When a temperature gradient is applied to a polymer solution, the polymer typically migrates to the colder regions of the fluid as a result of thermal diffusion (Soret effect). However, in recent thermodiffusion experiments on poly(ethylene-oxide) (PEO) in a mixed ethanol/water solvent it is observed that for some solvent compositions the polymer migrates to the cold side, while for other compositions it migrates to the warm side. In order to understand this behavior, a two-chamber lattice model for thermodiffusion in liquid mixtures and dilute polymer solutions has been developed. For mixtures of PEO, ethanol, and water, the compressibility and hydrogen bonding between PEO and water molecules are taken into account and Soret coefficients are calculated for a given temperature, pressure, and solvent composition. The sign of the Soret coefficient of PEO is found to change from negative (polymer enriched in warmer region) to positive (polymer enriched in cooler region) as the water content of the solution is increased, in agreement with experimental data. A close relationship between the solvent quality and the partitioning of the polymer between the two chambers is noted, which may explain why negative Soret coefficients for polymers are so rarely observed. The Soret effect in ethanol/water mixtures is also investigated and a change in sign of the Soret coefficient of water is found at high water concentrations, in qualitative agreement with experimental data.

KEY WORDS: ethanol; lattice model; PEO; poly(ethylene-oxide); polymer solution; Soret effect.


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1. INTRODUCTION

A temperature gradient applied to a fluid mixture generally induces a net mass flow, which results in the formation of a concentration gradient. This effect is known as thermodiffusion or the Ludwig–Soret effect [1–4].

The Soret coefficient \( S_T \) relates the steady-state concentration gradient to the imposed temperature gradient. By convention, the Soret coefficient of component \( i \) is positive if component \( i \) is enriched in the cooler region [5].

Thermal diffusion has long been used as an effective tool for separating mixtures of isotopes [4]. More recently, the effect has been used to characterize mixtures of complex fluids (see, for example, Refs. 5–8).

In liquid mixtures whose components differ widely in molecular mass, such as polymer solutions [6, 7] and colloidal suspensions [8], it is typically the heavier component that migrates to the cold region. There are, however, exceptions. In 1977, Giglio and Vendramini [9] found a negative Soret coefficient for poly(vinyl alcohol) in water. Very recently, de Gans et al. [10, 11] reported results of thermal-diffusion-forced Raleigh scattering (TDFRS) measurements on solutions of poly(ethylene oxide) (PEO) in mixtures of ethanol and water. In pure water, PEO shows the expected migration to the cold region of the fluid (\( S_T > 0 \)). However, in solutions with low water content, PEO is found to migrate to the warmer region of the fluid (\( S_T < 0 \)). Although changes in sign of the Soret coefficient have been reported for a number of liquid mixtures of small-molecule fluids, including alcohol solutions [12–16], the PEO/ethanol/water system appears to be the first polymer solution for which such a sign change has been observed.

Thermodiffusion in a binary fluid mixture is described by the flux of one of the components in response to a temperature and concentration gradient [1]. The flux is given by

\[
J_1 = -\rho D \nabla c_1 - \rho c_1 (1 - c_1) D' \nabla T, \tag{1}
\]

where \( D \) is the mutual diffusion coefficient, \( D' \) is the thermal diffusion coefficient of component 1, \( \rho \) is the total mass density, \( c_1 \) is the mass fraction of component 1, and \( T \) is the temperature. Here the pressure is assumed to be constant throughout the mixture and the flux \( J_1 \) describes the flow of component 1. Eventually, the system reaches a stationary state in which the flux \( J_1 \) vanishes. Inserting \( J_1 = 0 \) into Eq. (1) yields

\[
-\frac{1}{2} c_1 (1 - c_1) \nabla^2 c_1 \nabla^2 T = D'. \tag{2}
\]
The Soret coefficient of component 1 is the ratio of thermal and mutual diffusion coefficients:

$$S_T = \frac{D'}{D}.$$  \hspace{1cm} (3)

More generally, we define the Soret coefficient of component $i$ of a mixture as:

$$S_T = -\frac{1}{c_i} \left(1 - c_i \right) \frac{dc_i}{dT}.$$  \hspace{1cm} (4)

For ternary mixtures, such as PEO in a mixed solvent, concentration gradients and fluxes of two of the components are considered. While Eqs. (1)–(3) are generalized [1, 17], the Soret coefficient of component $i$ can still be defined through Eq. (4).

