

Figure 1. Solubility of hydrogen in α -methylstyrene at 1 atm pressure.

The experimental solubilities are summarized in Table II. The average of the four to six measurements at each temperature is plotted in Figure 1.

The points do not show a pronounced deviation from a linear solubility-temperature dependency. Assuming linearity, a straight-line relationship through the data points in Figure 1 was evaluated by minimizing the sum of the squares of the deviations. The relationship is

$$C_{\text{sat}} = (2.26 + 0.0145t) \times 10^{-6}, \text{ g-mol/cm}^3 \quad (1) \\ (15 \leq t \leq 74 \text{ } ^\circ\text{C})$$

The standard deviation is 0.064×10^{-6} or about 3%.

A literature search revealed no experimental studies other than the two commonly quoted references (3, 5). Solubility curves from these studies are also shown in Figure 1. The measurements of Polejes (3) covered the range 10–60 $^\circ\text{C}$, while the Satterfield et al. data were for 30–60 $^\circ\text{C}$. At low temperatures ($\sim 20 \text{ } ^\circ\text{C}$) all the results in Figure 1 agree within 15%,

but at higher temperatures ($\sim 60 \text{ } ^\circ\text{C}$) the data from ref 3 and 5 differ by about 40%. The solubilities from our studies are between the results of the earlier work. It also should be mentioned that preliminary measurements in our laboratory, with less sensitive apparatus and less accurate technique, gave solubilities that were scattered, but within 10% of the final data. It has been mentioned (6) that a Ph.D. thesis of Jawad K. Ali (University of Birmingham, England, 1974) reported a maximum at 58 $^\circ\text{C}$ in the solubility vs. temperature curve for hydrogen in α -methylstyrene. Our results given in Figure 1 show no maximum in the range 15–74 $^\circ\text{C}$.

Acknowledgment

The Dow Chemical Co. supplied α -methylstyrene.

Glossary

C_{sat}	concentration of hydrogen in α -methylstyrene in equilibrium with pure hydrogen gas at 25 $^\circ\text{C}$ and 1 atm pressure, g-mol/cm ³
t	temperature, $^\circ\text{C}$

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Volumetric Properties of Molten Calcium and Cadmium Nitrate Tetrahydrates with Rubidium and Cesium Nitrates

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Densities of molten calcium and cadmium nitrate tetrahydrates containing rubidium and cesium nitrates were measured at temperatures ranging between 288.2 and 363.2 K. Densities and equivalent volumes varied linearly with temperature. Trends in equivalent volume-composition isotherms suggest that Rb^+ and Cs^+ ions do not compete for water of hydration bound with divalent cations.

Molten hydrated salts containing 4–6 mol of water/mol of salt have been considered as an analogue of molten salts (1) since the water of hydration remains strongly bound to cation giving weak field species of the type $\text{M}(\text{H}_2\text{O})_n^{m+}$. Several alkaline earth metal nitrate hydrates-alkali metal nitrate mixtures show strong glass-forming and supercooling tendencies, enabling measurements well below the freezing points. In view of the recent interest in such systems (1, 2, 4, 6), densities of molten calcium and cadmium nitrate tetrahydrates containing rubidium and

cesium nitrates are reported in this paper.

Experimental Section

Calcium and cadmium nitrate tetrahydrates were Analar (BDH) grade; the water content of the salts, determined by volumetric titration using EDTA, were within ± 0.01 of the stoichiometric value. Rubidium and cesium nitrate, extra pure (E. Merck), were dried to constant mass at 150 $^\circ\text{C}$ and stored over anhydrous magnesium perchlorate until used.

Details of the densitometer, calibration and precision in the acquisition of data, etc., have been described earlier (8). Data were obtained both in heating and cooling cycles at 5 $^\circ\text{C}$ interval.

