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## ELECTROMEMBRANE RECYCLING OF LIQUID WASTES OF DAIRY INDUSTRY USING ORGANIC-INORGANIC MEMBRANES

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Organic-inorganic membranes were obtained by the modification of heterogeneous cation and anion exchange polymer substrates with zirconium hydrophosphate and hydrated zirconium dioxide, respectively, the modifier content was 3.5 to 4.3% wt. The inorganic modifiers were found to be mainly in a form of single nanoparticles and their aggregates (up to 500 nm). The effect of the modifiers on the porous structure of the membranes was investigated using the data of standard contact porosimetry. Aggregated nanoparticles are a barrier against additionally sorbed electrolyte improving migration flux of counter-ions through the membranes and minimizing concentration polarization when the current is lower than its limiting value. This allows us to avoid the precipitation of insoluble compounds directly inside membranes. The electro-dialytic desalination of milky whey was investigated; both pristine and organic-inorganic membranes were applied. The composites provide preferable removal of hardness and phosphorus-containing ions from whey; moreover, a higher desalination degree is reached. The current efficiency for inorganic ions reaches 89% under the optimal operation conditions which involve particularly a contact of one side of the organic-inorganic membrane with acidic solution.

**Keywords:** electro-dialysis, organic-inorganic membranes, milky whey, desalination, standard contact porosimetry.

### **Introduction**

Membrane separation (mainly baromembrane processes) is widely used in food industry, particularly for recovery of valuable components from corn distillery [1] or milky whey [2]. However, manufacture of some products from whey, such as protein supplements or infant formula, requires removal of mineral components from the concentrate. Desalination is especially important for baby food, in which the salt content is strictly controlled at the legislative level [3]. Since the amount of mineral components in milky whey is rather high (the order is 1 g·dm<sup>-3</sup>), electro-dialysis (ED) is much more attractive for desalination in a comparison with adsorption and ion exchange techniques [4].

Nowaday dairy industry processes about 3 million tons of way with ED involving 25 000 m<sup>2</sup> installed membranes [5]. The electromembrane technique allows one to recycle not only whey, but also both permeate and concentrate after its baromembrane separation [6]. The method is used for regulation of whey acidity in order to support a growth media for certain bacteria [7], for separation of acid and basic bioactive peptides [8].

A problem of ED is fouling of polymer membranes by organic and inorganic matters [9]. However, polymer material containing intraporous active layer of inorganic ion-exchanger is stable against fouling during baromembrane separation [1]. A similar approach could be applied to ion exchange membranes. The aim of the investigation is a development of materials for ED, establishment of interrelation of their structure and functional properties, ascertainment of main regularities of whey desalination using the composite membranes.

### **Experimental**

#### *Modification of the polymers*

The ion exchange separators were obtained similarly to [10] by means of modification of heterogeneous CM-40 cation exchange (further CM) and AM-40 anion exchange (AM) polymer supports (produced by Schekinoazot, RF) with zirconium hydrophosphate (ZHP) and hydrated zirconium dioxide (HZD) respectively. The modification procedure involved impregnation of polymers with a ZrOCl<sub>2</sub> solution followed by removal of additionally sorbed electrolyte and deposition of the inorganic constituents with a solution of phosphoric acid

(cation exchange membrane) or ammonia (anion exchange one) at 273 K. Then the membranes were washed with deionized water, dried at 343 K and treated with ultrasound. The composites were marked as CM-ZHP and AM-HZD.

The resins (CU 2-8 cation-exchanger and EDE-10P anion-exchanger), which were used by the producing company for membrane preparation, were modified as mentioned above and used further for nanoparticle visualization.

#### Characterization of the composites

The amount of the inorganic constituent in the polymer was determined as a mass difference before and after modification. Visualization of cross-sections of the membranes and resins was provided by means of transmission electron microscopy (TEM) [10,11]. The method of standard contact porosimetry (SCP) [12–14], which has been recognized by the IUPAC [12], was applied. In opposite to well-known measurements of water adsorption isotherm using a vacuum Mac-Ben apparatus [15], the SCP allows us to investigate porous structure in a wide diapason of pore size (from 1 nm to 300  $\mu\text{m}$ ). Unlike mercury porosimetry, the SCP method can be applied to swollen materials. It is important for polymer ion exchangers, which are characterized by porosity only in a swollen state.

