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Thermodynamics of Hydrogen-Bonding Mixtures. 2. G^E, H^E, and S^E of 1-Propanol + *n*-Heptane[1]

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A metal ebulliometer was used to measure total vapor-pressure (PTx) data on 18 mixtures of 1-propanol + *n*-heptane (and the pure components) between 380 and 445 K. Bubble-point data were measured at seven pressures between 200 kPa and 1 MPa. These data cover an intermediate region between previous data reported near atmospheric pressure and below and high-temperature data extending to the critical region. A Redlich–Kister G^E model fit isotherms between 373.15 and 463.15 K via Barker's method with an average standard error of 0.2 to 0.5% in pressure. The system exhibits large positive deviations from ideality (derived $\gamma^\infty = 2.7$–10.5) which decrease with temperature. Equimolar G^E/T values thus derived also decrease with increasing temperature, which predicts a positive H^E. An azeotrope exists under all conditions studied; the azeotropic composition increases in alcohol content with increasing temperature. These mixture thermodynamic data show that, above ≈345 K, the system 1-propanol + *n*-heptane belongs to the class of mixtures where $G^E > 0$, $H^E > 0$, and $TS^E > 0$. This probably occurs because the 1–1 orientational effect (in this case, hydrogen-bonding of the alcohol molecules) is more readily disrupted in the "inert" solvent than it would be at lower temperatures, where the effect of hydrogen-bonding is stronger.

KEY WORDS: azeotrope; G^E; H^E; S^E; heat of mixing; *n*-heptane; hydrogen-bonding; mixture thermodynamics; 1-propanol; vapor–liquid equilibria; vapor pressure.

1. INTRODUCTION

Vapor–liquid equilibria and excess-property data for 1-propanol (1) + *n*-heptane (2) have been reported at temperatures between 280 and 340 K

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[1–3] and between 423 and 573 K [4]. This work reports pressure–temperature–liquid mole fraction (PTx) data and derived G^E, H^E, and S^E between 380 and 445 K.

2. MEASUREMENTS

2.1. Materials

The 1-propanol was Aldrich HPLC grade (99.5%; <0.08% water) and the *n*-heptane was J. T. Baker HPLC grade (99.9%; <0.01% water). These materials were used as received. Mixtures were prepared gravimetrically with analytical balances.

2.2. Procedure

The ebulliometer has been briefly described previously [5]. It is a one-stage total-reflux boiler equipped with twin vapor-lift pumps to spray slugs of equilibrated liquid and vapor upon a thermometer well. A condenser cooled to 280 K provided connection to the manostat. Pressures were controlled with a Grove back-pressure regulator and were measured with an IMO CEC Instruments Model 1004-0006 pressure transducer to ±0.1 kPa. Temperatures on the IPTS-68 scale were measured to ±0.01 K with a Hart Model 1506 thermometer and a Hart Model 5614 platinum resistance probe traceable to NIST. Pure components and mixtures were charged to the ebulliometer and boiling points were measured at nominal pressures of 205, 275, 410, 620, 825, 930, and 1030 kPa.

3. RESULTS

Table I contains 140 PTx measurements on the pure components and 18 mixtures. The difference between x, the liquid-phase mole fraction, and z, the overall mole fraction charged to the ebulliometer, shows the magnitude of the vapor-holdup and condensed vapor-holdup correction computed as described previously [5]. The PT data for each mixture were fit with a three-constant Antoine equation in order to calculate isothermal Px data similar to the procedure described by Prengle and Palm [6]. The Antoine constants and derived Px data for 423.15 K are given in Table II.

