The ion-exchange equilibrium

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resulting not from the kinetics, but from an equilibrium prior to the rate-determining step.

Models for compensation in diffusion processes include local melting[15,16] (which can only be valid if the compensation temperature is equal to the melting temperature), Keyes' vacancy model,[17] and tunneling.[18] In a very recent, questionable model[19] the energy barrier from a given site to an equivalent site is overcome in many consecutive steps to ever higher energy; the series of steps forms a path that is assumed to be chosen randomly as a linear subset of a Cayley tree (Bethe lattice). As for the closely related problem of compensation in the case of conductivity of semiconductors, a good survey is given by Dyre.[20] For that case there is independent experimental evidence for an exponential distribution of states.

In relation to chemical reactions in aqueous media Melander[21] notes that due to the specific temperature dependence of the dielectric constant (permittivity) of water, the electrostatic contributions to entropy and enthalpy turn out to be related in an approximately linear way.

Patterson and Barbe[22] explain compensation in alkane and aqueous systems as a phenomenon due to the rapid decrease of the order Gibbs free energy change as a function of temperature. In their model the compensation temperature is essentially the experimental temperature.

Appendix B

In this appendix eq 15 is derived. We define a cumulant expansion[23-25] of $\langle \exp[-\beta(U - U_0)] \rangle$ by

$$\langle \exp[-\beta(U - U_0)] \rangle = \exp\left(-\beta \bar{\kappa}_1 + \frac{1}{2!}\beta^2 \bar{\kappa}_2 + ...\right) \quad (B1)$$

where the cumulants $\bar{\kappa}$ may be found by expanding left- and

right-hand sides and equating terms of the same power in β without accounting for the implicit β dependence of the averages (a more precise mathematical definition need not concern us here). The first and second cumulants are given by

$$\bar{\kappa}_1 = \langle U - U_0 \rangle$$

and

$$\bar{\kappa}_2 = \langle (U - U_0)^2 \rangle - \langle U - U_0 \rangle^2$$

The free energy difference is

$$A - A_0 - A_{\text{mix}} = \langle U - U_0 \rangle - \frac{1}{2}\beta \bar{\kappa}_2 + ... \quad (B2)$$

Since $A - A_0$ is an extensive quantity the cumulants can at most be linear in the number of particles N. For dimensional reasons one expects that the expansion parameter will be β times a characteristic energy per particle. If one uses for this energy the experimental energy per particle in ion exchange, this expansion parameter is of the order of unity. However, this condition may be relaxed. A different estimate is found by realizing that

$$\partial \langle U - U_0 \rangle / \partial \beta = \langle (U - U_0)(U_0 - \langle U_0 \rangle) \rangle \quad (B3)$$

Thus the ratio of the second to the first term on the right-hand side of eq B2, which must be small if the cumulant expansion makes sense, is given by

$$\frac{1}{2}\beta \bar{\kappa}_2 / \langle U - U_0 \rangle = \frac{1}{2}R \, \partial \ln \langle U - U_0 \rangle / \partial \ln \beta \quad (B4)$$

with

$$R = \frac{\langle (U - U_0)(U - U_0 - \langle U - U_0 \rangle) \rangle}{\langle (U - U_0)(U_0 - \langle U_0 \rangle) \rangle} \quad (B5)$$

In the case of ion exchange it turns out experimentally that the derivative in eq B4 is of order unity. Thus, for the cumulant expansion to hold, the modulus of the ratio R must be much smaller than unity. In this sense U must be close to U_0. For higher order cumulants similar conditions may be derived.

Longuet-Higgins also derives eq 15, but roughly estimates that it may be used if $\langle U - U_0 \rangle$ is much smaller than $\langle U_0 \rangle$. This estimate is useful as a guideline for the experimentalist but has the conceptual problem of defining the zero of the average energy. Thermodynamically only differences in average energies are of importance. The more rigorous estimate given above is independent of the value of a constant contribution to the average energy.

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The Ion-Exchange Equilibrium

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The ion-exchange equilibria of alkali-metal and alkaline-earth-metal ions are studied by using surface-sulfonated polystyrene–divinylbenzene resins. A chromatographic method is employed in which one of the exchanging ions is present in trace quantities only. It was found that the equilibrium coefficient was independent of the concentration of the liquid phase, and therefore specificity in ion exchange is due solely to interactions in the exchanger phase. The data could be interpreted according to the model of enthalpy–entropy compensation. Equations are derived that relate the equilibrium coefficient to a product of the difference between two interaction parameters and a factor that is a constant within a class of ions. It is shown that selectivity is determined by the interaction between adsorbed ions and not by the interaction of separate adsorbed ions with the resin. A consistent set of interaction parameters is derived for the former interaction.

