Acetic acid Separation as a Function of Temperature Using Commercial Pervaporation Membrane

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ABSTRACT: Acetic acid was separated from a dilute mixture using a commercial polyvinyl alcohol (PVA) membrane. Intrinsic separation characteristics of the membrane were studied as a function of temperature. The degree of membrane swelling decreased marginally with increase in feed temperature. At 25°C the maximum degree of swelling was found out to be 46.3%, which reduced to 39.5% at 65°C. Although the pervaporation flux increased with increasing temperature of the liquid feed mixture, the separation factor decreased. From the temperature dependence of diffusion and permeation values, the Arrhenius apparent activation parameters for water permeation were estimated. Diffusion and partition coefficient for water and acid were found to increase with temperature, but the diffusion coefficient of water was substantially higher than that of acetic acid at a constant feed concentration. The membrane used in the present study could tolerate highly concentrated corrosive acetic acid, thus may be useful for dehydration of other organics.

KEYWORDS Pervaporation; Acetic acid, PVA; Swelling, flux; Activation energy.

INTRODUCTION
Stringent environmental regulation and growing public awareness have driven an ongoing need to separate organic materials from industrial wastewater. It is desirable to remove such compounds from the wastewater for a variety of reasons, particularly reclamation of water to the recovery of the organic compounds dissolved therein. Recovery of acetic acid (HAc) from aqueous solution by a suitable method has been a focus of attention for quite some time, since acetic acid is one of the top fifty organic intermediates in the chemical industry. The bulk of the acetic acid produced in industry is mainly used for the manufacturing of vinyl plastics, hot-melt adhesives, textile finishes, latex paints, phthalic anhydride, terephthalic acid and acetic anhydrides [1]. The production process of these end-products and intermediates are invariably accompanied by waste and or recycle streams containing acetic acid-water mixtures thereby necessitating their efficient separation [2]. Furthermore, the synthesis of acetic acid itself results in the production of water as a by-product.

Mixtures containing HAc and water do not form an azeotrope nonetheless; the separation of HAc from water using distillation is constrained with associated high costs due to the requirement of a large number of plates which are as many as 45-60 [3]. This separation is energy intensive because the relative volatility between water and HAc is close to unity. The vapor-liquid equilibrium graph for the HAc/H2O system indicates that in the region...
of the low HAc (high water) concentration, it becomes even more difficult for distillation as the compositions of HAc in liquid and vapor phase approach each other. The main challenges of such a separation process are two-fold, firstly cost-minimization and secondly increase of separation efficiency.

Pervaporation is recognized as a separation process in which a binary or multi-component liquid mixture is separated by partial vaporization through membrane film. The feed liquid is brought into contact with a membrane and one component preferentially permeates the membrane in the form of vapor either by a sweeping carrier gas or by applying a vacuum. Further downstream of the vapor is usually obtained as a liquid in a condenser. Pervaporative separation of the aqueous acetic acid solution has been reported by several researchers, however with different membranes. Huang and Yeom [4] (1991) reported a separation factor of 13–42 and flux of 0.079 – 2.285 kg/m².h through cross-linked poly (vinyl alcohol) membranes. Miyoshi et al. [5] (1988) carried out dehydration of an aqueous acetic acid solution through commercial ion-exchange membranes. Separation of water-acetic acid mixtures by using a blend membrane composed of poly (vinyl alcohol) and several hydrophilic copolymers such as poly (vinyl pyrrolidone) could achieve the separation factor of 34 with a flux of 0.14 g/m².h at 25°C [6]. Yoshikawa et al. [1985] reported the separation of an aqueous acetic acid solution through poly (acrylic acid-co-acrylonitrile) and poly (acrylic acid-co-styrene) membranes [7]. Kulia and Ray (2011) reported the dehydration of acetic acid using a chemically modified polyvinyl alcohol membrane (full interpenetrating network membrane) [1]. In another study pervaporative dehydration of acetic acid was conducted using polyelectrolytes complex (PEC)/11-phosphotungstic acid hydrate (PW11) hybrid membrane (PEC/PW11). The hybrid membrane containing 9 wt% PW11 exhibited the best pervaporation performance, with flow of 0.440 kg/m².h and separation factor of 144 for 90 wt% aqueous solution of acetic acid at 50°C [8]. A few other membranes used in the dehydration of acetic acid solution include polydimethyl siloxane (PDMS) [9], organosilica membranes prepared from bis(triethoxysilyl)ethane (BTESE)[10], NaY zeolite and hybrid poly(vinyl alcohol) composite membrane [11], sulfonated polybenzimidazole[12], polyphenyl sulfone[13] and so on.

