Proc. Indian Acad. Sci. (Chem. Sci.), Vol. 89, Number 2, April 1980, pp. 193–200.

Molar volumes of ammonium chloride—ammonium salt solutions

R L BLOKHRA, S K AGARWAL and S S THAKUR
Chemistry Department, Himachal Pradesh University, Simla 171 005, India

MS received 15 May 1979 ; revised 25 October 1979

Abstract. The apparent molar volume of ammonium bromide and ammonium nitrate has been determined in various solutions of ammonium chloride at 30° C from density measurements using an hydrostatic balance. The molar volumes show a linear function of concentration. The values of NH_4Br, NH_4NO_3 are larger in NH_4Cl solutions than in pure water and this has been attributed to the increase in the interactions of NH_4Br and NH_4NO_3 with NH_4Cl. The mean apparent molar volume of NH_4Br–NH_4Cl and NH_4NO_3–NH_4Cl solutions have also been estimated directly from density measurements as well as from pure water data using Young's rule. The deviations are approximately studied as excess volume of mixing of NH_4Br and NH_4NO_3 with NH_4Cl.

Keywords. Molar volumes ; Young's rule ; solute-solvent interactions ; ammonium chloride ; ammonium salt.

1. Introduction

During recent years, volume studies in mixed electrolyte solutions have been extensively studied to understand the interactions among electrolytes (Billi *et al* 1974; Blokhra *et al* 1977; Millero 1971; Ward and Millero 1974 ; Wells *et al* 1975). However, the behaviour of mixed electrolyte solutions has not bean studied in detail. The mean apparent molar volume ϕ_v of electrolyte-electrolyte solutions has been correctly estimated as a first approximation from molar volume data of these electrolytes in water using the additivity rule developed by Young (1951). Young's rule when applied to an electrolyte mixture is given by (Ward and Millero 1974)

$$\phi_v = \sum_i y_i \varphi_v (i), \tag{1}$$

$\varphi_v (i)$ is the apparent molar volume for electrolyte component i in water at the same ionic strength as the total mixture and y_i is the molar weighting factor ($y_i = m_i/m_T$) where m_i is the molarity of the component i and $m_T = \Sigma_i m_i$ is total molarity. This formula holds good for various multicomponent solutions. The present investigation attempts to verify Young's rule for mixtures of ammonium salts and to study the deviations, if any, from Young's ruld in terms of excess volume of mixing of two electrolyte solutions at constant ionic strength.

2. Experimental

Ammonium chloride, ammonium bromide and ammonium nitrate of Analar grade were used without further purification. Water of specific conductance 10^{-6} ohm^{-1} cm^{-1} was used for making different solutions. The density was measured with a hydrostatic balance (Blokhra and Agarwal 1979). A glass float (116 g) of volume 26·17 ml was used. The glass sample cell has a bakelite top with hole in the centre and is placed in a water bath which was further kept in an air thermostat controlled to better than $\pm$ 0·02° C. The densities of the solutions were calculated from the equation

$$d - d^0 = (W^0 - W_f/V)$$

where d and d^0 are the density of the sample and pure water respectively, W and W^0 are the weights of float in the sample solution and pure water. V_f is the volume of the float.

The accuracy was checked by measuring the density of pure dioxane at 30° C. The value of $d = 1{\cdot}02230\,(4)$ g cm^{-3} obtained in the present work agrees with that of Timmermans (1950). The difference in weight of float in water and dioxane at 30° C was $\pm 3{\cdot}0 \times 10^{-5}$ g. All measurements in the present study were carried out at 30° C.

3. Results and discussion

The densities have been measured for H_2O-NH_4Cl, H_2O-NH_4Br, H_2O-NH_4NO_3 and NH_4Cl-NH_4X ($X = Br^-$, NO_3^-) solutions at 30° C at different concentrations. The apparent molar volume φ_v of NH_4Br, NH_4NO_3 in NH_4Cl solutions were calculated directly from density data using the equation :

$$\varphi_v = 1000\,(d^0 - d)/(mdd^0) + (M/d) \tag{2}$$

where m is the molarity of NH_4X ($X = Br^-$, NO_3^-) in NH_4Cl solutions. d is the density of the solution, d^0 is the density of the solvent (NH_4Cl solutions at $m = 0$) and M is the molecular weight of NH_4X.

The apparent molar volumes of NH_4X ($X = Br^-$, NO_3^-) φ_v thus calculated vary linearly with m in different NH_4Cl solutions at 30° C. The φ_v values calculated from (2) of NH_4Br and NH_4NO_3 in H_2O and in NH_4Cl solutions at different concentrations are given in tables 1 to 3.

