Modeling Viscosity of Multicomponent Electrolyte Solutions[1]

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[1] Paper presented at the Thirteenth Symposium on Thermophysical Properties, June 22-27, 1997, Boulder, Colorado, USA.

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ABSTRACT

A comprehensive model for calculating the viscosity of aqueous electrolyte solutions has been developed. The model includes a long-range electrostatic interaction term, contributions of individual ions and a contribution of specific interactions between ions or neutral species. The long-range electrostatic term is obtained from the Onsager-Fuoss theory whereas the individual ionic contributions are calculated using the Jones-Dole *B* coefficients. A technique for predicting the temperature dependence of the B coefficients has been developed on the basis of the concept of structure-breaking and structure-making ions. The contribution of specific interactions between species, which is dominant for concentrated solutions, has been found to be a function of the ionic strength. The model reproduces the viscosity of aqueous systems ranging from dilute to concentrated solutions (up to ca. 30 m) at temperatures up to 573 K with an accuracy that is appropriate for modeling industrially important systems. In particular, the viscosity of multicomponent systems can be accurately predicted using parameters obtained from single-solute systems.

KEY WORDS: viscosity, aqueous solutions, electrolytes

1. INTRODUCTION

Knowledge of viscosity of electrolyte solutions is needed for the design of numerous industrial processes and, at the same time, provides useful insights into solution structure and interactions. Theoretical investigations of viscosity have been focused mainly on systems containing a single solute in dilute solutions (cf. a review by Horvath [1]). A limiting law for viscosity was developed by Onsager and Fuoss [2] using the Debye-Hückel equilibrium distribution functions. For somewhat more concentrated solutions (up to 0.1-0.2 M), Jones and Dole [3] found that the relative viscosity is given by

$$\eta_r = \eta / \eta_0 = 1 + Ac^{1/2} + Bc \qquad (1)$$

where η_0 is the viscosity of pure water and the $Ac^{1/2}$ term is identical to that obtained from a limiting-law theory of long-range electrostatic interactions in a dielectric continuum [2]. The coefficient *B* was found to be an additive property of ions and give a useful measure of ion-solvent interactions. An extended version of eq. 1 was proposed by Kaminsky [4] and used by several authors [5, 1] to fit the results of viscosity measurements at higher concentrations:

$$\eta_r = \eta / \eta_0 = 1 + Ac^{1/2} + Bc + Dc^2 \qquad (2)$$

The Jones-Dole equation proved useful because the *B* coefficients could be related to the properties of ions [1]. However, eq. 2 is not valid for systems containing more than one salt and cannot reproduce data for concentrated solutions (beyond ca. 1-3 M). Alternative models developed for concentrated solutions [1] are also applicable only for single-solute systems or do not take into account the speciation of the solution. Therefore, there is a need for a model that would reproduce the viscosity of multicomponent solutions in the full ranges of concentration and temperature that are encountered in industrial applications.

The objective of this study is to develop a comprehensive, engineering-oriented method for calculating viscosity of aqueous systems ranging from dilute to very concentrated. The method should be consistent with a realistic speciation model so that the viscosity model can be used in conjunction with speciation-based models for thermodynamic properties. Emphasis

will be put on developing a formalism that makes it possible to predict viscosity of multicomponent solutions on the basis of information obtained from single-solute systems.

2. CONCENTRATION DEPENDENCE OF VISCOSITY

The main advantage of the Jones-Dole equation is the recognition of a clear distinction between the long-range electrostatic term, contributions of individual ions (as quantified by the B coefficients) and contributions of interactions between ions or neutral species. Therefore, we can write a general expression for the relative viscosity η_r , i.e.,

$$\eta_r = 1 + \eta_r^{LR} + \eta_r^{species} + \eta_r^{species-species} \quad (3)$$

where the superscript *LR* stands for the long-range contribution. The η_r^{LR} term can be calculated from a model that recognizes electrostatic interactions between point charges in a dielectric continuum. Onsager and Fuoss [2] developed an analytical solution for this model for systems containing any number of ions. Working equations resulting from the Onsager-Fuoss theory are summarized in the Appendix. To compute the η_r^{LR} term, it is necessary to know the limiting conductivities of individual ions in addition to the dielectric constant of the solvent. The ionic conductivities are calculated as a function of temperature using a method developed by Anderko and Lencka [6].

The additivity of the B coefficients, which is well documented for single-solute and two-solute systems [7], can be easily generalized for multicomponent systems. Therefore, the $\eta_r^{species}$ term is an additive sum of contributions of individual species, i.e.,

$$\eta_r^{species} = \sum_i c_i B_i \quad (4)$$

where c_i and B_i are the molar concentration and *B* coefficient of the i-th species.

In contrast to the $\eta_r^{species}$ term, the $\eta_r^{species-species}$ contribution depends on interactions between various species that exist in the system. In this work, we develop an expression for $\eta_r^{species-species}$ that is valid for multicomponent solutions. In the extended Jones-Dole equation for single-solute systems (eq. 2), the $\eta_r^{species-species}$ term is proportional to c^2 (i.e., Dc^2). Here, we postulate that the $\eta_r^{species-species}$ term for multicomponent systems is proportional to I^2.