For potentiometric measurements, a two-compartment divided cell supplied by Ag/AgCl electrodes and filled with NaCl solutions (0.5 and 1 M) was used [14]. Electrical conductivity of the membranes was measured using this cell, which was filled with NaCl solutions of equal concentration (1–40  $\text{mol}\cdot\text{m}^{-3}$ ) [10].

#### Electrodialysis

Experimental set-up involves three-compartment cell, power supplier, measuring instrumentations and two independent liquid lines [10]. The first line provides circulation of whey (1.5  $\text{m}^3$ ) through the desalination compartment with a flow velocity of 4  $\text{cm}^3\cdot\text{s}^{-1}$ , the second line was through the electrode (concentration) chambers. The cathode and anode compartments were separated from the desalination chamber with cation and anion exchange membranes respectively, a distance between them was 1 cm, their area was 16  $\text{cm}^2$ .

The initial elemental composition of milky whey

was,  $\text{mmol}\cdot\text{dm}^{-3}$ : K – 36; Na – 16; Ca – 24; Mg – 4.3; P – 30; Cl – 51. Na, K and Cl are in a form of completely dissociated compounds. A part of Ca, Mg and P forms dihydro- and hydrophosphates or citrates. Phosphorus is also a part of protein aminoacids.

Several ED processes have been carried out for  $\approx 20$  h at 282 K, other conditions are given in Table 1. Preliminary voltammetric curves were obtained according to two-electrode scheme.

Table 1

Conditions of ED processes

№	Membranes	Solution through the electrode compartments	Current density, $\text{A}\cdot\text{m}^{-2}$
1	pristine	0.1 M $\text{NH}_4\text{NO}_3$	25
2	pristine	0.1 M HCl	25
3	composite	0.1 M HCl	25
4	pristine	0.1 M HCl	56
5	composite	0.1 M HCl	56

Alkaline and hardness ions in the concentrate were determined with flame photometry and atomic absorption, the P content was found with a spectrophotometric method after transformation into molibdovanadophosphoric acid [10]. The amount of  $\text{Cl}^-$  anions in whey was determined with a titrimetric technique using  $\text{AgNO}_3$ . Total acidity of whey was found by titration with a 0.1 M NaOH solution using phenolphthalein. This parameter was expressed in terms of Turner degrees ( $T_a$ ) as  $10v$ , where  $v$  is the volume of the alkaline solution for titration of whey aliquot (10  $\text{cm}^3$ ). The acidity involves both free and bonded (with proteins, phosphate anions etc.)  $\text{H}^+$  ions. The pH and conductivity of whey as well as the cell voltage were also monitored.

#### Results and discussion

##### Visualization of inorganic constituent

Mass fraction of the modifiers ( $m$ ) (Table 2) is in  $\approx 5$  times lower than that in the composite ion-exchange resin, which has been obtained by similar manner, but without removal of additionally sorbed  $\text{ZrOCl}_2$  [11]. Swollen ion-exchanger involves gel areas and voids between them, which are formed by hydrophilic and hydrophobic parts of polymer chains

Table 2

Characteristics of membranes

	I	II	III	IV	V	VI	VII	VIII	IX
CM	–	2.6	5.77	$3.1 \times 10^{-4}$	0.68	0.44	0.64	179	9
CM-ZHP	0.043	–	5.72	$1.2 \times 10^{-3}$	0.67	0.43	0.64	74	6
AM	–	3.8	2.69	$2.5 \times 10^{-5}$	0.61	0.36	0.59	519	7
AM-HZD	0.035	–	2.62	$6.8 \times 10^{-5}$	0.61	0.32	0.52	147	1