Introduction

Ion-exchange properties of various materials, such as clay minerals and polyelectrolytes, have long been known. When these materials are brought into contact with an electrolyte solution, an equilibrium is established, in which part of the ions proper to the exchanger are replaced by ions from the solution. If different

species of the same valency show a different prefernce for the exchanger phase, the ion-exchange process may be termed specific.[1] This implies that the exchange equilibrium is not deter-

(1) Lyklema, J. In *Adsorption from Solution*; Parfitt, G. D., Rochester, C. D., Eds.; Academic Press: New York, 1983; pp 223–246.

mined solely by electrostatic forces but also by specific interactions depending on, e.g., shape and size of the ions.

Because of its importance in separation science, the exchange equilibrium has been the subject of numerous studies [e.g., ref 2-5]. When pertaining to synthetic, resin-based exchangers, the exchange equilibrium is commonly treated in terms of a Gibbs–Donnan membrane equilibrium between an "external" solution and the "internal" solution. The internal solution contains the polyelectrolyte in the form of acidic or basic groups fixed to the resin structure. Specificity is due to differences in ion activity coefficients in the external and the internal solution and to differences in osmotic pressure. Several attempts have been made to estimate activity coefficients in the exchanger phase [e.g., ref 6]. The ultimate goal of these theories was the calculation of the exchange equilibrium over the complete mole fraction range at a given total concentration, i.e., the calculation of the complete exchange isotherm. Due to the severe difficulties involved in calculating chemical potentials in the exchanger phase, this goal has never been reached.

Renewed interest in ion-exchange equilibria stems from the introduction of a new type of ion-exchange materials by Small, Stevens, and Bauman.[7] In contrast to the older materials, these resins are not functionalized throughout the bulk, but only in a thin shell in the proximity of the external surface of the resin particles. As a result, much higher rates of mass transfer can be achieved. Combined with a very elegant way of conductometric detection, this led to a branch of liquid chromatography, now generally known as ion chromatography. Over the past decade ion chromatography has become one of the most important techniques for the quantitative determination of anions. Despite this clear importance in analytical chemistry, there is a general lack of understanding of the origins of selectivity. Both for the control of separations and for the development of improved exchange materials such an understanding is of crucial importance.

We have measured the enthalpies and entropies of homovalent exchanges of monovalent and divalent cations using surface-sulfonated resins. The exchange of cations was chosen to avoid the occurrence of secondary equilibria, arising from, e.g., the interaction of polarizable ions with the aromatic backbone of the resin, as has been observed in anionic exchange.[8]

As ion chromatography is generally performed as linear-elution chromatography, we limit our description of the exchange equilibrium to the case in which one of the ions of the exchanging pair is present in small amounts with respect to the other ion. That is to say, our description refers to the linear ("Henry") part of the exchange isotherm. Due to this restriction and due to the low external concentrations used in chromatography, the description of the equilibrium is greatly simplified.

In the preceding paper[9] we discussed the phenomenon of linear enthalpy–entropy compensation. It was shown there that compensation occurs when (i) the species under consideration are sufficiently similar (values of the interaction parameters all nearly equal) and (ii) the enthalpy and entropy of exchange can be considered constant. If these conditions are fulfilled, a relatively simple expression can be derived for the difference between the Helmholtz free energy of a system and that of an arbitrary reference. Here we touch on the essence of the approach. Rather than having to derive expressions for the total Helmholtz free energy content of a system (e.g., using a lattice model[10]), and subtracting this (large) value from that obtained after the change of interest, we focus on the differences directly. Thus, a great

deal of the ambiguity necessarily involved in calculating Helmholtz free energies by using very detailed models is eliminated.

As enthalpy–entropy compensation is observed in both monovalent and divalent exchange, we applied the theory to our experimental data. We will show that specificity in ion exchange is determined by two-body interaction potentials. A consistent set of interaction parameters for this type of interaction is derived.

Theory

The purpose of this section is to describe the ion-exchange equilibrium between a solid exchanger containing a fixed number of exchange sites per unit volume and an aqueous solution. For reasons of convenience homovalent exchange of cations will be considered. Generalization to other systems does not pose any major problems. We thus have the exchange equilibrium

$$A^l + B^s = B^l + A^s \qquad (1)$$
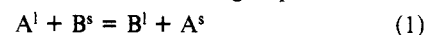
in which the superscripts l and s refer to the solid (exchanger) and liquid phases, respectively. Ion A is always present in very low concentrations relative to ion B. When there is mention of an exchanging pair in the following the first ion always refers to the ion present at low concentrations.

We will assume that both the chemical potential of the co-ions (ions of the same sign as the fixed groups) and that of the solvent do not change due to the exchange of a very small amount of cations. The assumptions require further discussion. According to Helfferich,[11] co-ions are completely excluded from the exchanger phase at low external concentrations. Hence, their chemical potential cannot change due to the exchange process. Experimental verification of co-ion exclusion, e.g., by measuring the chromatographic hold-up volumes of a series of co-ions of varying pK_a, was not readily possible due to the low total exchange capacities of the resins used. Assuming constancy of the solvent chemical potential is equivalent to saying that the swelling pressure, i.e., the osmotic pressure difference between the solid and liquid phases, does not change as a consequence of the exchange. Again the quality of the assumption cannot readily be assessed experimentally due to the small amounts exchanged.

