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Note

THE CALCIUM CHLORIDE—ETHANOL SYSTEM

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Compounds of $CaCl_2$ coordinated with ammonia, water, and alcohol have been proposed for use in solar energy concepts [1—3]. The ammoniates and hydrates of $CaCl_2$ are well characterized, but the same level of knowledge does not exist for coordination compounds formed with alcohol. This paper reports recent work on the $CaCl_2$—C_2H_5OH system.

Information on the $CaCl_2$—C_2H_5OH system is scant and of uncertain quality. Gerhold and Kahovec [4] have interpreted Raman spectra in terms of two compounds, $CaCl_2 \cdot C_2H_5OH$ and $CaCl_2 \cdot 3\ C_2H_5OH$. Parker et al. [5] have reported heats of formation for $CaCl_2 \cdot 3\ C_2H_5OH$ and $CaCl_2 \cdot 4\ C_2H_5OH$. It is noteworthy that a singly coordinated compound in the methanol system, $CaCl_2 \cdot CH_3OH$, was found not to exist [1], and that compounds triply coordinated with NH_3, H_2O and CH_3OH do not exist. Therefore, there is reason to suspect the reported existence of $CaCl_2 \cdot C_2H_5OH$ [4] and $CaCl_2 \cdot 3\ C_2H_5OH$ [4,5].

This work has focused on resolving some of the uncertainties in the $CaCl_2$—C_2H_5OH system, elucidating general features of the $CaCl_2$—C_2H_5OH phase diagram and determining the enthalpies of formation for ethanolates. Decomposition pressure measurements on several different compositions in the $CaCl_2$—C_2H_5OH system were made over the temperature range 298—360 K. From the pressure—temperature measurements the existence of $CaCl_2 \cdot nC_2H_5OH$ phases were inferred, and the enthalpies of decomposition and formation determined.

EXPERIMENTAL

The samples used in this study were prepared from $CaCl_2 \cdot 2\ H_2O$ (analytical reagent from Ventron Corporation) and ethanol (Baker analyzed reagent). Anhydrous $CaCl_2$ was prepared by heating the dihydrate in a vacuum oven for 24 h at 423 K. An X-ray powder diffraction analysis of the dried $CaCl_2$ showed only anhydrous $CaCl_2$ present. A known amount of anhydrous $CaCl_2$ was placed in a flask and allowed to react with ethanol vapors derived from a pool of ethanol held in a graduated cylinder. The overall sample composition was calculated from knowing the initial amount of anhydrous $CaCl_2$ and measuring the decrease in the ethanol level in the cylinder. The uncertainty in the measured ethanol volume was about 1 ml.

This uncertainty translated to a compositional uncertainty of ±0.1 mole of C_2H_5OH per mole of $CaCl_2$. Once the desired salt composition was attained, the ethanol pool was valved off from the system, and pressure measurements initiated.

Pressure measurements were made with a capacitance manometer (Datametrics, barocel electronic manometer). The sample temperature was concontrolled by placing the flask containing the sample into a controlled, constant-temperature oil bath which was held constant to within ±0.1 K. The temperature was measured by a thermocouple embedded in the salt. The entire apparatus, except for the flask in the oil bath, was heated to 340 K by heating tapes and heat lamps to prevent ethanol condensation.

RESULTS AND DISCUSSION

A variety of sample compositions were prepared to elucidate the features of the $CaCl_2$—C_2H_5OH system. Decomposition pressures as a function of temperature were measured for eight different compositions: $CaCl_2 \cdot nC_2H_5OH$, where $n = 0.7$, 1.7, 1.9, 2.7, 3.4, 3.8, 4.0 and 5.2. The experi-

