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Enthalpies of dilution of polyelectrolyte solutions and exchange enthalpies of polyelectrolyte counterions[1]

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Abstract

Experimental data of the enthalpies of dilution of aqueous polyelectrolyte solutions with water are presented, as well as the exchange enthalpies of polyelectrolyte counterions. Measurements were performed using a titration calorimeter. The procedure of obtaining exchange enthalpies is described. The knowledge of these exchange enthalpies reveals information about the enthalpies of formation of (polycation–polyanion) complexes which are the basic materials for the preparation of pervaporation membranes. The data obtained are also of interest for paper manufacturing industries because they provide a model of the interaction energies of polyelectrolytes with multiple-charged electrolytes, e.g. lignin sulfonate.

INTRODUCTION

New techniques for separating water from organics are of increasing importance. Using pervaporation and other membrane separation techniques, it is possible to obtain separation factors that are notably higher than those obtained by conventional thermal separation methods such as distillation.

The membranes that are very effective in this respect are the so-called "symplex membranes" which consist of cationic and anionic polyelectrolytes. These non-porous membranes have a hydrophilic character and are suitable for extracting water from organic solutions by pervaporation. The membranes are produced by phase inversion out of casting solutions of an anionic and a cationic polyelectrolyte according to the equation

$$PC^{x+}(Cl^-)_x + PA^{x-}(Na^+)_x \rightarrow PC^{x+}PA^{x-} + x\text{NaCl}$$

For the production of optimized symplex membranes with good separation properties, a knowledge of the interaction energy between the polycation and polyanion, as well as between the polyelectrolyte and water, is necessary. The interaction energies can be obtained by caloric

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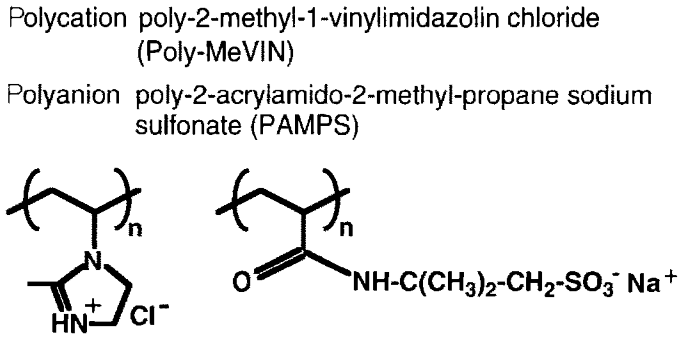

Fig. 1. The chemical structure of the polyelectrolytes Poly-MeVIN (polycation) and PAMPS (polyanion).

measurements. However, problems arise due to the high viscosity of solutions containing symplexes which make the measurements extremely difficult. In order to simulate the symplex formation process and to study the interaction energies associated with ion exchanges in polyelectrolytes, a TRONAC titration calorimeter was used to determine partial molar enthalpies of dilution of aqueous solutions of a polycation (poly-2-methyl-1-vinylimidazolin chloride (Poly-MeVIN)) and of a polyanion (poly-2-acrylamide-2-methyl-propane sodium sulfonate (PAMPS)). The chemical structure of the polymers is shown in Fig. 1. Measurements were also carried out by mixing aqueous solutions of Poly-MeVIN with salt solutions. Solutions of monovalent salts (sodium chloride), bivalent salts (sodium sulfate) and salts containing ions with two functional ionic groups in the molecule (nitrazine yellow) were used. The enthalpies of the exchange of polyelectrolyte counterions can be calculated from these calorimetric results as experimental data for the partial molar enthalpies of dilution for the polyelectrolyte solutions are available.

The experimental results are discussed below. The interaction energy between a polyelectrolyte and water, as well as the exchange of counterions, can be interpreted qualitatively from a molecular point of view.

