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Short Communication

Apparent molar volume of alkali metal formates in formic acid–water mixtures

K. CHOWDOJI RAO AND S. BRAHMAJI RAO
Department of Chemistry, Sri Krishnadevaraya University, Anantapur 515 003, India.
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Abstract

The apparent molar volumes of formates of lithium, sodium and potassium in different mixtures of formic acid and water at 30° C have been calculated from the experimentally determined densities. The molar volume increased with concentraton in pure water while it decreased with concentration in aqueous formic acid mixtures. At any concentration of the salt the volume varied non-linearly with the composition of the solvent and exhibited a maximum at about 40%, 60% and 80% of formic acid for lithium, sodium and potassium formates respectively.

Key words: Apparent molar volume, viscosity, density, alkali metal formates, formic acid.

1. Introduction

Our previous studies on the viscosity[1] and conductance[2] of sodium formate in formic acid–water mixtures indicated points of inflection at about 50% formic acid. In continuation of these studies we have studied the apparent molar volumes of formates of lithium, sodium and potassium in formic acid–water mixtures at 30° C. The results are communicated here.

2. Experimental

Formic acid (Riedel, 98–100%) purified by the standard procedure[3] (density 1·2058 g/ml lit.[4] 1·2073 g/ml ; viscosity 1.459 cp lit.[5] 1. 465 cp) and conductivity water are used in these studies. Salt solutions and solvent mixtures are prepared by weight. Density measurements are made with a pycnometer as reported[1] earlier.

Table I

Apparent molar volumes (ϕ_v) of alkali metal formates in formic acid-water mixtures at 30° C

% HCOOH	0·05	0·10	0·20	0·30	0·40	0·50
Lithium formate						
0	24·00	28·30	24·90	25·30	25·60	26·00
20	28·83	28·70	28·54	28·40	28·30	28·20
40	35·23	34·98	34·65	34·43	34·20	34·00
60	33·45	33·55	32·95	32·50	32·15	31·80
80	33·10	32·40	31·40	30·65	30·05	29·50
Sodium formate						
0	23·20	23·70	24·30	24·90	25·30	25·70
20	27·96	27·94	27·86	27·81	27·78	27·74
40	30·80	30·65	30·40	30·20	30·05	29·90
60	32·60	32·30	32·00	31·60	31·40	31·20
80	26·50	26·10	25·60	25·20	24·90	24·60
Potassium formate						
0	31·91	32·06	32·28	32·44	32·56	32·70
20	37·15	36·70	36·10	35·65	35·25	34·90
40	38·80	38·10	37·70	37·40	37·20	36·90
60	38·50	38·40	38·28	38·18	38·11	38·04
80	44·10	42·80	41·00	39·70	38·60	38·40

3. Results

Apparent molar volumes (ϕ_v) are calculated by equation[6] (1) and the data obtained are presented in Table I.

$$\phi_v = \frac{M}{d_0} - \frac{1000\ (d - d_0)}{d_0\, C} \qquad (1)$$

where d and d_0 are the densities of the solvent and of the solution, M is the molecular weight of the salt and C is the concentration.

4. Discussion

The apparent molar volume exhibited a linear decrease with salt concentration in aqueous formic acid in contrast to water. At any concentration of the salt the apparent molar

