Excess Properties for 1-Butanethiol + Heptane, + Cyclohexane, + Benzene, and + Toluene. 2. Excess Molar Enthalpies at 283.15, 298.15, and 333.15 K

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Excess molar enthalpies of binary mixtures of 1-butanethiol + heptane, + cyclohexane, + benzene, or + toluene have been determined at 283.15, 298.15, and 333.15 K with a flow mixing calorimeter, and at 283.15 and 298.15 K with a titration calorimeter. Partial molar enthalpies have been derived from the titration calorimetric results. Where results were obtained by both methods, they were combined to obtain the best estimate of excess enthalpy for all compositions. Equimolar excess enthalpies for 1-butanethiol + heptane or + cyclohexane are endothermic and are comparable to the equimolar excess enthalpies for 1-butanol + heptane or + cyclohexane. Excess enthalpies of 1-butanethiol + aromatic systems, however, are less endothermic than excess enthalpies of 1-butanethiol + alkane systems, which is contrary to the trend observed in 1-butanol + aromatic systems compared to 1-butanol + alkane systems. The excess enthalpy of 1-butanethiol + toluene is weakly exothermic.

Introduction

Thiols (mercaptans) are industrially important because of their occurrence in petroleum, their use as chemical intermediates, and their involvement in environmental problems. Excess molar enthalpies and activity coefficients for thiols with hydrocarbons are needed to develop and evaluate molecular models and correlations, and to design separation processes.

Very few thermophysical data are available for mixtures of thiols with hydrocarbons. This paper presents excess enthalpies, H^E, obtained at 283.15, 298.15, and 333.15 K by flow mixing calorimetry, and at 283.15 and 298.15 K by titration calorimetry, for binary mixtures of 1-butanethiol + heptane, + cyclohexane, + benzene, or + toluene. Densities and excess molar volumes for these mixtures are given in an earlier publication (Allred et al., 1990).

Flow mixing calorimetry was used to obtain excess enthalpies from $x = 0.05$ to $x = 0.95$; titration calorimetry was used to obtain precise values of the excess enthalpy with one component highly diluted in the other (Hansen et al., 1985). To most accurately model excess enthalpies for binary systems over the whole composition range, it is important to include data close to infinite dilution, because it is there that solute–solute interactions, such as hydrogen bonding, are most strongly manifested.

Experimental Section

Materials. The compounds used, their sources, purities, and treatments were described previously (Allred et al., 1990). The 1-butanethiol was the same used in the earlier work, but was distilled separately. Its density was 0.8508_6 and 0.8366_1 g·cm^{-3} at 283.15 and 298.15 K, respectively. Gas chromatography showed it to be 99.1% pure after distillation; the principal impurity was 1-methylethanethiol. The 1-butanethiol was stored under nitrogen to minimize oxidation. The purities of heptane, cyclohexane, benzene, and toluene, as stated by the manufacturers, were 99, 99.9, 99+, and 99.9 mole %, respectively. The heptane was purified further by distillation; cyclohexane, benzene, and toluene were used as supplied.

Flow Mixing Calorimetry. Excess enthalpy measurements were made at 283.15, 298.15, and 333.15 K, at 0.50 MPa, using a Hart 501 isothermal, flow mixing, power compensation calorimeter. The calorimeter temperature was controlled within ±0.004 K. The compounds to be mixed were delivered by two Varian 8500 high-pressure, digitally controlled, stepping-motor-driven syringe pumps. The pumps were held near 298 K, and controlled within ±0.1 K by thermostated water that flowed through copper tubes coiled around each pump cylinder. They were calibrated by weighing the amount of distilled water delivered in a known time. The total flow rate was 60 or 120 mL/h. The pressure was maintained within ±0.01 MPa by a back-pressure regulator arrangement similar to the one described by Christensen et al. (1985). The mass flow rates of the liquids delivered by the pumps were determined using previously measured densities (Allred et al., 1990) and the pump temperature. A computer controlled the pumps and recorded the calorimeter output.

From the repeatability of the average volumetric flow rate of the pumps, observed during calibration, and from the uncertainty in the liquid densities, we estimate the uncertainty in mole fractions for the mixtures delivered to the calorimeter to be ±0.3%.

