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Physicochemical Parameters of the Transport of Amines and Amino Acids through Liquid Membranes by Macrocyclic Ligands

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ABSTRACT

Both interphasic water/organic solvent transfer and transport through liquid membranes may be influenced to a certain extent by several physicochemical factors like the structure of the ligand, the nature of the cation, the type of the anion (acting as a counterion), the interfaces thermodynamic equilibria, and the nature of the membrane solvent. The effects of these factors upon both the transfer and the transport through liquid membranes of complexes of some amino acids (L-tryptophane, L-methionine, L-phenylalanine, L-leucine, L-isoleucine, and L-valine) and amines (methylamine, dimethylamine, and *n*-propylamine) in cationic forms with various macrocyclic ligands (18-crown-6, benzo-18-crown-6, and dibenzo-18-crown-6) have been investigated.

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Key Words. Amino acids; Amines; Transfer; Transport; Macrocyclic ligands

INTRODUCTION

Liquid membranes have been extensively investigated for their applications in separation and purification procedures, including the selective transport of transition metal ions, recovery of trace metals, analysis, separation of components of mixtures, and extraction of toxic species from biological fluids (1–6). The active transport of chemical species also provides models for biological transport mechanisms. All successful applications presume a quantitative understanding of the transport processes. Numerous attempts have been reported on modeling macrocyclic-mediated cation transport through liquid membranes (7–15).

The membrane transport of amino acids and amines plays an important role in many biological systems and provides means for further development of new methods in separation science. Generally, the main factors which influence both interphasic water/organic solvent transfer and transport through membranes are the structure of the ligand, the nature of the cation, the structure of the anion, and the nature of membrane solvent. The thermodynamic properties of a ligand–cation complex (stability, enthalpy, and the formation entropy) also have an important influence on the transfer and transport processes. The kinetic properties, such as the rates of complexation and the decomplexation of complexes at interfaces, play an important role not only in determining the stabilities of macrocyclic complexes but also in transport rates through liquid membranes. The concentration of compounds in the aqueous phases affects the extractibility into the membrane and, obviously, the transport rates. Further, the transport rates also depend on the geometry of the transport cell used in a specific experiment.

Some physicochemical factors involved in both interphasic water/organic solvent transfer and transport through liquid membranes (e.g., methylene chloride, chloroform, and 1,2-dichloroethane) of some cationic complexes of amino acids and amines ($R—NH_3^+$) with macrocyclic ligands (L) as ion pairs ($R—NH_3L^+A^-$) with various anions (A^-) have been investigated. They have been related to the structure of the ligand, the nature of the cation, the thermodynamic properties of the macrocyclic complexes, the type of anion, and the nature of the membrane solvent in the transfer and transport of the complexes of amino acids and amines.

EXPERIMENTAL

The following amines and amino acids were employed: methylamine (Fluka), dimethylamine (Fluka), *n*-propylamine (Fluka), L-tryptophane (L-

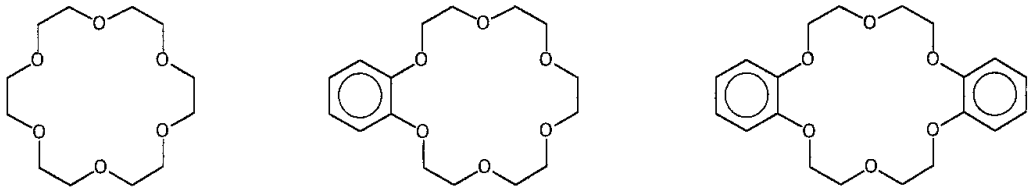

FIG. 1 The structure of the crown ethers utilized throughout the experiments: 18-crown-6 (18C6), benzo-18-crown-6 (B18C6), and dibenzo-18-crown-6 (DB18C6).

