= 0.76 and P = 560 Torr reported by Zurita et al. (*2*).

Glossary

B_{ii}	second virial coefficient of pure component i, cm^3/mol
B_{12}	cross virial coefficient, cm^3/mol
c_j	coefficient in eq 1, J/mol
G^E	excess molar Gibbs energy, J/mol
m	number of measurements on a system
n	number of coefficients in eq 1
n_D	refractive index for sodium D line
P_i°	vapor pressure of pure component i, Torr
p_i'	defined by eq 5, Torr
R	gas constant
T	thermodynamic temperature, K
V_i°	molar volume of pure liquid i, cm^3/mol
x_i	mole fraction of component i in liquid
y_i	mole fraction of component i in vapor
γ_i	activity coefficient of component i in liquid
ϵ	estimated experimental uncertainty
ρ	density, g/cm^3
σ	standard deviation, defined in the footnote of Table VI

Registry No. $CH_3(CH_2)_4CH_3$, 110-54-3; $CH_3(CH_2)_3CH_3$, 109-66-0; $H_2C{=}C(CH_3)CO_2Me$, 80-62-6; MeCOPr, 107-87-9; H_3CCO_2H, 64-19-7; H_3CCO_2Et, 141-78-6; H_3CCO_2Me, 79-20-9; $(CH_3CO)_2O$, 108-24-7.

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Excess Enthalpy of Four Partially Miscible Binary Liquid Mixtures near Their Critical Solution Temperatures

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Heats of mixing for the *n*-hexane + methanol, 2-methylpropanoic acid + water, nitroethane + 2,2,4-trimethylpentane, and nitromethane + 1-butanol systems were measured as a function of composition at from six to eight temperatures bracketing each system's critical solution temperature. The estimated uncertainty in the results is less than 1.0%. Heats of mixing were endothermic in all four systems. Above the critical solution temperature, heat of mixing curves plotted vs mole fraction of the first component were everywhere convex. Below the critical solution temperature, intersections of the straight (two-phase) and curved (one-phase) heat of mixing lines were used to provide a calorimetric estimate of the binodal compositions.

Introduction

The need for accurate prediction of liquid mixture properties for use in process design simulators has led to considerable interest in Gibbs free energy models. The local composition (LC) concept of Wilson (*1*) has been shown to be particularly effective in correlating vapor–liquid equilibrium (VLE). On the basis of the LC concept, several models have been developed to correlate VLE and liquid–liquid equilibrium (LLE) data (*2–6*), and simultaneously VLE and molar excess enthalpy h^E (*5*, *7–10*) data.

In order to facilitate multiproperty correlation based on the Gibbs–Helmholtz relation, several investigators have incorporated additional empirical temperature dependencies into the original versions of LC models for the molar Gibbs free energy g^E (*11–15*). While some success has been reported (*7–10*), other investigators have found simultaneous correlation of VLE and h^E with these models to be applicable to only a few mixtures (*5*, *12–14*). Studies have shown these empirically

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Table I. Experimental h^E (J/mol) for n-Hexane (1) + Methanol (2) Mixtures (CST = 306.95 K)[a]

	h^E at various T (K)							
x_1	303.15	307.15	307.90	308.40	309.15	310.15	313.15	318.15
0.0333	117						128	
0.0720	252	264	248	244	246	244	264	314
0.0938		307	310	302	305	302		385
0.1174	369	362	365	357	361	357	381	453
0.1433		404	406	402	408	405		506
0.1715	460	438	443	432	444	443	482	459
0.2026		466	470	463	478	475		588
0.2369	491*	491	492	485	503	505	560	629
0.2751		515	519	514	529	531		666
0.3178	500*	532	538	538	548	547	598	697
0.3658		551	555	552	565	569		716
0.4201	509*	564	571	568	576	581	627	736
0.4823		579	582	580	584	593		758
0.5540	511*	587	593	585	596	605	653	768
0.6376		604	587	581	590	597		760
0.7365	485	552	563	555	563	589	609	664
0.7812	436						565	
0.8295	385						515	
0.8551		436	444	427	421	423		482
0.8817	295						422	
0.9383							154	

[a] Values marked by asterisks are from a two-phase region.

modified models to be inadequate for general prediction of liquid-phase coexistence curves for both binary (*16*) and ternary (*17*, *18*) systems.