Values of G^E and y, the vapor-phase mole fraction, were computed by a Gauss–Newton nonlinear least-squares fit to the experimental mixture vapor pressures, coupled with a bubble-point calculation during each

Table I. *PTx* Data for 1-Propanol (1) + *n*-Heptane (2)

z_1	x_1	T (K)	P (kPa)
0.0000	0.0000	397.51	204.8
0.0511	0.0474	388.75	205.5
0.1000	0.0948	384.17	206.0
0.1500	0.1442	382.20	206.1
0.2000	0.1943	381.48	205.9
0.2500	0.2447	380.59	205.6
0.3000	0.2955	380.32	206.4
0.4000	0.3973	379.81	205.6
0.4500	0.4483	379.50	205.3
0.5000	0.4993	379.38	204.8
0.5500	0.5503	379.54	206.5
0.6000	0.6012	379.84	205.8
0.6606	0.6629	379.93	205.7
0.7000	0.7028	380.41	206.1
0.7500	0.7534	380.58	206.0
0.8000	0.8038	381.27	205.6
0.8500	0.8540	382.15	205.7
0.9000	0.9037	383.76	204.8
0.9500	0.9527	386.21	206.0
1.0000	1.0000	390.44	204.5
0.0000	0.0000	409.42	273.9
0.0511	0.0471	400.99	275.6
0.1000	0.0944	395.70	275.7
0.1500	0.1437	393.05	274.7
0.2000	0.1937	392.11	275.5
0.2500	0.2442	390.94	274.6
0.3000	0.2949	390.47	275.8
0.4000	0.3968	389.77	274.6
0.4500	0.4478	389.46	274.4
0.5000	0.4988	389.39	274.5
0.5500	0.5498	389.30	275.0
0.6000	0.6007	389.57	275.0
0.6606	0.6625	389.61	274.9
0.7000	0.7024	389.99	274.9
0.7500	0.7530	390.40	276.1
0.8000	0.8034	390.94	275.0
0.8500	0.8536	391.73	274.6
0.9000	0.9033	393.38	274.5
0.9500	0.9524	395.52	274.9
1.0000	1.0000	399.53	274.2

Table I. *(Continued)*

z_1	x_1	T (K)	P (kPa)
0.0000	0.0000	427.54	411.5
0.0511	0.0467	419.45	412.8
0.1000	0.0937	413.64	412.6
0.1500	0.1429	410.10	412.5
0.2000	0.1928	408.31	412.8
0.2500	0.2432	406.94	413.0
0.3000	0.2940	406.11	415.5
0.4000	0.3959	404.95	412.9
0.4500	0.4469	404.51	412.1
0.5000	0.4980	404.32	412.3
0.5500	0.5491	404.22	413.6
0.6000	0.6000	404.29	413.0
0.6606	0.6618	404.21	412.1
0.7000	0.7018	404.61	413.1
0.7500	0.7524	404.84	413.1
0.8000	0.8029	405.48	413.7
0.8500	0.8531	406.12	412.2
0.9000	0.9029	407.69	413.1
0.9500	0.9521	409.57	412.9
1.0000	1.0000	413.18	412.3
0.0000	0.0000	447.78	619.0
0.0511	0.0462	439.63	619.0
0.1000	0.0929	433.87	620.0
0.1500	0.1419	429.12	618.6
0.2000	0.1918	426.80	620.0
0.2500	0.2421	424.78	619.6
0.3000	0.2929	423.25	619.6
0.4000	0.3949	421.76	619.8
0.4500	0.4459	421.21	619.3
0.5000	0.4971	420.85	619.9
0.5500	0.5482	420.46	619.1
0.6000	0.5992	420.47	619.2
0.6606	0.6611	420.39	619.4
0.7000	0.7011	420.63	619.8
0.7500	0.7518	420.79	619.6
0.8000	0.8023	421.28	619.6
0.8500	0.8526	421.99	619.9
0.9000	0.9024	423.29	619.3
0.9500	0.9517	425.00	620.2
1.0000	1.0000	428.14	619.5

