Clathrate Hydrates in the System Tetraisopentylammonium Iodide–Water

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Abstract—Two clathrate hydrates *i*-Pent₄NI \cdot 36H₂O and *i*-Pent₄NI \cdot 32H₂O were revealed in the system (*i*-Pent)₄NI–H₂O. The hydrates melt incongruently at 14.2 and 14.8°C, respectively. Along with the polyhydrates, tetraisopentylammonium dihydrate was found.

All earlier attempts [1, 2] to obtain clathrate hydrates of ammonium iodides were unsuccessful. Later it was shown that certain iodides, such as tetraisopentylammonium iodide (i-Pent₄NI) [3, 4] and tributylisopentylammonium iodide (*i*-Bu₃PentNI) [3] form by one polyhydrate at atmospheric pressure. The hydrate of *i*-Bu₃PentNI melts at 7.1°C and comprises 25 to 35 water molecules per one salt molecule. According to [4], the hydrate in the *i*-Pent₄NI-H₂O system melts at 13.3°C, and the hydrate number, by very rough estimates, is 0.18 to 75.6. However, according to [3], one hydrate, *i*-Pent₄NI \cdot (36±3)H₂O is formed at atmospheric pressure, and it melts incongruently (with decomposition into salt and water) at 14.7°C. The density and unit cell parameters were determined. At 26 MPa, one more hydrate was found, with a lower hydrate number. The composition of the hydrate was established preparatively, and the large error in its determination was associated with the fact that crystalline tetraisopentylammonium iodide hydrate, unlike hydrates of other quaternary ammonium salts, quite readily lose water. Extensive studies on quaternary ammonium base-water systems showed that these systems, as a rule, contain several compounds with very close compositions but different structures (clathrates with the hydrate numbers 39, 38, 36, 35, 34, 32, etc. are known). Thus, the error limits in above estimates for the *i*-Pent₄NI-H₂O system include several hydrate numbers, and to find out whether this indeed relates to the determination error or we deal here with a mixture of different hydrates, the composition of the hydrate should be detemined as exactly as possible. To this end, in the present work we made use of the Schreinemakers method [5] which allows accurate and reliable detemination of the composition and number of compounds formed in a system.

We studied the *i*-Pent₄NI–MeCO₂H–H₂O ternary

polyhydrates, with 1:36 and 1:32 salt: water ratios, were revealed. The compositions were calculated by the program [6] that takes account of the intersects of the Schreinemakers rays with the axis of the *i*-Pent₄NI–H₂O binary system and equals $1:(35.94\pm$ 0.14) (number of Schreinemakers rays n = 15) and 1: $(32.02\pm0.17, n = 9)$. The solubility of both the hydrates in water is rather low (0.07-1.5 wt %); moreover, both the compounds, rather than forming two separate fields, are present throughout the entire crystallization range of clathrate hydrates, and this makes their stability (metastability) ranges difficult to separate. Most likely, the 1:36 hydrate is stable until some MeCO₂H concentration and then it crystallizes as a metastable phase, whereas the 1:32 hydrate gets more stable. We performed a special experiment, where the initially formed 1:32 hydrate was stirred in the range where its metastable existence was proposed (the solubility with respect to MeCO₂H was \sim 8.8 wt%) for 5 days (shorter time was insufficient), after which it passed into the 1:36 hydrate. This fact implies that it is the latter hydrate which is stable in the indicated concentration range. The same pattern was observed at a ~36% concentration of MeCO₂H. But in the latter case we first observed crystallization of the 1:36 hydrate which then, after ~5 days, too, passed into the 1:32 hydrate. On addition of a seed crystal of the corresponding hydrate, stable equilibrium is much faster attained (1-2 days). Then we studied several mixtures with compositions intermediate between 1:32 and 1:36 with gradually approaching stability regions, and, finally, the eutonic point between the 1:36 and 1:32 hydrates was obtained by mixing roughly equal quantities of these hydrates in a solution with a roughly specified MeCO₂H concentration. The eutonic point corresponds to 0.30 wt% of *i*-Pent₄NI and 23.9 wt% of

system at 0°C (Fig. 1, see table). As a result, two



Fig. 1. Solubility isotherm (0°C) in the system *i*-Pent₄NI–MeCO₂H–H₂O in the range of crystallization of clathrate hydrates. (*1–4*) Liquid phases of the 1:36, 1:32, and 1:2 hydrates and salt, respectively, (5) wet residues of the 1:36 and 1:2 hydrates and salt, and (6) wet residue of the 1:32 hydrate. (*I*) *i*-Pent₄NI(35.94±0.14)·H₂O, (*II*) *i*-Pent₄NI(32.02±0.17)·H₂O, (*III*) *i*-Pent₄NI–2H₂O, and (*IV*) *i*-Pent₄NI. Three-phase regions are shaded.

