High Temperature High Pressure Thermodynamic Measurements for Coal Model Compounds

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Authors: Vinayak N. Kabadi

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North Carolina A&T State University
Chemical Engineering Department
331B McNair Hall
Greensboro, North Carolina 27411

SIMULTANEOUS REPRESENTATION OF HIGH TEMPERATURE VLE AND EXCESS ENTHALPY DATA

It is well known that the fluid phase equilibria can be represented by a number of γ -models , but unfortunately most of them do not function well under high temperature. In this calculation, we mainly investigate the performance of UNIQUAC and NRTL models under high temperature, using temperature dependent parameters rather than using the original formulas. The other feature of this calculation is that we try to relate the excess Gibbs energy G^E and enthalpy of mixing H^E simultaneously. In other words, we will use the high temperature and pressure G^E and H^E data to regress the temperature dependent parameters to find out which model and what kind of temperature dependent parameters should be used.

LITERATURE DATA USED:

Because it is very difficult to generate high temperature high pressure data we have only three binary system data available: tetralin-quinoline^{1,5}, m-cresol- tetralin^{1,4,6}, m-cresol-quinoline^{2,3,5,6,7}. We used the raw data of vapor liquid equilibria to generate the G^E data for the three systems at first, then use the formula provided and the enthalpy data of pure tetralin, quinoline and m-cresol to generate H^E data for the three systems.

REGRESSIONS AND CALCULATIONS:

Upon review of the literature we concluded that no activity coefficient model is available that systematically represents VLE and excess enthalpy data simultaneously. Our goal is to use the data for the above three systems and attempt to represent them by UNIQUAC and NRTL models using temperature dependent interaction parameters. We have tried to fit several forms of temperature dependent parameters as shown below:

a. Four parameters UNIQUAC model:

the original UNIQUAC model for binary system can be expressed as :

$$\frac{G_c^E}{RT} = x_1 \ln \frac{f_1}{x_1} + x_2 \ln \frac{f_2}{x_2} + \frac{z}{2} (x_1 q_1 \ln \frac{q_1}{f_1} + x_2 q_2 \ln \frac{q_2}{f_2}) \quad \text{While } z=10 \quad \dots\dots(1)$$

$$\frac{G_r^E}{RT} = -(q_1 x_1 \ln(q_1 + q_2 t_{21}) + q_2 x_2 \ln(q_1 t_{12} + q_2)) \quad \dots\dots(2)$$

$$G^E = G_c^E + G_r^E \quad \dots\dots(3)$$

$$q_1 = \frac{x_1 q_1}{(x_1 q_1 + x_2 q_2)} \quad \dots\dots(4)$$

$$q_2 = \frac{x_2 q_2}{(x_1 q_1 + x_2 q_2)} \quad \dots\dots(5)$$

$$f_1 = \frac{x_1 r_1}{(x_1 r_1 + x_2 r_2)} \quad \dots\dots(6) \quad f_2 = \frac{x_2 r_2}{(x_1 r_1 + x_2 r_2)} \quad \dots\dots(7)$$

$$t_{21} = e^{-a_{21}/T} \quad \dots\dots(8) \quad t_{12} = e^{-a_{12}/T} \quad \dots\dots(9)$$

$$a_{21} = a_1 + a_2/T \quad \dots\dots(10) \quad a_{12} = a_3 + a_4/T \quad \dots\dots(11)$$

from the Gibbs-Helmoltz equation we have:

$$\frac{H^E}{T^2} = - \left[\frac{\partial(G^E/T)}{\partial T} \right]_{p,x} \quad \dots\dots(12)$$

$$H^E = R \left(\frac{q_1 x_1 q_2 t_{21} (a_1 + 2a_2/T)}{q_1 + q_2 t_{21}} + \frac{q_2 x_2 q_1 t_{12} (a_3 + 2a_4/T)}{q_2 + q_1 t_{12}} \right) \quad \dots\dots(13)$$