Note: I –  $m$ ; II –  $A_p$ ,  $\text{mmol}\cdot\text{g}^{-1}$ ; III –  $n$ ; IV – isoconductivity point,  $\text{Ohm}^{-1}\cdot\text{m}^{-1}$ ; V – pore volume,  $\text{cm}^3\cdot\text{g}^{-1}$ ; VI – volume of transport pores,  $\text{cm}^3\cdot\text{g}^{-1}$ ; VII –  $\alpha$ ; VIII –  $(\kappa^{1-\alpha}/\kappa_n)$ , IX –  $(\kappa^{1-\alpha}/\kappa^\alpha)$ .

respectively [14]. Gel areas are penetrated by clusters and channels, so called “transport pores”, since functional groups are located therein. Porous structure involves also defects and the largest pores between ion-exchanger and binder (for heterogeneous membranes). Inorganic particles can be placed everywhere depending on modification technique [10].

Both single nanoparticles (up to 20 nm, they can be located in transport pores) and their aggregates (30–500 nm, in voids between gel areas) are visible in TEM image of ion exchange resin (Fig. 1). Only a small amount of aggregates in structure defects was found. Pores between polymer ion-exchanger and binder are free from the aggregates of a comparable size.

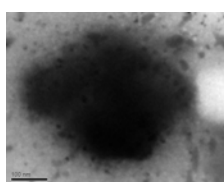


Fig. 1. TEM image of organic-inorganic cation exchange resin

#### *Isotherms of water adsorption, pore size distributions*

Since thermal pretreatment (at 343 K) before the SCP measurements is not able to remove water from the inorganic constituent, the results are related only to the polymer. Low content of the inorganic constituents causes an inconsiderable change of water adsorption isotherms (Fig. 2,a). The value of water adsorption ( $A_{H_2O}$ ), which corresponds to the plateau (adsorbate monolayer), was used for calculation of amount of water molecules ( $n$ ) in hydrate shells of counter-ions of functional groups of the polymer.

This magnitude was calculated as  $n = \frac{A_{H_2O}}{A_p V_{H_2O}}$  for the

pristine membranes and  $n = \frac{A_{H_2O}}{A_p V_{H_2O} (1-m)}$  for the

composite (here  $V_{H_2O}$  is the molar volume of water,  $A_p$  is the total exchange capacity of the pristine membrane). A slight decrease of the  $n$  value was found for the composites (see Table 2). This is evidently due to screening of transport pores with nanoparticles.

Several half-waves are visible in integral pore size distributions, which are plotted as functions of pore volume ( $V$ ) vs logarithm of pore radius ( $r$ ) (Fig. 2,b). Intersections of the plots with the ordinate axis correspond to micropores. They and the first build-up ( $r=2.5$  nm) are related to channels, the second step (16 nm) is attributed to clusters, the next one (40 nm) is due to voids between gel field. The  $V$  growth at 1–10  $\mu\text{m}$  is caused by structure defects, the largest pores are related to voids between ion-exchange polymer and binder. The “bonded” water confined in hydrate shells of ion-dipole associates of fixed ions with counter-ions [14]. This type of water is located in channels (region I), this region corresponds to the energy of water bonding ( $A \geq 1700 \text{ J}\cdot\text{mol}^{-1}$ ). ZHP causes practically no decrease of bonded water in opposite to HZD. This is probably due to higher swelling pressure in transport pore containing ZHP, since the modifier provides additional osmotically active species ( $H^+$ ) in neutral medium. HZD shows isoelectric point under these conditions – nanoparticles mainly screen transport pores of AM. The AM-HZD sample contains larger amount of free water (region II) in a comparison with CM-ZHP. This difference is due to pores between polymer and binder.

#### *Charge selectivity and electrical conductivity*

Transport numbers of counter-ions through the membrane ( $\bar{t}$ ) were determined from measurements of membrane potential ( $E_m$ ) followed by calculations from the formula [14]:

$$E_m = (2\bar{t} - 1) \frac{RT}{zF} \ln \frac{a_2}{a_1}, \quad (1)$$

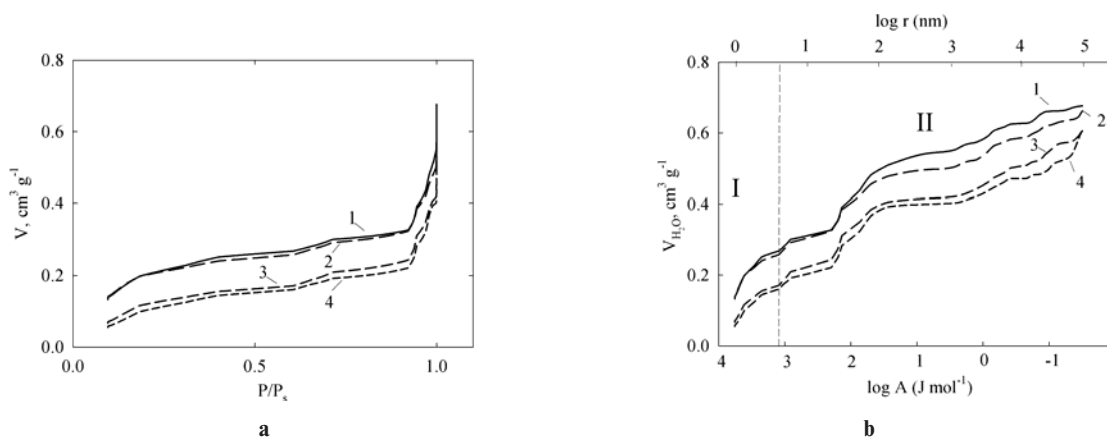


Fig. 2. Isotherms of water adsorption (a), integral distributions of pore size and binding energy of water for CM (1), CM-ZHP (2), AM (3), AM-HZD (4). Regions I and II of Fig. 2,b correspond to bonded and free water respectively

where  $z$  is the charge number,  $a_1$  and  $a_2$  are the activity of less and more concentrated solutions,  $R$  and  $F$  are the gas and Faraday constants respectively,  $T$  is the temperature. Modification improves charge selectivity of CM evidently due to screening of non-transport pores with inorganic constituent (see Table 2), the particles of which form secondary porosity. The “secondary membrane” is a barrier against additionally sorbed electrolyte due to high charge density of ZHP and small pores between nanoparticles. However, slight deterioration of anion permittivity was found for the AM-HZD in a comparison with AM. This is due to ability of HZD to sorb both anions and cations in neutral medium.

Fig. 3 illustrates electrical conductivity of the membranes ( $\kappa_m$ ) as a function of solution conductivity ( $\kappa$ ). When these values are equal (isoconductivity point), following relation is valid [14]:

$$\kappa_m = \bar{\kappa}^\alpha \kappa^{1-\alpha} \quad (2)$$

Here  $\bar{\kappa}$  is the conductivity of gel areas,  $\alpha$  is the fraction of transport pores (this value was determined from Fig. 2,b, a sum of fractions of volumes of transport and non-transport pores is equal to 1). The isoconductivity point was found as an intersection of the  $\kappa_m, \kappa$  lines by their extrapolation. The relations of  $\kappa^{1-\alpha}/\bar{\kappa}^\alpha$  and  $\kappa^{1-\alpha}/\kappa_m$  indicate screening of electrolyte by gel areas and whole polymer respectively. They are lower for the composites evidently due to aggregates, which are a barrier against additionally sorbed electrolyte. It means, at least one side of organic-inorganic membrane should be in a contact with highly concentrated solution. Moreover, in order to provide high charge selectivity of the AM-HZD membrane, one side of the separator has to be in a contact with acidic solution.

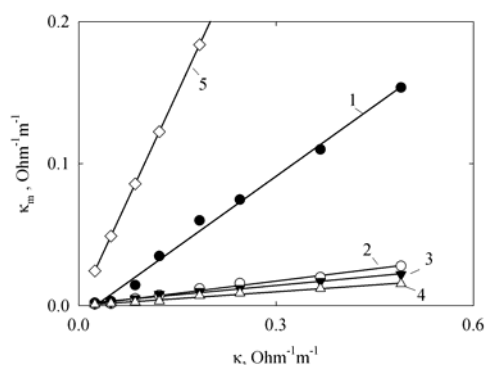


Fig. 3. Conductivity of membranes CM (1), AM (2), CM-ZHP (3), AM-HZD (4) and solution (5) as a function of solution conductivity