Further, we postulate that this term is made up of contributions of all species pairs in the system. This implies that $\eta_r^{species-species}$ is expressed by summation over all species pairs, i.e.,

$$\eta_r^{species-species} = \sum_i \sum_j f_i f_j D_{ij} I^2 \quad (5)$$

where f_i and f_j are fractions if the *i*-th and *j*-th species, respectively, and D_{ij} is the interaction parameter between *i* and *j*. The definition of the fraction of the *i*-th ion in eq. 5 should be guided by the empirical effectiveness of the final expression for multicomponent systems. Tests made using a total of 17 systems with two or three solutes revealed that the best agreement is obtained when f_i is a molar fraction adjusted for the charge of species, i.e.,

$$f_i = \frac{c_i / \max(1,|z_i|)}{\sum_k c_k / \max(1,|z_k|)} \quad (6)$$

where the factor $\max(1,|z_i|)$ ensures that f_i reduces to the molar fraction for neutral species. For concentrated solutions, it has been found that the parameter D_{ij} in eq. 5 depends on the ionic strength. The frequently observed steep increase in viscosity for very concentrated systems necessitates the use of an exponential function, i.e.,

$$D_{ij} = d_1 + d_2 I + d_3 \exp(0.08 I^{3/2}) \quad (7)$$

where d_1, d_2 and d_3 are empirical parameters. The parameters d_2 and d_3 are required only for systems with a substantial ionic strength (usually above 5 molal).

3. TEMPERATURE DEPENDENCE OF PARAMETERS

For most electrolyte systems, viscosity data are available only at one temperature (such as 298.15 K) or over narrow temperature ranges. Therefore, it is necessary to establish the temperature dependence of the parameters B and D so that viscosity can be extrapolated well beyond the range of experimental data.

To express the temperature dependence of the parameter B, it is convenient to use the equation of Out and Los [5], i.e.,

$$B = B_E + B_s \exp\left[-k(T - 273.15)\right] \quad (8)$$

This equation accurately reproduces the gradual decrease of the absolute value of *dB/dT*, which tends to zero at high temperatures. To evaluate the coefficients of eq. 8, the parameters B have been calculated by extrapolating the function $B + Dc = (\eta / \eta_0 - 1 - Ac^{1/2}) / c$ to zero concentration. Experimental data from the compilation of Lobo and Quaresma [8] have been used for this purpose. Subsequently, the *B* parameters for individual electrolytes have been decomposed into ionic contributions using the standard convention $B_{K^+} = B_{Cl^-}$ [5]. Then, the coefficients of eq. 8 have been evaluated for a total of 41 ions for which the temperature range of experimental data was sufficient. It has been found that the coefficient *k* in eq. 8 can be assigned a common value of 0.023 without impairing the quality of reproducing the *B* parameters. Therefore, eq. 8 with *k*=0.023 can be further used as a starting point for developing a generalized correlation for predicting the temperature dependence of *B*.

A generalized expression for *B* has to recognize the structural effects caused by the interactions of ions with the H_2O hydrogen-bonded network. In particular, these effects manifest themselves in the positive values of dB/dT for structure-breaking ions and negative values for structure-making ones [5, 9]. As a measure of the structure-making and structure-breaking effects, we utilize the standard entropy of hydration (ΔS_{hyd}), which is widely available from thermodynamic measurements [9]. The correlation between the parameter B_s and ΔS_{hyd} is shown in Fig. 1. It is noteworthy that three linear relationships are obtained for monovalent, divalent and trivalent ions. These relationships are represented by:

$$B_s = -0.00233\Delta S_{hyd} - 0.297 \quad \text{for monovalent ions} \tag{9}$$

$$B_s = -0.0020\Delta S_{hyd} - 0.520 \quad \text{for divalent ions} \tag{10}$$

$$B_s = -0.0020\Delta S_{hyd} - 0.840 \quad \text{for trivalent ions} \tag{11}$$

The correlation between B_s and ΔS_{hyd} appears to be more significant that the correlations that have been previously reported between the *B* coefficients at constant temperature and ΔS_{hyd} or related quantitites [1]. Eqs. 9-11 can be used in conjunction with a single value of *B*

(usually, at 298.15 K) to predict the complete temperature dependence of the ionic *B* parameters according to eq. 8.

The temperature dependence of the interaction parameters (i.e., *D* in eq. 5) is weaker that that of the single-ion parameters (i.e., *B*). For ion-ion interactions, the *D* parameters are almost always positive in contrast to the *B* parameters, which can be either positive or negative. Negative values of *D* are observed only for interactions between neutral aqueous species. For the representation of accurate viscosity data over wide temperature ranges, an exponential temperature dependence is used for the parameters d_i in eq. 7, i.e.,

$$d_i = d_{i,0} \exp[d_{i,1}(T - 273.15)] \qquad (12)$$

4. RESULTS AND DISCUSSION

The proposed model requires the knowledge of speciation in the system of interest so that the summations over individual species (eqs. 4 and 5) can be computed. To obtain the speciation, the thermodynamic model developed by OLI Systems [10] has been used in this study. The parameters of the viscosity model have been derived using a two-step procedure, i.e.,

(1) The B coefficients were obtained from experimental data for dilute solutions and decomposed into individual ionic contributions. Subsequently, the parameters of eq. 8 were calculated by fitting eq. 8 to the ionic B coefficients. If the ionic B coefficients were available only at one temperature or in a narrow temperature interval, their temperature dependence was predicted using eqs. 9-11.

