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Apparent Molal Volumes of Aqueous Ammonium Salts-Glucose Solution

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Present paper reports the mean apparent molal volumes of aqueous NH_4X (X = Cl, Br, NO_3)-glucose solution directly determined at 40°C from density measurements. The modified Young's rule has been found to be applicable to these solutions. The deviations from the modified Young's rule have been taken as the excess apparent molal volumes of mixing NH_4X and glucose solutions.

Key Words: Molal volumes, Ammonium salts, Glucose solution.

INTRODUCTION

Thermodynamical treatment of multicomponent solutions has been given considerable attention for the last few years[1–4]. Many volume studies have been made on solutions containing several electrolytes. The volume of mixing[5–9] electrolyte solutions constitutes an excellent way for the study of ion-ion and ion-solvent interactions. The Young's rule[10] provides the way to calculate mean apparent molal volume of ternary solutions. The Young's rule holds good for electrolytic solutions. Some workers[11, 12] have extended such studies to electrolytic-non-electrolytic solutions, which are important and useful due to the deficiency of ϕ_V data for these solutions. The present study has been carried out in order to test the validity of the modified Young's rule[10] for aqueous NH_4X-glucose solutions, which is an electrolyte-non-electrolyte system, and to study the change of ϕ_V on addition of glucose to the system.

EXPERIMENTAL

The chemicals NH_4Cl, NH_4Br, NH_4NO_3 and glucose were of either BDH or E. Merck quality. They were used without any further purification. Water used as a solvent was obtained by distillation of distilled water over a little $KMnO_4$ and NaOH until its specific conductance was of the order of 10^{-6} mho cm^{-1}. The densities were measured with the help of a double capillary pyknometer and an analytical balance with an accuracy of 0.0001 g. The temperature of the solutions was controlled in a water-thermostat.

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RESULTS AND DISCUSSION

The densities of aqueous solutions containing 0.05, 0.10, 0.15 or 0.20 M NH_4X and various molalities of glucose were measured at 40°C and their mean apparent molal volumes, ϕ_V, were calculated from the equation[1]

$$\phi_V = \frac{1000(d_0 - d)}{d_0 d m_T} + \frac{M_T}{d} \quad (1)$$

where d_0 and d are the densities of pure water and the solution respectively, m_T is the molality ($m_T = \Sigma m_i$) and M_T is the mean molecular weight of the solutes, which is determined by $M_T = \Sigma Y_i M_i$, where M_i is the molecular weight of component i and Y_i is the molal weighing factor defined as $Y_i = m_i/m_T$, m_i being the molality of component i and m_T being the total molality.

The mean apparent molal volume ϕ_V of the solutions can also be calculated from the Young's rule[10] which, for a ternary system, is expressed as

$$\phi_V = \sum_{i=1}^{2} Y_i \phi_V(i) + \frac{\Delta V}{m_T} \quad (2)$$

where Y_i is the molal weighing factor as described earlier, $\phi_V(i)$ is the apparent molal volume for the electrolytic component i in water at the same ionic strength as the total mixture and ΔV is the increase in volume on mixing and m_T is the total molality of the solution. $\Delta V/m_T$ is called the excess apparent molal volume of mixing. In Young's rule expressed by eqn. (2), the term $\Delta V/m_T$ is ignored[10]. Thus the modified Young's rule for a ternary system is

$$\phi_V = Y_1\phi_1 + Y_2\phi_2 \quad (3)$$

The modified Young's rule for the present study may be written as

$$\phi_V\,(\text{cal}) = Y_{NH_4X}\,\phi_V(NH_4X) + Y_{\text{glucose}}\,\phi_V(\text{glucose}) \quad (4)$$

where $\phi_V(\text{cal})$ is the mean apparent molal volume calculated from pure water molal volume data; $Y_{NH_4X} = m_{NH_4X}/m_T$ and $Y_{\text{glucose}} = m_{\text{glucose}}/m_T$. $\phi_V(NH_4X)$ is the apparent molal volume of NH_4X in pure water at ionic strength of the solution, *i.e.*, m_{NH_4X}, and ϕ_V (glucose) is the apparent molal volume of glucose in pure water at the total molality m_T of the solution.

The difference between $\phi_V(\text{obs})$, *i.e.*, mean apparent molal volume of the solution directly determined from eqn. (1) and $\phi_V(\text{cal})$ calculated from the modified Young's rule as represented in eqn. (4) is considered as the excess apparent molal volume, ϕ_V (excess), of mixing aqueous solutions of NH_4X and glucose. Thus ϕ_V (excess) may be expressed as:

$$\phi_V(\text{excess}) = \phi_V(\text{obs}) - \phi_V(\text{cal}) \quad (5)$$

where

$$\phi_V(\text{excess}) = \frac{\Delta V}{m_T} \quad (6)$$

$\phi_V(\text{excess})$ is the deviation from Young's rule approximation.

