Thermochimica Acta, 154 (1989) 71–79
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

EXCESS ENTHALPIES FOR ETHANE + ACETONITRILE AT 298.15, 323.15, AND 348.15 K AND AT 7.5 AND 15 MPa *

J.B. OTT **, B.J. NEELY, J.E. PURDY, and R.L. OWEN

Department of Chemistry, Brigham Young University, Provo, UT 84602 (U.S.A.)

(Received 12 December 1988)

ABSTRACT

Excess enthalpies have been determined for acetonitrile + ethane at 298.15, 323.15 and 348.15 K and at pressures of 7.5 and 15 MPa. The critical point for ethane is at 305.50 K and 4.914 MPa. Hence, the measurements at 298.15 K are with liquid ethane while those at 323.15 and 348.15 K are with supercritical ethane. This system enables us to make interesting comparisons of excess enthalpies and phase equilibria for a non-polar liquid (or supercritical fluid) with a second polar liquid. For example, pressure has a large effect on H_m^E at 323.15 and 348.15 K where the ethane is supercritical, but not at 298.15 K where the ethane is liquid. Liquid ethane + acetonitrile have a miscibility gap which continues into the supercritical region. The H_m^E results at 15 MPa have been used to obtain the fluid + liquid phase diagram at this pressure.

INTRODUCTION

In a recent paper [1], the measurement of H_m^E with an isothermal flow calorimeter over a range of temperature and pressure was described for cyclohexane + acetonitrile. This was the first in a series of systems to be studied in which relatively simple polar and non-polar substances are mixed. The liquid + liquid phase equilibrium is present in the cyclohexane + acetonitrile system. The liquid + liquid phase diagram was measured at ambient pressure and the results were compared with those obtained from breaks in the H_m^E against mole fraction curves; excellent agreement was found, demonstrating that calorimetric measurements can be used to obtain reliable liquid + liquid results.

This paper reports H_m^E results for $\{xC_2H_6 + (1-x)CH_3CN\}$ at 298.15, 323.15 K and 348.15 K and at pressures of 7.5 and 15 MPa. The critical points T_c and P_c are 305.50 K, and 4.91 MPa, and 547.9 K, and 4.83 MPa

---

* Dedicated to Professor James J. Christensen in memory of his contribution to innovation in calorimetry

** Author to whom all correspondence should be addressed.

0040-6031/89/$03.50

TABLE 1

Experimental excess enthalpies H_m^E for $\{xC_2H_6+(1-x)CH_3CN\}$. δH_m^E is the deviation of the experimental results from eqn. (1) or eqn. (2). The composition range where each equation applies is given in Tables 2 and 3

x	H_m^E (J mol^{-1})	δH_m^E (J mol^{-1})	x	H_m^E (J mol^{-1})	δH_m^E (J mol^{-1})	x	H_m^E (J mol^{-1})	δH_m^E (J mol^{-1})
$T = 298.15$ K, $p = 7.5$ MPa								
0.0112	36	−1	0.2652	611	3	0.6678	401	−9
0.0226	70	−5	0.3088	585	−2	0.7283	390	9
0.0341	111	−1	0.3541	563	−2	0.7916	339	−10
0.0693	224	2	0.4012	553	11	0.8578	328	11
0.1058	338	6	0.4503	499	−18	0.9272	275	−8
0.1435	434	−7	0.5013	505	12	0.9511	274	3
0.1826	553	2	0.5545	458	−8	0.9753	254	0
0.2231	629	0	0.6099	445	7			
$T = 298.15$ K, $p = 15$ MPa								
0.0368	133	7	0.2521	799	−5	0.8044	458	4
0.0619	220	1	0.2810	782	6	0.8672	415	−1
0.0939	346	6	0.3525	739	6	0.9104	386	−3
0.1135	411	−1	0.4206	686	−5	0.9324	383	7
0.1268	450	−10	0.5040	636	−3	0.9546	368	6
0.1536	549	−1	0.5921	582	−3	0.9659	329	−14
0.1788	623	−6	0.6853	525	−3	0.9727	288	4
0.1948	676	2	0.7438	481	−11	0.9863	177	25
0.2250	760	12	0.7840	465	−2			
$T = 323.15$ K, $p = 7.5$ MPa								
0.0112	17	−5	0.2652	321	−6	0.6099	156	−3
0.0341	64	1	0.2795	316	−3	0.6678	129	−2
0.0693	125	1	0.3088	305	−1	0.7283	103	1
0.1058	179	1	0.3541	290	6	0.7916	69	−2
0.1435	229	1	0.4012	262	1	0.8578	37	−2
0.1826	268	−4	0.4503	241	5	0.9272	5	0
0.2231	310	3	0.5013	217	5	0.9511	−6	1
0.2370	316	−1	0.5545	184	−2	0.9753	−17	0