Thermal diffusion in liquid mixtures is not well understood and even the sign of the Soret coefficient cannot generally be predicted (see, e.g., Refs. 4–6). Due to the complexity of the task, attempts to extend the kinetic gas theory [18] of thermodiffusion to the liquid state have so far been unsuccessful [4, 6]. Molecular dynamics simulations (for a review, see Ref. 19) have become an important tool in the investigation of thermodiffusion in small-molecule liquids. Long computation times make it difficult, however, to address thermodiffusion in polymeric systems.

In this work, we investigate the Soret effect in dilute polymer solutions and liquid mixtures with the aid of a recently developed [20, 21] two-chamber lattice model. Following traditional experimental methods [1–4], we consider a system divided into two chambers of equal size that are maintained at slightly different temperatures. Particles are free to move between the chambers, which do not otherwise interact. If the pressure differences between the chambers are small enough to be neglected, the Soret coefficient can be determined from the difference in composition of the solutions in the two chambers [1–4]. We start by describing the lattice model for PEO in ethanol-water mixtures in Section 2. In Section 3 we introduce our two-chamber lattice model to determine Soret coefficients of liquid mixtures. Results of our calculations are presented in Section 4 and compared with experimental data, where available. In Section 5 we discuss the work presented here.

2. LATTICE MODEL FOR PEO IN ETHANOL/WATER MIXTURES

Solutions of high molecular weight poly(ethylene oxide) (PEO) in ethanol and water have interesting properties. Hydrogen bonding between PEO and water molecules plays an important role in aqueous solutions...
of PEO (see, e.g., Refs. 22, 23). Water is a good solvent for PEO at standard temperature and pressure. However, the solvent quality decreases with temperature and a miscibility gap opens above a lower critical solution temperature [23]. Ethanol, on the other hand, is a poor solvent for PEO at room temperature but the solubility increases with temperature [10]. In mixtures of ethanol and water at standard temperature and pressure, the water content determines the solubility of PEO. For the molecular weight considered in this work, the transition between poor and good solvent condition appears between a water content of 5% and 10% by mass [10, 11]. Light scattering experiments [10] show that the PEO chains expand with increasing water content, indicating that the addition of water improves the solvent quality.

In order to describe dilute solutions of PEO in mixtures of ethanol and water, we have developed a simple lattice model for a polymer chain in a mixed compressible solvent. At a given temperature, pressure, and composition, the solution is represented by a simple cubic lattice with $N$ sites, of which $N_c$, $N_s$, and $N_w$ are occupied by the polymer (PEO), the first solvent (ethanol), and the second solvent (water), respectively. In order to account for compressibility, we allow sites to be unoccupied so that $N = N_c + N_s + N_w + N_v$, where $N_v$ is the number of voids. The total volume of the lattice is $V = v_0 N$, where $v_0$ is the volume of one elementary cube.

Interactions between occupied nearest-neighbor sites are described by interaction energies $\epsilon_{ij}$, where the subscripts indicate the occupants of the sites (p for polymer, s and w for the solvents; voids are assumed to have zero interaction energies). In aqueous solutions, hydrogen bonding between PEO and water plays an important role (cf. Ref. 22). In order to account for these specific interactions, we introduce an orientational degree of freedom in the description of water. Each elementary cube occupied by water is assumed to have one special face. If this face is exposed to a polymer segment, the interaction energy is $\epsilon_{pw}$; otherwise $\epsilon_{pw}$ (non-specific); see the left panel of Fig. 1 for an illustration.

From an exact enumeration of all self-avoiding walks of length $N_c - 1$ on a simple cubic lattice (cf. Refs. 24 and 25), we determine the number $c(m)$ of chain conformations with $m$ segment pair contacts and the average squared radius of gyration $\bar{R}_g^2(m)$ as a function of $m$. In this work, $N_c = 17$. In solution, a chain conformation with $m$ pair contacts has $n_n = 4N_c + 2 - 2m$ nearest neighbor (nn) sites, which are occupied by $n_i, i \in \{s, w, v\}$ solvent particles and voids. With the aid of the random mixing approximation for all but the polymer contacts, the canonical partition function of the system can be written as
Fig. 1. Two-dimensional illustration of the two-chamber lattice model for PEO in mixtures of ethanol and water. In this figure, chamber A contains the polymer chain, indicated by circles connected by line segments. The unconnected circles represent sites occupied by ethanol, while the angular shapes represent sites occupied by water.

\[ Z_{\text{pol}}(N, T, N_w, N_s) = \sum_{m} c(m) \left[ \sum_{n_w} n_w (n_w - n_w(n_w - N_w - n_w)) \times \sum_{n_s} (n_s - n_w n_s) (N - n_s - N_c - (N_w - n_w N_s - n_s)) \right] e^{-\beta(m \epsilon_{pp} + n_s \epsilon_{ps}) \left( 5 e^{-\beta \epsilon_{pw}} - n + e^{-\beta \epsilon_{pw}}; n \right)} e^{-\beta E_r}, \] (5)

where, as before, \( c(m) \) is the number of chain conformations with \( m \) polymer–polymer contacts. The square brackets around the summation indices indicate that the summation is performed consistent with the available nearest-neighbor sites and the total filling of the lattice. The energy \( E_r \) denotes the contribution to the total energy due to solvent-solvent interactions evaluated in the random mixing approximation [26], cf. Eq. (8) below.