Trp, Fluka), L-leucine (L-Leu, Fluka), L-phenylalanine (L-Phe, Aldrich), L-isoleucine (L-Ile, Fluka), L-methionine (L-Met, Sigma) and L-valine (L-Val, Fluka), all of the highest purity commercially available. The macrocyclic ligands were 18-crown-6 (18C6), benzo-18-crown-6 (B18C6), and dibenzo-18-crown-6 (DB18C6) from Merck; they were used without further purification (Fig. 1).

The values of the extraction constants (log K_{ex}) have been determined by spectrophotometric measurements. Equal volumes of 6×10^{-4}–3×10^{-3} M for the amino acid and 8×10^{-5} M for the picric acid or tropaeolin 00 at pH 2.02 in the aqueous phase were extracted with a macrocyclic ligand of 4×10^{-3}–2×10^{-2} M in the organic phase. The complexing ratio $RNH_3^+ : L : A^-$ was 1:1:1, where RNH_3^+ stands for the protonated amino acid, L is the macrocyclic ligand, and A^- is the counterion of picric acid or tropaeolin 00. The volume ratio of the aqueous and organic phases in the extraction process was 1:1. The organic solvent and water were saturated with each other prior to use in order to prevent volume change during extraction. A Perkin-Elmer UV-Visible Spectrometer, Model 559 was used for recording the electronic spectra of the organic phases. The pH determinations were carried out by a digital MV-870 Pracitronic pH-meter with a glass electrode and saturated calomel reference electrode. The stability constants for the reactions of several amino acids or amines with 18C6 in methanol were determined using calorimetric titrations (Tronac Model 450). Anhydrous methanol (Merck; H_2O content less than 0.01%) was used as the solvent. All solvents (1,2-dichloroethane, chloroform, and methylene chloride) were spectroscopically pure. Extraction of the amino acids amphionic species from water onto an organic solvent as the ion pair $R—NH_3L^+A^-$ may be evaluated by using Eq. (3). Picric acid and tropaeolin 00 [4-(4′-anilinophenylazo)benzenesulfonic acid, Fluka] were used as counterions.

The transport experiments were performed using a device reported earlier (14). The device consists of two concentric tubes. The inner tube contains

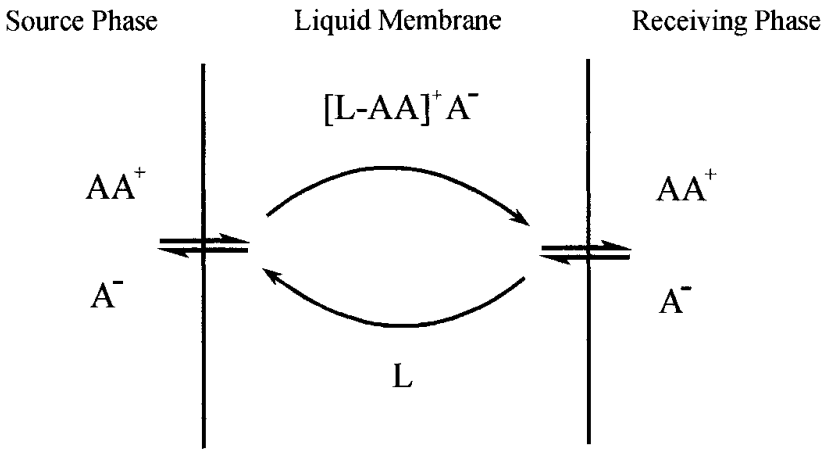

FIG. 2 Mechanism of the ion pair mediated transport through liquid membrane. AA^+: amino acid or amine; A^-: anion; L: ligand; $[L\text{-}AA]^+A^-$: ion pair.

the source phase (5 mL solution of 0.16 mM protonated amino acid or 0.20 mM protonated amine and 1.6 mM picric acid) and acts as a stirrer. The receiving phase (5 mL of 0.1 N LiOH) and the membrane phase (30 mL solution of macrocyclic ligand, 10 mM, in organic solvent) are introduced in the outer tube. The pH 2.02 in the source phase is ensured by the use of HCl. The phases are stirred at 180 rpm for 6 hours. Each experiment was repeated three times. Reproducibility was within $\pm 10\%$.

