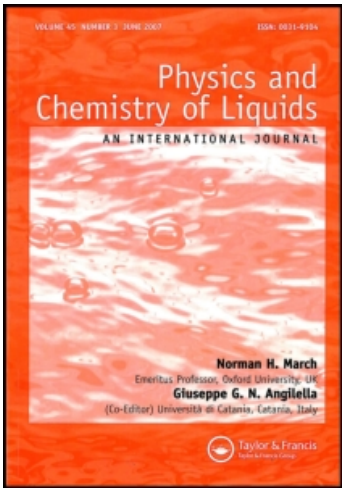

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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To cite this Article Kumar, Anil(1990) 'A Study on Partial Molar Volume and Expansion Of oagnesium Butyrate', Physics and Chemistry of Liquids, 21: 1, 29 — 34
To link to this Article: DOI: 10.1080/00319109008028461
URL: http://dx.doi.org/10.1080/00319109008028461

Phys. Chem. Liq., 1990, Vol. 21, pp. 29–34
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A STUDY ON PARTIAL MOLAR VOLUME AND EXPANSION OF MAGNESIUM BUTYRATE

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(Received 9 May 1989)

The partial molar expansibilities for aqueous solutions of magnesium butyrate at various temperatures were evaluated from the temperature dependence of their partial molar volumes. Both partial molar volume and expansibility for these solutions increased with increasing the temperature. The results of partial molar volumes and expansibilities at different temperatures provide information on the structure-sensitive factors in these aqueous soap solutions.

KEY WORDS: Aqueous soap solutions, conductance, viscosity.

INTRODUCTION

Density measurements were employed to determine the critical micelle concentration of copper[1] and cobalt[2] soaps of lower fatty acids in non-aqueous media. Masson[3] studied the variation of densities of aqueous solutions of 4-amino butyric acids with their concentrations. The apparent and limiting apparent molar volume data for electrolytes[4] and non-electrolytes[5] furnished informations on solute–solute, solute–solvent and solvent–solvent interactions in solutions. Hepler[6] and Jolicoeur *et al.*[7] investigated the effect of temperature on partial molar volumes of hydrophobic solutes as to obtain significant conclusions on solute-solvent interactions.

The present study on partial molar volume and expansibility has been initiated with a view to secure information on micellisation, solute-solvent/ion-ion interactions and structure-sensitive factors in aqueous solutions of magnesium butyrate. The results are viewed as supplementary and in furtherance to previous findings as obtained from conductance[8] and viscosity[9] measurements for aqueous solutions of metal soap.

EXPERIMENTAL

AnalaR grade magnesium carbonate (Glaxo laboratories, Bombay, India) was used without further purification and n-butyric acid (Sigma Chem. Co. U.S.A.) was purified by distillation under reduced pressure (B.P. 163.0°C).

The calculated amount of magnesium carbonate and n-butyric acid were suspended in water and heated upto 80°C with constant stirring. After the evolution of carbon dioxide ceased, the solution was evaporated to obtain the metal soap. The soap was

recrystallised from ethanol, dried initially in an air oven (100–105°C) and, finally, under reduced pressure at room temperature and stored over calcium chloride. The soap was characterised by the elemental analysis and the results were found in agreement with the theoretically calculated values.

Pyrex glass dilatometers with 15 cm^3 reservoir were employed to determine the molar volume of soap solutions at a constant temperature (± 0.05°C). Dilatometers were calibrated with water and benzene. The reproducibility of the results was ± 0.0002 g cm^{-3}. The accuracy of the results was checked by determining the molar volume of sodium chloride at 45°C. The experimental value (17.50 cm^3 mol^{-1}) was found in agreement with the value (17.59 cm^3 mol^{-1}) determined by Millero[10].

RESULTS AND DISCUSSION

The density for aqueous solutions of magnesium butyrate increases with increasing soap concentration and decreasing temperature. The density results have been explained in terms of Roots' equation[2],

$$d = d_0 + AC - BC^{3/2} \quad \text{(i)}$$

where, d, d_0, C are density of the solution, density of the solvent and concentration of the aqueous soap solutions. A,B are the constants.

The breaks in the plots of $(d - d_0)/C$ vs. $C^{1/2}$ (Figure 1) agree with the values of CMC (I) and CMC (II) (corresponding to the formation of ionic micelles and neutral colloid, respectively) as was also determined by conductance[8] and viscosity measurements[9]. The values of CMC (I) are found to decrease with increasing temperature whereas the data for CMC (II) are independent of temperature (Table 1). It may, therefore, be affirmed that the association of long chain ions to form ionic micelles is a reversible process and is affected favourably by increasing temperature. The values of constants A and B have been evaluated from the intercepts and slopes of these plots (Figure 1) and are recorded in Table 1.