Under the above two assumptions, the condition for stable phase equilibrium leads to the following relation between chemical potentials:

$$\hat{\mu}^l_A + \hat{\mu}^s_B + RT \ln x^l_A \gamma^l_A + RT \ln x^s_B \gamma^s_B =$$
$$\hat{\mu}^l_B + \hat{\mu}^s_A + RT \ln x^l_B \gamma^l_B + RT \ln x^s_A \gamma^s_A \quad (2)$$

In this equation $\hat{\mu}^l$ and $\hat{\mu}^s$ are the standard chemical potentials in the liquid and solid phases, respectively. x^l and x^s refer to the mole fraction in the liquid phase and the equivalent fraction in the solid phase. The latter quantity is defined by $x^s_A = N^s_A(N^s_A + N^s_B)$, where N denotes molar amounts. Activity coefficients are indicated by γ. The activity coefficients in the aqueous phase are defined in the usual way: $\gamma_i \rightarrow 1$ as $x_i \rightarrow 0$. The definition of the reference states and activity coefficients for the exchanger phase will be discussed more fully below. Rewriting eq 2 we obtain

$$\ln \frac{x^s_A x^l_B}{x^l_A x^s_B} = \frac{-\Delta \hat{\mu}^{l,s}}{RT} + \ln \frac{\gamma^s_B}{\gamma^s_A} + \ln \frac{\gamma^l_A}{\gamma^l_B} \qquad (3)$$

The left-hand side of eq 3 is the logarithm of the so-called equilibrium coefficient (ln $\tilde{K}_{AB}$). It can be assessed experimentally through the corresponding ratio of concentrations. Also, through variation of the temperature, the enthalpy and entropy of exchange can be measured. The tilde is used to distinguish the equilibrium coefficient from the thermodynamic equilibrium constant (this latter quantity being a ratio of activities rather than one of concentrations). Entropies and enthalpies derived from the temperature variation of $\tilde{K}_{AB}$ will also be indicated by a tilde to avoid confusion with standard enthalpies and entropies.

We now proceed by assuming that the last term on the right-hand side of eq 3 vanishes at low total concentrations. This

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implies that the activity coefficient in solution is only determined by electrostatic forces and not by ion specific forces. That the assumption does indeed apply under our conditions is shown by experiment (see Results and Discussion).

We have now arrived at a point where Gibbsian thermodynamics can take us no further. As indicated in the Introduction one usually proceeds from here by devising detailed models for the interactions in the exchanger phase. We will proceed in a more general way, only assuming that compensation occurs and that interaction parameters for the various ionic species do not differ very much. Expressions will be derived for the cases that either one-body or two-body interactions are dominant. It was argued in ref 9 that these two possibilities are generally mutually exclusive.

For the case that the interaction potential is determined by a two-body potential we have (eq 31 of ref 9):

$$RT \ln \gamma^s_A = (x^s_B)^2 \left(\frac{\partial \hat{\mu}}{\partial f}\right)_{f=f_0} \{2f_{AB} - f_{AA} - f_{BB}\} \qquad (4)$$

and

$$RT \ln \gamma^s_B = (x^s_A) \left(\frac{\partial \hat{\mu}}{\partial f}\right)_{f=f_0} \{2f_{AB} - f_{AA} - f_{BB}\} \qquad (5)$$

In these equations $\hat{\mu}$ is the standard chemical potential in the solid phase of a reference compound, e.g., one of the ions under consideration. The so-called interaction parameters between ions i and j are indicated by f_{ij}. These parameters are scaling parameters in the expression for the interaction potential between these ions. The f values are temperature independent. It is assumed that all the differences between different compounds in a compensation class show up in these parameters. At a given temperature the derivative of $\hat{\mu}$ to f is hence a constant. It should be noted that activity coefficients are temperature dependent. This implies that an entropy contribution is contained in the terms describing the deviation from ideality. Thus, the Bragg–Williams approximation (i.e., the random-mixing approximation used in regular solution models) is not made in the present model.[9]

As component A is present in the solid phase in trace amounts only, $(x^s_A)^2$ is very small and hence $\ln \gamma^s_B \ll \ln \gamma^s_A$ so that the former can be neglected. We thus obtain, as x is almost 1

$$RT \ln \tilde{K}_{AB} = -\Delta \hat{\mu}^{l,s} - \left(\frac{\partial \hat{\mu}}{\partial f}\right)_{f=f_0} \{2f_{AB} - f_{AA} - f_{BB}\} \qquad (6)$$