While partially miscible ternary systems are of more practical importance to the chemical processing industry, the study of partially miscible binary systems provides information about the temperature dependence of LLE that is more significant to development of the correct temperature dependence in Gibbs free energy models. For example, an enthalpy-based local-composition model (EBLCM) (*16*–*18*) has been developed in an attempt to accurately predict LLE from only VLE and h^E data for binary and ternary systems. The existing literature, however, contains very few data for excess enthalpies of partially miscible binary systems (*19*). To help alleviate that paucity and to provide data from which better g^E models can be developed to simultaneously correlate h^E and LLE, we report here h^E values for four partially miscible binary systems at several temperatures just above and below their critical solution temperature (CST).

Experimental Section

Excess enthalpies were measured with use of a commercial Tronac Model 450/550 isothermal flow calorimeter with a flow insert similar in design to that used by Christensen et al. (*20*). The calorimeter and experimental technique have been described elsewhere (*17*). Two ISCO precision positive displacement pumps were used to establish constant flow rates through the mixing cell. The pumps' stepper motors were driven at constant, but variable, flow rates by a microcomputer using a frequency-to-voltage converter. The pumps were calibrated over the range 0.0017–0.0217 cm^3/s through replicate runs of distilled water. The calibrated flow rates were linear with a reliability of better than 99.8% over the entire flow range. Experiments were performed with one pure component in each pump. The mixture composition was varied over the entire composition range by adjusting the flow rates of the two pumps subject to the constraint of constant total flow rate at 0.016 67 cm^3/s. In addition to thorough cleaning and purging of the pumps between changes in components, densities of the pure fluids were measured and compared to values available in the literature to ensure complete purging of the system and to maintain purity of components. A Mettler/Paar 4-digit densitometer with a calibrated accuracy of ±0.0001 kg/dm^3 was used for the density determinations.

The calorimeter, submerged in a constant temperature bath, was maintained to within ±0.0006 K of the set point with a Tronac Model PTC-41 precision temperature controller as monitored with a Hewlett-Packard Model 2804A quartz thermometer. Feed streams to the calorimeter's mixing/measurement coil were equilibrated to the bath temperature in stainless steel heat-exchange coils immersed in the same bath. A back-pressure regulator in the effluent line maintained a constant pressure of 101.3 kPa.

Excess enthalpies were determined from the calibrated flow rates, the fluid densities, the change of the control heater's pulse rate at each composition from the base-line value, and the electrical calibration constant for the pulse heat rate. Three replicate measurements were made over the entire composition range at each temperature for the four systems. The agreement between replicate runs was found to be better than 99.2%

All organic chemicals used in this study were spectrophotometric grade of at least 99.9% specified purity. All were used without further purification. Water used in this study was deionized and then distilled in a Sybron/Barnstead Fistreem glass still. A test of the accuracy of the calorimeter was made by comparing measured excess enthalpies for cyclohexane + benzene mixtures with values reported by Elliott and Wormald (*21*); the resultant average absolute deviation was 0.41%, and the maximum error was 0.75%. On the basis of this test and the precision of the measurements, we estimate the uncertainty of the reported excess enthalpies to be less than 1.0%.

Results

Experimental heats of mixing for n-hexane + methanol, 2-methylpropanoic acid + water, nitroethane + 2,2,4-trimethylpentane, and nitromethane + 1-butanol mixtures are reported in Tables I–IV. The critical solution temperatures of these systems, as reported elsewhere (*6*), are also shown in these tables for reference purposes. Values of the heat of mixing reported for the n-hexane + methanol system agree with previously reported data (*22*, *23*) to within experimental error. Literature data for the nitroethane + 2,2,4-trimethylpentane system, only available at 298.15 K (*24*), are slightly larger than those measured in this study. The authors know of no literature values for the remaining two systems.

Table II. Experimental h^E (J/mol) for 2-Methylpropanoic Acid (1) + Water (2) Mixtures (CST = 298.65 K)[a]

	h^E at various T (K)						
x_1	293.15	298.15	298.65	299.15	300.15	303.15	308.15
0.0461						92	147
0.0765						200	237
0.0882	180*	200*	201	207			
0.1007					228		
0.1142	243*	268*	270	276	264	293	347
0.1288					299		
0.1447	307*	335	339	343	333		
0.1620					377	416	490
0.1810	381*	404	410	411	413		
0.2018					454		
0.2248	447	487	488	489	496	561	617
0.2504					536		
0.2789	523	570	575	621	581		
0.3109					633	733	783
0.3471	606	654	664	717	682		
0.3885					733		
0.4361	671	766	774	805	785	916	1006
0.4916					836		
0.5569	758	861	862	867	896	1024	1120
0.6351					941	1073	1160
0.7302	816	891	897	914	957	1094	1168
0.7744	824	883	884	896			
0.8227	741	807	809	853			
0.8486					783	929	900
0.8759	599	667	671	690			
0.9347	379	415	406	445			

[a] Values marked by asterisks are from a two-phase region.