The mechanism proposed for ion pair mediated transport (5, 7, 14, 24) is presented in Fig. 2. The transport mechanism is of the active type (a coupled transport of amines or amino acids and hydrogen ions from the source phase to the receiving phase is ensured) assisted by a pH gradient. The overall transport process consists of a mixture of diffusion steps and complexation/decomplexation reactions at two independent and possible different interfaces (14). The chromatographic determinations were performed with a Carlo Erba 6000 apparatus, while the concentrations of the amino acids in the two phases of the system were determined with a Carlo Erba 3A28M amino acid analyzer.

RESULTS AND DISCUSSION

The possibility of transferring some amines and amino acids from water onto an organic phase (membrane) may be investigated by changing them into hydrophobic entities. The ability of the macrocyclic ligands 18C6, B18C6, and DB18C6 to lipophilize amines and amino acids cations by complexation suggests their potential use as selective extraction agents and carriers through liquid membranes.

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The equilibria of the distribution in extraction processes at the water/organic solvent interfaces of the complexes of amines and amino acids during the transport through liquid membranes were studied.

The liquid/liquid equilibrium of extraction is described by

$$(R—NH_3^+)_w + (L)_s + (A^-)_w = (R—NH_3LA)_s \quad (1)$$

where w and s define the aqueous and the organic phases, respectively.

The distribution coefficient (D) of the amino acid between the organic phase and the aqueous phase is presented by

$$D = [R—NH_3LA]_s/[R—NH_3^+]_w \quad (2)$$

The extraction equilibrium constant, K_{ex}, is given by

$$K_{ex} = \frac{[R—NH_3LA]_s}{[R—NH_3^+]_w[L]_s \cdot [A^-]_w} \quad (3)$$

Modification of Eq. (3) leads to the expression

$$K_{ex} = \frac{D}{[L]_s \cdot [A^-]_w} \quad (4)$$

The distribution coefficient, K_d, of the ligand between the organic and the aqueous phases is given by

$$K_d = [L]_s/[L]_w \quad (5)$$

The equilibrium constant K of the reaction between the amino acid or amine and the macrocyclic ligand is given by

$$K = \frac{[R—NH_3L^+]}{[R—NH_3^+] \cdot [L]} \quad (6)$$

The Distribution of the Crown Ether

The values of K_d for the partitioning of 18C6 between the organic and the aqueous phases are given in Table 1 as a function of the pH values. Their

TABLE 1
Distribution Coefficients (K_d)[a] of 18C6 in the 1,2-Dichloroethane/Water System at 25 ± 1°C

pH of the aqueous phase	K_d
2.02	0.760
6.45	1.035
13.05	1.204

[a] $K_d = [18C6]_s/[18C6]_w$.

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TABLE 2
Experimental Data of the Transport of Some Amino Acids and Amines through 1,2-Dichloroethane by Various Macrocyclic Ligands at 25 ± 1°C[a]

Amino acids and amines	18C6 (%)[b]	B18C6 (%)[b]	DB18C6 (%)[b]
L-Met	81	41	37
L-Ile	81	47	38
L-Phe	81	55	45
L-Leu	81	43	42
L-Val	79	67	35
$CH_3NH_3^+$	25	18	20
$(CH_3)_2NH_2^+$	38	26	22
n-$C_3H_7NH_3^+$	40	31	25

[a] *Source phase*: [amino acid] = 0.16 mM, [picric acid] = 1.6 mM, HCl 0.05 N (pH 2.02), 5 mL; or [amine] = 0.20 mM, [picric acid] = 0.20 mM, HCl 0.05 N (pH 2.02); 5 mL. *Membrane*: 1,2-dichloroethane, [macrocyclic ligand] = 10 mM, 30 mL. *Receiving phase*: LiOH 0.1 N (pH 13.01), 5 mL.
[b] Amino acid or amine percentage found in the receiving phase after 6 hours of stirring;

distributions have been examined by chromatographic measurements on both the aqueous and the organic phases apart from the equilibrium mixture. Generally, the values of K_d are dependent on the macrocycle structure and solvent type. Nevertheless, as shown in Table 1, the distribution of 18C6 is also influenced by the pH value. Benzo- and dibenzo-18-crown-6 have been shown to be practically insoluble in water (15).

