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Note

THE APPARENT AND PARTIAL MOLAL PROPERTIES OF POTASSIUM SALTS OF SOME FATTY ACIDS IN FORMAMIDE AT DIFFERENT TEMPERATURES

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As a part of an earlier work, where the determination of the apparent and partial molal volumes of potassium halides [1] and sodium salts of some fatty acids [2] in formamide was reported, we have now undertaken similar determination on potassium salts of formic, acetic, propionic, *n*-butyric and *n*-valeric acids in this solvent over the temperature range 15—45°C, and also the effect of the increase in chain length upon the change in apparent and partial molal volumes and expansibilities of the potassium salts.

EXPERIMENTAL

The method of preparation and purification of the potassium salts of the fatty acids was described elsewhere [3]. These salts were dried at 100° for 2 h and kept in a vacuum desiccator before use. The method of purification of formamide and the procedure for density measurements were essentially similar to that described in our previous article [1].

RESULTS AND DISCUSSION

The values of the apparent molal volume (ϕ_v), and partial molal volume ($\overline{V}_2$) calculated from the usual relations [1,2] for the potassium salts of formic, acetic, propionic, *n*-butyric and *n*-valeric acids in formamide are presented in Table 1 for different temperatures ranging from 15 to 45°C along with the values of apparent molal volume at infinite dilution (ϕ_v^0) and the limiting slope (S_v) obtained from the linear plots of ϕ_v versus $c^{1/2}$. The increments in ϕ_v^0 due to an increase in chain length of a CH_2 grouping and the partial molal volumes at the highest concentration ($\overline{V}_{2\max}$) are also included in Table 1.

The densities of the potassium salt solutions in formamide calculated by

TABLE 1

Values of ϕ_v^0, S_v, A and B constants [of eqn (1)], $\overline{V}_{2max}$ and ϕ_v^0 for potassium formate, acetate, propionate, butyrate and valerate at different temperatures

Temp (°C)	Salt [a]	ϕ_v^0 (ml mole^{-1})	S_v (ml$^{3/2}$ mole$^{-3/2}$)	$A \times 10^3$	$B \times 10^3$	$\overline{V}_{2max}$ (ml mole^{-1})	Mean $\Delta\phi_v^0$ (ml mole^{-1}) per CH_2 increase
15	a	37.21	2 71	41.774	3 078	42.94	16.09
	b	53 17	2.86	37 557	3.197	58.85	
	c	69.20	3 34	33.368	3.793	75.50	
	d	85.38	3.59	29.003	4 112	92 00	
	e	101.57	3 87	24.580	4 419	108.76	
20	a	37.50	2.66	41 599	3.018	43 13	16.13
	b	53 51	2 82	37.453	3 203	59.10	
	c	69.58	3 30	33 245	3 740	75.77	
	d	85.79	3 54	28.871	4 013	92.30	
	e	102.00	3 82	24 494	4 336	109.09	
25	a	37 81	2.62	41.106	2 958	43.34	16.15
	b	53.84	2 79	37.310	3 151	59.35	
	c	69.94	3 26	33.110	3 666	76 06	
	d	86.20	3 49	28 780	3.956	92 61	
	e	102.42	3 79	24 444	4 277	109.44	

30	a	38.13	2.56	41.173	2.867	43.53	16.18
	b	51 20	2.73	37.115	3 065	59.58	
	c	70 32	3 21	33.114	3.718	76.34	
	d	86.59	3.45	28 695	3 906	92.92	
	e	102 86	3 74	24.359	4.197	109.78	
35	a	38 45	2.52	40 999	2 819	43 73	16.21
	b	54 53	2 69	36 973	3.024	59.83	
	c	70.69	3 17	32.859	3.553	76.61	
	d	86.99	3 41	28 582	3.824	93 23	
	e	103 30	3 69	24 316	4.155	110.11	
40	a	38 71	2.49	40 887	2.797	43 93	16.26
	b	54.89	2 63	36.813	2 953	60.06	
	c	71.07	3 11	32 723	3 479	76.88	
	d	87 40	3 36	28.471	3 735	93.45	
	e	103.75	3 63	24.239	4 061	110.45	
45	a	39 02	2.44	40 687	2.707	44.13	16 29
	b	55 22	2 60	36.668	2 886	60.32	
	c	71 43	3 08	32.643	3 436	77.17	
	d	87 80	3.33	28 445	3.710	93 86	
	e	104.16	3.62	24 247	4 032	110.81	

[a] a = Potassium formate; b = potassium acetate; c = potassium propionate, d = potassium butyrate; e = potassium valerate

the usual relation [1] are expressed in the general form

$$d = d_0 + Ac - Bc^{1/2} \tag{1}$$

which agree fairly well with the observed values of the density. The constants A and B of eqn. (1) are also included in Table 1.

As usual [2] the values of the apparent molal expansibility (ϕ_E) and the partial molal expansibility ($\overline{E}_2$) of the potassium salt solutions were calculated by using the equations

$$\phi_E = \alpha_0 \phi_v + (\alpha - \alpha_0) \frac{1000}{c} \tag{2}$$

and

$$\overline{E}_2 = \phi_E + \left(\frac{1000 - c\phi_E}{2000 + S_E c^{3/2}}\right) S_E c^{1/2} \tag{3}$$

where the symbols have their usual significance. The values of α, α_0 and S_E for various potassium salts were obtained from the relations [1,2]

$$\alpha_0 = -\frac{1}{d_0}\left(\frac{\partial d_0}{\partial T}\right)_p \tag{4}$$

$$\alpha = \alpha_0 + A'c - Bc^{3/2} \tag{5}$$

and

$$\phi_E = \phi_E^0 + S_E c^{1/2} \tag{6}$$

The constants for eqns. (5) and (6) are listed in Table 2 for different temperatures and one atmosphere together with the increments in ϕ_E^0 due to an increase in the chain length of a CH_2 grouping.