Both operating conditions and membrane characteristics have a decisive role in determining the separation performance of a pervaporation process because they not only manipulate the driving forces to transport permeants but also affect intrinsic membrane permeability and selectivity. As a result, both permeation (and pervaporation) flux and separation factor are closely linked with the operating conditions. It is, therefore, necessary to study the effect of operating parameters in order to optimize or scale up a pervaporation process. While a number of researchers have studied the effects of process conditions on pervaporation system [8-13], correlating separation performance with temperature and intrinsic separation characteristics of commercial PVA membranes remain to be an underexploited area of research. Keeping in mind, the effect of temperature on the separation performance during pervaporation of binary mixture of acetic acid-water in a pilot plant has been studied.

A commercial hydrophilized PVA-PES composite membrane was employed for separation of water–acetic acid mixture. Activity and partition coefficient, diffusivity, pervaporation flux, separation factor, and selectivity were evaluated under different experimental conditions. From the temperature dependence of the permeation flux and diffusion coefficients, the Arrhenius activation parameters were estimated. Studies covered the entire concentration range of 10-90 wt% of acetic acid.

EXPERIMENTAL SECTION

Chemicals and membranes

Acetic acid (AR grade) from S D.fine-chem, Mumbai, India was used as received without further purification. Preparation of stock solutions was carried out with deionized water, having a conductivity of 20 µS/cm, produced from a reverse osmosis system. Hydrophilized and flat sheet polyvinyl alcohol (PVA) membrane of thickness 115 µm, with polyether sulfone (PES) support and cross linked with glutaraldehyde was used in the study. The asymmetric PVA-PES composite membrane was supplied by M/s Permionics Membrane Pvt. Ltd, Baroda, India. The membrane was prepared by solution casting and phase inversion gelling. According to the manufacturer’s data, the effective membrane area was 0.016 m².

Pervaporation experiment

Pervaporation experiments were conducted in a small
pilot plant assembly as shown in Fig. 1. The permeation cell consisted of two detachable Stainless Steel (SS 316) parts which were provided with inlet and outlet openings for the flow of feed solution and an outlet opening for the withdrawal of the permeated product. The effective area of the membrane in the pervaporation cell was 164.8 cm².

The liquid feed-mixture is circulated in contact with the membrane using a peristaltic pump (capacity 180 l/h) from a feed tank, equipped with an overhead condenser to prevent any loss of feed due to evaporation. The constant temperature of feed was maintained by using a thermostat bath and controlled on the inlet and outlet of cell according to the need of the experiment. The optimal operating pressure above the active layer of the membrane was atmospheric [9, 14]. This condition was thought to avoid partial vaporization of the feed; thus, a pressure of 1 atm was used in this work. Before starting the PV experiments, test membranes were equilibrated for 1 h with the feed mixture.

The pervaporate compositions were evaluated by measuring its refractive index with an accuracy of ±0.0005 units using a refractometer. The obtained refractive index was then compared to a standard curve for acetic acid and water mixtures. Each of the pervaporation experiments was repeated two times and the results were averaged to minimize error. The experimental data points were reproducible and the experimental errors were estimated to be less than 3%.

**Swelling study**

Degree of swelling of the membrane was estimated by immersing the membrane samples into deionized water at a particular temperature for 24 h to ensure equilibrium. Subsequently, the samples were taken out and removed the residual water on surfaces and weighed immediately. The samples were then dried in vacuum at 80°C for 24 h and weighed again. The water uptake was calculated in terms of swelling ratio as given by the following equation

\[
S_R = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \tag{1}
\]

where \(W_{\text{dry}}\) and \(W_{\text{wet}}\) are the weight of dry and swollen membrane, respectively.