By performing partial summations over the terms in Eq. (5), the probabilities for specific sets of states can be determined. If we write the partition function as

\[ Z_{\text{pol}} \equiv \sum_{m, [n_w], [n_s]} Z_{m, n_w, n_s}, \] (6)

the average radius of gyration \( \langle R_g^2 \rangle \) is given by

\[ \langle R_g^2 \rangle = \frac{1}{Z_{\text{pol}}} \sum_{m, [n_w], [n_s]} \bar{R}_g^2(m) Z_{m, n_w, n_s}. \] (7)
In order to describe properties of ethanol–water mixtures and to perform the two-chamber calculations discussed below, the canonical partition function of a chamber without polymer is required. Consider a lattice of \( N \) sites occupied by the two types of solvent and voids, \( N = N_s + N_w + N_v \). Denoting the filling fractions of ethanol and water by \( \phi_s = N_s/N \) and \( \phi_w = N_w/N \) and assuming random mixing, the internal energy is given by Ref. 26

\[
E_{\text{nop}} = z^2 N \left( \epsilon_{ss} \phi_s^2 + \epsilon_{ww} \phi_w^2 + 2 \epsilon_{ws} \phi_s \phi_w \right).
\]

(8)

Accordingly, the canonical partition function of the lattice without polymer takes the form

\[
Z_{\text{nop}}(N,T,N_s,N_w) = 6^N (N_s N_w)^{N_s} e^{-\beta E_{\text{nop}}}.
\]

(9)

For a calculation of properties at a given temperature, pressure and composition, occupation numbers of the lattice are determined with an iterative procedure [20]. For a given value of the concentration of the polymer and one of the solvents, the concentration of the remaining solvent is calculated from the requirement that the pressure, given by

\[
P = k_B T v_0 \left( \frac{\partial \ln Z_{\text{pol}}}{\partial N} \right)_{N_s,N_w,N_P},
\]

(10)

has the desired value. The integer nature of the occupation numbers causes such an iterative procedure to not converge to the desired values. The determined system parameters have shown good agreement with the observed phenomena. The degree of freedom in the initial step was reduced by the use of a geometric-mean approximation for ethanol–water interactions. The Soret coefficient of water in ethanol–water mixtures changes sign at a water concentration of around 72% by mass.
In order to investigate thermodiffusion in ethanol–water mixtures, we determined a value of $\epsilon_{ws}$ from a comparison with tabulated values for the density of ethanol–water mixtures [27], weighted to insure a good fit at high water concentrations. In Fig. 2, we compare calculated and tabulated values for the density of ethanol–water mixtures at $T = 293$ K and $P \approx 0.1$ MPa. Symbols represent tabulated values [27], and the line represents densities calculated from our lattice model.

Since chain dimensions are an indicator for solvent quality, we present in Fig. 3 graphs for the chain dimensions calculated with the aid of the system-dependent parameters presented in Table I. The chain expands (solvent quality improves) with increasing water content of the solution, in qualitative agreement with experimental observation [10, 11]. For PEO in ethanol, the chain dimensions increase with increasing temperature while they decrease with temperature for PEO in water, in agreement with observed changes in solvent quality, cf. Ref. 23.
Table I. System-Dependent Parameters for the PEO/Ethanol/Water System