EXPERIMENTAL

Details of the procedure using the TRONAC 1250 calorimeter (Tronac, Inc., Orem, UT, USA) have been described previously [1, 2]. The calorimeter is shown schematically in Fig. 2. The dilution or mixing process takes place in the reaction vessel, of approximate volume 32 ml, which is immersed in a large water bath of 80 l capacity. The caloric measurements were made at 298.15 K in a quasi-isothermal process. Water or salt solution (2 ml) is titrated continuously into approx. 20 ml of polyelectrolyte solution by means of a precision buret (Gilmont Instr., Inc., Great Neck, NY, USA). A Peltier cooler in the bottom of the reaction vessel removes energy from

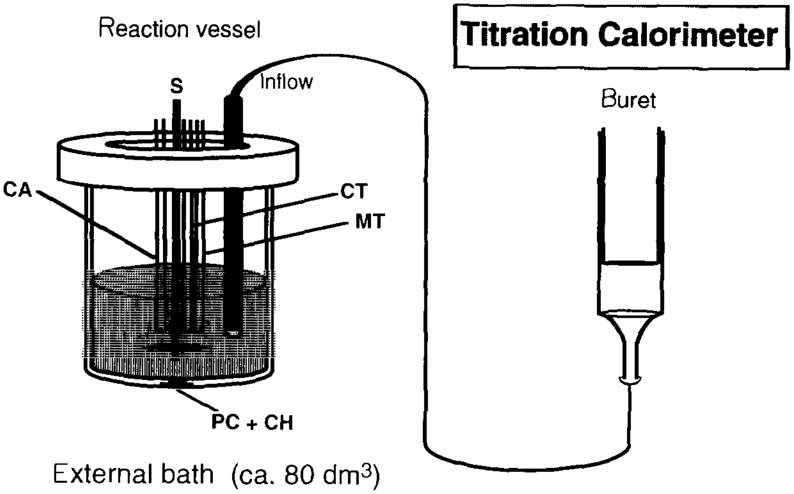

Fig. 2. Schematics of the TRONAC titration calorimeter. The figure shows the external water bath with the reaction vessel and the precision buret. S, stirrer; CA, calibration heater; CT, control thermistor; MT, monitor thermistor; PC, Peltier cooler; CH, control heater.

the solution at a constant rate. A control heater compensates for this energy and for the energy released or absorbed by the mixing process, maintaining the solution in the reaction vessel at practically constant temperature ($\pm 5 \times 10^{-4}$ K). The difference in the compensating heating power during and before the mixing process is a direct measure of the heat of dilution or mixing ΔQ. A stirrer assures a homogeneous temperature within the solution. Using a calibration heater, a well-defined energy can be generated, thus making calibration of the whole system possible. Corrections to ΔQ arising from heat effects associated with the change in the vapor space during the titration proved to be small [1] compared to other sources of experimental error limits and, therefore, have been neglected.

The partial molar enthalpies of dilution Δh_1 (excess partial molar enthalpies of water) in aqueous polyelectrolyte solutions are related to the integral heat of dilution ΔQ by the equation

$$\Delta Q = \int_{w_{2,A}}^{w_{2,E}} \Delta h_1 \, dn_1$$

where dn_1 is the differential molar amount of water added to the solution, and $w_{2,A}$ and $w_{2,E}$ are the molar weight fractions of polyelectrolyte at the beginning and at the end of a titration.

For small differences between $w_{2,A}$ and $w_{2,E}$, Δh_1 can be obtained directly from the relationship

$$\Delta h_1 = \Delta Q / \Delta n_1$$

where Δn_1 is the number of moles of water added to the solution.

The exchange enthalpy of polyelectrolyte counterions is obtained from the heats of mixing of polyelectrolyte solutions with salt solutions, provided the enthalpies of dilution of the different components are taken into account.

The polycation and polyanion used for the measurements were supplied by BASF A.G. (Ludwigshafen, FRG): Poly-MeVIN as a solid, and PAMPS as an aqueous stock solution of 20.8 wt.%. The average molecular weight of both polyelectrolytes is about 50000. Sodium chloride, p.a., and sodium sulfate, p.a., were supplied by Merck (Darmstadt, FRG) (purity >99.95% and >99%, respectively). Nitrazine yellow (dye content approx. 85%) was supplied by Aldrich (Gillingham, UK). The water used was supplied by J.T. Baker (Deventer, The Netherlands), HPLC reagent (purity >99.99% by GLC). The materials were used without further purification.