The experimental values of density, $\phi_V(\text{obs})$, $\phi_V(\text{cal})$ and $\phi_V(\text{excess})$ have been tabulated in Tables 1–3 for aqueous NH_4Cl-glucose, NH_4Br-glucose and NH_4NO_3-glucose solutions respectively as a function of glucose concentration.

It is evident from Tables 1–3 that the value of excess apparent molal volume of mixing, ϕ_V(excess), is not very high. Therefore the modified Young's rule is applicable to aqueous NH_4X-glucose solutions.

TABLE-1
DATA FOR AQUEOUS NH_4Cl-GLUCOSE SOLUTIONS AT 40°C

M NH_4Cl (mol L^{-1})	$m_{glucose}$ (mol kg^{-1})	Density (g mL^{-1})	ϕ_V(obs) (mL mol^{-1})	ϕ_V(cal) (mL mol^{-1})	ϕ_V(excess) (mL mol^{-1})
0.05 M	0.07621	0.9987	78.08	79.89	−1.81
	0.10190	1.0004	83.92	85.17	−1.25
	0.15371	1.0038	91.23	91.88	−0.65
	0.20613	1.0072	95.63	95.97	−0.34
0.10 M	0.10190	1.0016	70.29	73.27	−2.98
	0.20613	1.0083	84.95	86.57	−1.62
	0.25916	1.0116	89.29	90.65	−1.36
	0.31284	1.0145	93.56	94.14	−0.58
0.20 M	0.07621	1.0012	55.60	56.75	−1.15
	0.15371	1.0066	67.05	68.97	−1.92
	0.20613	1.0107	71.08	74.75	−3.67
	0.31284	1.0161	82.39	83.26	−0.87

TABLE-2
DATA FOR AQUEOUS NH_4Br-GLUCOSE SOLUTIONS AT 40°C

M NH_4Br (mol L^{-1})	$m_{glucose}$ (mol kg^{-1})	Density (g mL^{-1})	ϕ_V(obs) (mL mol^{-1})	ϕ_V(cal) (mL mol^{-1})	ϕ_V(excess) (mL mol^{-1})
0.10 M	0.08903	1.0041	73.08	75.94	−2.86
	0.11479	1.0059	77.25	80.33	−3.08
	0.23257	1.0134	90.01	91.74	−1.73
	0.35351	1.0198	98.73	98.35	+0.38
0.15 M	0.08903	1.0064	68.53	70.33	−1.80
	0.17984	1.0127	79.24	82.08	−2.84
	0.27253	1.0179	88.13	89.29	−1.16
	0.36717	1.0236	92.94	94.12	−1.18
0.20 M	0.07621	1.0076	63.97	64.82	−0.85
	0.15371	1.0131	73.08	75.31	−2.23
	0.31284	1.0227	86.05	87.41	−1.36
	0.42219	1.0280	92.97	92.62	+0.35

TABLE-3
DATA FOR AQUEOUS NH_4NO_3 – GLUCOSE SOLUTIONS AT 40°C

M NH_4NO_3 (mol L^{-1})	$m_{glucose}$ (mol kg^{-1})	Density (g mL^{-1})	ϕ_V(obs) (mL mol^{-1})	ϕ_V(cal) (mL mol^{-1})	ϕ_V(excess) (mL mol^{-1})
0.10 M	0.10190	1.0029	76.95	79.82	–2.87
	0.15371	1.0061	84.92	86.37	–1.45
	0.20613	1.0094	89.93	91.24	–1.31
	0.31284	1.0162	95.71	96.67	–0.96
0.15 M	0.06432	1.0014	66.87	67.66	–0.79
	0.12772	1.0058	76.31	77.64	–1.33
	0.25916	1.0134	89.96	89.51	+0.45
	0.42219	1.0226	98.06	96.81	+1.25
0.20 M	0.07621	1.0037	65.64	66.72	–1.08
	0.15371	1.0088	75.52	76.80	–1.28
	0.31284	1.0179	88.94	88.69	+0.25
	0.42219	1.0235	94.94	93.46	+1.48