The values of apparent molar volume ϕ_v of magnesium butyrate have been calculated by using the equation[11]

$$\phi_v = \frac{M}{d_0} - \frac{(d - d_0)}{Cd_0} \times 10^3 \quad \text{(ii)}$$

where M, d, d_0 and C are the molecular weight of the soap, density of soap solution, density of water and concentration of soap solution, respectively. Figure 1 explicitly shows that the apparent molar volume at first decreases rapidly, then slowly, and finally increase with increasing concentration of soap. The various factors such as hydration of amphiphilic solutes, electrostriction of water molecules by charged moieties, nature of ionic head group and length of non-polar portion of amphiphilic molecules may contribute to apparent molar volume and thus affect the volume differently and upto a different extent. The change in apparent molar volume as such is to be governed by all these factors. The decrease in apparent molar volume ϕ_v of NaDDS beyond CMC is also observed by Frank *et al.*[12]

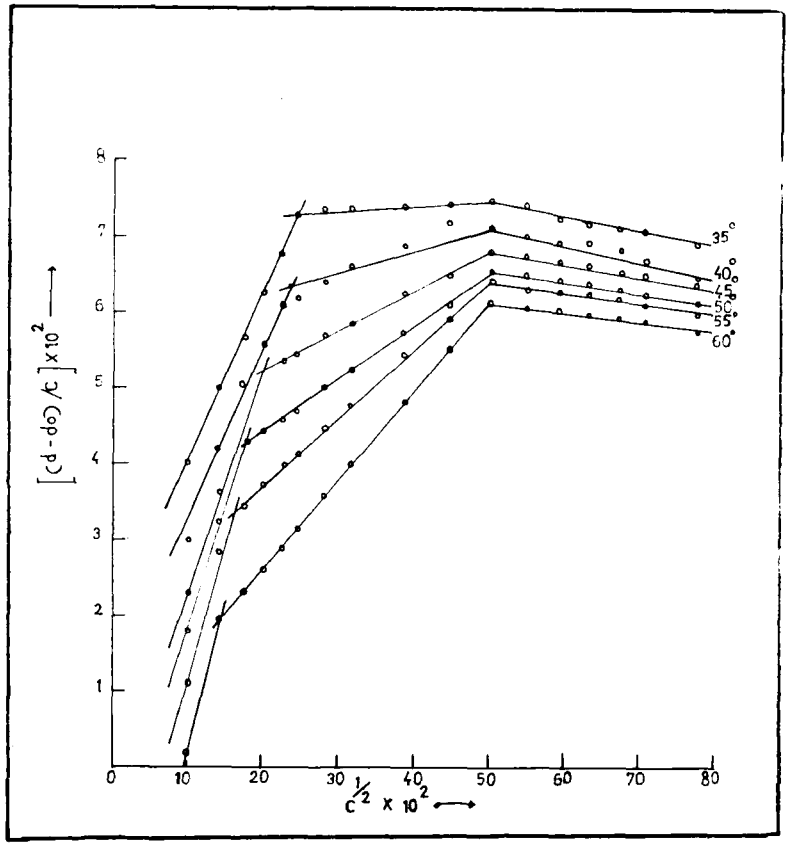

Figure 1 $(d - d_0)/C$ vs. $C^{1/2}$.

The two breaks observed in the plots of ϕ_v vs. $C^{1/2}$ (Figure 2) again correspond to CMC (I) CMC (II) as was determined by conductance[8] and viscosity measurements[9] of these soap solutions. The values of limiting apparent molar volumes, also referred to as partial molar volume, ϕ_v^0, have been obtained by extrapolating the linear plot of ϕ_v vs. $C^{1/2}$ (Figure 2) for dilute soap solutions according to Masson's equation[13]

$$\phi_v = \phi_v^0 + S_v C^{1/2} \qquad \text{(iii)}$$

Table 1 Values of constant A and B, ϕ_v^0, $\bar{v}$ and S_v, and CMC (I) and CMC (II) of magnesium butyrate.

Temperature (°C)	*A*	*B*	ϕ_v^0	$\bar{v}$	$-S_v$	*CMC (I)* × 10^2	*CMC (II)*
35°	0.018	0.225	180	0.90	200	6.0	0.25
40°	0.005	0.255	187	0.94	220	5.0	0.25
45°	−0.006	0.295	193	0.97	230	4.0	0.25
50°	−0.001	0.335	216	1.08	330	3.0	0.25
55°	−0.034	0.440	230	1.15	400	2.5	0.25
60°	−0.046	0.475	244	1.22	490	2.0	0.25