A systematic error in this type of flow mixing calorimeter has been reported by Gruszkiewicz et al. (1992), who determined that the error, which depends on placement of the calibration heater, affects the absolute value of the measured enthalpy of mixing, and is independent of pressure, temperature, flow rate, and fluid composition. To evaluate the accuracy of our flow mixing calorimeter, we obtained excess enthalpies for benzene + cyclohexane at 298.15 K at 24 points over the binary composition range. Smoothed values of the excess enthalpy obtained with our calorimeter (relative standard deviation 0.35%) were 2.25% smaller in absolute value than those reported by Stokes et al. (1969). The difference was independent of flow rate. Because our calorimeter has the same configuration as the one studied by Gruszkiewicz et al., we assume that the systematic error in our instrument is also independent of temperature and fluid composition. Therefore, all excess enthalpies reported in this paper have been corrected to

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Table 1. Excess Molar Enthalpies from Flow Calorimetry for 1-Butanethiol (1) + Hydrocarbon (2) at 0.50 MPa

	H^E/(J·mol^{-1})				H^E/(J·mol^{-1})				H^E/(J·mol^{-1})		
x_1	283.15 K	298.15 K	333.15 K	x_1	283.15 K	298.15 K	333.15 K	x_1	283.15 K	298.15 K	333.15 K
1-Butanethiol (1) + Heptane (2)											
0.0406			103.5	0.3474	643.2	627.0	583.6	0.7529	510.4	502.1	
0.0540	147.4	145.3		0.4027	678.2	662.0	619.4	0.7958			413.6
0.0672			158.2	0.4562	694.7	676.8	637.7	0.8042	428.2	423.0	
0.0934			222.3	0.4978	698.3	681.9		0.8374			342.3
0.1064	279.4	267.3		0.5080			641.4	0.8537	328.6	335.7	
0.1192			264.6	0.5483	689.5	673.1		0.8779			266.5
0.1447	357.4	350.5	320.6	0.5582			631.4	0.9016	225.6	232.1	
0.1822			385.2	0.5973	665.3	651.9		0.9172			182.3
0.2068	475.7	462.7	425.0	0.6069			611.3	0.9479		116.9	
0.2431			472.4	0.6540	623.5	610.2	576.7	0.9630			72.0
0.2550	544.0	520.8		0.6998	578.8	568.6	535.9				
0.3018	592.1	584.8	543.4	0.7442			484.5				
1-Butanethiol (1) + Cyclohexane (2)											
0.0503	164.6	151.1	135.6	0.4016	675.0	673.9	597.4	0.7513	487.9	466.1	424.0
0.1006	302.9	286.4	249.3	0.4517	682.5	680.8	613.2	0.8011	416.9	402.1	355.7
0.1509	414.4	398.1	350.4	0.5017	676.3	675.4	607.2	0.8509	324.2	311.7	277.9
0.2011	520.2	488.6	434.6	0.5517	668.4	652.2	591.4	0.9006	225.1	211.7	196.3
0.2513	573.8	554.3	490.3	0.6016	631.6	629.4	569.4	0.9503	115.9	111.7	103.0
0.3014	613.8	611.0	540.5	0.6515	593.6	579.2	527.5				
0.3515	656.7	650.3	578.4	0.7014	553.8	534.7	480.3				
1-Butanethiol (1) + Benzene (2)											
0.0502		35.8	23.8	0.3461	145.2		82.8	0.6482	109.8		64.5
0.1014	74.5	65.9	42.8	0.3556		117.2		0.6589		88.8	
0.1538	101.7	84.5	57.5	0.4038	146.7	118.4	83.3	0.7020	97.2	80.4	57.9
0.1982	118.9	97.9	67.4	0.4529	143.1	116.9	82.4	0.7458	86.0	73.3	50.5
0.2527	133.9	107.8	75.0	0.5029	136.7	112.0	80.7	0.8016	68.9	61.0	40.2
0.2619		109.5		0.5539	131.6	106.0	75.5	0.8471	53.2	47.6	31.8
0.2989	141.4	115.6	80.8	0.5954	124.8		72.0	0.9049	34.2	30.3	19.9
0.3083		114.1		0.6059		99.1		0.9521	18.1	15.2	9.9
1-Butanethiol (1) + Toluene (2)											
0.0198	−7.9			0.2978	−81.8	−76.1	−56.4	0.6476	−78.8	−70.8	−54.9
0.0495	−19.1	−17.0	−13.5	0.3476	−87.1	−80.5	−60.1	0.6978	−70.9	−64.7	−49.1
0.0693	−26.0			0.3974	−89.9	−82.1	−62.2	0.7480	−62.7	−57.8	−43.4
0.0990	−35.5	−33.0	−25.5	0.4474	−91.2	−82.9	−63.6	0.7983	−52.3	−47.9	−36.2
0.1486	−50.8	−47.3	−35.6	0.4973	−91.0	−81.6	−62.8	0.8486	−41.3	−37.2	−28.4
0.1983	−62.1	−59.5	−43.7	0.5474	−89.3	−79.1	−62.1	0.8990	−29.5	−25.9	−19.5
0.2480	−72.4	−68.3	−50.5	0.5974	−84.6	−75.1	−58.8	0.9495	−15.0	−13.1	−10.6

