development of vapor-phase membrane methods for separation of organic substances.

Materials, Methods of Measurement and Calculation

Membranes based on poly(1-trimethylsilyl-1-propyne) (PTMSP), poly-4-methyl-1-pentine (PMP) and polyvinyltrimethylsilane (PVTMS) were selected for the study. All studied membranes are hydrophobic: industrial asymmetric membrane based on PVTMS (production of Kuskovsky chemical plant, Moscow, Russia) with selective layer thickness of 0.2 μm and porous support thickness of 200-250 μm; laboratory PTMSP-based membrane (homogeneous film) with thickness 30 μm; laboratory PMP-based membrane (homogeneous film) with thickness 32 μm [13]. Conditions of synthesis of PTMSP and PMP polymers and main physical and chemical properties of PVTMS, PTMSP and PMP including hydrophobicity are described in [13, 25-27]. Vapor transfer of water, methanol, ethanol, n-propanol and n-butanol was investigated. Basic physical and chemical properties of alcohols and water are presented in Table **1**. Method of the vapor permeability experimental measurement is described in [13, 14].

Liquid-to-vapor phase transition in case of diluted water-alcohol mixtures leads to significant change of the vapor phase composition compared to liquid phase, in order to determine the permeability and selectivity of membrane the additional information about vapor-liquid equilibrium is needed for calculation of the driving force of each component transfer:

$$Q_i = \frac{J_i}{A\left(p_i - p_i'\right)} \tag{1}$$

$$\alpha_{i/j} = \frac{Q_i}{Q_j} \tag{2}$$

where *Q* is the permeability of membrane, *J* is the vapor volumetric (reduced to STP as it is traditionally used for gases) or molar flow rate of component, *A* is membrane area, p_i and p_i' are partial pressures of the

Table 1: The Physical-Chemical Properties of Alcohols and Water

Liquid	Boiling point, °C	Density, g/cm^3 [28]	Molecular weight, g/mol	Molecular volume, Å^3	Kinetic diameter, nm [29,30]	Solubility parameter, (J/cm^3)$^{1/2}$ [30, 31]
n-BuOH	117.8	0.810	74.1	151.8	0.505	23.1
n-PrOH	97.2	0.803	60.1	124.1	0.469	24.5
EtOH	78.3	0.789	46.1	96.8	0.430	26.5
MeOH	64.7	0.792	32.0	67.1	0.380	29.6
Water	100.0	1	18.0	29.9	0.296	47.8

component over and under membrane, respectively, $\alpha_{i/j}$ is ideal selectivity of membrane.If thickness of membrane selective layer is known it is possible to determine the vapor permeability coefficient of the membrane material for each component:

$$P_i = Q_i h \qquad (3)$$

where P is the vapor permeability coefficient of the membrane, h is the thickness of the selective layer of the membrane.

Permeability coefficient of vapor, as permeability coefficient of gas, can be considered as the product of diffusion and solubility coefficients:

$$P_i = D_i S_i \qquad (4)$$

where D is diffusion coefficient, S is solubility coefficient.

The ideal selectivity of the membrane can also be expressed through the respective components:

$$\alpha_{i/j} = \frac{P_i}{P_j} = \frac{D_i S_i}{D_j S_j} = \alpha_D \alpha_S \qquad (5)$$

where α_D is diffusion selectivity that is related to the characteristic size of diffusing molecules, α_S is selectivity of solubility or thermodynamic selectivity, associated with a boiling point (or critical temperatures) of components. In the absence of specific interactions, typically $\alpha_D > 1$ for smaller molecules relatively to large ones (for example, water/alcohols), while $\alpha_S < 1$ in this case. As a result, depending on the diffusion and thermodynamic contributions hydrophobic membranes can be water-selective or alcohol-selective.