Table I. (*Continued*)

z_1	x_1	T (K)	P (kPa)
0.0000	0.0000	462.94	824.6
0.0511	0.0459	455.09	826.1
0.1000	0.0922	449.07	826.8
0.1500	0.1411	444.08	826.5
0.2000	0.1908	441.17	826.0
0.2500	0.2412	438.82	826.7
0.3000	0.2919	436.89	826.1
0.4000	0.3940	434.83	825.9
0.4500	0.4451	434.12	825.3
0.5000	0.4963	433.60	825.6
0.5500	0.5475	433.11	825.6
0.6000	0.5986	433.05	826.7
0.6606	0.6605	432.82	826.1
0.7000	0.7006	432.95	825.9
0.7500	0.7513	433.11	826.7
0.8000	0.8019	433.51	826.2
0.8500	0.8522	434.13	826.2
0.9000	0.9021	435.38	826.5
0.9500	0.9515	436.87	826.1
1.0000	1.0000	439.55	821.0
0.0000	0.0000	469.53	928.7
0.0511	0.0457	461.65	929.2
0.1000	0.0919	455.41	930.2
0.1500	0.1407	450.56	930.3
0.2000	0.1904	447.52	929.3
0.2500	0.2407	444.94	929.1
0.3000	0.2915	442.79	928.7
0.4000	0.3935	440.55	929.4
0.4500	0.4447	439.76	929.1
0.5000	0.4959	439.18	929.5
0.5500	0.5472	438.64	929.8
0.6000	0.5983	438.44	929.7
0.6606	0.6602	438.23	930.3
0.7000	0.7003	438.37	931.5
0.7500	0.7511	438.41	930.2
0.8000	0.8017	438.74	929.7
0.8500	0.8520	439.32	929.2
0.9000	0.9020	440.51	929.8
0.9500	0.9514	442.01	929.4
1.0000	1.0000	444.58	929.6

Table I. (*Continued*)

z_1	x_1	T (K)	P (kPa)
0.0000	0.0000	475.45	1030.2
0.0511	0.0455	467.67	1031.9
0.1000	0.0916	461.57	1032.0
0.1500	0.1403	456.24	1032.0
0.2000	0.1899	453.04	1032.1
0.2500	0.2402	450.61	1032.3
0.3000	0.2910	448.06	1031.8
0.4000	0.3931	445.66	1031.7
0.4500	0.4443	444.90	1031.9
0.5000	0.4956	444.24	1032.3
0.5500	0.5468	443.65	1032.3
0.6000	0.5980	443.42	1032.8
0.6606	0.6599	442.93	1032.0
0.7000	0.7001	443.13	1032.8
0.7500	0.7509	443.15	1031.6
0.8000	0.8015	443.43	1032.7
0.8500	0.8519	444.07	1031.9
0.9000	0.9019	445.17	1032.1
0.9500	0.9513	446.67	1032.3
1.0000	1.0000	449.06	1031.1

iteration (Barker's method). The equation which describes thermodynamic equilibrium between the phases at T and P is

$$\phi_i y_i P = x_i \gamma_i P_i^0 \phi_i^0 \exp[(P - P_i^0) V_i/(RT)], \qquad i = 1, 2 \qquad (1)$$

where ϕ is the vapor-phase fugacity coefficient, γ is the liquid-phase activity coefficient (reference state: pure liquid at system T and P), P_i^0 is the pure-component vapor pressure, and V_i is the pure-component saturated-liquid molar volume. Saturated liquid volume data were taken from the DIPPR databank [7] and the vapor-phase fugacity coefficients were computed from the second-virial equation of state. Second virial coefficients were estimated from the Hayden–O'Connell correlation [8].

The G^E model is the Redlich–Kister equation:

$$G^E = x_1 x_2 [A + B(x_1 - x_2) + C(x_1 - x_2)^2 + D(x_1 - x_2)^3 + \cdots] \qquad (2)$$

$$RT \ln \gamma_i = G^E + x_j (\partial G^E / \partial x_i)_{TP}, \qquad i, j = 1, 2 \qquad (3)$$

where A, B, C, D,... are parameters to be estimated in a least-squares fit.