#### Whey demineralization

Typical voltammetric curves for membrane systems given in Fig. 4. Two half-waves and linear

region can be observed for the pair of CM and AM. Nonlinearity at  $i < 0.75i_{lim}$  (here  $i$  is the current density,  $i_{lim}$  is the limiting current) is due to concentration polarization inside pores between the ion-exchange polymer and binder. As shown earlier in the example of NaCl solution, the limiting current due to anions is higher than that caused by cations [10]. It is the same for whey, since ions of alkaline metals and  $Cl^-$  are dominant. Thus, the first half-wave is attributed both to cations ( $i \leq i_{lim}$ ) and anions ( $i < i_{lim}$ ), the second one is due to anion transport through AM ( $i < i_{lim}$ ), limiting and overlimiting current of cations. The linear region corresponds to overlimiting current caused by transport of both cations and anions as well as water split at the membrane surface.

In opposite to pristine membranes, the composites show linear regions at  $i < 0.75i_{lim}$  for two half-waves. It means no concentration polarization inside membranes due to screening effect of nanoparticle aggregates. This is important from the practical point of view, since the polarization slows down ion transport and supports precipitation of insoluble matters inside membrane. Since the composites show higher limiting currents, the curves for pristine membranes were taken into consideration for chosen of ED conditions ( $i = 0.75i_{lim}$  for two half-waves).

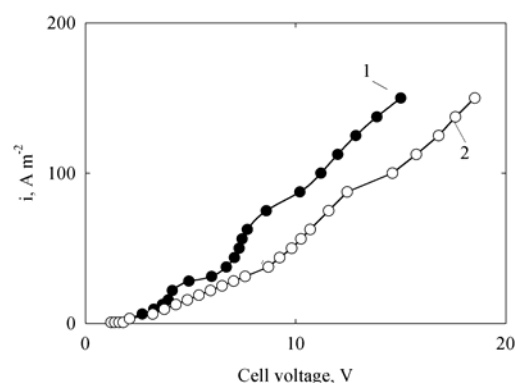


Fig. 4. Voltammetric curves for the system containing pairs of CM and AM (1), CM-ZHP and AM-HZD (2)

During electrodialysis, the whey conductivity ( $k$ ) falls off (Fig. 5), the cell voltage slightly grows due to whey depletion (Table 3). A change of neutral solution in the concentration compartments into acid leads to intensification of whey desalination. This is evidently due to diffusive fluxes of acid, a direction of which is opposite to migration flux. The acid prevents blockage of outer surface of all membranes and volume of pristine separators with insoluble substances. Replacement of polymer membranes by organic-inorganic materials leads to intensification of desalination evidently due to their improved charge selectivity.

Typical dependences of cation amount ( $n$ ) in

Electrodialysis of whey

№	Cell voltage*, V	pH	T <sub>a</sub> *	CE**, %		
				alkaline ions	hardness ions	anions***
1	increases from 4.4 to 5.6	4.3	decreases from 62 to 55	decreases from 44 to 32	decreases from 17 to 11	decreases from 84 to 82
2	increases from 4.3 to 5.8	4.3	decreases from 62 to 43	decreases from 36 to 27	decreases from 18 to 11	86
3	increases from 4.8 to 5.6	4.4	decreases from 62 to 56	decreases from 42 to 27	increases from 6.5 to 13	89
4	increases from 5.3 to 16.8	4.3	decreases from 62 to 56	decreases from 30 to 26	decreases from 14 to 11	decreases from 70 to 60
5	increases from 5.9 to 12.8	4.4	decreases from 61 to 31	decreases from 35 to 25	increases from 4 to 13	decreases from 80 to 51

Note: \* – Lower limit of the interval corresponds to  $\tau=0$ ; \*\* – Lower limit of the interval corresponds to  $\tau=1$  h, further the CE values were practically constant; \*\*\* – Only  $H_2PO_4^-$  ions were taken into account for CE calculations for phosphorus-containing species.