The plots of φ_v versus $\sqrt{m}$ for NH_4Cl-H_2O, NH_4Br-H_2O, and NH_4NO_3-H_2O are linear as shown in figure 1. The apparent molar volume at infinite dilution has been calculated for different solutions by extrapolating the linear plots of φ_v versus m. The limiting slope S_v^* of these plots and φ_v^0 values have been recorded in table 4.

Since S_v^* is the measure of ion-ion interactions (Horne 1972), higher values of S_v^* suggest the formation of multi ions in the solutions at higher concentrations of ammonium chloride.

The volume properties of multicomponent solutions can also be conveniently treated (Ward and Millero 1974) by using the concept of mean apparent molal volume ϕ_v. The mean apparent molar volume ϕ_v is given by

$$\phi_v = 1000\,(d^0 - d)/(m_T dd^0) + (M_T/d), \tag{3}$$

Table 1. The apparent molar volume φ_v of NH_4X in water at 30° C.

m_{NH_4Cl}	$-1000\Delta d$	φ_v
0·05	0·67	36·33
0·10	1·68	36·88
0·15	2·47	37·16
0·20	3·10	37·55
0·25	4·02	38·16
0·30	4·38	39·00
0·35	5·09	39·12
0·40	5·55	39·79
m_{NH_4Br}		
0·05	2·62	45·70
0·10	5·13	46·86
0·15	7·44	48·64
0·20	9·89	48·77
0·25	12·25	49·23
0·30	14·41	50·19
0·35	16·28	50·71
0·40	17·35	51·34
$m_{NH_4NO_3}$		
0·05	1·55	49·21
0·10	3·08	49·37
0·15	4·52	50·16
0·20	5·90	50·73
0·25	7·16	51·28
0·30	8·28	52·62
0·35	9·47	53·19
0·40	10·65	53·39

where d^0 is the density of pure water, d is the density of solution, m_T is the total molarity and M_T is the mean molecular weight. M_T of the solution is determined by equation (4)

$$M_T = \sum_i y_i M_i, \tag{4}$$

where M_i is the molecular weight of the component i and Y_i is the molar weighing factor. The mean apparent molar volumes of NH_4X–NH_4Cl solutions were determined by using equation (3) and ϕ_v at 30° C are plotted against $\sqrt{m_T}$ in figure 2.

The curves representing various concentration of NH_4X solutions in NH_4Cl solutions could not be extrapolated to a point corresponding to zero concentration of NH_4X salts. This suggests solute–solute interactions in these multicomponent electrolyte solutions and ϕ_v^0 cannot therefore be considered to be made up of two components.

Table 2. The density and apparent molar volume φ_v of NH_4Br in NH_4Cl solutions at 30° C.

m_{NH_4Br}	$-1000 \Delta d$	φ_v
$m_{NH_4Cl} = 0{\cdot}01$; $d^0 = 0{\cdot}99583$ (5)		
0·05	2·27	52·73
0·10	4·73	50·87
0·15	7·40	48·83
0·20	10·02	48·11
0·25	12·90	46·58
0·30	16·08	44·58
$m_{NH_4Cl} = 0{\cdot}03$; $d^0 = 0{\cdot}99613$ (6)		
0·05	2·50	48·13
0·10	5·03	47·90
0·15	7·53	47·09
0·20	10·26	46·87
0·25	13·32	44·90
0·30	17·08	42·23
$m_{NH_4Cl} = 0{\cdot}05$; $d^0 = 0{\cdot}99633$ (6)		
0·10	6·48	36·24
0·15	8·45	41·79
0·20	11·24	41·94
0·25	13·21	45·31
0·30	15·78	45·54
$m_{NH_4Cl} = 0{\cdot}070$; $d^0 = 0{\cdot}99648$ (2)		
0·10	5·95	38·63
0·15	8·28	42·92
0·20	10·82	44·04
0·25	13·05	45·95
0·30	15·15	47·66
$m_{NH_4Cl} = 0{\cdot}09$; $d^0 = 0{\cdot}99660$ (0)		
0·05	2·86	40·80
0·10	5·26	45·54
0·15	7·70	46·77
0·20	9·90	48·66
0·25	12·16	49·50
0·30	14·38	50·21

Ward and Millero (1974) used Young's method of estimating mean apparent molar properties of mixed electrolyte solutions by considering the weighted additivity of the properties of electrolyte components in pure water to be equal to the properties of mixed electrolyte solutions. If we apply this to our system, the

Table 3. Density and apparent molar volume of NH_4NO_3 in NH_4Cl solutions at 30° C.