$T = 323.15$ K, $p = 15$ MPa								
0.0122	38	−9	0.3261	883	−5	0.7438	657	5
0.0368	124	−15	0.3726	867	6	0.8044	619	0
0.0493	177	−7	0.4206	833	−2	0.8672	590	7
0.0746	267	−4	0.4701	818	12	0.9104	553	−5, −5 [a]
0.1135	407	12	0.5212	769	−9	0.9236	514	24
0.1536	523	8	0.5741	749	1	0.9324	467	26
0.1948	631	3	0.6287	712	−6	0.9546	268	−42
0.2373	739	5	0.6853	683	−3	0.9772	128	−35
0.2810	822	−12						
$T = 348.15$ K, $p = 7.5$ MPa								
0.0112	−0.2	2	0.2370	−187	−4	0.7491	271	1
0.0226	−0.3	5	0.2454	−186	4	0.7575	275	−3
0.0341	−13	−4	0.2482	−185	10	0.7702	289	−1
0.0457	−14	0	0.2510	−189	4	0.8133	332	2
0.0574	−23	−3	0.2566	−185	3	0.8578	367	−4
0.0693	−30	−4	0.2795	−163	4	0.8805	388	−5
0.0935	−40	3	0.3088	−139	0	0.9272	443	7
0.1182	−60	4	0.3696	−87	−5	0.9607	473	6
0.1435	−87	0	0.4337	−27	−4	0.9656	479	7
0.1694	−110	4	0.5013	29	−11	0.9704	483	41
0.1826	−129	−2	0.5727	100	−6	0.9753	326	−53
0.1959	−142	−1	0.6482	171	−6	0.9901	174	10
0.2231	−171	−2	0.7078	232	0			
$T = 348.15$ K, $p = 15$ MPa								
0.0122	28	−7	0.4206	934	1	0.8251	766	−3
0.0493	154	3	0.4534	919	0	0.8672	727	−2
0.1004	314	0	0.4870	912	6	0.8887	680	−6
0.1536	467	−3	0.5212	884	−8	0.9104	630	5
0.2088	616	6	0.5921	860	−3	0.9324	549	11
0.2663	728	−4	0.6662	833	0	0.9546	415	−1
0.3261	832	−2	0.7438	808	6	0.9772	226	−16
0.3884	917	3						

---

[a] This mole fraction was taken as the solubility limit and hence, the intersection of eqns. (1) and (2). The two numbers are the deviations from eqns. (1) and (2) respectively.

for ethane and acetonitrile, respectively. Thus, acetonitrile will be liquid for all of the measurements while the ethane will be a supercritical fluid at all the temperatures except 298.15 K. This is a different condition than for cyclohexane + acetonitrile where both components were liquid at all the temperatures and pressures at which the measurements were made.

EXPERIMENTAL

Matheson 99.0 mass per cent ethane and B and J ChromPure 99.8 mass per cent acetonitrile were used without further purification. The acetonitrile was stored over Davison 3A molecular sieve to remove water.

The automated isothermal high-pressure and high-temperature flow calorimeter has been described in detail in an earlier paper [2]. We reported the accuracy of the calorimeter as better than 0.5% but then indicated in a later paper [1] that in systems such as the one reported here where phase separation occurs, the uncertainty increases to 1% in the one-phase region and to as much as 2% in the two-phase region.

Bath temperatures were set and monitored with a Hart Model 1006 platinum resistance thermometer which was calibrated against a Rosemount thermometer (IPTS-68). Pressures were measured with a Sensotec Model 450D transducer checked by a Heise gauge. Both the Heise gauge and the transducer were calibrated against a dead-weight gauge. We estimate our temperature and pressure scales to be accurate to ±0.02 K and ±0.1 MPa, respectively.

RESULTS AND DISCUSSION

H_m^E results for $\{xC_2H_6 + (1-x)CH_3CN\}$ at 298.15, 323.15, and 348.15 K and 7.5 and 15.0 MPa are given in Table 1. The values in the one-phase region were fitted to the equation

$$H_m^E(\mathrm{J\ mol^{-1}}) = x(1-x)\sum_{j=0}^{n} a_j(1-2x)^j \tag{1}$$

The coefficients a_j for eqn. (1) are summarized in Table 2 along with the standard deviations, and the deviations from this equation are given in Table 1.