The Structure of the Ligand and the Nature of the Cation

It is known that both the stability and selectivity of the complexes depend on the size of the crown ether ring in the sense that the best bound cation is the one which fits the best into the cavity. For instance, the ring of 18C6 with $r = 1.4$ A and the group $—NH_3^+$ with $r = 1.42$ A (16–18) fit reasonably. The number, the type, the arrangement of donor atoms, and the substituents of the crown ether may influence the complexation. The effect on the transport of some amines and amino acids through a liquid membrane with different macrocyclic ligands used as carriers has been examined. The experimental data of the transport of some amino acids and amines through a 1,2-dichloroethane liquid membrane containing 18C6, B18C6, or DB18C6, as the carriers are presented in Table 2.

Following the data in Table 2, the transport of the amino acids and the amines decreases in the following sequence: 18C6 > B18C6 > DB18C6. The ring substitutions of 18C6 with benzo and dibenzo groups resulted in different changes in transport through a liquid membrane or the extraction

equilibrium constant K_{ex} of complexes of amino acids and amines (19). In these cases the data indicate that the addition of hydrophobicity to the macrocycle is accompanied by a decrease in the transport value.

The properties of the cation (e.g., ionic radius, polarizability) influence the selection of the ligand to be involved in complexation. It is important for the cation to have complementary properties relative to the selected ligand.

It has been proved that crown ethers, such as 18C6, interact with the —NH_3^+ group through hydrogen bond formation (20, 21). In some previous works (14, 22) the influence of the molecular structure of the amino acid on the distribution between the phases of the system was presented. The transfer and transport through liquid membranes of amino acids may be further influenced by the hydrophobic or hydrophilic character of the chain —R.

The Thermodynamic Properties

It is important for efficient transport that the effect of complex stability on the distribution equilibrium be evaluated. Knowledge of the extraction and equilibrium constants, K_{ex} and K, respectively, is essential to the modeling process. Most experiments have suggested a diffusion-limited process of amino acid transport through liquid membranes (23–25). In a diffusion-controlled process, the rates depend on the thermodynamic equilibria at the interphases. It is generally necessary to have the optimal complex stability for optimum transport rates. The stability constants values and the extraction constants of the complexes of some amino acids with 18C6 in the presence of picrate anion are presented in Table 3.

TABLE 3
Stability Constants log K (K in M^{-1}) and Extraction Constants log K_{ex} of the Complexes of Protonated Amino Acids with 18C6 at 25 ± 1°C

Amino acid	log K* [42]	log K_{ex} [b]
L-Met	3.23 ± 0.01	4.70 ± 0.04
L-Trp	3.19 ± 0.09	5.05 ± 0.03
L-Phe	3.18 ± 0.01	5.16 ± 0.08
L-Leu	3.14 ± 0.02	5.76 ± 0.07
L-Val	2.99 ± 0.09	4.36 ± 0.05
L-Ile	2.98 ± 0.05	4.90 ± 0.04

[a] $C_{\text{amino acid}} = 1 \times 10^{-3}$ M, $C_{18C6} = 1.6 \times 10^{-2}$ M in methanol.

[b] $C_{\text{amino acid}} = 6 \times 10^{-4}$ M, $C_{18C6} = 4 \times 10^{-3}$–$10^{-2}$ M, $C_{\text{picric acid}} = 8 \times 10^{-5}$ M.