for meta-cresol $r=4.2867$, $q=3.2480$, for tetralin $r=5.5531$, $q=4.0000$, for quinoline $r=4.7932$, $q=3.1530$

b. Six parameters UNIQUAC model:

$$\frac{G_c^E}{RT} = x_1 \ln \frac{f_1}{x_1} + x_2 \ln \frac{f_2}{x_2} + \frac{z}{2} (x_1 q_1 \ln \frac{q_1}{f_1} + x_2 q_2 \ln \frac{q_2}{f_2}) \quad \text{While } z=10 \quad \dots\dots(1)$$

$$\frac{G_r^E}{RT} = -(q_1 x_1 \ln(q_1 + q_2 t_{21}) + q_2 x_2 \ln(q_1 t_{12} + q_2)) \quad \dots\dots(2)$$

$$G^E = G_c^E + G_r^E \quad \dots\dots(3)$$

$$q_1 = \frac{x_1 q_1}{(x_1 q_1 + x_2 q_2)} \quad \dots\dots(4) \quad q_2 = \frac{x_2 q_2}{(x_1 q_1 + x_2 q_2)} \quad \dots\dots(5)$$

$$f_1 = \frac{x_1 r_1}{(x_1 r_1 + x_2 r_2)} \quad \dots\dots(6) \quad f_2 = \frac{x_2 r_2}{(x_1 r_1 + x_2 r_2)} \quad \dots\dots(7)$$

$$t_{21} = e^{-a_{21}/T} \quad \dots\dots(8) \quad t_{12} = e^{-a_{12}/T} \quad \dots\dots(9)$$

$$a_{21} = a_1 + a_2(T - T_0) + a_3(T \ln \frac{T_0}{T} + T - T_0) \quad \dots\dots(14)$$

$$a_{12} = a_4 + a_5(T - T_0) + a_6\left(T \ln \frac{T_0}{T} + T - T_0\right) \quad \text{.....(15)}$$

$$H^E = R \left(\frac{q_1 x_1 q_2 t_{21} (a_1 - a_2 T_0 + a_3 (T - T_0))}{q_1 + q_2 t_{21}} + \frac{q_2 x_2 q_1 t_{12} (a_4 - a_5 T_0 + a_6 (T - T_0))}{q_2 + q_1 t_{12}} \right) \quad \text{.....(16)}$$

c. Six parameter UNIQUAC model suppose that q is a function of temperature

compared with part b everything is the same except that we suppose

$$q_1 = q_1' - a_7(T - T_0) \quad \text{.....(17)}$$

$$q_2 = q_2' - a_8(T - T_0) \quad \text{.....(18)}$$

here q_1' and q_2' are the original q value of the compounds, thus the H^E expression becomes

$$H^E = -T^2 (H_c^E + H_r^E) \quad \text{.....(19)}$$

$$H_c^E = -\frac{z}{2} R \left(a_7 x_1 \ln \left(\frac{q_1}{f_1} \right) + a_8 x_2 \ln \left(\frac{q_2}{f_2} \right) \right) \quad \text{.....(20)}$$

$$H_r^E = -R (F_1 - a_7 x_1 \ln B_1 + F_2 - a_8 x_2 \ln B_2) \quad \text{.....(21)}$$

$$F_1 = \frac{q_1 x_1}{B_1} (A(1 - t_{21}) + E_1 q_2) \quad \text{.....(22)}$$

$$F_2 = \frac{q_2 x_2}{B_2} (A(t_{21} - 1) + E_2 q_1) \quad \text{.....(23)}$$

$$A = x_1 x_2 (a_8 q_1 - a_7 q_2) \quad \text{.....(24)}$$

$$E_1 = t_{21} (a_1 - a_2 T_0 + a_3 (T - T_0)) / T^2 \quad \text{.....(25)}$$

$$E_2 = t_{12} (a_4 - a_5 T_0 + a_6 (T - T_0)) / T^2 \quad \text{.....(26)}$$

$$B_1 = q_1 + q_2 t_{21} \quad \text{.....(27)} \quad B_2 = q_2 + q_1 t_{12} \quad \text{.....(28)}$$