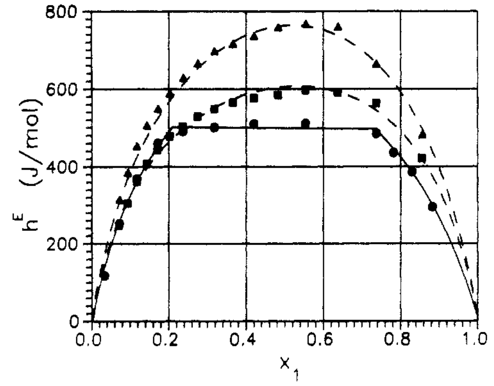

Figure 1. Experimental h^E for *n*-hexane (1) + methanol (2) mixtures at 303.15 (●), 209.15 (■), and 318.15 K (▲). Dashed lines represent single-phase values correlated by using EBLCM; solid lines represent the two-phase isotherm estimated from the calorimetric data.

Measured excess enthalpies in the single-phase region were correlated by using the EBLCM equation of Rowley and Battler (*16*)

$$h^E = x_1x_2\left[\sum_{i=1}^{2}\sum_{j=1}^{2}\frac{H_{ij}G_{ij}}{\sum_{k=1}^{2}x_kG_{kj}} + b[(T/\mathrm{K}) - 300]\right] \qquad (1)$$

where

$$G_{ij} = \exp\left(-\frac{a_{ij}}{RT}\right) \qquad (2)$$

and $H_{ij} = 0$ for $i = j$. This equation provides good correlation of experimental h^E data over a wide temperature range using a relatively small number of parameters. The values of the parameters H_{ij}, a_{ij}, and b in eqs 1 and 2 are presented in Table V for each system, along with the overall standard deviation of the fit. Figures 1–4 show both experimental and correlated h^E values for selected temperatures.

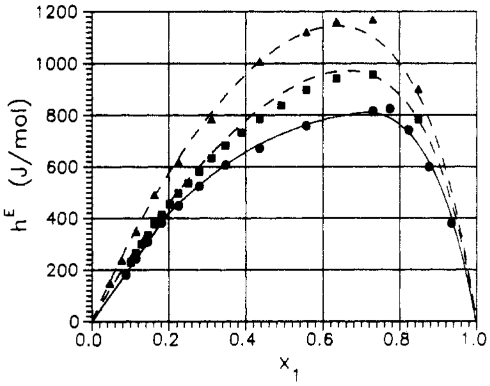

Figure 2. Experimental h^E for 2-methylpropanoic acid (1) + water (2) mixtures at 293.15 (●), 300.15 (■), and 308.15 K (▲). Line attributes are the same as in Figure 1.

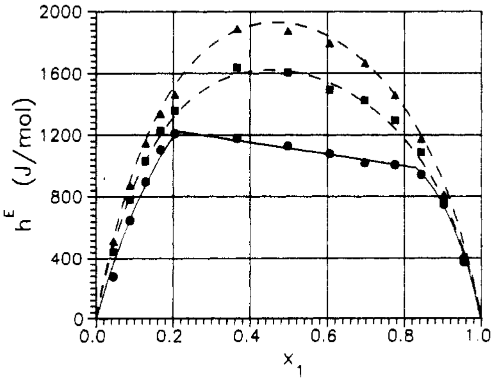

Figure 3. Experimental h^E for nitroethane (1) + 2,2,4-trimethylpentane (2) mixtures at 293.15 (●), 304.15 (■), and 313.15 K (▲). Line attributes are the same as in Figure 1.