(2) The interaction coefficients d_i (cf. Eq. 7) were obtained for pairs of species by regressing experimental data for single-solute systems using the previously developed data base of B coefficients.

Figures 2-4 show the representation of experimental data [8] for single-solute systems. In all cases the model represents the experimental data within experimental uncertainty. Fig. 2 shows the results for both strong and weak 1:1 electrolytes. It is noteworthy that the

viscosity of strong electrolytes rapidly increases with concentration whereas that of weak electrolytes slowly increases or decreases. The behavior of weak electrolytes, such as acetic acid or HCN, is similar to the behavior of nonelectrolyte solutions. Fig. 3 shows the results for 2:1 electrolytes. In general, the viscosity of 2:1 electrolytes rises more rapidly with concentration than that of 1:1 electrolytes. This is especially notable for the 2:1 electrolytes that do not form strong complexes. In the case of electrolytes that show strong complexation (e.g. zinc halides), the complexation limits the ionic strength of the solution and, subsequently, moderates the increase in viscosity as concentration increases. Fig. 4 shows the viscosity of 3:1 electrolytes. In this case, the viscosity rises even more steeply with concentration so that the relative viscosity can even exceed 100.

Multicomponent systems provide a stringent test of the performance of the model. To validate the model against multicomponent data, the interaction parameters obtained from data for single-solute systems were used to predict the viscosity of systems with two or three solutes. The results are shown in Figs. 5 and 6 for the systems NaCl + HCl + KCl and $(NH_4)_2SO_4$ + KCl + Na_2SO_4, respectively. As illustrated in Figs. 5 and 6, the quality of predicting the viscosity of multicomponent systems is similar to the quality of reproducing the data for single-solute systems.

5. CONCLUSIONS

The proposed model is capable of accurately reproducing the viscosity of complex aqueous solutions that are encountered in industrial practice. The model is applicable for concentrated solutions (up to ca. 30 m) at temperatures up to 573 K. It is particularly important that the conductivity of multicomponent systems can be predicted using parameters obtained from data for single-solute systems.

6. APPENDIX

According to the Onsager-Fuoss [2] theory, the η_r^{LR} term is given by

$$\eta_r^{LR} = a\frac{1}{\eta_0}\left(\frac{2I}{\varepsilon T}\right)^{1/2}\left(\sum_i^{N_I}\frac{\mu_i z_i}{\lambda_i}\right) - 4\mathbf{r}\sum_{n=0}^{\infty} c_n \mathbf{s}^n \qquad \text{(A-1)}$$

where a is a numerical constant defined by

$$a = \frac{Fe^2 10^8}{480\pi}\left(\frac{N_A}{1000\varepsilon_0 k}\right)^{1/2} = 0.36454 \qquad \text{(A-2)}$$

where F, e, N_A, ε_0 and k are the Faraday constant, electron charge, Avogadro constant, permittivity of vacuum and Boltzmann constant, respectively. The numerical factors in eq. A-2 are consistent with the use of concentrations in mol/dm^3 and ionic conductivity in Ω^{-1} mol^{-1}cm^2. I is the ionic strength in mol/dm^3. In the first summation on the right hand side of eq. A-1, N_I is the total number of different ions in the mixture, z_i is the absolute value of the ionic charge, λ_i is the equivalent conductance of ion i and μ_i is defined as

$$\mu_i = \frac{c_i z_i^2}{\sum_j^{N_I} c_j z_j^2} \qquad \text{(A-3)}$$

The vector **r** is given by

$$r_i = 1 - \frac{z_i \lambda_i}{\overline{(z/\lambda)}} \qquad i = 1, \ldots, N_I \qquad \text{(A-4)}$$

where the average $\overline{(z/\lambda)}$ is calculated as

$$\overline{(z/\lambda)} = \frac{\sum_i^{N_I} c_i z_i^2 (z_i/\lambda_i)}{\sum_i^{N_I} c_i z_i^2} \qquad \text{(A-5)}$$

In the second summation in eq. (A-1), c_n is a numerical factor defined as

$$c_0 = -3 + \sqrt{2} \qquad \text{(A-6)}$$

$$c_n = -2\sqrt{2}\left\{\sqrt{2} - \sum_{p=0}^{n}\binom{1/2}{p}\right\} \qquad n = 1, \ldots, \infty \qquad \text{(A-7)}$$

The vectors $\mathbf{s}^n$ are given by a recursive formula, i.e.,

$$\mathbf{s}^0 = \mathbf{s} \qquad \text{(A-8)}$$

$$\mathbf{s}^n = \mathbf{H}\mathbf{s}^{n-1} \qquad \text{(A-9)}$$

where the elements of the vector **s** are defined as

$$s_j = \mu_j \left(\frac{z_j}{\lambda_j} - \frac{\overline{(z/\lambda)^2}}{\overline{(z/\lambda)}} \right) \tag{A-10}$$

The second-order average $\overline{(z/\lambda)^2}$ is calculated as

$$\overline{(z/\lambda)^2} = \frac{\sum_i^{N_I} c_i z_i^2 (z_i/\lambda_i)^2}{\sum_i^{N_I} c_i z_i^2} \tag{A-11}$$

The matrix **H** in eq. A-9 is defined as

$$h_{ji} = 2\delta_{ji} \sum_k^{N_I} \mu_k \frac{\lambda_k / z_k}{\lambda_k / z_k + \lambda_j / z_j} + 2\mu_j \frac{\lambda_j / z_j}{\lambda_i / z_i + \lambda_j / z_j} - \delta_{ji} \tag{A-12}$$

where δ_{ij} is the Kronecker symbol. The second summation in eq. (A-1) usually reaches convergence for n ranging from 4 to 6.