Vapors unlike gases are easily condensable components, therefore, the diffusion of vapors through nonporous polymeric membranes may occur with specific interactions of components with membrane material (non-linearity of the sorption isotherms, plasticization, swelling), as well as among themselves (for example, formation of associates). Therefore, diffusion and solubility coefficients in the case of condensable components transfer, as a rule, are not constant values and are functions of components concentrations. Permeability and selectivity of membrane may depend on the process conditions and composition of mixture. If such dependence presents, it is the more stronger, the more higher the activity of vapors.

Since water-alcohol mixtures separation by vapor-phase membrane method is two-stage process, involving liquid-to-vapor phase transition and membrane separation, the separation factor consists of two components:

$$\alpha' = \alpha'_{PT} \alpha'_M \qquad (7)$$

where α' is the overall separation factor, α'_{PT} is the separation factor of phase transition, α'_M is the separation factor of membrane [13]. Thus, only in the case of considering the phase transition contribution one can get an objective assessment of the separation characteristics of the membrane and its contribution to the separation process.

Correlation Analysis of Gases and Vapors Transfer Parameters in Polymers

By now, transport parameters mainly of permanent gases (permeability P, diffusion D and solubility S coefficients and corresponding temperature characteristics E_P, E_D, ΔH_S) are known for more than 2000 polymers. Analysis of experimental data shows the existence of the upper limit of the dependency of separation selectivity for gas pairs such as O_2/N_2, CO_2/CH_4, H_2/N_2, He/N_2, H_2/CH_4, He/CH_4, He/H_2, H_2/CO_2 and He/CO_2 in the coordinates $\ln(P_i/P_j)=f(\ln P_i)$ (Robeson's diagram) [32, 33]. 3D correlations, *e.g.*, in the coordinates $\ln(P_i/P_j)=f(\ln(P_i/P_k), \ln P_k)$ are

considered as well [23]. Unfortunately, the data of vapors permeability in polymers are represented in the literature quite poor, moreover, existing values are obtained under different experimental conditions that does not allow using of available data for systematic consideration of vapor transfer parameters (permeability, diffusion and solubility coefficients). However, well-known correlations of membrane transfer and separation characteristics that have been found for gases can be used for vapors as well. For this purpose it is necessary to have data for gases and vapors permeability (diffusion, solubility) measured in the same conditions and similar samples. Unfortunately, such kind of studies have not been carried out by now. Data of inert gases and alcohols vapors diffusion in polyvinyl chloride (PVC) [34], presented in [15], seem to be the most relevant to the theme of this work.

These unique data allow to use the results of studies [22, 23], where statistically reasonable correlation equation is proposed based on comparative analysis of inert (He, Ne, Ar, Kr, Xe,[222]Rn) and permanent gases diffusion through a large number of polymers:

$$\lg D_i = K_1 - K_2 d_{efi}^2 \qquad (8)$$

where K_1 and K_2 are isothermal constant coefficients, individual for each homopolymer; d_{ef} is the characteristic diameter of gas molecules which is effective in the diffusion process. The effective cross-section d_{ef}^2 of the diffusing molecule is expressed from its characteristic diameter, it is permanent for each gaseous molecule (atom) and independent on the nature of polymeric material. It is noteworthy that correlations include noble gases with atomic masses from 4 to 222 a.u., therefore these correlations might be suitable for a great number of low molecular weight substances including water and C₁-C₄ alcohols molecules in case of specific interactions absence. Selectivity of diffusion is determined by the magnitude of K_2 and agrees qualitatively with the change of the cohesion energy density of the polymer [23]. It is also important to note that the activation energy of gases diffusion E_D is proportional to the specified effective molecular cross-sections mentioned above.

