Densities of Aqueous KCl and UO_2SO_4 from 25° to 374° C.

J. T. BELL, D. M. HELTON, and T. G. ROGERS[1]
Oak Ridge National Laboratory, Oak Ridge, Tenn. 37830

The densities of 0.1, 0.5, and 1.0*M* solutions of KCl and of 1.27*M* UO_2SO_4 have been observed at temperatures between 25° and 374° C. These data are reported as density vs. temperature, and the isotherms of density vs. concentration are shown for the KCl solutions. The change in the densities of the KCl solutions at 25° C. is a linear function of the KCl concentration, but this linear relationship disappears at higher temperatures, and the greatest change in the solution density per unit of KCl concentration occurs between 0 and 0.1*M*. Between 0.1 and 1.0*M* KCl, the density change for the KCl solutions at the higher temperatures is a linear function of the KCl concentration. The change in the density of the UO_2SO_4 solution over any temperature range is greater than the density changes for the KCl solutions over the same range, and is most notable at temperatures above 250° C.

DENSITY changes of aqueous solutions at high temperatures are of interest in various areas of research, and the data are very important to general solution theories concerning the properties and structures of solutions.

Ellis and Golding reported the densities of NaCl solutions at temperatures between 150° and 350° C. (*4*). Copeland *et al.* (*3*) studied phase equilibria in the NaCl–H_2O system at high temperatures (near 400° C.) and pressures (200 to 300 atm.), but gave little information on the densities of solutions in closed containers—i.e., under their own vapor pressures. Others (*7*) reported the concentrations of NaCl in the gas and liquid phases at high temperatures, greater than 350° C., and various pressures for the NaCl–H_2O system. Krohn and Wymer (*5*) used an x-ray dilatometer method to determine the densities of 35.2% UO_2SO_4 solution to 300° C. Their results agreed well with Secoy's data (*6*) for 34.9% UO_2SO_4 solution. However, these authors (*5*) agree that their dilatometer system was not as accurate as the present system (*2*). Moreover, it was limited to temperatures below 300° C.

The authors have measured the densities of 0.0999, 0.498, and 0.997*M* KCl solutions and of 1.27*M* UO_2SO_4 from 25° to 374° C., using the x-ray dilatometer method (*2*). This report presents these results and correlations with other published data.

EXPERIMENTAL

A detailed description of the x-ray dilatometer for observing the volume changes of solutions at high temperatures was given previously (*2*). The procedure for calculating the solution density from the observed data was given also. This dilatometer system is improved over the previous system (*5*) by three major modifications. The dilatometer is made from titanium and is more resistant than stainless steel to corrosion by aqueous solutions at high temperatures. The sealing technique employs a Haskel seal (Haskel Engineering and Supply Co., Burbank, Calif.) between two surfaces. This seal is capable of containing samples at higher temperatures and pressures than the conical-type seals. The temperature is measured as a small differential voltage between a calibrated thermocouple and a bucking voltage from a Leeds and Northrup K-3 potentiometer. The differential voltage is observed on a Speedomax G recorder having a 10-mv. range, and is added to the bucking voltage of the potentiometer. This gives the total e.m.f. of the thermocouple with high precision.

The KCl solutions (0.0999, 0.498, and 0.997*M*) were prepared by dissolving reagent-grade KCl in distilled water, and the solutions were analyzed for Cl^-. The 1.27*M* UO_2SO_4 solution was prepared from $UO_2SO_4 \cdot XH_2O$ and was coulometrically analyzed for uranium.

RESULTS

The densities of the three KCl solutions and one UO_2SO_4 solution over the 25° to 374° C. range are shown in Figure 1, with the corresponding densities of water (*1*); the densities at specific temperatures are given in Table I. The changes in the density of the KCl solutions closely parallel the corresponding changes for water, but some deviations occur with the higher temperatures. Isotherms of density *vs.* concentration are shown in Figure 2. The measured densities for the KCl solutions agree to within 3% of the reported densities for similar NaCl solutions to 350° C. (*4*).

The densities of KCl solutions with concentrations between 0 and 1*M* can be determined at any temperature between 25° and 375° C. from Table I. The density *vs.* temperature curves for the KCl solutions could not be described by simple polynomial functions, and thus the density at temperatures other than those in Table I must be interpolated.

When the published data for NaCl (*4*) are plotted as isotherms of density *vs.* concentration at 25° C., the solution density appears to be a linear function of the concentration over the 0 to 1*M* range for temperatures to 350° C. However, the NaCl data (*4*) did not include a solution concentration between 0.0 and 0.5 molal (0.502*M*), and this concentration region is very important in describing the changes in densities of solutions at elevated temperatures.