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FIGURE CAPTIONS

Fig. 1. Relationship between the parameter B_s (eq. 8) and the entropy of hydration of ions. The circles represent the values obtained by fitting eq. 8 to experimental values of the viscosity B coefficients. The lines are obtained from eqs. 9-11.

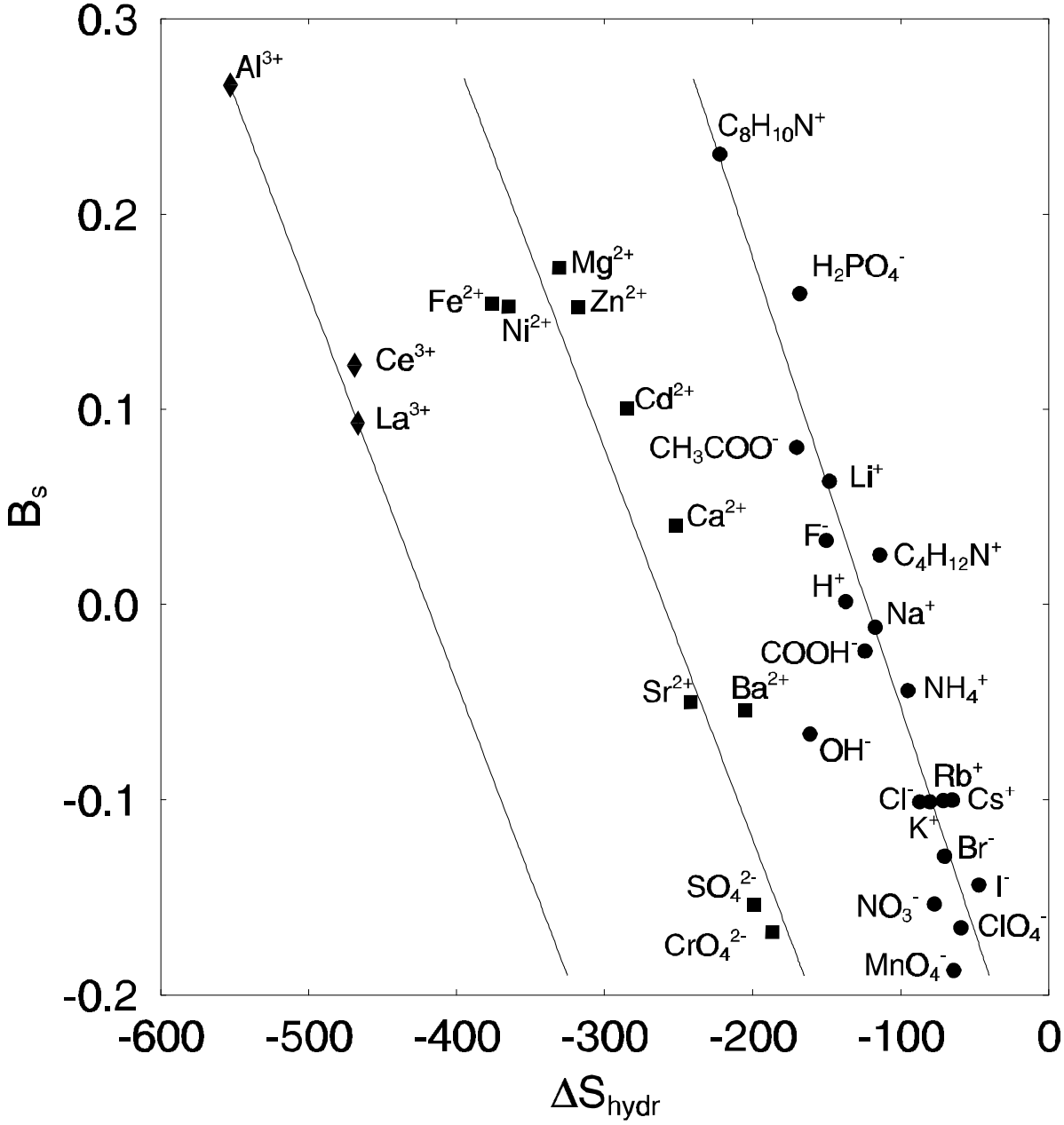
Fig. 2. Representation of viscosity for strong and weak 1:1 electrolytes at 298.15 K. The symbols denote experimental data [8] and the lines have been calculated using the model.

Fig. 3. Representation of viscosity for 2:1 electrolytes at 298.15 K. The symbols denote experimental data [8] and the lines have been calculated using the model.

Fig. 4. Representation of viscosity for 3:1 electrolytes at 298.15 K. The symbols denote experimental data [8] and the lines have been calculated using the model.