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The values of the extraction constants (log K_{ex}) of the reactions of protonated amino acids with 18C6 in 1,2-dichloroethane have been found to be in the 4.36 to 5.76 range. The values of the stability constants have been found to be between 2.98 for L-Ile and 3.23 for L-Met. As shown in Table 3, the values of the extraction constants decrease in the following sequence: L-Leu > L-Phe > L-Trp > L-Ile > L-Met > L-Val, while the values of the stability constants follow the sequence L-Met > L-Trp > L-Phe > L-Leu > L-Val > L-Ile.

The stability constants of the complex and the extraction constants (26) reveal no strict proportionality because, in contrast with the R—NH_3L^+ formation of the in methanol solution, complex the extraction process involves the formation of the ion pair R—$NH_3L^+A^-$, and the effect of anion (A^-) on the extraction constant has been demonstrated in extraction experiments (27, 28). The strength of cation–solvent interactions also plays an important role in the thermodynamics of cation extraction and the transport process (29, 30).

The Nature of the Anion

In many systems the extractibility of cations and the rates of cation transport are influenced by the structure of the anion used as the anion pair for cation–ligand complexes.

The cationic complex R—NH_3L^+ of an amino acid or amine with a macrocyclic ligand may be extracted in an organic solvent or transported through liquid membranes as ion pairs, R—$NH_3L^+A^-$, with some counterions (31–38) The anion used as a counterion (e.g., picrate or sulfophthaleinic anions) in the ion pair will affect the rate in both processes, the extraction and the transport, by modifying the phase distribution of the protonated amino acid and amine.

Lamb et al. (39) presented the effects of anions on cation transport and suggested that anions with smaller hydration energies and higher lipophilicities allow faster cation transport. A linear correlation of extractibility and anion hydration energy has been reported (39).

The values of the extraction constants (log K_{ex}) of some amino acids with 18C6 in the presence of tropaeolin 00 (**1**) and picric acid (**2**) as the anion pair in 1,2-dichloroethane are presented in Table 4. The difference in the extraction constants for the complexation of some amino acids with 18C6 in the presence of the **1** and **2** anion, is not significant. The lowest values of the extraction constants (log K_{ex}) were obtained for the complexes of L-Val (4.36 in the presence of anion **2** and 4.48 in the presence of anion **1**).

The Nature of the Membrane Solvent

The nature of the solvent of the membrane phase influences the distribution equilibria at the interfaces of the complex in the membrane. Solvent polarity

TABLE 4
Extraction Constants log K_{ex} of the Complexes of Some Amino Acids with 18C6 and Different Anions at 25 ± 1°C

Amino acid[a]	**1**[b]	**2**[b]
L-Leu	5.25 ± 0.05	5.76 ± 0.1
L-Ile	5.15 ± 0.04	4.90 ± 0.04
L-Phe	5.08 ± 0.02	5.16 ± 0.02
L-Met	4.38 ± 0.02	4.70 ± 0.04
L-Val	4.48 ± 0.03	4.36 ± 0.03

[a] $c = 7 \times 10^{-4}$–3×10^{-3} M.
[b] Tropaeolin 00 (**1**) and picric acid (**2**). $c = 8 \times 10^{-5}$ M, $c_{18C6} = 5 \times 10^{-3}$–$2 \times 10^{-2}$ M.

is also important in solvent extraction, and the relative cation selectivity is quite often sensitive to the polarity change (29). A large effect of solvent type on transport but a minimal effect of solvent type on membrane selectivity has been observed (40). The stability of a membrane is also influenced by the possibility of maintaining the organic solvent between the aqueous source and receiving phases. In order to increase membrane integrity (higher boiling point and low water solubility), it is necessary to increase the chlorination and the carbon chain length (41).