We also have from eq 30 of ref 9

$$\hat{\mu}^s_A = \left(\frac{\partial \hat{\mu}}{\partial f}\right)_{f=f_0} (f_{AA} - f_0) \quad \text{and} \quad \hat{\mu}^s_B = \left(\frac{\partial \hat{\mu}}{\partial f}\right)_{f=f_0} (f_{BB} - f_0) \qquad (7)$$

We recall that standard states for the aqueous phase are defined at infinite dilution. Additionally, we will suppose that the state of solvation does not change upon dilution. That is to say, the partial molar enthalpy of the ions at our reference is determined solely by electrostatic interactions. Hence, the standard states for ions of the same valency are equal. Substituting the result of eq 7 into eq 6 and using $\hat{\mu}^l_A = \hat{\mu}^l_B$, we obtain

$$RT \ln \tilde{K}_{AB} = -\left(\frac{\partial \hat{\mu}}{\partial f}\right)_{f=f_0} 2(f_{AB} - f_{BB}) \qquad (8)$$

Similarly, if one-body interaction potentials dominate, one obtains using eq 22–24 of ref 9

$$RT \ln \tilde{K}_{AB} = -\left(\frac{\partial \hat{\mu}}{\partial f}\right)_{f=f_0} (f_A - f_B) \qquad (9)$$

From eq 4 it follows that the activity coefficients in the solid phase are defined so that $\gamma^s_A \to 1$ as $x^s_B \to 0$. From eq 7 we have that the standard states for the solid phase are taken to be the pure (completely filled) states of A and B, respectively. The corresponding entropy and enthalpy changes are obtained from eq 8 using

$$\Delta \tilde{S} = -\left(\frac{\partial \Delta \tilde{G}}{\partial T}\right)_p, \quad \Delta \tilde{H} = T \Delta \tilde{S} + \Delta \tilde{G} \qquad (10)$$

The results are

$$\Delta \tilde{S}_{AB} = -2(f_{AB} - f_{BB}) \frac{\partial}{\partial T} \left\{ \left(\frac{\partial \hat{\mu}}{\partial f}\right)_{f=f_0} \right\} \qquad (11)$$

$$\Delta \tilde{H}_{AB} = -2(f_{AB} - f_{BB}) \left\{ T \frac{\partial}{\partial T} \left(\frac{\partial \hat{\mu}}{\partial f}\right)_{f=f_0} - \left(\frac{\partial \hat{\mu}}{\partial f}\right)_{f=f_0} \right\} \qquad (12)$$

The ratio of $\Delta \tilde{H}$ and $\Delta \tilde{S}$ has the dimension of temperature and is called the compensation temperature:

$$T_c(T) = \left(\frac{\partial \hat{\mu}}{\partial f}\right)_{f=f_0} \bigg/ \left[\frac{\partial}{\partial T} \left(\frac{\partial \hat{\mu}}{\partial f}\right)_{f=f_0} \right] + T \qquad (13)$$

By combining eq 10 and eq 9 similar expressions can be obtained for the case that the interaction potentials are determined by one-body potentials. Using a zeroth-order approximation, i.e., neglecting the temperature dependence of $\Delta \tilde{H}$ and $\Delta \tilde{S}$, the compensation temperature (eq 13) is a constant. The adequacy of the present theory can be verified from the internal consistency of equations of the type (12). That is to say, from a set of exchange equilibria, an internally consistent set of differences between f_{ij} values should be derivable.

Experimental Section

Apparatus and Materials. Throughout this work a PU 4100 binary liquid chromatograph (Philips Scientific, Cambridge, U.K.), equipped with a PU 4700 autoinjector was used. The system was adapted to suit the requirements of ion chromatography by replacing all stainless steel tubing with Tefzel (Omnifit, Cambridge, U.K.) and replacing the injection valve with a metal-free Rheodyne 7125 injection valve (Rheodyne, Cotati, CA). A guard column (Waters/Millipore, Etten-Leur, The Netherlands) was installed between the pump and the injector. It was found that, when the above precautions are taken, several hundred standard solutions could be injected without a decrease of the exchange capacity of the column due to irreversible exchange with heavy-metal ions. Conductometric detection was performed using a LDC Mark III ConductoMonitor (LDC/Milton Roy, Riviera Beach, FL). The temperature of the eluent and the column was controlled by using the PU 4100 column-oven accessory. Oven set temperatures were calibrated with a calibrated chromel/alumel thermocouple inserted in a T-piece junction. Temperatures measured up- and downstream of the column were always equal to within 2 K. The average was taken to be the column temperature. Chromatograms were recorded and analyzed with a Model 10B integrator (LDC/Milton Roy).

Both commercial and experimental columns (sulfonated polystyrene–divinylbenzene; courtesy of Prof. M. Verzele, State University of Ghent, Belgium) were used. Commercial columns were obtained from Waters/Millipore (IC-PAK C). Dimensions are 50 mm and 4.6 mm i.d.; the exchange capacity was measured to be 14 μequiv/g. All alkali-metal and alkaline-earth-metal salts used were nitrates of Suprapur or comparable quality (Merck, Darmstadt, FRG). High-purity deionized water was used to make up the solutions.