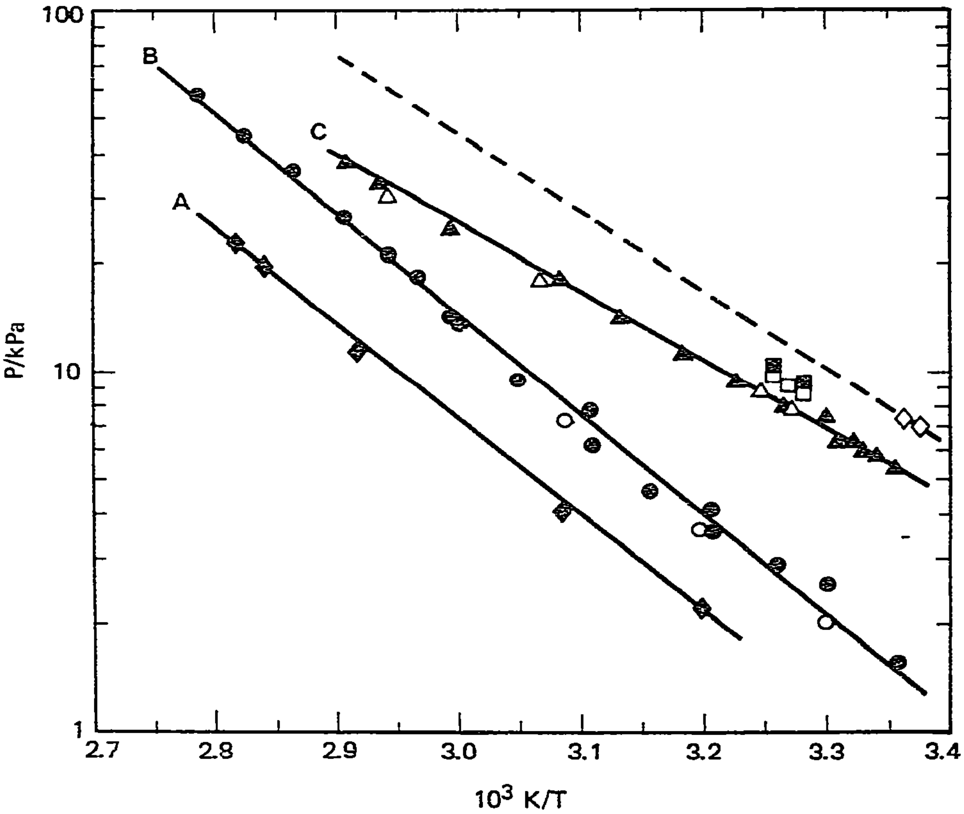

Fig. 1. Decomposition pressure measurements for $CaCl_2 \cdot nC_2H_5OH$. A, $CaCl_2 \cdot C_2H_5OH$; B, $CaCl_2 \cdot 2\ C_2H_5OH$; C, $CaCl_2 \cdot mC_2H_5OH$, ◆, $n = 0.7$; ●, $n = 1.7$; ○, $n = 1.9$; ▲, $n = 2.7$; △, $n = 3.4$; □, $n = 3.8$; ■, $n = 4.0$; ◇, $n = 5.2$; - - - - - -, vapor pressure of ethanol.

TABLE 1

Experimental pressure—temperature data

T (K)	P (kPa)	T (K)	P (kPa)
$CaCl_2 \cdot 0.7\ C_2H_5OH$		$CaCl_2 \cdot 2.7\ C_2H_5OH$	
313	2.28	298	5.36
324	4.00	299	5.75
343	11.5	299	5.68
352	19.4	300	6.08
355	22.7	301	6.27
$CaCl_2 \cdot 1.7\ C_2H_5OH$		302	6.35
298	1.69	303	7.51
303	2.57	304	7.51
307	2.96	306	8.01
312	3.65	310	9.36
312	4.19	314	11.3
317	4.69	319	14.3
322	7.83	324	17.8
322	6.39	334	25.5
328	9.33	341	33.5
333	13.4	344	38.8
334	13.8	$CaCl_2 \cdot 3.4\ C_2H_5OH$	
337	18.7	305	7.96
340	21.1	308	8.89
344	27.0	326	18.2
349	35.6	340	31.2
354	45.1	$CaCl_2 \cdot 3.8\ C_2H_5OH$	
359	58.9	305	8.64
$CaCl_2 \cdot 1.9\ C_2H_5OH$		306	9.27
303	2.08	307	9.53
313	3.69	$CaCl_2 \cdot 4\ C_2H_5OH$	
324	7.47	305	9.13
		306	9.73
		$CaCl_2 \cdot 5.2\ C_2H_5OH$	
		296	6.95
		297	7.21

mental pressure—temperature measurements are given in Table 1 and plotted in Fig. 1. Curve A in Fig. 1 is attributed to the reaction

$$CaCl_2 \cdot C_2H_5OH(s) = CaCl_2(s) + C_2H_5OH(g) \tag{1}$$

and the pressure data were fitted to the equation $\ln(P/\mathrm{kPa}) = 20.4 \pm 0.5 - (61.3 \pm 1.4)10^2\,(T/\mathrm{K})^{-1}$ by the method of least squares, where the uncertainties are standard deviations. Evidence for the existence of $CaCl_2 \cdot C_2H_5OH$ stems from the fact that different pressure—temperature curves were obtained for $CaCl_2 \cdot 0.7\ C_2H_5OH$ and $CaCl_2 \cdot 1.7\ C_2H_5OH$ (cf. Fig. 1).