Fig. 5. Viscosity of the system NaCl + HCl + KCl for various molar ratios of components. The symbols denote experimental data [11, 12]. The dashed and solid lines have been calculated for single-solute and mixed systems, respectively.

Fig. 6. Viscosity of the system $(NH_4)_2SO_4$ + KCl + Na_2SO_4 for various molar ratios of components. The symbols denote experimental data [8, 11]. The dashed and solid lines have been calculated for single-solute and mixed systems, respectively.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-300
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B_s
ΔS_{hydr}
Al^{3+}
Ce^{3+}
La^{3+}
Fe^{2+}
Ni^{2+}
Mg^{2+}
Zn^{2+}
Cd^{2+}
Ca^{2+}
Sr^{2+}
Ba^{2+}
SO_4^{2-}
CrO_4^{2-}
$C_8H_{10}N^+$
$H_2PO_4^-$
CH_3COO^-
Li^+
F^-
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H^+
Na^+
$COOH^-$
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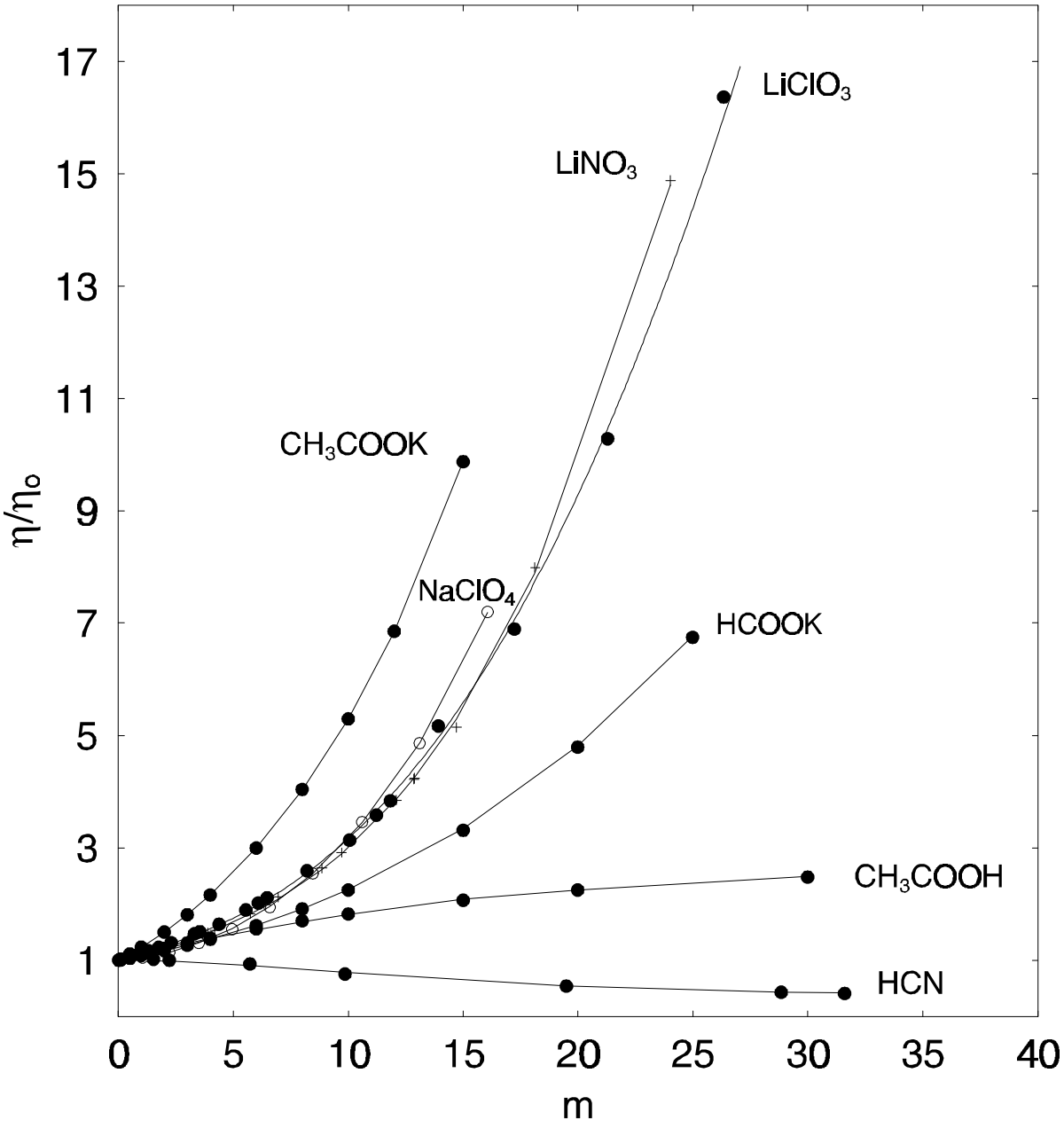
MnO_4^-