The published data [15, 34] were analyzed in the frames of correlation approach (equation (8)) [22] for the diffusion of gases in glassy PVC (the respective regression is shown in Figure **1**), that allowed to determine coefficients K_1 and K_2 in correlation equation 8 for PVC (K_1 = -3.7492, K_2 = 0.5602). The effective

diffusion diameters of molecules [34] were calculated (Table **2**) on the basis of obtained correlation coefficients and known experimental data of water and lower alcohols (C₁-C₄) vapors diffusion in PVC.
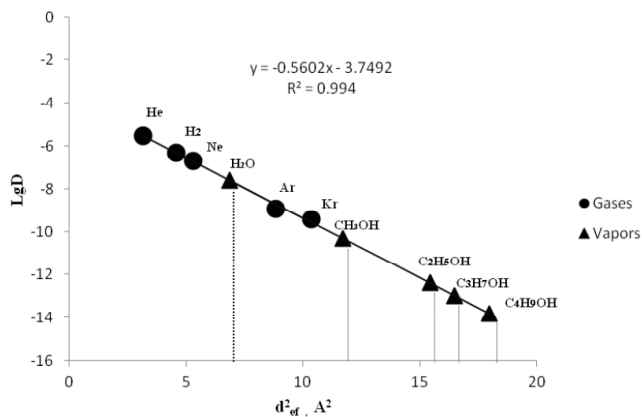

Figure 1: The dependence of diffusion coefficient logarithm in PVC on diffusing molecule effective cross-section: ● – gases ▲ – water and lower alcohols vapors (experimental data [34], methodology [22]).

Calculated effective diameters are represented in Table **2**. These diameters and values of K_1 and K_2 correlation coefficients obtained earlier for PTMSP and PVTMS in [22] using gas transfer data were substituted in equation (8) in order to evaluate diffusion coefficients of water and C₁-C₄ alcohols vapors in these glassy polymers for the first time (Table **3**).

Table **3** shows that difference of C₁-C₄ alcohols diffusion coefficients reach approximately two decimal orders of magnitude in PVTMS and one decimal order of magnitude in PTMSP. As a result diffusion selectivity (α_D) in PVTMS significantly exceeds the one in PTMSP and its contribution can control vapor separation properties of the polymer.

Currently, polymers for vapor separation, especially for water/alcohol mixtures separation, are studied as a rule in the form of membranes with thin selective layers that makes difficult the determination of diffusion coefficients (time-lags are too short), therefore correlation analysis in the frames of equation (8) is not possible. However, the analysis can be performed by using only values of experimental gas and vapor permeability.

A quantitative correlation of solubility coefficient of gases as function of $(\varepsilon/k)_{ef}$ was proposed for a number of homopolymers in [22]:

$$\lg S_i = K_3 + K_4 (\varepsilon/k)_{efi} \qquad (9)$$

Table 2:   Evaluation of Effective Diameters of Water and C_1-C_4 Alcohols Molecules in PVC [15, 22, 23, 34]

Gas	Diffusion Coefficient lg(D[cm^2/s])	Effective Diameter of Molecule, Å	Vapor	Diffusion Coefficient, lg(D[cm^2/s])	Effective Diameter of Molecule, Å
He	-5.5	1.78	H_2O	-7.6	2.62
H_2	-6.3	2.14	CH_3OH	-10.3	3.42
Ne	-6.7	2.30	C_2H_5OH	-12.4	3.93
Ar	-8.9	2.97	n-C_3H_7OH	-13.0	4.06
Kr	-9.4	3.22	n-C_4H_9OH	-13.8	4.24

Table 3:   Estimation of Diffusion Coefficients of Water and C_1-C_4 Alcohols Vapors in PVTMS and PTMSP at 25 °C

Polymer	K_1^*	K_2^*	D(H_2O), cm^2/s	D(CH_3OH), cm^2/s	D(C_2H_5OH), cm^2/s	D(C_3H_7OH), cm^2/s	D(C_4H_9OH), cm^2/s
PVTMS	-7.770	0.765	$2.2\cdot10^{-6}$	$5.5\cdot10^{-8}$	$3.1\cdot10^{-9}$	$1.4\cdot10^{-9}$	$4.5\cdot10^{-10}$
PTMSP	-7.260	0.374	$5.4\cdot10^{-5}$	$8.9\cdot10^{-6}$	$2.2\cdot10^{-6}$	$1.5\cdot10^{-6}$	$8.5\cdot10^{-7}$

