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Molar excess enthalpies of ethyl acetate + alkanols at $T = 298.15$ K, $p = 10.0$ MPa

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Abstract

A commercial flow-mixing isothermal calorimeter was tested by measuring heat of mixing curves for exothermic, endothermic, S-shaped and double minimum molar excess enthalpy mixtures at high pressure. The results show this calorimeter is able to produce good quality data. Molar excess enthalpies for ethyl acetate mixed with a series of simple alkanols were measured at $T = 298.15$ K and $p = 10$ MPa.

Keywords: Flow-mixing; Calorimeter; Molar excess enthalpy

1. Introduction

Real behavior of binary systems is frequently described through excess properties [1]. Knowledge of molar excess enthalpies, H_m^E, is fundamental in designing and developing industrial processes [2], and data on molar excess enthalpies of mixtures are valuable source of thermodynamic information [3], elucidate microscope structures of the solutions and interactions among the components [4]. The flow-mixing isothermal calorimeters are widely used to determinate molar excess enthalpies of mixed solvents [5].

Many data on excess enthalpies for binary systems exist at $T = 298.15$ K and $p = 0.1$ MPa, e.g. the Dortmund data bank (DDB) [6], but fewer data are available at higher temperature and pressure [7,8]. To investigate the effects of temperature and pressure on excess enthalpies, a high pressure flow-mixing isothermal calorimeter system was evaluated by measurement of molar excess enthalpies H_m^E of four binary mixtures ($\{xCH_3OH + (1-x)H_2O\}$, $\{xC_2H_5OH + (1-x)H_2O\}$, $\{xCH_3COCH_3 + (1-x)H_2O\}$ at $T = 298.15$ K and $p = 0.2$ MPa, $\{xC_2H_5OH + (1-x)H_2O\}$ at $T = 333.15$ K and $p = 0.4$ MPa); and the result was compared with reliable literature data. The comparison shows this calorimeter produces good quality data. Molar excess enthalpies for ethyl acetate mixed with a series of simple alkanols were also measured at $T = 298.15$ K and $p = 10.0$ MPa.

2. Experimental

2.1. Chemicals

Methanol (HPLC grade), ethanol (HPLC grade) and acetone (HPLC grade) were purchased from Tedia (Fairfield, USA). 1-Propanol (AR grade), 2-propanol (AR grade), 1-butanol (AR grade) and ethyl acetate (AR grade) were purchased from Tianjin Chemical Reagent Co. All chemicals were distilled at a reflux ratio of approximately 50 in a 2 m distillation column and loaded directly into the pump to avoid absorbing atmospheric water. Comparison of the measured densities and the literature data is shown in Table 1. They were found to be in good agreement. Water was distilled by using a quartz sub-boiling purifier and degassed before it was loaded into the pumps.

2.2. Apparatus

A commercial isothermal calorimeter (model 4400 IMC, Calorimeter Science Corporation, USA) with a

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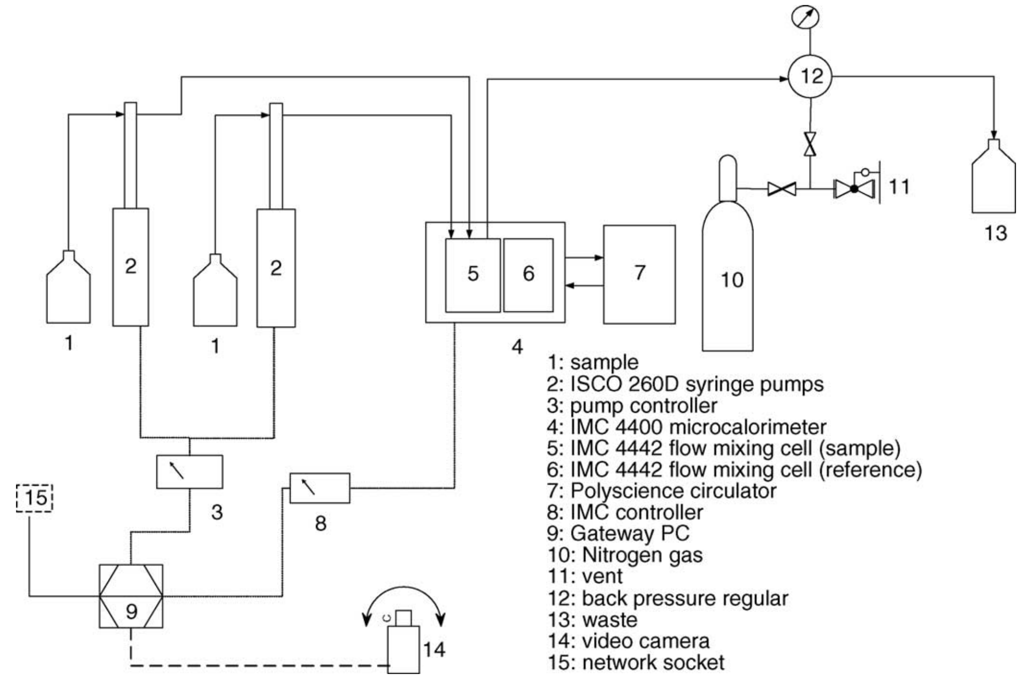