Below the CST, h^E vs x_1 plots exhibit a linear behavior characteristic of the two-phase region and a discontinuity in slope at the binodal curve. This has been observed previously for similar systems (*25*). The linear dependence of excess enthalpy on composition in the two-phase region results from

Table III. Experimental h^E (J/mol) for Nitroethane (1) + 2,2,4-Trimethylpentane (2) Mixtures (CST = 302.15 K)[a]

	h^E at various T (K)						
x_1	293.15	302.15	303.15	304.15	305.15	308.15	313.15
0.0449	275	393	412	442	481	467	513
0.0876	648	738	755	780	813	855	872
0.1282	895	1000	1009	1031	1065	1108	1146
0.1670	1102	1177	1220	1225	1272	1302	1332
0.2039	1209	1318	1337	1357	1385	1410	1461
0.3656	1177*	1490	1571	1636	1666	1791	1888
0.4969	1127*	1449	1525	1605	1663	1779	1873
0.6058	1078*	1387	1454	1491	1601	1710	1795
0.6974	1017*	1284	1367	1423	1467	1578	1663
0.7756	1005*	1172	1228	1292	1319	1410	1454
0.8432	941	1027	1073	1087	1098	1145	1173
0.9021	749	763	765	771	782	796	809
0.9540	372	381	387	393	399	414	424

[a] Values marked by asterisks are from a two-phase region.

Table IV. Experimental h^E (J/mol) for Nitromethane (1) + 1-Butanol (2) Mixtures (CST = 291.15 K)[a]

	h^E at various T (K)					
x_1	291.15	292.15	293.15	295.15	298.15	303.15
0.0817	572	568	582	574	581	605
0.1582	1143	1133	1140	1147	1156	1164
0.2298	1490	1531	1527	1563	1595	1620
0.2972	1692	1707	1741	1814	1894	1912
0.3605	1794	1842	1872	1932	2061	2106
0.4202	1865	1925	1928	2018	2151	2242
0.4766	1912	1972	1996	2087	2203	2293
0.5300	1961	1990	2049	2144	2222	2312
0.5805	1938*	2009	2023	2098	2252	2320
0.6284	1920*	1975	1994	2084	2200	2271
0.6740	1886*	1931	1966	2044	2149	2221
0.7173	1858	1890	1909	1986	2088	2122
0.7585	1781	1797	1819	1888	1968	2002
0.7978	1686	1723	1741	1770	1837	1881
0.8354	1560	1572	1588	1605	1653	1725
0.8712	1386	1388	1381	1385	1406	1492
0.9055	1114	1116	1113	1107	1124	1214
0.9384	791	796	795	786	800	873

[a] Values marked by asterisks are from a two-phase region.

constant partial molar enthalpies in the two coexisting phases. The slope discontinuity can be utilized as an enthalpic measurement of the binodal curve. The lowest isotherms displayed in Figures 1–4 were used to estimate the coexisting phase compositions; values are reported and compared with smoothed experimental values (*6*) in Table VI. Values of h^E obtained in the two-phase region between these compositions are marked with an asterisk in Tables I–IV. Binodal composition estimates can be made graphically or by determining the intersection of a polynomial fitted only from single-phase data with the straight line that characterizes the two-phase region. Equilibrium phase compositions estimated in this manner for the *n*-hexane + methanol and nitroethane + 2,2,4-trimethylpentane systems are reasonable as is the value obtained for one of the coexisting phases in the 2-methylpropanoic acid + water system. Estimation of the composition for the second phase of this latter system was impossible because of its proximity to that of pure water. A similar analysis for the nitromethane + 1-butanol system indicates some phase separation at the reported CST, possibly due to either slight impurities in the mixture or a slight error in the reported CST. In general, the calorimetric method for determination of LLE is most accurate for temperatures several degrees below an upper CST, where there is a distinct change in slope at the binodal compositions.

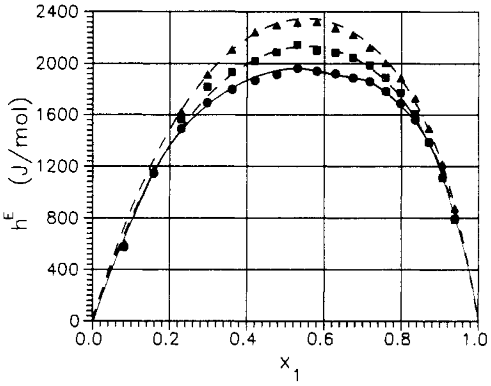

Figure 4. Experimental h^E for nitromethane (1) + 1-butanol (2) mixtures at 291.15 (●), 295.15 (■), and 303.15 K (▲). Line attributes are the same as in Figure 1.

