METHODS FOR PREDICTING PROPERTIES AND
TAILORING SALT SOLUTIONS FOR INDUSTRIAL PROCESSES

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ABSTRACT

An algorithm developed at Oak Ridge National Laboratory (1) accurately and quickly predicts thermodynamic properties of concentrated aqueous salt solutions. This algorithm is much simpler and much faster than other modeling schemes and is unique because it can predict solution behavior at very high concentrations and under varying conditions. Typical industrial applications of this algorithm would be in manufacture of inorganic chemicals by crystallization, thermal storage, refrigeration and cooling, extraction of metals, emissions control, etc.

INTRODUCTION

The use of electrolytes is ubquitious in commerce and industry, and much work has been done to describe the properties of electrolytes, especially aqueous electrolytes. Description of the properties of such electrolytes in terms of electrostatic interactions has made the treatment cumbersome and difficult to apply in a practical sense because of the requirement for a large number of experimentally determined parameters.

Until this algorithm was developed at the Oak Ridge National Laboratory, no modeling scheme could quickly predict the relative performance of salt solutions in the concentration range from 2 to 98 mole %. Earlier modeling schemes address many parameters to evaluate a solution's performance. Such complex modeling schemes are slow, are limited to predicting the performance of low (~6 molal) concentrations, and do not permit extrapolation from one set of conditions to another. The algorithm runs on a personal computer and can easily generate in a day the equivalent of one year experimental work. Only two or three parameters are required by the algorithm. For many salts, these parameters are included in a data base that can be augmented and edited by the user. The algorithm is user friendly with pull-down menus. Results can be obtained in either tabulated or graphical form, depending upon user preference.

COMPARISON OF COMPUTED VS. MEASURED DATA

Comparisons of the computed and empirical data on vapor pressure-composition-temperature, molar volume-composition-temperature, enthalpy-concentration-temperature, and solid phase behavior for electrolytes are shown in Figures 1-3 and Tables 1 and 2.

USER FRIENDLY SOFTWARE

A user friendly software for use on IBM personal computers is available for licensing.

REFERENCES

1.   Ally, M.R., and Braunstein, J., (1991). Process for Preparing Salt Mixtures with Predicted Crystalline Phases. Patent Pending.
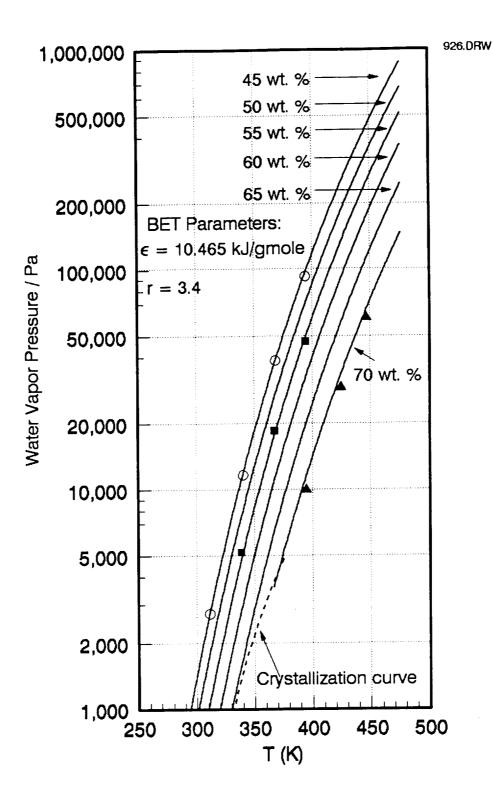
Fig. 1. Vapor pressure-composition-temperature for aqueous LiBr solutions. Solid lines indicate fitted experimental data. Symbols represent predicted values from ORNL algorithm.
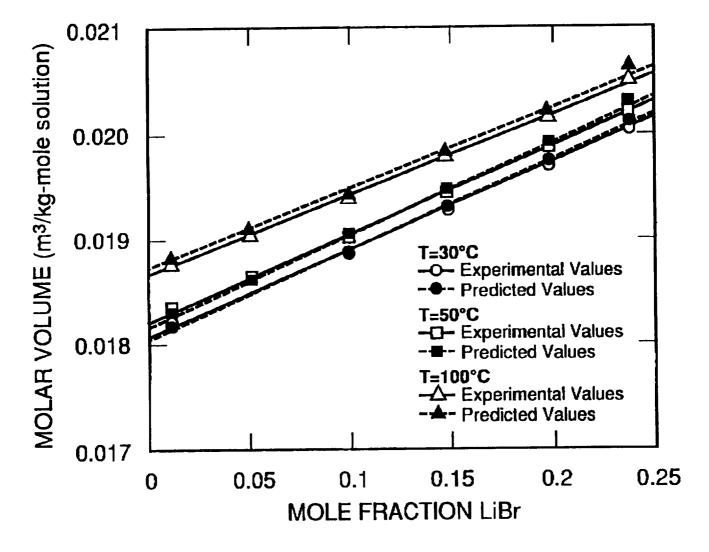
Fig. 2. Comparison of predicted and experimental molar volume-composition-temperature data for aqueous LiBr solutions.
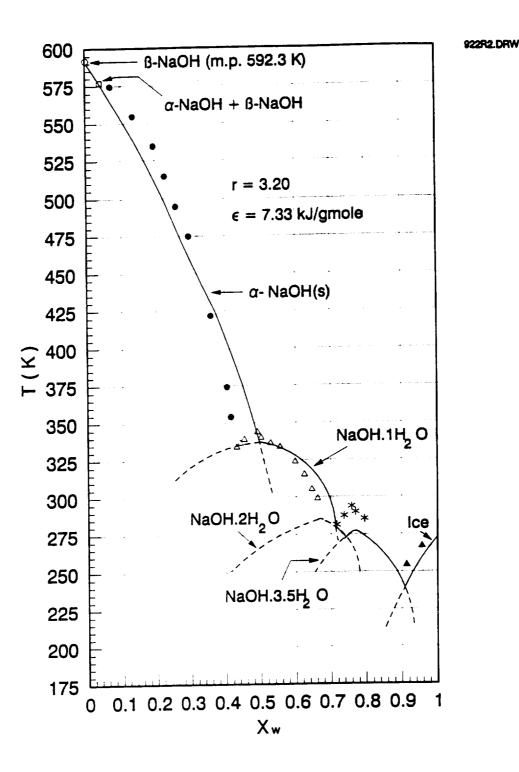
Fig. 3. Some crystalline phases in aqueous NaOH solutions. ____ Prediction of stable phases from ORNL algorithm. - - - - Prediction of metastable phases from ORNL algorithm. Symbols represent experimental data on crystalline phases.

