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Note

Physico-chemical properties of solutions of potassium halides in formamide at different temperatures

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The view that in concentrated aqueous solutions and in some different solvents the apparent molal volumes of electrolytes increase with increase in concentration and obey the Masson's equation[1], inspired a large number of research workers to test the validity of the fact in determining the apparent molal volume of various electrolytes in varying concentration ranges in different solvents. Bruno and Della Monica[2], from density measurements of alkaline and alkaline-earth metal salts in formamide, reported that the apparent molal volumes of these salts do not change with concentration. On the other hand, Gopal and Singh[3] studying tetraalkylammonium salt series in this solvent observed the variation of apparent molal volume with concentration. With a view to obtaining an independent check, the present work aims at determining the apparent molal volume of potassium halides in formamide from density measurements in varying ranges of concentration at different temperatures. The coefficients of thermal expansion, and the apparent and partial molal expansibility of solutions of potassium halides have also been determined in this solvent at 25 °C.

EXPERIMENTAL

Potassium chloride, potassium bromide (B.D.H. Analar), and potassium iodide (Guaranteed Reagent) were dried at 100 and 200 °C, respectively, for 2 h and kept in a vacuum desiccator before use. Formamide (B.D.H., L.R.) was purified by the method as adopted by Dash and Nayak[4]. Density measurements were carried out by following the procedure of Bruno and Della Monica[2].

RESULTS AND DISCUSSION

The apparent molal volumes were calculated from the observed densities by means of the relation given by[5]

$$\phi_v = \frac{1000}{cd_0}(d_0 - d) + \frac{M_2}{d_0} \tag{1}$$

TABLE 1

VALUES OF $\phi_v{}^0$, S_v, A AND B CONSTANTS (OF EQN. 4), $\bar{V}_{2\,\max}$ AND V_m FOR POTASSIUM CHLORIDE, BROMIDE AND IODIDE, AT DIFFERENT TEMPERATURES

T (°C)		$\phi_v{}^0$ (ml mole^{-1})	S_v (ml$^{3/2}$ mole$^{-3/2}$)	A	B	$\bar{V}_{2\,max}$ (ml mole^{-1})	V_m (ml mole^{-1})
15	KCl	31.25	3.17	0.03901	0.00361	35.51	
	KBr	38.21	3.85	0.07555	0.00441	43.42	
	KI	50.11	5.12	0.10899	0.00582	57.31	
20	KCl	31.62	3.10	0.03871	0.00350	35.77	
	KBr	38.53	3.81	0.07533	0.00432	43.66	
	KI	50.33	5.14	0.10896	0.00583	57.55	
25	KCl	31.97	3.01	0.03844	0.00341	36.02	20.77
	KBr	38.91	3.68	0.07508	0.00419	43.87	24.23
	KI	50.78	4.95	0.10866	0.00559	57.69	30.20
30	KCl	32.39	2.93	0.03814	0.00331	36.27	
	KBr	39.26	3.61	0.07491	0.00416	44.12	
	KI	51.11	4.90	0.10846	0.00544	57.94	
35	KCl	32.75	2.88	0.03787	0.00325	36.57	
	KBr	39.57	3.59	0.07466	0.00404	44.37	
	KI	51.48	4.78	0.10828	0.00534	58.13	
40	KCl	33.07	2.87	0.03760	0.00318	36.87	
	KBr	39.90	3.55	0.07445	0.00396	44.65	
	KI	51.81	4.71	0.10815	0.00526	58.34	
45	KCl	33.42	3.21	0.03737	0.00314	37.33	
	KBr	40.12	3.66	0.07424	0.00387	44.98	
	KI	52.09	4.70	0.10805	0.00522	58.60	

where c is the molar concentration of the solution, M_2 is the molecular weight of the solute, and d_0 and d are the densities of the pure solvent and solution, respectively.

The apparent molal volumes thus obtained were found to vary linearly with $c^{1/2}$, agreeing fairly well with the relation[1]

$$\phi_v = \phi_v^0 + S_v c^{1/2} \tag{2}$$

over the range in which the densities were determined, where ϕ_v^0 is the apparent molal volume at infinite dilution and $S_v (= \partial\phi_v/\partial c^{1/2})$ is the slope of the plot of ϕ_v vs. $c^{1/2}$.

The densities of the solutions were calculated by using the equation[5]

$$d = d_0 + \frac{(M_2 - d_0\,\phi_v^0)c}{1000} - \frac{(S_v d_0)c^{3/2}}{1000} \tag{3}$$

Equation (3) can be represented by the relation of the form

$$d = d_0 + Ac - Bc^{3/2} \tag{4}$$

Observed values of the density are reproduced by these equations to at least 1 part in 10 000.

In Table 1 are presented the values of ϕ_v^0, S_v, A and B constants for the potassium halides at each of the seven temperatures. The partial molal volumes, $\overline{V}_2$, were calculated by the relation[5]

$$\overline{V}_2 = \phi_v + \left(\frac{1000 - c\,\phi_v}{2000 + S_v c^{3/2}}\right) S_v C^{1/2} \tag{5}$$

for these salts at different temperatures for various concentrations of the solutions. The partial molal volumes at the highest concentration, $\overline{V}_{2\,\mathrm{max}}$ for the seven investigated temperatures are also included in Table 1, along with the molal volume values V_m calculated by means of the following equation

$$V_\mathrm{m} = 4/3\,\pi\,(r_\mathrm{a}^3 + r_\mathrm{c}^3)N \tag{6}$$

where r_a and r_c are the ionic radii of the corresponding ions, and are reported in the literature[6].