**Flux and separation factor**

Flux and separation factors are two important performance indices of any pervaporation process. Pervaporation data are usually reported in terms of membrane separation factor and flux. The trans membrane flux in pervaporation is generally expressed
as a mass flux \( (J) \) with typical unit \( \text{kg/} \text{m}^2 \text{h} \). It can be determined for any species (say ‘i’, i.e. \( J_i \)) as Eq. (2) [15]:

\[
P_i^G = \frac{J_i}{\left( \gamma_i x_i P_{i, \text{sat}} - \gamma_i P_p \right)}
\]

(2)

Where \( P_i \) is the membrane permeability, \( l \) is the membrane thickness and \( \gamma \) is the activity coefficient, which may be calculated using Van Laar equation. The mole fraction in the feed solution is denoted as \( x \), \( P_{i, \text{sat}} \) is the saturated vapor pressure calculated with Antoine’s equation, \( y \) is the mole fraction in the permeate and \( P_p \) is the permeate pressure obtained for the component during the PV experiment?

In gas separation, flux is normally given as a molar flux \( (j) \) with units \( \text{cm}^3 \text{STP}/\text{cm}^2 \text{s} \) or \( \text{m}^3 \text{STP}/\text{m}^2 \text{s} \). Ignoring simple numerical conversion terms (\( \text{m}^2 \) to \( \text{cm}^2 \), \( \text{h} \) to \( \text{s} \)) this means:

\[
\dot{W}_i = \frac{j_i M_{wi}}{V_i}
\]

(3)

Where \( V_i \) is the molar volume of gas \( i \) (22.4 l(STP)/mol) and \( M_{wi} \) is the molecular weight of component \( i \).

The membrane separation factor \( (\beta) \) can be defined as the ratio of the molar component concentrations in the fluids on either side of the membrane. Hence:

\[
\beta = \frac{y(1-x)}{x(1-y)}
\]

(4)

Where ‘x’ and ‘y’ represent the feed and permeate concentrations of the faster permeating component \( i \) which is water in the present case.

**Permeability and selectivity**

The membrane permeability, \( (P_i^G) \) (or permeability coefficient) is a component flux normalized for membrane thickness and driving force [16]. It is defined as the transport flux of material through the membrane per unit driving force per unit membrane thickness, given as Eq. (5)

\[
P_i^G = \frac{1}{\left( \gamma_i x_i P_{i, \text{sat}} - \gamma_i P_p \right)}
\]

(5)

It is generally denoted as Barrers (1 Barrer = \( 1 \times 10^{-10} \text{ cm}^3 \text{STP}/\text{cm}^2 \text{s cm Hg} \)) for the gas separation. Alternatively, when the membrane thickness is not known, membrane permeance \( (P_i^G/l) \), the ratio of membrane permeability to membrane thickness can be used. Permeance is most commonly reported as gas permeation unit (GPU) \( (1 \text{GPU} = 1 \times 10^{-6} \text{ cm}^3 \text{STP}/\text{cm}^2 \text{s cm Hg}) \)

Membrane selectivity \( (\alpha_{\text{mem}}) \), defined as the ratio of the permeabilities or permeances of components \( i \) and \( j \) through the membrane is given by Eq. (6)

\[
\alpha_{\text{mem}} = \frac{P_i^G}{P_j^G}
\]

(6)

**Diffusion and partition coefficient**

In a binary mixture, Fick’s law is often used to describe the binary diffusion, which can be expressed as

\[
J = -D \frac{dC}{dh}
\]

(7)

Where \( J \) is the permeation flux per unit area (\( \text{kg/} \text{m}^2 \text{h} \)), \( D \) is the diffusion coefficient(\( \text{m}^2/\text{s} \)), \( C \) is the concentration of permeant (\( \text{kg/} \text{m}^3 \)) and \( h \) is the diffusion length (m).The concentration profile in this study is assumed to be linear along the diffusion length. As a result, Eq.(7) can be rewritten as [17]:

\[
D_i = \frac{J \delta}{C}
\]

(8)

Where \( \delta \) is the membrane thickness. Thus the partition coefficient \( (K) \) of species \( i \) between membrane and feed can be determined using Eq.(9)

\[
\left[ \frac{P}{1} \right] = D_i K_i
\]

(9)

**Thermogravimetric analysis**

The thermal decomposition behaviour of the new and used membranes was characterized with a TGA 2050 Thermogravimetric Analyzer (TA Instruments), with a ramp of 5°C/min at the temperature ranging from 40 to 900°C, under nitrogen atmosphere. The weights of the samples were around 6 mg.