Table III presents results from fitting the one-, two-, three-, and four-constant Redlich–Kister models to the derived Px data at 423.15 K. The

Table II. Antoine Equation Constants and Derived Px Data at 423.15 K for 1-Propanol (1) + n-Heptane (2)[a]

x_1 (423.15 K)	$A(z_1)$	$B(z_1)$	$C(z_1)$	P(423.15 K) (kPa)
0.0000	6.4406045	1573.875	−16.328	373.2
0.0471	6.7092025	1832.282	28.120	445.6
0.0938	6.4143285	1547.387	−6.491	501.8
0.1425	5.9041915	1101.291	−75.322	547.0
0.1921	5.7855145	986.836	−97.120	573.7
0.2422	5.6774515	895.209	−114.518	598.2
0.2928	5.8630825	981.792	−103.586	617.7
0.3946	6.0091075	1040.950	−98.190	639.4
0.4456	6.0842565	1079.696	−93.279	647.4
0.4968	6.1345195	1100.852	−91.488	653.6
0.5480	6.2344085	1156.909	−84.417	659.2
0.5990	6.2599505	1162.365	−85.316	659.6
0.6610	6.4623625	1288.826	−69.268	661.3
0.7010	6.4065285	1244.521	−76.301	658.3
0.7518	6.4954075	1302.085	−69.202	655.6
0.8024	6.6029035	1366.718	−62.665	648.0
0.8527	6.5110855	1297.624	−73.062	637.6
0.9025	6.5379075	1302.542	−75.590	616.9
0.9518	6.3769445	1179.880	−95.852	591.6
1.0000	6.4035485	1157.900	−107.559	542.7

[a] $\log P(z_1) = A(z_1) - B(z_1)\,[T + C(z_1)]$; log = base 10, $P(z_1)$ = kPa, T = K.

standard rms error from the least-squares fit is reduced with the addition of each of the four constants. The pressure residuals from the four-constant least-squares fit display no systematic trends and the overall rms error is reduced to the expected level of experimental error ($\approx 0.2\%$). Derived Px data between 373.15 K and 463.15 K were analyzed in a similar fashion to produce G^E data that could be analyzed with the Gibbs–Helmholtz equation to produce H^E and TS^E data as described in Section 4.

Table III. Redlich–Kister G^E Parameters at 423.25 K for 1-Propanol (1) + n-Heptane (2)

No. parameters	A (J · mol^{-1})	B (J · mol^{-1})	C (J · mol^{-1})	D (J · mol^{-1})	Standard rms error (P) (kPa)
0	0				155.614
1	4625.3				4.077
2	4622.1	67.036			4.033
3	4583.3	71.985	437.54		1.950
4	4573.6	30.534	494.00	267.86	1.402

4. DISCUSSION

The precision of the results is indicated by the standard rms error in the Barker's method fit, 0.2 to 0.5% in pressure. The evaluation of the accuracy of experimental measurements in the absence of exactly known reference values is a difficult and ill-defined process [9]. If systematic errors (bias) are absent, the experimental uncertainty is the same as the uncertainty from random error as described in the precision. Agreement with literature values for the pure-component vapor pressure data indicates that serious systematic errors are absent.