* The values of correlation coefficients were taken from [22]

where K_3 and K_4 are isothermally permanent coefficients, individual for each homopolymer, $(\varepsilon / k)_{efi}$ is the characteristic value of the force constant of the Lennard-Jones potential. Values of the solubility coefficients of a large number of gases in homopolymers were calculated using equation (9) [22-24]. The sum of equations (8) and (9) gives the general expression for the permeability coefficient:

$$\lg P_i = \lg D_i + \lg S_i = K_1 - K_2 d_{efi}^2 + K_3 + K_4(\varepsilon / k)_{efi} \qquad (10)$$

Equation (10) takes into account the correlation of gas transfer parameters with the properties of diffusing molecules (d_{efi}^2, $(\varepsilon / k)_{efi}$) and the nature of the polymer matrix (fixed K_1, K_2, K_3, K_4 coefficients for a given polymeric material).

The method is quite versatile in itself since for its application it is enough to know permeability coefficients of several gases through the polymer to be able to predict desired permeability coefficients of other gases. The limitation of the method is the need of experimental data of permeability for several (at least three) gases in a new (not previously studied) polymer. Actually, this limitation is applicable to water and C_1-C_4 alcohols vapors as well.

Unfortunately, data on gases and vapors solubility in polymers obtained under comparable conditions are almost not represented in literature. Evaluation of the permeability of water and alcohols vapors on the basis of data on gas permeability by using equation (10) is difficult to carry out. However, only data on permeability of gases and vapors in polymeric membranes

published in [13, 14, 22, 23] and obtained in the course of this work can be used for determination of force constant of the Lennard-Jones potential $(\varepsilon / k)_{efi}$ for the vapors, using the system of equations (11), when the thickness of selective membrane layer is known:

$$\ln P_1 = (K_1 + K_3) - K_2 d_1^2 + K_4(\varepsilon_1 / k),$$
$$\ln P_2 = (K_1 + K_3) - K_2 d_2^2 + K_4(\varepsilon_2 / k),$$
$$\text{..} \qquad (11)$$
$$\ln P_i = (K_1 + K_3) - K_2 d_i^2 + K_4(\varepsilon_i / k)$$

when the thickness of the selective layer of the membranes is unknown the system of equations (12) can be used:

$$\ln Q_1 = (K'_1 + K'_3) - K'_2 d_1^2 + K'_4(\varepsilon_1 / k),$$
$$\ln Q_2 = (K'_1 + K'_3) - K'_2 d_2^2 + K'_4(\varepsilon_2 / k),$$
$$\text{..} \qquad (12)$$
$$\ln Q_i = (K'_1 + K'_3) - K'_2 d_i^2 + K'_4(\varepsilon_i / k)$$

where $P_{1..i}$ are values of the permeability coefficients of gas or vapor in polymer; $Q_{1..i}$ are values of the gas or vapor permeability of membrane.

It seems that characteristic correlations developed for gas transfer in polymeric media can be applied for evaluation of vapors transfer as well. For this purpose it is necessary to know (or to measure experimentally) under isothermal conditions the permeability of certain gases and alcohols vapors (at least 3 variants) which values of d_{efi}^2 are known for. Solving systems of linear equations (11) or (12) allows to determine values of $(K'_1+K'_3)$, K'_2 and K'_4 under isothermal conditions of the

experiment and, as a result, to calculate $(\varepsilon / k)_{efi}$ of the vapors studied.

This approach is tested with commercial membranes based on PVTMS. Gas, water and C$_1$-C$_4$ alcohols vapors permeability and calculated values of the force constant of Lennard-Jones potential for the investigated alcohols are shown in Table **4**.