Table 1. Comparison of experimental and predicted molar volumes of aqueous $(Li,K,Na)NO_3$ solutions			
Parameters: r =2.0, ϵ = 3.8 kJ/g-mole ϵ' =20.3x10^{-4} kJ/kg-mole-Pa (20.3x10^{-1} m^3/kg-mole)			
Wt. % $(Li,K,Na)NO_3$	Mole Fraction $(Li,K,Na)NO_3$, x_s	Correlated Experimental Molar volume * m^3/kg-mole	Predicted Molar volume ∇, m^3/kg-mole
t = 50° C (323.15 K)			
4.231	0.0100	0.01833	0.01840
18.71	0.0500	0.01905	0.01907
32.70	0.1000	0.01993	0.01993
43.56	0.1500	0.02082	0.02080
52.23	0.2000	0.02173	0.02170
59.31	0.250 •	0.02266	0.02263
65.21	0.300	0.02364	0.02359
70.19	0.350	0.02468	0.02459
74.46	0.400	0.02579	0.02562
78.16	0.450	0.02699	0.02667
t = 100° C (373.15K)			
4.231	0.010	0.01906	0.01898
18.71	0.050	0.01979	0.01973
32.70	0.100	0.02071	0.02067
43.56	0.150	0.02165	0.02164
52.23	0.200	0.02259	0.02263
59.31	0.250	0.02355	0.02365
70.19	0.300	0.02452	0.02470
74.46	0.400	0.02651	0.02690

* Goodness of fit defined by (a) average absolute deviation = $(\sum |d_i|)$/Nx100%, d_i = (ρ(observed) - ρ(predicted))/ρ(observed); (b) Residual sum of squares = $\sum(\rho$(observed) - ρ(predicted))^2. Number of data points, N, between 440 and 524 for each wt. % solution (Ally et al., 1991). ϵ evaluated from mixing rules at 120°C.

Table 2. Comparison of correlated and predicted molar enthalpies of aqueous LiBr solutions

Parameters: $r = 3.4$, $\epsilon = 10.465$ kJ/g-mole

Wt. % LiBr(dry) in Solution	Mole Fraction LiBr, x_3	Correlated Molar Enthalpy kJ/kg-mole sol'n $\tilde{H}$	Predicted Molar Enthalpy kJ/kg-mole sol'n $\tilde{H}$
t = 100 F (311 K)			
10	.02253	2.85	2.75
30	0.08165	2.13	2.51
40	0.12150	2.04	2.38
50	0.1718	2.31	2.31
60	0.2373	3.82	3.01
70	0.3262	7.07	6.13
t = 220 F (378 K)			
10	.02253	7.88	7.68
30	0.08165	6.54	7.18
40	0.12150	6.40	6.90
50	0.1718	6.70	6.71
60	0.2373	8.26	7.26
70	0.3262	11.64	9.78
t = 280 F (411 K)			
10	.02253	10.44	10.18
30	0.08165	8.78	9.54
40	0.12150	8.59	9.17
50	0.1718	8.89	8.90
60	0.2373	10.44	9.35
70	0.3262	13.89	11.57
t = 360 F (456 K)			
10	.02253	13.92	13.56
30	0.08165	11.82	12.67
40	0.12150	11.55	12.17
50	0.1718	11.84	11.75
60	0.2373	13.35	11.98
70	0.3262	16.79	13.73