d. Eight parameters UNIQUAC model

$$\frac{G_c^E}{RT} = x_1 \ln \frac{f_1}{x_1} + x_2 \ln \frac{f_2}{x_2} + \frac{z}{2} (x_1 q_1 \ln \frac{q_1}{f_1} + x_2 q_2 \ln \frac{q_2}{f_2}) \quad \text{While } z=10 \quad \dots\dots(1)$$

$$\frac{G_r^E}{RT} = -(q_1 x_1 \ln(q_1 + q_2 t_{21}) + q_2 x_2 \ln(q_1 t_{12} + q_2)) \quad \dots\dots(2)$$

$$G^E = G_c^E + G_r^E \quad \dots\dots(3)$$

$$q_1 = \frac{x_1 q_1}{(x_1 q_1 + x_2 q_2)} \quad \dots\dots(4) \quad q_2 = \frac{x_2 q_2}{(x_1 q_1 + x_2 q_2)} \quad \dots\dots(5)$$

$$f_1 = \frac{x_1 r_1}{(x_1 r_1 + x_2 r_2)} \quad \dots\dots(6) \quad f_2 = \frac{x_2 r_2}{(x_1 r_1 + x_2 r_2)} \quad \dots\dots(7)$$

$$t_{21} = e^{-a_{21}/T} \quad \dots\dots(8) \quad t_{12} = e^{-a_{12}/T} \quad \dots\dots(9)$$

$$a_{21} = T_0 \left(a_1 \left(1 - \frac{T}{T_0} \right) + a_2 \left(1 - \frac{T}{T_0} \right)^{1.5} + a_3 \left(1 - \frac{T}{T_0} \right)^3 + a_4 \left(1 - \frac{T}{T_0} \right)^6 \right) \quad \dots\dots(29)$$

$$a_{12} = T_0 \left(a_5 \left(1 - \frac{T}{T_0} \right) + a_6 \left(1 - \frac{T}{T_0} \right)^{1.5} + a_7 \left(1 - \frac{T}{T_0} \right)^3 + a_8 \left(1 - \frac{T}{T_0} \right)^6 \right) \quad \dots\dots(30)$$

$$H^E = R \left(\frac{q_1 x_1 q_2 t_{21} c_1}{q_1 + q_2 t_{21}} + \frac{q_2 x_2 q_1 t_{12} c_2}{q_2 + q_1 t_{12}} \right) \quad \dots\dots(31)$$

$$C_1 = T \left(a_1 + 1.5 a_2 \left(1 - \frac{T}{T_0} \right)^{0.5} + 3 a_3 \left(1 - \frac{T}{T_0} \right)^2 + 6 a_4 \left(1 - \frac{T}{T_0} \right)^5 \right) + a_{21} \quad \dots\dots(32)$$

$$C_2 = T \left(a_5 + 1.5 a_6 \left(1 - \frac{T}{T_0} \right)^{0.5} + 3 a_7 \left(1 - \frac{T}{T_0} \right)^2 + 6 a_8 \left(1 - \frac{T}{T_0} \right)^5 \right) + a_{12} \quad \dots\dots(33)$$

Here $T_0 = 850K$

e. Ten parameters NRTL model :

$$\frac{G^E}{RT} = x_1 x_2 \left(\frac{t_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{t_{12} G_{12}}{x_2 + x_1 G_{12}} \right) \quad \text{.....(34)}$$

$$G_{21} = e^{-at_{21}} \quad \text{.....(35)} \quad G_{12} = e^{-at_{12}} \quad \text{.....(36)}$$

$$a = a_9 + a_{10}/T \quad \text{.....(37)}$$

$$t_{21} = a_{21}/T \quad \text{.....(38)} \quad t_{12} = a_{12}/T \quad \text{.....(39)}$$