**RESULTS AND DISCUSSION**

**Membrane swelling**

Pervaporation performance is affected by the extent of membrane swelling. Degree of swelling of the PVA-PES
Fig. 2: Degree of swelling as a function of feed water concentration at different feed temperature.

the composite membrane used in the present study at three different temperatures viz. 25, 45 and 65°C for different concentrations of acetic acid are presented in Fig. 2. In general it was observed that % degree of swelling decreased gradually with increase in water concentration of the binary (water-acetic acid) feed mixture irrespective of temperature. Moreover, with increase in feed temperature degree of swelling decreased marginally. At 25°C the maximum degree of swelling was found out to be 46.3%, which reduced to 39.5% at 65°C. The sorption (swelling) mechanism of pervaporation membranes depends on many factors, such as membrane morphology, affinities of the components towards membrane and their mutual interaction [13, 18]. This was due to an increase in preferential sorption of water. Water molecules absorbed by the hydrophilic groups, such as – NH₂, – COO⁻, or –OH in the membrane resulted in the swelling of the membrane thereby assisting transport through the membrane. As the acetic acid concentration in the feed mixture increases because of a strong interaction between acetic acid and membrane, the membranes may become more swollen. This further results in more flexibility of polymeric chains and transport may become easier. Since the molar mass of HAc (60.05 g/mol) is higher than that of water (18.01 g/mol), the total degree of swelling of PVA-PES membrane was higher in HAc compared to water [1].

Equilibrium mass uptake is a strong function of acetic acid concentration and also depends weakly on temperature. It is what causes PVA-PES composite membrane to swell among other things. Both temperature and solvent activity strongly affects the viscoelastic response of the membrane. In general creep increases significantly with increasing temperature. This is because bonding strength between polymer chains decreases with increasing temperature. However, combined effects of temperature and solvent activity are complicated. Acetic acid concentration strongly affects the viscoelastic response of membrane at all temperatures. It was shown at room temperature increased acetic acid concentration had increased the creep as well.

The efficiency of liquid permeation separations through polymer films depends primarily on whether there is an interaction, chemical or physical, between the solvent solute and polymer. The extent of the liquid-polymer interaction determines whether solvent, solute or neither is preferentially sorbed at the membrane-solution interface. As expected, the membrane selectivity decreases dramatically with a reduction of the water permeance and an increment of the HAc permeance when changing to a 55% wt HAc concentration feed. The swelling from the high acetic acid concentration feed increases the free volume and changes the free volume distribution. The HAc-induced plasticization helps itself through the membrane much more than water, resulting in the low membrane selectivity. This has been discussed a little later.

Flux and separation factor

The temperature dependence of pervaporation data was investigated over a temperature range from 50 to 90°C with a constant feed concentration of 50% by volume acetic acid. These are presented in Fig. 3, which indicates that Total molar fluxes, as well as molar fluxes of both water and acetic acid, increased with increasing temperatures. Generally, temperature influences both the permeate transport behavior and the ease of swelling by the polymer chain in the membrane structure. At higher temperature, frequency and amplitude of segmental motion of the polymeric chains increase with increased free volume and lower degree of swelling. This increased free volume facilitates transport of permeants. Further, vapor pressure of the permeating molecules also increases at higher temperatures. The combined effects of increased free volume and driving force (vapor pressure difference) results in the increased flux at higher temperature irrespective of concentrations.
It is worth mentioning that the rate of increase of molar flux of water with temperature was found to be substantially higher and closer to overall flux than the rate of increase of acetic acid molar flux. At 70°C the molar flux of water was found out to be 0.3342 m³(STP)/m²h, which is around 81.45% of total flux whereas the acetic acid flux was 0.0526 m³(STP)/m²h, almost about six fold lower. Although the pervaporation flux increased with increasing temperature of the liquid feed mixture, the separation factor decreased. At 50°C the separation factor was estimated to be 2.3, which decreased to 1.52 and 1.35 at 80°C and 90°C respectively.

These results can be explained following the free volume theory. The thermal motion of polymer chains in the amorphous regions randomly produces free volume. As the temperature increase, the frequently and amplitude of the chain jumping increase and the resulting free volumes become larger. The diffusion rate of isolated permeating molecules and associated permeating molecules are high when the temperature is high so that total permeation rate is high and the separation factor is low [18].