Similarly, $CaCl_2 \cdot 2\ C_2H_5OH$ is shown to exist due to the difference in pressure—temperature curves for $CaCl_2 \cdot 1.7\ C_2H_5OH$ and $CaCl_2 \cdot 1.9\ C_2H_5OH$, and $CaCl_2 \cdot 2.7\ C_2H_5OH$. Curve B in Fig. 1 represents the equilibrium reaction

$$CaCl_2 \cdot 2\ C_2H_5OH(s) = CaCl_2 \cdot C_2H_5OH(s) + C_2H_5OH(g) \qquad (2)$$

The pressure—temperature relationship for this reaction is given by $\ln(P/\mathrm{kPa}) = 21.6 \pm 0.5 - (63.2 \pm 1.3)10^2\ (T/\mathrm{K})^{-1}$.

The superposition of decomposition pressures for compositions $CaCl_2 \cdot 2.7\ C_2H_5OH$ and $CaCl_2 \cdot 3.4\ C_2H_5OH$ (curve c in Fig. 1) presents evidence for the non-existence of $CaCl_2 \cdot 3\ C_2H_5OH$ over the temperature range in this study. If the $CaCl_2 \cdot 3\ C_2H_5OH$ were stable, one would have observed different pressure—temperature curves for each sample. Since liquid was observed to be present in these samples, curve C is taken to represent the equilibrium between $CaCl_2 \cdot 2\ C_2H_5OH$ and a solution of the liquidus composition

$$CaCl_2 \cdot m\ C_2H_5OH\ (liq) = CaCl_2 \cdot 2\ C_2H_5OH(s) + (m - 2)C_2H_5OH(g) \qquad (3)$$

where $CaCl_2 \cdot mC_2H_5OH(liq)$ is the solution of the liquidus composition and $m > 3.4$.

Vapor pressure measurements were extended to compositions of higher C_2H_5OH levels, namely $CaCl_2 \cdot nC_2H_5OH$, where $n = 3.8$, 4.0, and 5.2; the results are in excellent agreement with previous measurements of vapor pressures of ethanolic solutions of calcium chloride [6,7]. The pressures appeared to vary with composition; as the C_2H_5OH content increased, the vapor pressure increased. This behavior suggests that these compositions were in the single phase liquid solution region. However, visual observation revealed the presence of a solid in the bottom of the container. The pressure—composition behavior is not consistent with this observation of two phases; reasons for this discrepancy are not readily apparent.

To summarize, the pressure—temperature curves have been used to define the general features of the $CaCl_2$—C_2H_5OH phase diagram. At the temperatures of this study (i.e., 298—359 K) only two compounds exist, $CaCl_2 \cdot C_2H_5OH$ and $CaCl_2 \cdot 2\ C_2H_5OH$. Contrary to previously reported studies [4,5], no evidence was found to support the existence of $CaCl_2 \cdot 3\ C_2H_5OH$ and $CaCl_2 \cdot 4\ C_2H_5OH$. However, one cannot discount the possibility that these and other compounds are stable at temperatures other than those used in this study.

The enthalpies of decomposition for reactions (1) and (2) have been derived by the second-law method and are 51.0 ± 1.2 kJ and 52.5 ± 1.4 kJ, respectively, per mole of C_2H_5OH. It is assumed that the enthalpy at 298.15 K is equivalent to the uncorrected second-law value. The magnitude of the enthalpy correction from the mean experimental temperature to 298.15 K has been shown to be negligible over such small temperature differences [8]. Enthalpies of formation for $CaCl_2 \cdot C_2H_5OH$ and $CaCl_2 \cdot 2\ C_2H_5OH$ were calculated by appropriately combining the second-law enthalpies of decomposition with the enthalpies of formation for solid $CaCl_2$ [9] (—795.8 kJ) and gaseous C_2H_5OH [10] (—234.8 kJ). Enthalpies of formation for $CaCl_2 \cdot C_2H_5OH$ and $CaCl_2 \cdot 2\ C_2H_5OH$ were calculated to be —1082 and —1369 kJ mole^{-1}, respectively. The latter quantity compares favorably with the value determined recently by solution calorimetry, —1394 kJ mole^{-1} [11]. No thermodynamic data have been previously reported for the $CaCl_2 \cdot C_2H_5OH$ compound.

SUMMARY

Decomposition pressure measurements have been carried out on eight different compositions in the $CaCl_2$—C_2H_5OH system. The resulting data suggest that only two compounds exist at temperatures of 298—359 K, $CaCl_2 \cdot C_2H_5OH$ and $CaCl_2 \cdot 2\,C_2H_5OH$. Enthalpies of formation for these compounds were determined to be —1082 and —1369 kJ mole^{-1} by a second-law analysis of the data.

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