



OLI Systems, Inc.

BINCON_INT.EXE (MSE)

For transport properties and data regression

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Disclaimer:

This manual was produced for use along with the OLI Software version 9.5.4 or later. Use with earlier versions is not supported.

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Installing and running the BINCON_INT.EXE file¹

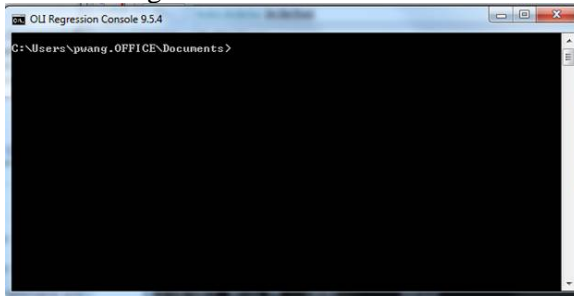
The BINCON_INT.EXE file needs to run with a set of files stored in a local folder. Download a ZIP file with the most recent version of the program from this location:

http://wiki.olisystems.com/wiki/images/1/16/BINCON_INT.zip

Now follow these instructions to install and then execute the program.

1. Extract the files.
2. Right click on the “CopyBinConToESP95.bat” file and run it as administrator. That will automatically generate a “C:\BinCon” folder and then will copy all the necessary .dat files from ESP 9.5 folder to this C:\BinCon folder.
3. Now, you can use the OLI Regression Console for your data regression from Start menu -> OLI Systems -> ESP 9.5 -> Tools -> OLI Regression Console.

- a. The OLI Regression Console window looks like this:



- b. In OLI Regression Console window, go to your working directory: e.g. C:\>cd My-work
- c. Run BINCON_INT: C:\My-work>BINCON_INT

Your input file, dbs file and all .dat files should be in the working directory

4. You should already have the input file (including your electrical conductivity data) as well as generated “.mod” and “.dbs” files available in the local folder C:\BinCon. At this step, consult the instructions below to see how you can create an input file and to become familiar with the parameters of the model.

¹ Earlier versions of this program were called BINCON.EXE. For version 9.5.4 and later it was renamed to BINCON_INT.EXE

5. From the command window of OLI Regression Console, go to your local folder C:\BinCon. Now, type bincon_int to start the program. Select "1" to use the program for electrical conductivity regression/prediction and follow the instructions from the document below.

Files to be used by BINCON_INT.EXE:

An input file and a model file (dbs file) are required to run BINCON_INT.EXE.

The dbs file can be generated with the usual procedure using OLI/ESP, with MSE framework.

The input file (no extension) must have the same name as the dbs file. For example, if the dbs file name is "SO3W.DBS", the input file name must be "SO3W".

Format of the input file used for electrical conductivity optimization or calculations is as follows:

The 1st line gives a list of the inflow component names (must include H₂O). These names must be identical with the names used in the databank and are separated by space(s).

The 2nd line gives multipliers for calculating equivalent conductivities and molecular weights for the inflow components. The number of multipliers and the number of molecular weights must be the same as the number of inflow components listed in the 1st line. For MSE conductivity model, only specific conductance is calculated, and the multipliers are not used, but are needed to hold the space.

From the 3rd line on, the conductivity data are given in each line in the order of:

- Temperature
- Concentrations of the inflow components (in the order of the 1st line components)
- Specific conductance (in unit of S.cm⁻¹)
- Temperature code (1 for Celsius, 0 for Kelvin)
- Concentration code (1 for molality, 2 for weight percent, 3 for mole-fraction)
- Code for conductivity unit – The only option in MSE conductivity model is 0, i.e. specific conductance in the unit of S.cm⁻¹.

The last line in the input file must be a series of 0 (zero), and the number of zeros must be equal to the number of entries in the data lines.

