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1-Methyl-2-pyrrolidinone Solvates of Alkali Metal Salts

ROSS D. HUNTER and DEAN C. LUEHRS*

Department of Chemistry and Chemical Engineering, Michigan Technological University, Houghton, Mich. 49931, U.S.A.

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1-Methyl-2-pyrrolidinone (NMP) is an excellent dissociating solvent with good donor properties [1–9]. A large number of solvates of NMP with salts of multiply charged cations have been prepared and characterized [10–17]. Several NMP solvates of alkali metal salts have been reported [17–21], but the melting points were not usually given and in the case of LiCl·NMP there was no agreement on the value of the melting point. Because of the interest here in the application of solvates of alkali metal salts as electrolytes in thermal power cells [22], it was desirable to know the values of the melting points of known solvates and prepare as many additional NMP solvates as possible for evaluation as thermal cell electrolytes. Also the characterization of solid solvates is one approach to studying the solvation of electrolytes in solution [23, 24].

Experimental

Aldrich NMP was purified by distillation under vacuum from calcium hydride. The IR spectra of the solvates were obtained from KBr pellets on the Perkin-Elmer 283B or 735B infrared spectrophotometer. All other work was done as before [25, 26].

Results

The solvates prepared together with the elemental analyses, melting points, and CO stretch frequencies are given in Table I.

Discussion

The melting point for LiCl·NMP did not agree with the value of Madan [17] or Asahara's first report [20] but did agree with the value of Asahara's second report [21]. This is not the first time that values from Asahara's first report did not agree with other workers [26]. Perhaps one source of confusion here is that LiCl·NMP melts incongruently, and this phenomenon is not as familiar as a congruent melting point. Generally when a pure compound melts incongruently, there is a large amount of liquid phase formed initially, and the remaining solid dissolves gradually as the temperature is raised. The congruent melting of an impure solid is superficially similar except that a relatively small amount of liquid phase

TABLE I. NMP Solvates of Alkali Metal Salts.

	m.p.[a] (°C)	CO stretch ($\mathrm{cm^{-1}}$)	% Anion		% C		% H		% N	
			calc.	found	calc.	found	calc.	found	calc.	found
LiCl·NMP	65*i*	1635	25.05	23.42	42.46	43.88	6.41	7.24	9.90	10.1
LiBr·NMP	215	1621	42.97	37.02	32.29	34.30	4.88	5.98	7.53	7.61
$\mathrm{LiNO_3}$·NMP	84–85	1630			35.73	33.83	5.40	5.73	16.67	14.80
LiSCN·NMP	65–66*i*	1628	35.38	32.87	43.90	44.41	5.53	5.83	17.07	16.93
$\mathrm{LiClO_4}$·NMP	139*i*	1647	48.39	46.63	29.22	23.13	4.41	1.87	6.82	5.34
$\mathrm{LiClO_4}$·3.5NMP	42–45	1623	21.99	21.99	46.36	43.85	7.00	6.82	10.82	10.11
NaI·3NMP	43*i*	1654	28.37	28.16	40.28	37.19	6.08	5.82	9.39	8.80
NaSCN·2NMP	54–57	1649	20.80	19.40	47.30	44.85	6.50	6.58	15.05	14.14
$\mathrm{NaClO_4}$·2.5NMP	55	1666	26.86	27.08	40.55	37.71	6.13	5.90	9.46	8.83
KSCN·2.5NMP	39*i*	1663	16.83	17.03	47.00	43.67	6.57	6.30	14.21	13.64
KI·3NMP	67*i*	1653	27.39	26.92	38.88	36.17	5.87	5.75	9.07	8.52
NMP		1685								

[a] *i* denotes an incongruent melting point.

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*Author to whom correspondence should be addressed.

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forms gradually as the temperature is raised and finally the remaining solid liquifies as the melting point of the pure solid is approached [27].

The melting points of the solvates of lithium perchlorate and sodium perchlorate agree with those of Madan [17]. However, there is disagreement as to the exact composition of the solid phase due to difficulties in completely excluding water and separating the hygroscopic, very soluble crystals from the viscous mother liquor. Every reasonable precaution was taken in this study to dry the salts, NMP, and solvents before use and to minimize exposure to air during preparation of a solvate.

The frequency of the CO stretch of the NMP was decreased in all cases upon coordination to the alkali metal ion. This indicates coordination through the oxygen [12, 17, 19]. The decrease was greatest with lithium ion, as expected for the most intense electric field, and on the average least for potassium ion. There were no other significant effects in the IR spectra above 600 cm^{-1}.

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