Thermochimica Acta, 68 (1983) 223–232
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THE EXCESS ENTHALPIES OF LIQUID FREON-22 + 2,3-DIMETHYLBUTANE MIXTURES FROM 363 TO 423 K AT 5.5 MPa *

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(Received 29 March 1983)

ABSTRACT

The excess enthalpies, H^E, for liquid Freon-22 + 2,3-dimethylbutane mixtures were measured in the vicinity of the critical point of Freon-22. Measurements were made from 363 to 423 K at 5.5 MPa with an isothermal flow calorimeter with a reproducibility of better than 1%. Mixtures at 363 K show mainly moderate endothermic mixing with a very small region of exothermic mixing in the Freon-22 rich region. Mixtures at 383 K show very exothermic mixing with a minimum value of H^E (maximum exothermic mixing) in the Freon-22 rich region. Mixtures at 403 and 423 have an exothermic section in the 2,3-dimethylbutane rich region and an endothermic section in the Freon-22 rich region. The Redlich–Kister equation was found to give a good fit of the H^E data over the entire composition and temperature ranges investigated. The changes observed in H^E with temperature are discussed in terms of the behavior of the components near the critical point of Freon-22 and in terms of the chemical and physical bonding occurring between the components. The observed behavior was found to be consistent with previously measured H^E data obtained as a function of temperature near the critical point of one of the components.

INTRODUCTION

We have developed 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 positive or negative H^E values from 253 to 443 K and from 0.1 to 41 MPa (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], alcohol + alcohol [10], and CO_2 + hydrocarbon [11–13] binary mixtures.

We have initiated a program to measure H^E for several refrigerant-absorbent fluid mixtures that are possible working fluids for advanced absorp-

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* Contribution No. 310 from the Thermochemical Institute.

tion cycles. Results for Freon-22 (monochlorodifluoromethane) + N,N-dimethylacetamide from 263 to 423 K at 5.5 MPa [14,15] and Freon-12 (dichlorodifluoromethane) + N,N-dimethylacetamide from 263 to 413 K at 4.33 to 4.53 MPa [16] have already been reported. The present work reports H^E values for Freon-22 + 2,3-dimethylbutane over the entire composition range at 363, 383, 403, 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 are described in the literature [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 0.0030 $cm^3\ s^{-1}$ 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% mainly due to instability of the components near the critical point of the Freon.

Materials

The materials employed were Freon-22 (E.I. DuPont de Nemours&Co., 99 + % pure) and 2,3-dimethylbutane (Phillips Petroleum Company, 99 + % pure). The 2,3-dimethylbutane 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 [17] 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 5.5 MPa for Freon-22 was obtained by interpolation of the data of Zander in E.I. DuPont de Nemours Pamphlet X-36E [18]. A density of 0.6627 g cm^{-3} at 298.15 K and 5.5 MPa for 2,3-dimethylbutane was obtained by making an isothermal compressibility correction to the density at 298.15 K and 101 kPa [19].

RESULTS AND DISCUSSION

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

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

were found by a least squared curve-fitting program and are given in Table 2 together with standard deviations, s. Values of H^E (calcd.) reported in Table 1 were calculated from eqn. (1).

Figure 1 is a plot of H^E vs. mole fraction of Freon-22 at the temperatures of 363, 383, 403, and 423 K. As shown in Table 1 and Fig. 1 the H^E values follow the characteristic pattern which has been observed before for binary mixtures near the critical point of one of the components [11–16]. The critical temperature and pressure of Freon-22 are 369.15 K and 4.98 MPa, respectively. The H^E values at constant pressure rapidly become more negative as the temperature increases from below to above the critical temperature of Freon-22 (363–383 K). With further increases in temperature above the critical temperature (383–423) the values of H^E progressively become less negative, with the maximum negative values occurring at lower Freon-22 mole fractions.