$m_{NH_4NO_3}$	$-1000\,\Delta d$	φ_v
$m_{NH_4Cl} = 0{\cdot}01$; $d^0 = 0{\cdot}99583\,(5)$		
0·05	0·22	75·73
0·10	1·19	68·37
0·15	2·64	62·04
0·20	4·83	56·42
0·25	6·95	52·42
0·30	8·66	51·32
$m_{NH_4Cl} = 0{\cdot}03$; $d^0 = 0{\cdot}99613\,(6)$		
0·05	0·50	70·27
0·10	1·13	67·89
0·15	2·80	61·52
0·20	4·91	55·63
0·25	7·14	51·63
0·30	9·56	48·30
$m_{NH_4Cl} = 0{\cdot}05$; $d^0 = 0{\cdot}99636\,(3)$		
0·05	2·30	34·02
0·10	4·48	35·27
0·15	6·14	39·16
0·20	7·64	41·92
0·25	9·29	42·99
0·30	9·74	45·71
$m_{NH_4Cl} = 0{\cdot}07$; $d^0 = 0{\cdot}99648\,(2)$		
0·05	2·22	35·63
0·10	4·38	36·25
0·15	6·18	39·91
0·20	7·69	42·68
0·25	9·22	43·27
0·30	9·72	47·76
$m_{NH_4Cl} = 0{\cdot}09$; $d^0 = 0{\cdot}99660\,(0)$		
0·05	2·02	39·65
0·10	3·75	42·59
0·15	4·99	46·96
0·20	6·29	48·69
0·25	7·67	49·46
0·30	8·91	50·45

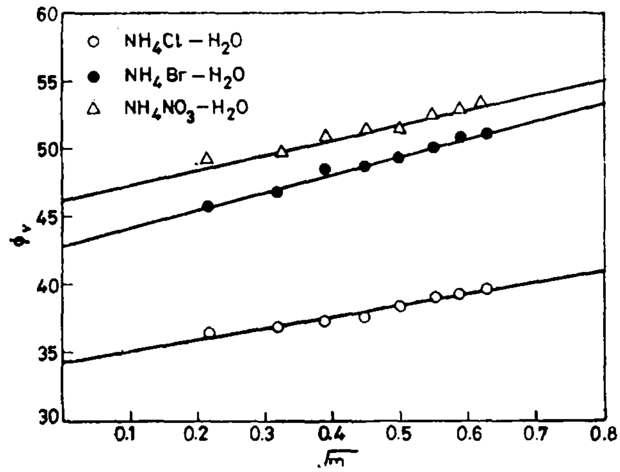

Figure 1. Plot of φ_v *vs.* $\sqrt{m}$ for NH_4X-H_2O at 30° C.

Table 4. The partial molar volume at infinite dilution for NH_4Br, NH_4NO_3 i NH_4Cl solutions at 30° C.

m_{NH_4Cl}	φ_v^0 (NH_4Br)	S_v^* (NH_4Br)	φ_v^0 (NH_4NO_3)	S_v^* (NH_4NO_3)
0·01	53·00	−31·43	81·60	−105·50
0·03	50·00	−24·00	79·40	−88·80
0·05	34·00·	40·00	31·60	53·36
0·07	37·00	42·80	33·40	76·40
0·09	41·00	43·37	39·00	92·85