Procedure. The ion-exchange equilibrium was studied by using a chromatographic method. Exchange is between a mobile external liquid phase (eluent), consisting of a solution of the nitrate salt of one of the ions of the exchanging pair (concentrations typically around 10^{-3} M) and a stationary exchanger phase. A small amount (10 μL; 10^{-4}–10^{-5} M) of a solution containing the cation to be studied is introduced into the eluent at the top of the column. The measured quantity is the retention time t_R of this cation or, preferably, the retention time relative to the retention time of an unsorbed solute (t_0)

$$k' = \frac{t_R - t_0}{t_0} \qquad (14)$$

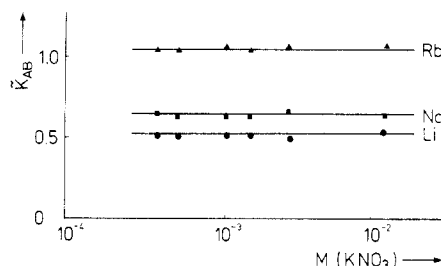The capacity factor (k') thus represents a dimensionless retention,

Figure 1. Plot of equilibrium coefficient vs eluent concentration. Column, Waters IC PAK C; eluent, KNO_3: flow rate, 1.2 mL/min; temperature, 295 K.

Figure 2. van't Hoff plot for alkali exchanges. Column, Waters IC PAK C; flow rate, 1.2 mL/min.

in which the influence of changing flow rates has been eliminated. It is the fundamental tenet of chromatographic theory that a solute band travelling through the column is continuously at equilibrium with the packing material of the column. This assertion can be checked by verifying the invariance of k' with changes in the flow rate.

Evaluation of eq 13 requires knowledge of t_0: the retention time of an unsorbed solute. Several different dead times can be defined depending on the different volumes explored by the unsorbed probe molecule/ion. Different definitions include the interparticle volume or the interparticle volume plus various intraparticle volumes. As probes we used the nitrate ion (by injecting solutions with slightly higher concentrations than the eluent) and water. No significant differences in dead time could be detected, in accordance with the notion that the stationary phase consists of a surface-functionalized resin. In such pellicular type stationary phases intraparticle volumes are thought to be negligible compared to the interparticle volume.

Retention time was measured from the peak apex. As it is only the center of mass of the concentration distribution that is at equilibrium with the stationary phase, this procedure is strictly correct only for symmetrical peaks. In liquid chromatography peaks very rarely are symmetrical. However, using the approximative procedure of Foley and Dorsey[13] to estimate the first statistical moment of the concentration distribution it could be shown that the first moment value does not differ by more than 1% from the peak apex under our conditions.

The capacity factor (k') provides us with the ratio of times spent in the stationary and mobile phases, respectively. This ratio will be equal to the corresponding ratio of average amounts of solute in stationary and mobile phases. Multiplication by the appropriate ratio of volumes (Φ) transforms k' into a concentration ratio. To bring the product $k'\Phi$ into coincidence with the left-hand side of eq 3 we have to multiply it by c^l_B/c^s_B. Both concentrations refer to the equilibrium concentrations of ion B. As the amounts of ion A are very small compared to B, c^l_B and c^s_B are considered to be equal to the eluent concentration and the exchange capacity of the column, respectively. The exchange capacity was measured by using a breakthrough method[14] and conductivity detection. It is expressed in moles per liter. The phase ratio (Φ) then simply is the ratio of the column void volume and the volume occupied by the stationary phase.

It is the variation of the equilibrium coefficient (left-hand side of eq 3) with temperature and eluent concentration that is studied in this work. On the present instrument a series of different experiments at different temperatures could be run automatically. Equilibrium coefficients reported are the average of at least four injections, taken during both heating-up and cooling-down cycles. Columns were regenerated with 0.1 M solution of the eluent when deviations in retention time larger than 2% were detected. All sample solutions were made up from 1000 ppm stock solutions and diluted with eluent to avoid undesirable system peaks.

Results and Discussion

We will first investigate the influence of the external (eluent) concentration on the equilibrium coefficient. In Figure 1 the
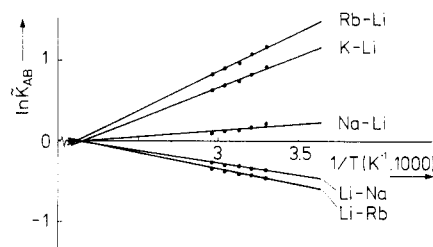
equilibrium coefficient is plotted against the eluent concentration and found to be independent of this concentration in the range normally used in ion chromatography. This observation has been made before, mostly presented as a linear relationship between ln k' and ln c.[15] However, we are now able to interpret it s physical significance. Looking at the right-hand side of eq 3, we notice that the first term is a sum of standard chemical potentials and hence is concentration independent. The second term is the ratio of activity coefficients in the exchanger phase and depends on concentrations in that phase. However, in the linear part of the adsorption isotherm the concentration of the eluent ion stays virtually constant (equivalent fraction in the exchanger phase very close to 1). Also, the chemical environment of the solute ions does not change (only interaction with eluent ions and not with other solute ions). Therefore, the activity coefficient of the solute in the exchanger phase is not expected to change either. Thus, the ratio γ^l_A/γ^l_B is independent of the external concentration. From the limiting behavior of the activity coefficients, we may confidently assume this constant ratio to be equal to 1. Fundamentally, this means that all differences between $\tilde{K}$ values of different ions are due to differences in the exchanger phase. From a practical point of view it implies that we have the freedom to choose the external concentrations so as to measure retention times in the chromatographically optimum range without influencing the equilibrium coefficient.