compensate for this systematic error. We estimate the overall uncertainty of smoothed, corrected excess enthalpies from the flow mixing calorimeter (allowing for errors in composition, flow rate, and calorimeter response) to be ±2%.

Titration Calorimetry. Enthalpy of dilution measurements were made at 283.15 and 298.15 K, at ambient pressure, using a Tronac 450 continuous titration, isoperibol, temperature rise calorimeter. A calibrated, precision micrometer buret delivered from 0.3 to 2 mL of titrant into a known mass (~50 mL) of titrate contained within a Dewar-type reaction vessel; the density of the titrant had been determined previously (Allred et al., 1990). A computer recorded the calorimeter temperature at intervals of 2, 4, or 5 s while the buret ran, and every 10 s at other times. An effective zero reading of the buret was obtained by plotting the mixture temperature against elapsed time and locating the intersection of the line formed just before with the one formed just after the titrant began to enter the reaction vessel. The mole fraction of each component was calculated at each temperature reading during the titration, and the cumulative energy evolved was calculated according to the method described by Eatough et al. (1974). Mole fractions were corrected for evaporation into the vapor space using pure component vapor pressures, ideal solution behavior, and the ideal gas law. The excess enthalpy at each point was calculated and corrected for the enthalpy of vaporization. Corrections to the titrant mole fraction were no greater than 0.016%; the largest correction to H^E was 1.3%.

The accuracy of the titration calorimeter was checked by titration of aqueous tris(hydroxymethyl)aminomethane with 0.1 M aqueous HCl; results agreed with accepted values for this reaction (Grenthe et al., 1970) within ±0.2%.

Results and Discussion

Excess molar enthalpies were calculated from the results of both flow mixing calorimetry and titration calorimetry. Excess molar enthalpies obtained by flow mixing calorimetry are given in Table 1.

For the titration experiments, a series of values for H^E was calculated from each enthalpy of dilution titration, results from replicate titrations were combined, and all replicate results were fit to

$$H^E = A_1x + A_2x^2 \qquad (1)$$

where x is the mole fraction of the titrant at each point. The standard deviation of the fit was in no case greater than 0.53% of the maximum value for the titration. The coefficient A_1 in eq 1 is equal to the infinite dilution enthalpy of dilution, or the infinite dilution partial molar enthalpy, h^∞. Coefficients A_i from eq 1 are given in Table 2.

