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Biophysical Chemistry 76 (1999) 73–82

Biophysical Chemistry

# Effect of cation and anion of an electrolyte on apparent molar volume, isentropic compressibility and refractive index of glycine in aqueous solutions

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Received 18 August 1998; received in revised form 16 November 1998; accepted 17 November 1998

## Abstract

Experiments at 298.15 K have been performed to measure the density, velocity of sound and refractive index in three water + glycine + electrolyte systems. The electrolytes studied were KCl, $KNO_3$ and $NaNO_3$. The values of apparent molar volume and isentropic compressibility of glycine in aqueous electrolyte solutions were calculated from the measured data. The results obtained in this study and those reported previously for water + glycine + NaCl system have been comparatively studied. The results show that the nature of both the cation and the anion of an electrolyte influence the behaviour of glycine in aqueous solutions. For all four electrolytes studied, the comparison shows a positive volume transfer for glycine from an electrolyte solution to a more concentrated solution of the same electrolyte. The results also show a negative apparent isentropic compressibility for glycine in the presence of the electrolytes studied. These effects indicate that the volume of a glycine molecule is larger in solutions with higher electrolyte concentration and the water molecules around the glycine molecules are less compressible than the water molecules in the bulk solution. These effects were attributed to the doubly charged behaviour of glycine and to the formation of physically bonded ion-pairs between the charged groups of glycine and the cation and the anion of the electrolyte. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Cation; Anion; Glycine; Isentropic compressibility; Molar volume; Refractive index

## 1. Introduction

The interactions between charged biomolecules and ions can highly influence their behaviour and conformation in aqueous solutions. The study of these interactions provides an insight into the conformational stability and unfolding behaviour of some biomolecules, such as globular proteins. This study also has application in the development and design of separation processes containing electrolytes, such as electrolyte-induced precipitation of biomolecules. However, the complex

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PII:S0301-4622(98)00223-3

structure of most biomolecules makes it difficult to study the effect of different factors influencing their behaviour. Amino acids are the simplest biomolecules, which are the building blocks of other more complex biomolecules, such as proteins and antibiotics. Thus, they can be used as the model compound for the study of the behaviour of complex biomolecules. In addition, in the absence of the experimental data for large biomolecules, it would be desirable to predict their properties from the properties of their constituent amino acids using a group contribution method.

Among thermodynamic properties, which directly or through other exact thermodynamic relations represent the interactions in a system, partial molar volume and isentropic compressibility are particularly important. This is due to the fact that not only do they provide important information about the interactions and the behaviour of molecules in solutions, they can be measured accurately. Measurement of the partial molar volume and isentropic compressibility of amino acids in aqueous solutions without the presence of an electrolyte has been the subject of several studies [1–5]. Some studies have also been conducted to calculate the properties of complex biomolecules from the properties of their constituent amino acids. For example, Iqbal and Verrall [2] showed that the partial-specific volumes of some proteins could be calculated, with a reasonable accuracy, from the partial-specific volume of their constituent amino acids. Despite the ample use and importance of amino acids in many industries, their interactions with electrolytes and physicochemical properties in electrolyte solutions have been the subject of few investigations [6,7]. Recently, we have reported the partial molar volume and isentropic compressibility and refractive index in water + glycine + NaCl solutions and developed a model to correlate the experimental data [8]. The results of this study and other previously measured data revealed that the presence of an electrolyte greatly influences the behaviour of amino acids in solutions.

In this study experiments at 298.15 K have been performed to measure the density, sound velocity and refractive index in three water + glycine + electrolyte systems. The electrolytes studied are KCl, $KNO_3$ and $NaNO_3$. The values of apparent molar volume, $V_\phi$, and apparent molar isentropic compressibility, $K_\phi$, were calculated from the measured data. To determine the effect of the anion and the cation of an electrolyte on its interactions with glycine the results obtained from this study and those reported previously for water + glycine + NaCl system [8] are comparatively studied.