In Figure 2 the logarithm of the equilibrium coefficient for a number of alkali-metal ion exchanges is plotted against the reciprocal temperature. From the good linearity of the plots in our range of measurement we conclude that $\Delta\tilde{H}$ and $\Delta\tilde{S}$ can be considered to be independent of temperature. Visual inspection suggests that there is a compensation of enthalpy and entropy changes. An unbiased interpretation of the data is not trivial, however. Krug et al.[16] have shown that the usual way of data analysis, i.e., regressing ΔH onto ΔS to obtain an estimate of the compensation temperature, leads to results that are heavily confounded with, if not dominated by, statistical error. The origin of statistical compensation is to be found in the fact that errors in enthalpies and entropies obtained from plots such as Figure 2 are highly correlated. To distinguish between statistical and physical compensation, the above authors suggest a hypothesis test. The hypothesis that the observed line in the enthalpy–entropy plane is a manifestation of only the statistical compensation pattern may be rejected if the slope estimate is sufficiently different from T_{hm} (the harmonic mean of the experiment temperatures) as determined by a t test. Applied to the data of Figure 2, we find that coincidence of the slope of the ΔH–ΔS plot with the harmonic mean temperature can be rejected at the 1% level of significance. We hence conclude that the compensation found is of physical origin.

In the following we will present our data as plots of $\Delta\tilde{H}$ vs $\Delta\tilde{G}_{T_{hm}}$, the Gibbs free energy evaluated at the harmonic mean of the experimental temperatures, instead of $\Delta\tilde{H}$ vs $\Delta\tilde{S}$ plots. The great advantage of this transformation of variables is that the abscissa and ordinate values are now no longer correlated and an unbiased estimation of the compensation temperature may be

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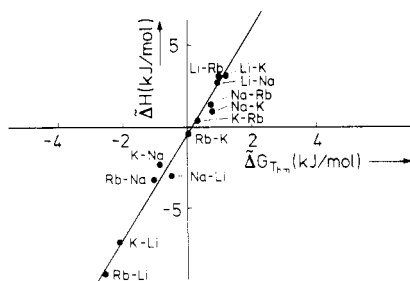(16) Krug, R. R.; Hunter, W. G.; Grieger, R. A. *J. Phys. Chem.* **1976**, *80*, 2335.

Figure 3. Plot of $\Delta \tilde{H}$ vs $\Delta \tilde{G}_{T_{hm}}$ for the alkali-metal exchanges. Column, Waters IC PAK C. The data are evaluated at $T_{hm} = 319.1$ K. The observed linear compensation corresponds to a compensation temperature of 480 ± 20 K.

obtained. That a compensation between ΔH and $\Delta G_{T_{hm}}$ should also appear if an enthalpy–entropy compensation exists follows directly from the first and second laws of thermodynamics.

In Figure 3 the exchange enthalpy has been plotted against $\Delta \tilde{G}_{T_{hm}}$ for 12 monovalent cation exchanges. Values of $\Delta \tilde{H}$ and $\Delta \tilde{G}_{T_{hm}}$ were obtained by regressing $\ln \tilde{K}$ onto $\{1/T - \langle 1/T \rangle\}$. From the slope ($a$) and the intercept ($b$) estimates of $\Delta \tilde{H}$ end $\Delta \tilde{G}_{T_{hm}}$ are calculated according to $\Delta \tilde{G}_{T_{hm}} = -RT_{hm}b$ and $\Delta \tilde{H} = -Ra$. The value of the compensation temperature indicated in the figure was obtained by regressing $\Delta \tilde{H}$ onto $\Delta \tilde{G}_{T_{hm}}$ using ordinary linear regression. As the error in $\Delta \tilde{G}_{T_{hm}}$ is much smaller than that in $\Delta \tilde{H}$ use of the modified regression algorithm suggested by Krug et al.[17] did not lead to significantly different results. The compensation temperature can be obtained from the slope of the plot (c) according to $T_c = T_{hm}/(1 - 1/c)$.

