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Simultaneous correlation of VLE, H^E and $c_p{}^E$ of some diether + *n*-alkane systems by the Kohler polynomial

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Abstract: The simultaneous correlation of VLE and excess properties (H^E, $c_P{}^E$) for diether + *n*-alkane systems was performed in our previous paper by the cubic equation of state which incorporates the activity coefficient model (CEOS/G^E). With the same aim, in the present work, a completely different approach based on a polynomial equation (Kohler model) was considered. This method gave results on the same systems which could be estimated as being comparable to GEOS/G^E models for the simultaneous correlation of two and, with considerably improved fits, of three properties.

Keywords: Kohler polynomial, thermodynamic properties, simultaneous correlation, diether, *n*-alkane.

INTRODUCTION

Knowledge of phase equilibria: vapor–liquid equilibria VLE, liquid–liquid equilibria LLE, gas solubility *etc.* and excess properties, such as excess enthalpy H^E, excess heat capacity $c_P{}^E$, excess volume V^E *etc.*, of liquid systems are of great importance for industrial purposes, particularly for the analysis and design of chemical processes. Also, thermodynamic understanding of the structure of molecules and their behaviour is of primary interest for many studies. Many approaches (G^E models, cubic equation of state, *etc.*) have already been used for single and the simultaneous correlation of two properties, while those considering three properties are very rare in the literature.[1]

Various empirical equations of the polynomial type have also been very frequently used to adequately describe the thermodynamic behaviour of complex systems. Well known expressions, such as the Redlich–Kister,[2–4] Scatchard,[5,6] Tsao–Smith,[7,8] Toop,[9,10] Jacob–Fitzner,[11,12] Radojković,[13,14] Cibulka,[15,16] Kohler,[17–20] Nagata[20–22]

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etc., are widely used for the fitting of thermodynamic data of binaries and correlating and predicting those of ternaries. Such equations may often be adequate to represent binary data with high precision to the accuracy of the experiments.

In this work the Kohler model was chosen as a representative polynomial for the simultaneous correlation of VLE+H^E+$c_P{}^E$ and their combination of two properties VLE+H^E, VLE+$c_P{}^E$ and H^E+$c_P{}^E$ data of diethers (1,4-dioxane, 1,3-dioxolane) with *n*-alkanes (heptane, octane and nonane). The present calculations are compared to already published results[1] of the CEOS/G^E models for the same systems, bearing in mind that those complex mixture have a W-shaped $c_P{}^E$–x curve which is very difficult to fit.

KOHLER MODEL

The Kohler polynomial equations used in this work are given as follows:

$$G^E = x_1 x_2 \sum_{i=0}^{3} (a_i + b_i T + c_i T \ln T) Q_i \tag{1}$$

$$H^E = x_1 x_2 \sum_{i=0}^{3} (a_i - c_i T) Q_i \tag{2}$$

$$c_P{}^E = -x_1 x_2 \sum_{i=0}^{3} c_i Q_i \tag{3}$$

Model parameters Q_i are determined by the following expression:

$$\text{for } i = 0,\ Q_i = 1 \tag{4}$$

$$\text{for } i = 1,\ Q_i = x_2 - x_1 \tag{5}$$

$$\text{for } i = 2,\ Q_i = \frac{1}{2}[3(x_2 - x_1)^2 - 1] \tag{6}$$

$$\text{for } i = 3,\ Q_i = \frac{1}{2}[5(x_2 - x_1)^3 - 3(x_2 - x_1)] \tag{7}$$

DATA REDUCTION PROCEDURE

The calculated pressure P and the vapor mole fraction y of the component i for each data point of the isothermal VLE, were evaluated by the bubble point calculation, equating the fugacity of the vapor and liquid phase for each component.

The Kohler polynomial was used with twelve optimized coefficients given in Eqs. (1–3). All coefficients in the expressions for temperature dependent parameters of the polynomial model were generated from the corresponding fits of VLE+H^E, VLE+$c_P{}^E$, H^E+$c_P{}^E$ or VLE+H^E+$c_P{}^E$ data by minimizing the following objective function:

$$OF = OF_1 + OF_2 + OF_3 + OF_4 = \frac{1}{k}\sum_{i=1}^{k}\left(\frac{P_{\mathrm{exp}} - P_{\mathrm{cal}}}{P_{\mathrm{exp}}}\right)_i^2 + \frac{1}{q}\sum_{i=1}^{1}\left(\frac{y_{\mathrm{exp}} - y_{\mathrm{cal}}}{y_{\mathrm{exp}}}\right)_i^2 +$$