 $MeCO_2H$ (see table). An eutonic point separating the crystallization ranges of the clathrate hydrates and tetrapentylammonium iodide dihydrate (Fig. 1) was found. This point could be fixed because one of the solid phases (tetraisopentylammonium iodide dihydrate) proved lighter than the equilibrium liquid phase and floated, while the second solid phase (1:32 hydrate) was under the solution.

To find the melting points and stability regions of the hydrates, we performed DTA and solubility studied of the *i*-Pent₄NI–H₂O binary system in the clathrate-formation range (Fig. 2). By DTA we revealed two peritectic lines corresponding to formation of two polyhydrates that melted incongruently at 14.8 and 14.2°C (solidus lines). The liquidus lines for this system were constructed on the basis of solubility measurements, since, in view of the poor solubility of the polyhydrates and salt in water, we failed to extract required data from DTA analysis. The hydrates were isolated either from the binary system (1:36 hydrate) or from the *i*-Pent₄NI–MeCO₂H–H₂O ternary system (1:32 hydrate) and analyzed. The resulting hydrate numbers (35.93 and 32.24) are nicely consistent with those obtained by the Schreinemakers method.

Thus, together our findings point to formation in the *i*-Pent₄NI–H₂O system of two polyhydrates that have stability ranges, as well as a dihydrate. The melting point of the 1:36 hydrate is 14.2°C, whereas the melting point of 14.7°C, assigned to it earlier [3], relates to the 1:32 hydrate (the present value for the latter compound is 14.8°C). The 1:36 hydrate, as found in [3], has a rhombic unit cell [a 12.1(1), b 21.6(2), c 49.9(5) Å] which can be considered as quadruplicate rhombic similar to that reported for the *i*-Pent₄NF·38H₂O hydrate (a 12.1, b 21.6, c 12.8 Å; Z 2) [7]. The 1:32 hydrate has been found in almost Solubility isotherm (0°C) in the *i*-Pent₄NI–MeCO₂H–H₂O system

Liquid phase, wt%		Residue, wt%		Solid
<i>i</i> -Pent ₄ NI	MeCO ₂ H	<i>i</i> -Pent ₄ NI	MeCO ₂ H	phase
0.07	_	_	_	
0.04	0.90	20.72	0.49	
0.09	4.19	18.43	2.27	
0.16	13.27	24.72	4.90	
0.15	15.89	25.27	5.62	
0.14	16.05	20.57	7.73	
0.18	21.07	21.93	9.46	
0.24	21.39	20.55	10.38	1:36
0.18	21.45	23.51	8.83	
0.25	21.50	20.74	10.20	
0.27	22.58	23.68	9.22	
0.32 ^a	25.74	19.25	13.44	
0.31 ^a	27.45	21.23	12.96	
0.28 ^a	28.03	23.62	11.60	
0.31 ^a	28.45	24.74	10.88	
0.58 ^a	31.95	22.21	14.33	
0.30	23.90	19.06	12.32	1:36+1:32
0.15	3.17	20.39	1.66	
0.10	4.49	24.29	1.94	
0.28	5.95	24.50	2.55	
0.22	7.25	20.08	3.83	
0.10	7.56	24.26	3.24	1:32
0.15	8.56	24.08	3.69	
0.18	14.75	20.65	7.57	
0.53 ^a	31.48	24.20	13.71	
1.48 ^a	38.33	24.98	16.33	
2.13	38.53	15.50	25.98	
2.04	44.00	16.31	32.43	1:32+1:2
3.04	44.90	31.78	31.19	
2.51	39.18	24.56	29.53	1.2
2.80	39.39	19.36	32.06	1.2
3.04	44.90	31.78	31.19	· A NIT
3.04	51.24	22.14	41.07	<i>i</i> -Am ₄ NI

^a Metastable phases.

all systems containing quaternary ammonium salts, and it most likely has a tetrahedral structure characteristic of salt hydrates of the same composition [6].