The apparent molal expansibility of the solute, ϕ_E, was calculated from densities and their temperature coefficients by using the equations[5]

$$\phi_E = \frac{1000}{c}(\alpha - \alpha_0) + \alpha_0\phi_v \tag{7}$$

where α and α_0 are the coefficients of thermal expansion of solution and solvent, respectively, and are given by

$$\alpha \equiv -\frac{1}{d}\left(\frac{\partial d}{\partial T}\right)_p \tag{8}$$

and

$$\alpha_0 \equiv -\frac{1}{d_0}\left(\frac{\partial d_0}{\partial T}\right)_p \tag{9}$$

The values of ϕ_E like ϕ_v can also be represented by the expression

$$\phi_E = \phi_E^0 + S_E c^{1/2} \tag{10}$$

where

$$\phi_E = 0.0718 - 0.0127\,c^{1/2} \tag{11}$$

$$\phi_E = 0.0669 - 0.0136\,c^{1/2} \tag{12}$$

and

$$\phi_E = 0.0642 - 0.0135\,c^{1/2} \tag{13}$$

for potassium chloride, bromide and iodide, respectively, at 25 °C and 1 atm pressure. By substituting the values of ϕ_E and S_E for potassium salts in place of ϕ_v and S_v in eqn. (5), the partial molal expansibility $\bar{E}_2$ has also been calculated at this temperature.

The coefficients of thermal expansion for potassium salts at 25°C and 1 atm pressure have been represented by the equations

$$\alpha(\text{KCl}) = 7.393 \times 10^{-4} + 0.479 \times 10^{-4}c - 0.146 \times 10^{-4}c^{3/2} \tag{14}$$

$$\alpha(\text{KBr}) = 7.393 \times 10^{-4} + 0.382 \times 10^{-4}c - 0.164 \times 10^{-4}c^{3/2} \tag{15}$$

and

$$\alpha(\text{KI}) = 7.393 \times 10^{-4} + 0.288 \times 10^{-4}c - 0.199 \times 10^{-4}c^{3/2} \tag{16}$$

It has been found that Masson's law is obeyed by potassium halides in formamide over a considerable concentration range within an accuracy of 0.01 % in the density determinations. Unlike Monica et al.'s investigation on alkaline and alkaline-earth metal salts in this solvent, the apparent molal volumes of potassium halides are found to increase with increase of concentration in the present study, lending support to the applicability of Masson's law in formamide.

It is interesting to compare the present set of data with that available in aqueous medium[5] at 25°C. The slopes, s_v, of the plot of ϕ_v vs. $c^{1/2}$ are expected to be positive because of the electrostatic ion–ion interaction in both the solvents but in formamide these are found to be more positive, pointing to the greater electrostatic ion–ion interaction in this solvent than in water. The reverse order in the slope values for the potassium halides observed in formamide in comparison with that in water indicates that the extent of anionic solvation is affected more in formamide than in water. The decreasing trend in the slope values (Table 1) for the three salts with increase of temperature points to the enhanced ion–solvent interaction in this solvent.

The limiting apparent molal volume, ϕ_v^0, of potassium halides like that of tetraalkyl ammonium salts reported in formamide[7] increases with increase of temperature and has been given in the form of equations (variation of ϕ_v^0 with any temperature T in °C,)

$$\phi_v^0(\text{KCl}) = 30.17 + 0.0728\,T$$

$$\phi_v^0(\text{KBr}) = 37.26 + 0.0652\,T$$

and

$$\phi_v^0(\text{KI}) = 49.04 + 0.0686\,T$$

Comparing the ϕ_v^0 values of KCl, KBr, and KI (31.97, 38.91 and 50.78 ml mole^{-1}, respectively) obtained in formamide at 25°C with that available in water[5], 26.52, 33.73, and 45.36 ml mole^{-1} at this temperature for KCl, KBr and KI, respectively, it is observed that the ϕ_v^0 values are greater in formamide than in water, lending support to the view that the higher dielectric constant favours a higher value of ϕ_v^0 as a result of stronger electrostatic ion–solvent interaction. It is interesting to note a similar order of ϕ_v^0 for the potassium salts in both formamide and water. Our ϕ_v^0

values at 25 °C are in good agreement with those reported earlier at this temperature[8].

Unlike Monica et al.'s investigation, the partial molal volumes, $\overline{V}_2$, for the potassium salts increase with increase in concentration for each temperature. This increasing trend is also observed in the case of copper sulphamate studied in aqueous solution[9]. However, the $\overline{V}_2$ tends to a constant value with increase in concentration in the present study. The decrease of the partial molal volume values in the low concentration region in the case of the potassium salts is in contradiction to the electrostriction phenomenon, according to which the partial molal volume should increase because of the increase of the available number of solvent molecules for each ion in dilute solutions, yet appears reasonable owing to the structure breaking of the solvent molecules in concentrated solution of high charge density ions like potassium and halide ions characterized by very strong interaction forces with the solvent molecules. It is evident from Table 1 that there seems to be no agreement between the molal volume values, V_m, of eqn. (6), the partial molal volume in the highly concentration solution, $\overline{V}_{2\max}$, and ϕ_v^c values for the potassium halides in this solvent.

By means of eqns. (11)–(13), the apparent molal expansibilities for potassium halides have been calculated at 25 °C. Comparing the limiting apparent molal expansibility, ϕ_E^0 of KCl obtained in formamide at 25 °C (0.0718 ml mole^{-1} deg^{-1}) with that available in water[5] (0.0850 ml mole^{-1} deg^{-1}) it is seen that ϕ_E^0 is greater in water than in formamide. The reason for this might be that the apparent molal volume is affected more in changing the solvent from water to formamide.

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