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THE EXCESS ENTHALPIES OF LIQUID FREON-22 + *N,N*-DIMETHYLACETAMIDE MIXTURES FROM 373 TO 423 K AT 5.5 MPa *

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ABSTRACT

The excess enthalpies, H^E, for liquid Freon-22 + *N,N*-dimethylacetamide mixtures were measured from 373 to 423 K at 5.5 MPa using an isothermal flow calorimeter with a reproducibility of better than two percent. At all temperatures the mixtures showed negative (exothermic) non-ideal behavior of H^E. The H^E data were correlated with the Redlich–Kister equation over the entire composition and temperature ranges investigated except for those linear sections representing two phase behavior where a linear equation was used. The changes observed in the excess enthalpy with temperature are discussed in terms of hydrogen bonding between the two components and the behavior of the components near the critical point of Freon-22.

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 accurately predict 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 443 K and from 0.1 to 41 MPa (6000 psia). Energy effects from 0.15 to 30 J min^{-1} can be measured to an accuracy of ± 1%. The units

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have been used to determine H^E values for hydrocarbon + alcohol [4–9], alcohol + alcohol [10] and CO_2 + hydrocarbon [11–13] binary mixtures.

We have initiated a program to determine H^E for several refrigerant–absorbent fluid mixtures that are possible working fluids for advanced absorption cycles. Results for Freon-22 (monochlorodifluoromethane) + *N*,*N*-dimethylacetamide from 263 to 363 K at 5.5 MPa [14] and Freon-12 (dichlorodifluoromethane) + *N*,*N*-dimethylacetamide from 263 to 413 K at 4.33 to 4.53 MPa [15] have been reported earlier. The earlier results for Freon-22 indicated that the heat of mixing was beginning to behave in an unusual fashion as the temperature approached the critical temperature of Freon-22 at a constant pressure. The present work extends the previous measurements on the Freon-22 + *N*,*N*-dimethylacetamide system and reports H^E values over the entire composition range at 373, 383, 393, 403, 413 and 423 K and 5.5 MPa.

EXPERIMENTAL

Calorimetric measurements

The high temperature, high pressure flow calorimeter used for the measurements and the experimental procedure have been described [1,3]. All runs were made at 5.5 MPa. 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 0.00389 $cm^3\ s^{-1}$ for all runs. Previous results obtained with this calorimeter were reproducible to ±0.5% or better over most of the mole fraction range ($0.2 < x < 0.8$) [2]. Reproducibility of results in the present investigation was ±1 to ±2% with the uncertainty being due primarily to instability of the components near the critical point of the Freon.

Materials

The materials employed were Freon-22 (DuPont de Nemours, 99 + % pure) and *N*,*N*-dimethylacetamide (Aldrich, 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 [16] 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 mole s^{-1} and to mole fractions using the densities of the two pure materials estimated as described. A density of 1.2154 $g\ cm^{-3}$ at

298.15 K and 5.5 MPa for Freon-22 was obtained by interpolation of the data of Zander in ref. 17. A density of 0.9422 g cm^{-3} at 298.15 K and 5.5 MPa for *N*,*N*-dimethylacetamide was obtained by making an isothermal compressibility correction to the density at 298.15 K and 101 kPa [18].