$$a_{21} = T_0 \left(a_1 \left(1 - \frac{T}{T_0} \right) + a_2 \left(1 - \frac{T}{T_0} \right)^{1.5} + a_3 \left(1 - \frac{T}{T_0} \right)^3 + a_4 \left(1 - \frac{T}{T_0} \right)^6 \right) \quad \text{.....(29)}$$

$$a_{12} = T_0 \left(a_5 \left(1 - \frac{T}{T_0} \right) + a_6 \left(1 - \frac{T}{T_0} \right)^{1.5} + a_7 \left(1 - \frac{T}{T_0} \right)^3 + a_8 \left(1 - \frac{T}{T_0} \right)^6 \right) \quad \text{.....(30)}$$

$$H^E = \frac{R x_1 x_2 (C_1 G_{21} E_1 - x_1 G_{21} D_1 t_{21})}{E_1^2} + \frac{R x_1 x_2 (C_2 G_{12} E_2 - x_2 G_{12} D_2 t_{12})}{E_2^2} \quad \text{.....(31)}$$

$$C_1 = T \left(a_1 + 1.5 a_2 \left(1 - \frac{T}{T_0} \right)^{0.5} + 3 a_3 \left(1 - \frac{T}{T_0} \right)^2 + 6 a_4 \left(1 - \frac{T}{T_0} \right)^5 \right) + a_{21} \quad \text{.....(32)}$$

$$C_2 = T \left(a_5 + 1.5 a_6 \left(1 - \frac{T}{T_0} \right)^{0.5} + 3 a_7 \left(1 - \frac{T}{T_0} \right)^2 + 6 a_8 \left(1 - \frac{T}{T_0} \right)^5 \right) + a_{12} \quad \text{.....(33)}$$

$$D_1 = a C_1 + a_{10} t_{21} \quad \text{.....(40)} \quad D_2 = a C_2 + a_{10} t_{12} \quad \text{.....(41)}$$

$$E_1 = x_1 + x_2 G_{21} \quad \text{.....(42)} \quad E_2 = x_2 + x_1 G_{12} \quad \text{.....(43)}$$

In estimating the temperature dependant parameters, data for G^E and H^E were used simultaneously. The following objective function was minimized:

$$F = \frac{1}{N} \sum_N \left[100 \left(\frac{G_{i,\text{exp}}^E - G_{i,\text{cal}}^E}{G_{i,\text{exp}}^E} \right) \right]^2 + \frac{1}{M} \sum_M \left[100 \left(\frac{H_{i,\text{exp}}^E - H_{i,\text{cal}}^E}{H_{i,\text{exp}}^E} \right) \right]^2 \quad \text{.....(44)}$$

Where N and M are ,respectively, the number of experimental G^E and H^E data points, for minimizing the function F, a packaged program called UNLSF in the MATH/LIBRARY provided by IMSL Inc. is employed, this program solve nonlinear least squares problems using a modified Levenberg-Marquardt

algorithm and a finite-difference Jacobian. this method is one of the most effective methods for parameter seeking.

REGRESSION RESULTS:

We set up two criteria to judge how the models fit the data no matter whatever the parameters are. Of course the first are the errors between the experimental and calculated values the other is the variance of the fit S , which can be expressed as

$$S = \sqrt{\frac{1}{M_1 - N} \sum_{M_1} \left(\frac{G_{i,\text{exp}}^E - G_{i,\text{cal}}^E}{G_{i,\text{exp}}^E} \right)^2 + \frac{1}{M_2 - N} \sum_{M_2} \left(\frac{H_{i,\text{exp}}^E - H_{i,\text{cal}}^E}{H_{i,\text{exp}}^E} \right)^2} \quad \dots\dots(45)$$

Where M_1 and M_2 are the number of data of G^E and H^E respectively, N is the number of parameters. by fitting the five models, one by one, mentioned above to all the G^E and H^E data points of the three systems, we found out that the ten parameters NRTL model yield the best fit though the results even by the ten parameters NRTL model are far not desired at all. The regression result is given as the following:

Table 1 : Best regression results for the three systems by using 10 parameters model

systems	Parameters generated										Error For G^E %	Error For H^E %	S
	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8	a_9	a_{10}			
Tetralin- Quinoline	4.2637	-5.5079	-3.0595	21.7246	0.9078	-3.5268	8.5044	-20.5378	4.8506	-1510.988	47.273	53.504	
Meta-cresol -tetralin	-74.3467	122.234	71.9595	-3235.53	3.9721	-7.5490	9.1036	-10.9895	-2.7256	695.7518	15.136	38.755	
Meta-cresol -quinoline	-1.3184	1.3157	-4.1925	8.9071	2.4568	-4.5695	1.7565	-1.3163	0.1584	157.4738	7.3453	9.3462	

We will show in the following how the calculated result corresponds to the experimental data:

Graph 1 comparison of experimental and calculated G^E data for tetralin-quinoline system

Graph 2 comparison of experimental and calculated H^E data for tetralin-quinoline system

Graph 3 comparison of experimental and calculated G^E data for m-cresol –tetralin system

Graph 4 comparison of experimental and calculated H^E data for m-cresol tetralin system

Graph 5 comparision of experimental and calculated G^E data for m-cresol quinoline system

Graph 6 : comparison of experimental and calculated H^E data for tetralin-quinoline system

DISCUSSION:

We have noticed that different results were generated by applying ten parameters NRTL model to the three systems. The fitting of this model to the m-cresol quinoline system is very good, while that of the m-cresol-tetralin system, though not very satisfactory, is relatively fine. But the fit for the tetralin –quinoline system is totally errand.

First of all, we tried to regress the best parameter sets for the three systems using the G^E and H^E data simultaneously based on the Gibbs-Helmoltz equation :

$$\frac{H^E}{T^2} = - \left[\frac{\partial(G^E/T)}{\partial T} \right]_{p,x} \dots\dots\dots(12)$$

whether our G^E and H^E data satisfy equation (12) or not is one of the most important factors that affect the regression calculation. From our data source we numerically got the $\frac{H^E}{T^2}$ and the $-\left[\frac{\partial(G^E/T)}{\partial T} \right]_{p,x}$ values, compared them and saw how they differ with each other.

Table 2 comparisons of $\left[\frac{\partial(G^E/T)}{\partial T} \right]_{p,x}$ and $-\frac{H^E}{T^2}$ values of tetralin-quinoline system

Temperature K	Xt=0.25		Xt=0.5		Xt=0.6667	
	$\partial(G^E/T)/\partial T$	$-\frac{H^E}{T^2}$	$\partial(G^E/T)/\partial T$	$-\frac{H^E}{T^2}$	$\partial(G^E/T)/\partial T$	$-\frac{H^E}{T^2}$
523.15	-0.0003336	-0.000283	-0.00551	-0.001315	-0.003689	-0.000968
548.15	-0.00229	-2.8E-05	-0.004255	-0.001153	-0.004115	-0.000816
573.15	-0.001738	0.000571	-0.003334	-0.000775	-0.002997	-0.000473
598.15	-0.001364	0.001516	-0.00223	-0.000179	-0.000626	6.37E-05
623.15	-0.000719	0.002799	-0.001357	-0.000631	-0.001094	0.000791
648.15	-0.000996	0.004063	-0.002062	0.00143	-0.002711	0.001508

Graph 7: comparison of $\frac{\partial \left(\frac{G^E}{T} \right)}{\partial T}$ and $-\frac{H^E}{T^2}$ values of different temperatures for tetralin-quinoline system $X_t=0.25$

Graph 8 : : comparison of $\frac{\partial \left(\frac{G^E}{T} \right)}{\partial T}$ and $-\frac{H^E}{T^2}$ values of different temperatures for tetralin-quinoline system $X_t=0.50$