Table 4:   The Permeability of Gases and Vapors Through PVTMS Membrane at 50 °C

Penertant[1]	Permeability, L(STP)/(m^2·h·atm)	d_{ef} , Å	$(\varepsilon / k)_{ef}$, °K
He	2300	1.78	9.5
O$_2$	560	2.89	112.7
N$_2$	220	3.04	83
CH$_4$	560	3.18	154.7
C$_3$H$_8$	115	4.09	305
C$_4$H$_{10}$	70	4.4	364
H$_2$O	10400	2.62	248*
CH$_3$OH	3100	3.42	341*
C$_2$H$_5$OH	930	3.93	397*
n-C$_3$H$_7$OH	670	4.06	414*
n-C$_4$H$_9$OH	1600	4.24	520*

[1]Data [14, 24] and the present study; the values of gases permeability extrapolated to 50 °C for the temperature characteristics of [22]; data for alcohols [14] and the present study.
* - Calculated values

For commercial PVTMS membrane it was obtained: $K'_1+K'_3$ = 9.1841; K'_2 = 0.5558; K'_4 = 0.0157

Similarly, values of the force constant of the Lennard-Jones potential of water, ethanol and n-butanol molecules using the parameters of the gas and vapor permeability were estimated for other hydrophobic glassy polymers. Experimental data of the present study (permeability of gases in PTMSP) and published data of lower hydrocarbons permeability in PMP [26, 27] were used for this purpose. Data of alcohols permeability in PTMSP and PMP were taken from [35], obtained results are shown in Table **5**.

It is important to note that results represented in Tables **2-5** are preliminary and show probable correlation of gas and vapor permeability parameters. Systematic study of possibility of application of the proposed approach requires the accumulation of a rather large array of experimental data of transfer of gases and vapors in polymeric membranes under the similar conditions in order to obtain statistically valid values for the correlation equations. It should be particularly noted that for the vapors it is important to carry out experiments with taking into account variation of activities and possible concentration dependencies of the permeation parameters. However, even the first approximation gives important information about vapor transfer in membranes. Tables **6** and **7** represents experimental data of water and alcohols vapors permeability in PTMSP and PMP, demonstrating various levels of selectivity. It can be noted that data obtained for membranes based on hydrophobic glassy polymers are divided into three groups: (1) butanol-selective properties of membranes based on PTMSP and PMP; (2) practically non-selective properties of membranes based on PTMSP and PMP for the pair ethanol-water and (3) water-selective properties of membranes based PVTMS in both cases. To explain this fact as a first approximation we can consider diffusion coefficients of water, ethanol and butanol vapors in the polymers, obtained using the proposed correlation approach.

Table 5:   Evaluation of the Force Constant Lennard-Jones Potential of Water, Ethanol and Butanol Molecules

Polymer	$K'_1+K'_3$	K'_2	K'_4	ε/k (H$_2$O) °K	ε/k (C$_2$H$_5$OH) °K	ε/k (C$_4$H$_9$OH) °K
PTMSP	9.0589	0.1712	0.0137	213	362	439
PMP	8.2666	0.3097	0.0168	199	380	509

Table 6:   Vapor Transfer Parameters for Individual Components Through PTMSP Membrane at 50 °C [35]

Penetrant	Flux, kg/(m^2·h)	Permeability, L(STP)/(m^2·h·atm)	Permeability Coefficient, Barrer (10^{-10} cm^3·cm/(cm^2·s·cmHg))	Alcohol/Water Ideal Selectivity
H$_2$O	0.183	2700	30000	-
C$_2$H$_5$OH	1.343	2900	32000	1.1
n-C$_4$H$_9$OH	0.293	6100	67000	2.2

Table 7:   Vapor Transfer Parameters for Individual Components Through PMP Membrane at 50 °C [35]

Penetrant	Flux, kg/(m^2·h)	Permeability, L(STP)/(m^2·h·atm)	Permeability Coefficient, Barrer (10^{-10} cm^3·cm/(cm^2·s·cmHg))	Alcohol/Water Ideal Selectivity
H_2O	0.069	1000	12000	-
C_2H_5OH	0.431	1000	12000	1.0
n-C_4H_9OH	0.184	4200	50000	4.2