Two things should be noted in Figure 3. First, within experimental error the compensation line passes through the origin. This is in accordance with basic thermodynamic principles. One would not expect any enthalpic or entropic effect, when the two ions of the exchanging pair are identical. In liquid chromatography incomplete compensation, i.e., compensation lines not passing through the origin, has been reported.[18] If, following Everett,[19] adsorption from solution is envisaged as an exchange, this is clearly impossible. However, it is common practice to plot the logarithm of the capacity factor rather than the logarithm of the equilibrium coefficient against reciprocal temperature. Referring to eq 3 it is readily seen that this procedure introduces a trivial constant corresponding to $\ln \Phi \; x^l_B/x^s_B$.

Second, it is seen from Figure 3 that A–B and B–A exchanges are not symmetrical with respect to inversion in the origin. As eq 9 predicts inversion symmetry, we can conclude that specificity in ion exchange is not determined by one-body interaction potentials. We, therefore, analyzed our data according to eq 8 and corresponding equations. For the 12 exchanges among the four alkali-metal ions we thus have 12 equations and 10 unknown interaction parameters. This offers the possibility of predicting the equilibrium position of any remaining two exchanges. As our goal here is to test the model developed in ref 9, we took a somewhat different approach. We have solved the overdetermined system using an algorithm that finds the least-squares solution.[20] Note that the f_{ij} values cannot be obtained absolutely, e.g., by inspection of eq 12. Differences can be calculated that are known to within an unknown constant. Absolute values of the interaction parameters thus are arbitrary. The internal consistency of the obtained set of parameters, however, can be checked by comparing measured thermodynamic properties with those predicted by differences between interaction parameters by using eq 8 and related equations. In Table I measured $\Delta \tilde{H}_{AB}$ values are shown together with those calculated by substituting the fitted f_{ij} values into eq 12. It is seen that they agree to within experimental error. We therefore conclude that our results can be adequately described

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(19) See e.g.: Everett, D. H. *J. Phys. Chem.* **1981**, *85*, 3263.

(20) NAG Fortran Library, Routine F04JGF.

TABLE I: Comparison of Measured and Fitted Exchange Enthalpies[a] (kJ/mol)

exchange	fitted	measd	exchange	fitted	measd
Na–Li	−3.44	−3.10	Li–K	2.98	2.99
K–Li	−7.18	−7.23	Na–K	1.12	1.00
Rb–Li	−8.77	−9.05	Rb–K	−0.78	−0.67
Li–Na	3.18	2.84	Li–Rb	2.71	3.04
K–Na	−2.46	−2.34	Na–Rb	1.50	1.28
Rb–Na	−3.35	−3.13	K–Rb	0.48	0.37

[a] Fitted values were derived from the solutions of f_{AB} and f_{BB} obtained from the set of equations of the type (12). Estimated standard deviations of measured $\Delta \tilde{H}$ values range from 5 to 10%.
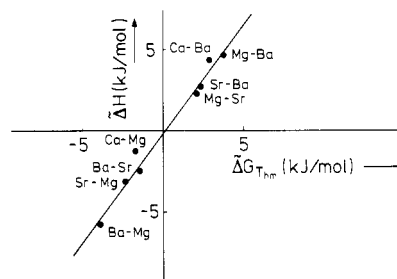

Figure 4. Plot of $\Delta \tilde{H}$ vs $\Delta \tilde{G}_{T_{hm}}$ for alkaline-earth-metal exchanges. Column, Waters IC PAK C. The data are evaluated at $T_{hm} = 319.1$ K. The compensation temperature (excluding Ca exchanges) is 1250 ± 100 K.
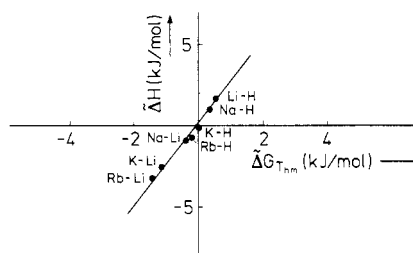

Figure 5. Plot of $\Delta \tilde{H}$ vs $\Delta \tilde{G}_{T_{hm}}$ for alkali-metal exchanges. Column, polystyrene–divinylbenzene (home made). Harmonic mean temperature, 319.1 K. The compensation temperature derived from this plot is 540 ± 50 K. Note the good correspondence with T_c obtained by using the commercial column (Figure 3).

assuming that two-body interactions are dominant.

In Figure 4 the exchange of divalent ions is illustrated. Again, a compensation line passing through the origin is found, in accordance with basic thermodynamic notions. Points referring to exchanges with Ca appear to be somewhat off the line. The reason for this is not quite clear. Secondary equilibria with hydroxyl or bicarbonate ions might cause the equilibrium concentration of calcium to be lower than expected. The compensation temperature is more than twice the compensation temperature observed in the case of monovalent exchange. Qualitatively, this seems a reasonable result. We have shown that selectivity is introduced through two-body interaction potentials. The geometrical configuration of divalent ions relative to one another and relative to the fixed charges on the exchanger is expected to differ considerably from the case of monovalent ions. One would not expect the interaction potential to behave in the same way in this case.