It should be noted that tetraisopentylammonium halides almost do not vary in stability in going from F^- to Br^- , and their melting points span the range 28–32.5°C [8–10]. Obviously, the lower stability of tetraisopentylammonium iodide hydrate is explained by the relatively high stability of the crystal structure

RUSSIAN JOURNAL OF GENERAL CHEMISTRY Vol. 73 No. 3 2003

of the salt itself, and its developed crystallization field overlaps considerably the crystallization fields of the clathrate hydrates (peritectic type of melting). Had the hydrate melted congruently (distectic type), its melting point would has been higher, like in other systems of this series, containing congruently melting compounds. Probably, the stability of the iodide hydrates is determined by the fact that the iodide ion much stronger than the other halide ions differs from the water molecule both in size and in the ability to H-bond formation, thus producing some additional distortion in the carcass on insertion. These factors contribute much more in the tetrabutylammonium halide hydrate series, since the tetrabutylammonium cation worse than tetraisopentylammonium stabilizes voids in the clathrate carcass. Therefore, the melting points of tetrabutylammonium halide hydrates vary considerable in going from F⁻ to Br⁻, and the iodide does not form clathrate hydrates at all [11].

EXPERIMENTAL

Tetraisopentylammonium iodide was prepared by the Menshutkin reaction. To this end, an equimolar mixture of triisopentylamine and isopentyl iodide in acetonitrile was heated under reflux for ~36 h. The product was thrice recrystallized from ethyl acetate and then dried in a dessicator over P_2O_5 . The content



Fig. 2. Phase diagram of the *i*-Pent₄NI–H₂O system in the crystallization range of clathrate hydrates (the numerals along the composition line are hydrate numbers; triangles are DTA data; and circles are solubility-derived data).

of the main substance $(99.8\pm0.2 \text{ wt\%})$ was determined by potentiometric titration of the salt with a solution of sodium tetraphenylborate using an ion-selective electrode [12].

The fusibility curve was studied by solubility measurements and DTA. For solubility measurements, a mixture of salt and water (supersaturated solution) was stirred for some hours (4–7 h) at different temperatures, and after which the salt concentration was determined as described above. The reproducibility of temperature measurements in the DTA analysis was $\pm 0.05^{\circ}$ C, and the heating rate was 0.2 deg/min.

The ternary system was studied by the Schreinemakers method, by analysis of the liquid phase and wet residue after the equilibrium had been attained. The wet residue was dissolved in a water–ethanol mixture. The equilibration time (under mechanical stirring) was 4–6 h. The tetraisopentylammonium salt was determined as described above. The acetic acid was titrated with ~0.04 N NaOH (indicator thymol blue).

The preparative isolation of crystals was performed at $3-8^{\circ}$ C. The crystals were squeezed between filter paper sheets, after which their composition was determined.

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REFERENCES

- 1. McMullan, R.K. and Jeffrey, G.A., J. Chem. Phys., 1959, vol. 31, no. 5, p. 1231.
- 2. Dyadin, Yu.A., Zhurko, F.V., and Zelenin, Yu.M., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, no. 2, p. 479.
- Dyadin, Yu.A., Zhurko, F.V., Zelenin, Yu.M., Aladko, E.Ya., Gaponenko, L.A., and Sinitskii, V.P., *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1984, issue 1, no. 2, p. 13.
- Nakayama, H., Bull. Chem. Soc. Jpn., 1981, vol. 54, no. 12, p. 3717.
- 5. Schreinemakers, F.A.H., Z. Phys. Chem., 1906, vol. 55, p. 71.
- 6. Yurchenko, V.K. and Dyadin, Yu.A., Available from VINITI, 1975, Moscow, no. 3115-75.
- 7. Jeffrey, G.A. and McMullan, R.K., Prog. Inorg. Chem., 1967, vol. 8, no. 43, p. 43.
- Lipkowski, J., Suwinska, K., Podionova, T.V., Udachin, K.A., and Dyadin, Yu.A., J. Incl. Phenom., 1994, vol. 17, no. 2, p. 137.
- Aladko, L.S., Rodionova, T.V., and Dyadin, Yu.A., *Zh. Obshch. Khim.*, 2000, vol. 70, no. 12, p. 1972.
- Dyadin, Yu.A. and Kiseleva, L.S., *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1980, issue 1, no. 2, p. 124.
- Dyadin, Yu.A. and Terekhova, I.S., *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1980, issue 4, no. 9, p. 88.
- Smolyakov, B.S., Dyadin, Yu.A., and Aladko, L.S., *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1980, issue 1, no. 14, p. 66.