$$+\frac{1}{m}\sum_{i=1}^{m}\left(\frac{H^E_{\mathrm{exp}} - H^E_{\mathrm{cal}}}{H^E_{\mathrm{exp}}}\right)_i^2 + \frac{1}{n}\sum_{i=1}^{n}\left(\frac{c^E_{p\,\mathrm{exp}} - c^E_{p\,\mathrm{cal}}}{c^E_{p\,\mathrm{exp}}}\right)_i^2 \rightarrow \min \tag{8}$$

In Eq. (8) k, q, m and n are the number of the experimental P, y, H^E and $c_P{}^E$ data points, respectively. For the minimization of the objective function, the Hooke–Jeeves technique[23] was used.

The correlating results of VLE, H^E and $c_P{}^E$ data representation are given by the following deviations:

– The average absolute deviation $D(Z)$:

$$D(Z) = \frac{1}{n}\sum_{i=1}^{n}|Z_{\mathrm{exp}} - Z_{\mathrm{cal}}|_i \tag{9}$$

where Z stands for y.

– The percentage average absolute deviation $PD(Z)$:

$$PD(Z) = \frac{100}{n}\sum_{i=1}^{n}\left|\frac{Z_{\mathrm{exp}} - Z_{\mathrm{cal}}}{(Z_{\mathrm{exp}})_{\mathrm{max}}}\right|_i \tag{10}$$

where Z stands for P or H^E or $c_P{}^E$.

RESULTS AND DISCUSSION

For the purpose of simultaneous fitting of VLE+H^E+$c_P{}^E$ data and their combination of two properties, and comparison with CEOS/G^E models, the diether+n-alkane systems already used in our recent work[1] were selected. All calculations were performed by the Kohler polynomial model and compared with those of the MHV1 and MHV2 as CEOS/G^E models applied in our previous work.[1] The coefficients of this polynomial for all cases studied here are given in Appendix A.

Simultaneous correlation of two properties

For the simultaneous correlation of VLE+H^E data, the unique set of optimized coefficients of the Kohler model for all systems (Table AI) were generated using two objective functions $OF = OF_1 + OF_3$ (type I) and $OF = OF_1 + OF_2 + OF_3$ (type II). For the 1,4-dioxane+n-alkane systems, in most cases good performance was acieved when the coefficients were generated from the type I objective function. The results in $D(y)$ for the 1,4-dioxane+heptane system, obtained using the type II objective function were considerably better than those attained with type I, but the error in $PD(P)$ was somewhat higher, as can be seen from Table I. A similar behaviour was observed for the system 1,4-dioxane+nonane. It is evident from Table I that for the 1,4-dioxane+octane

TABLE I. Calculated results for the simultaneous correlation of VLE, H^E and $c_P{}^E$ binary data by the Kohler model

Properties	Deviations	1,4-Dioxane+heptane		1,4-Dioxane+octane		1,4-Dioxane+nonane		1,3-Dioxolane+heptane	
		I[a]	II[b]	I[a]	II[b]	I[a]	II[b]	I[a]	II[b]
VLE+H^E	$PD(P)$	0.48	0.94	0.43	0.43	0.34	0.74	0.92	0.93
	$D(y)$	0.0101	0.0050	0.0058	0.0058	0.0064	0.0039	0.0099	0.0099
	$PD(H^E)$	0.27	0.22	0.32	0.21	0.42	0.31	0.20	0.30
VLE+$c_P{}^E$	$PD(P)$	0.52	0.93	0.42	0.42	0.33	0.69	0.34	0.46
	$D(y)$	0.0083	0.0050	0.0058	0.0058	0.0064	0.0046	0.0081	0.0081
	$PD(c_P{}^E)$	2.93	2.71	1.46	1.36	2.28	2.15	1.85	1.75
H^E+$c_P{}^E$	$PD(H^E)$	0.34		0.32		0.41		0.20	
	$PD(c_P{}^E)$	2.27		1.39		2.22		1.00	

[a] The adjusted coefficients obtained by the objective function without the part OF_2 to the fitting of the VLE+H^E and VLE+$c_P{}^E$ data; [b] The adjusted coefficients obtained by the objective function including the part OF_2 to the fitting of VLE+H^E and VLE+$c_P{}^E$ data