The small positive values of H^E measured at 363 K are characteristic of

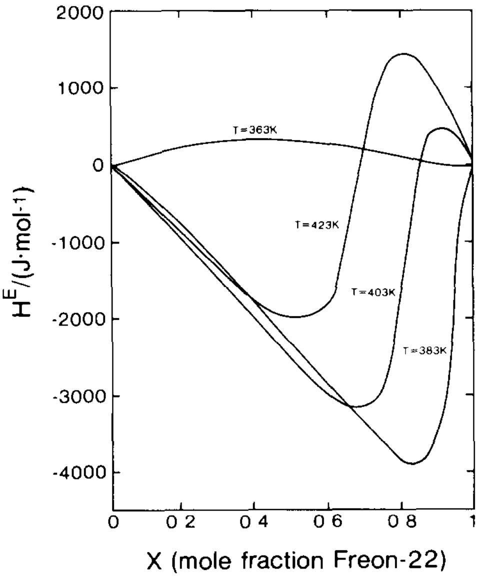

Fig. 1. Plot of H^E against x for mixtures of (x)Freon-22 + $(1-x)$2,3-dimethylbutane at 363, 383, 403, and 423 K.

TABLE 1

Experimental and calculated excess enthalpies, H^E, at 5.5 MPa and various temperatures for (x)Freon-22 + $(1-x)$2,3-dimethylbutane

x	H^E(J mole^{-1})		x	H^E(J mole^{-1})	
	Exptl.	Calcd.		Exptl.	Calcd.
$T = 363.15$ K					
0.0360	18.3	25.5	0.5696	294	290
0.0708	60.0	62.5	0.6089	272	269
0.1045	99.1	103.8	0.6463	247	244
0.1371	148	145	0.6821	213	216
0.1688	186	183	0.7162	183	186
0.1995	223	217	0.7489	147	153
0.2293	253	245	0.7801	117	120
0.2863	284	288	0.8100	89.4	87.2
0.2863	287	288	0.8388	54.8	55.7
0.3401	302	313	0.8663	31.5	27.4
0.3910	319	325	0.8928	6.7	3.6
0.4392	324	326	0.9182	−14.8	−13.7
0.4392	332	326	0.9427	−22.8	−23.1
0.4849	322	320	0.9663	−27.2	−22.6
0.5283	309	307	0.9890	−8.2	−10.7
$T = 383.15$ K					
0.0360	−62.3	−77.2	0.7801	−3774	−3784
0.1045	−391	−349	0.8100	−3912	−3880
0.1688	−634	−650	0.8100	−3903	−3880
0.2293	−970	−949	0.8245	−3853	−3908
0.2863	−1204	−1238	0.8245	−3846	−3908
0.3401	−1535	−1515	0.8388	−3947	−3917
0.3910	−1764	−1781	0.8388	−3902	−3917
0.4392	−2010	−2034	0.8527	−3851	−3901
0.4849	−2246	−2276	0.8663	−3929	−3851
0.5283	−2566	−2506	0.8928	−3605	−3601
0.5696	−2770	−2726	0.9182	−3262	−3034
0.6089	−2970	−2936	0.9427	−1900	−2018
0.6463	−3075	−3135	0.9663	−595	−735
0.6821	−3332	−3322	0.9777	−247	−238
0.7162	−3473	−3495	0.9890	−85.4	18.2
0.7489	−3629	−3652			
$T = 403.15$ K					
0.0360	−92.9	−142	0.7162	−3129	−3127
0.1045	−452	−448	0.7489	−2878	−2822
0.1688	−792	−772	0.7647	−2613	−2546
0.2293	−1118	−1101	0.7801	−2019	−2179
0.2863	−1406	−1421	0.7952	−1696	−1732
0.3401	−1696	−1723	0.8100	−1166	−1238
0.3910	−1981	−2002	0.8245	−624	−746
0.4392	−2284	−2254	0.8388	−220	−304
0.4849	−2512	−2482	0.8663	250	287