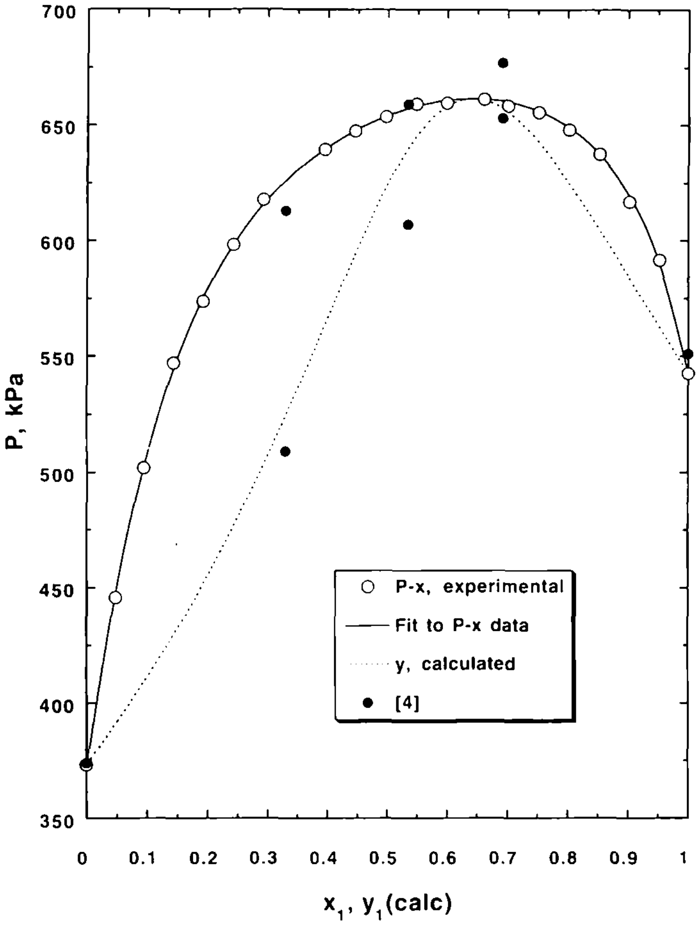

Fig. 1. P-x-y data at 423.15 K for 1-propanol (1) + n-heptane (2).

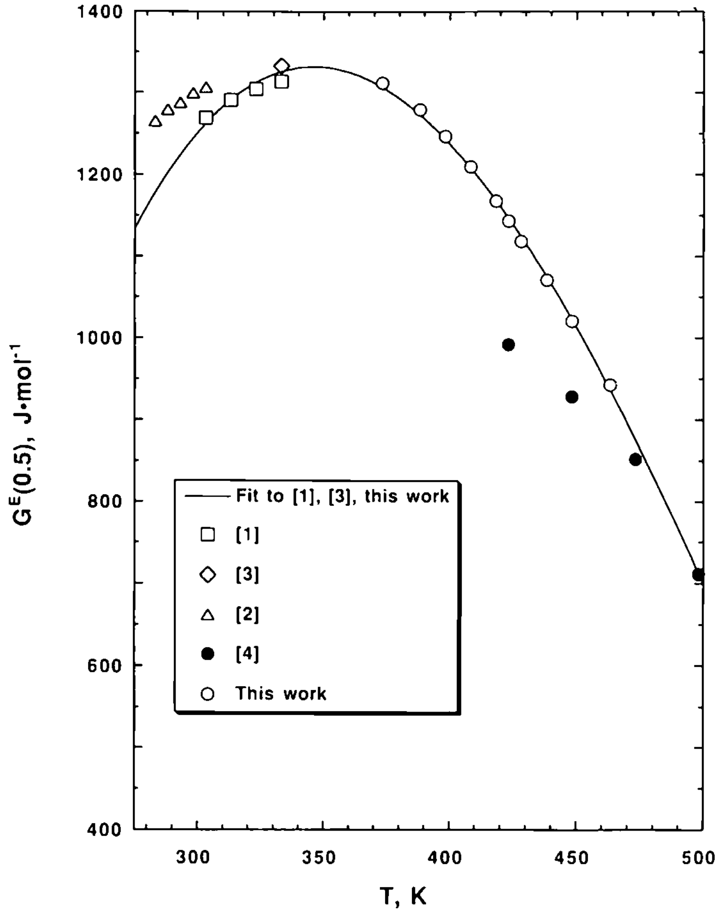

Fig. 2. Equimolar excess Gibbs energy of mixing (G^E) vs temperature for 1-propanol (1) + *n*-heptane (2).

A comparison at 423.15 K with Zawisza and Verjrosta [4] is shown in Fig. 1. Note that their reported azeotropic composition, $x_1(\mathrm{az}) = 0.62$, is close to the value measured here, $x_1(\mathrm{az}) = 0.64$. However, Fig. 1 shows that the bubble and dew points reported in [4] at 423.15 K are not in agreement with our data.