Figure 1.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15
13
11
9
7
5
3
1
η/η₀
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5
10
15
20
25
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m
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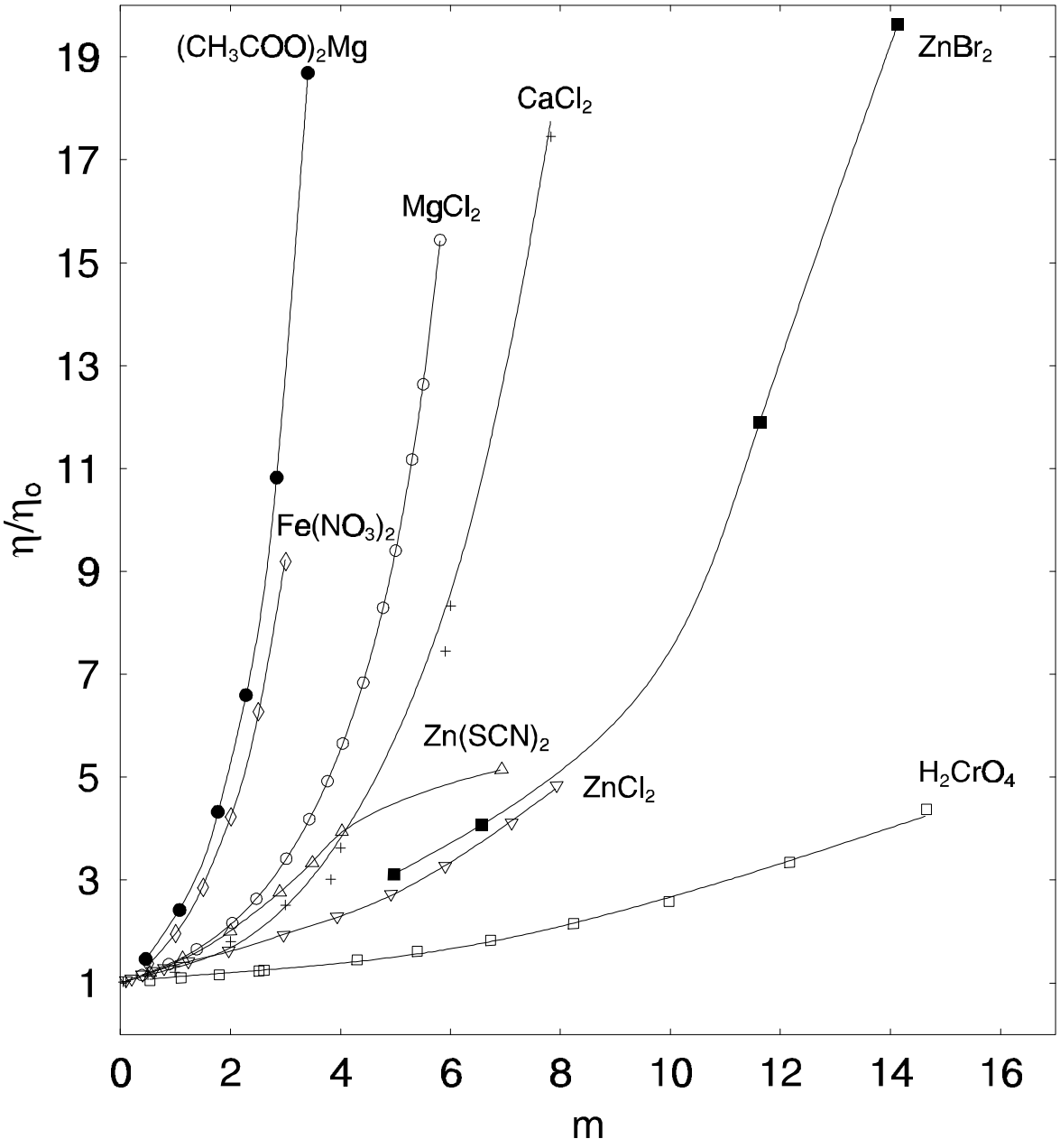
HCOOK
CH3COOH
HCN