The H_m^E results in the two-phase region were fitted to the linear equation

$$H_m^E = b_0 + b_1 x \tag{2}$$

The coefficients b_0 and b_1, along with the standard deviations, are given in Table 3 with deviations from this equation given in Table 1. In Tables 2 and 3, x_1 and x_2 give the composition limits over which eqns. (1) and (2) apply.

TABLE 2

Coefficients for eqn. (1). This equation and these coefficients apply for $\delta \leq x \leq x_1$, and $x_2 \leq x \leq 1$, where x_1 and x_2 are the liquid+liquid solubility limits and δ is the standard deviation of H_m^E from eqn. (1)

p(MPa)	T(K)	a_0	a_1	a_2	a_3	δ(J mol^{-1})	x_1	x_2
7.5	298.15	5359.0	−3756.5	1781.7	–	3.8	0.2126	0.9747
15.0	298.15	3696.2	449.1	3778.0	−4775.3	9.7	0.2481	0.9644
7.5	323.15	1198.3	1389.7	−648.4	–	2.3	0.2591	0.9737
15.0	323.15	4723.5	−1781.5	984.3	–	19.0	0.3103	0.9104
7.5	348.15	−207.4	−5168.4	8801.9	−3562.8	16.2	0.2497	0.9679
15.0	348.15	3939.7	−339.3	−177.3	1019.7 [a]	6.3	0.4103	0.8469

[a] At 348.15 K and 15.0 MPa, $a_4 = 3810.4$ and $a_5 = -3406.8$ must be added.

They correspond to the points of intersection for these equations and hence, to the compositions of the phases in equilibrium at the temperatures and pressures of the measurements.

Figure 1 compares H_m^E values at 298.15, 323.15, and 348.15 K at a pressure of 15.0 MPa, while Fig. 2 makes the same temperature comparison at 7.5 MPa. At the higher pressure, H_m^E changes only a small amount with temperature in the composition regions where complete mixing occurs. This is true even though the ethane is liquid at the lower temperature but supercritical at the two higher temperatures. The supercritical ethane at 15 MPa could be described as behaving very "liquid-like". This behavior is also in evidence in the liquid + liquid or fluid + liquid phase diagram shown in Fig. 3. The curve is obtained by fitting the solubilities obtained from the calorimetric measurements (x_1 and x_2 in Tables 2 and 3) to the equation

$$T = T_c + k(y - y_c)^n \tag{3}$$

where

$$y = \alpha x / \{1 + x(\alpha - 1)\} \tag{4}$$

$$y_c = \alpha x_c / \{1 + x_c(\alpha - 1)\}. \tag{5}$$

TABLE 3

Coefficients for eqn. (2). This equation applies for $x_1 \leq \delta \leq x_2$, where x_1 and x_2 are the liquid+liquid solubility limits given in Table 2 and δ is the standard deviation from eqn. (2)

p(MPa)	T(K)	b_0	b_1	δ(J mol^{-1})	x_1	x_2
7.5	298.15	738.7	−491.8	8.7	0.2126	0.9747
15.0	298.15	949.4	−615.4	5.1	0.2481	0.9644
7.5	323.15	455.7	−486.5	3.3	0.2591	0.9737
15.0	323.15	1071.2	−562.8	5.9	0.3103	0.9104
7.5	348.15	−426.2	929.8	5.3	0.2497	0.9679
15.0	348.15	1102.4	−404.3	4.3	0.4103	0.8469

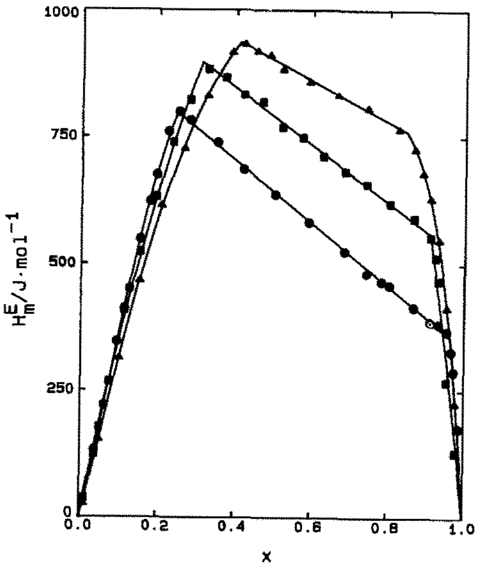

Fig. 1. Excess enthalpies at 15 MPa for $\{xC_2H_6+(1-x)CH_3CN\}$: ●, 298.15 K; ■, 323.15 K; ▲, 348.15 K.