## 2. Materials and methods

Potassium chloride, potassium nitrate and sodium nitrate with nominal purity of greater than 99.0 mass% were purchased from SIGMA (Madrid, Spain) and were oven-dried for 72 h prior to use. Glycine with a purity of greater than 99.0 mass% was purchased from ICN (Barcelona, Spain) and was used without further purification. In all experiments deionized water produced by a Milli-Q water deionizer was used. Prior to the use, the deionized water was ultrasonically degassed. The pH of the deionized water was measured on a Mettler Toledo MP225 and it was equal 7.0.

All the solutions were prepared by weight on a Mettler AE 240 balance precise to within ±0.0001 g. In order to prepare the solutions under investigation, aqueous solutions of each salt at different concentrations were first prepared. Known amount of glycine was then added to a salt solution prepared in advance and stirred until a homogeneous solution was obtained.

The densities and sound transmission speeds of the mixtures were measured on an Anton Paar DSA-48 densimeter and sound analyser. The instrument precision was within $\pm 0.0001$ g/cm$^3$ for the density and ±1.0 m/s for the velocity of sound. The refractive indices were measured on an ATAGO RX-1000 refractometer precise to within ±0.0001. In order to maintain the sample temperature constant during the experiments, all the instruments were equipped with a thermostatic bath and the temperature was kept constant at $298.15 \pm 0.02$ K throughout the experiments. All measurements were repeated three times for each sample, and were repeatable to within the precision quoted for each apparatus.

## 3. Results and Discussion

The measured values at 298.15 K of density, sound velocity and refractive index in water + glycine + KCl, water + glycine + $NaNO_3$ and water + glycine + $KNO_3$ systems are presented in Tables 1–3, respectively. The values of the apparent molar volumes, $V_\phi$, and apparent molar isentropic compressibility, $K_\phi$, of glycine in solutions with different electrolyte concentration were calculated from the following relations:

$$V_\phi = \frac{M}{\rho} - \frac{\rho - \rho_0}{m \rho \rho_0} \tag{1}$$

$$K_\phi = \frac{M \kappa_S}{\rho} - \frac{\kappa_{S0}\, \rho - \kappa_S\, \rho_0}{m \rho \rho_0} \tag{2}$$

where $M$ denotes the molecular weight of glycine, $m$ is the molality of glycine, $\rho$ and $\rho_0$ are the densities of the solution and the solvent, respectively. The terms $\kappa_S$ and $\kappa_{S0}$ in Eqs. (1) and (2) refer, respectively to the isentropic compressibilities of the solution and the solvent calculated from the velocity of sound, $u$, according to the following relation:

$$\kappa_S = \frac{1}{u^2 \rho} \tag{3}$$

The values of $V_\phi$ and $K_\phi$ of glycine at different electrolyte molalities, calculated from Eqs. (1)–(3), are also presented in Tables 1–3. It is important to mention that for systems containing

Table 1
Measured values of density, sound velocity and refractive index, and calculated values of apparent molar volume and isentropic compressibility in water + glycine + KCl system