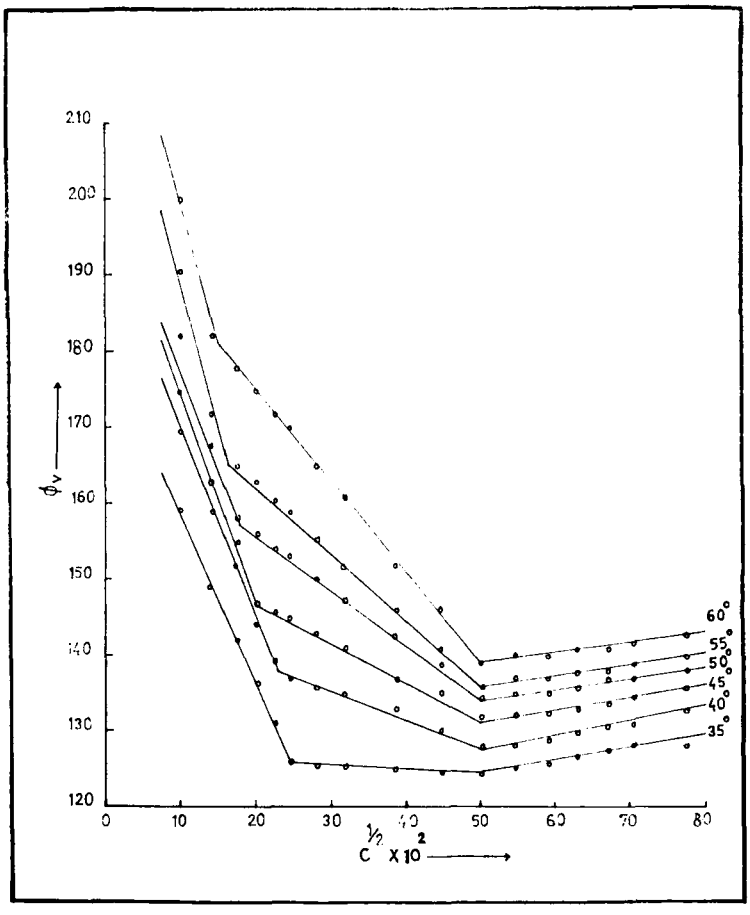

Figure 2 ϕ_v vs. $C^{1/2}$.

The values of intercept (limiting apparent molar volume, ϕ_v^0) and slope (S_v), recorded in Table 1, are a measure of solute-solvent and ion-ion interactions, respectively. The values of ϕ_v^0 for aqueous solutions of magnesium butyrate increase, and those of S_v decrease with increasing temperature (Table 1).

Partial molar quantities are very significant as these allow one to represent the properties of a solution in terms of properties of its components. The partial specific volumes, $\bar{v}$ (Table 1) for these aqueous soap solutions are evaluated by drawing an analogy between ϕ_v^0 and $\bar{v}$. Partial molar volume ϕ_v^0 is the change in the solution volume v per mole n_i of component i added, with the temperature, pressure, and all other composition variables n_j held constant. The partial molar volume $\phi_{v_i}^0$ may then be written as

$$\phi_{v_i}^0 = \left(\frac{\partial v}{\partial n_i}\right) T, P, n_j \neq i \qquad \text{(iv)}$$

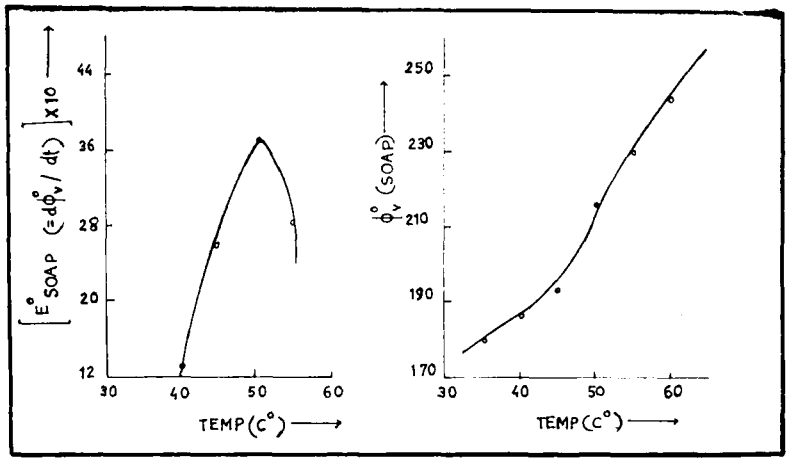

Figure 3 $[d\phi_v^0/dt]$ vs. temp.

It is also possible to define the change of an extensive property per unit mass of component i added; these are called partial specific quantities. The partial specific volume, v_i may be written

$$\bar{v}_i = \left(\frac{\partial v}{\partial w_i}\right) T, P, W_j \neq i \qquad \text{(v)}$$

where w_i is the mass of component i. From the above discussion one can write

$$\phi_{v_i}^0 = M_i \bar{v}_i \qquad \text{(vi)}$$

where M_i is the molecular weight of component i.

The partial molar expansibilities $(d\phi_v^0/dT)$ of magnesium butyrate (Figure 3) increase with increasing temperature which may either be due to the decrease in electrostriction or due to the loosening of water structure at higher temperatures. The plots of molar expansibilities and limiting apparent molar volume vs. temperature (Figure 3) confirm that the metal soap appears to be structure breaker above 50°C and that may be due to the fact that at higher temperature the increased thermal agitation does not allow structure formation by the metal soap to an extent detectable by the present technique.

The results suggest the presence of both ionic micelles and neutral colloid in aqueous solutions of magnesium butyrate. The temperature dependence of partial molar volume facilitates the evaluation of partial molar expansibilities for aqueous soap solutions. Both partial molar volume and expansibilities increase with increasing temperature.

Acknowledgement

The author is grateful to Dr. K. N. Mehrotra, Professor and Head of the Chemistry Department. The financial assistance by U.G.C., New Delhi is thankfully acknowledged.

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