Graph 9: comparison of $\frac{\partial \left(\frac{G^E}{T} \right)}{\partial T}$ and $-\frac{H^E}{T^2}$ values of different temperatures for tetralin-quinoline system $X_t=0.6667$

Table 3 comparisons of $\left[\frac{\partial \left(\frac{G^E}{T} \right)}{\partial T} \right]_{p,x}$ and $-\frac{H^E}{T^2}$ values of m-cresol-tetralin system (numbers timed by 10^4)

Temperature K	Xm=0.1667		Xm=0.3333		Xm=0.5		Xm=0.6667		Xm=0.75		Xm=0.8333	
	$\frac{\partial \left(\frac{G^E}{T} \right)}{\partial T}$	$-\frac{H^E}{T^2}$	$\frac{\partial \left(\frac{G^E}{T} \right)}{\partial T}$	$-\frac{H^E}{T^2}$	$\frac{\partial \left(\frac{G^E}{T} \right)}{\partial T}$	$-\frac{H^E}{T^2}$	$\frac{\partial \left(\frac{G^E}{T} \right)}{\partial T}$	$-\frac{H^E}{T^2}$	$\frac{\partial \left(\frac{G^E}{T} \right)}{\partial T}$	$-\frac{H^E}{T^2}$	$\frac{\partial \left(\frac{G^E}{T} \right)}{\partial T}$	$-\frac{H^E}{T^2}$
523.15	-11.63	-3.367	-10.13	-6.129	-16.32	-6.908	-6.177	-6.253	4.330	-2.856	-10.41	-3.568
548.15	-14.43	-2.683	-12.60	-5.387	-18.17	-5.849	-8.416	-5.686	5.865	-2.923	-13.88	-2.93
573.15	-20.32	-1.814	-17.78	-4.495	-21.90	-4.72	-13.08	-4.974	9.043	-3.118	-21.13	-2.045
598.15	-23.40	-0.76	-20.48	-3.451	-23.78	-3.529	-15.51	-4.118	10.687	-3.435	-24.91	-0.919

Graph 10 comparison of $\frac{\partial \left(\frac{G^E}{T} \right)}{\partial T}$ and $-\frac{H^E}{T^2}$ values of different temperatures for m-cresol-tetralin system $X_m=0.3333$

Graph 11 comparison of $\frac{\partial \left(\frac{G^E}{T} \right)}{\partial T}$ and $-\frac{H^E}{T^2}$ values of different temperatures for m-cresol-tetralin system $X_m=0.5$

Graph 12 comparison of $\frac{\partial \left(\frac{G^E}{T} \right)}{\partial T}$ and $-\frac{H^E}{T^2}$ values of different temperatures for m-cresol-tetralin system Xm=0.6667

Table 4 comparison of $\left[\frac{\partial (G^E/T)}{\partial T} \right]_{p,x}$ and $-\frac{H^E}{T^2}$ values of m-cresol-quinoline system (numbers timed by 10^4)

Temperatur K	Xm=0.2		Xm=0.3333		Xm=0.5		Xm=0.6667		Xm=0.8000	
	$\frac{\partial \left(\frac{G^E}{T} \right)}{\partial T}$	$-\frac{H^E}{T^2}$	$\frac{\partial \left(\frac{G^E}{T} \right)}{\partial T}$	$-\frac{H^E}{T^2}$	$\frac{\partial \left(\frac{G^E}{T} \right)}{\partial T}$	$-\frac{H^E}{T^2}$	$\frac{\partial \left(\frac{G^E}{T} \right)}{\partial T}$	$-\frac{H^E}{T^2}$	$\frac{\partial \left(\frac{G^E}{T} \right)}{\partial T}$	$-\frac{H^E}{T^2}$
523.15	6.821	10.877	11.60	12.35	15.817	15.735	10.44	15.278	10.338	13.968
548.15	7.345	9.334	10.797	10.314	14.739	13.361	12.795	12.583	8.453	12.023
573.15	5.414	7.858	9.161	8.501	10.806	11.44	9.375	10.353	4.192	10.449
598.15	2.959	6.432	8.328	6.877	7.950	9.930	3.599	8.552	1.816	9.219