TABLE 1

Experimental and calculated excess enthalpies, H^E, at 5.5 MPa 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.	Calcd.		Expt.	Calcd.
T = *373.15 K*			T = *393.15 K*		
0.0258	262	260	0.0258	480	374
0.1015	1053	1037	0.0766	1132	1143
0.1746	1802	1786	0.1262	1897	1916
0.2452	2459	2485	0.1746	2704	2674
0.3135	3100	3116	0.2220	3333	3405
0.3795	3656	3664	0.2682	4090	4096
0.4434	4135	4117	0.3135	4765	4742
0.5052	4483	4465	0.3578	5314	5338
0.5651	4701	4702	0.3578	5302	5338
0.6232	4836	4820	0.4010	6022	5879
0.6795	4806	4811	0.4434	6359	6368
0.7341	4649	4668	0.4848	6845	6801
0.7872	4370	4378	0.5254	7124	7182
0.8387	3898	3921	0.5651	7411	7510
0.8887	3269	3257	0.6040	7840	7786
0.9373	2330	2293	0.6422	7983	8011
0.9845	785	767	0.6795	8181	8180
			0.7161	8317	8290
T = *383.15 K*			0.7520	8369	8334
0.0258	172	328	0.7520	8306	8334
0.1015	1308	1342	0.7872	8318	8295
0.1746	2437	2364	0.8217	8157	8150
0.2452	3373	3355	0.8555	7778	7856
0.3135	4300	4287	0.8887	7411	7340
0.3795	5092	5134	0.9050	6345	6408
0.4434	5910	5879	0.9212	5304	5204
0.5052	6492	6505	0.9373	4021	4006
0.5651	6958	7001	0.9532	2781	2824
0.6232	7350	7357	0.9689	1613	1656
0.6795	7549	7566	0.9845	531	496
0.7341	7652	7620			
0.7872	7514	7510			
0.8387	7271	7222			
0.8887	6783	6722			
0.9373	5822	5883			

TABLE 1 (continued)

x	$-H^E$(J mole^{-1})	
	Expt.	Calcd.
T = *403.15 K*		
0.258	284	361
0.0766	1127	1112
0.1262	1907	1875
0.1746	2617	2625
0.2219	3354	3347
0.2682	4027	4030
0.3135	4640	4667
0.3577	5265	5254
0.3577	5268	5254
0.4010	5767	5792
0.4434	6300	6282
0.4848	6690	6721
0.5254	7128	7115
0.5651	7509	7460
0.6422	7967	7998
0.6795	8163	8177
0.7161	8282	8281
0.7520	8298	8290
0.7872	8183	8177
0.8217	7900	7904
0.8555	6461	6524
0.8887	5093	4907
0.9212	3335	3324
0.9532	1684	1765
0.9845	248	240
T = *413.15 K*		
0.0258	200	217
0.0766	1231	1309
0.1262	1893	1954
0.1746	2672	2659
0.2219	3406	3358
0.2682	4089	4037
0.3135	4629	4684
0.3577	5255	5288
0.4010	5891	5846
0.4434	6315	6351
0.4848	6750	6798
0.5254	7286	7185
0.5651	7504	7509
0.6040	7756	7769
0.6422	7951	7965
0.6795	8077	8096
0.6795	8098	8096
0.7161	8194	8166
0.7520	8183	8179
0.7520	8146	8179
0.7858	7740	7767
0.8217	6367	6317
0.8555	4903	4953
0.8887	3640	3613
0.9212	2335	2301
0.9532	974	1009
T = *423.15 K*		
0.0258	−1	8
0.0766	995	891
0.1262	1739	1769
0.1746	2565	2571
0.2219	3368	3307
0.2682	3991	3988
0.3135	4558	4617
0.3577	5114	5194
0.4010	5807	5723
0.4434	6203	6203
0.4848	6652	6631
0.5254	7035	7005
0.5651	7241	7321
0.6040	7633	7573
0.6422	7712	7756
0.6795	7872	7858
0.7161	7875	7871
0.7520	7265	7259
0.7872	6103	6082
0.8217	4921	4929
0.8555	3803	3799
0.8887	2635	2689
0.9212	1598	1602
0.9532	535	532
0.9689	39	7

TABLE 2

Coefficients and standard deviations, s, for least-squares representations of H^E [(x) Freon-22 + (1 − x) N,N-dimethylacetamide] by eqns. (1) and (2)

Equation (1)

T (K)	C_0	C_1	C_2	C_3	D_1	D_2	D_3	s (J mole^{-1})
373.15	−17759.7	−5305.6	4454.1		0.8587			21
383.15	−25825.7	−6470.5	7525.4		0.9788			66
393.15	−27797.6	−4836.4	2133.2	4008.5	0.8594			64
403.15	−27492.8	2377.9	−3498.0	6452.8	0.6269			55
413.15	−27796.8	20612.1	19626.7	−10185.2	−0.04294	−1.1589		59
423.15	−27106.3	46622.7	−19010.6		−1.0287	0.4828	0.5222	68

Equation (2)

