Thermochimica Acta, 50 (1981) 73—79
Elsevier Scientific Publishing Company, Amsterdam — in The Netherlands

THE EXCESS ENTHALPIES OF LIQUID FREON-22 + *N,N*-DIMETHYLACETAMIDE MIXTURES FROM 263 TO 363 K AT 5500 kPa *

J.J. CHRISTENSEN **, M.E. POST, T.A. MCFALL and R.M. IZATT **

Departments of Chemical Engineering and Chemistry, Brigham Young University, Provo, UT 84602 (U.S.A.)

(Received 9 February 1981)

ABSTRACT

The excess enthalpies, H^E, for liquid Freon-22 + *N,N*-dimethylacetamide mixtures were measured from 263 to 363 K at 5500 kPa using isothermal flow calorimeters with a reproducibility of better than 1%. At all temperatures the mixtures showed negative (exothermic) nonideal behavior of H^E. The H^E values are essentially invariant with temperature from 263 to 363 K, but H^E values become successively more negative for 343, 353, and 363 K. The Redlich—Kister equation was found to give a good fit of the H^E data over the entire composition and temperature ranges investigated.

INTRODUCTION

Recent activities in the development of solar-powered absorption and Rankine air conditioning technologies have established a need to obtain more detailed thermal characteristics of fluids used in these applications. Proper design of any refrigeration cycle is dependent upon the ability to model and predict accurately the thermodynamic properties of the working fluid. If the working fluid is a mixture, heat of mixing, H^E, data are one of the important thermodynamic properties to be determined. We have developed high temperature, high pressure flow calorimeters suitable for making H^E measurements over wide temperature and pressure ranges [1—3]. The calorimeters are suitable for measuring either endothermic or exothermic H^E values from 253 to 423 K and from 100 to 41 000 kPa (6000 psi). Energy effects from 0.15 to 30 J min^{-1} can be measured to an accuracy of ±1%. The units have been used to measure H^E values for several hydrocarbon—alcohol [4—9] and alcohol—alcohol [10] binary mixtures.

We have initiated a program to measure H^E for several refrigerant—absorbent fluid mixtures that are possible working fluids for advanced absorption cycles. The present work reports H^E for Freon-22 (monochlorodifluoromethane) and *N,N*-dimethylacetamide mixtures over the entire composition range at 263, 283, 303, 323, 343, 353 and 363 K and 5500 kPa.

---

* Contribution No. 246 from the Thermochemical Institute, Brigham Young University.
** To whom correspondence should be addressed.

EXPERIMENTAL

Calorimetric measurements

The two high pressure flow calorimeters that were used for the measurements and the experimental procedure are described in the literature [1,3]. One unit was used to measure H^E from 263 to 323 K (low temperature unit) while the other unit was used from 323 to 363 K (high temperature unit). Measurements made at 323 K using either calorimeter agreed within experimental error. All runs were made at 5500 kPa. This operating pressure was chosen to insure that the pure components and the mixtures were liquid in the calorimeter. All runs were made in the steady state (fixed composition) mode. The total flow rate was 0.0042 $cm^3\ s^{-1}$ at 263, 283, 303 and 323 K. The flow rate was reduced to 0.0039 $cm^3\ s^{-1}$ for the runs of 343, 353 and 363 K to decrease the rate of energy generation in the calorimeter.

Materials

The materials employed were Freon-22 (E.I. DuPont De Nemours and Co., 99+% pure) and *N,N*-dimethylacetamide (Aldrich Chemical Company, 99+% pure). The *N,N*-dimethylacetamide was stored in sealed bottles over approximately 50 cm^3 of Davison molecular sieves (3 nm effective pore size) and, just prior to use, was filtered through a Gelman Alpha Metrical filter (0.45 μm pore diameter) and degassed for 10 min in an ultrasonic bath. Further purification of either material is not necessary [11] since the other substances present in small amounts are expected to be sufficiently close in nature to the primary substance that H^E is not significantly affected. Flow rates measured in $cm^3\ s^{-1}$ were corrected to moles s^{-1} and to mole fractions using the densities of the two pure materials estimated as follows. A density of 1.2154 g cm^{-3} at 298.15 K and 5500 kPa for Freon-22 was obtained by interpolation of the data of Zander in ref. 12. A density of 0.9422 g cm^{-3} at 298.15 K and 5500 kPa for *N,N*-dimethylacetamide was obtained by making an isothermal compressibility correction to the density at 298.15 K and 101 kPa [13].