Figure 2.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H2CrO4
η/ηo
m
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2
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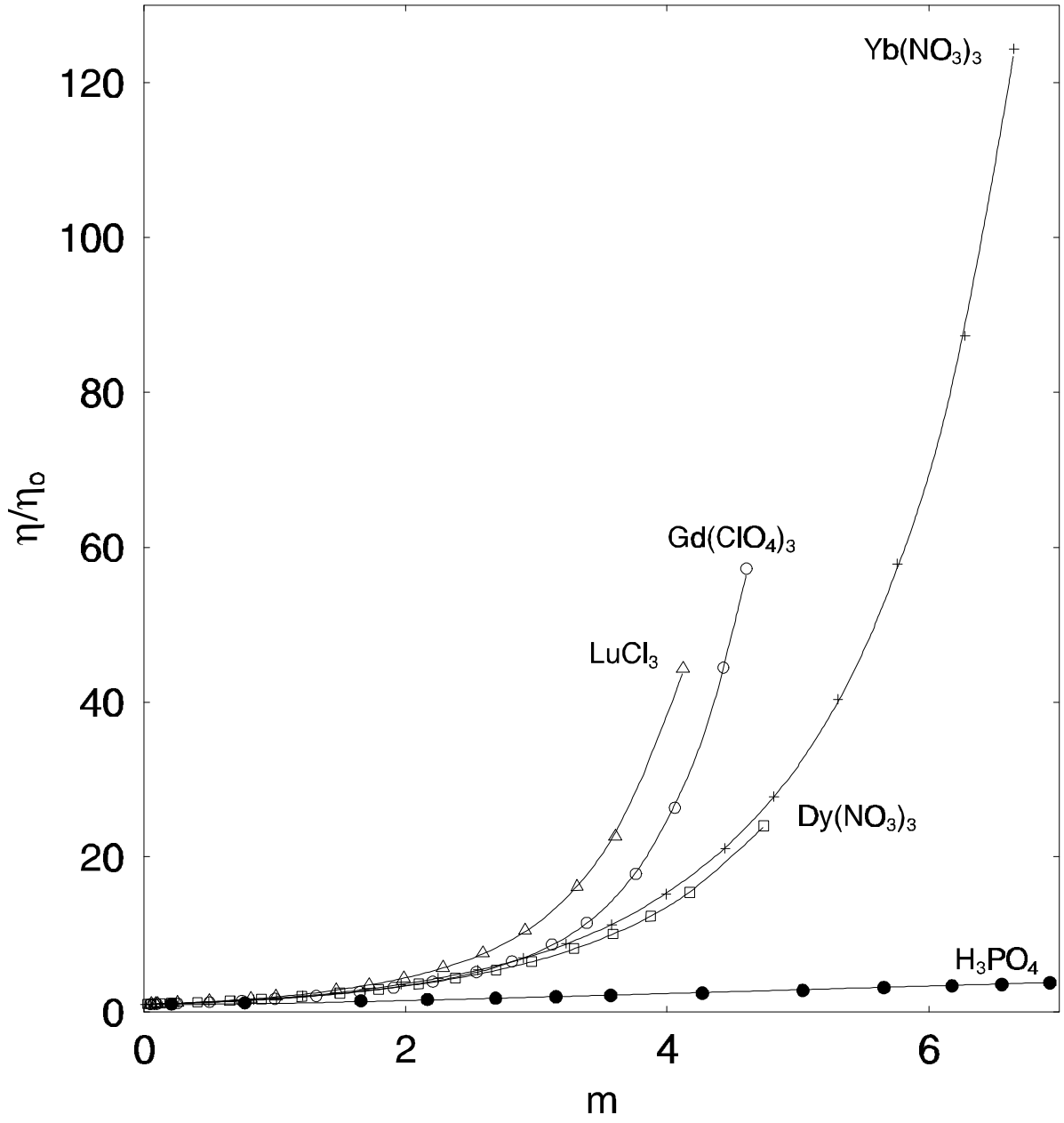
Figure 3.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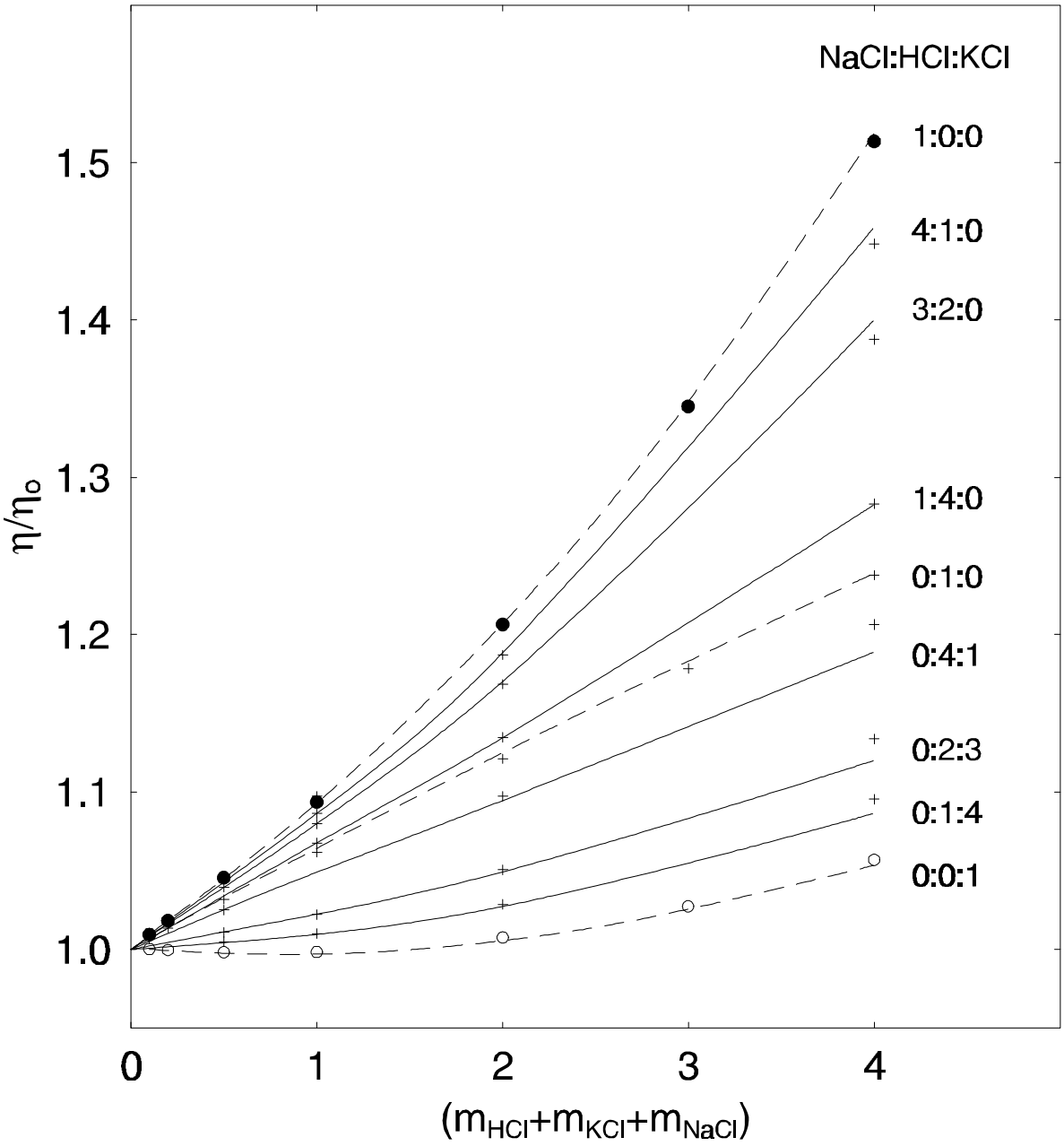
4
6