T (K)	A_0	A_1	s (J mole^{-1})	Interval
393.15	−73705.4	74361.5	62	$0.892 < x < 0.984$
403.15	−48192.7	48707.1	192	$0.827 < x < 0.984$
413.15	−39488.1	40368.3	42	$0.782 < x < 0.974$
423.15	−32399.5	33431.7	25	$0.734 < x < 0.969$

RESULTS AND DISCUSSION

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

$$\frac{H^{E}}{(\mathrm{J\ mole^{-1}})}=\left[\frac{x(1-x)}{1+\sum_{n=1}^{B} D_n(1-2x)^n}\right]\sum_{n=0}^{A} C_n(1-2x)^n \qquad (1)$$

were found by a least-squares curve-fitting program and are given in Table 2 together with the standard deviation, s. Values of H^{E} (calcd.) reported in Table 1 were calculated from eqn. (1). The excess enthalpies vary linearly with mole fraction in the Freon-22-rich region (the only exceptions are the values obtained at 373.15 and 383.15 K) and have been fitted in this region to the equation

$$H^{\mathrm{E}}/(\mathrm{J\ mole^{-1}})=A_0+A_1x \qquad (2)$$

The values of the coefficients A_0 and A_1, the standard deviation, s, and the mole fraction intervals for the linear sections are also given in Table 2.

Figure 1 is a plot of H^{E} vs. mole fraction of Freon-22 at the temperatures of 303, 353, 373, 383, 393 and 423 K. The values at 303 and 353 K were taken from our earlier results [14]. As shown in Table 1 and Fig. 1, all the H^{E} values are negative and large in magnitude. The H^{E} values become progressively more negative as the temperature increases from 373 to 393 K with the maximum negative values of H^{E} occurring at higher Freon-22 mole fractions. Further increases in temperature from 393 to 423 K result in less negative values of H^{E} with the maximum negative values of H^{E} occurring at lower Freon-22 mole fractions. Also, at the higher temperatures of 393, 403, 413 and 423 K the H^{E} curves demonstrate a linear section in the Freon-22-rich region. In other systems, similar linear sections have been found to correspond to two-phase regions [11,12,19]. The beginning of the two-phase region becomes very pronounced at 423 K as indicated by the sharp break in the curve at $x \simeq 0.73$.

The observed changes in H^{E} with temperature are now examined in terms of the chemical interactions in the system and the changes in the fluid properties of Freon-22 near its critical point ($T_{\mathrm{c}} = 369.33$ K, $P_{\mathrm{c}} = 4.989$ MPa) [20]. The large negative values of H^{E} at temperatures below the critical temperature of Freon-22 indicate strong chemical interactions probably resulting from extensive hydrogen bonding between the Freon-22 hydrogen and the nitrogen on the acetamide. The hydrogen bonding is undoubtedly promoted by the presence of the electronegative fluorine and chlorine atoms in the Freon-22. The data reported earlier for this system over a temperature range of 263–363 K show large negative H^{E} values which remained fairly

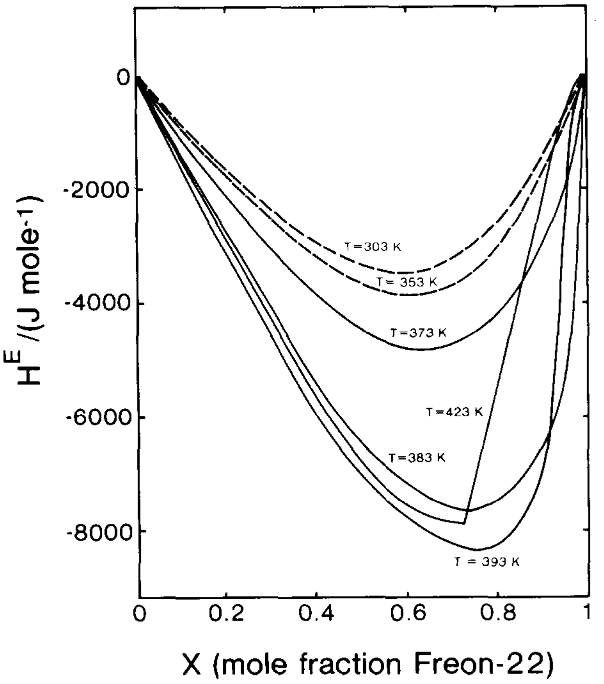

Fig. 1. Plot of H^E vs. x for mixtures of (x)Freon-22 + $(1-x)$ *N,N*-dimethylacetamide at 303 and 353 K (broken line, taken from ref. 14) and at 373, 383, 393 and 423 K (solid line, this work).

