Subscript

2MN = 2-methylnaphthalene
nBB = *n*-butylbenzene

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The Solubility of Potassium Chloride in Ordinary and Heavy Water

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Using the sealed tube method the solubility of KCl has been redetermined in D_2O in the temperature range 21–88 °C and compared with new determinations in ordinary water. The present work confirms earlier work published about 40 years ago; however, many more determinations have been made and a higher precision has been obtained. Both of these sets of data have been subjected to least-squares treatment, and polynominal equations have been obtained.

For several years after the discovery of heavy water its solubility relations with a number of substances were studied. Experimental work was hampered due to the difficulty in procuring D_2O and the lack of knowledge of its fundamental properties. The passage of considerable time has resulted in marked changes in both respects; it therefore seemed desirable to redetermine the solubility of one salt in both ordinary and heavy water and compare the results with what seemed the best of earlier work. Potassium chloride was chosen largely because it could be obtained in a relatively high state of purity fairly easily.

Experimental Section

Chemicals. The heavy water was purchased from The Stuart Oxygen Co. who claimed a 99.7% D_2O content; it was used without further purification. Care was taken to avoid unnecessary contact with the atmosphere or ordinary water. The solvent ordinary water was laboratory deionized water. The KCl was the best grade of J. T. Baker; it was twice recrystallized from deionized water and fused.

Appartus and Method. All of the determinations were made using the sealed tube method which involves introducing weighed quantities of solute and solvent into a tube and sealing. Then the tube is heated slowly with shaking to determine the temperature at which the last small crystal remains. Mercury in glass thermometers were employed throughout this work. No important change has been made from that described earlier (*2*, *3*).

Results. In Table I will be found the contents of the 16 tubes containing KCl and ordinary water. The third column gives the solubility in moles of KCl per 55.51 mol of ordinary water. The last column gives the temperature at which the last small crystal remained. Corresponding results for 15 runs with 99.7% D_2O are given in Table II.

The values in the third column of Table II were calculated with the aid of the apparent molecular weight of the 99.7% D_2O, 20.028; this value is very close to that of pure D_2O, 20.029. Shearman and Menzies (*1*) expressed their results on the basis of pure D_2O. To do this required a short linear extrapolation from 98.2% D_2O to 100.0% D_2O. This slight difference in the

Table I. Observed Solubility of KCl in Ordinary Water

Wt KCl (g)	Wt H_2O (g)	*M*	Temp, °C
0.3343	1.0174	4.407	16.13
0.2559	0.7360	4.668	21.97
0.3009	0.8556	4.716	23.50
0.3803	1.0622	4.803	26.32
0.3856	1.0307	5.018	30.80
0.3679	0.9663	5.050	31.59
0.3850	0.9817	5.264	37.62
0.4528	1.1233	5.406	41.00
0.3023	0.7116	5.698	48.12
0.4013	0.9178	5.903	53.27
0.3212	0.7313	5.891	53.82
0.4310	0.9378	6.164	62.88
0.4534	0.9619	6.322	66.23
0.5565	1.1630	6.418	69.12
0.5860	1.1759	6.684	77.07
0.6816	1.3145	6.955	85.26

Table II. Observed Solubility of KCl in D_2O

Wt KCl (g)	Wt D_2O (g)	*M*	Temp, °C
0.2746	0.9843	4.160	21.51
0.3248	1.1182	4.331	25.78
0.3202	1.0644	4.486	28.99
0.3709	1.1279	4.904	39.48
0.3372	0.9880	5.089	43.16
0.4027	1.1744	5.113	44.53
0.3841	1.0800	5.304	49.19
0.3105	0.8394	5.516	55.54
0.3464	0.9225	5.600	56.87
0.3142	0.8245	5.683	58.72
0.3627	0.9269	5.835	63.00
0.3571	0.8751	6.085	70.06
0.4055	0.9862	6.132	71.45
0.4570	1.0667	6.389	79.36
0.4062	0.9048	6.695	88.42

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Table III. Solubility of KCl in Ordinary and Heavy Water. Summary of Data Obtained by Various Investigators with Results of Calculations

Experimentor	Solvent	Temp range, °C	No. of determinations	Values of constants in the polynomial equations			Av difference Mex − Mca
				A	$B \times 10^2$	$-C \times 10^5$	
Baumbach	H_2O	16–85	16	3.706	4.486	8.05	0.0137
Baumbach	99.7% D_2O	21–88	15	3.165	4.800	9.12	0.0093
Schmude	H_2O	26–57	6	3.761	4.253	6.02	0.031
Schmude	99.5% D_2O	24–67	6	3.199	4.660	7.77	0.0058
Shearman and Menzies	H_2O	7–175	10	3.852	3.752	1.08	0.028
Shearman and Menzies.	98.2% D_2O[a]	5–177	10	3.317	4.153	2.10	0.057

[a] See text for clarification of this procedure.

meaning of M still allows a comparison of the two results because the difference is much less than the experimental error.

Treatment of Experimental Results. The data in Tables I and II, along with those of others to be discussed, were fitted to a second power polynomial ($M = A + Bt - Ct^2$) using the method of least squares; the results are given in Table III.

Discussion

The work of Schmude was carried out in this laboratory before that of Baumbach. Lack of time restricted the number of determinations to six in each solvent. Since the results are in satisfactory agreement with those of Baumbach, further details will be omitted. Table III also gives the results of the first least-squares treatment of the work of Menzies on KCl. At 0, 10, 90, and 100 °C that work using ordinary water is on the average a little over 1% different from the present work while at temperatures between 10 and 90° the difference is reduced to about ½%, higher in both cases. For heavy water the differences are the same in the 10–90° interval, but about 3% higher at the other temperatures. It should be stated that over twice as many determinations were made in the present work in the 10–90° interval but that some extrapolation at lower and higher temperatures was necessary in order to make these comparisons.

The last column of Table III gives the average difference between the experimental values (Mex) and the calculated values (Mca). In all but one case the precision of the present work and that of Schmude is higher than that of Shearman and Menzies. apparatus and technique whereby about 1 g of solvent would suffice for ten determinations, the amount of solvent being changed without opening the apparatus, the agreement and precision are very satisfactory, indeed.

In Tables I and II temperatures are given to the nearest 0.01°, as a result of making the usual calibration and exposed stem corrections. No claim to a higher precision than ±0.05° is made for the majority of runs. It appears that equilibrium is attained more slowly in inorganic systems, such as the present one, than in organic systems where the sealed tube method has been used so extensively.

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