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Method for Evaluating Exchangeable-Ion Excess Gibbs Energy Models In Systems with Many Species

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We have developed a method for evaluating excess Gibbs energy (G_{excess}) models for exchangeable ions by exploiting the relationship between the Vanselow selectivity coefficient and the exchange equilibrium constant. Unlike presently available methods, the "rational approach" may be used to fit G_{excess} models to systems with any number of exchangeable ions. To demonstrate its utility, the method was used to evaluate three G_{excess} models in both binary and ternary cation-exchange systems. The Wilson model described best the chemical behavior of exchangeable cations in both binary and ternary cation-exchange systems.

Despite years of research, there is still no generally accepted activity-coefficient model for exchangeable ions. Until a reliable statistical-mechanical model is developed, the most popular source of exchangeable-ion activity-coefficient models will remain excess Gibbs energy (G_{excess}) models found in the thermodynamic theory of mixtures.[1] While G_{excess} models have been applied successfully to binary ion-exchange systems,[2-4] it is not clear if these models are generally applicable as no one has successfully estimated G_{excess} model parameters from experiments with more than two exchangeable ions.[5,6] To settle the matter, we have developed a method, called the rational approach, which can be used to evaluate statistically G_{excess} models in systems with any number of exchangeable ions.

The molar excess Gibbs energy (G_{excess}, J mol^{-1}), may be defined as[1]

$$\frac{G_{excess}}{RT} = \sum_{i=1}^{n} x_i \ln f_i \tag{1}$$

where R is the molar gas constant (J K^{-1} mol^{-1}); T, temperature, (K); x_i, the mole fraction of species i; and f_i, its rational activity coefficient. Expressions for $\ln f_i$ in systems with two or more exchangeable ions can be derived from eq 1 using the Gibbs–Duhem equation. For binary systems, this results in

$$\ln f_1 = \frac{1}{RT} \left[G_{excess} + x_2 \frac{d(G_{excess})}{dx_1} \right] \tag{2}$$

while for ternary systems

$$\ln f_1 = \frac{1}{RT} \left[G_{excess} + x_2 \left(\frac{dG_{excess}}{dx_3} \right)_{x_1} + (x_2 + x_3) \left(\frac{dG_{excess}}{dx_1} \right)_{x_2} \right] \tag{3}$$

Similar expressions may be derived for systems with more than three exchangeable species.

The rational approach is based on the identity

$$\ln k^a_{(V)1/2} = \ln K_{ex1/2} + z_1 \ln f_2 - z_2 \ln f_1 \tag{4}$$

where $k^a_{(V)1/2}$ is the Vanselow selectivity coefficient,[7] $K_{ex1/2}$, the exchange equilibrium constant,[8] and z_1, the valence of exchangeable ion 1. The method is called the "rational approach" since exponentiation of eq 4, after rearrangement, relates the ratio $k^a_{(V)1/2}/K_{ex1/2}$ to the ratio $f_2^{z_1}/f_1^{z_2}$. The method is applied by determining $k^a_{(V)1/2}$ for the system under consideration and then fitting by nonlinear regression techniques eq 4 in which $\ln f_1$ and $\ln f_2$ have been replaced by expressions derived from G_{excess} model under consideration using relations such as eq 2 or 3. For systems with more than two exchangeable ions, and thus more than one Vanselow selectivity coefficient, eq 4 may be reformulated so that the sum

$$\sum_{i=1}^{n-1} \sum_{n \geq j > i} \left(\ln k^a_{(V)i/j} - \ln K_{exi/j} - z_i \ln f_j + z_j \ln f_i \right)^2 \tag{5}$$

is minimized by a nonlinear regression procedure. This method has been used earlier,[9] though to our knowledge this is the first

(1) Gokcen, N. A. *Statistical Thermodynamics of Alloys*; Plenum Press: New York, 1986; Chapter 1.
(2) Freeman, D. H. *J. Chem. Phys.* **1961**, *35*, 189.
(3) Elprince, A. M.; Babcock, K. L. *Soil Sci.* **1975**, *120*, 332.
(4) Elprince, A. M.; Vanselow, A. P.; Sposito, G. *Soil Sci. Soc. Am. J.* **1980**, *44*, 964.
(5) Fletcher, P.; Franklin, K. R.; Townsend, R. P. *Philos. Trans. R. Soc. London, A* **1984**, *312*, 141.
(6) Chakravarti, A. K.; Fritzsch, G. *React. Polym.* **1988**, *8*, 51.