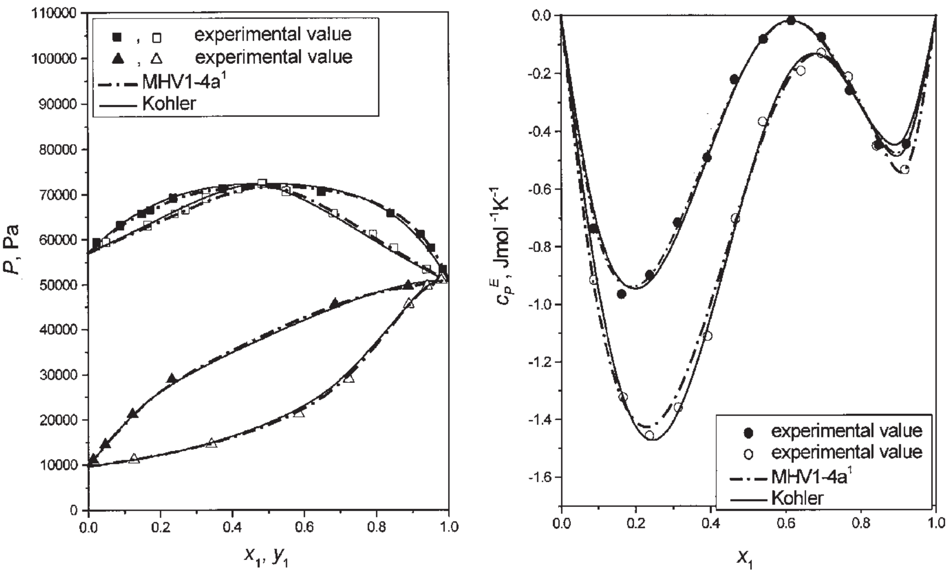


Fig. 1. The simultaneous correlation of VLE data at 353.15 K and $c_P{}^E$ data at 298.15 K. The points are experimental data: a) ■,□ – VLE at 353.15 K for the system 1,4-dioxane (1)+heptane (2),[24] ▲,Δ – VLE at 353.15 K for the system 1,4-dioxane (1)+nonane (2);[24] b) ● – $c_P{}^E$ at 298.15 K for the system 1,4-dioxane (1)+heptane (2),[25] O – $c_P{}^E$ at 298.15 K for the system 1,4-dioxane (1)+nonane (2).[25]

and 1,3-dioxolane+heptane systems, the type of objective function employed had no influence on the results of the VLE calculation.

The simultaneous correlation of VLE+$c_P{}^E$ data was carried out employing a single set of optimized coefficients (Table AI) generated from the data of these properties. As can be seen from Table I, the results obtained for the 1,4-dioxane+*n*-alkane systems, as well as for the 1,3-dioxolane + heptane system are satisfactory. Both objective functions (type I and II) function very similarly for each individual system. From Fig. 1a it is evident that the Kohler (type I) and MHV1-4a[1] models give good representation of the 1,4-dioxane+heptane and 1,4-dioxane+nonane systems. A similar conclusion can be drawn for the fitting of the $c_P{}^E$ data for both systems, as shown in Fig. 1b, where comparison is made with the same CEOS/G^E model. It is clear that both models are able to follow the W-shape of the $c_P{}^E$–x curve over the whole concentration range of the mole fraction of the liquid phase x.

TABLE II. Calculated results for the simultaneous correlation of VLE+H^E + $c_P{}^E$ binary data by the Kohler model

System	Deviations	I[a]	II[b]
1,4-Dioxane+heptane	$PD(P)$	0.59	0.94
	$D(y)$	0.0083	0.0050
	$PD(H^E)$	0.32	0.24
	$PD(c_P{}^E)$	2.96	2.91

TABLE II. Continued

System	Deviations	I[a]	II[b]
1,4-Dioxane+octane	$PD(P)$	0.42	0.42
	$D(y)$	0.0058	0.0058
	$PD(H^E)$	0.32	0.33
	$PD(c_P{}^E)$	1.57	1.39
1,4-Dioxane+nonane	$PD(P)$	0.34	0.70
	$D(y)$	0.0064	0.0041
	$PD(H^E)$	0.42	0.36
	$PD(c_P{}^E)$	2.29	2.19
1,3-Dioxolane+heptane	$PD(P)$	0.91	0.93
	$D(y)$	0.0110	0.0109
	$PD(H^E)$	0.20	0.29
	$PD(c_P{}^E)$	1.86	1.77