RESULTS AND DISCUSSION

Values of the mole fraction, x, and experimental excess enthalpies, H^E (expt.), are given in Table 1 for the seven temperatures studied. The values of the coefficients, C_i, in the equation

$$H^E\ (\text{J mole}^{-1}) = x(1-x)\sum_{i=0}^{N} C_i\,(1-2x)^i \qquad (1)$$

were found by a least squares curve-fitting program and are given in Table 2 together with standard deviations, σ. Values of H^E (calc.) reported in Table 1 were calculated from eqn. (1). The numerical values of H^E(expt.) and

TABLE 1

Experimental and calculated excess enthalpies, H^E, at 5500 kPa and various temperatures for (x)Freon-22 + (1 — x)*N*,*N*-dimethylacetamide

x	$-H^E$ (J mole^{-1})		x	$-H^E$ (J mole^{-1})	
	Expt.	Calc.		Expt.	Calc.
T = 263.15 K					
0.0258	161	208	0.5944	3552	3534
0.1015	732	759	0.6232	3554	3526
0.1746	1276	1262	0.6516	3474	3479
0.2452	1786	1755	0.6795	3396	3396
0.3135	2259	2237	0.7070	3298	3276
0.3795	2674	2683	0.7341	3096	3119
0.4434	3043	3063	0.7872	2738	2706
0.5052	3320	3346	0.8387	2166	2178
0.5354	3420	3443	0.8887	1575	1563
0.5651	3499	3506	0.9373	850	897
T = 283.15 K					
0.0258	281	236	0.5944	3560	3579
0.1015	831	854	0.6232	3563	3566
0.1746	1425	1399	0.6795	3449	3435
0.2452	1866	1907	0.7341	3175	3165
0.3135	2413	2382	0.7872	2725	2763
0.3795	2791	2807	0.8387	2273	2246
0.4434	3152	3161	0.8887	1629	1634
0.5052	3460	3418	0.9373	961	955
0.5651	3545	3558			
T = 303.15 K					
0.0258	259	223	0.5651	3493	3503
0.0640	518	535	0.6232	3505	3506
0.1015	809	826	0.6516	3453	3456
0.1384	1083	1103	0.6795	3377	3373
0.1746	1364	1371	0.7070	3265	3256
0.2102	1639	1630	0.7341	3128	3107
0.2452	1905	1882	0.7609	2925	2925
0.3135	2392	2357	0.7872	2707	2714
0.3795	2790	2778	0.8131	2492	2474
0.4117	2931	2962	0.8387	2213	2208
0.4434	3134	3124	0.8638	1933	1920
0.4745	3226	3261	0.8887	1585	1610
0.5052	3362	3371	0.9131	1277	1285
0.5354	3461	3453	0.9373	923	944
T = 323.15 K					
0.0258	216	229	0.5651	3665	3629
0.0640	541	552	0.5944	3665	3650
0.1015	850	857	0.6232	3622	3638
0.1384	1149	1149	0.6516	3596	3593
0.1746	1440	1430	0.6795	3531	3514
0.2452	1969	1964	0.7070	3396	3400
0.2796	2237	2215	0.7341	3231	3254
0.3135	2455	2455	0.7609	3073	3074
0.3467	2682	2679	0.7872	2883	2863
0.3795	2867	2886	0.8131	2616	2622
0.4117	3083	3074	0.8387	2333	2352
0.4434	3227	3239	0.8638	2054	2057
0.4745	3346	3378	0.8887	1747	1736
0.5052	3471	3492	0.9131	1410	1395
0.5354	3589	3576	0.9373	1020	1033