(7) Introduced by A. P. Vanselow (*Soil Sci.* **1932**, *33*, 95), this corrected exchange selectivity coefficient may be defined by

$$k^a_{(V)i/j} = \left(\frac{x_i}{a^s_i} \right)^{z_j} \left(\frac{a^s_j}{x_j} \right)^{z_i}$$

where x_i is the mole fraction of exchangeable ion i, a^s_i, the activity of the ion's electrolyte in solution, and z_i, the ion's valence.
(8) This is defined here to be

$$K_{exi/j} = \left(\frac{a^e_i}{a^s_i} \right)^{z_j} \left(\frac{a^s_j}{a^e_j} \right)^{z_i}$$

where a^e_i is the activity of the exchangeable ion i.
(9) Sposito, G. *The Thermodynamics of Soil Solutions*; Clarendon Press: Oxford, 1981; Chapter 5. D. H. Freeman[2] fit the Gaines–Thomas selectivity coefficient (in which the exchangeable ion is represented by its equivalent fraction) to a general G_{excess} model.

TABLE I: Expression for Exchangeable-Ion Activity Coefficients in Binary and Ternary Systems Derived from Three Excess Gibbs Energy Models

	activity coefficient models	
excess Gibbs energy model	for binary systems	for ternary systems
regular-solution model	$\ln f_1 = a_{12}(x_2)^2$	$\ln f_1 = a_{13}x_3^2 + (a_{13} - a_{23} + a_{12})x_2x_3 + a_{12}x_2^2$
subregular-solution model	$\ln f_1 = (x_2)^2[A_{21} + 2x_1(A_{21} - A_{12})]$	$\ln f_1 = (A_{31} + A_{32})x_2x_3^2 + (((A_{31} + A_{32}) + (A_{21} + A_{23}))x_2^2 + (2(A_{12} + A_{13}) - 2(A_{31} + A_{32}))x_1x_2)x_3^2 + ((A_{21} + A_{23})x_2^3 + (2(A_{12} + A_{13}) - 2(A_{21} + A_{23})x_1x_2^2 - (A_{12} + A_{13})x_1^2x_2)x_3$

Wilson model

$$\ln f_1 = -x_2 \ln (1 - a_{2/1}x_2) + x_2\left(\frac{a_{2/1}x_2}{1 - a_{1/2}x_1} - \frac{a_{1/2}x_1}{1 - a_{2/1}x_2}\right)$$

$$\ln f_1 = -x_1 \ln (1 - a_{3/1}x_3 - a_{2/1}x_2) + x_2(\ln (1 - a_{3/2}x_3 - a_{1/2}x_1) + \frac{a_{3/2}x_2}{1 - a_{3/2}x_3 - a_{1/2}x_1} - \frac{(a_{2/1} - a_{3/1})x_1}{1 - a_{3/1}x_3 - a_{2/1}x_2} - \frac{a_{2/3}x_3}{1 - a_{2/3}x_2 - a_{1/3}x_1} - \ln (1 - a_{2/3}x_2 - a_{1/3}x_1) - \ln (1 - a_{3/2}x_3 - a_{1/2}x_1)) - x_3 \ln (1 - a_{2/3}x_2 - a_{1/3}x_1) + (x_3 + x_2) \times$$

$$\left(\ln (1 - a_{2/3}x_2 - a_{1/3}x_1) - \ln (1 - a_{3/1}x_3 - a_{2/1}x_2) - \frac{(a_{3/2} - a_{1/2})x_2}{1 - a_{3/2}x_3 - a_{1/2}x_1} - \frac{a_{3/1}x_1}{1 - a_{3/1}x_3 - a_{2/1}x_2} + \frac{a_{1/3}x_3}{1 - a_{2/3}x_2 - a_{1/3}x_1} \right)$$