[a,b] The same as in Table I

Values of the sets of optimized coefficients (Table AI) appearing in the Kohler model were generated from the simultaneous correlation of H^E+$c_P{}^E$ data using the objective function $OF=OF_3+OF_4$. The results of the correlation are given in Table I. The Kohler model gave excellent results in terms of $PD(H^E)$ for all mixtures, while the errors in $PD(c_p{}^{E)}$ were slightly greater (above 2 %) for the of 1,4-dioxane+heptane and 1,4-dioxane+nonane systems and around 1 % for the 1,4-dioxane+octane and 1,3-dioxolane+heptane systems. As an example, the very good

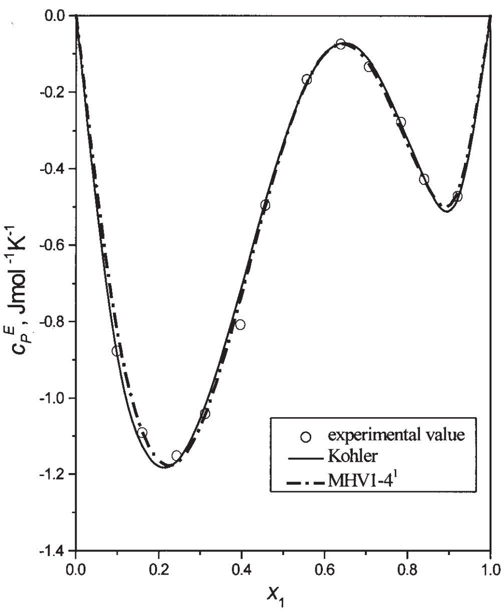
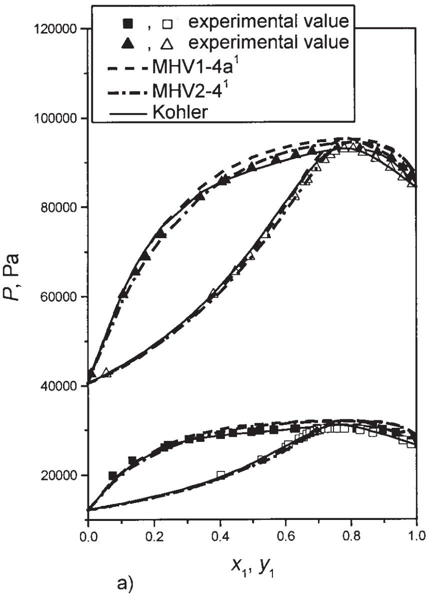
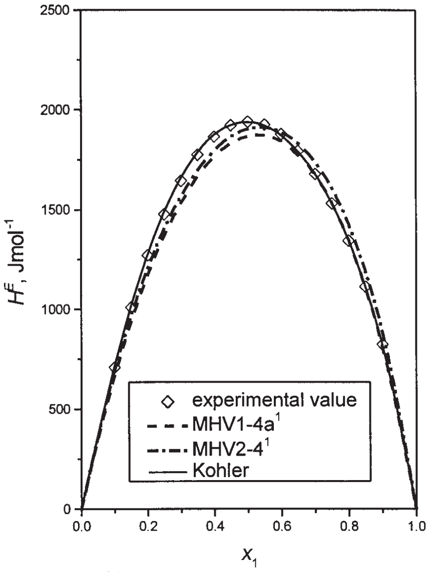


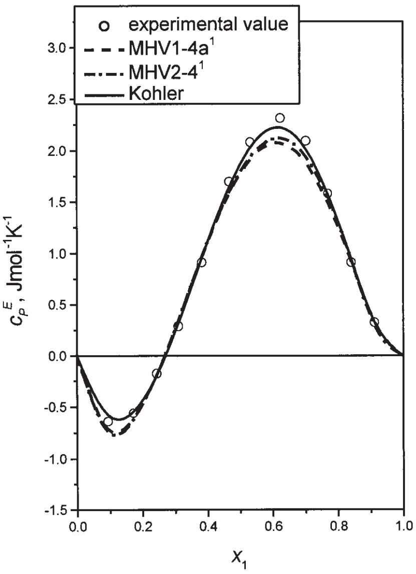
Fig. 2. Correlation of $c_P{}^E$ data at 298.15 K with the parameters of the models generated from the H^E+$c_P{}^E$ data for the system 1,4-dioxane (1)+octane (2). The points O are experimental data.[25]



a)



b)



c)