Results and Discussion

Densities of several mixtures of calcium and cadmium nitrate tetrahydrates with rubidium and cesium nitrates, obtained at temperatures ranging between 288.2 and 363.2 K, are presented

Table I. Densities of Calcium Nitrate Tetrahydrate with Rubidium and Cesium Nitrates

T, K	X_{Rb}			X_{Cs}					
	0.026	0.063	0.096	0.020	0.048	0.092	0.168	0.233	0.377
288.2				1.7672					
293.2	1.7604	1.7740	1.7863	1.7625	1.7894	1.8261	1.8952	2.0200	
298.2	1.7560	1.7695	1.7819	1.7580	1.7850	1.8218	1.8909	2.0158	2.1247
303.2	1.7516	1.7651	1.7775	1.7536	1.7807	1.8174	1.8866	2.0116	2.1205
308.2	1.7472	1.7607	1.7731	1.7498	1.7763	1.8130	1.8823	2.0075	2.1162
313.2	1.7429	1.7563	1.7687	1.7444	1.7720	1.8087	1.8781	2.0032	2.1120
318.2	1.7385	1.7520	1.7643	1.7400	1.7676	1.8043	1.8737	1.9990	2.1079
323.2	1.7342	1.7478	1.7600	1.7356	1.7633	1.7998	1.8695	1.9949	2.1036
328.2	1.7298	1.7434	1.7557	1.7312	1.7589	1.7955	1.8652	1.9906	2.0995
333.2	1.7256	1.7390	1.7514	1.7267	1.7546	1.7912	1.8608	1.9864	2.0953
338.2	1.7212	1.7345	1.7472	1.7222	1.7502	1.7868	1.8565	1.9822	2.0910
343.2	1.7170	1.7302	1.7432	1.7177	1.7459	1.7825	1.8523	1.9782	2.0868
348.2	1.7126	1.7260	1.7390	1.7132	1.7415	1.7781	1.8479	1.9738	2.0825
353.2	1.7082	1.7216	1.7349	1.7088	1.7372	1.7738	1.8436	1.9696	2.0785
358.2	1.7040	1.7173	1.7307	1.7044	1.7328	1.7694	1.8395	1.9655	2.0742
363.2	1.6998	1.7130	1.7265	1.6998	1.7285	1.7651	1.8350	1.9612	2.0699

Table II. Densities of Cadmium Nitrate Tetrahydrate with Rubidium and Cesium Nitrates

T, K	X_{Rb}				X_{Cs}			
	0.072	0.133	0.231	0.373	0.063	0.113	0.215	0.287
288.2								
293.2	2.3039	2.3169	2.3344	2.3688	2.3160	2.3468	2.4178	2.4746
298.2	2.2978	2.3112	2.3286	2.3623	2.3102	2.3411	2.4122	2.4691
303.2	2.2922	2.3055	2.3239	2.3650	2.3044	2.3354	2.4065	2.4636
308.2	2.2867	2.2998	2.3172	2.3498	2.2984	2.3298	2.4010	2.4582
313.2	2.2806	2.2934	2.3111	2.3429	2.2926	2.3240	2.3952	2.4527
318.2	2.2749	2.2876	2.3050	2.3375	2.2870	2.3182	2.3892	2.4472
323.2	2.2689	2.2814	2.2984	2.3309	2.2815	2.3122	2.3844	2.4418
328.2	2.2630	2.2753	2.2923	2.3244	2.2752	2.3068	2.3785	2.4361
333.2	2.2571	2.2693	2.2863	2.3179	2.2696	2.3012	2.3730	2.4306
338.2	2.2513	2.2633	2.2804	2.3119	2.2640	2.2952	2.3672	2.4250
343.2	2.2454	2.2572	2.2744	2.3058	2.2580	2.2896	2.3615	2.4195
348.2	2.2393	2.2610	2.2683	2.2998	2.2520	2.2840	2.3562	2.4140
353.2	2.2353	2.2450	2.2622	2.2939	2.2462	2.2784	2.3505	2.4086
358.2	2.2304	2.2391	2.2562	2.2880	2.2406	2.2727	2.3450	2.4032
363.2	2.2245	2.2320	2.2500	2.2820	2.2348	2.2672	2.3394	2.3975

