J. Chem. Eng. Data **1985**, *30*, 144–145

Solubilities of Inorganic Salts and Tetraalkylammonium Iodides in Sulfolane at Several Temperatures

Pankaj Srivastava,* Mohd. M. Husain, and Ram Gopal†

Department of Chemistry, Lucknow University, Lucknow—226007, India

Solubilities of some common salts and tetraalkylammonium iodides (R_4NI) in sulfolane have been determined at different temperatures. In general, solubilities of alkali metal halides are in the order iodides > bromides > chlorides. The solubilities of R_4NI salts increase with growing alkyl chain from Me_4NI to n-Bu_4NI. Enthalpies of solution of sparingly soluble halides have been estimated from the solubility data and are used to evaluate the solvation enthalpies in studying the solute–solvent interaction in sulfolane.

Introduction

A reference to the literature reveals that the solubilities of electrolytes in sulfolane (*1*) are, in general, not available except for some perchlorates and the sparingly soluble chlorides at 40 °C only. It is, therefore, desirable to obtain the useful solubility data in detail and thus to have an idea of solute–solvent interaction in this solvent. As mentioned earlier, the solubilities of some sparingly soluble salts have been determined in sulfolane at 40 °C radiochemically (*1*); it would be interesting to verify them by conductivity method and extend the data to other temperatures as well. The present communication reports some studies in this direction.

Experimental Section

Sulfolane (Fluka, puriss) was purified as reported earlier (*2*); the melting points of samples used were close to 27 °C, density ($d_{40 °C}$), being 1.2515 g mL^{-1}. The common salts were recrystallized twice from conductivity water and dried under vacuum before use and the R_4NI salts were purified as described elsewhere (*3, 4*). In order to conserve the costly solvent, care was taken to use its minimum quantity; the solubilities of fairly soluble salts were determined by either evaporation (*5*) or synthetic method (*6*), according to suitability. A brief description of the methods used is given below.

Evaporation Method. A petri dish containing a weighed sample of clear saturated solution, at a desired temperature, was heated carefully in an oven and finally on an electrical heater to expel the solvent completely. Too rapid heating was avoided to check the spurting of solution and charring of sulfolane. The dish was then cooled in a dry nitrogen box and weighed. The process was repeated to obtain a constant weight of solute from which the solubility was calculated as usual. The results are, in general, the mean of solubilities with three different samples at given temperatures and are satisfactorily reproducible.

Synthetic Method. Known amounts of finely grounded solute (R_4NI) and sulfolane were sealed in a Corning glass tube. The ampule was then placed in a thermostat whose temperature could be raised slowly in 0.10 °C intervals, when desired. The temperature of the bath was held constant (±0.03 °C) for sufficient time to ensure saturation. The ampule containing the solute–solvent mixture was shaken from time to time and the temperature at which the last crystal disappeared was taken as the saturation temperature of the sample. In general, the saturation temperatures were observed to differ by ±0.01 °C for the three samples of nearly equal compositions and the mean of these temperatures was taken.

Table I. Solubilities of Some Common Salts in Sulfolane at Different Temperatures by the Evaporation Method

	solubility,[a] g per 100 g of sulfolane			
salt	40 °C	45 °C	50 °C	55 °C
$NaNO_2$	0.0155	0.0822	0.1429	0.2048
$NaNO_3$[b]	0.4553	0.4021	0.3672	0.3370
NaI[b]	29.41	22.48	18.89	15.19
KNO_3	0.0450	0.0990	0.1955	0.2945
KBr	0.1363	0.1658	0.2921	0.3370
KI[b]	19.69	18.40	17.71	17.03
KIO_4	0.0589	0.0869	0.1207	0.2110
KCNS	18.59	20.59	21.44	22.38
$SrCl_2$	0.1434	0.1638	0.2349	0.3609
$PbCl_2$[b]	0.4829	0.2674	0.0934	0.0805

[a] Correct within ±1%. [b] Solubilities decrease with temperature.

Table II. Solubilities of Sparingly Soluble Ammonium and Alkali Metal Halides in Sulfolane by the Conductivity Method

	solubility,[a] $10^3 \times$ g per 100 g of sulfolane	
halide	40 °C	50 °C
NH_4Cl	2.091 (2.675)	2.420
NaCl	1.886 (5.148)[b]	1.979
NaBr	187.2	191.2
KCl	4.305 (3.948)[b]	4.968
RbCl	14.75 (10.57)[b]	16.46
CsCl	46.93 (18.52)[b]	49.75
CsBr	272.9	273.5

[a] The data agree, in general, within ±0.1%. [b] Reference *1*.

For the determination of solubilities of sparingly soluble salts by conductivity method, a solubility flask–conductivity cell combine, as shown in Figure 1, was used. The working of the combine is self-evident and is given briefly as follows.