The Gibbs–Helmholtz equation was used to derive enthalpy-of-mixing data from the temperature dependence of the G^E data:

$$H^E = -T^2(\partial g/\partial T)_x \tag{4}$$

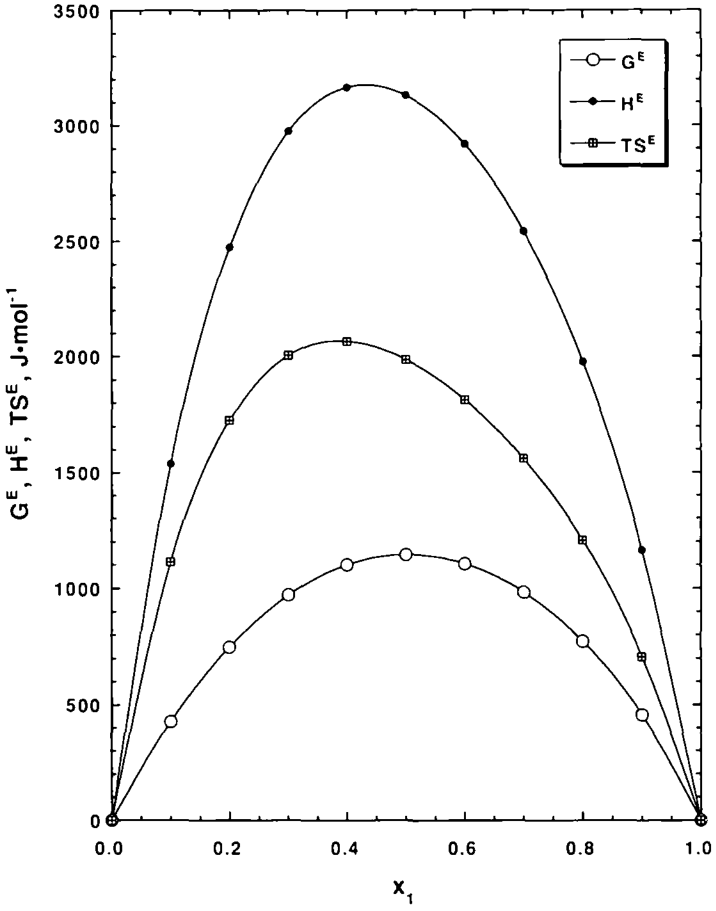

Fig. 3. Excess functions of mixing at 423.15 K for 1-propanol (1) + *n*-heptane (2).

where $g = G^E/T$. TS^E was then determined from the thermodynamic relation,

$$TS^E = H^E - G^E \tag{5}$$

Figure 2 shows the equimolar G^E from this work compared to data at higher and lower temperatures. The maximum in equimolar G^E at ≈ 345 K indicates that equimolar TS^E has changed from negative to positive. Figure 3 shows the mixture thermodynamic excess functions derived from our PTx data at 423.15 K. Note that $G^E > 0$, $H^E > 0$, and $TS^E > 0$ for all compositions, in contrast to the low-temperature data [1]. At 318.15 K, $G^E > 0$ and

Table IV. Azeotropic Composition vs Temperature for 1-Propanol (1) + *n*-Heptane (2)

Temperature (K)	x_1(az)	Ref. No.
283.17	0.25	2
293.15	0.26	2
303.15	0.28	2
303.15	0.26	1
313.15	0.29	1
323.15	0.32	1
333.15	0.36	1
333.15	0.37	3
398.15	0.57	This work
423.15	0.64	This work
423.15	0.62	4
448.15	0.70	This work
448.15	0.62	4
473.15	0.62	4
498.15	0.62	4

$H^E > 0$ but TS^E is positive in the dilute alcohol region (up to $x_1 \approx 0.15$) and negative from $x_1 \approx 0.15$ to $x_1 = 1.00$.

Malesinski [10] has classified binary mixtures according to the signs of the their excess functions. He relates this classification to the like interactions (1–1, 2–2) and unlike (1–2) interactions of the two different molecules in solution. The excess-function behavior of alcohol + hydrocarbon systems at low temperatures [1] suggests that the orientation of alcohol molecules through hydrogen bonding is disrupted only at high dilution. Our data suggest that, at higher temperatures, hydrogen-bonding is diminished by kinetic energy effects, and loss of alcohol molecule orientation leads to $TS^E > 0$ over the entire composition range.

Because of the large positive mixture nonidealities and the similarity of the pure-component vapor pressures, a maximum-pressure homoazeotrope was found at all temperatures studied. Azeotropic composition vs temperature data are given in Table IV.

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