The density-to-concentration relationship for the KCl solutions near 25° C. is linear (Figure 2) and indicates

---

[1] Present address, Department of Chemistry, University of California, Riverside; Riverside, Calif.

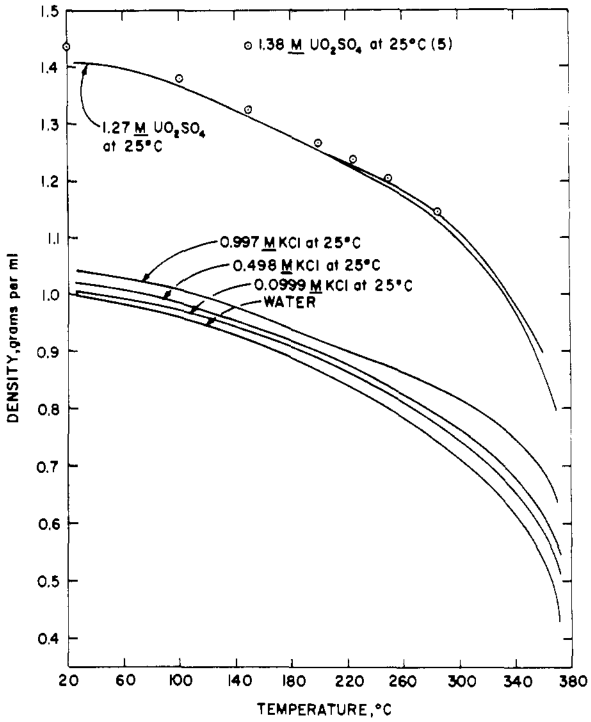

Figure 1. The densities of KCl and UO_2SO_4 solutions, and of water at temperatures to 374° C.

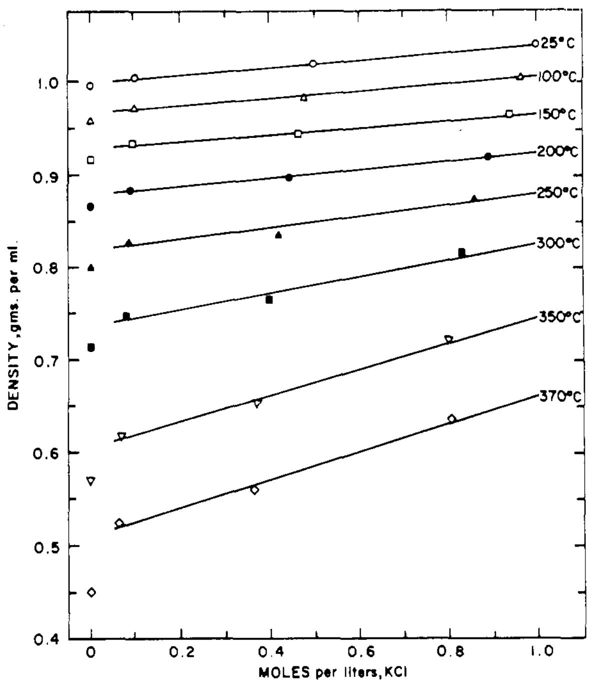

Figure 2. Isotherms of density vs. concentration for aqueous KCl

Table I. Densities (Grams per Ml.) of Aqueous KCl and UO_2SO_4 Solutions to 370° C.