TABLE II: Ternary Excess Gibbs Energy Model Coefficient Values Estimated by Nonlinear Regression from Binary and Ternary Cation-Exchange Data

		cation-exchange data used			
		ternary		binary	
excess Gibbs energy model	coefficient	estimate	asymptotic std error	estimate	asymptotic std error
regular solution	a_{12}	0.0885	0.2168	0.4232	0.2948
	a_{23}	−0.0986	0.1734	1.3766	0.4653
	a_{13}	−0.4584	0.0930	−1.3200	0.3746
subregular solution	$A_1 (=A_{12} + A_{13})$	0.0597	1.4001	−1.5077	0.9718
	$A_2 (=A_{21} + A_{23})$	2.1859	2.0886	2.6614	0.9582
	$A_3 (=A_{31} + A_{32})$	−2.9212	1.5239	−0.1254	0.8159
Wilson	$A_{1/2}$	−0.0809	1.2693	−0.8768	1.1766
	$A_{1/3}$	0.6695	1.0017	−0.5413	0.7543
	$A_{2/1}$	0.4609	0.8899	0.9271	0.4176
	$A_{2/3}$	−0.5807	2.2311	0.7847	0.4319
	$A_{3/1}$	−1.4857	2.6209	−1.2842	1.6311
	$A_{3/2}$	0.5751	1.2624	0.4171	0.4996

time it has been used systematically to evaluate several G_{excess} models or used to estimate G_{excess} model parameters from ternary ion-exchange data.

In the implementation of the rational approach, $\ln K_{exi/j}$ may be treated as another coefficient to be fit during regression evaluation of eq 4 or it may be calculated separately and its calculated value treated as a constant during the regression evaluation. In most situations, its estimated value will be affected, sometimes dramatically, by the G_{excess} model from which $\ln f_1$ and $\ln f_2$ in eq 4 are derived. If several G_{excess} models are to be evaluated using the rational approach, it may be better to estimate $\ln K_{exi/j}$ by the Argersinger approach[10] before evaluating these models. Similarly, if three complimentary binary ion-exchange systems (e.g., NH_4–Ba, Ba–La, and La–NH_4) are to be studied, the values of the three $\ln K_{exi/j}$ values are related by the triangle rule.[11] This constraint is not easily inserted into the regression evaluation of each set of binary ion-exchange data.

To demonstrate the utility of the rational approach, three G_{excess} models (regular-solution, subregular-solution and Wilson) were evaluated in a ternary and three binary cation-exchange systems.[12-14] Representations of eq 2 and 3 for each of these models

in both binary and ternary systems are presented in Table I.[15] Two aspects of the candidate models were evaluated: (1) their ability to describe accurately $\ln k^a_{(v)i/j}$ in binary and ternary systems and (2) whether model-coefficient estimates calculated from binary data accurately predicted $\ln k^a_{(v)i/j}$ in ternary experiments. The data of Elprince et al., who studied NH_4–Ba–La exchange on a montmorillonite clay, were analyzed.[4] The Vanselow selectivity coefficient was calculated by

$$k^a_{(v)i/j} = \left(\frac{x_i}{m_i^s(\gamma \pm iCl_{z_i})^{z_i+1}}\right)^{z_j}\left(\frac{m_j^s(\gamma \pm jCl_{z_j})^{z_j+1}}{x_j}\right)^{z_i} \quad (6)$$

where m_i^s is aqueous molality (mol kg^{-3}) of the chloride salt of cation "i" and $\gamma \pm iCl_{z_i}$, the mean ionic activity coefficient for this salt in solution. The mean ionic activity coefficients for each salt at a given ionic strength were calculated from the data tabulated by Harned and Owen.[16] The exchange-equilibrium constants were calculated before the models were tested.[17] Equations 2–5 for each G_{excess} model were evaluated using MACSYMA.[18]

(10) Argersinger, W. J.; Davidson, A. W.; Bonner, O. D. *Trans. Kansas Acad. Sci.* **1950**, *53*, 404. The exchange equilibrium constant may be calculated by evaluating the integral

$$\ln K_{exi/j} = \int_0^1 \ln k^a_{(v)i/j}\, dE_i$$

where E_i is the equivalent fraction of exchangeable ion i.