invariant in magnitude at a given concentration [14]. This is illustrated in Fig. 1 where the H^E values show a relatively small change with temperature in going from 303 to 353 K as compared with larger changes at the higher temperatures. To investigate the effect of hydrogen bonding, the excess enthalpies of Freon-12 (dichlorodifluoromethane) + *N,N*-dimethylacetamide were measured over a temperature range of 263–413 K [15]. The only difference between Freon-12 and Freon-22 is that Freon-12 has a chlorine atom in place of the Freon-22 hydrogen atom. Thus, the possibility of hydrogen bonding between Freon-12 and *N,N*-dimethylacetamide is eliminated. The H^E values at temperatures below the critical point of the Freon-12 are all positive indicating only physical interactions (van der Waal type) between the molecules in the mixture.

The observed H^E values at temperatures below the critical temperature of Freon-22 can be explained in terms of hydrogen bonding but it is necessary to look to other explanations for the behavior near the critical temperature of Freon-22. The increasingly larger negative H^E values observed from 373 to 393 K reaching a maximum negative value at 393 K and then becoming less negative as the temperature increases to 423 K can be examined in terms of the changes in the fluid properties of Freon-22 near its critical temperature. Similar behavior near the critical point has been observed for the Freon-12 + N,N-dimethylacetamide system and has been discussed in terms of the effect of the critical point on the physical properties of the various components in the mixture [15]. The change in H^E with temperature at constant pressure can be expressed as

$$\left(\frac{\partial H^E}{\partial T}\right)_p = \Delta C_p = C_p(\text{mixture}) - xC_p(\text{Freon-22}) \\ - (1-x)C_p(N,N\text{-dimethylacetamide}) \tag{3}$$

where C_p is the molar heat capacity at constant pressure. Large changes in the value of C_p (Freon-22) can be expected in the vicinity of the critical point of the Freon (the critical temperature of N,N-dimethylacetamide is far removed from the temperatures in this study). In fact, for a one-component system, C_p becomes infinite at the critical point [21,22]. Figure 2 shows how the value of C_p for CH_4 changes as a function of temperature for three pressures near the critical point. Figure 3 demonstrates how the pressures and temperatures corresponding to the maximum values of C_p as given in Fig. 2 fall on or near the line representing the extension of the vapor pressure curve beyond the critical point. It would be expected [looking at eqn. (3)] that if the magnitude of ΔC_p were primarily determined by the value

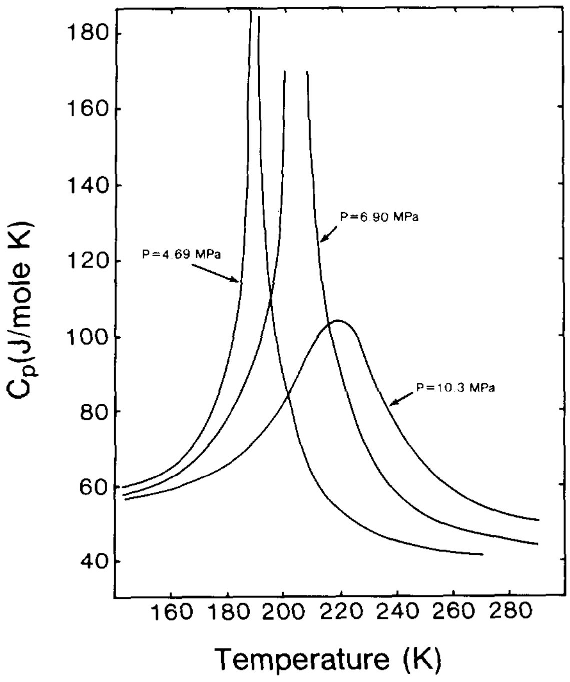

Fig. 2. Plot of C_p vs. temperature (K) for CH_4 at the supercritical pressures 4.69, 6.90 and 10.3 MPa. For CH_4, $T_c = 190.5$ K and $P_c = 4.64$ MPa. C_p data are taken from ref. 21.

