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# Prediction of Maxwell–Stefan diffusion coefficients in polymer–multicomponent fluid systems



Andrzej Kubaczka

Department of Process Engineering, Opole University, ul. Dmowskiego 7-9, 45-365 Opole, Poland

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## ABSTRACT

Calculations of mass fluxes in multicomponent fluids based on the system of generalized Maxwell–Stefan equations (GMSE) is preferably used because Maxwell–Stefan (M–S) diffusion coefficients are symmetrical and have a clear physical meaning, as they reflect the binary friction forces between compounds in the system. For the calculation of the mass transport of a multicomponent fluid in the polymer basing on GMSE, it is necessary to have M–S diffusion coefficients. This paper proposes a method that allows their calculation using widely available self-diffusion coefficients and binary diffusion coefficients for infinitely diluted mixtures. The proposed method was compared with the method of J.S. Vrentas and Ch.M. Vrentas [Restrictions on friction coefficients for binary and ternary diffusion, *Ind. Eng. Chem. Res.* 46 (2007) 3422–3428] that allows to predict diffusion coefficients of the generalized Fick's equation (GFE) for ternary systems based on self-diffusion coefficients. In the computational experiment, values of molar fluxes of methanol and toluene in poly(vinyl acetate) calculated in a wide range of concentrations using both methods were compared. Because the proposed method calculates molar fluxes relative to the average molar velocity and the method cited above – mass fluxes relative to the average mass velocity, for the sake of clarity of the comparison, the derivation of J.S. Vrentas and Ch.M. Vrentas was repeated using molar concentrations and mole fractions instead of mass density and mass fractions and molar fluxes were obtained as in the proposed method. In both methods, derivatives of chemical potentials were calculated in the same way, using the UNIFAC-FV method for which equations on derivatives of activity coefficients were derived. The computational experiment showed that the values of fluxes calculated in ternary methanol–toluene–poly(vinyl acetate) system using both significantly different methods are very close.

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## 1. Introduction

Membrane separations technologies are likely to play an increasingly important role in reducing the environmental impact and operational costs of industrial processes [1]. Membrane techniques are promising to replace energy inefficient classic

E-mail address: [kubaczka@uni.opole.pl](mailto:kubaczka@uni.opole.pl)

separation processes that require a phase change in the mixture that is to be separated. Furthermore, membrane separation units are smaller than other types of plants. With the decrease in the ratio between the equipment size and the production capacity, membrane technologies address the requirements of process intensification.

Separation through membranes is usually based on the transport phenomenon of the molecules in the membrane material. The importance of this phenomenon has led to the development of numerous physical theories for the estimation of mass fluxes in the membrane materials [2–17]. An estimation of these fluxes is essential for processes developing (membrane materials, plants) and requires the availability of mutual diffusion coefficients or Maxwell–Stefan (M–S) diffusion coefficients. Different diffusion coefficients are required for processes based on porous membrane, and different – for a non-porous one [16, 17].

At present, diffusion coefficients in polymers are often determined by measurements that are usually complex and time-consuming, and demand expensive instruments to provide the required accuracy. In many cases, it is easier to carry out self-diffusion experiments than to perform experiments which measure mutual or M–S diffusion coefficients exclusively for more than binary systems [18–20].

Because self-diffusion coefficients describe the mobility of molecules, a number of molecular theories develop expressions for self-diffusion coefficients rather than for mutual or M–S ones. Among others, such expressions were derived using the free-volume theory of diffusion. [2–5, 7, 10].

Numerous works of Vrentas et al. [21, 24–28] and works [22, 23, 29–32] have shown, however, that with certain assumptions, the mutual diffusion coefficients may be related by dependences with self-diffusion coefficient. Values of mutual diffusion coefficients can then be calculated using the self-diffusion coefficients determined either experimentally or using predictive methods.

The works [12, 29–32] share a common concept involving the assumption that the ratio of the friction coefficients  $\psi_{ij}$  defined by Bearman [33] is constant and respectively equal to the molar volume ratio or the molar mass ratio. Additional equations obtained this way enable to solve the system of Bearman's equations and express mutual diffusion coefficients with the function dependent on self-diffusion coefficients and concentration of components in the system.

