Journal of Molecular Structure 480–481 (1999) 563–567

Journal of
MOLECULAR
STRUCTURE

Potassium transport through liquid membranes using spectral and chemometric methods

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Received 24 August 1998; received in revised form 2 November 1998; accepted 2 November 1998

Abstract

Chemometric techniques were applied to follow the transport of potassium through a chloroform membrane, using ternary mixtures of the isomeric anions, 2,4-dinitrophenolate (2,4-DNP) and 2,5-dinitrophenolate (2,5-DNP) with also 2-nitrophenolate (*ortho*-). Some spectral differences can be observed in the UV–Vis region, although 2,4- and 2,5-DNP have very similar spectra. Using the trilinear decomposition method (TLD), it is possible to estimate the spectra of the pure components and simultaneously their kinetic profiles. The estimated spectral profiles are in excellent agreement with experimental results and the kinetic profiles agree with those obtained by ordinary least squares (OLS). The transport rates are calculated and compared. The *ortho*- isomer has a very small rate of transport. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Chemometrics; Liquid membranes; Trilinear decomposition; Nitrophenolates

1. Introduction

Membrane systems yield high selectivity as well efficiency in the separation of neutral and ionic chemical species when compared to many other systems [1,2]. In particular, carrier-mediated transports are highly specific in molecular recognition and can be used on a continuous basis in performing separation [3]. This capability of making efficient and selective separations has led to the study of several membrane types as well as many carrier molecules. Among all membrane systems, the bulk liquid membrane is the one most frequently used to make screening and modeling studies of specific carrier-mediated systems, although it is not appropriate to be used in practical large scale separation schemes [4].

Macrocycles such as crown ethers are ideal candidates for use as carrier reagents as they have highly hydrophobic exteriors, but the inner hydrophilic cavity has a high affinity for cations and selectivity among them [5,6]. Members of the crown ether class of macrocyclic compounds interact with specific alkali metal cations according to their fitting into the crown cavity. Macrocycles containing an 18-crown-6 macrocyclic core show size-based selectivity for K^+ over the other alkali metal cations. When neutral macrocycle carriers are used to transport cations, anions must accompany the cation-carrier complex in order to maintain electrical neutrality. Hence, the extraction of the anions is important in determining transport rates and the total efficiency of the transport [7].

Born's equation shows that the potential energy (w) of the transfer of a species with anionic radius r and charge z from a phase of dielectric constant ϵ to

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PII: S0022-2860(98)00823-0

Table 1
Mixture concentrations used for transport experiments

Mixture #	(*ortho*) × 10^3 mol l^{-1}	(2,4-DNP) × 10^3 mol l^{-1}	([2,5-DNP) × 10^3 mol l^{-1}
01	3.0	1.5	4.0
02	1.5	1.5	5.0
03	3.0	1.0	3.0
04	—	1.5	5.0

another phase of dielectric constant ϵ_m, at constant temperature T, decreases as the ionic radius of this species increases [8] according to the following equation

$$w = \frac{z^2 e_0^2}{8\pi\kappa T\epsilon_0 r}\left(\frac{1}{\epsilon_m} - \frac{1}{\epsilon}\right)$$

where κ is the Boltzmann's constant, e_0 the electron charge, and ϵ_0 the vacuum electric permitivity.

In the present work, all the counterions used have the same charge ($-$ 1), so it was possible to quantify K^+ by analyzing the anion at the receiving phase by UV–Vis measurements [9], as for any anion being transported, a K^+ was simultaneously transported.

2. Experimental

In this work, the isomeric anions, 2,4-dinitrophenolate (2,4-DNP) and 2,5-dinitrophenolate (2,5-DNP), and also 2-nitrophenolate (*ortho*-) were employed. Some spectral differences can be observed in the UV–Vis region, although 2,4- and 2,5-DNP have very similar spectra.