Fig. 3. Simultaneous correlation of the VLE + H^E + c_P^E data of the system 1,3-dioxolane(1) + heptane (2). The points are experimental data: a) ■,□ – VLE at 313.15 K,[26] ▲,Δ – VLE at 343.15 K,[26] b) ◇ – H^E at 298.15 K,[27] c) O – c_P^E at 298.15 K.[27]

agreement between the experimental and the values calculated using the Kohler and MHV1-4[1] models for the 1,4-dioxane+octane system is shown in Fig. 2.

Simultaneous correlation of three properties

The simultaneous fittings of VLE+H^E+c_P^E binary data for the 1,4-dioxane+n-alkane systems and 1,3-dioxolane+heptane system with the Kohler model are presented in Table II. The following remarks can be made: (*i*) the results of the simultaneous correlation of three properties by the Kohler model are very good and better than those obtained using the CEOS/G^E models,[1] (*ii*) introducing a part of the objective function OF_2 into the overall OF slightly decreases the errors in the vapor phase composition and increases the errors in pressure P for the 1,4-dioxane+heptane and 1,4-dioxane+nonane systems, while for other systems the influence of OF_2 on the improvement of the overall results can be neglected. The very good correlating results for the 1,3-dioxolane+heptane system, are shown in Fig. 3, from which it can be seen that for all properties the fitting curves agree most closely with the experimental data points than the CEOS/G^E models, where, for example, the MHV2-4[1] model gave a considerably higher error, $PD(c_P{}^E) = 3.85$.

CONCLUSION

Thermodynamic modelling of the diethers (1,4-dioxane and 1,3-dioxolane) with *n*-alkanes (heptane, octane and nonane) using the Kohler polynomial equation has proven to be a powerful tool for providing sufficient information on the simultaneous correlation of VLE and excess properties (H^E, $c_P{}^E$).

The simultaneous description of two properties (VLE+H^E, VLE+$c_P{}^E$ and H^E+$c_P{}^E$) of these systems can be very successfully performed by the Kohler model, as was the case with CEOS/G^E models.[1] However, the correlation of three properties (VLE+H^E+$c_P{}^E$) shows that the Kohler model is more suitable than the relatively simple CEOS/G^E models. The simultaneous correlation of three investigated thermodynamic properties is extremely rarely encountered in the literature, and bearing in mind their importance from the theoretical and practical points of view, further investigations in this field could be very promising.

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ИЗВОД

СИМУЛТАНО КОРЕЛИСАЊЕ VLE, H^E И $c_P{}^E$ ПОДАТАКА ДИЕТАР + *n*-АЛКАН СИСТЕМА ПОМОЋУ КОХЛЕРОВОГ ПОЛИНОМА

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Симултано корелисање VLE и допунских величина (H^E, $c_P{}^E$) извршено је у претходном раду на системима диетри+*n*-алкани коришћењем кубне једначине стања која укључује модел за коефицијенте активности (CEOS/G^E). Са истим циљем, у овом раду примењен је потпуно другачији приступ базиран на коришћењу полинома (Кохлеров модел). Овај приступ дао је резултате на истим системима који су у случају симултаног корелисања две особине сличног квалитета као и при коришћењу CEOS/G^E модела док су резултати при симултаном корелисању три особине значајно побољшани.

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APPENDIX

The numerical values of the optimized coefficients, existing in the Kohler polynomial used for the correlation of diverse combinations of VLE, H^E and $c_P{}^E$ data are summarized in Tables AI and AII.

TABLE AI. Optimized coefficients for the simultaneous correlation of VLE, H^E and $c_P{}^E$ binary data by the Kohler model