The following is an input sample file for NiCl₂+H₂O system.

```

NiCl2  H2O          ← inflow names
2      1  129.576  18.0152 ← multipliers for NiCl2 and H2O and molecular weights
25 0.00001807 0.99998193 0.0002499 1 3 0 ← T (°C), x(NiCl2), x(H2O), κ (S.cm-1), and
25 0.00009034 0.99990966 0.001146 1 3 0 codes for T, concentration, and conductivity.
25 0.00054182 0.99945818 0.006078 1 3 0
25 0.00180431 0.99819569 0.01803 1 3 0
25 0.00898675 0.99101325 0.069915 1 3 0
25 0.02687992 0.97312008 0.13908 1 3 0
25 0.06342345 0.93657655 0.12565 1 3 0
25 0.07288616 0.92711384 0.10476 1 3 0
0 0          0          0          0 0 0 ← indicate the end of data block

```

The following is the sample input for NaCl+H2O system, where concentrations are given in molalities. It is noted that in this case, H2O concentrations are at a constant value of 55.509, and must be in the input (the aqueous transport program does not require H2O and its concentration to be in the input file).

```

NaCl  H2O
1      1  58.443  18.0152
25 0.05000  55.509  0.005509 1 1 0
25 0.10000  55.509  0.010660 1 1 0
25 1.00000  55.509  0.084050 1 1 0
25 3.00000  55.509  0.189000 1 1 0
25 5.00000  55.509  0.239700 1 1 0
100 0.00100  55.509  0.000342 1 1 0
100 0.00502  55.509  0.001680 1 1 0
100 0.01000  55.509  0.003277 1 1 0
100 0.04942  55.509  0.015048 1 1 0
100 0.10000  55.509  0.028701 1 1 0
300 0.00100  55.509  0.000684 1 1 0
300 0.00502  55.509  0.003328 1 1 0
300 0.01000  55.509  0.006272 1 1 0
300 0.04942  55.509  0.027018 1 1 0
300 0.10000  55.509  0.049811 1 1 0
0 0          0          0          0 0 0

```

For the viscosity data file, the first 2 lines are the same as those for electrical conductivity, from the 3rd line on, the viscosity data are given in each line in the order of:

- Temperature
- Concentrations of the inflow components (in the order of the 1st line components)
- Viscosity (in unit of cP for absolute viscosity)
- Temperature code (1 for Celsius, 0 for Kelvin)
- Concentration code (1 for molality, 2 for weight percent, 3 for mole-fraction)
- Code for viscosity unit (1 for absolute viscosity in cP, 0 for relative viscosity).

The last line in the input file must be a series of 0 (zero), and the number of zeros must be equal to the number of entries in the data lines.

Conductivity data regression using BINCON_INT.EXE

Depending on the range of temperature and concentration, there are options of adjusting up to 12 parameters. The OLI/MSE conductivity paper² is referred for the following parameters and their symbols/names (Eqs. 18-21 in ref 1).

Table 1. Adjustable Interaction Parameters for Electrical Conductivity

Number of adjustable parameters (N)	Which parameters are adjusted
1	$\sigma(0)$
2	$\sigma(0), \sigma(1)$
3	$\sigma(0), d1(0), d2(0)$
4	$\sigma(0), d1(0), \sigma(1), d1(1)$
5	$\sigma(0), d1(0), d2(0), d3(0), \sigma(1)$
6	$\sigma(0), d1(0), d2(0), \sigma(1), d1(1), d2(1)$
7	$\sigma(0), d1(0), d2(0), d3(0), \sigma(1), d1(1), d2(1)$
8	$\sigma(0), d1(0), d2(0), d3(0), \sigma(1), d1(1), d2(1), d3(1)$
9	$\sigma(0), d1(0), d2(0), d3(0), \sigma(1), d1(1), d2(1), d3(1), \sigma(2)$
10	$\sigma(0), d1(0), d2(0), d3(0), \sigma(1), d1(1), d2(1), d3(1), \sigma(2), d1(2)$
11	$\sigma(0), d1(0), d2(0), d3(0), \sigma(1), d1(1), d2(1), d3(1), \sigma(2), d1(2), d2(2)$
12	$\sigma(0), d1(0), d2(0), d3(0), \sigma(1), d1(1), d2(1), d3(1), \sigma(2), d1(2), d2(2), d3(2)$