TABLE 1 (*continued*)

x	$-H^E$ (J mole^{-1})		x	$-H^E$ (J mole^{-1})	
	Expt.	Calc.		Expt.	Calc.
T = 343.15 K					
0.0891	767	770	0.5944	3785	3800
0.1262	1080	1082	0.6040	3828	3800
0.1626	1368	1383	0.6327	3782	3779
0.1865	1589	1579	0.6516	3746	3746
0.2452	2053	2049	0.6609	3706	3724
0.3022	2493	2484	0.6795	3680	3669
0.3577	2865	2873	0.6887	3636	3636
0.4117	3235	3207	0.7070	3564	3558
0.4434	3374	3377	0.7252	3475	3464
0.4642	3487	3475	0.7959	2969	2944
0.4950	3576	3600	0.8387	2475	2504
0.5153	3666	3667	0.8638	2229	2201
0.5354	3700	3721	0.8804	1961	1983
0.5454	3731	3743	0.9212	1373	1385
0.5651	3778	3777	0.9452	995	995
T = 353.15 K					
0.0258	240	235	0.5651	3913	3879
0.1015	915	907	0.5944	3907	3906
0.1746	1521	1536	0.6232	3888	3899
0.2452	2118	2120	0.6516	3870	3860
0.3135	2665	2647	0.6795	3789	3786
0.3795	3095	3102	0.7070	3679	3679
0.4117	3295	3297	0.7341	3503	3536
0.4434	3501	3469	0.7872	3170	3148
0.4745	3590	3614	0.8387	2627	2626
0.5052	3708	3732	0.8887	1989	1975
0.5354	3813	3821	0.9373	1179	1202
T = 363.15 K					
0.0258	271	246	0.5651	4143	4158
0.1015	989	975	0.5944	4219	4200
0.1746	1642	1664	0.6232	4226	4211
0.2452	2287	2294	0.6795	4121	4136
0.3135	2873	2852	0.7341	3900	3923
0.3795	3309	3325	0.7872	3539	3561
0.4434	3690	3707	0.8387	3047	3039
0.4745	3857	3860	0.8887	2379	2346
0.5052	4002	3987	0.9373	1463	1470
0.5354	4112	4087			

H^E(calc.) are estimated to be accurate to within ±2%.

Figure 1 is a plot of H^E vs. mole fraction of Freon-22 at the temperatures of 303, 323, 353, and 363 K. Values of H^E at 263, 283 and 303 are essentially identical (Table 1) and only the curve for 303 K is given in Fig. 1. As shown in Table 1 and Fig. 1, all the H^E values are exothermic and large in magnitude. In Table 3 representative H^E values for different binary mixtures at $x = 0.5$ are compared. Positive H^E values are usually indicative of only

TABLE 2

Coefficients and standard deviation, σ, for least-squares representation of H^E for (x)Freon-22 + $(1-x)$*N*,*N*-dimethylacetamide by eqn. (1)

T (K)	C_0	C_1	C_2	C_3	σ (J mole^{-1})
263	−13 307	7731.0	2020.5	−4870.1	29.40
283	−13 602	6937.8	1059.1	−3896.1	31.95
303	−13 419	6629.3	1196.7	−3327.8	20.28
323	−13 899	6803.1	645.5	−2645.6	17.28
343	−14 473	6951.9	308.9	−1701.1	17.27
353	−14 859	7113.9	−243.6	−1206.8	20.38
363	−15 872	7753.0	−2302.9	916.9	22.33

physical interactions between the molecules in the mixture while negative H^E values usually indicate some degree of chemical interaction in the mixture. The large negative value of H^E for the Freon-22 + *N*,*N*-dimethylacetamide system indicates much stronger chemical interaction in this system than is found in any of the other systems in Table 3. This large negative H^E value most likely results from extensive hydrogen bonding between the Freon-22 hydrogen and the nitrogen on the acetamide. The hydrogen bonding is undoubtedy promoted by the presence of the electronegative fluorine and chlorine atoms in the Freon-22. Investigation of similar systems involving other Freons should allow correlations to be developed between H^E and the electronegativity of the Freon carbon atom.