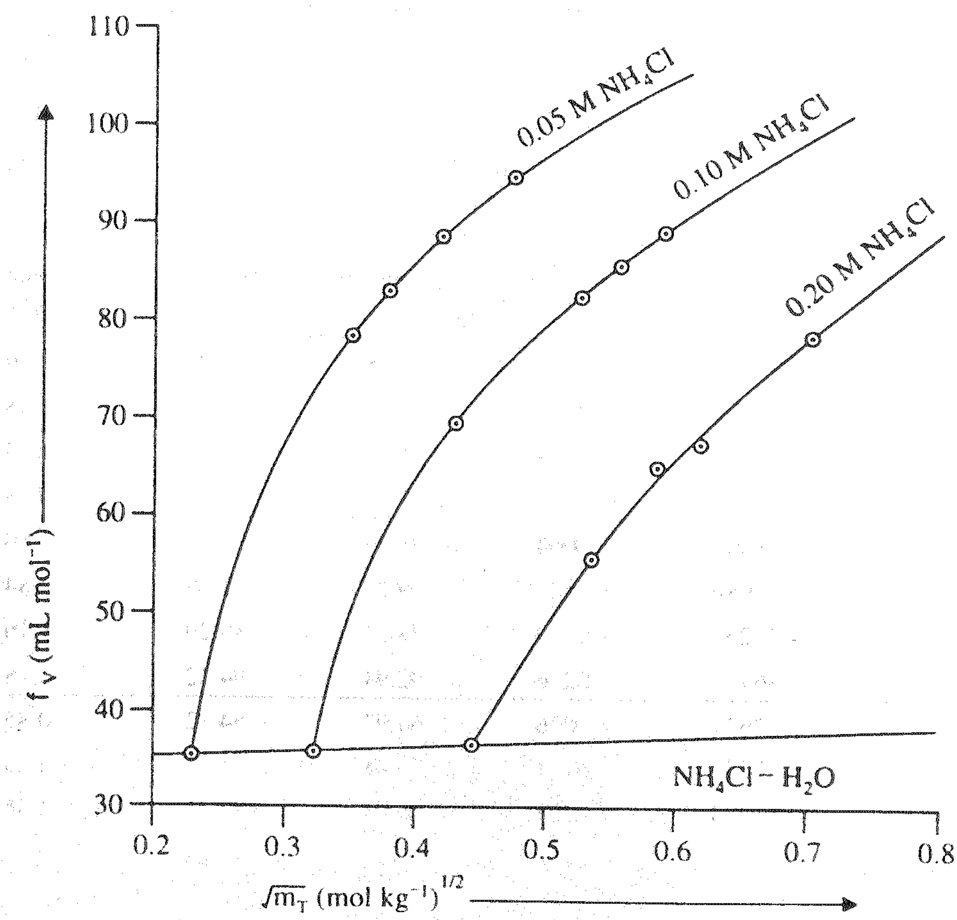

Fig. 1. Apparent molal volume of aqueous NH_4Cl-glucose solutions at 40°C

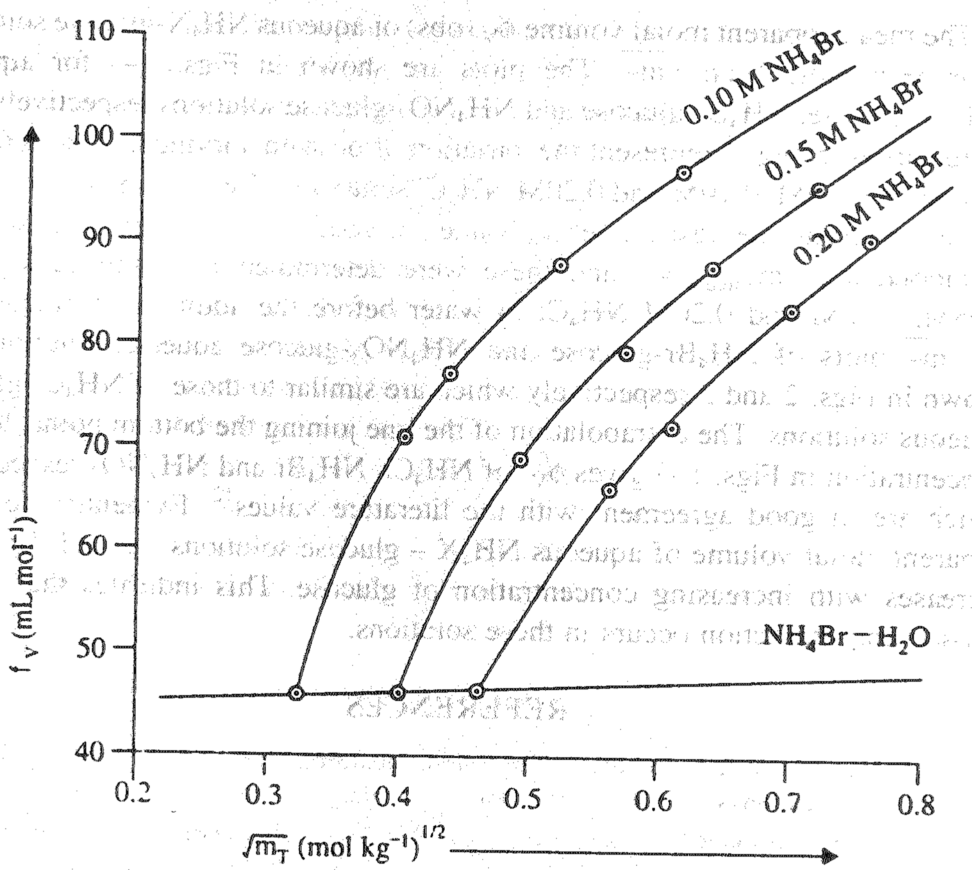

Fig. 2. Apparent molal volume of aqueous NH_4Br-glucose solution at 40°C

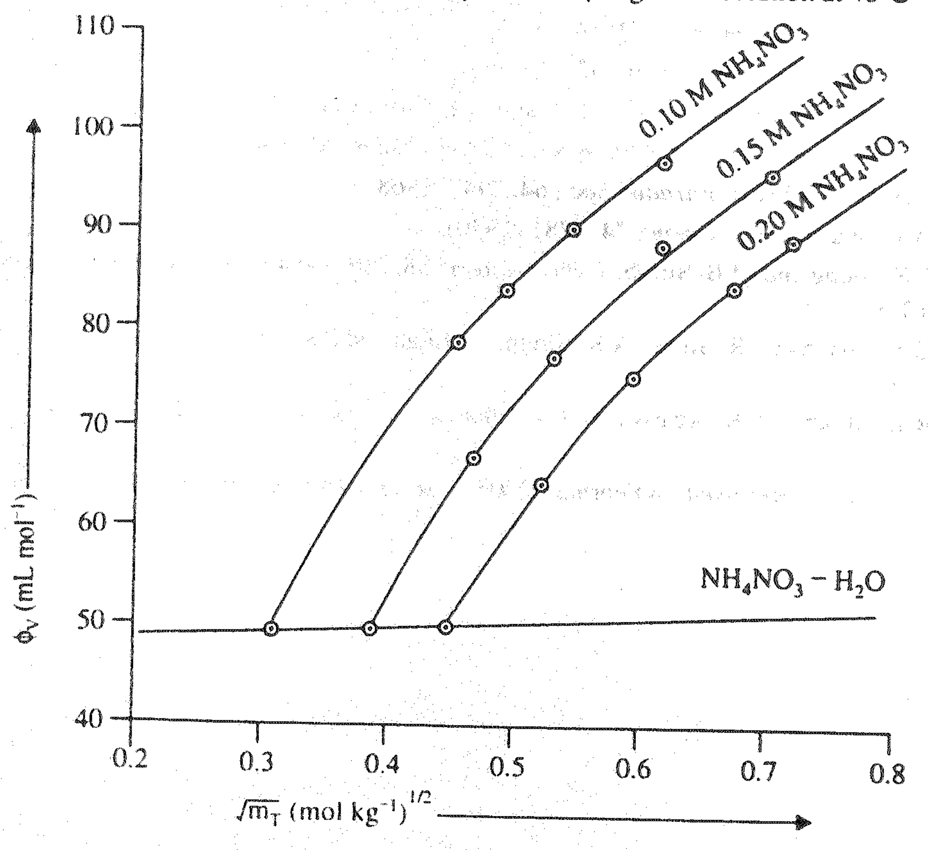

Fig. 3. Apparent molal volume of aqueous NH_4NO_3-glucose solutions at 40°C

The mean apparent molal volume ϕ_V (obs) of aqueous NH_4X-glucose solutions have been plotted *vs.* $\sqrt{m_T}$. The plots are shown in Figs. 1–3 for aqueous NH_4Cl-glucose, NH_4Br-glucose and NH_4NO_3-glucose solutions respectively. The three curves in Fig. 1 represent the variation of ϕ_V with varying concentration of glucose in 0.05M, 0.10M and 0.20M NH_4Cl solutions. The bottom points of each curve represent the respective ϕ_V value of aqueous NH_4Cl-glucose solution extrapolated to $m_{glucose} = 0$ and these were determined from the densities of 0.05M, 0.10M and 0.20M NH_4Cl in water before the addition of glucose. ϕ_V *vs.* $\sqrt{m_T}$ plots of NH_4Br-glucose and NH_4NO_3-glucose aqueous solutions are shown in Figs. 2 and 3 respectively which are similar to those of NH_4Cl-glucose aqueous solutions. The extrapolation of the line joining the bottom points to zero concentration in Figs. 1–3 gives ϕ_V^0 of NH_4Cl, NH_4Br and NH_4NO_3 respectively which are in good agreement with the literature values[12]. Evidently the mean apparent molal volume of aqueous NH_4X – glucose solutions ($X = Cl, Br, NO_3$) increases with increasing concentration of glucose. This indicates that strong ion-solvent interaction occurs in these solutions.

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