In eqns. (3)–(5), T is the temperature and x is the mole fraction, with T_c and x_c as the values at the UCST.

The solubility results fitted to eqns. (3)–(5) with the exponential n set at the theoretical value of 3.1, give $T_c = 361.4$ K, $x_c = 0.633$, $k = -1.36 \times 10^3$,

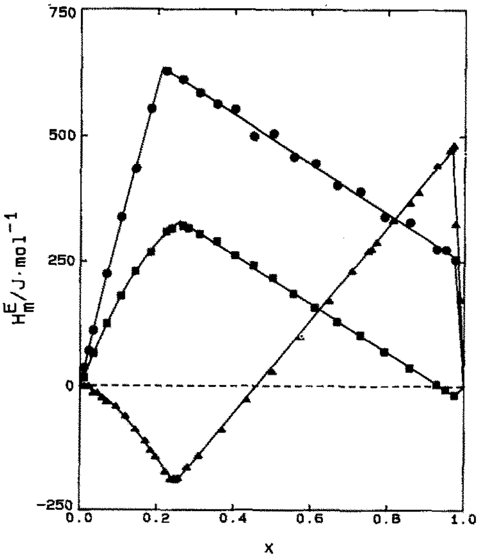

Fig. 2. Excess enthalpies at 7.5 MPa for $\{xC_2H_6+(1-x)CH_3CN\}$: ●, 298.15 K; ■, 323.15 K; ▲, 348.15 K.

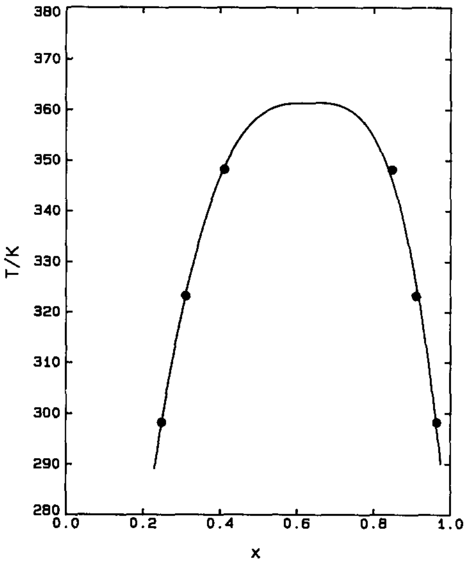

Fig. 3. Liquid + liquid phase diagram at 15 MPa for $\{xC_2H_6+(1-x)CH_3CN\}$: ●, points obtained from the discontinuities in the H_m^E curves; ———, curve obtained from the best fit of the experimental results to eqns. (3)–(5) with $n=3.1$.

and $\alpha=0.812$ with a standard deviation of 1.4 K. In earlier papers [1,3,4], it has been shown that eqns. (3)–(5) adequately fit liquid + liquid equilibria and can be used to predict the solubility curve without using experimental results near the UCST where the calorimetric method is less accurate.

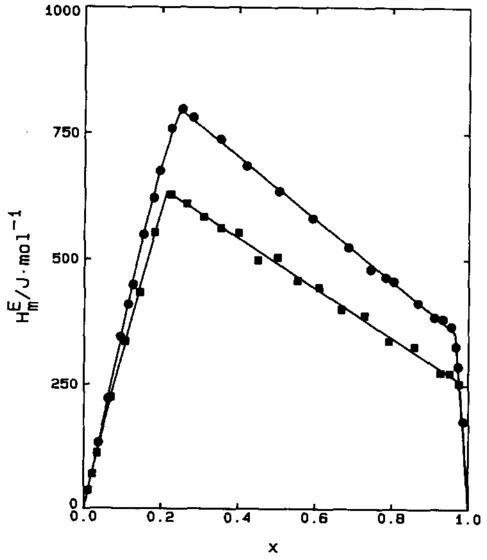

Fig. 4. Excess enthalpies at 298.15 K for $\{xC_2H_6+(1-x)CH_3CH\}$: ●, 15 MPa; ■, 7.5 MPa.