Values of log K_{ex} for some amino acids using 18C6 as a function of the solvent under experiment are given in Table 5. In all solvents for this system the values of log K_{ex} are sufficiently high to allow transport processes. As shown in Table 5, the solvent type has a minimal effect on the selectivity. The differences among the values of the extraction constants in the cases of

TABLE 5
Extraction Constants log K_{ex} of the Complexes of Some Amino Acids with 18C6 in Different Solvents at 25 ± 1°C[a]

Amino acid	Methylene chloride	Chloroform	1,2-Dichloroethane
L-Trp	4.80 ± 0.02	5.68 ± 0.04	5.80 ± 0.01
L-Leu	4.64 ± 0.04	4.98 ± 0.02	5.25 ± 0.05
L-Ile	4.37 ± 0.04	5.04 ± 0.01	5.15 ± 0.04
L-Phe	4.67 ± 0.02	5.22 ± 0.03	5.08 ± 0.02
L-Met	4.42 ± 0.04	4.83 ± 0.02	4.98 ± 0.02
L-Val	3.73 ± 0.02	4.31 ± 0.04	4.48 ± 0.03

[a] Tropaeolin 00 as counterion. $C_{18C6} = 5 \times 10^{-3}$–$2 \times 10^{-2}$ M, $C_{\text{amino acid}} = 4 \times 10^{-3}$ M, $C_{\text{anion}} = 4 \times 10^{-4}$ M.

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complexation of some amino acids with 18C6 in CH_2Cl_2, $CHCl_3$, and $C_2H_4Cl_2$ solvents with their increasing chlorination will have a minimal effect on the magnitude of the values of log K_{ex}.

CONCLUSIONS

The effects of some factors that might influence both the extraction and the transport through liquid membranes of some complexes of protonated amines and amino acids with macrocyclic ligands have been reported.

The structure of the ligand, the nature of the cation, the type of the anion, and the nature of the solvent have been proved to influence the distribution equilibria at the interfaces, the stability and selectivity of the complex in the membrane, and, consequently, the transport rates.

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REFERENCES

1. J.-M. Lehn, *Supramolecular Chemistry, Concepts and Perspectives*, VCH, Weinheim, 1995, Chapter 6.
2. M. Newcomb, J. L. Toner, R. C. Hegelson, and D. C. Cram, *J. Am. Chem. Soc.*, *101*, 4941 (1979).
3. T. B. Stolwijk, E. J. R. Sudholter, and D. N. Reinhoudt, *J. Am. Chem. Soc.*, *111*, 6321 (1989).
4. W. Simon, W. E. Morf, and P. C. Meier, *Struct. Bonding*, *16*, 113 (1973).
5. J.-P. Behr and J.-M. Lehn, *J. Am. Chem. Soc.*, *95*, 6108 (1973).
6. E. Drioli, *Recents Prog Genie Proc.*, *22*, 339 (1992).
7. C. F. Reusch and E. L. Cussler, *AIChE J.*, *19*, 736 (1973).
8. J. D. Lamb, J. J. Christensen, J. L. Oscarson, B. L. Nielsen, W. B. Asay, and R. M. Izatt, *J. Am. Chem. Soc.*, *102*, 6820 (1980).
9. T. B. Stolwijk, E. J. R. Sudholter, and D. N. Reinhoudt, *Ibid.*, *109*, 7042 (1987).
10. J. Ibanez, L. Victoria, and A. Hernandez, *Sep. Sci. Technol.*, *25*, 739 (1990).
11. L. A. J. Chrisstoffels, W. Struijk, F. de Jong, and D. N. Reihoudt, *J. Chem. Soc., Perkin Trans. 2*, 1617 (1996).
12. J.-P. Behr, M. Kirck, and J.-M. Lehn, *J. Am. Chem. Soc.*, *107*, 241 (1985).
13. R. Mutihac and L. Mutihac, in *Procedings, Euromembrane '95, Vol. 1* (W. R. Bowen, R. W. Field, and J. A. Howell, Eds.), University of Bath, UK, September 1995, p. 63.
14. L. Mutihac, R. Mutihac, and H.-J. Buschmann, *J. Incl. Phenom.*, *23*, 167 (1995).
15. Y. Inoue, F. Amano, N. Okada, H. Inada, M. Ouchi, A. Tai, T. Hakushi, Y. Liu, and L.-H. Tong, *J. Chem. Soc., Perkin Trans., 2*, 1239 (1990).
16. F. Vogtle and E. Weber, in *The Chemistry of Ethers, Crown Ethers, Hydroxy Groups, and Their Sulphur Analogues* (S. Patai, Ed.), Wiley, New York, NY, 1980, Chapter 2.