In the experiments involving simultaneous transport of three salts, an U-tube system connected to a continuous flow system which consists of a HP 8452 A diode array spectrophotometer, a peristaltic pump, a magnetic stirrer and a thermostated water bath. Each one of the mixtures indicated in Table 1 was employed as source phase. A 1.0×10^{-2} mol l^{-1} solution of 18-crown-6 in chloroform was used as membrane. Such concentration ensures that there was enough carrier in the membrane, avoiding alterations in the transport rate behavior caused by a limited concentration of this component. Spectra at the receiving phase (distillated water at the beginning) were recorded for the three ternary mixtures at one-minute intervals for 85 min, within the range from 190 to 820 nm, at 2 nm intervals.

A third order array of intensity values (316 × 85 × 3) was obtained by stacking the sequential spectra of all the samples along the membrane transport time.

3. Theory

Hyphenated instruments (such as Diode Array Spectrophotometers) are ideal to follow experiments of transport through membranes and can generate third order data. Rank annihilation factor analysis (RAFA), introduced by Ho et al. [10], was later reformulated and extended by Sanchez and Kowalski [11,12], giving rise to the non-iterative methods GRAM (Generalized Rank Annihilation Method) [11,13] and TLD (TriLinear Decomposition) [12]. These are efficient methods for analyzing three-way data sets, although, GRAM is restricted to the analysis of two samples while TLD has no such restriction. TLD performs a triadic decomposition on the data set obeying the trilinear model described by the following equation

$$R_{ijk} = \sum_{n=1}^{N} X_{in} Y_{jn} Z_{kn} + E_{ijk},$$

where R_{ijk} represent the elements of the third-order array and N is the number of factors in the model. **X**, **Y** and **Z** are matrices describing the pure spectra, the kinetics and the relative contribution of each physical component, respectively. The rank of each pure component matrix is unitary in the absence of noise, so that the number of pure components is equal to the total rank. In the presence of spectral non-linearities and noise, the rank of each pure component is no longer one and to correct it, additional factors are added to the model. Analyzing the estimated profiles,

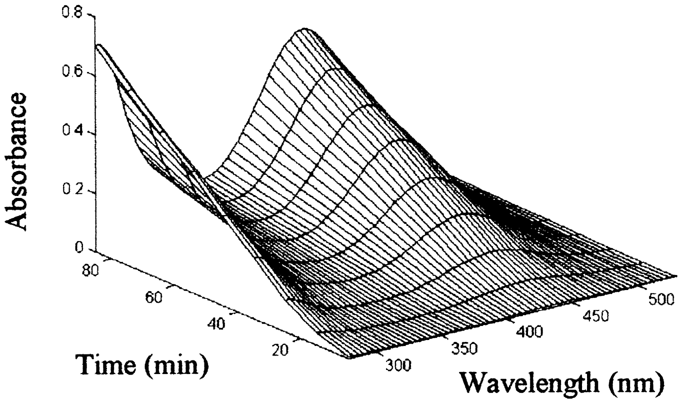

Fig. 1. Experimental data for a representative mixture sample.

it is possible to determine if a minor factor describes a nonlinear affect or a particular chemical species.

4. Results and discussion

The analyses were performed on the (81 × 126) truncated matrices with wavelengths ranging from 278 to 530 nm, below 278 nm the chloroform has a strong absorbance and above 530 nm there is no significant visual absorption of any compound. The time interval was 5–85 min. The spectra recorded for times less than 5 min were discarded to ensure stability of the system. Fig. 1 shows the 3D plot for one of the samples.

Singular value decomposition (SVD) was applied to determine the number of factors needed to model the transport through the membrane. Each individual sample is well described by two factors although a quite small third factor could describe non-random variance. The same result is obtained when the first three mixtures (01, 02 and 03) are juxtaposed either row-wise or column-wise and analyzed as a single matrix (Table 2). That is a strong indication that two of the isomers are freely transported through the membrane. The slight discrepancy between the column-wise and row-wise analysis suggests the presence of non-linearities in the X mode (time domain).