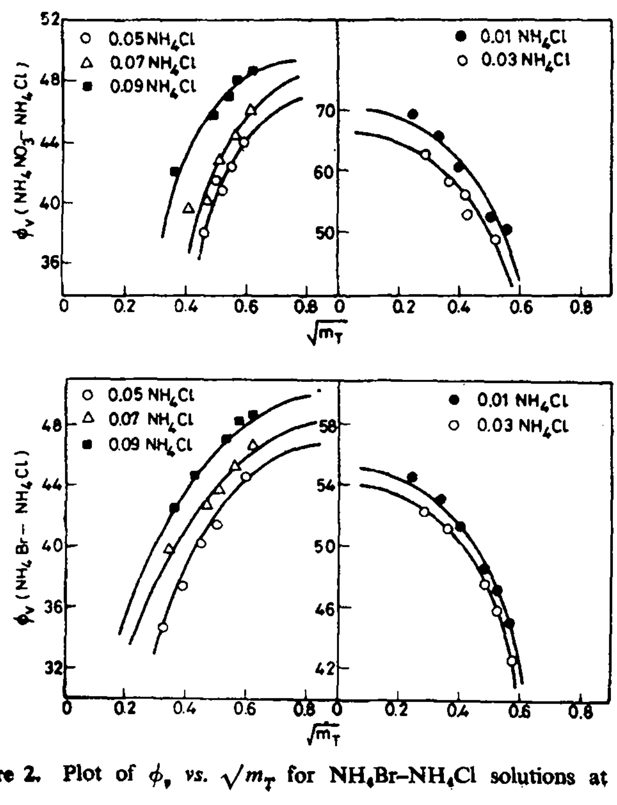

Figure 2. Plot of ϕ_v *vs.* $\sqrt{m_T}$ for NH_4Br-NH_4Cl solutions at 30° C.

mean apparent molar volume can be calculated from pure water molar volume data using equation (5) :

$$\phi_v\,(\text{cal.}) = y_{NH_4Cl}\,\varphi_v\,(NH_4Cl) + y_{NH_4X}\,\varphi_v\,(NH_4x), \quad (5)$$

where ϕ_v (cal) is the mean apparent molar volume calculated from pure water molar volume data

$$y_{NH_4X} = \frac{m_{NH_4X}}{m_T}, \quad y_{NH_4Cl} = \frac{m_{NH_4Cl}}{m_T}$$

$\varphi_v\,(NH_4X)$ is the apparent molar volume of NH_4X in water at m_T and $\varphi_v\,(NH_4Cl)$ is the apparent molar volume of NH_4Cl in pure water at m_T.

The difference in the observed ϕ_v values and values obtained from equation (5) is the excess molar volume for the mixing of two electrolytes and is given by equation (6) :

$$\phi_v\,(\text{obs.}) - \phi_v\,(\text{cal.}) = \triangle\phi_v\,(\text{excess}). \quad (6)$$

The change in volume of mixing of the solutions of two electrolytes, $\triangle V_m$, calculated from equation (7) (Ward and Millero 1974)

$$\triangle\phi_v\,(\text{excess}) = \triangle V_m/m_T, \quad (7)$$

for NH_4X-NH_4Cl solutions are plotted versus Y_B ($Y_B = m_B/m_T$) in figure 3. This is of a large magnitude but parabolic curve with maxima around $Y_B = 0{\cdot}5$ for 0·01, 0·03, 0·05 m NH_4Cl solutions is similar to the curves for volume of mixing of other compounds. The large value of $\triangle V_m$ may be attributed to the non-validity of equation (5). However in case of 0·07 and 0·09 m NH_4Cl solutions, $\triangle V_m$ has been found to be more or less constant with Y_B in the concentration range reported in the present investigation.

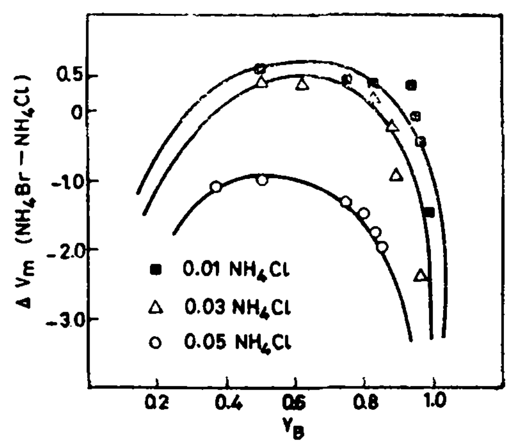

Figure 3. Plot of $\triangle V_m$ *vs.* Y_B for NH_4Br-NH_4Cl solutions at 30° C.

Acknowledgements

Two of the authors (SKA and SST) thanks the Council of Scientific and Industrial Research, New Delhi for the award of fellowships.

References

Billi A, Indelli A, Malatesta F and Zambomi R 1974 *J. Chem. Phys.* **61** 4877
Blokhra R L, Agarwal S K and Sakhuja Neerja 1977 *Electrochim. Acta* **22** 1083
Blokhra R L and Agarwal S K 1979 *J. Chem. Thermodyn.* **11** 229
Horne R A 1972 *Water and aqueous solutions* (New York : John Wiley) p. 522
Millero F J 1971 *Chem. Rev.* **71** 147
Timmermans J 1950 *Physicochemical constants of pure organic compounds* (Amsterdam : Elsevier) p. 502
Ward G K and Millero F J 1974 *J. Solution Chem.* **3** 431
Wells H L, Kustek M J and Lindstorm R E 1975 *J. Solution Chem.* **4** 391
Young T F 1951 *Rec. Chem. Progr.* **12** 81