Graph 13 comparison of $\frac{\partial \left(\frac{G^E}{T} \right)}{\partial T}$ and $-\frac{H^E}{T^2}$ values of different temperatures for m-cresol-quinoline system $X_m=0.3333$

Graph 14 comparison of $\frac{\partial \left(\frac{G^E}{T} \right)}{\partial T}$ and $-\frac{H^E}{T^2}$ values of different temperatures for m-cresol-quinoline system $X_m=0.5$

Graph 15 comparison of $\frac{\partial \left(\frac{G^E}{T} \right)}{\partial T}$ and $-\frac{H^E}{T^2}$ values of different temperatures for m-cresol-quinoline system $X_m=0.6667$

Though visually we might say that the m-cresol –quinoline system has the best correspondence for the $\frac{\partial \left(\frac{G^E}{T} \right)}{\partial T}$ and $-\frac{H^E}{T^2}$ values, and the tetralin-quinoline system has the worst, we still need to analyze the

correspondence numerically. let $g = \frac{\partial \left(\frac{G^E}{T} \right)}{\partial T}$ and $h = -\frac{H^E}{T^2}$ we develop a variable d to check the correspondence.

$$d = \sqrt{\frac{\left(\frac{(g_i - h_i)}{g_i} \right)^2}{N}} \quad \dots\dots\dots(45)$$

where N is number of the data sets. After the calculation we got different d for different system

m-cresol-quinoline	1.0815
m-cresol-tetralin	0.9134
tetralin-quinoline	2.0253

from the numbers we got we still cannot explain why we got better fit for m-cresol-quinoline than that of the m-cresol-tetralin system. This might relate to the G^E and H^E data themselves, which means that we need to check the smoothness and the reliability of the G^E and H^E data used. Hence we fit the model to G^E and H^E data separately, and obtained the average errors and variances for the three data sets.

Table 5: regression results generated by applying the model to G^E and H^E data respectively

m-cresol-quinoline	Error of H^E %	7.6102
	Variance of fit for H^E S_{He}	0.0997
	Error of G^E %	6.2013
	Variance of fit for G^E S_{Ge}	0.0940
m-cresol-tetralin	Error of H^E %	37.903
	Variance of fit for H^E S_{He}	0.5343
	Error of G^E %	10.399
	Variance of fit for G^E S_{Ge}	0.1478
Tetralin-quinoline	Error of H^E %	53.525
	Variance of fit for H^E S_{He}	0.7376
	Error of G^E %	11.830
	Variance of fit for G^E S_{Ge}	0.1670

With the variances of the fits given above combined with the d values of equation 45, we might develop criteria to evaluate relatively the internal consistency of the G^E and H^E data sets used in the regressions. This way it should be possible to assign errors in model predictions appropriately to the the model deficiencies on one hand and data inconsistencies on the other.

$$\text{Let } \mu = d \sqrt{\frac{S_{He}^2 + S_{Ge}^2}{2}} \quad \dots\dots\dots(46)$$

The μ values for different systems are listed below

Tetralin-quinoline	1.083
m-cresol-tetralin	0.3580
m-cresol-quinoline	0.1047

it is apparent that the smaller the μ value is the better regression result we can get.

FUTURE WORK:

This study was quite revealing, in that we see clearly that before one goes about regressing parameters in a temperature dependent activity coefficient model for simultaneous representation of VLE excess enthalpy data, internal consistency of the data needs to be carefully evaluated. If the thermodynamic inconsistencies in the data are large, no model will be able to represent the data. Future work in this area needs to be in the development of clear and very easy to use thermodynamic consistency tests for high temperature VLE and excess enthalpy data. Such work will be a part of the future efforts in this project.

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