Vrentas and Vrentas [28] demonstrate that Bearman's equations system can also be solved by assuming that there are geometric dependences between friction coefficients. Although these dependences result also from accepting the constant ratio of the coefficients, this assumption is only sufficient but not necessary conditions for the geometric dependence to be true. Therefore, the assumption of the geometric relationships between the coefficients is a preferable solution because it demonstrates that their ratio does not need to be constant, but may vary with concentrations in the system. The solution of Bearman's equations [33] for the binary system involving the geometric dependence shows that the identification of one self-diffusion coefficient does not determine the value of the second one, as in case of assuming a constant ratio. Both self-diffusion coefficients can be independently determined and their ratio determines the value of the ratio between friction coefficients.

Based on these findings and on the demonstration that neither the postulate of thermodynamics of irreversible processes regarding the entropy inequality in the system, nor the Gibbs–Duhem equation imposes any restrictions on friction coefficients, Vrentas and Vrentas [28] suggest to assume for the ternary system that geometric dependences – similar to that of the binary system – appropriately apply between all friction coefficients in the system. This assumption enables the work [28] to derive equations that define the mutual diffusion coefficients (coefficients of the generalized Fick's equation (GFE)) as a function of self-diffusion

coefficients, system concentrations and chemical potential derivatives.

In parallel with works intending to determine the components mass fluxes in the polymer, based on the generalized Fick's equation, for which mutual diffusion coefficients have been determined either experimentally or as a function of the self-diffusion coefficient and derivatives of chemical potentials, many studies [13–17, 35, 36] have been published in which the solution has been derived from the generalized Maxwell–Stefan equations whose advantages in comparison with the generalized Fick's equation are shown on examples, among others, in [17].

The selection of the Maxwell–Stefan equations has been dominated by the argument that the diffusion coefficients in this equation, the so-called Maxwell–Stefan (M–S) diffusion coefficients, represent the binary interaction of friction forces between molecules; therefore they are symmetrical and also less sensitive to the change of the concentration in the system. The symmetry of the coefficients means that to determine fluxes e.g. for the ternary system, the knowledge of three coefficients (instead of four as in case of the generalized Fick's equation) is sufficient; furthermore, the coefficients are free from chemical potential derivatives.

Most of the existing GMSE used in systems with the polymer, bypasses the original form of the GMS equations in which concentrations are expressed as mole fractions [16, 34], whereas mass fluxes – as molar fluxes relative to the average molar velocity. However, the applied GMSE form involves mass or molar fluxes relative to the mass or volume average velocity and concentrations expressed by mass or volume fractions [13, 14], as well as the form with molar fluxes relative to the fixed coordinate system and concentrations expressed as above [15, 35, 36]. This selection of the reference of the system is justified by the fact that the molar mass of the polymer is usually not accurately defined and, thus, the molar concentration of polymer in the system is not well-defined. Elimination of this disadvantage by using mass or volume fractions in the system has turned out to be apparent only, as it required the introduction of modified diffusion coefficients that do not retain the Maxwell symmetry and also depend on the molar mass of the polymer [13–15]. Therefore, the molar mass of the polymer has remained in the system, only that it has been moved from concentrations into diffusion coefficients. The loss of symmetry of modified M–S diffusion coefficients hinders the process of their experimental determination because e.g. for the ternary system, one needs to determine six instead of three coefficients.

In [13, 15, 35], the GMS system has been a platform to calculate mass fluxes and diffusion coefficients have been determined experimentally or calculated from empirical relationships for which parameters have also been determined experimentally. In [36], the M–S diffusion coefficients have been calculated using the method proposed in [37]. The method, based on the free-volume theory, enables to calculate M–S coefficients using universal constant and molecular parameters of the polymer and compounds. The authors of [37] do not recommend their method for mixtures whose compounds greatly differ in shape or size.

Considering the benefits resulting from the GMSE system compared with the GFE system and the current ability to predict the value of self-diffusion coefficients, for systems of various compounds with different (amorphous, cross-linked, crystalline) polymers enabled by the method derived from the free-volume theory [38–45], and examples [28, 29] of possible relations of mutual diffusion coefficients with self-diffusion coefficients, this work propose the method for predicting M–S diffusion coefficients. This method enables the calculation of M–S diffusion coefficients if both self-diffusion coefficients and the values of binary liquid diffusion coefficients at infinite dilution are known.

Because the application of the concentrations system different from the original to GMSE, does not release them from the polymer molar mass and subsequent modifications of the M–S

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