According to SVD/Variance analysis, the application of the TLD method to the combined mixtures yielded the pure spectra and the respective kinetic profiles (conc. × time) for the isomers (2,4-DNP and 2,5-DNP). Although this two-factor model seems quite adequate to describe the phenomenon, it is known that the source phase contains a third component. Also, the results from Table 2 indicate that the data does not follow a perfectly linear model. So, the third factor could describe non random variance and the model should be tested with additional factors. The third factor in the model yields a spectral profile but its kinetic profile does not have a physical meaning, supporting the conclusion that this extra factor does not describe the third (*ortho*-) compound in the mixtures. The estimated spectral profiles for 2,4-DNP and 2,5-DNP, done by a three-factor model

Table 2
Singular values and total percent variance of mixtures 01, 02 and 03 column- and row-wise juxtaposed (C- and R-, respectively) for the first four factors

C-Singular values	Total % Variance	R-Singular Values	Total % Variance
33.2497	99.9494	33.2031	99.6692
0.7180	0.0466	1.8774	0.3187
0.1916	0.0033	0.3316	0.0099
0.0805	0.0006	0.1503	0.0020

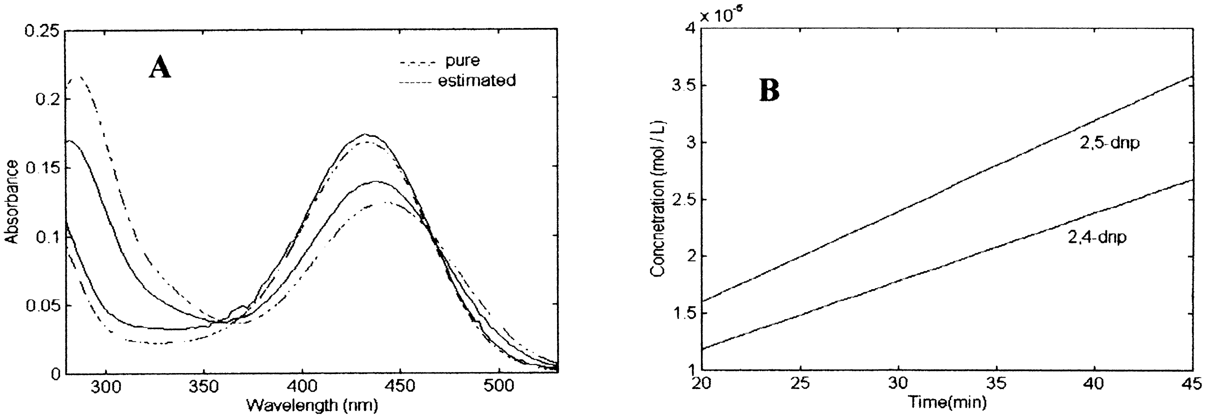

Fig. 2. TLD results. (a) Pure experimental and estimated absorption spectra (normalized intensities); (b) estimated kinetic profiles.

and their respective pure spectra, are presented in Fig. 2(a). The estimated spectra, with peaks at 436 and 439 nm for 2,4- and 2,5-DNP respectively, show excellent agreement (within the experimental error) with the respective pure spectra, which have peaks at 434 and 444 nm. In summary, these results indicate that only 2,4-DNP and 2,5-DNP are diffused through the membrane in reasonable amounts, when compared to the *ortho*-nitrophenolate. In Fig. 2(b), the kinetic curves for the two resolved isomers are shown.

As the pure experimental spectra are available, the ordinary least squares (OLS) method was applied separately to each mixture. Their kinetic profiles are very similar and the results for one of the mixtures are shown in Fig. 3(a). As can be seen, the *ortho*- has an extremely low concentration at the receiving phase, which is in agreement with the previous results from TLD. One extra sample (mixture 04, with two components) was also studied, aiming to verify the behavior of the *ortho*- compound. Fig. 3(b) shows that, in the absence of this compound, the transport of 2,4- and 2,5-DNP are greatly affected, being increased.