		KCl		KCl		KCl		UO_2SO_4		UO_2SO_4	
Temp., ° C.	Water Density	Moles per liter	Solution density	Moles per liter	Solution density	Moles per liter	Solution density	Moles per liter	Solution density	Moles per liter	Solution density
25	0.997	0.0999	1.003	0.498	1.018	0.997	1.039	1.270	1.4102	1.270	1.411
30	0.995	0.1001	1.003	0.498	1.017	0.997	1.038	1.270	1.4099	1.269	1.409
40	0.992	0.0999	1.001	0.497	1.015	0.992	1.036	1.269	1.4047	1.265	1.408
50	0.987	0.0996	0.997	0.494	1.012	0.987	1.033	1.265	1.3971	1.262	1.401
60	0.982	0.0994	0.993	0.493	1.007	0.982	1.028	1.253	1.3907	1.258	1.395
70	0.977	0.0990	0.988	0.492	1.002	0.979	1.023	1.247	1.3854	1.251	1.390
80	0.972	0.0987	0.983	0.488	0.996	0.973	1.018	1.240	1.3795	1.246	1.381
90	0.964	0.0979	0.977	0.484	0.989	0.970	1.011	1.233	1.3708	1.237	1.372
100	0.957	0.0975	0.971	0.481	0.982	0.963	1.003	1.227	1.3637	1.229	1.363
110	0.950	0.0966	0.965	0.479	0.975	0.959	0.998	1.219	1.3547	1.220	1.356
120	0.942	0.0960	0.958	0.475	0.968	0.953	0.990	1.213	1.3464	1.216	1.347
130	0.933	0.0953	0.950	0.473	0.960	0.945	0.982	1.205	1.3366	1.205	1.335
140	0.925	0.0946	0.942	0.469	0.952	0.938	0.973	1.197	1.3267	1.197	1.327
150	0.916	0.0938	0.933	0.464	0.943	0.936	0.963	1.187	1.3147	1.186	1.313
160	0.907	0.0928	0.925	0.460	0.933	0.920	0.954	1.176	1.2998	1.178	1.303
170	0.896	0.0919	0.918	0.455	0.924	0.911	0.943	1.165	1.2879	1.172	1.289
180	0.887	0.0908	0.905	0.451	0.913	0.902	0.935	1.156	1.2768	1.164	1.278
190	0.876	0.0901	0.894	0.447	0.905	0.897	0.926	1.148	1.2648	1.157	1.268
200	0.865	0.0892	0.883	0.444	0.897	0.890	0.918	1.135	1.2538	1.147	1.256
210	0.852	0.0883	0.874	0.438	0.887	0.884	0.908	1.126	1.2408	1.138	1.245
220	0.839	0.0875	0.863	0.434	0.876	0.877	0.899	1.118	1.2295	1.128	1.234
230	0.825	0.0864	0.852	0.430	0.863	0.871	0.891	1.107	1.2163	1.117	1.222
240	0.813	0.0856	0.840	0.425	0.851	0.864	0.882	1.098	1.2035	1.114	1.210
250	0.798	0.0846	0.826	0.421	0.838	0.860	0.873	1.086	1.1896	1.105	1.197
260	0.783	0.0834	0.812	0.416	0.824	0.854	0.862	1.077	1.1737	1.096	1.184
270	0.765	0.0823	0.797	0.412	0.810	0.848	0.852	1.065	1.1589	1.086	1.170
280	0.750	0.0811	0.781	0.407	0.795	0.842	0.842	1.049	1.1417	1.074	1.154
290	0.732	0.0799	0.765	0.402	0.780	0.836	0.830	1.034	1.1158	1.062	1.134
300	0.713	0.0785	0.747	0.398	0.763	0.830	0.813	1.016	1.0951	1.053	1.109
310	0.691	0.0770	0.728	0.393	0.746	0.823	0.802	0.997	1.0690	1.035	1.081
320	0.665	0.0754	0.704	0.390	0.727	0.818	0.786	0.975	1.0340	1.021	1.053
330	0.639	0.0734	0.678	0.383	0.705	0.811	0.767	0.948	1.0036	1.005	1.024
340	0.607	0.0712	0.650	0.377	0.680	0.807	0.746	0.917	0.9678	0.989	0.990
350	0.572	0.0689	0.618	0.372	0.653	0.801	0.720	0.882	0.9269	0.970	0.950
360	0.526	0.0663	0.579	0.368	0.615	0.801	0.688	0.835	0.8606	0.947	0.898
370	0.451	0.0624	0.525	0.363	0.560	0.807	0.635	0.771	0.7940	0.921	0.796
375[a]	0.400	0.0582	0.482	0.361	0.518	0.810	0.550	0.714	0.750	0.905	

[a] Values at 375° C. were extrapolated.

that the density change per unit concentration is constant. One might assume the linear relationship for all temperatures if the data for the 0.1*M* solution were not available. However, at higher temperatures the density change per unit concentration is greatest over the 0.0 to 0.1*M* region (Table I), and the linear relationship between the density and the concentration of KCl solutions applied only to the 0.1 to 1.0*M* region (Figure 2).