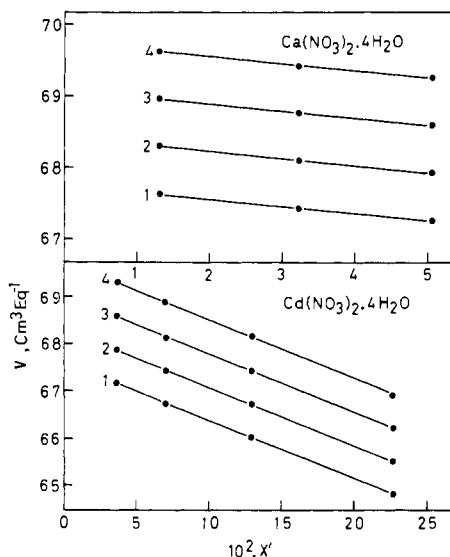


Figure 1. Equivalent volume (V) vs. equivalent fraction (X') of rubidium nitrate isotherms for calcium and cadmium nitrate tetrahydrate-rubidium nitrate systems: 1, 303.2 K; 2, 323.2 K; 3, 343.2 K; 4, 363.2 K.

in Tables I and II. Equivalent volumes were calculated using the mass of the mixture containing 1 mol of NO_3^- ions; the implication being that the number of these ions, the main space filling species, would then be independent of the composition for the "per equivalent" unit and thus, the changes in the volume with composition will directly reflect the changes in the packing density (cf. 3, 7).

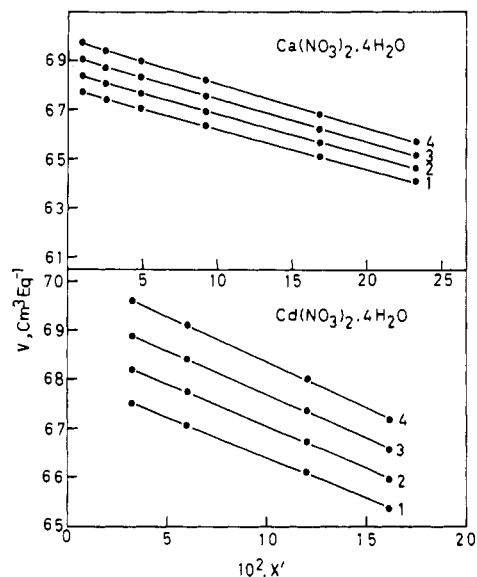


Figure 2. Equivalent volume (V) vs. equivalent fraction (X') of cesium nitrate isotherms for calcium and cadmium nitrate tetrahydrate-cesium nitrate systems: 1, 303.2 K; 2, 323.2 K; 3, 343.2 K; 4, 363.2 K.

At all compositions, temperature variation of density (ρ) and equivalent volume (V) could be least-squares fitted into the linear equation

$$Y(\rho, V) = A \pm B(T - 300) \quad (1)$$

the coefficients of the equations and the standard deviations are given in Tables III and IV.

Table III. Least-Squares Equations of Density and Equivalent Volume Data for Mixtures of Calcium Nitrate Tetrahydrate with Rubidium and Cesium Nitrates

X_{MNO_3}	Temp range (T, K)	Data points	$\rho = A - B(T - 300), \text{g cm}^{-3}$			$V = A' + B'(T - 300), \text{cm}^3 \text{equiv}^{-1}$		
			A	$10^3 B$	10^3SE^a	A'	$10^2 B'$	SE^a
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{RbNO}_3$								
0.026	290-365	15	1.754 35	0.866 00	0.09	67.5234	3.3325	0.003
0.063	290-365	15	1.767 90	0.870 43	0.09	67.3233	3.3326	0.003
0.096	290-365	15	1.780 08	0.853 20	0.07	67.1593	3.3376	0.003
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{CsNO}_3$								
0.020	285-365	16	1.756 50	0.897 32	0.05	67.6562	3.5551	0.003
0.048	290-365	15	1.783 46	0.870 02	0.03	67.2605	3.3760	0.002
0.092	290-365	15	1.820 15	0.872 10	0.05	66.8918	3.3003	0.002
0.168	290-365	15	1.889 37	0.859 23	0.06	66.2175	3.0982	0.002
0.232	290-365	15	2.014 30	0.839 40	0.06	65.0217	2.7782	0.001
0.377	295-365	14	2.123 16	0.841 54	0.06	64.0243	2.5911	0.001

^a SE = standard error.