Excess molar enthalpies may be correlated as a function of composition by the Redlich–Kister equation

$$H^E/x_1x_2 = \sum B_i(x_2 - x_1)^i \qquad i = 0, 1, 2, ... \qquad (2)$$

Where excess enthalpies were obtained by both flow mixing and titration calorimetry, they were combined to get the

Table 2. Coefficients of Eq 1 Determined from Titration Calorimetry Results

T/K	x[a]	A_1/(J·mol^{-1})	A_2/(J·mol^{-1})	n_1[b]	n_2[c]	σ[d]/(J·mol^{-1})
1-Butanethiol + Heptane (x = mole fraction of heptane)						
283.15	0.0227	2839.7 (1.6)[e]	−3328 (97)	3	519	0.11
298.15	0.0231	2512.5 (1.2)		2	390	0.31
1-Butanethiol + Cyclohexane (x = mole fraction of cyclohexane)						
283.15	0.0183	2494.10 (0.75)	−2854 (52)	1	140	0.023
298.15	0.0192	2385.2 (2.5)	4317 (170)	2	597	0.17
1-Butanethiol + Benzene (x = mole fraction of benzene)						
283.15	0.0447	354.9 (1.2)	307 (35)	1	73	0.068
298.15	0.0354	323.36 (0.35)	-98 (13)	2	230	0.027
1-Butanethiol + Toluene (x = mole fraction of toluene)						
283.15	0.0375	−305.43 (0.11)	127.7 (3.9)	1	72	0.0053
298.15	0.0303	−273.45 (0.10)		2	234	0.028
Heptane + 1-Butanethiol (x = mole fraction of 1-butanethiol)						
283.15	0.0412	2906.7 (2.7)	−3250 (86)	2	374	0.31
298.15	0.0426	2784.7 (1.6)	−2925 (47)	2	391	0.19
Cyclohexane + 1-Butanethiol (x = mole fraction of 1-butanethiol)						
283.15	0.00868	3469.0 (6.5)	8238 (960)	1	129	0.093
298.15	0.0305	3396.8 (4.3)	-6079 (200)	2	237	0.30
Benzene + 1-Butanethiol (x = mole fraction of 1-butanethiol)						
283.15	0.0242	906.45 (0.48)	−1587 (26)	1	111	0.018
298.15	0.0247	815.02 (0.43)	−1332 (22)	1	116	0.017
Toluene + 1-Butanethiol (x = mole fraction of 1-butanethiol)						
283.15	0.0293	−411.09 (0.32)	353 (14)	1	112	0.014
298.15	0.0296	−370.24 (0.16)	303.9 (6.8)	1	116	0.0073

[a] Maximum mole fraction of the dilute component. [b] Number of replicate titrations. [c] Total number of temperature readings (and corresponding data points) for all replicate titrations. [d] Standard deviation of the fit. [e] Standard deviation of the coefficient determined from regression.

Table 3. Coefficients of Eq 2

T/K	B_0/(J·mol^{-1})	B_1/(J·mol^{-1})	B_2/(J·mol^{-1})	B_3/(J·mol^{-1})	n[a]	σ[b]/(J·mol^{-1})
1-Butanethiol (1) + Heptane (2)						
283.15	2771.7 (26.7)[c]	33.50 (3.14)	101.5 (26.5)		18	7.6
298.15	2749.7 (17.8)	136.1 (2.0)	−101.1 (17.7)		19	6.4
333.15	2572.7 (6.8)	5.6 (25.5)	−82.4 (28.0)	126.4 (61.4)	23	4.3
1-Butanethiol (1) + Cyclohexane (2)						
288.15	2751.4 (17.5)	487.5 (6.5)	230.2 (16.2)		19	9.2
298.15	2687.9 (13.8)	428.2 (34.4)	203.1 (12.9)	77.6 (34.0)	19	4.1
333.15	2427.9 (4.4)	360.8 (8.8)	75.7 (20.2)		19	2.7
1-Butanethiol (1) + Benzene (2)						
283.15	558.99 (2.81)	250.4 (6.8)	71.7 (2.5)	25.3 (6.7)	18	1.1
298.15	450.05 (2.19)	178.0 (5.5)	119.1 (2.1)	67.8 (5.5)	21	1.1
333.15	320.74 (0.66)	128.9 (2.5)	48.1 (3.0)	30.4 (6.6)	19	0.4
1-Butanethiol (1) + Toluene (2)						
283.15	−363.3 (1.2)	−56.7 (2.9)	5.03 (1.11)	3.9 (2.9)	21	0.5
298.15	−332.9 (1.8)	−70.2 (4.7)	11.0 (1.8)	21.8 (4.7)	19	1.1
333.15	−252.3 (0.5)	−42.1 (0.9)	4.0 (2.1)		19	0.3