RESULTS

Enthalpies of dilution

Figures 3 and 4 show the enthalpies of dilution of Poly-MeVIN and PAMPS, respectively, expressed as partial molar excess enthalpy of water

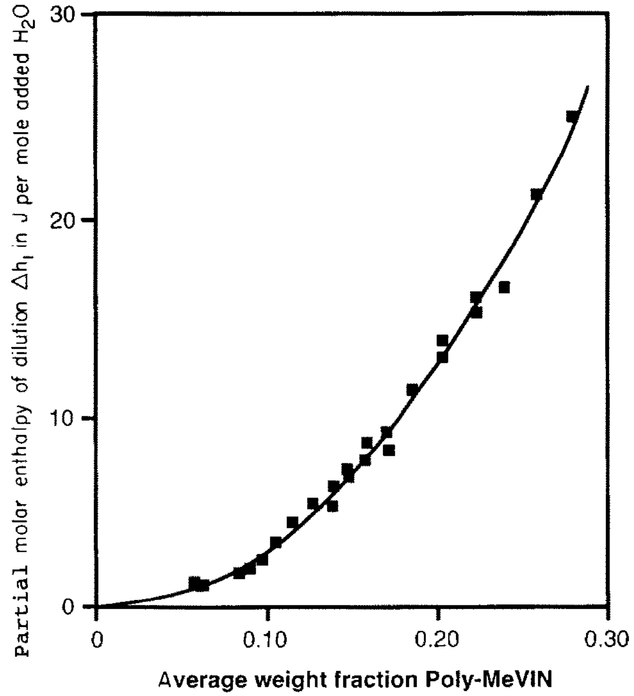

Fig. 3. Partial molar enthalpy of dilution Δh_1 (in J per mole added water) versus average weight fraction of Poly-MeVIN in water for the system (Poly-MeVIN + water): ■, experimental data.

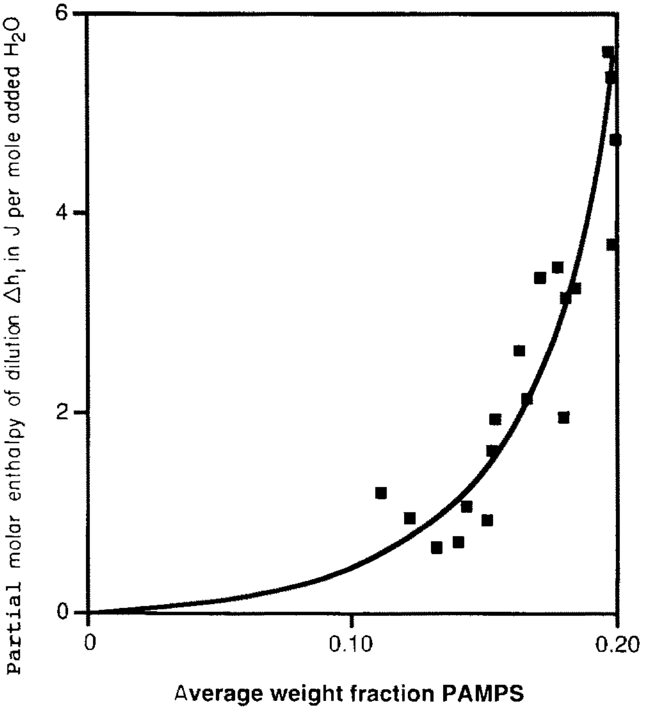

Fig. 4. Partial molar enthalpy of dilution Δh_1 (in J per mole added water) versus average weight fraction of PAMPS in water for the system (PAMPS + water): ■, experimental data.

as a function of the weight fraction of polyelectrolyte in water given as an arithmetic mean of the weight fraction at the beginning and at the end of each titration. Obviously, Δh_1 is lower for the polyanion–water system than for the polycation–water system. This difference might arise from a different extent of conformational changes of the polyelectrolytes when the solvent is added. The experimental error of Δh_1 is estimated to be within ±2.5% at $w_2 = 0.23$, and ±17% for $w_2 = 0.08$. This error results from a summation of errors due to the heat effect of dilution, the heat effect of the calibration heater, and the accuracy of the flow rate of the solvent.