Permeability and selectivity

Intrinsic membrane selectivity and permeability of acetic acid and water as a function of temperature is presented in Fig. 4. A perusal of Fig. 4 indicates that permeability of both water and acetic acid increase and membrane selectivity decreases with an increase in temperature, although the permeability of water was higher than that of acetic acid. At 90°C the selectivity was found out to be 44% of that obtained at 50°C.

The HAc solubility in the polymer plays an important role in the membrane selectivity, unlike near-negligible water sorption. The swelled polymer chains due to the high HAc concentration feed favour more HAc sorption into the polymer (solubility). This swelling, in turn, enables large increase in diffusivity and permeability. In other words, the HAc permeability and solubility can increase significantly in high HAc concentration solutions. Nevertheless, the membrane selectivity decreases since the water permeability exhibits a rather limited increment under the HAc-induced swelling condition. This is believed to occur since the swelling effect benefits the larger penetrant more than the smaller one[19]. Thus, the PVA-PES membrane used in the present study may be suitably used at higher temperatures with increased flux, however at the cost of a considerable decrease in membrane selectivity.

Activation energy

The effect of temperature on pervaporation can be conveniently described by the Arrhenius type relationship [13]. The relationship of flux or permeance of a penetrant across a membrane with operating temperature can be described by the Arrhenius equations as follows:

$$X = X_0 \exp \left( - \frac{E_X}{RT} \right)$$  \hspace{1cm} (10)

Where $X$ is the pervaporation flux (J), $X_0$ is the pre-exponential factor (permeation rate constant) R is the universal gas constant (J/mol K), T is the operation...
variation of \( \ln J_\text{w} \) with temperature for two different acetic acid concentrations using PVA-PES membrane. Good linearity exists between logarithmic flux vs. reciprocal temperature and the values of regression coefficients, \( R^2 \) are close to unity, indicating the experimental data fit the Arrhenius equation well. Activation energies for water and acetic acid permeation for two different feed concentrations are presented in Fig. 5 and Fig. 6 respectively. It is observed from Fig. 5 and Fig. 6 that the apparent activation energy of water permeation (\( E_{\text{pw}} \)) (56.82 kJ/mol) was significantly lower than those of acetic acid permeation (\( E_{\text{pHAc}} \)) (79.35 kJ/mol), suggesting a higher separation efficiency of the membranes. If the activation energy is positive, the permeation flux increases with an increase in temperature, which has also been reported in most pervaporation experiments in the literature [20]. The present study also corroborates the same observation. Due to its molecular size and shape, the activation energy of diffusion for acetic acid becomes greater than that for water. With the decrease in water content in the feed the polymeric membrane become less swollen and the mobility of chain segments decreases, thereby increasing the energy required for the diffusive jump of acetic acid molecules. The interaction between permeants is thought to have an enhancing effect on the permeation activation energy because associated molecules require more energy for permeation than isolated ones. On the contrary, the plasticization action could diminish the activation energy by making the polymeric chain segments even more flexible [4].

**Diffusion and partition coefficient**

The mass transfer of a binary liquid mixture through a non-porous polymeric membrane during pervaporation is generally governed by the solution-diffusion mechanism. This is assumed to take place in three steps, namely sorption, diffusion, and evaporation [19]. The selectivity and solute permeation rates depend closely on the solubility and diffusivity of each component of the feed mixture to be separated. Thus, it is important to estimate the diffusion coefficient, \( D_i \) of penetrating (or pervaporating) molecules to understand transport mechanism. Diffusion and partition coefficients were determined using Eq. (7) to (9) as discussed in section 2.5. Fig. 7 presents diffusion and partition coefficient of acetic acid and water at different temperatures for a fixed concentration of feed mixture. A perusal of Fig. 7 shows that the diffusion coefficient of water and acetic acid increases with increase in feed temperature at fixed feed concentration of 50 vol%. However, the increase in diffusion coefficient of water was observed to be much higher than that of acetic acid at all the temperatures. At around 80°C the diffusion coefficient of water is \( 28.21 \times 10^{-12} \text{ m}^2/\text{s} \) and that of acetic acid is \( 18.46 \times 10^{-12} \text{ m}^2/\text{s} \), which is 1.5 fold lower than water.