² Wang, P.; Anderko, A. Young, R. D. *Ind. Eng. Chem. Res.* 2004, **43**, 8083-8092

Viscosity data regression using BINCON_INT.EXE

Depending on the range of temperature and concentration, there are options of adjusting up to 7 parameters. The OLI/MSE viscosity paper³ is referred for the following parameters and their symbols/names (Eqs. 14-15 in ref. 2).

Table 2. Adjustable Interaction Parameters for Viscosity

Number of adjustable parameters (N)	Which parameters are adjusted
1	$d^{(10)}$
2	$d^{(10)}, d^{(20)}$
3	$d^{(10)}, d^{(20)}, d^{(30)}$
4	$d^{(10)}, d^{(20)}, d^{(30)}, b$ in ENGINE
4	$d^{(10)}, d^{(20)}, d^{(11)}, d^{(21)}$ in BINCON program
6	$d^{(10)}, d^{(20)}, d^{(30)}, d^{(11)}, d^{(21)}, d^{(31)}$
7	$d^{(10)}, d^{(20)}, d^{(30)}, b, d^{(11)}, d^{(21)}, d^{(31)}$

Self-diffusivity data regression using BINCON_INT.EXE

Depending on the range of temperature and concentration, there are options of adjusting up to 3 parameters. The OLI/MSE diffusivity papers^{4,5} are referred for the following parameters and their symbols/names $\{\sigma_{ij} = \sigma_{ij}^0 \exp(a_{ij}I), \sigma_{ij}^0 = \sigma_{ij,1}^0 + \sigma_{ij,2}^0(T-298.15), I = (\sum z_i^2 c_i)/2, c_i$ is in mol/dm³ $\}$.

Table 2. Adjustable Interaction Parameters σ_{ij} for Self-diffusivity

Number of adjustable parameters (N)	Which parameters are adjusted
1	$\sigma_{ij,1}^0$
2	$\sigma_{ij,1}^0, a_{ij}$
3	$\sigma_{ij,1}^0, a_{ij}, \sigma_{ij,2}^0$
-2	$\sigma_{ij,1}^0, \sigma_{ij,2}^0$

³ Wang, P.; Anderko, A. Young, R. D. *Fluid Phase Equil.* 2004, **226**, 71-82

⁴ Anderko, A.; Lencka, M. *Ind. Eng. Chem. Res.* 1998, **37**, 2878-2888

⁵ Wang, P.; Anderko, A. *Ind. Eng. Chem. Res.* 2003, **42**, 3495-3504

Program options

BINCON.EXE provides functions for optimization or calculation of three transport properties for mixed solvent electrolyte systems:

1. Electrical conductivity
2. Viscosity
3. Self-diffusivity

You will be prompted to select among:

- 1 - Regression
- 2 - Calculate electrical conductivity (or viscosity or diffusivity) with existing parameters

Auxiliary data files for using BINCON.EXE

There is a total of 7 auxiliary ASCII files needed to run BINCON.EXE.

1. **Limcon.dat** – store limiting conductivity of ions or limiting diffusivity of aqueous species, and coefficients for thermal conductivity Riedel-term:

Line 1: SPECIES_NAME BE BS K SOLVENT_NAME α_1 α_2 K
BE, BS, K are coefficients in viscosity B equation – Eq. (13) of OLI/MSE viscosity paper.²
SOLVENT_NAME is the solvent name. If no solvent is given, H2O is the solvent.
 α_1 , α_2 , K are Riedel-term coefficients in OLI thermal conductivity model.⁶

Line 2: N BT RI
N - Number of points in limiting conductivity data,
BT - coefficient for temperature extrapolation,
RI - ionic radius

Line 3: T(1) T(2) T(N) (temperature in C)

Line 4: $\lambda^\infty(1)$ $\lambda^\infty(2)$ $\lambda^\infty(N)$ (molar limiting conductivity in $\text{cm}^2 \cdot \Omega^{-1} \cdot \text{mol}^{-1}$)

2. **VPURE.dat** – store parameters in pure liquid density, dielectric constant, and viscosity equations. H2O is not in this file because it is treated differently using a separate EOS.