[a] Number of data points (mixtures), not including titration data (see text). [b] Standard deviation of the fit. [c] Standard deviation of the coefficient determined from regression.

best estimate of H^E for all compositions. We considered two possible methods for combining mixing and titration data before choosing a third. Either the infinite dilution partial molar enthalpies of dilution at $x_1 = 0$ and $x_2 = 0$ derived by eq 1 from titration experiments or the excess enthalpies themselves from titration experiments may be combined with flow excess enthalpy data in a linear regression of eq 2. In either case, some means must be chosen to appropriately weight the data obtained by different methods. In choosing a weighting scheme, the fact that titration data are more reliable than flow mixing data at the extremes of composition must be considered. We found no satisfactory weighting scheme. Therefore, we chose a third method, which incorporates titration data by using it to fix the end points in a plot of H^E/x_1x_2 vs x_1, or the limiting slopes in a plot of H^E vs x_1.

For component 1, as x_1 approaches 0, H^E/x_1x_2 approaches h_1^∞, the infinite dilution partial molar enthalpy of component 1 in component 2. Similarly, as x_1 approaches 1, H^E/x_1x_2 approaches h_2^∞. Equation 2 then becomes

$$\lim_{x_1\to 0} H^E/x_1x_2 = h_1^\infty = B_0 + B_1 + B_2 + B_3 + \ldots \quad (3)$$

or

$$\lim_{x_1\to 1} H^E/x_1x_2 = h_2^\infty = B_0 - B_1 + B_2 - B_3 + \ldots \quad (4)$$

The infinite dilution enthalpy of dilution obtained from titration calorimetry may now be integrated into the H^E model. Adding or subtracting eqs 3 and 4, we obtain

$$d^+ = (h_1^\infty + h_2^\infty)/2 = B_0 + B_2 + \ldots \quad (5)$$

and

$$d^- = (h_1^\infty - h_2^\infty)/2 = B_1 + B_3 + \ldots \quad (6)$$

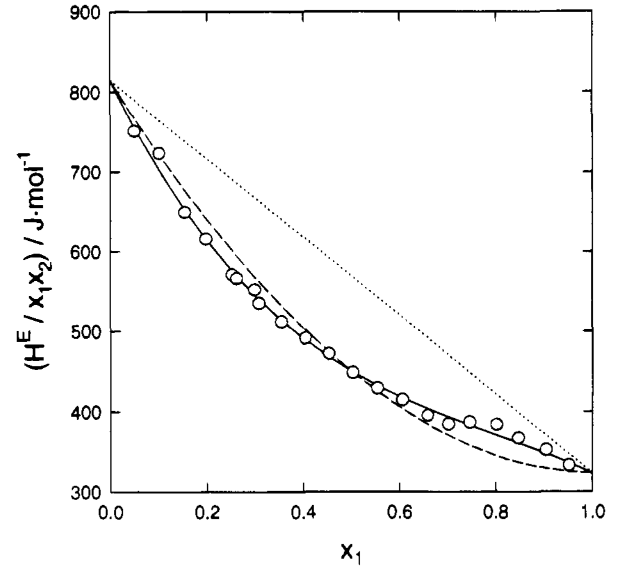

Figure 1. Excess molar enthalpy of 1-butanethiol (1) + benzene (2) at 298.15 K: (○) experimental values, (···) eq 2 with two coefficients, (- - -) eq 2 with three coefficients, (—) eq 2 with four coefficients.