Fig. 1. Schematic diagram of the flow-mixing calorimeter.

refrigerating/heating circulator (model 9000, PolyScience Inc., USA) was used in these measurements. The flow-mixing system is comprised of two CSC4442 flow-mixing cells [9,10], two syringe pumps (model: 260D, ISCO Inc., USA) and a back pressure regulator. It can be used to measure heat of mixing at pressures up to 15 MPa and at temperatures from −20 to 200 °C. The IMC data acquisition software was provided by Calorimetry Sciences Corporation, the pumps scheduler/monitor program was developed by our group. An Anton Paar densimeter (DMA55, with accuracy of $\pm 5 \times 10^{-5}$ g cm^3) and Sartorius analytical balance (with accuracy of ±0.1 mg) were used to check flow rates of the syringe pumps. The flow rate resolution of 260D syringe pumps is 0.1 μl min^{-1}. The measured short-term (1 h) and

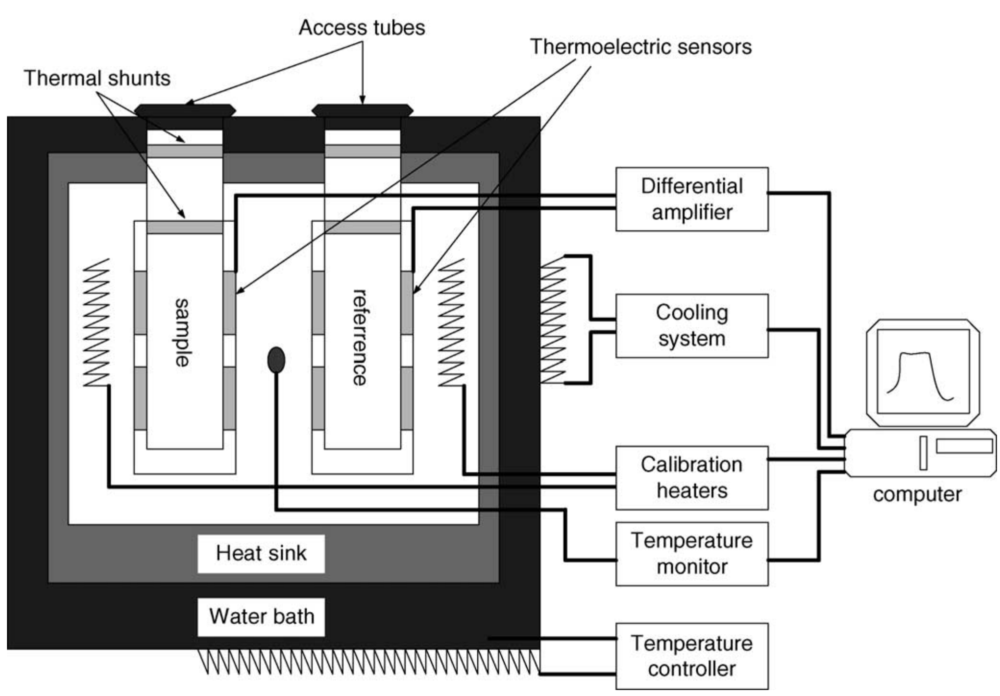

Fig. 2. General setup of the model 4400 isothermal calorimeter (Calorimetry Sciences Corporation, UT).