Line 1: SPECIES_NAME

Line 2: Aden Bden Cden Cden Edie Fdie (coefficients in LDEN equation & in ϵ equation)

Line 3: ID, A, B, C, D, E, Tmin, Tmax (coefficients in viscosity equation, T-range in K)

ID=1 viscosity (η) is calculated using DIPPR equation:

$$\eta = \exp [A + B/T + C \cdot \ln T + D \cdot T^E] \text{ in Pa.s}$$

ID=2 η is calculated using DECHEMA equation:

$$\eta = \exp [A/T^2 + B/T + C + D \cdot T] \text{ in Pa.s (E=0)}$$

Line 4: A, B, C, D, E: coefficients in DIPPR thermal conductivity equation

$$\lambda = A + BT + CT^2 + DT^3 + ET^4 \text{ in W.m}^{-1} \cdot \text{K}^{-1}$$

⁶ Wang, P. Anderko, A. *Ind. Eng. Chem. Res.* 2008, **47**, 5698-5709

Line 5: A, B, C, D, E, IE, Tc

A, B, C, D, E: Coefficients in DIPPR surface tension equation

IE=100: σ (N/m) = A + BT + CT² + DT³ + ET⁴

IE=106: σ (N/m) = A(1-Tr)^B + CTr + DTr² + ETr³, Tr=T/Tc

Tc is critical temperature in K (used in Eq# 106)

3. **CONPAR.dat** – store parameters for limiting conductivity in mixed solvent. For the limiting conductivity of an ion (ION) in a mixed solvent containing SOLVENT_1 and SOLVENT_2, the entries are:

Line 1: SOLVT1_NAME SOLVT2_NAME ION

Line 2: k_0, g_0, k_1, g_1 mixing-rule parameters, refer to Eqs(3)-(6) in OLI/MSE conductivity paper¹

4. **VISSOL.dat** – store “mixing-rule” parameters for viscosity, thermal conductivity, and surface tension of the mixed solvent

Line 1: SOLVT1_NAME SOLVT2_NAME

Line 2: $k_0, k_1, k_2, g_0, g_1, g_2, k_{ij}^{(0)}, k_{ij}^{(1)}, k_{ij}^{(2)}, p_{ij}, p_{ji}, k_{ij}, k_0^{ij}, k_t^{ij}, k_0^{ji}, k_t^{ji}$

Where

$k_0, k_1, k_2, g_0, g_1, g_2$: Viscosity – see reference 2

$k_{ij}^{(0)}, k_{ij}^{(1)}, k_{ij}^{(2)}$: Thermal conductivity – see reference 3

p_{ij}, p_{ji}, k_{ij} : Surface tension – Refer to OLI surface tension paper.⁷

$k_0^{ij}, k_t^{ij}, k_0^{ji}, k_t^{ji}$: Interfacial tension – refer to OLI interfacial tension paper.

5. **BINPAR.dat** – store MSE electrical conductivity interaction parameters between an ion (ION) with another species (ION or AQ). Refer to Table 1 for the arrangement of parameters in this file. Examples are given below. After the regression is completed, simply copy the lines that have the names of species pair and their parameters in BINCON.OUT and paste to this file. Because the interaction parameters in the MSE transport model are "solvent-dependent", e.g. interactions between CATION/ANION may be different in H2O and in METHANOLAQ, the solvent in which a specific pair interaction is valid is also specified following the names of the pair. For example, the following line in BINPAR.dat gives interaction parameters between H3OION and H3P2O7ION in H2O:

```
H3OION      H3P2O7ION  H2O          H2O          (4A16)
8 0.592197 -3.99262  3.42256 -0.589099 0.189337E-04 0.616707E-01 -0.117124 0.610509E-01 340.15
                                                    (I3, 14G13.6)
```