(11) The so-called triangle rule (see Helfferich, F. G. *Ion Exchange*; McGraw-Hill: New York, 1962; Chapter 5) relates three complementary exchange equilibrium constants algebraically by $z_k \ln K_{exi/j} + z_i \ln K_{exj/k} + z_j \ln K_{exk/i} = 0$.

(12) Hildebrand, J. H. *J. Am. Chem. Soc.* **1929**, *51*, 66.

(13) Hardy, H. K. *Acta Metall.* **1953**, *1*, 202.

(14) Wilson, G. M. *J. Am. Chem. Soc.* **1964**, *86*, 127.

(15) The following served the sources for the G_{excess} models evaluated: binary and ternary regular solution, Gokcen,[1] eq 4.7 (for $S_{excess} = 0$); binary subregular solution, Hardy,[13] eq 1; ternary subregular solution, J. Grover, (In *Thermodynamics in Geology*; Fraser, D. G., Ed.; D. Reidel: Dordrecht, The Netherlands, 1977), eq 37; binary and ternary Wilson, Wilson,[14] eq 1.

(16) Harned, H. S.; Owen, B. B. *The Physical Chemistry of Electrolyte Solutions*; Reinhold: New York, 1958; Appendix.

(17) $\ln K_{exLa/Ba}$, 2.216 027 78; $\ln K_{exLa/NH_4}$, −0.917 694 4; $\ln K_{exBa/NH_4}$, −1.350 472 2.

(18) Symbolics, Inc. *VAX UNIX MACSYMA Reference Manual Version 11*; Symbolics, Inc.: Cambridge, MA, 1985; Chapter 2.

TABLE III: Total Sums of Squares and Residual Sums of Squares after Fitting ln $k^a_{(v)i/j}$ by Nonlinear Regression to Three Excess Gibbs Energy Models

exchange system modeled	TSS	excess Gibbs energy model	RSS
La–Ba	11.827	regular solution	12.919
		subregular solution	10.503
		Wilson	11.415
La–NH$_4$	8.751	regular solution	4.604
		subregular solution	4.541
		Wilson	4.532
Ba–NH$_4$	9.319	regular solution	5.840
		subregular solution	5.690
		Wilson	5.569
La–Ba–NH$_4$	3.895	regular ternary data	3.086
		regular binary data	34.845
		subregular ternary data	4.825
		subregular binary data	6.955
		Wilson ternary data	1.597
		Wilson binary data	98.692

Statistical evaluations of the G_{excess} models were performed using the Gauss–Newton method of the NLIN procedure in the SAS statistical package.[19]

In some cases it may be assumed that exchangeable cations behave as if in an ideal mixture; that is, f_i and, consequently, $k^a_{(v)i/j}$ are independent of exchangeable-cation composition. This would be the case if the experimentally estimated coefficients for the simplest G_{excess} model, the regular solution, were zero. Inspection of the binary regular-solution model-coefficient estimates and their asymptotic standard errors presented in Table II indicated that coefficients in two of the binary cation-exchange systems were not zero. Accordingly, it is appropriate with these data to develop or select an exchangeable-cation activity-coefficient model.

Table III presents the total sum of squares (TSS), corrected for the mean, for the ln $k^a_{(v)i/j}$ values in both the binary and ternary experiments along with the residual sums of squares (RSS) associated with the nonlinear regression of each model.[20] Two RSS values are presented for each model when applied to ternary systems; one was calculated using the G_{excess} model coefficients estimated from ternary data and the other using coefficients estimated from binary data. These RSS values indicate that all three of the G_{excess} models evaluated could be used to describe the binary cation-exchange data. Use of either the regular-solution or Wilson models with ternary cation-exchange data reduced the RSS below the TSS. With the regular-solution model, the reduction in the RSS was modest, indicating that the Wilson model might be conditionally preferred. Still, it should be noted that the differences in the predictions by the regular-solution and Wilson models in ternary cation-exchange systems were small,

(19) SAS Institute Inc. *SAS User's Guide: Statistics, Version 5 Edition*; SAS Institute Inc.: Cary, NC, 1985; Chapter 25.