On the other hand, partition coefficients of acetic acid and water increased marginally with temperature. In the process, because of establishing the fast equilibrium distribution between the bulk feed and the upstream surface of a membrane, diffusion step controls the migration of penetrants. Although, it is not equally functional throughout all the feed concentrations.
It appears that for permeation of acetic acid, the diffusion contributes more and thereby sorption becomes less significant. But in the case of water permeation, the occurrence of strong interaction between the water molecules leads to decreased plasticization effect, which suppresses the sorption. The effect is more pronounced at higher water concentration. In case of acetic acid, diffusion coefficients increased continuously with increasing water composition in the feed. This was plausibly due to a deterioration of membrane selectivity towards water with increasing water composition in the feed [21]. However, further experiments need to be conducted to obtain more insight into the diffusion and sorption phenomena during pervaporation of water and acetic acid mixture.

**Thermogravimetric analysis**

ThermoGravimetric Analysis (TGA) signifies the heat resistance and thermal stability of the polymer. TGA characterizations of the pristine and used PVA-PES composite pervaporation membranes are shown in Fig. 8(a) and (b) respectively.

The results show that the weight loss for both the pristine and used PVA membrane begins at about 100°C, while there are two consecutive stages of weight loss. The first weight loss starting at about 100°C is mainly due to the adsorbed moisture; the 2nd stage of weight loss from 280°C to 300°C is probably contributed by the degradation of the sulfonic groups or the thermal desulfonation. In general the thermal degradation of PVA is initiated from the amorphous phase and extends to the crystalline region after melting [22]. The first stage of weight loss was very small about 2.07% but the weight loss at the second stage was significant (about 71.75%). A further small percent of weight loss (2.61%) took place at the 3rd stage at about 500°C. This was corresponding to the degradation of the polymeric backbone [12]. The primary decomposition temperatures of PVA membrane is 275°C for control PVA sample but it shifted to nearly 300°C for cross-linked PVA sample, which suggests the thermal stability of PVA membrane was significantly enhanced due to the formation of homogeneous cross linked layer. Clearly, cross linked PVA membrane used in the study imparted sufficient thermal stability. Additionally, we notice that the difference in weight loss of the used PVA membrane after a repeated cycle of operation was not much different from the original membrane.

**CONCLUSIONS**

Effect of temperature on molar flux, selectivity, and intrinsic membrane permeability was investigated with a commercial PVA-PES composite membrane crosslinked with glutaraldehyde during the pervaporation of water-acetic acid binary mixture over a wide concentration range. The degree of swelling increased almost linearly with increasing acetic acid concentration in the feed mixture ultimately resulting in an increase of the total flux. With an increase in feed temperature degree of swelling decreased marginally. At 25°C the maximum degree of swelling was found out to be 46.3%, which reduced to 39.5% at 65°C. The rate of increase of molar flux of water with temperature was found to be substantially higher than the rate of increase of acetic acid molar flux. At 70°C the total molar flux was found to be 0.4103 m³(STP)/m²h whereas the molar flux of water was found out to be 0.3342 m³(STP)/m²h and the acetic acid flux was 0.0526 m³(STP)/m²h, almost about seven fold lower. However the separation factor decreased with increasing temperature. At 50°C the separation factor was estimated to be 2.3, which decreased to 1.52 and 1.35 at 80°C and 90°C respectively. The apparent activation energy value of water permeation ($E_{pw}$) was significantly lower than that of acetic acid permeation ($E_{pHAc}$), indicating a higher separation efficiency of the membrane. Diffusion and partition coefficient for water and acid were also found to increase with temperature,
but the diffusion coefficient of water was substantially higher than that of acetic acid at a constant feed concentration. The membrane used in the present study could tolerate highly concentrated corrosive acetic acid, thus may be useful for dehydration of other organics. However, further efforts for flux enhancement are needed in the future.

Acknowledgment

The authors are grateful to The Institution of Engineers (India) for providing grant (File No: RDDR2015007) to carry out the work and Suggestions by the anonymous reviewers to improve the manuscript are also gratefully acknowledged.

Received : Nov. 19, 2017 ; Accepted : Nov. 19, 2018

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Research Article