Exchange enthalpies of polyelectrolyte counterions

According to the reaction

$$PC^{x+}(Cl^-)_x + (x/2)Na_2SO_4 \rightarrow PC^{x+}(SO_4^{2-})_{x/2} + xNaCl \quad (1)$$

the exchange of polyelectrolyte-bonded chloride for sulfate is assumed to be complete if the total molar amount of sulfate added is at least half of the equivalent molar amount of bonded chloride ions. The resulting thermal effect is the sum of several heat effects: (a) the enthalpy associated with the exchange of two chloride ions for one sulfate ion, (b) the enthalpy of

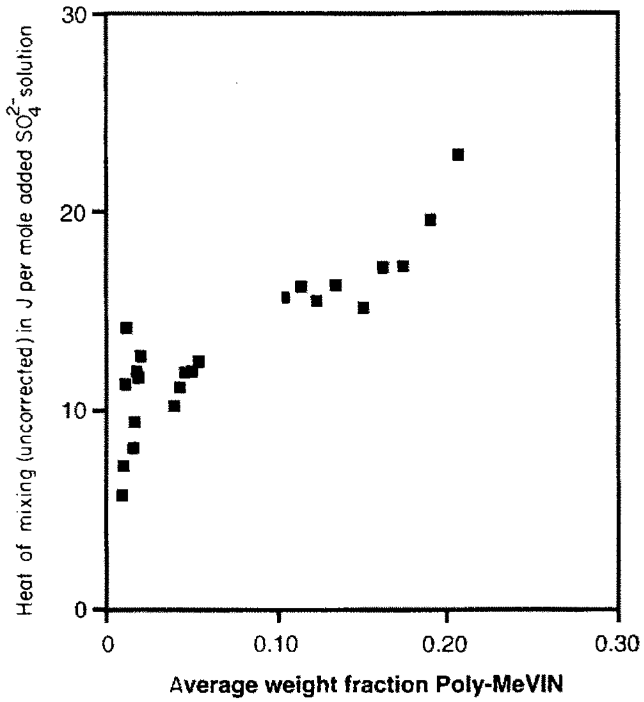

Fig. 5. Heat of mixing (see text) in J per mole of added salt solution versus average weight fraction of Poly-MeVIN in water for the system (Poly-MeVIN + 0.1 M Na_2SO_4): ■, experimental data before corrections were made.

dilution of the polyelectrolyte solution, (c) the enthalpy of dilution of the added salt solution, and (d) the enthalpy of solution of the generated sodium chloride.

The exchange enthalpy measurements for Poly-MeVIN chloride (see eqn. (1)) were obtained by titrating 2 ml of 0.1 M aqueous sodium sulfate solution several times into Poly-MeVIN solution (20 ml) present in the reaction vessel. The measured heat effect (Fig. 5) has to be corrected by the partial molar enthalpy of dilution of Poly-MeVIN, as presented in Fig. 3, and by the heat of dilution of the sodium sulfate solution added to the reaction vessel. This heat effect was measured by a separate series of experiments titrating sodium sulfate solution into pure water. The heat of dilution of the generated sodium chloride is very small and can be neglected. The corrected heat of mixing data are shown in Fig. 6 and are given in joules per mole of the added salt solution. The solid line indicates the averaged values obtained. Below a certain weight fraction of Poly-MeVIN, the heat of mixing data decrease drastically, because all Cl^- ions have been exchanged by SO_4^{2-} at this state of dilution. Adding more SO_4^{2-} ions has no heat effect because the exchange process has already been completed and the SO_4^{2-} ions are now present in excess. The exchange

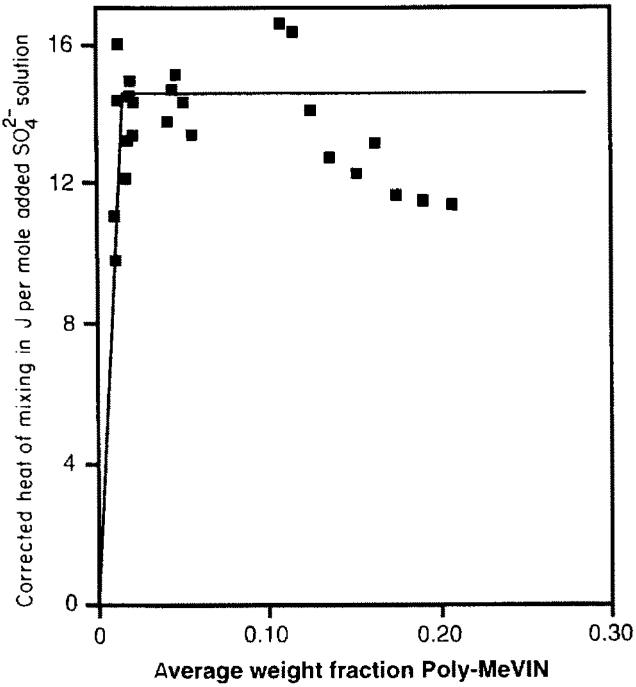

Fig. 6. Corrected heat of mixing (see text) in J per mole of added salt solution versus average weight fraction of Poly-MeVIN in water for the system (Poly-MeVIN + 0.1 M Na_2SO_4): ■, experimental data after corrections were made; exchange enthalpy, +8.0 kJ per mol SO_4^{2-}.