17. F. De Jong and D. N. Reinhoudt, *Stability and Reactivity of Crown Ether Complexes*, Academic Press, New York, NY, 1981.
18. J.-P. Behr, J.-M. Lehn, and P. Vierling, *Helv. Chim. Acta*, *62*, 1853 (1982).
19. L. Mutihac, D. O. Popescu, and R.-I. Stefan, *Anal. Lett.*, *28*, 835 (1995).
20. J.-M. Lehn, in *Perspectives in Coordination Chemistry* (A. F. Williams, C. Floriani, and A. E. Merbach, Eds.), VHCA, Basel, 1992, p. 447.
21. A. F. Danil de Namor, *Pure Appl. Chem.*, *62*, 2121 (1990).
22. L. Mutihac, H.-J. Buschmann, C. Bala, and R. Mutihac, *Anal. Quim., Int. Ed.*, *93*, 332 (1997).
23. R. M. Izatt, D. K. Roper, R. L. Bruening, and J. D. Lamb, *J. Membr. Sci.*, *45*, 73 (1989).
24. R. M. Izatt, R. L. Bruening, M. L. Bruening, G. C. Lindh, and J. J. Christensen, *Anal. Chem.*, *61*, 1140 (1989).
25. L. Mutihac and R. Mutihac, *Acta Chim. Hung.—Models Chem.*, *129*, 573 (1992).
26. H.-J. Buschmann and L. Mutihac, *Thermochim. Acta*, *237*, 203 (1994).
27. Y. Takeda, *Top. Curr. Chem.*, *121*, 1 (1984).
28. A. Brandstrom, *Adv. Phys. Org. Chem., C.*, *15*, 267 (1977).
29. H.-J. Buschmann, G. Wenz, E. Schollmeyer, and L. Mutihac, *Thermochim. Acta*, *261*, 1 (1995).
30. D. O. Popescu, T. Constantinescu, and L. Mutihac, *Anal. Quim., Int. Ed.*, *93*, 182 (1997).
31. C. J. Pedersen, *J. Am. Chem. Soc.*, *89*, 7017 (1967).
32. H. K. Frensdorff, *Ibid.*, *93*, 4684 (1971).
33. P. Beronius and A. Brandstrom, *Acta Chem. Scand.*, *A30*, 687 (1976).
34. M. Yoshio and H. Noguchi, *Anal. Lett.*, *15*, 1197 (1982).
35. H. Noguchi, H. Nakamura, and M. Yoshio, *Bull. Chem. Soc. Jpn.*, *55*, 152 (1982).
36. Yu. A. Nazarenko and Z. Z. Nizhnik, *Zh. Anal. Chim.*, *39*, 1308 (1984).
37. I. M. Kolthoff and M. K. Chantooni Jr. *J. Chem. Eng. Data*, *42*, 49 (1997).
38. I. M. Coelhoso, J. P. S. G. Crespo, and M. J. T. Carrondo, *Sep. Sci. Technol.*, *31*, 491 (1996).
39. J. D. Lamb, J. J. Christensen, S. R. Izatt, K. Bedke, M. S. Astin, and R. M. Izatt, *J. Am. Chem. Soc.*, *102*, 3399 (1980).
40. R. M. Izatt, D. W. McBride Jr., P. R. Brown, J. D. Lamb, and J. J. Christensen, *J. Membr. Sci.*, *28*, 69 (1986).
41. R. M. Izatt, R. L. Bruening, M. L. Bruening, and J. D. Lamb, *Isr. J. Chem.*, *30*, 239 (1990).
42. H.-J. Buschmann, E. Schollmeyer, and L. Mutihac, *J. Incl. Phenom.*, *30*, 21 (1998).

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