time ( $\tau$ ) are given in Fig. 6. After the initial growth ( $Na^+$  through CM and CM-ZHP,  $Ca^{2+}$  through CM), a slope of the curves to the abscissa axes decreases, the plots become practically linear. The current efficiency (CE), which is calculated as  $\frac{zFN}{i} \times 100\%$  (here N is the flux of species,  $N = \frac{1}{A_m} \frac{dn}{d\tau}$ , where  $A_m$  is the membrane area), also decreases (see Table 3). Regarding cation transport at  $25 A \cdot m^{-2}$ , a decrease of their concentration in whey causes a fall of limiting current and current efficiency. It is the same for transport of  $Na^+$ ,  $K^+$  and anions at  $56 A \cdot m^{-2}$ . In the case of process 1, a decrease of anion flux is due to deposition of insoluble compounds of hardness ions.

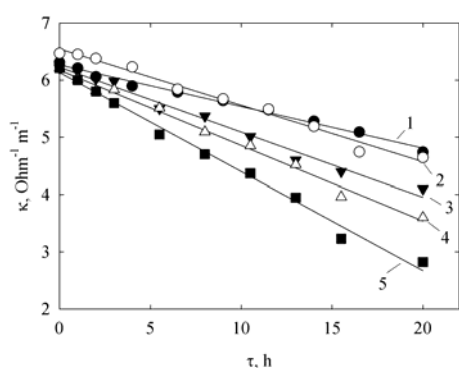


Fig. 5. Whey conductivity as a function of time. Numbering of curves correspond to that of ED processes given in Table 1

Replacement of polymer membranes by organic-inorganic separators causes intensification of transport of  $Ca^{2+}$  ions (see Fig. 6). Moreover, their flux increases after the initial induction period evidently due to accumulation in the membrane. The flux of  $Na^+$  is depressed. Maximal ratio of fluxes of hardness ions and alkaline metal ions is reached

under  $25 A \cdot m^{-2}$  (Fig. 7). It is the same for P-containing species and  $Cl^-$  anions. This is evidently affected by the modifiers, which demonstrate high sorption affinity towards  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $HPO_4^-$  and  $H_2PO_4^-$  ions. A decrease of these ratios under higher current is caused by precipitation of phosphates. Thus, desalination is mainly due to removal of  $Na^+$ ,  $K^+$  and  $Cl^-$  ions at  $56 A \cdot m^{-2}$ ,  $Ca^{2+}$ ,  $Mg^{2+}$  are precipitated as phosphates.

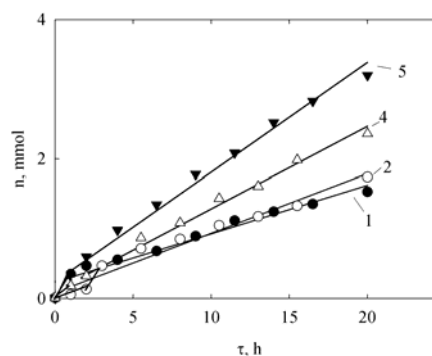


Fig. 6. Amount of  $Ca^{2+}$  (1, 2) and  $Na^+$  (3, 4) ions in the concentration compartments, which were willed with acidic solution, as a function of time. Pairs of pristine (1, 3) and composite (2, 4) membranes were used,  $i=25 A \cdot m^{-2}$

No changes of the pH of whey was found (see Table 3) due to several buffers (proteinaceous, phosphate, cytrate). The pH of buffers, which is formed by weak acid and its salt (for instance, by  $H_2PO_4^-$  and  $HPO_4^-$  species), is determined as:

$$pH = pK_{acid} - \log \frac{C_{acid}}{C_{salt}}, \quad (3)$$

In the case of higher anion flux towards concentration compartment, alkalization of whey is expected. The alkalization can be compensated by a

leakage of acid from the concentration compartment (processes 2–5). However, no alkalization was found, when this compartment was filled with a neutral solution (process 1). Thus, the constancy of whey pH is due to predominance of  $\text{H}_2\text{PO}_4^-$  ions. Alkalization causes their transformation to  $\text{HPO}_4^{2-}$  species:

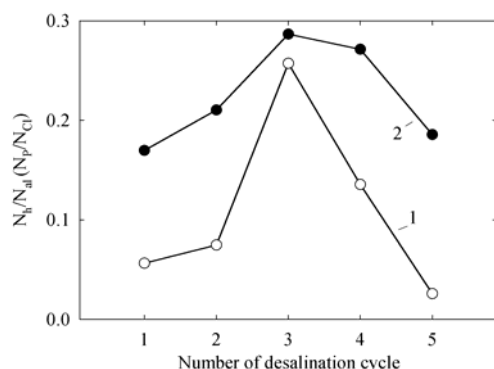
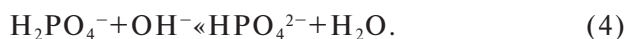


Fig. 7. Ratio of fluxes of alkaline and hardness ions (1),  $\text{Cl}^-$  and phosphorus-containing anions (2) for EDI processes (their numbering is in Table 1),  $\tau > 1$  h

In owing to this transformation and also due to removal of phosphorus-containing ions, the acidity expressed in Terner degrees decreases in time.

### Conclusions

Particles of inorganic ion-exchanger incorporated into polymer membrane can give two effects: they screen pores and change swelling pressure. The SCP technique shows a screening effect (a decrease of the  $n$  value). However, no considerable change of amount of bonded water was found for CM-ZHP in a comparison with the pristine membrane probably due to an increase of swelling pressure in transport pores. Screening effect of amphoteric HZD in transport pores of the anion exchange composite is dominant due to isoelectric point of this inorganic constituent in neutral medium. In owing to this, HZD deteriorates charge selectivity of AM under these conditions in opposite to ZHP in CM. Thus, at least one side of anion exchange membrane can be in a contact with acidic solution. Since ZHP is weakly acidic ion-exchanger, one side of the composite cation exchange membrane has to be in a contact with a neutral or weakly acidic solution.

Nanoparticles form secondary porosity in non-transport pores (mainly in voids between gel areas). Pores between nanoparticles as well as high surface charge density provide a barrier against additionally sorbed electrolyte. This causes depolarization of composite heterogeneous membranes at  $i < 0.75i_{lim}$  and prevents precipitation inside them. Thus, periodic

use of acid for dissolution of the precipitate is unnecessary, only disinfection and cleaning of outer surface of the membranes are needed. Softer reagents can be applied to disinfection, cleaning can be carried out by means of hydrodynamic pulsations. This allows us to increase life-time of separators. Moreover, lower amount of water is needed for washing of the membrane system.

The composite membranes show higher ion transport during whey desalination in a comparison with polymer materials. Hardness and phosphorus-containing ions are removed preferably. When these ions are removed almost completely, operation under overlimiting current conditions could be proposed in order to increase the efficiency of desalination. Precipitation of insoluble inorganic compounds can be avoided by this manner.

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#### **ELECTROMEMBRANE RECYCLING OF LIQUID WASTES OF DAIRY INDUSTRY USING ORGANIC-INORGANIC MEMBRANES**

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*Organic-inorganic membranes were obtained by the modification of heterogeneous cation and anion exchange polymer substrates with zirconium hydrophosphate and hydrated zirconium dioxide, respectively, the modifier content was 3.5 to 4.3% wt. The inorganic modifiers were found to be mainly in a form of single nanoparticles and their aggregates (up to 500 nm). The effect of the modifiers on the porous structure of the membranes was investigated using the data of standard contact porosimetry. Aggregated nanoparticles are a barrier against additionally sorbed electrolyte improving migration flux of counter-ions through the membranes and minimizing concentration polarization when the current is lower than its limiting value. This allows us to avoid the precipitation of insoluble compounds directly inside membranes. The electro-dialytic desalination of milky whey was investigated; both pristine and organic-inorganic membranes were applied. The composites provide preferable removal of hardness and phosphorus-containing ions from whey; moreover, a higher desalination degree is reached. The current efficiency for inorganic ions reaches 89% under the optimal operation conditions which involve particularly a contact of one side of the organic-inorganic membrane with acidic solution.*

**Keywords:** electro-dialysis; organic-inorganic membranes; milky whey; desalination; standard contact porosimetry.

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