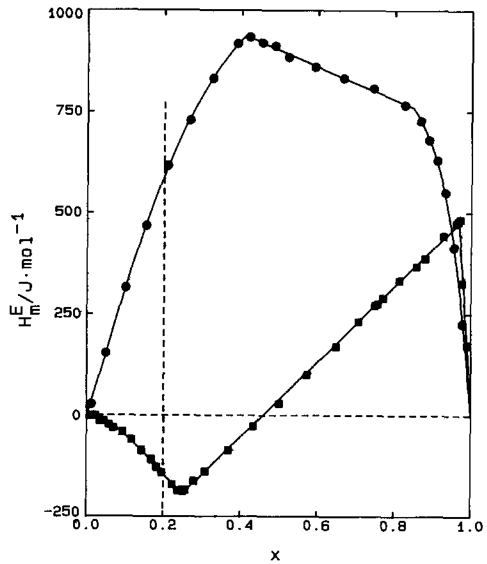

Fig. 5. Excess enthalpies at 348.15 K for $\{xC_2H_6+(1-x)CH_3CH\}$: ●, 15 MPa; ■, 7.5 MPa. The dashed line is the $x = 0.2$ isopleth along which the results shown in Fig. 6 were taken.

As can be seen in Fig. 2, the temperature effect at 7.5 MPa is very different from that at 15 MPa. Figure 4 shows the pressure effect on H^E_m at 298.15 K. Liquids are being mixed and $\partial H^E_m/\partial p$ is small. However, in the supercritical region, the pressure effect is large. At 348.15 K, H^E_m changes

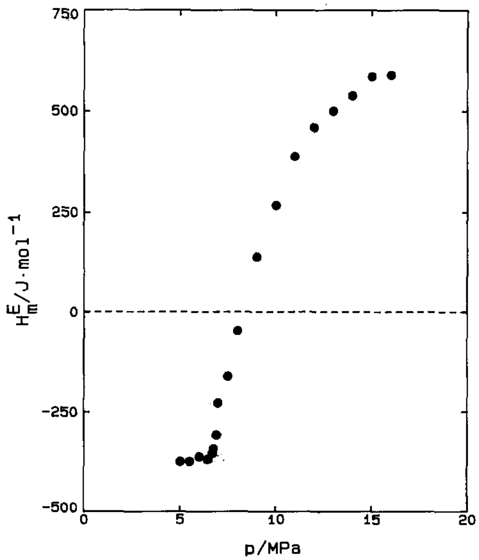

Fig. 6. Excess enthalpies at 348.15 K for $\{xC_2H_6+(1-x)CH_3CN\}$ as a function of pressure along the isopleth $x = 0.2$ (dashed line in fig. 5).

from positive to negative as the pressure decreases (Fig. 5). A simplified explanation for these changes in H_m^E is as follows. At 7.5 MPa and 348.15 K, supercritical ethane has "gas-like" properties. At low x, this "gaseous" ethane dissolves in the liquid acetonitrile. In the process, the gas condenses to a liquid and H_m^E is negative due to the enthalpy of condensation. At high x, the reverse process occurs. That is, liquid acetonitrile vaporizes into the gaseous ethane and a large endothermic enthalpy of mixing is obtained, resulting from the enthalpy of vaporization of the acetonitrile.

In Fig. 6, the pressure effect can be seen in more detail as p is plotted versus H_m^E at 348.15 K and at the $x = 0.2$ isopleth (the dashed line in Fig. 5). H_m^E goes through a minimum of approximately -350 J mol^{-1} at around 5 MPa (which is very nearly the critical pressure), then increases rapidly to approximately 600 J mol^{-1} at 15 MPa after which the pressure effect becomes small.

ACKNOWLEDGEMENT

The authors express appreciation to Brigham Young University for financial help in making the measurements.

REFERENCES

1 J.B. Ott, J.E. Purdy, B.J. Neely and R.A. Harris, J. Chem. Thermodyn., 20 (1988) 1079.

2 J.B. Ott, C.E. Stouffer, G.V. Cornett, B.F. Woodfield, R.C. Wirthlin, J.J. Christensen and U.K. Deiters, J. Chem. Thermodyn., 18 (1986) 1.

3 I.F. Hölscher, G.M. Schneider and J.B. Ott, Fluid Phase Equilibria, 27 (1986) 153.

4 J.B. Ott, I.F. Hölscher and G.M. Schneider, J. Chem. Thermodyn., 18 (1986) 815.