Table 1
Experimental and literature (DDB) values of densities at $T = 298.15$ K

Compound	d (exp) (g cm^{-3})	d (lit) (g cm^{-3})
Ethanol	0.78554	0.7850
Methanol	0.78676	0.7866
Acetone	0.78454	0.7844
1-Propanol	0.79967	0.7997
2-Propanol	0.78134	0.7813
1-Butanol	0.80612	0.8060
Ethyl acetate	0.89455	0.8946

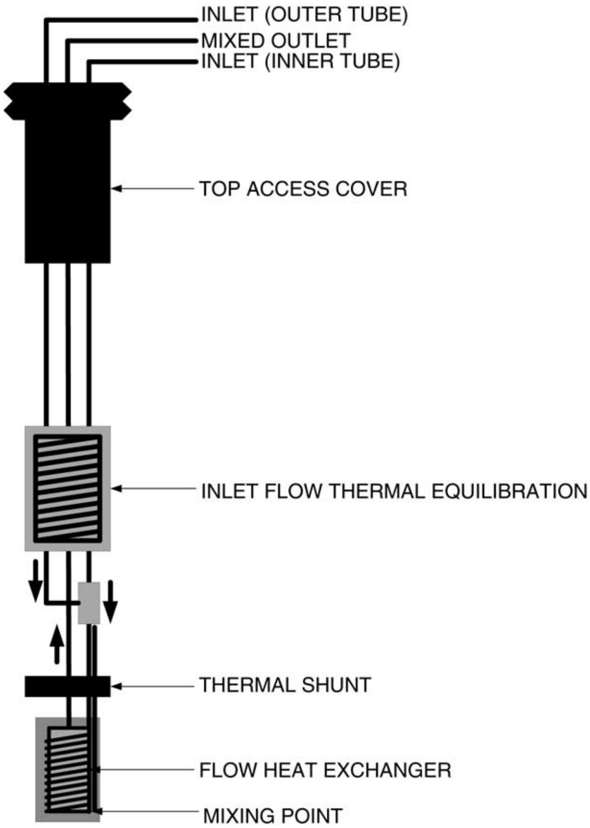

Fig. 3. Model 4442 flow-mixing cell (Calorimetry Sciences Corporation, UT).

long-term (24 h) stability of CSC 4400 IMC show that changes in heat flow as small as 0.1 μW and heat effects as small as 40 μJ are detectable. When the output signal corresponding to the mixture ($\{x\mathrm{CH_3OH} + (1 - x)\mathrm{H_2O}\}$) reaches the stationary state, the signal noise ratio is larger than 80 dB at normal flow rate (150:150 μl min^{-1}) and about 20 dB at baseline flow rate (300:0 or 0:300 μl min^{-1}) (Figs. 1–3).

3. Calculation

The molar excess enthalpy was obtained from the following equation:

$$H^{\mathrm{E}} = \frac{P - P_{\mathrm{b}}}{V_1\rho_1/M_1 + V_2\rho_2/M_2} \tag{1}$$

Table 2
Densities of $\{x\text{ethanol} + (1 - x)\text{water}\}$ mixtures at $T = 298.15$ K, $p = 0.1$ MPa

x	d (g cm^{-3})
0.00000	0.99729
0.09971	0.96369
0.19995	0.93392
0.28662	0.90969
0.34653	0.89305
0.50049	0.85913
0.59197	0.84241
0.69750	0.82568
0.78469	0.81232
0.89920	0.79902
1.00000	0.78554

where V_i, ρ_i and M_i are the volumetric flow rate (ml min^{-1}), density (g cm^{-3}) and molecular weight (g mol^{-1}) of solvent i, respectively. The power P (J s^{-1}) is the measured variable read from the IMC data acquisition system. To reduce background heat effect of the physical process, the baseline power, P_{b} was measured and calculated from the following equation:

$$P_{\mathrm{b}} = \frac{V_1 P_1 + V_2 P_2}{V_1 + V_2} \tag{2}$$

where P_i is the baseline power of heat flow for solvent i at flow rate V_i. However, this non-compensated effect is less than 1.0% in this work.