TABLE 1 (continued)

x	H^E(J mole^{-1})		x	H^E(J mole^{-1})	
	Exptl.	Calcd.		Exptl.	Calcd.
0.5283	−2690	−2686	0.8928	428	503
0.5696	−2884	−2868	0.9182	461	485
0.6089	−3024	−3025	0.9427	403	365
0.6089	−3029	−3025	0.9663	272	215
0.6463	−3163	−3145	0.9890	133	67.9
0.6821	−3188	−3200			
$T = 423.15$ K					
0.0360	−156	−160	0.6821	−68.4	−96.5
0.1045	−477	−482	0.7162	758	687
0.1688	−807	−790	0.7489	1220	1213
0.2293	−1062	−1072	0.7801	1399	1449
0.2863	−1330	−1322	0.8100	1451	1480
0.3401	−1507	−1542	0.8388	1381	1388
0.3910	−1756	−1733	0.8663	1231	1232
0.4392	−1895	−1889	0.8928	1064	1041
0.4849	−2007	−1999	0.9182	838	831
0.5283	−2017	−2028	0.9427	607	606
0.5696	−1922	−1915	0.9663	375	371
0.6089	−1653	−1568	0.9890	82.1	126
0.6463	−857	−933			

H^E values for systems exhibiting only physical interactions between the two components [15,16]. The large negative values of H^E observed at 383, 403, and 423 K can be explained in terms of the changes in the fluid properties of Freon-22 near its critical point. Similar behavior has been observed and discussed in terms of the effect of the critical point on the heat capacity, C_p, of the various components in the mixture [11–16]. The changes in H^E with temperature at constant pressure can be expressed as

$$\left(\frac{\partial H^E}{\partial T}\right)_p = \Delta C_p = C_p(\text{mixture}) - xC_p(\text{Freon-22}) - (1-x)C_p(\text{2,3-dimethylbutane}) \tag{2}$$

The heat capacity at constant pressure for a one component system near the critical point exhibits a maximum as a function of temperature and this maximum becomes larger and sharper as the critical pressure and temperature are approached. Thus if the magnitude of ΔC_p were primarily determined by the value of C_p(Freon-22), then the large negative values of H^E at 383, 403, and 423 K can be explained in terms of the large changes in the value of C_p(Freon-22) occurring as the critical point of Freon-22 is ap-

TABLE 2

Coefficients and standard deviations, s, for least-squares representation of H^{E} $\{(x)$Freon-22 + $(1-x)$2,3-dimethylbutane$\}$ by eqn. (1)

T (K)	C_0	C_1	C_2	C_3	C_4	D_1	D_2	D_3	D_4	s (J mole^{-1})
363	1264.4	520.7	−303.9	272.7	−1307.1					5
383	−9422.8	−409.8	9492.7			1.171	−0.716	−0.924		74
403	−10216.8	−14564.4				2.355	1.495	0.580	1.160	62
423	−8081.2	−24702.1	−12145.5	−6038.3	13588.6	3.329	4.394			40

proached. The appearance of an increasingly positive value of H^E at 403 and 423 K in the Freon-22 rich region and the decreasing negative values of H^E accompanied by a shift in the maximum of these values toward the 2,3-dimethylbutane rich region can also be explained in terms of changes in the heat capacities in eqn. (1). Figure 2 is a plot of the vapor pressure vs. temperature for Freon-22 showing the extrapolation of the vapor pressure curve through the region where the H^E measurements were made. Also shown is the critical point of 2,3-dimethylbutane. 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 (Freon) and H^E can be expected as discussed above. The magnitude of these changes is related to the distance from the critical point [15]. As the temperature increases from 363 to 383 K the values of H^E decrease (becoming more negative), indicating that C_p (Freon-22) has passed through a maximum. Further increases in temperature from 382 to 423 K result in the values of H^E increasing (becoming more positive), indicating that C_p(mixture) has become the dominant quantity in eqn. (1). If the temperature were to continue to increase to beyond the critical temperature of 2,3-dimethylbutane, C_p(2,3-dimethylbutane) should also pass through a maximum resulting in the values of H^E becoming more negative as they did near the critical temperature of the Freon-22. These changes are consistent with results reported by Mosedale and Wormald [21] for the (argon + methane) system. They presented a graph of H^E against temperature which showed how, as the temperature increased