Conclusions

Heats of mixing for the *n*-hexane + methanol, 2-methylpropanoic acid + water, nitroethane + 2,2,4-trimethylpentane, and nitromethane + 1-butanol systems were measured at from six to eight temperatures bracketing each system's CST. An analysis of the experimental data below the critical solution temperature shows the characteristic linear relationship for h^E vs composition in the two-phase region. Intersection of this linear region with the single-phase curve provides reasonable estimates of the binodal compositions for the four systems reported here. This calorimetric determination of LLE becomes less accurate and more difficult to use the closer the temperature is to the CST.

Table V. EBLCM Parameters Regressed from Single-Phase Data

parameters	*n*-hexane (1) + methanol (2)	2-methylpropanoic acid (1) + water (2)	nitroethane (1) + 2,2,4-trimethylpentane (2)	nitromethane (1) + 1-butanol (2)
a_{21}, J/mol	6208.6	2946.4	4031.5	1695.79
a_{12}, J/mol	5083.9	3925.0	5123.3	4712.20
H_{21}, J/mol	4907.8	892.8	11025.1	7411.46
H_{12}, J/mol	4489.1	9098.5	9752.4	15225.04
b, J/(mol·K)	57.88	79.01	109.63	77.09
AAD,[a] %	3.8	4.1	5.1	2.8
AAD,[a] J/mol	14	20	42	35

[a] Average absolute deviation.

Table VI. Binodal Compositions Estimated from the h^E Data

system	T, K	estimated		literature	
		x_1'	x_1''	x_1'	x_1''
n-hexane (1) + methanol (2)	303.15	0.21	0.74	0.269	0.758
2-methylpropanoic acid (1) + water (2)	293.15		0.20	0.054	0.224
nitroethane (1) + 2,2,4-trimethylpentane (2)	293.15	0.20	0.83	0.236	0.834
nitromethane (1) + 1-butanol (2)	291.15	0.53	0.72	at CST	

Glossary

h^E	molar excess enthalpy (J/mol)
g^E	molar excess Gibbs free energy (J/mol)
R	molar gas constant [J/(mol·K)]
T	temperature (K)
x_i	mole fraction of component i
a_{ij}	adjustable parameter for i–j interactions (J/mol)
H_{ij}	adjustable parameter for i–j interactions (J/mol)
G_{ij}	nonrandomness weighting factor, defined by eq 2
b	adjustable parameter for i–j interactions [J/(mol·K)]

Registry No. Hexane, 110-54-3; methanol, 67-56-1; 2-methylpropanoic acid, 79-31-2; nitroethane, 79-24-3; 2,2,4-trimethylpentane, 540-84-1; nitromethane, 75-52-5; 1-butanol, 71-36-3.

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Excess Volumes of Binary Mixtures of 1,3-Dichlorobenzene with 1-Alkanols at 303.15 K

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Excess molar volumes for binary mixtures of 1,3-dichlorobenzene with 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol have been determined at 303.15 K. V^E is negative in mixtures rich in alcohols and positive in mixtures rich in 1,3-dichlorobenzene.

Introduction

This forms a part of a study of excess thermodynamic properties of binary mixtures that include chlorinated benzenes as common components and a homologous series of alcohols as noncommon components. Excess volumes for mixtures of 1,2-dichlorobenzene with 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol were reported earlier (*1*). We report here new experimental data for binary mixtures of 1,3-dichlorobenzene with the five alcohols. This work was undertaken to study the isomeric effect arising due to the replacement of 1,2-dichlorobenzene by 1,3-dichlorobenzene.

Table I. Densities ρ of Pure Liquid Components at 303.15 K

component	$\rho/(\text{g cm}^{-3})$	
	present work	literature
1,3-dichlorobenene	1.27716	1.27718 (*5*)
1-butanol	0.80206	0.8022 (*6*)
1-pentanol	0.80760	0.8079 (*6*)
1-hexanol	0.81205	0.8121 (*6*)
1-heptanol	0.81572	0.8148 (*6*)
1-octanol	0.82188	0.8184 (*6*)

Experimental Section

Excess volumes were measured as described previously (*1*) by using a single composition per loading type dilatometer described by Rao and Naidu (*2*). Measurements were made employing a thermostatic bath maintained to 303.15 ± 0.01 K.

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