The complete setup, containing suitable quantities of solute and solvent in the bulb B (about 50-mL capacity), was kept in a thermostat running at the desired temperature. After the solute–solvent mixture was stirred for 3–4 h, with an electrically driven glass stirrer, T, provided with a mercury trap, the contents of the bulb were allowed to settle. The clear supernatant solution was then sucked into the conductivity cell, C, with a slight suction with the help of a pipet. The capillary stopcock, S, was closed and the conductivity of the solution measured. The solution was then allowed to flow back into the bulb B of the flask by opening the stopcock. The procedure was repeated until reproducible conductance values were obtained. The limiting equivalent conductances at 40 and 50 °C of the salts concerned, required for solubility calculations, were computed from available ionic conductance data (*7*) at 30 °C. For this purpose, the temperature coefficient of conductance was taken as 2% deg^{-1}, which is usually applicable for strong

---

* Address correspondence to this author at the Department of Chemistry, Dayalbagh Educational Institute, Dayalbagh, Agra 282 005, India.

† Deceased, October 15, 1984.

0021-9568/85/1730-0144$01.50/0

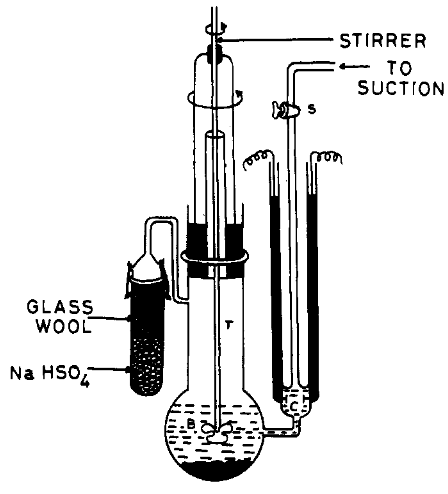

Figure 1. Solubility flask-conductivity cell combine.

electrolytes and also appears to be justified from the unpublished conductance data, obtained in sulfolane in this laboratory.

Results and Discussion

The solubilities of some common electrolytes, thus obtained, are recorded in Tables I and II, from which it appears that the solubility process in most of the cases is endothermic. In general, the solubility and its temperature coefficient are smaller in sulfolane than in water, formamide (*5*), *N*-methylacetamide (NMA) (*6*), and dimethyl sulfoxide (Me_2SO) (*4*). KCNS, however, is found to be more soluble in sulfolane than in water. Ammonium and most of the alkali metal chlorides and bromides appear to be sparingly soluble, contrary to their behavior in water and some other nonaqueous solvents (*4*–*6*). To a large extent, this poor solubility trend is also maintained by $NaNO_2$, KNO_3, KBr, KIO_4, and $SrCl_2$. The solubilities of alkali metal halides are in the order $I^- > Br^- > Cl^-$, as in water ($\epsilon_{25^\circ C} = 78.54$), formamide ($\epsilon_{25^\circ C} = 109.4$), NMA ($\epsilon_{35^\circ C} = 171$), and Me_2SO ($\epsilon_{25^\circ C} = 48.9$) but are, in general, much lower in sulfolane than the corresponding values in the latter solvents, apparently due to its lower dielectric constant ($\epsilon_{30^\circ C} = 43.3$) and the absence of hydrogen bonding (*8*). As is clear from Table II, ammonium chloride and alkali metal chlorides and bromides are sparingly soluble, in general agreement with the results reported by Starkovich et al. (*1*) with apparent exceptions, to NaCl and CsCl. However, there appears to be no possible explanation for this departure. Solubilities of alkali metal halides have been found to increase with increasing size of the cation as in water.

The dilute saturated solution solubility data, recorded in Table II at 40 and 50 °C, offer an opportunity to obtain meaningful enthalpies of solution ($\Delta H_{solution}$) and solvation ($\Delta H_{solvation}$) in order to throw some light on solute–solvent interaction. By combining $\Delta H_{solution}$ with the lattice energy, U_0, of the salt in question, one gets the $\Delta H_{solvation}$ by the relation

$$\Delta H_{solvation} = \Delta H_{solution} - U_0$$

Table III gives the values of $\Delta H_{solvation}$ of some uni-univalent halides in sulfolane.

A comparison of $\Delta H_{solvation}$ data of different alkali metal halides in sulfolane, water (*9*), and formamide (*9*) (Table III) appears to give no clear-cut picture, in general. Probably, this may be accounted for in the light of the aprotic nature of sulfolane unlike water and formamide. However, with the growing size of alkali metal cation, a general increase of $\Delta H_{solvation}$ in all three solvents is noteworthy. Anionic solvation in sulfolane is expected to be negligible; the only interaction, could be on account of feeble anion–solvent dipole interaction, as is pointed out by the conductance study of Monica et al. (*10*).