Interaction parameters between H3P2O7ION and H3OION in H3PO4AQ (which has been treated as a "solevnt" component) are given in this file as

```
H3P2O7ION  H3OION      H3PO4AQ      H3PO4AQ      (4A16)
8 6.30771  18.3964 -40.1075  20.3661 0.105500 5.80538 -11.4631 5.80092 340.15
                                                    (I3, 14G13.6)
```

The last number (optional) in the parameter lines gives the maximum temperature (Tmax in K) where these parameters are determined or valid. A minimum temperature (Tmin) may

⁷ Wang, P.; Anderko, A. Young, R. D. *Ind. Eng. Chem. Res.* 2011, <http://pubs.acs.org/doi/abs/10.1021/ie101915n>

also be given following the T_{max}, to indicate a temperature range where these parameters are valid. Conductivity values beyond this T-range will be determined based on an extrapolation technique.

6. **VISPAR.dat** – store MSE viscosity interaction parameters. Refer to Table 2 for the arrangement of the parameters in this file. After the regression is completed, simply copy the lines that have the names of species pair and their parameters in BINCON.OUT and paste to this file. The viscosity interaction parameters are also solvent dependent.
7. **DIFPAR.dat** – store MSE self-diffusivity interaction parameters. After the regression is completed, simply copy the lines that have the names of species pair and their parameters in BINCON.OUT and paste to this file.

These data files (with extension “dat”) need to be in the working directory when BINCON.EXE is used (the same directory where you run BINCON.EXE). For optimization and calculation of electrical conductivity, only limcon.dat, conpar.dat, vpure.dat, and binpar.dat are important.

Running BINCON_INT.EXE for conductivity data regression

You will be prompted to type in the input file (no extension should be given), then select “1” for regression. You will then be asked the number of binary parameters to be adjusted. Your choices can be from 1 to 12, as listed in Table 1 for electrical conductivity; or from 1-7 (Table 2) for viscosity, depending on the ranges of temperature and concentration covered by the experimental data.

Next, you will be asked to select the solvent in which the interaction parameters are determined. For water-dominated systems, option 1 is the choice, i.e. select the option with “H₂O H₂O” (we tried to introduce the interactions in “cross-solvent” in earlier days of this project, and found it unnecessary for the systems we studied. But this option has been left open).

For the next selection, we recommend to choose option 1, i.e. “select from all non-negligible species” for species pairs which will be selected for interaction parameters optimization.

You will then see a list of species and be asked to give the number of species pairs for which parameters will be regressed. You can then specify the number of pairs and the select among the list which pairs are to be regressed.

The next prompt will be related to simultaneous determination of the limiting conductivity of the ions in mixed-solvent. In water-dominated systems, you may simply select “No” (2) to skip.

The optimization process then begins.

The result of the optimization (or calculation) is in an output file called BINCON.OUT. The optimized parameters will be listed at the beginning of this file in the same format that is used in the BINPAR.dat (or VISPAR.dat). This makes it easy to update the dat files by simply copying the parameters from BINCON.OUT to the dat files.

The rest of the BINCON.OUT file gives comparison of the calculated and experimental specific conductivity result at each data point, together with the temperature, concentrations, and the relative deviation. At the end of the OUT file, the average relative deviation is printed.

How the transport property parameters are used by OLI/ESP (and Analyzers)

Currently, databank entries in MSEPUB have not been created to store parameters from MSE transport property calculations. Once the parameters are finalized from the regression, the above 7 ASCII dat files must be put in the same directory as the other databank files, i.e. the "ESP" directory, in order to calculate transport properties using OLI/ESP or Analyzers.