4. Results and discussion

4.1. Validation of the reliability of syringe pumps

Various $\{x\text{ethanol} + (1 - x)\text{water}\}$ mixtures were prepared by using weighing method. Their densities were determined by densimeter and listed in Table 1. The data was correlated with a polynomial equation:

$$x = -56.813d^3 + 165.07d^2 - 162.97d + 54.703 \tag{3}$$

A serious of $\{x\text{ethanol} + (1 - x)\text{water}\}$ mixtures were obtained by using the ISCO syringe pumps at different volumetric flow rates. Their compositions x_{cal} were calculated

Table 3
Molar fraction of $\{x\text{ethanol} + (1 - x)\text{water}\}$ at $T = 298.15$ K, $p = 0.1$ MPa

Pump 1 (ml min^{-1})	Pump 2 (ml min^{-1})	x_{cal}	d (g cm^{-3})	x_{exp}
0.0500	0.3500	0.0422	0.98249	0.0459
0.1000	0.3000	0.0932	0.96609	0.0969
0.1500	0.2500	0.1561	0.94629	0.1589
0.2000	0.2000	0.2356	0.92264	0.2371
0.2500	0.1500	0.3394	0.89531	0.3386
0.3000	0.1000	0.4805	0.86290	0.4837
0.3500	0.0500	0.6833	0.82742	0.6862

Table 4
Excess enthalpies for test systems

x_1	H^E (J mol^{-1})
{$x$ethanol + (1 − x)water} at T = 333.15 K, p = 0.4 MPa	
0.0244	−117.9
0.0478	−216.0
0.0736	−272.6
0.1242	−313.9
0.1734	−293.0
0.2233	−248.1
0.2717	−197.1
0.323	−142.2
0.3718	−93.0
0.4213	−47.5
0.4706	−12.6
0.5222	15.8
0.5719	37.0
0.6225	49.3
0.6735	51.3
0.7243	44.3
0.7742	30.3
0.8222	12.7
0.8542	1.1
0.8878	−6.7
0.9232	−11.8
{$x$methanol + (1 − x)water} at T = 298.15 K, p = 0.2 MPa	
0.0230	−150.87
0.0411	−263.30
0.0600	−378.18
0.0797	−476.95
0.1004	−559.50
0.1221	−640.43
0.1448	−702.51
0.1687	−761.34
0.1938	−801.14
0.2202	−837.55
0.2481	−859.25
0.2775	−880.10
0.3086	−879.80
0.3416	−881.35
0.3765	−868.17
0.4137	−849.60
0.4533	−828.29
0.4955	−799.50
0.5406	−764.37
0.5890	−722.31
0.6410	−671.84
0.6970	−605.32
0.7576	−523.20
0.8232	−425.42
0.8945	−276.83
0.9197	−218.48
{$x$ethanol + (1 − x)water} at T = 298.15 K, p = 0.2 MPa	
0.016	−136.3
0.029	−270.7
0.042	−381.1
0.056	−482.6
0.072	−574.8
0.088	−644.9
0.105	−699.5
0.123	−738.3
0.142	−762.6
0.163	−771.2
0.185	−769.6
0.21	−752.4
0.236	−722.3
0.264	−683.1
0.294	−642.5
0.328	−595.1
0.364	−546.1
0.404	−498.9
0.448	−459.2
0.497	−414.8
0.552	−371.5
0.614	−323.8
0.683	−280.7
0.763	−229.5
0.854	−176.3
0.913	−133
{$x$acetone + (1 − x)water} at T = 298.15 K, p = 0.2 MPa	
0.0128	−125.29
0.0230	−207.65
0.0339	−282.74
0.0455	−354.58
0.0579	−419.35
0.0711	−481.82
0.0853	−528.73
0.1005	−574.68
0.1169	−601.93
0.1345	−625.75
0.1537	−640.5
0.1745	−645.86
0.1973	−639.68
0.2221	−623.02
0.2495	−602.22
0.2798	−558.65
0.3134	−504.38
0.3509	−442.53
0.3931	−364.43
0.4410	−270.95
0.4957	−155.2
0.5588	−28.03
0.6324	115.59
0.7193	243.46
0.8236	306.52
0.8632	287.72
0.9077	239.06

with equation:

$$x_{cal} = \frac{V_1 \rho_{EtOH}/M_{EtOH}}{V_1 \rho_{EtOH}/M_{EtOH} + V_2 \rho_{Water}/M_{Water}} \quad (4)$$

The densities of these mixtures were determined and compositions x_{exp} were calculated with Eq. (3) (Table 2).

The results show that differences between x_{cal} and x_{exp} are less than 0.003 in Table 3.

4.2. Test systems

To verify the reliability of calorimeter, molar excess enthalpies of binary systems ({$x$ethanol + (1 − x)water} at T = 298.15 K, p = 0.4 MPa, {$x$methanol + (1 − x)water}, {$x$ethanol + (1 − x)water} and {$x$acetone + (1 − x)water} at T = 298.15 K, p = 0.2 MPa) were measured. The experimental data was listed in Table 4.