The densities of 1.27*M* UO_2SO_4 at temperatures to 374° C. are also shown in Figure 1, together with the data of Krohn and Wymer for 1.38*M* UO_2SO_4 (*5*). The general effect of temperature on the density of the uranyl sulfate solution is similar to that on the density of the KCl solutions. However, the density of the UO_2SO_4 solution decreases much faster than the density of the KCl solutions, especially at temperatures above 250° C. The divergence of the two sets of density data for the UO_2SO_4 solution (Figure 1) is the result of different solution concentrations at the higher temperatures. Different initial volumes of 1.27*M* UO_2SO_4 induced different vapor volumes above the solution. Therefore, the mass transfer of solvent to the vapor phase was greater for the lower initial volume, and the concentration of that solution was greater at the higher temperatures.

The densities of 0.1, 0.5, and 1.0*M* KCl and of 1.27*M* and 1.344 molal UO_2SO_4 at various temperatures (Table II) have been determined by linear interpolation of the density *vs.* concentration plots at the various temperatures. These data for the KCl solutions were interpolated from the data in this report only. These data for UO_2SO_4 were interpolated from the data in this report and the data of Krohn and Wymer (*5*), obtained in numerical form from those authors.

The density change of the UO_2SO_4 solution from 25° to 350° C. is 0.464 gram per ml., whereas the corresponding change for the 1.0*M* KCl solution is only 0.320 gram per ml. This difference in the change of the densities might be due to differences in the concentrations or the molecular weights of the two salts. However, the linear relationship between the density and concentration of the KCl solutions indicates that the densities of 1.27*M* KCl solution at all temperatures would be higher than the densities of the 1.0*M* KCl; but the rate of density change would not approach that observed for UO_2SO_4. Also, normalizing the concentrations in terms of molality and normality and plotting the densities against these terms does not change the trends of, and the differences in, the densities of the KCl and UO_2SO_4 solutions.

Table II. Interpolated Densities of Solutions Having Constant Concentrations at Temperatures to 370° C.

Temp., ° C.	Density, Grams per Ml. 0.1 *M* KCl	0.5 *M* KCl	1.0 *M* KCl	1.27 *M* UO_2SO_4	1.344 *m* UO_2SO_4
25	1.003	1.018	1.039	1.411	1.411
100	0.971	0.985	1.004	1.370	1.363
150	0.933	0.947	0.964	1.319	1.314
200	0.882	0.900	0.922	1.278	1.253
225	0.858	0.876	0.899	1.258	1.223
250	0.823	0.848	0.878	1.233	1.189
275	0.788	0.867	0.856	1.207	1.144
285	0.773	0.804	0.846	1.186	1.124
300	0.743	0.780	0.816	1.149	1.088
350	0.618	0.674	0.744		
370	0.525	0.586	0.659		

LITERATURE CITED

(1) Bain, R. W., "Steam Tables 1964," Department of Scientific and Industrial Research, National Engineering Laboratory, Great Britain.

(2) Bell, J. T., Biggers, R. E., Rogers, T. G., Rom, A. M., *Rev. Sci. Instr.* **40,** 985 (1969).

(3) Copeland, C. S., Silverman, J., Benson, S. W., *J. Chem. Phys.* **21,** 12 (1952).

(4) Ellis, A. J., Golding, R. M., *Am. J. Sci.* **261,** 47 (1963).

(5) Krohn, N. A., Wymer, R. G., *Anal. Chem.* **34,** 121 (1962).

(6) Secoy, C. H., Oak Ridge National Laboratory, Chem. Div. Quart. Rept. ORNL-**336,** pp. 24, 26–7 (Dec. 1948).

(7) Sourirajan, S., Kennedy, G. C., U. S. Atomic Energy Commission Rept. No. UCRL-**6175** (1960).

RECEIVED for review April 1, 1969. Accepted October 6, 1969. Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

Vapor-Liquid Equilibrium Relations of Binary Systems. The Propane–*n*-Alkane Systems. *n*-Butane and *n*-Pentane

WEBSTER B. KAY
Department of Chemical Engineering, The Ohio State University, Columbus, Ohio 43210

IN THE COURSE of a long-range study of the critical properties of hydrocarbon mixtures, *P-V-T-x* data have been obtained for a series of binary systems of the normal and branched-chain hydrocarbons. In the selection of the systems of study, members of the homologous series of the paraffin hydrocarbons have been paired with a member of the same series, but of lower molecular weight. By this method, the effect of such variables as molecular weight and molecular structure on the phase behavior can be investigated as parameters for the correlation of the *P-V-T* data. This first paper summarizes the data obtained for the two binary systems composed of *n*-butane and *n*-pentane, with propane as the common component. The work has been carried out by graduate students, each binary system serving as the thesis problem for the M.S. degree in chemical engineering.