Proper-ties	Coeficients	1,4-Dioxane+heptane		1,4-Dioxane+octane		1,4-Dioxane+nonane		1,3-Dioxolane+heptane	
		I[a]	II[b]	I[a]	II[b]	I[a]	II[b]	I[a]	II[b]
VLE+H^E	a_1	0.665348E+4	0.684074E+4	0.611879E+4	0.731962E+4	0.551006E+4	0.7227874E+4	0.739226E+4	0.796704E+4
	b_1	0.517853E+1	0.103244E+1	0.231410E+2	–0.355580E+1	0.443801E+2	0.564892E+1	0.438430E+1	–0.883112E+1
	c_1	–0.257706E+1	–0.19504E+1	–0.540240E+1	–0.142737E+1	–0.878073E+1	–0.304112E+1	–0.252435E+1	–0.647280E+0
	a_2	–0.671737E+3	–0.847541E+3	–0.913828E+3	–0.103236E+4	–0.125122E+4	–0.114698E+4	–0.680559E+3	–0.213671E+4
	b_2	0.172659E+1	0.637456E+1	–0.175724E+1	0.225371E+1	0.934520E+0	–0.640400E-1	–0.131130E+0	0.337877E+2
	c_2	–0.212520E+0	–0.845060E+0	0.474650E+0	–0.152310E+0	0.126980E+0	0.221870E+0	0.215880E+0	0.215880E+0
	a_3	0.511997E+3	0.529189E+3	0.466585E+3	0.614746E+3	0.739558E+3	0.498617E+3	0.769729E+3	0.104768E+4
	b_3	0.161330E+0	–0.940760E+0	0.768900E-1	–0.215093E+1	–0.535970E+1	0.359860E+0	–0.111853E+1	–0.799592E+1
	c_3	–0.943700E-1	–0.115970E+0	–0.205520E+0	0.972800E-1	0649520E+0	–0.265260E+0	–0.926000E-1	0.806010E+0
	a_4	–0.451298E+3	–0.247594E+3	–0.634889E+3	–0.445322E+3	–0.457868E+3	–0.494858E+3	–0.443337E+3	–0.386498E+3
	b_4	0.232318E+1	–0.172493E+1	0.157009E+1	–0.830180E+0	–0.104563E+3	0.241503E+1	–0.651050E+0	–0.139422E+1
	c_4	–0.192750E+0	0.395390E+0	0.170000E-1	0.333720E+0	0.36529E+0	–0.225960E+0	0.333190E+0	0.401991E+0
VLE+$c_P{}^E$	a_1	–0.306532E+4	–0.198527E+4	–0.416520E+4	–0.335902E+4	–0.435099E+4	–0.406250E+4	0.110213E+5	0.115814E+5
	b_1	–0.378140E+1	–0.712845E+1	–0.569556E+1	–0.781120E+1	–0.100322E+2	–0.109705E+2	–0.368392E+1	–0.549610E+1
	c_1	0.365749E+1	0.369963E+1	0.447887E+1	0.444822E+1	0.525332E+1	0.521005E+1	–0.305820E+1	–0.307281E+1
	a_2	0.139763E+5	–0.290466E+4	–0.579200E+2	–0.323091E+4	–0.376770E+4	–0.419623E+4	0.554356E+4	0.566744E+4
	b_2	–0.546914E+2	–0.628184E+1	–0.178536E+2	–0.815175E+1	–0.131094E+2	–0.115183E+2	–0.606710E+2	–0.606710E+2
	c_2	0.236489E+1	0.230511E+1	0.278022E+1	0.268304E+1	0.373556E+1	0.367202E+1	0.737780E+1	0.734886E+1
	a_3	–0.561078E+4	–0.661094E+4	–0.326339E+4	–0.592272E+4	–0.6017763E+4	–0.609394E+4	0.430127E+4	0.641707E+4