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \epsilon_{ij} ) in J/mol(^{-1} )</td>
<td></td>
</tr>
<tr>
<td>Lattice site volume ( v_0 )</td>
<td>5.255 \times 10^{-5} m(^3)/mol</td>
</tr>
<tr>
<td>Ethanol ( \epsilon_{ss} )</td>
<td>-2306 ( \text{s} )</td>
</tr>
<tr>
<td>Water ( \epsilon_{ww} )</td>
<td>0.3362</td>
</tr>
<tr>
<td>PEO ( \epsilon_{pp} )</td>
<td>0.6318</td>
</tr>
</tbody>
</table>
| Ethanol/Water mixed interaction \( \epsilon_{ws} \) | -3600 \( \text{s} \)
| PEO/Water mixed interaction \( \epsilon_{pw} \) | 2660 \( \text{s} \) \( n = 2660 \) \( \text{s} \) |
| PEO/Ethanol mixed interaction \( \epsilon_{ps} \) | 2660 |
Radius of gyration squared, $R_g^2$, as calculated from Eq. (7). The left panel shows chain dimensions as a function of solvent composition at a temperature $T = 293$ K, pressure $P \approx 0.1$ MPa, and a PEO concentration of 5 g·L$^{-1}$. The right panel shows the temperature variation at constant pressure of the chain dimensions of PEO in the two pure solvents, ethanol and water. The dashed line indicates the chain dimensions, $R_g^2(\theta^*)$, of the isolated 17 bead chain at the $\theta^*$ temperature of the infinite chain.

where, as before, square brackets indicate summations consistent with the total numbers of particles and lattice sites. Chamber A is considered the warmer chamber so that $\delta T = T_A - T_B > 0$, and equal-sized chambers are used, $N_A = N_B = N/2$. As we are performing the calculation of the terms in the sum of states, we monitor for each chamber the composition and the pressure of the mixtures. This allows us to calculate the average quantities for each chamber by performing weighted sums. For example, the average mass fraction of component $i$ in chamber A, $c_i, A$, is calculated from

$$c_i, A = \frac{1}{Q} \sum_{N_p, A=0}^{N} \left[ N_w, A \right] \sum_{N_s, A} \left[ N_s, A \right] c_i(N_w, A, N_s, A, N_p, A) \times Z(N_A, T_A, N_w, A, N_s, A, N_p, A) \times Z(N_B, T_B, N_w - N_w, A, N_s - N_s, A, 1 - N_p, A),$$

(13)

where $c_i(N_w, A, N_s, A, N_p, A)$ is the mass fraction of component $i$ in chamber A at this occupation of the chamber.
mixture without polymer, the equation simplifies to

\[ c_i, A = \sum [N_{w, A}] \sum [N_{s, A}] c_i (N_{w, A}, N_{s, A}, N_p, A) \times Z(N_{A, T_A, N_{w, A}, N_{s, A}, N_p, A}) \times Z(N - N_{A, T_B, N_{w, A}, N_{s, A}, N_p, A}). \]  

(14)

Following Eq. (4), the Soret coefficient of component \( i \) is calculated from

\[ S_T = -\frac{1}{c_i (1 - c_i)} \delta c_i \delta T, \]  

(15)

where \( c_i \) is the overall mass fraction of component \( i \), \( \delta c_i = c_i, A - c_i, B \), and \( \delta T = T_A - T_B \). 

S\(_T\) values determined in this way are independent of \( \delta T \) for a wide range of temperature differences (about \( 10^{-8} - 10^{-2} \)), in agreement with the definition of the Soret coefficient. While the lattice occupation numbers \( N_{k, A} \) are integers and yield discrete values for \( c_i (N_{w, A}, N_{s, A}, N_p, A) \), the mass fractions \( c_i, A \) and \( c_i, B \) are averages over very large numbers of lattice occupations. This leads to a smooth variation of calculated Soret coefficients with temperature and composition.

The probability to find the polymer in chamber A in this model is given by

\[ q_A = \frac{1}{Q} \sum [N_{w, A}] \sum [N_{s, A}] Z_{pol}(N_A, T_A, N_{w, A}, N_{s, A}, N_p, A) \times Z_{nop}(N - N_{A, T_B, N_{w, A}, N_{s, A}, N_p, A}). \]  

(16)

This probability is related to an internal energy difference of two chambers at the same temperature:

\[ q_A - \frac{1}{2} \approx -\frac{1}{4} \langle U_{nop} \rangle - \langle U_{pol} \rangle k_B T \delta T. \]  

(17)

The angular brackets indicate an average over all configurations of particles in two chambers at the same temperature, where the polymer is confined to one of the chambers. \( U_{pol} \) and \( U_{nop} \) are the average internal energies of the chamber with and without polymer at fixed composition. For the small temperature differences \( \delta T = 10^{-4} K \), corresponding to \( \delta T/T \approx 3 \times 10^{-7} \), employed in our calculations, values for the probability \( q_A \) calculated from Eqs. (16) and (17) agree to more than five digits. The excess probability \( q_A - \frac{1}{2} \) is proportional to the temperature difference and independent of the polymer concentration for dilute solutions.
We have applied our lattice model to ethanol–water mixtures and to solutions of PEO in ethanol/water mixtures under a variety of conditions. In Fig. 4 we present values for the Soret coefficient of water in ethanol–water mixtures calculated according to Eqs. (14) and (4). For comparison, we include experimental data by Kolodner et al. [14], Zhang et al. [15], and Dutrieux et al. [16]. The deviations between calculated values and experimental data are smallest at high water concentrations. This illustrates the importance of a good description of the thermodynamic properties of the mixture. In our earlier work [20], where we employed a geometric mean approximation for the mixed interactions, we found no sign change for the Soret coefficient of water.