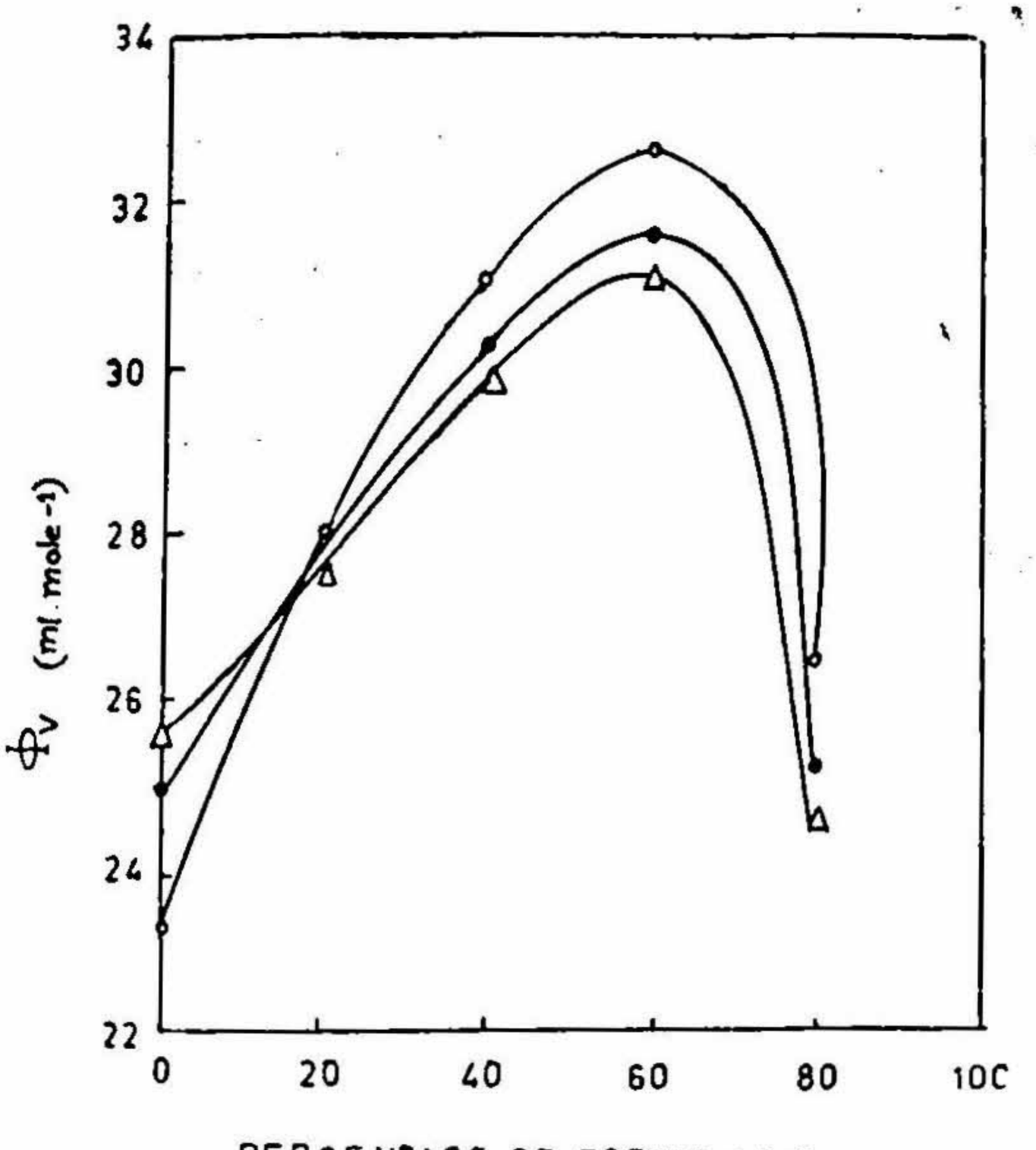

FIG. 1. Plot of ϕ_V *vs.* percentage of formic acid at 30° C ; O, 0·1 molar ; ●, 0·3 molar ; △, 0·5 molar sodium formate solutions.

volume changed with the composition of the solvent in a non-linear fashion exhibiting a maximum (*cf.* fig. 1). This maximum occurred at 40%, 60% and 80% formic acid for lithium, sodium and potassium formates respectively. The change in viscosity and the packing[7] of the solvent molecules in the ion-solvent complex may be responsible for this maximum. The greater the packing the smaller is the apparent molar volume. It appears that smaller the size of the cation, the minimum solvation (maximum molar volume) occurs at lower percentages of formic acid.

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