As for those of the sodium salts of fatty acids [2], the limiting apparent molal volume (ϕ_v^0) and the limiting apparent molal expansibility (ϕ_E^0) of potassium salts of the same fatty acids tend to increase with increase in temperature, and these are expressed as a function of temperature by equations of the form,

$$\phi_v^0 = C + Dt \tag{7}$$

and

$$\phi_E^0 = C't + D't \tag{8}$$

respectively. The constants of eqns. (7) and (8) are presented in Table 3 for different potassium salts. The increase in the values of ϕ_v^0 and ϕ_E^0 with the increase in the chain length of a CH_2 grouping is in agreement with our earlier observations on sodium salts in formamide lending support to the greater electrostatic ion—ion interaction in this solvent. This is consistent with the positive values of S_v presented in Table 1 for the potassium salts. Further the

TABLE 2

Values of ϕ^0_E, S_E, A' and B' constants [of eqns. (5) and (6)] and ϕ^0_E for potassium formate, acetate, propionate, butyrate and valerate at different temperatures and one atmosphere

Temp (°C)	Salts [a]	$\phi^0_E \times 10^2$ (ml mole^{-1})	$-S_E \times 10^2$ (ml$^{3/2}$ mol$^{-3/2}$)	$A' \times 10^4$	$B' \times 10^4$	Mean $\Delta\phi^0_E \times 10^2$ (ml mole^{-1}) per CH_2 increase
15	a	5.85	0.93	0.3112	0.1122	0 648
	b	6.65	0.96	0.2749	0.1170	
	c	7.20	0.90	0.2123	0.1147	
	d	7.86	0.97	0.1592	0.1234	
	e	8.44	0.95	0.0982	—0.1230	
20	a	5.92	0.94	0.3152	0.1139	0.643
	b	6.73	0.98	0.2792	0.1194	
	c	7.27	0.91	0.2147	0.1165	
	d	7.95	1 01	0.1628	0.1267	
	e	8.49	0.95	0.0985	—0.1236	
25	a	6.00	0.97	0.3200	0.1161	0.658
	b	6.83	1.02	0 2841	0 1221	
	c	7.37	0.96	0.2192	0.1191	
	d	8.01	1.01	0.1644	0.1275	
	e	8.63	1 03	0.1048	—0.1297	
30	a	6 07	0.99	0.3249	0.1184	0.658
	b	6.91	1.05	0.2886	0.1249	
	c	7.46	0 99	0.2241	0.1226	
	d	8.11	1.06	0.1687	0.1314	
	e	8.70	1.04	0 1057	—0.1311	
35	a	6.13	1.00	0 3265	0.1185	0 658
	b	6.95	1.04	0.2905	0.1253	
	c	7.51	0.99	0 2250	0.1231	
	d	8.17	1.06	0.1689	0.1316	
	e	8.76	1 05	0.1060	—0.1317	
40	a	6.21	1.02	0.3302	0.1201	0 658
	b	7.05	1 08	0.2948	0.1276	
	c	7.61	1.03	0 2296	0.1265	
	d	8.25	1.09	0.1709	0.1333	
	e	8.84	1.08	0 1065	—0.1327	
45	a	6.25	1.03	0.3318	0.1204	0.650
	b	7.11	1 09	0.2956	0.1278	
	c	7.62	1.00	0.2261	0.1234	
	d	8.29	1.09	0.1687	0.1318	
	e	8 85	1.04	0.1037	—0 1318	

[a] a = Potassium formate; b = potassium acetate, c = potassium propionate; d = potassium butyrate; e = potassium valerate.

TABLE 3

Parameters for equations (7) and (8)

Salts	C	$D \times 10^2$	$C' \times 10^2$	$D' \times 10^4$
Formate	36.299	6.06	5.652	1.36
Acetate	52.137	6.86	6 431	1.53
Propionate	68.086	7.44	6 989	1.49
n-Butyrate	84.178	8.05	7.652	1.46
n-Valerate	100 262	8.68	8.231	1.47

values of $\overline{V}_2$ and $\overline{V}_{2\max}$ obtained for the potassium salts in the present study also follow a similar trend to those of sodium salts in formamide. The increase in the value of $\overline{V}_{2\max}$ with an increase in the chain length is consistent with the structure breaking of the solvent molecules in concentrated solutions of larger anions as observed in the case of sodium salts in this solvent.

It is interesting to compare the ϕ_v^0 values of potassium salts with those of sodium salts of the same fatty acids in formamide. It is found that the ϕ_v^0 values of potassium salts are higher than those of sodium salts suggesting that the electrostatic ion—solvent interaction and solvation predominate over the ion—ion interaction in the case of potassium salts in comparison with that in sodium salts or, in other words, potassium salts breakdown more of the structure in formamide than do the sodium salts. This is again reflected in the lower values of S_v for the potassium salts compared with for the sodium salts.

The ϕ_v^0 values shown in Table 1 give a value of approximately 16.15 ml per CH_2 increase at infinite dilution and is in reasonably good agreement with 16.13 ml obtained earlier from the study of sodium salts.

REFERENCES

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