Figure 5 illustrates the influence of the exchange material. For the exchange of the alkali-metal ions the compensation temperature mains the same but the positions on the line change. Due to the lower selectivity of the resin the actual enthalpies and entropies have all moved to lower values. Thus, differences between different columns are determined solely by geometric factors. The way in which $\hat{\mu}$ depends on the reference f_0 and its temperature dependence—one is inclined to call this the mechanism of exchange—remain the same.

Let us now review the position we have arrived at. We have found that entropy–enthalpy compensation occurs for all cases of ion exchange studied. From a very general formalism we have
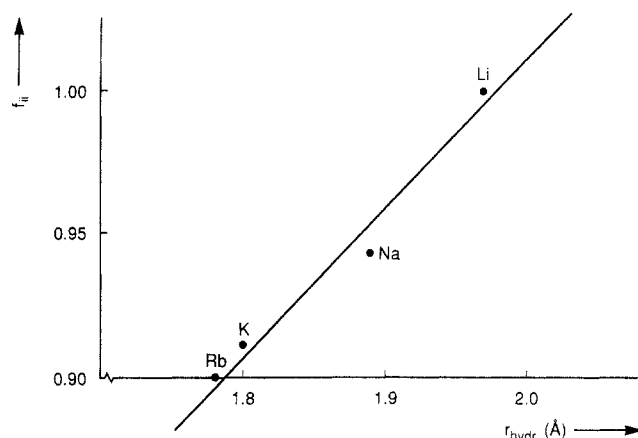
Figure 6. Plot of f_{ii} vs hydrated ionic radii (ref 22).

shown that a consistent set of interaction parameters can be derived assuming that two-body interactions determine specificity. Dominance of the interaction of the ions with the exchanger was shown to be inconsistent with the results. We would like to note that currently used models to describe selectivity in ion-exchange and ion-pair chromatography, especially the double-layer model,[21] do not take interactions between adsorbed species into account.

From the constancy of $\Delta\bar{H}$ and $\Delta\bar{S}$ we know that $(\partial\bar{\mu}/\partial f)_{f=f_0}$ changes linearly with temperature over the experimental range. The compensation temperature is, hence, equal to the negative of the ratio of the intercept and the slope of this line. As the constancy of the tangent to a possibly very complicated function is measured, the compensation temperature should not be given

the physical significance of a critical temperature.[9] A more detailed model is needed to allow interpretation of the compensation temperature and of the differences found between different compensation classes. Also, one would want to be able to predict f_{ij} from the geometric properties of the ions in the resin phase. As a first attempt, it is shown in Figure 6 that as reasonable correlation is obtained between values for the interaction parameters and the hydrated ionic radii. The interaction parameters are scaled to 1 and 0.9 for the largest and the smallest, respectively. Values for the hydrated ionic radii of the alkali-metal ions are the corrected Stokes radii taken from Marcus.[22]

In conclusion, it can be stated that a framework has been built to interpret selectivity in ion exchange. More detailed models are needed for a complete specification of the system, however. The elaboration of these models is the subject of further research.

Conclusions

(i) Enthalpy–entropy compensation occurs for all cases of ion exchange studied.

(ii) Using the information contained in enthalpy–entropy compensation one can explain the ion-exchange equilibrium from first principles assuming that the interaction potentials differ only in one parameter.

(iii) For the ion-exchange equilibrium a consistent set of interaction parameters can be derived assuming that the dominant feature determining specificity is the interaction between adsorbed ions.

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Light Scattering of Liquids and Liquid Mixtures. 3. Thermodynamic Interaction Data for Selected Binary Mixtures

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A modified experimental and analytical procedure for characterizing liquid–liquid mixture interactions from light scattering data was presented in a preceding work. The accuracy and resolving power of the method have been assessed here by applying the technique to six binary systems: benzene–octane, toluene–octane, toluene–decane, benzene–carbon tetrachloride, cyclohexane–carbon tetrachloride, and benzene–methanol. The attainable accuracy depends mainly on the difference of the refractive indices of the two components of the mixture and on the experimental precision in the determination of isotropic Rayleigh ratio and isothermal compressibility.

Introduction

In a previous paper,[1] theoretical and experimental framework was presented for the utilization of light scattering for thermodynamic study of binary liquid mixtures. In a model investigation, the method was illustrated on the system benzene–cyclohexane. The concept of excess isothermal compressibility of mixing was

introduced into the data treatment procedure as a means of boosting the precision of the technique. Neglect of the excess compressibility was found to introduce a systematic error into the thermodynamic functions obtained, which in some cases can be quite significant.

In this work, light scattering is used to evaluate thermodynamic interaction functions for six binary systems: benzene–octane, toluene–octane, toluene–decane, benzene–carbon tetrachloride, cyclohexane–carbon tetrachloride, and benzene–methanol. The

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