Table IV. Least-Squares Equations of Density and Equivalent Volume Data for the Mixtures of Cadmium Nitrate Tetrahydrate with Rubidium and Cesium Nitrates

X_{MNO_3}	Temp range (T, K)	Data points	$\rho = A - B(T - 300), \text{g cm}^{-3}$			$V = A + B(T - 300), \text{cm}^3 \text{equiv}^{-1}$		
			A	$10^3 B$	10^3SE^a	A	$10^2 B$	SE^a
$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{RbNO}_3$								
0.072	290-365	15	2.295 93	1.168 74	0.16	67.0612	3.4904	0.006
0.133	290-365	15	2.300 20	1.191 46	0.30	66.8410	3.5289	0.012
0.231	290-365	15	2.326 67	1.214 96	0.30	65.9062	3.5029	0.011
0.373	290-365	15	2.372 49	1.251 06	0.35	64.3511	3.4697	0.013
$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{CsNO}_3$								
0.063	290-365	15	2.308 07	1.150 05	0.15	67.3943	3.4876	0.010
0.113	290-365	15	2.338 98	1.139 88	0.16	66.9756	3.3577	0.007
0.215	290-365	15	2.410 07	1.119 53	0.19	66.0240	3.1460	0.007
0.287	290-365	15	2.467 17	1.101 42	0.09	65.2776	2.9890	0.009

^a SE = standard error.

Table V. Computed Partial Equivalent Volumes of the Components of Molten Hydrated Salt Mixtures

System $\text{M}'(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{MNO}_3$	T, K	$\bar{V}_{\text{M}'(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}}$	\bar{V}_{MNO_3}
$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{RbNO}_3$	303.2	67.60	55.39 (54.37) ^b
	323.2	68.30 (68.08) ^a	55.80 (54.73) ^b
	343.2	69.01	56.45 (55.06) ^b
	363.2	69.73	57.12 (55.47) ^b
	303.2	68.03	50.58 (47.91) ^b
$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{CsNO}_3$	323.2	68.74	51.05 (48.22) ^b
	343.2	69.46	51.52 (48.54) ^b
	363.2	70.19	51.90 (48.86) ^b
	303.2	67.75	55.15
	323.2	68.42 (68.76) ^a	55.90
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{RbNO}_3$	343.2	69.08	56.52
	363.2	69.75	57.10
	303.2	67.82	50.44
	323.2	68.52	50.91
	343.2	69.10	51.32
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{CsNO}_3$	363.2	69.82	51.74

^a Moynihan et al. (6). ^b Extrapolated from molten salt data (5).

Equivalent volume (V)-equivalent fraction (X') isotherms (Figures 1 and 2) show a decrease in V with increase in monovalent nitrate content; this appears logical as the larger hydrated cations $\text{Ca}(\text{H}_2\text{O})_4^{2+}$ (3.75 Å) and $\text{Cd}(\text{H}_2\text{O})_4^{2+}$ (3.77 Å) are gradually replaced by Rb^+ (1.43 Å) and Cs^+ (1.67 Å) ions. Large scale plots (not shown) showed that for $V-X'$ plots deviations from linearity were less than 0.1%, so that volumetrically the systems may be considered as ideal in the composition range studied. Partial equivalent volumes, evaluated from $V-X'$ isotherms by graphical extrapolation and also by least-squares fitting of $V-X'$ data into a linear equation, are given in Table V. Computed partial equivalent volumes of the hydrated salts may be compared with the measured volumes of the pure component (1, 2, 4, 6) and those of rubidium and cesium nitrates with the volumes extrapolated from molten salt data (5); in both

cases the extrapolated and computed values are in good agreement. The additivity of volumes and the close agreement between computed and extrapolated partial equivalent volumes also suggest that Rb^+ and Cs^+ ions do not compete for water of hydration originally present in the coordination of divalent cations (1, 2)

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Vapor-Liquid Equilibrium of the Methane-Toluene System at Low Temperatures

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Measurements of the bubble-point compositions are reported at 40, 0, -40, and -120 °F. The pressure ranges from 50.0 to 7070 psia. *K* values were evaluated by combining with earlier dew-point data from this laboratory at 40 and 0 °F and from BWRS predictions at -40° and -120 °F. Limited liquid-liquid miscibility at temperatures below the critical temperature of methane was observed. The *P*-*x* plot shows reverse solubility of methane in the liquid at high pressures resulting in *K* values of methane at lower temperatures crossing over the ones at higher temperatures.