Table 5
Coefficients a_i, k in Eq. (5), and RMSD for the results in Table 4

	Ethanol + water, T = 333.15 K, p = 0.4 MPa	Methanol + water, T = 298.15 K, p = 0.2 MPa	Ethanol + water, T = 298.15 K, p = 0.2 MPa	Acetone + water, T = 298.15 K, p = 0.2 MPa
k	−0.4416	0.9848	0.9981	0.4169
a_0 ($\times 10^3$ J mol^{-1})	0.0185	−3.1839	−1.6434	−0.5900
a_1 ($\times 10^3$ J mol^{-1})	−1.1172	1.6387	0.0330	−3.9040
a_2 ($\times 10^3$ J mol^{-1})	−2.0025	−0.6881	−1.0284	1.0998
a_3 ($\times 10^3$ J mol^{-1})	−1.4673	1.1532	−0.9563	−1.5132
a_4 ($\times 10^3$ J mol^{-1})	−2.5445	0.7958	0.2174	−0.9062
a_5 ($\times 10^3$ J mol^{-1})	−1.8082	0.2319	3.4804	−0.1857
RMSD (J mol^{-1})	2.54	2.25	1.38	1.99

Table 6
Comparison of smooth value of experimental data and literature data

x_1	H^E (J mol^{-1})							
	Ethanol + water, T = 333.15 K, p = 0.4 MPa		Methanol + water, T = 298.15 K, p = 0.2 MPa		Ethanol + water, T = 298.15 K, p = 0.2 MPa		Acetone + water, T = 298.15 K, p = 0.2 MPa	
	Experimental	Reference [10]	Experimental	Reference [11]	Experimental	Reference [12]	Experimental	Reference [13]
0.100	−302.1	−301.4	−560.4	−545.0	−685.7	−685.2	−569.3	−573.0
0.200	−273.2	−268.0	−812.7	−806.2	−758.5	−784.0	−639.1	−636.5
0.300	−165.3	−159.3	−880.8	−880.2	−634.4	−660.1	−528.6	−516.4
0.400	−66.5	−61.9	−858.7	−857.9	−505.0	−511.1	−351.0	−335.1
0.500	4.6	5.9	−796.0	−797.9	−410.9	−403.5	−147.5	−132.4
0.600	44.8	41.8	−711.2	−720.7	−337.0	−329.4	54.4	68.9
0.700	49.0	44.4	−603.4	−618.5	−268.6	−264.8	220.1	235.4
0.800	20.8	19.4	−460.5	−470.9	−207.1	−203.3	303.6	319.4
0.900	−9.4	−9.4	−265.6	−263.5	−144.6	−142.6	249.8	263.8

The results in Table 4 were fitted to the modified Redlich–Kister (R–K) equation:

$$H_m^E\,(\mathrm{J\,mol^{-1}}) = x(1-x)\sum_{j=0}^{m}\frac{a_j(1-2x)^j}{1-k(1-2x)} \quad (-1 < k < 1) \qquad (5)$$

the following objective function was used:

$$\mathrm{RMSD} = \sqrt{\frac{1}{n}\sum_{i}^{n}(H^E_{\mathrm{calc}(i)} - H^E_{\mathrm{expt}(i)})^2} \qquad (6)$$

the coefficients k, a_i and RMSD are summarized in Table 5. Smooth values of experimental data were compared with literature data in Table 6.

Table 6 shows this isothermal calorimeter is producing good quality data.

4.3. *The molar excess enthalpies of ethyl acetate + alcohols systems*

The molar excess enthalpies at T = 298.15 K, p = 10 MPa for ethyl acetate mixed with a series of 1-alkanols are reported in Table 7. The H^E data were fitted to modified Redlich–Kister (R–K) equation (5). The coefficients a_i and RMSD are summarized in Table 8.