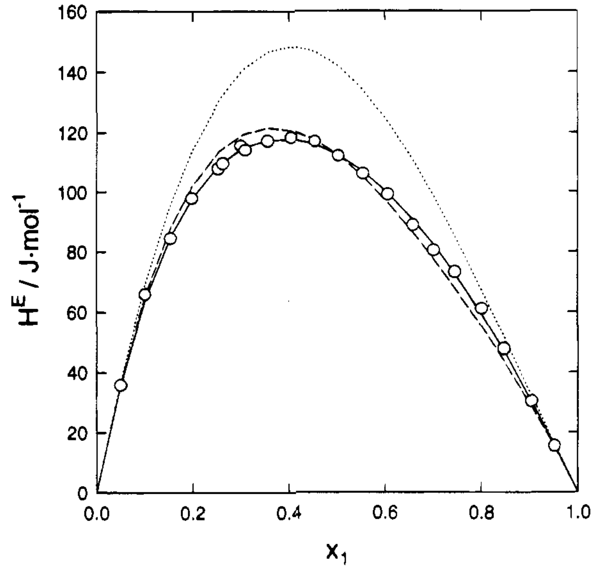

Figure 2. Excess molar enthalpy of 1-butanethiol (1) + benzene (2) at 298.15 K: (○) experimental values, (···) eq 2 with two coefficients, (- - -) eq 2 with three coefficients, (—) eq 2 with four coefficients.

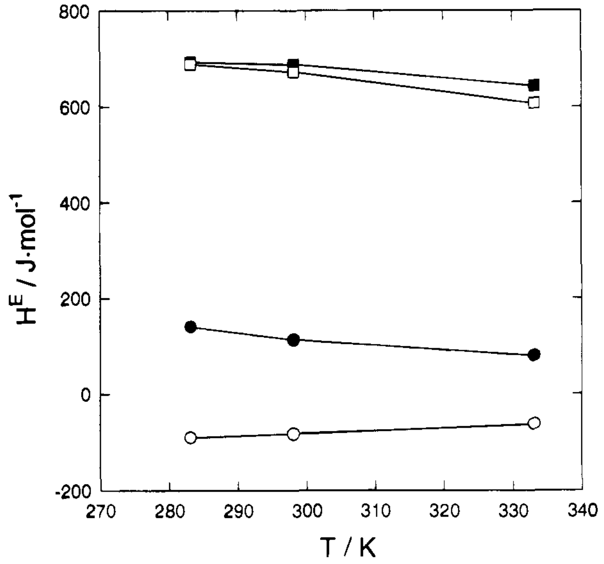

Figure 3. Equimolar excess enthalpy plotted against temperature: (■) 1-butanethiol + heptane, (□) 1-butanethiol + cyclohexane, (●) 1-butanethiol + benzene, (○) 1-butanethiol + toluene.

If we restrict eq 2 to a cubic equation, then

$$B_0 = d^+ - B_2 \qquad (7)$$

and

$$B_1 = d^- - B_3 \qquad (8)$$

Combining eqs 2, 7, and 8

$$H^E/x_1x_2 - d^+ - d^-(x_2 - x_1) = B_2[(x_2 - x_1)^2 - 1] + B_3[(x_2 - x_1)^3 - (x_2 - x_1)] \qquad (9)$$

The constants d^+ and d^- are obtained from titration calorimetry, coefficients B_2 and B_3 are obtained from eq 9 by linear regression, and B_0 and B_1 come from eqs 7 and 8. When only three coefficients in eq 2 are justified to model H^E, we calculate B_2 by regression; then $B_0 = d^+ - B_2$, and $B_1 = d^-$. H^E may also be estimated using two coefficients derived from titration data alone: $B_0 = d^+$ and $B_1 = d^-$.

The coefficients B_i of eq 2 for each system, determined by linear regression using eq 9 with x_1 as the mole fraction of 1-butanethiol, are given in Table 3. The standard deviation of the fit was in no case greater than 1.3% of the maximum enthalpy of mixing; the maximum deviation for any one mixture was no greater than 3.4% of the maximum enthalpy of mixing for the binary. Increasing the number of parameters by adding a further term to eq 2 does not significantly improve the fit.

Experimental values of H^E/x_1x_2 from flow mixing calorimetry for benzene + 1-butanethiol at 298.15 K with smoothed curves calculated from eq 2 are shown in Figure 1. Figure 2 shows the same data, plotted as H^E. In Figure 2, the curve calculated using the two coefficients derived from titration calorimetry, compared with the regression fits obtained using a third or fourth coefficient derived by including flow mixing calorimetry, shows that titration data alone give a good estimate of H^E over the whole composition. Figure 3 shows the equimolar excess enthalpy for each system at each temperature.