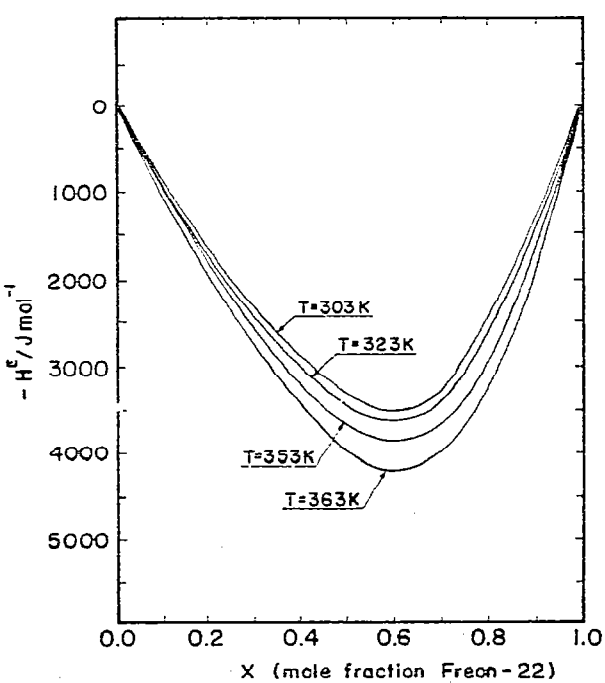

Fig. 1. Plot of H^E vs. x for mixtures of (x) Freon-22 + $(1-x)$ *N*,*N*-dimethylacetamide at 303, 323, 353, and 363 K.

TABLE 3

Representative H^E values at $x = 0.5$ for several binary systems at 298 K

Binary mixtures	H^E (J mole^{-1})
Cyclohexane + hexane [1]	210
n-Pentanol + decanol [10]	150
Ethane + hexanol [8]	350
Water + ethyl alcohol [15]	−140
Freon-22 + *N*,*N*-dimethylacetamide	−3350

The H^E values in Table 1 and Fig. 1 at a given mole fraction of Freon-22 are essentially invariant with temperature from 263 to 303 K. However, successively greater increases in $-H^E$ are seen for the temperatures 343, 353, and 363 K. This change in $-H^E$ with temperature indicates a corresponding change in the value of ΔC_p [C_p(mixture) − C_p(Freon-22) − C_p(*N*,*N*-dimethylacetamide)] for the mixing process from approximately zero in the 263—303 K range to an increasingly larger negative number in the 343—363 K range. This is in agreement with the statement in Hirschfelder et al. [14] that the heat capacity of a one-component system at constant pressure, C_p, becomes infinite at the critical point. The critical temperature and pressure of Freon-22 are 369.33 K and 4989 kPa, respectively. It will now be of interest to extend our measurement of H^E values for this system into the critical temperature range of Freon-22.

REFERENCES

1 J.J. Christensen, L.D. Hansen, D.J. Eatough and R.M. Izatt, Rev. Sci. Instrum., 47 (1976) 730.
2 J.J. Christensen, R.M. Izatt, D.J. Eatough and L.D. Hansen, J. Chem. Thermodyn., 10 (1978) 25.
3 J.J. Christensen, L.D. Hansen, R.M. Izatt, D.J. Eatough and R.M. Hart, Rev. Sci. Instrum., in press.
4 J.J. Christensen, B.E. Rossiter, T.K. O'Neill and R.W. Hanks, J. Chem. Thermodyn., 10 (1978) 829.
5 J.J. Christensen, R.M. Izatt, B.D. Stitt and R.W. Hanks, J. Chem. Thermodyn., 11 (1979) 261.
6 J.J. Christensen, R.M. Izatt, B.D. Stitt, R.W. Hanks and K.D. Williamson, J. Chem. Thermodyn., 11 (1979) 1029.
7 S.G. Collins, J.J. Christensen, R.M. Izatt and R.W. Hanks, J. Chem. Thermodyn., 12 (1980) 609.
8 T.A. McFall, M.E. Post, S.G. Collins, J.J. Christensen and R.M. Izatt, J. Chem. Thermodyn., 13 (1981) 41.
9 M.E. Post, T.A. McFall, J.J. Christensen and R.M. Izatt, J. Chem. Thermodyn., 13 (1981) 77.
10 H.H. Sun, J.J. Christenser., R.M. Izatt and R.W. Hanks, J. Chem. Thermodyn., 12 (1980) 95.
11 C.G. Savini, D.R. Winterhalter and H.C. Van Ness, J. Chem. Eng. Data, 10 (1965) 168.

12 E.I. DuPont De Nemours and Company, Freon Products Division, Wilmington, Delaware, Pamphlet X-36E.
13 R.C. Weast (Ed.), Handbook of Chemistry and Physics, CRC Press, Cleveland, Ohio, 56th edn., 1975—1976.
14 J.O. Hirschfelder, C.F. Curtiss and R.B. Bird, Molecular Theory of Gases and Liquids, John Wiley and Sons, New York, 1954, p. 367.
15 J.A. Larkin, J. Chem. Thermodyn., 7 (1975) 137.