Accordingly to Table **3** for the water-ethanol system α_D for PVTMS is approximately 700, for PTMSP is approximately 25; for the system water-butanol α_D for PVTMS is approximately 4900, for PTMSP is approximately 64. Considering that the solubility of the components in the polymers increases from water to ethanol to butanol and solubility selectivity of vapors is almost similar (values of correlation coefficients K'_4 are 0.0157 for PVTMS, 0.0137 for PTMSP, 0.0168 for PMP), it can be concluded that for PVTMS diffusion selectivity of water for both systems (water-ethanol and water-butanol) is dominated, for PTMSP and PMP the solubility selectivity provides significant contribution for the system water-butanol.

Thus, the proposed approach unites the correlations of gas and vapor transfer that can be useful for the preliminary selection of polymeric membranes for application in gas-vapor and vapor mixtures separation. From the fundamental point of view proposed approach can also be applied for explanation of the observed features of water and C_1-C_4 aliphatic alcohols vapors transfer in polymeric membranes.

CONCLUSION

A comparison of gas and vapor (water and C_1-C_4 aliphatic alcohols) transfer through polymeric membranes shows the existence of correlations between parameters of gas and vapor transport characteristics in accordance with solution-diffusion mechanism. The possibility of application of gas transfer correlation coefficients for evaluation of water and C_1-C_4 aliphatic alcohols vapors transfer parameters in polymeric membranes was demonstrated. Obtained data for considered membranes based on hydrophobic glassy polymers are divided into three groups: (1) butanol-selective properties of membranes based on PTMSP and PMP, (2) almost non-selective properties of membranes based on PTMSP and PMP for the pair ethanol-water and (3) water-selective properties of membranes based PVTMS in both cases. The estimation of diffusion coefficients values of water, ethanol and n-butanol vapors in these polymers showed that for PVTMS diffusion selectivity of water for systems water-ethanol and water-butanol is dominated,

for PTMSP and PMP the solubility selectivity provides significant contribution for system water/butanol.

The proposed approach allows to explain observed characteristics of studied vapors permeability in polymeric membranes. It seems that obtained results can be useful for the development of vapor-phase membrane methods of separation of organic substances.

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REFERENCES

[1]   Vane LM. A review of pervaporation for product recovery from biomass fermentation processes. Chem Technol Biotechnol 2005; 80: 603-629.
http://dx.doi.org/10.1002/jctb.1265

[2]   Vane LM. Separation technologies for the recovery and dehydration of alcohols from fermentation broths. Biofuels Bioprod Bioref 2008; 2: 553-588.
http://dx.doi.org/10.1002/bbb.108

[3]   Kazuhiko Z, Nagase Yu, Matsui K. Pervaporation of alcohol/water mixtures through poly[l-(trimethylsily1)-1-propyne] membrane. Makromol Chem Rapid Commun 1986; 7: 43-46.
http://dx.doi.org/10.1002/marc.1986.030070201

[4]   Wang Ya, Goh SH, Chung TS, Na P. Polyamide-imide/polyetherimide dual-layer hollow fiber membranes for pervaporation dehydration of C1–C4 alcohols. J Membr Sci 2009; 326: 222-233.
http://dx.doi.org/10.1016/j.memsci.2008.10.005

[5]   Huang RYM, Jarvis NR. Separation of liquid mixtures by using polymer membranes. II. Permeation of aqueous alcohol solutions through cellophane and poly(vinyl alcohol). J Appl Polym Sci 1970; 14: 2341.
http://dx.doi.org/10.1002/app.1970.070140914

[6]   Volkov VV, Separation of liquids by pervaporation through polymeric membranes. Russian Chemical Bulletin 1994; 43: 187-197.
http://dx.doi.org/10.1007/BF00695808

[7]   Semenova S, Haruhiko O, Soontarapa K. Hydrophilic membranes for pervaporation: An analytical review. Desalination 1997; 110: 251-286.
http://dx.doi.org/10.1016/S0011-9164(97)00103-3