The transport rates, which are the slope of the kinetic curves, were calculated and are shown, together with some previous results, in Table 3. In the first column are the rates when only one compound is transported at a time [14]. Some previous results from our group showed that the Gibbs free energy of complexation of *ortho*- with the carrier (18C6) in chloroform is smaller (in module) than that of the dinitro isomers. Hence, it has a smaller tendency to complex and shows a

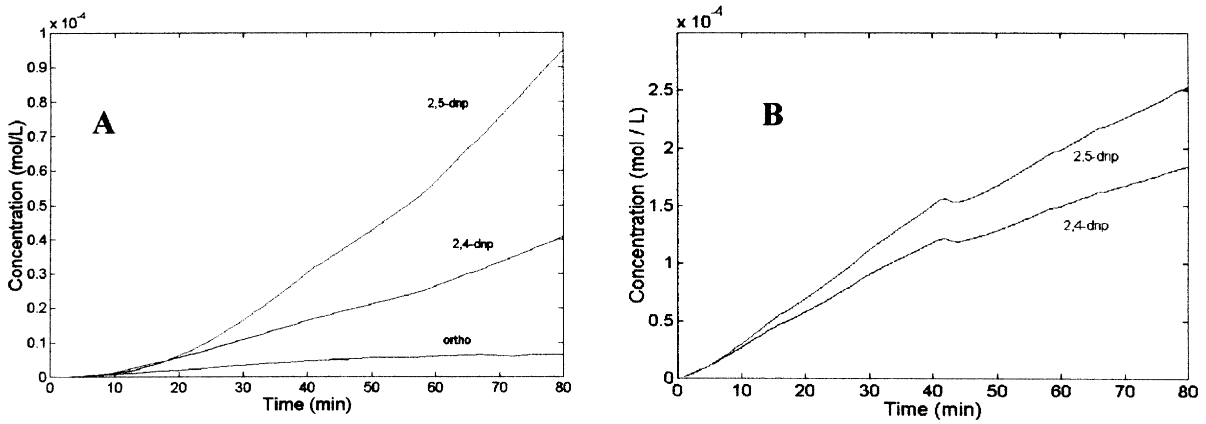

Fig. 3. Kinetic profiles obtained by OLS method. (a) Mixture 02; (b) mixture 04.

Table 3
Transport rates of each compound in different situations (mol min^{-1})

	Single [14][a]	Binary[b]	Ternary[c] OLS	Ternary TLD
Ortho	4.44×10^{-6}	—	7.55×10^{-8}	—
2,4-DNP	1.37×10^{-5}	2.29×10^{-6}	4.54×10^{-7}	3.84×10^{-7}
2,5-DNP	2.38×10^{-5}	3.21×10^{-6}	1.25×10^{-6}	1.51×10^{-6}

[a] Results for univariate method.
[b] Without *ortho*- compound.
[c] Mean values.

smaller rate of transport. The third and fourth columns contain the results obtained from this work for the ternary mixtures. Note that the rates obtained by TLD method are in very good agreement with those from OLS, which are the mean values for mixtures 01, 02 and 03. Comparing these values with the respective values from column one, it can be seen that rates for ternary mixtures are much lower. In addition for the binary mixture studied, where *ortho*- was absent, the transport observed for the two isomers is faster (second column in Table 2). As the experiments were designed so to have enough carriers at the membrane, it is possible that *ortho*- accumulates at the interface source phase/membrane and does not cross the membrane easily, reducing the effective free area of complexation.

5. Conclusions

It was shown in this work, that chemometrics, specially the TLD method which does not need any prior knowledge of pure component spectra, is an excellent option in studying transport phenomena. The pure spectra are estimated, even though when they are so similar and overlapped as in this case, and simultaneously, the kinetic profiles. The results are in excellent agreement with experimental results and the kinetic profiles agree with those obtained by OLS. It was shown that only 2,4-DNP and 2,5-DNP are diffused through the membrane in reasonable amounts, when compared to the *ortho*-nitrophenolate. The calculated transport rates show that the *ortho*-nitrophenolate besides having a very small rate of transport when compared to the two isomers also slow their transport in the ternary mixtures.

Acknowledgements

The authors acknowledge the financial support from CNPq and FAPESP for carrying out this work.

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