Table 7
Excess enthalpies for {$x$ethyl acetate + (1 − x)alcohols} systems

x_1	H^E (J mol^{-1})
{$x$ethyl acetate + (1 − x)methanol} at T = 298.15 K, p = 10.0 MPa	
0.057	182.6
0.086	272.5
0.113	333.8
0.188	523.2
0.257	680.3
0.319	809.4
0.377	897.1
0.430	968.3
0.478	995.8
0.524	1013.3
0.566	1009.1
0.605	987.0
0.641	977.4
0.675	945.3
0.707	910.2
0.738	869.6
0.766	821.8
0.793	767.6
0.818	711.3
0.842	651.3
0.864	585.4
0.886	518.1
0.906	446.5
0.926	367.7
0.944	284.6
0.962	200.1
0.979	105.9

Table 7 (*Continued*)

x_1	H^E (J mol^{-1})
{xethyl acetate + (1 − x)ethanol} at T = 298.15 K, p = 10.0 MPa	
0.030	141.0
0.054	247.4
0.078	365.9
0.104	469.6
0.130	566.0
0.157	660.9
0.184	755.1
0.213	845.9
0.243	931.1
0.274	1007.3
0.306	1082.3
0.339	1148.0
0.373	1204.2
0.409	1250.7
0.446	1297.6
0.485	1328.2
0.525	1337.5
0.567	1330.4
0.611	1309.3
0.657	1259.2
0.705	1192.7
0.754	1087.9
0.807	947.1
0.861	763.2
0.919	508.9
0.939	399.5
0.960	274.4
{xethyl acetate + (1 − x)1-propanol} at T = 298.15 K, p = 10.0 MPa	
0.039	250.6
0.068	397.1
0.098	541.6
0.129	674.2
0.160	796.3
0.192	919.1
0.225	1017.4
0.258	1120.4
0.291	1204.9
0.326	1280.3
0.361	1365.0
0.396	1412.6
0.433	1459.2
0.470	1483.9
0.508	1511.2
0.547	1514.4
0.586	1503.0
0.627	1463.7
0.668	1418.4
0.710	1344.1
0.753	1236.4
0.797	1108.4
0.842	932.2
0.888	724.7
0.935	457.4
0.951	350.9
0.968	239.6

Table 7 (*Continued*)

x_1	H^E (J mol^{-1})
{xethyl acetate + (1 − x)2-propanol} at T = 298.15 K, p = 10.0 MPa	
0.039	271.9
0.070	475.1
0.100	647.1
0.132	805.2
0.163	952.4
0.196	1081.8
0.229	1207.2
0.262	1309.7
0.296	1406.0
0.331	1491.5
0.366	1556.7
0.402	1617.4
0.439	1652.8
0.476	1690.3
0.514	1712.3
0.553	1696.7
0.592	1683.3
0.632	1630.8
0.673	1566.8
0.715	1467.6
0.758	1344.3
0.801	1186.1
0.845	999.0
0.891	761.1
0.937	482.3
0.952	378.0
0.969	254.1
{xethyl acetate + (1 − x)1-butanol} at T = 298.15 K, p = 10.0 MPa	
0.047	297.4
0.082	499.8
0.118	691.7
0.153	839.7
0.189	1003.0
0.225	1134.8
0.262	1258.0
0.298	1350.0
0.335	1446.3
0.371	1515.5
0.408	1583.1
0.446	1627.1
0.483	1671.6
0.520	1694.4
0.558	1686.8
0.596	1676.0
0.634	1619.1
0.673	1565.9
0.711	1481.0
0.750	1379.0
0.789	1238.3
0.828	1090.3
0.867	905.5
0.907	680.5
0.947	431.2
0.960	323.6
0.974	216.9

Table 8
Coefficients a_i in Eq. (5), and RMSD for the results in Table 7

	Ethyl acetate + methanol	Ethyl acetate + ethanol	Ethyl acetate + 1-propanol	Ethyl acetate + 2-propanol	Ethyl acetate + 1-butanol
a_0 ($\times 10^3$ J mol^{-1})	4.0238	5.3193	6.0313	6.8084	6.7156
a_1 ($\times 10^3$ J mol^{-1})	0.6257	−0.7553	−0.7392	−0.6457	−1.0160
a_2 ($\times 10^3$ J mol^{-1})	−0.1507	0.4006	0.7175	0.8319	0.6384
a_3 ($\times 10^3$ J mol^{-1})	1.7513	−0.0181	−0.4706	0.7641	0.9269
a_4 ($\times 10^3$ J mol^{-1})	0.8486	0.6028	0.5832	0.4591	0.5065
a_5 ($\times 10^3$ J mol^{-1})	−1.4976	−0.6385	0.7258	−0.7631	−1.1418
RMSD (J mol^{-1})	3.4971	2.7906	3.8954	3.2084	5.0475

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