In Fig. 5 we present values for the Soret coefficient of PEO at room temperature (293 K), atmospheric pressure (0.1 MPa), and a PEO concentration of 5 g·L⁻¹, calculated according to Eqs. (4) and (13). For comparison, we include experimental data by Wiegand and coworkers [10, 28].
Both experimental and theory give a change in sign of the Soret coefficient as the water content of the solution is increased. For low water concentrations, the polymer is more likely to be found in the higher temperature chamber; for high water concentrations, the opposite is true. Differences between theory and experiments are most pronounced at low water concentrations, where our calculations overestimate the Soret effect. This is a consequence of our choosing a mixed interaction parameter $\epsilon_{ps}$ that emulates for short chains the poor solvent conditions that long PEO chains experience in ethanol [21]. A comparison of Fig. 5 with the chain-dimension graph (Fig. 3) shows a correlation between solvent quality and thermodiffusion. In general, as the solvent quality increases, indicated by an increase in chain dimensions, the Soret coefficient becomes more positive.
Lattice Model for Thermodiffusion in Polymer Solutions

We present a detailed enumeration of partition functions for polymer-solvent systems to study thermodiffusion. By considering the polymer-solvent system as a whole, we avoid the common approximation of treating the polymer and solvent as non-interacting species. We focus on the interactions between solvent solvent particles and solvent-polymer sites, which are evaluated in a random-mixing approximation. The radius of gyration of the polymer chain in solution is calculated using these partition functions, allowing us to monitor the solvent quality of the solution. To investigate thermodiffusion, we divide the lattice into two non-interacting sublattices of equal size, maintained at slightly different temperatures. The Soret coefficient of component $i$ is determined from the difference between the average concentrations of component $i$ in the warm and cold chambers. Kinetic-energy contributions are neglected, but the heat of transport is approximated by the difference in potential energy. The probability to find the polymer in the warmer chamber is related to the difference in average internal energy, reflecting both enthalpic and entropic contributions.

We have investigated the Ludwig–Soret effect in mixtures of ethanol and water, observing a qualitative agreement with experimental data. Since our model is simple, we do not expect quantitative agreement with experiment. We are currently developing a model that includes specific interactions between molecules to improve the description of ethanol–water mixtures and solutions of PEO in such mixtures.

Our model reproduces some of the important thermodynamic properties of the PEO/ethanol/water system. For PEO in mixed solvents, the solvent quality, as monitored by the radius of gyration, increases with the water content of the solution [10, 11]. Similarly, an increase in temperature increases the solvent quality for mixtures with low water content. However, for mixtures with high water content, an increase in temperature reduces the solvent quality, in agreement with observations on PEO in water (cf. Ref. 23). Our two-chamber approach allows us to calculate Soret coefficients of PEO for given temperatures, pressures, and compositions of the solution.
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solutions [30], the results are independent of the polymer concentration. In qualitative agreement with experimental data of de Gans et al. [10, 11] and Kita et al. [28], the calculated Soret coefficients are negative for solutions with low water content and positive for solutions with high water content. This is consistent with the expectation that the partitioning of the polymer between the chambers is influenced by the solvent quality. In good solvent conditions, the Soret coefficient of the polymer becomes more positive as the solvent quality increases. On the other hand, the values of $S_T$ diverge near a mixture critical point [32] and are thus expected to increase near the coil-globule transition in a dilute polymer solution. Recent experiments of Kita and Wiegand [33] show indeed a maximum in $S_T$ at the coil-globule transition of poly(N-isopropylacrylamide) in water and suggest a minimum in $S_T$ near the transition. The calculations presented here cannot be applied to systems near phase transitions. However, we are currently working on an extension of our model that we hope will allow us to investigate the PNIPAM/water system.

While a typical experiment on polymers in good solvents is expected to yield positive Soret coefficients, we expect negative Soret coefficients to be observed for polymers that would be insoluble were it not for specific interactions between solvent molecules and sites on the polymer. It appears that both polymer systems for which negative Soret coefficients have been observed, the solutions of PEO in a mixed ethanol/water solvent [10, 11, 28] and the solution of poly(vinyl alcohol) in water [9, 31], belong to this category.

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