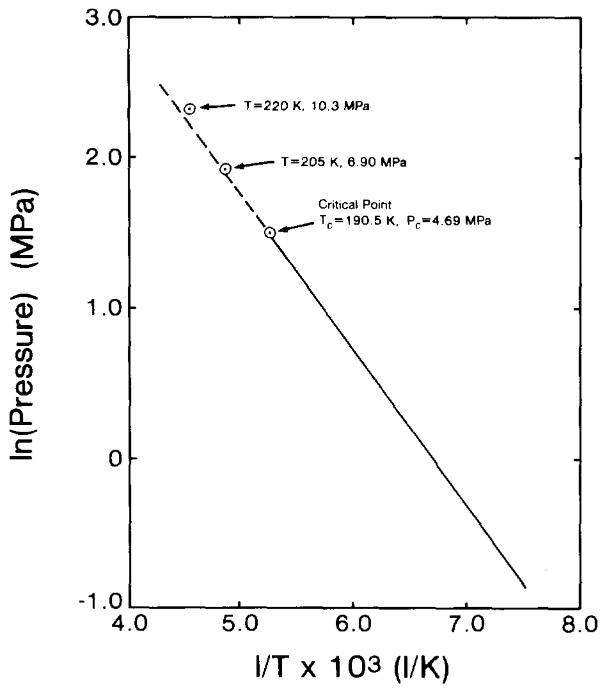

Fig. 3. Vapor pressure curve for CH_4 extrapolated beyond the critical point. Circles indicate temperatures and pressures corresponding to maximum values of C_p as determined from Fig. 2. Vapor pressure data were taken from ref. 21.

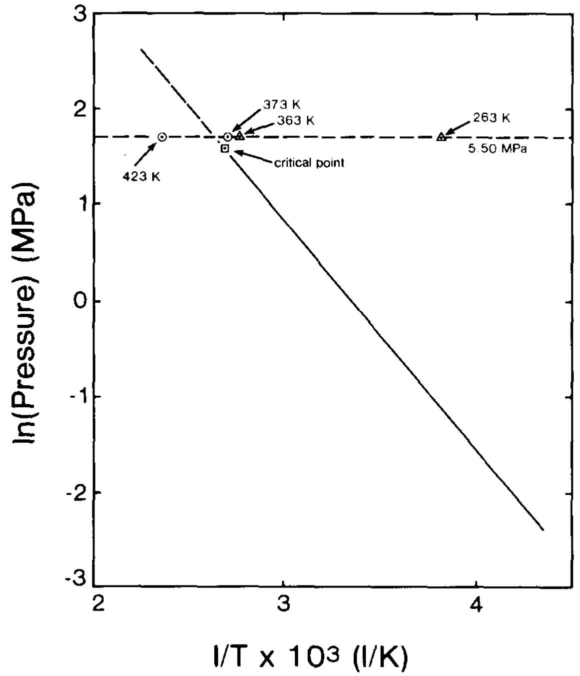

Fig. 4. Vapor pressure curve for Freon-22 extrapolated beyond the critical point. ○, This study; △, ref. 14. Vapor pressure data were taken from ref. 20.

of the C_p for Freon-12, then the maximum value of ΔC_p would occur for a given supercritical pressure near the line representing the extension of the vapor pressure curve beyond the critical point. Figure 4 is a plot of vapor pressure vs. temperature for Freon-22. It shows that the extrapolation of the vapor pressure curve passes through the temperature–pressure region where the measurements reported here were made. Thus, in the supercritical region, as one proceeds at constant pressure across the extension of the vapor pressure curve large changes in the value of C_p (also molar volume and thermal expansion coefficient) can be expected. The magnitude of these changes is related to the distance from the critical point as illustrated in Fig. 2. These changes in C_p of Freon-22 and thus in ΔC_p for the mixture could thus explain the observed behavior in H^E with temperature. Unfortunately, there are not enough data to quantitatively apply eqn. (3) to the Freon-22 + *N*,*N*-dimethylacetamide system.

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