[8]   Fadeev AG. Extraction of butanol from aqueous solutions by pervaporation through poly(1-trimethylsilyl-1-propyne). J Membr Sci 2001; 186: 205-217.
http://dx.doi.org/10.1016/S0376-7388(00)00683-9

[9]   Fadeev AG, Selinskaya YaA, Kelley SS, Meagher MM, Litvinova EG, Khotimsky VS, Volkov VV. Extraction of butanol from aqueous solutions by pervaporation through

poly(1-trimethylsilyl-1-propyne). J Membr Sci 2001; 186: 205-217.
http://dx.doi.org/10.1016/S0376-7388(00)00683-9

[10] Volkov VV, Fadeev AG, Litvinova EG, McMillan JD, Kelley SS. Effects of synthesis conditions on the pervaporation properties of poly[1-(trimethylsilyl)-1-propyne] useful for membrane bioreactors. Appl Polym Sci 2004; 91: 2271-2277.
http://dx.doi.org/10.1002/app.13358

[11] Vane LM. Pervaporation and Vapor Permeation Tutorial: Membrane Processes for the Selective Separation of Liquid and Vapor Mixtures. Sep Sci Technol 2013; 48: 429-437.
http://dx.doi.org/10.1080/01496395.2012.725792

[12] Sosa MA, Paredes DA, Basilico JC, Bruggen BV, Espinosa J. Screening of pervaporation membranes with the aid of conceptual models: An application to bioethanol production. Sep Purif Technol 2015; 146: 326-341.
http://dx.doi.org/10.1016/j.seppur.2015.04.001

[13] Baker RW. Membrane technology and application. 2nd ed. California, USA: John Wiley &Sons Ltd 2004; 538.
http://dx.doi.org/10.1002/0470020393

[14] Yampolskii Y, Pinnau I, Freeman B. Materials Science of Membranes for Gas and Vapor Separation. John Wiley & Sons Ltd The Atrium Southern Gate Chichester England 2006; 437.

[15] Yakovlev AV, Shalygin MG, Matson SM, Khotimskiy VS, Teplyakov VV. Separation of diluted butanol-water solutions via vapor phase by organophilic membranes based on high permeable polyacetylenes. J Membr Sci 2013; 434: 99-105.
http://dx.doi.org/10.1016/j.memsci.2013.01.061

[16] Basile A, Figoli A, Khayet M, Eds. Pervaporation, Vapour Permeation and Membrane Distillation. Principles and Applications. Woodhead Publishing Series in Energy 2015.

[17] Stern SA, Mi Y, Yamamoto H. Structure/permeability relationships of polyimide membranes. Applications to the separation of gas mixtures. J Polym Sci Part B Polym Phys Ed 1989; 27: 1887-1909.
http://dx.doi.org/10.1002/polb.1989.090270908

[18] Schultz J, Pienemann KV. Membranes for separation of higher hydrocarbons from methane. J Membr Sci 1996; 110: 37-45.
http://dx.doi.org/10.1016/0376-7388(95)00214-6

[19] Robeson DR, Smith CD, Langsam MA. Group contribution approach to predict permeability and permselectivity of aromatic polymers. J Membr Sci 1997; 132: 33-54.
http://dx.doi.org/10.1016/S0376-7388(97)00031-8

[20] Mulder M. Basic Principles of Membrane Technology, 2nd edition. Dordrecht Kluwer academic publishers 1996; 564: 110-119.
http://dx.doi.org/10.1007/978-94-009-1766-8

[21] Park JY, Paul DR. Correlation and prediction of gas permeability in glassy polymer membrane materials via a modified free volume based group contribution method. J Membr Sci 1997; 125: 23-39.
http://dx.doi.org/10.1016/S0376-7388(96)00061-0