(20) In Table 2, the total sum of squares, corrected for the mean, is defined to be

$$\sum_{i=1}^{n} (\ln k^a_{(v)1/2}(i) - \overline{\ln k^a_{(v)1/2}})^2$$

and the residual sum of squares

$$\sum_{i=1}^{n} (\ln k^a_{(v)1/2}(i) - \hat{y}(i))^2$$

where $\overline{\ln k^a_{(v)1/2}}$ is the mean value of ln $k^a_{(v)1/2}$ in the data set under consideration and $\hat{y}(i)$ is the value of ln $k^a_{(v)1/2}$ predicted using the G_{excess} model under consideration.
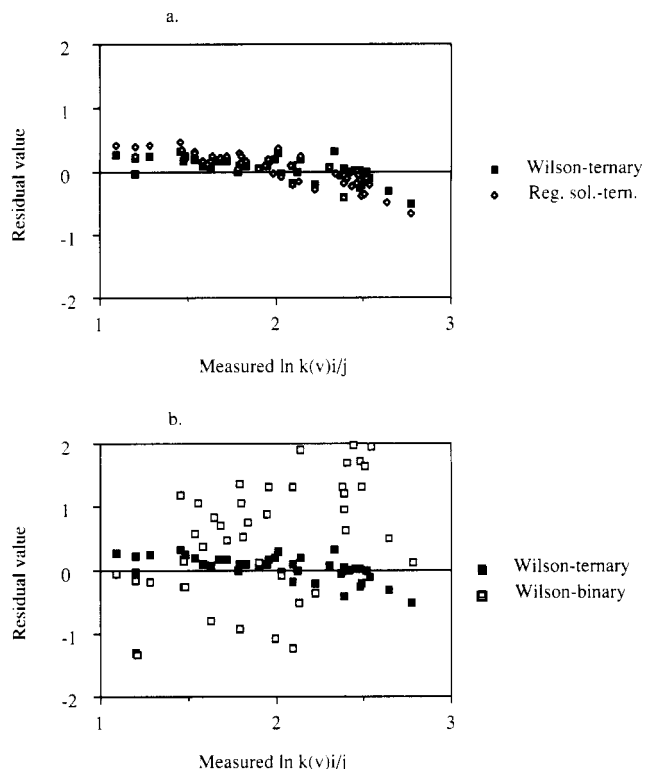

Figure 1. (a) Plot of residuals of ln $k^a_{(v)i/j}$ values measured in ternary cation-exchange experiments and those predicted by using Wilson and regular-solution model coefficients estimated using the ternary cation-exchange data. (b) Plot of residuals of ln $k^a_{(v)i/j}$ values measured in ternary cation-exchange experiments and those predicted by using Wilson model coefficients estimated using either binary or ternary cation-exchange data.

as can be seen in Figure 1a, which shows a plot of the residuals for the ln $k^a_{(v)i/j}$ values predicted by these two models.

Wilson model coefficients determined from binary cation-exchange experiments could not be applied successfully to ternary systems. The ternary system RSS for the Wilson model coefficients determined in binary systems were many times higher than the RSS resulting from using coefficients determined in the ternary system. This disparity is presented graphically in Figure 1b.

Excess Gibbs energy models have been widely used to describe the thermodynamic properties of solid and liquid mixtures,[1,21] but until now the appropriateness of these models for exchangeable ions could not be tested conclusively since no technique existed to apply these models to multispecies ion-exchange systems. Using the rational approach, three candidate G_{excess} models in both binary and ternary ion-exchange systems could be evaluated directly and the appropriate model coefficients estimated. We believe that this tool will facilitate the development and evaluation of exchangeable-ion G_{excess} models for systems with numerous exchangeable species.

(21) Abrams, D. S.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 116. See also Wilson[14] and Grover.[15]