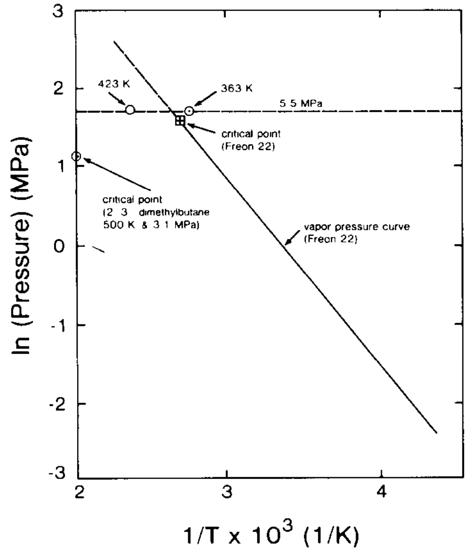

Fig. 2. Vapor pressure curve for Freon-22 extrapolated beyond the critical point. Circles correspond to range of temperatures at which experimental runs were made in the present study. Vapor pressure data were taken from ref. 20.

TABLE 3

Representative H^E values for three binary mixtures at temperatures removed and near the critical temperatures of the components

System	Type of interaction between components in mixture	Typical maximum negative or positive values of H^E	
		$T < T_c$	T near T_c
Freon-22(CHF_2Cl)+ *N,N*-dimethylacetamide ($CH_3C(O)N(CH_3)_2$)	Chemical (hydrogen bonding)	−3500 to −4000	−8000
Freon-12(CF_2Cl_2)+ *N,N*-dimethylacetamide	Physical	0 to 200	−5000
Freon-22+ 2,3-dimethylbutane ($CH_3CH(CH_3)CH(CH_3)CH_3$)	Physical	300	−4000

through the critical temperatures of argon and methane, H^E first decreased (near the critical temperature of argon), then increased from a negative to a positive value, then decreased again (near the critical temperature of methane) returning near to its original value. A more detailed analysis of the effect of temperature on ΔC_p and on H^E for the present system will have to wait until the heat capacities of the pure components and the mixture can be measured.

To investigate the effect of chemical and physical bonding in the mixture on the values of H^E near the critical point we have also measured H^E values for Freon-22 + *N,N*-dimethylacetamide [14,15] and Freon-12 + *N,N*-dimethylacetamide [16]. These two systems together with the present system are listed in Table 3 with respect to their chemical structure, type of bonding, and typical and maximum values of H^E as a function of temperature. As seen from the structures given in Table 3, there is the possibility of chemical interaction (hydrogen bonding) between Freon-22 and *N,N*-dimethylacetamide but not between either Freon-12 and *N,N*-dimethylacetamide or Freon-22 and 2,3-dimethylbutane. The observed maximum values (either maximum negative or maximum positive) of H^E at temperatures below the critical temperature of Freon-22 and Freon-12 given in Table 3 are typical for chemical bonding (Freon-22 + *N,N*-dimethylacetamide) and for physical bonding (Freon-12 + *N,N*-dimethylacetamide and Freon-22 + 2,3-dimethylbutane). It can also be seen that the maximum values of H^E near the critical points are essentially the same for the two systems that exhibit physical bonding and differ from the value for the system which exhibits chemical bonding by a quantity equal to the typical value of H^E at a temperature less than T_c(H^E value for chemical bonding). Thus the observed changes of H^E values with temperature near the critical temperature of one of the components are the same for the three systems and seem to be independent of whether chemical or physical interactions are predominant in the mixture. Also the value of H^E seems to exhibit approximately the same change in direction and amount as indicated by the three systems given in Table 3.

ACKNOWLEDGEMENT

This work was funded by U.S. Department of Energy Contract No. DE-AC02-82ER13024 and the American Chemical Society Petroleum Research Fund.

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