A number of studies of the vapor-liquid equilibrium of the methane-toluene binary system have been reported in the literature. Savvina and Velikovski (12) reported some results from 40 to 150 °C with pressures up to the critical at each temperature. Elbishlawi and Spencer (6) studied the equilibrium relations at 150 °F from 100 psia up to the critical pressure of the mixture. Chang and Kobayashi (2) reported measurements from 0 down to -100 °F with pressures up to 3500 psia. No experimental bubble point data for the methane-toluene system exist for temperatures between 0 and 100 °F and for pressures above 3500 psia at temperatures below 100 °F.

Dew point loci for the methane-toluene system using the elution method were reported by Hwang and Kobayashi (8) from this laboratory at 40, 20, and 0 °F and pressures up to 2500 psia.

This study and that by Chang and Kobayashi (2) show some discrepancies in both dew points (8) and bubble points as shown in Figure 2.

Two liquid phases were observed at temperatures below the critical temperature of methane. An earlier study from this laboratory (2) defined the phase behavior.

Experimental Method and Procedure

The recycle equilibrium apparatus is the same as that used by Mraw et al. (10) in the methane-carbon dioxide investigation with some modifications. The sampling lines were all heated to above the boiling point of toluene (231.13 °F) at 300 °F to transform and keep the sample in the vapor phase at essentially atmospheric conditions. The precooler was disconnected due to the operation of a closed system in methane-toluene mixtures.

Toluene was charged to the cleaned and evacuated cell first, methane was then added to the desired pressure. Temperature was controlled by applying liquid nitrogen and a heater from the Thermostat to ± 0.02 °F and was determined with a Leeds and Northrup platinum resistance thermometer. A magnetic pump was used to recycle the gas mixture through the liquid at the

bottom of the cell until an equilibrium state is reached. It usually took over an hour to reach the equilibrium state, after which at least six analyses were made.

A stirred pot made of stainless steel with a volume of approximately 150 mL was used to homogenize the sample of the liquid phase (as a vapor) by mixing.

The experimental equipment and technique for the dew-point concentration measurements have been reported in earlier publications (3-5, 9) which should be consulted for itemized information.

In the bubble-point concentration investigation, a TRACOR Model 550 gas chromatograph with thermal conductivity detector was used for analysis. The chromatographic column was a 4-ft length of 1/8-in. o.d. stainless steel tubing packed with 80-100 mesh Duropack (OPN/Porasil C). Helium was used as a carrier gas. The flow rate of helium was determined to give maximum response. Sample was introduced into the sample loop and then bubbled through a water column to indicate the flow rate of the sample. The signal from the detector was integrated by an Autolab minigrator and recorded on a Leeds and Northrup strip chart recorder.

The peak areas were calibrated by preparing samples from two metering pumps. A 500-cm³ pump was used to deliver a certain flow rate of methane and an 8-cm³ pump was used to deliver a precise quantity of toluene. The two components were then going through a mixing valve and to the sample loop to be analyzed. Samples with methane mole fractions ranging from 5 to 95 % were prepared and analyzed. The area ratios were plotted as a function of the mole fraction ratios. In the region of study, this is a linear relation. See Figure 1.

The isotherms were usually investigated in order of decreasing temperature and increasing pressure. Additional points were sometimes taken on later dates to verify the consistency of the measurements.

The pressure in the system was indicated by four (0-1000, 0-3000, 0-6000, 0-10 000 psia) Heise gauges with accuracy of 0.1% of the full scale reading.

Materials Used

Ultra-high-purity methane (99.97 mol % minimum) was purchased from Matheson Gas Products. The research grade (99.94 mol %) toluene used was donated by the Phillips Petroleum Co. All materials were used without further purification.

Error Analysis

The contributing factors of errors are temperature, controlled to ± 0.02 °F, pressure, measured by Heise gauges calibrated