Table III. Enthalpies of Solution and Solvation of Some Sparingly Soluble Halide Salts in Sulfolane, Water, and Formamide

halide	U_0, kcal mol^{-1}	$\Delta H_{solution}$, kcal mol^{-1}	$-\Delta H_{solvation}$, kcal mol^{-1} sulfolane	water	formamide
NH_4Cl	162	2.937	159.1	158.1	---
NaCl	184	0.962	183.0	184.9	187.9
NaBr	176	0.425	175.6	176.8	181.0
KCl	168	2.877	165.1	156.5	168.1
RbCl	163	2.206	160.8	158.8	162.1
CsCl	157	1.170	155.8	151.1	154.3
CsBr	151	0.046	151.0	142.8	147.2

Table IV. Solubilities of Tetraalkylammonium Iodides in Sulfolane at Different Temperatures by the Synthetic Method

salt	solubility,[a] g per 100 g of sulfolane 40 °C	45 °C	50 °C	55 °C
Me_4NI	0.376	0.489	0.643	0.856
Et_4NI	0.880	1.32	1.92	2.90
n-Pr_4NI	16.22	17.95	19.77	22.13
n-Bu_4NI	31.12	41.88	46.13	48.87
n-Pen_4NI	2.82	4.94	8.51	14.22
n-Hex_4NI	6.11	8.81	13.18	17.78
n-Hep_4NI	4.07	6.14	8.85	13.21

[a] Reproducibility within ±0.5%.

The solubility trend of R_4NI salts (Table IV) appears to be similar to that in Me_2SO (4) but opposite to that in water (*11*–*13*) where the larger R_4NI salts are almost insoluble. This difference in behavior is very likely due to the absence of solvophobic interaction in sulfolane as in Me_2SO; i.e., the solubility increases regularly from Me_4NI to *n*-Bu_4NI, then decreases for *n*-Pen_4NI, and increases once again for *n*-Hex_4NI before decreasing for *n*-Hep_4NI.

An increasing trend of solubility from Me_4NI to *n*-Bu_4NI may be reasonably explained in terms of a growing amount of organic moiety of the salts concerned, thereby offering a larger hydrocarbon surface to interact with the solvent. Moreover, higher solubility of *n*-Hex_4NI as compared to *n*-Pen_4NI and *n*-Hep_4NI appears to be due to the presence of an even number of carbon atoms in the alkyl chain which somehow tends to induce their more compact packing with the solvent dipoles.

Registry No. $NaNO_2$, 7632-00-0; $NaNO_3$, 7631-99-4; NaI, 7681-82-5; KNO_3, 7757-79-1; KBr, 7758-02-3; KI, 7681-11-0; KIO_4, 7790-21-8; KCNS, 333-20-0; $SrCl_2$, 10476-85-4; $PbCl_2$, 7758-95-4; NH_4Cl, 12125-02-9; NaCl, 7647-14-5; NaBr, 7647-15-6; KCl, 7447-40-7; RbCl, 7791-11-9; CsCl, 7647-17-8; CsBr, 7787-69-1; Me_4NI, 75-58-1; Et_4NI, 68-05-3; *n*-Pr_4NI, 631-40-3; *n*-BuNI, 311-28-4; *n*-Pen_4NI, 2498-20-6; *n*-Hex_4NI, 2138-24-1; *n*-Hep_4NI, 3535-83-9; sulfolane, 126-33-0.

Literature Cited

(1) Starkovich, J. A.; Janghorbani, M. *J. Inorg. Nucl. Chem.* **1972**, *34*, 789–91.
(2) Pankaj; Gopal, R. *Indian J. Chem., Sect. A* **1982**, *21A*, 404–5.
(3) Conway, B. E.; Verrall, R. E.; Desnoyers, J. E. *Trans. Faraday Soc.* **1966**, *62*, 2738–49.
(4) Gopal, R.; Jha, J. S. *Indian J. Chem.* **1974**, *12*, 618–9.
(5) Gopal, R.; Husain, M. M. *J. Indian Chem. Soc.* **1963**, *40*, 272–4.
(6) Gopal, R.; Chandra, D. *J. Indian Chem. Soc.* **1970**, *47*, 154–6.
(7) Della Monica, M.; Lamanna, U.; Senatore, L. *J. Phys. Chem.* **1968**, *72*, 2124–6.
(8) Parker, A. J. *Chem. Rev.* **1969**, *69*, 1–32.
(9) Gopal, R., Husain, M. M.; Bhatnager, O. N. *J. Indian Chem. Soc.* **1967**, *44*, 1005–8.
(10) Della Monica, M.; Lamanna, U. *J. Phys. Chem.* **1968**, *72*, 4329–31.
(11) Levien, B. J. *Aust. J. Chem.* **1965**, *18*, 1161–70.
(12) Lindenbaum, S.; Boyd, G. E. *J. Phys. Chem.* **1964**, *68*, 911–7.
(13) Franks, F.; Clarke, D. L. *J. Phys. Chem.* **1967**, *71*, 1155–6.

Received for review February 7, 1983. Revised manuscript received June 25, 1984. Accepted July 18, 1984. We are thankful to the UGC, New Delhi, for financial assistance.