[22] Teplyakov VV, Meares P. Correlation aspects of the selective gas permeabilities of polymeric materials and membranes. Gas Sep Purif 1990; 4: 68-72.
http://dx.doi.org/10.1016/0950-4214(90)80030-O

[23] Malykh OV, Golub AYu, Teplyakov VV. New aspects of empirical approaches to prediction of gas permeability parameters in relation to permanent gases linear lower hydrocarbons and some toxic gases. Advances in Colloid and Interface Science 2011; 164: 89-99.
http://dx.doi.org/10.1016/j.cis.2010.10.004

[24] Teplyakov VV, Malykh OV, Amosova OL, Golub AYu, Yastrebov RA. Functional Database for the permeability of permanent and acid gases, lower hydrocarbons and toxic gaseous species through polymer materials and membranes with the function of estimating of values for which data are missing». Certificate № 2011620549 / 28.07.2011.

[25] Yushkin A, Grekhov A, Matson S, Bermeshev M, Khotimsky V, Finkelstein E, Budd P, Volkov V, Vlugt TJH, Volkov A. Study of glassy polymers fractional accessible volume (FAV) by extended method of hydrostatic weighing: Effect of porous structure on liquid transport. React Func Polym 2015; 86: 269-281.
http://dx.doi.org/10.1016/j.reactfunctpolym.2014.06.010

[26] Matson SM, Rätzke K, Shaikh MQ, Litvinova EG, Shishatskiy SM, Peinemann KV, Khotimskiy VS. Macrochain configuration, structure of free volume and transport properties of poly(1-trimethylsilyl-1-propyne) and poly(1-trimethylgermyl-1-propyne) . Polym Sci 2012; 54: 671-677.

[27] Sultanov EY, Ezhov AA, Shishatskiy SM, Buhr K, Khotimskiy VS. Synthesis, characterization, and properties of poly(1-trimethylsilyl-1-propyne)-block-poly(4-methyl-2-pentyne) block copolymers. Macromolecules 2012; 45: 1222-1229.
http://dx.doi.org/10.1021/ma202140c

[28] Qiao X, Chung TS, Guo WF, Matsuura T, Teoh MM. Dehydration of isopropanol and its comparison with dehydration of butanol isomers from thermodynamic and molecular aspects. J Membr Sci 2005; 252: 37-49.
http://dx.doi.org/10.1016/j.memsci.2004.11.014

[29] Wijmans JG. Process performance = membrane properties + operating conditions. J Membr Sci 2003; 220: 1-3.
http://dx.doi.org/10.1016/S0376-7388(03)00221-7

[30] Huang RYM, Jarvis NR. Separation of liquid mixtures by using polymer membranes. II. Permeation of aqueous alcohol solutions through cellophane and poly(vinyl alcohol). J Appl Polym Sci 1970; 14: 2341-2356.
http://dx.doi.org/10.1002/app.1970.070140914

[31] Leeuwen ME. Derivation of Stockmayer potential parameters for polar fluids. Fluid Phase Equlibr 1994; 99: 1-18.
http://dx.doi.org/10.1016/0378-3812(94)80018-9

[32] Freeman BD. Basis of permeability/selectivity tradeoff relations in polymeric gas separation membranes. Macromolecules 1999; 32: 375-380.
http://dx.doi.org/10.1021/ma9814548

[33] Robeson L.M. Correlation of separation factor versus permeability for polymeric membranes. J Membr Sci 1991; 62: 165-185.
http://dx.doi.org/10.1016/0376-7388(91)80060-J

[34] Gruen F, Diffusionmessungen an Kautschuk (Diffusion in Rubber), Experimenta 3, 490 (1947).
http://dx.doi.org/10.1007/BF02154561

[35] Shalygin MG, Kozlova AA, Teplyakov VV. Membrane vapor-phase concentrating of bioethanol and biobutanol with the use of hydrophobic membranes based on glassy polymers, Membrany i Membrannaia Technologia. 2016; 6:3, 313-321, DOI 10.1134/S221811721603010X (In Russian)