Figure 4.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0:0:1
1.5
1.4
1.3
1.2
1.1
1.0
η/η₀
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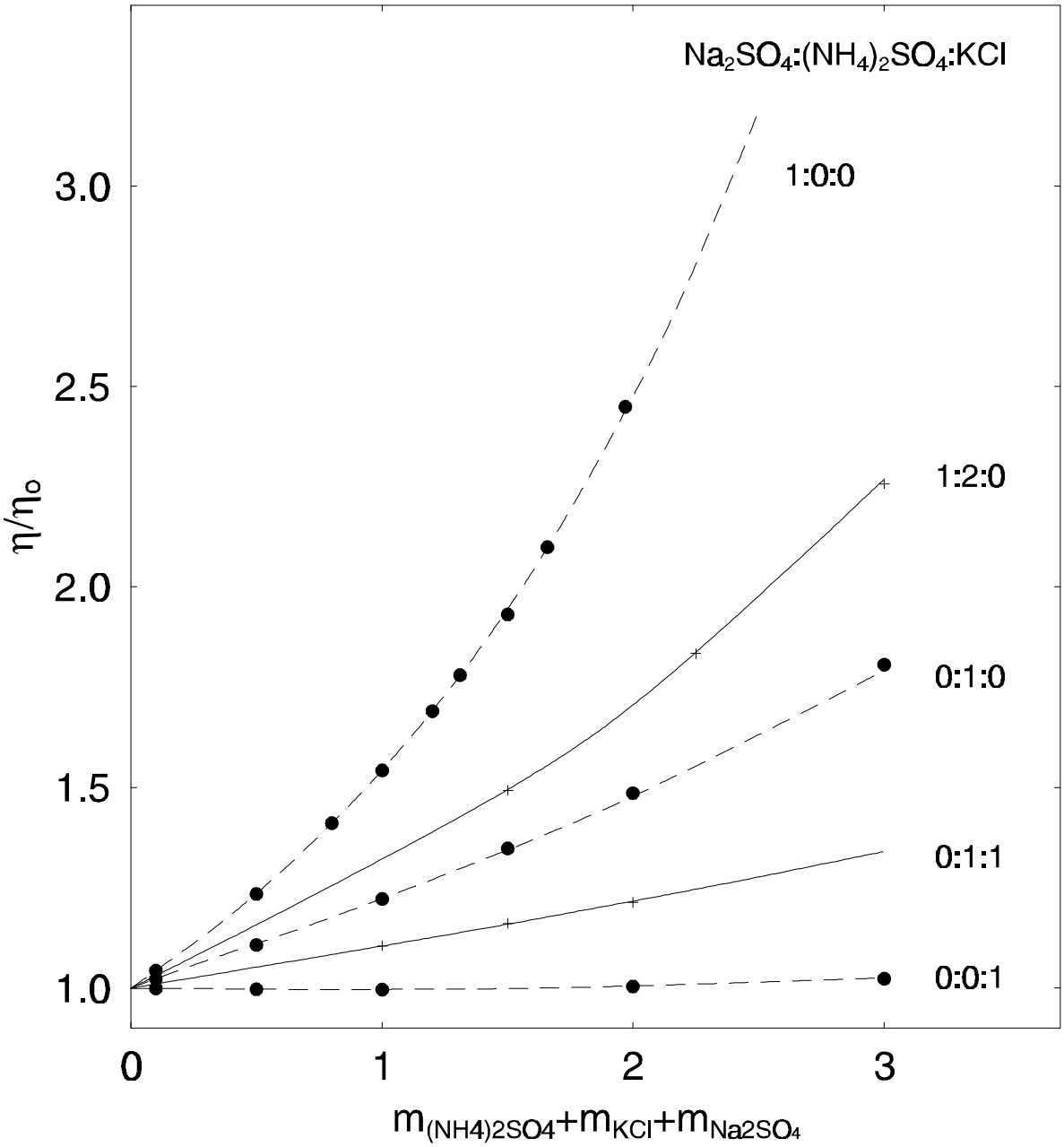
2
3
4
(m_HCl+m_KCl+m_NaCl)

Figure 5.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2.5
2.0
1.5
1.0
η/ηo
0
1
2
3
m(NH4)2SO4+mKCl+mNa2SO4

Figure 6.