Conclusions

For these four binary thiol + hydrocarbon mixtures, the equimolar excess enthalpy decreases in the order heptane > cyclohexane > benzene > toluene; the excess enthalpy for 1-butanethiol + toluene is exothermic, while the others are endothermic.

Equimolar excess enthalpies for 1-butanethiol + heptane and + cyclohexane are similar to equimolar excess enthalpies for 1-butanol + heptane (Oswald et al., 1986) and + cyclohexane (Saris et al., 1986). Equimolar excess enthalpies for 1-butanol + aromatics, e.g., benzene (Saris et al., 1986) and toluene (Mrazek and Van Ness, 1961), are more endothermic than for 1-butanol + alkanes. Instead of being more endothermic, the 1-butanethiol + benzene system is less endothermic, and the 1-butanethiol + toluene system is exothermic. This difference must be considered when correlating or predicting the temperature dependence of activity coefficients needed for the design or simulation of separations involving thiols.

To most accurately model excess enthalpies for binary systems, it is important to include data close to infinite dilution, of the type obtained by titration calorimetry. It is in dilute mixtures where the effects of solute–solute interactions, such as hydrogen bonding, are most evident. Because most distillation processes strive to eliminate certain components, dilute solution properties are particularly important.

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Literature Cited

Allred, G. C.; Beets, J. W.; Parrish, W. R. Excess Properties for 1-Butanethiol + *n*-Heptane, Cyclohexane, Benzene, and Toluene. 1. Excess Molar Volumes at 283.15 and 298.15 K. *J. Chem. Eng. Data* **1990**, *35*, 328–331.

Christensen, S. P.; Christensen, J. J.; Izatt, R. M. Enthalpies of Solution of CO_2 in Aqueous Diglycolamine Solutions. Research Report RR-85; Gas Processors Association: Tulsa, OK, 1985.

Eatough, D. J.; Christensen, J. J.; Izatt, R. M. *Experiments in Thermometric Titrimetry and Titration Calorimetry*; Brigham Young University Press: Provo, UT, 1974.

Gruszkiewicz, M. S.; Sipowska, J. T.; Ott, J. B.; Graham, R. C. Excess Enthalpies for (Butane + Chloromethane) at the Temperatures (298.15, 323.15, and 348.15) K and Pressures (5 and 15) MPa and at the Temperature 293.15 K and Pressure 15 MPa. *J. Chem. Thermodyn.* **1992**, *24*, 1057–1064.

Grenthe, I.; Ots, H.; Ginstrup, O. A Calorimetric Determination of the Enthalpy of Ionization of Water and the Enthalpy of Protonation of THAM at 5, 20, 25, 35, and 50 °C. *Acta Chem. Scand.* **1970**, *24*, 1067–1080.

Hansen, L. D.; Lewis, E. A.; Eatough, D. J. In *Analytical Solution Calorimetry*; Grime, K., Ed.; Wiley: New York, 1985.

Mrazek, R. V.; Van Ness, H. C. Heats of Mixing: Alcohol-Aromatic Binary Systems at 25°, 35°, and 45 °C. *AIChE J.* **1961**, *7*, 190–195.

Oswald, G.; Schmittecker, B.; Wagner, D.; Lichtenthaler, R. N. Excess Enthalpies and Excess Volumes of Alkanol + *n*-Heptane Mixtures at High Pressures. *Fluid Phase Equilib.* **1986**, *27*, 119–135.

Saris, P.; Rosenholm, J. B.; Sjoblom, E.; Henriksson, U. A Thermometric Investigation of the Association Equilibria of Alcohols and Hydrocarbons. *J. Phys. Chem.* **1986**, *90*, 660–665.

Stokes, R. H.; Marsh, K. N.; Tomlins, R. P. An Isothermal Displacement Calorimeter for Endothermic Enthalpies of Mixing. *J. Chem. Thermodyn.* **1969**, *1*, 211–221.

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