TABLE AI.Continued

Proper-ties	Coeficients	1,4-Dioxane+heptane		1,4-Dioxane+octane		1,4-Dioxane+nonane		1,3-Dioxolane+heptane	
		I[a]	II[b]	I[a]	II[b]	I[a]	II[b]	I[a]	II[b]
	b_3	–0.185591E+2	–0.174093E+2	–0.273031E+2	–0.194161E+2	–0.172656E+2	–0.169207E+2	–0.632285E+2	–0.701370E+2
	c_3	0.603958E+1	0.613494E+1	0.626400E+1	0.619864E+1	0.593846E+1	0.587422E+1	0.875756E+1	0.87757E+1
	a_4	0.235767E+4	0.103036E+4	0.460800E+3	0.291118E+4	0.415145E+4	0.494918E+4	–0.869390E+3	–0.106596E+4
	b_4	0.254920E+1	0.656015E+1	0.143213E+2	0.773480E+1	0.870759E+1	0.623176E+1	0.195275E+2	0.205133E+2
	c_4	–0.157822E+1	–0.163260E+1	–0.268338E+1	–0.274338E+1	–0.352156E+1	–0.351468E+1	–0.292921E+1	–0.300501E+1
$H^E+c_P^E$	a_1	0.855135E+4		0.905414E+4		0.968789E+4		0.721732E+4	
	b_1	–0.491630E+0		0.767850E+0		0.250700E-1		–0.873380E+0	
	c_1	0.380513E+1		0.444516E+1		0.523337E+1		–0.309881E+1	
	a_2	0.688070E+2		–0.261840E+3		–0.161640E+3		0.142264E+4	
	b_2	–0.590970E+0		–0.342190E+0		0.973220E+0		–0.941590E+0	
	c_2	0.235178E+1		0.266617E+1		0.369693E+1		0.720906E+1	
	a_3	0.242393E+4		0.236987E+4		0.228194E+4		0.352209E+4	
	b_3	0.729340E+0		–0.958300E+0		0.533090E+0		–0.119390E+0	
	c_3	0.638918E+1		0.618426E+1		0.590016E+1		0.913710E+1	
	a_4	–0.919264E+3		–0.146600E+4		–0.15266E+4		–0.153160E+4	
	b_4	0.337700E+0		0.358630E+0		0.936290E+0		–0.705840E+0	
	c_4	–0.159530E+1		–0.276356E+1		–0.350640E+1		–0.369020E+1	

[a,b] The same as in Table I

TABLE AII. The optimized coefficients for the simultaneous correlation of VLE+H^E+c_P^E binary data

System	Coefficients	I[a]	II[b]
1,4-Dioxane+heptane	a_1	0.850612E+4	0.851109E+4
	b_1	–0.363750E+2	–0.366519E+2
	c_1	0.364219E+1	0.366661E+1
	a_2	0.442874E+2	0.111794E+3
	b_2	–0.149984E+2	–0.153965E+2
	c_2	0.231447E+1	0.240258E+1
	a_3	0.231265E+4	0.234230E+4
	b_3	–0.409838E+2	–0.423067E+2
	c_3	0.600669E+1	0.605939E+1
	a_4	–0.918545E+3	–0.819744E+3
	b_4	0.119980E+2	0.113170E+2
	c_4	–0.161052E+1	–0.155115E+1
1,4-Dioxane+octane	a_1	0.907504E+4	0.905860E+4
	b_1	–0.434031E+2	–0.430238E+2
	c_1	0.451435E+1	0.445804E+1
	a_2	–0.200698E+3	–0.255701E+3
	b_2	–0.178540E+2	–0.167749E+2
	c_2	0.287473E+1	0.271590E+1
	a_3	0.241815E+4	0.237611E+4
	b_3	–0.438578E+2	–0.430033E+2
	c_3	0.634212E+1	0.621925E+1
	a_4	–0.142833E+4	–0.146095E+4
	b_4	0.193280E+2	0.199824E+2
	c_4	–0.262641E+1	–0.272250E+1
1,4-Dioxane+nonane	a_1	0.969548E+4	0.968023E+4
	b_1	–0.498404E+2	–0.498133E+2
	c_1	0.525678E+1	0.521620E+2
	a_2	–0.163403E+3	–0.152429E+3
	b_2	–0.234463E+2	–0.229390E+2
	c_2	0.375890E+1	0.365437E+1
	a_3	0.232032E+4	0.228771E+4
	b_3	–0.409424E+2	–0.406523E+2
	c_3	0.595068E+1	0.586435E+1
	a_4	–0.159663E+4	–0.150734E+4
	b_4	0.248467E+2	0.247930E+2
	c_4	–0.349951E+1	–0.355470E+1

TABLE AII.Continued

System	Coefficients	I[a]	II[b]
1,3-Dioxolane+heptane	a_1	0.723155E+4	0.723641E+4
	b_1	0.797387E+1	0.752390E+1
	c_1	–0.305693E+1	–0.308884E+1
	a_2	0.145728E+4	0.151670E+4
	b_2	–0.481333E+2	–0.483767E+2
	c_2	0.737936E+1	0.734313E+1
	a_3	0.340117E+4	0.340833E+4
	b_3	–0.603922E+2	–0.610696E+2
	c_3	0.875679E+1	0.872253E+1
	a_4	–0.141450E+4	–0.141059E+4
	b_4	0.211850E+2	0.215972E+2
	c_4	–0.292872E+1	–0.302811E+1

[a,b] The same as in Table I