enthalpy can be calculated from these data in joules per mole of exchanged sulfate. The value is +8.0 kJ per mol SO_4^{2-}. Owing to the relatively small heat effects observed, a considerable scattering of the data is obtained. The exchange enthalpy of 8 kJ mol^{-1} is estimated as having an experimental error of ±1.0 kJ mol^{-1}. The measurements were also carried out with a 0.01 M solution of sodium sulfate. The resulting exchange enthalpy was +8.5(±2.4) kJ per mol SO_4^{2-}. In spite of the endothermic value, the reaction of exchange chloride for sulfate is complete, because it is accompanied by an increase in the entropy (one sulfate ion replaces two chloride ions).

Figure 7 presents the corresponding enthalpy values for the exchange of chloride ions for nitrazine yellow (2-[2,4-dinitrophylazo]naphthol-3,6-disulfonic acid, disodium salt). The exchange enthalpy is −18.2(±2.1) kJ per mol nitrazine yellow. Nitrazine yellow is an azo compound with two sulfonate groups. These charges are separated on the molecule by a distance of approx. 1.4 nm. The dilution measurements presented in Fig. 7 were made with 0.00875 M nitrazine yellow solution. Measurements with a solution half of this concentration give an exchange enthalpy of −23.1(±4.3) kJ per mole nitrazine yellow. Both results agree within the estimated experimental error.

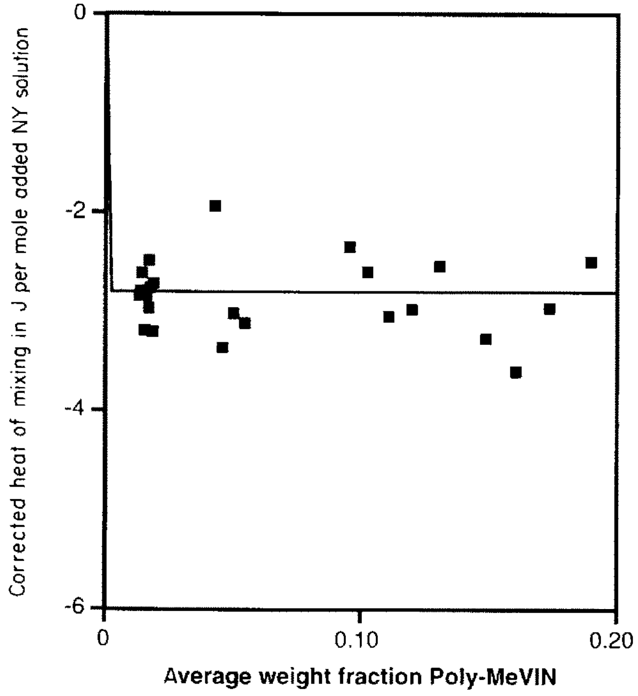

Fig. 7. Corrected heat of mixing (see text) in J per mole of added nitrazine yellow (NY) solution versus average weight fraction of Poly-MeVIN in water for the system (Poly-MeVIN + 0.00875 M nitrazine yellow solution): ■, experimental data after corrections were made; exchange enthalpy, −18.2 kJ per mol NY^2.

Obviously, the exchange of chloride for sulfate is an endothermic process while the exchange for a nitrazine yellow anion is exothermic. The difference in the exchange enthalpies reflects the different kinds of interaction of the negative ions with the polycation. According to polyelectrolyte theories [3, 4], it might be suggested that the sulfate ions are bonded in the ion cloud dispersed in the apparent volume of the polyelectrolyte molecule, resulting in only weak binding. However, nitrazine yellow has two separated charges with an "ideal" distance of 1.4 nm. It is suggested that the anion is bonded directly at certain positive charges fixed on the polyelectrolyte molecule in a kind of complexation process. This leads to a distinct exothermic value for the exchange enthalpy.

ACKNOWLEDGEMENT

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