| Glycine molality | Density (kg/m$^3$) | Sound velocity (m/s) | Refractive index | $V_\phi \times 10^6$ (m$^3$/mol) | $K_\phi \times 10^{15}$ (m$^3$/kPa.mol) |
|---|---|---|---|---|---|
| KCl concentration = 0.0 m | | | | | |
| 0.000 | 997.0 | 1497 | 1.3325 | – | – |
| 0.4972 | 1012.4 | 1523 | 1.3389 | 43.46 | −25 865.1 |
| 1.0226 | 1027.4 | 1548 | 1.3454 | 44.05 | −23 312.9 |
| 1.4867 | 1039.9 | 1569 | 1.3508 | 44.36 | −21 830.6 |
| 1.9724 | 1052.2 | 1591 | 1.3562 | 44.67 | −19 818.5 |
| 2.4091 | 1062.6 | 1609 | 1.3606 | 44.94 | −19 074.2 |
| 2.9291 | 1074.3 | 1630 | 1.3657 | 45.24 | −17 724.4 |
| KCl concentration = 0.2 m | | | | | |
| 0.0000 | 1006.4 | 1508 | 1.3344 | – | – |
| 0.4776 | 1020.6 | 1532 | 1.3405 | 44.60 | −21 892.8 |
| 1.0035 | 1035.3 | 1557 | 1.3469 | 44.87 | −20 256.0 |
| 1.4535 | 1047.1 | 1577 | 1.3520 | 45.12 | −18 857.7 |
| 2.0076 | 1060.7 | 1600 | 1.3580 | 45.43 | −17 257.6 |
| 2.2753 | 1067.0 | 1612 | 1.3607 | 45.55 | −16 883.1 |
| 2.7854 | 1078.4 | 1632 | 1.3658 | 45.79 | −15 729.2 |
| KCl concentration = 0.4 m | | | | | |
| 0.0000 | 1015.4 | 1518 | 1.3365 | – | – |
| 0.4763 | 1029.2 | 1541 | 1.3424 | 45.21 | −19 180.8 |
| 0.9772 | 1042.8 | 1564 | 1.3483 | 45.50 | −17 786.1 |
| 1.4701 | 1055.3 | 1586 | 1.3538 | 45.80 | −16 686.2 |
| 1.9790 | 1067.6 | 1607 | 1.3592 | 45.98 | −15 507.1 |
| 2.4186 | 1077.5 | 1625 | 1.3635 | 46.20 | −14 678.7 |
| 2.7146 | 1083.9 | 1637 | 1.3664 | 46.33 | −14 199.3 |

Table 1 (*Continued*)

| Glycine molality | Density ($kg/m^3$) | Sound velocity (m/s) | Refractive index | $V_\phi \times 10^6$ ($m^3$/mol) | $K_\phi \times 10^{15}$ ($m^3$/kPa.mol) |
|---|---|---|---|---|---|
| KCl concentration = 0.6 m | | | | | |
| 0.0000 | 1024.3 | 1528 | 1.3383 | – | – |
| 0.5000 | 1038.4 | 1552 | 1.3445 | 45.78 | −17 499.5 |
| 0.9985 | 1051.5 | 1574 | 1.3502 | 46.10 | −15 818.5 |
| 1.4763 | 1063.3 | 1595 | 1.3554 | 46.34 | −14 919.4 |
| 1.9702 | 1074.8 | 1615 | 1.3606 | 46.56 | −13 828.2 |
| 2.4462 | 1085.2 | 1634 | 1.3653 | 46.78 | −12 994.9 |
| 2.7863 | 1092.4 | 1646 | 1.3684 | 46.87 | −12 286.7 |
| KCl concentration = 0.8 m | | | | | |
| 0.0000 | 1032.9 | 1537 | 1.3401 | – | – |
| 0.4928 | 1046.4 | 1560 | 1.3460 | 46.39 | −15 431.4 |
| 0.9812 | 1058.9 | 1582 | 1.3516 | 46.66 | −14 441.3 |
| 1.4759 | 1070.8 | 1602 | 1.3570 | 46.89 | −13 070.1 |
| 1.8945 | 1080.3 | 1619 | 1.3612 | 47.06 | −12 338.5 |
| 2.3520 | 1090.2 | 1637 | 1.3657 | 47.22 | −11 633.5 |
| 2.9707 | 1102.8 | 1660 | 1.3713 | 47.41 | −10 715.0 |
| KCl concentration = 1.0 m | | | | | |
| 0.0000 | 1041.4 | 1547 | 1.3419 | – | – |
| 0.5067 | 1054.9 | 1570 | 1.3479 | 46.91 | −13 523.8 |
| 0.9916 | 1066.9 | 1590 | 1.3534 | 47.21 | −12 018.3 |
| 1.5464 | 1079.9 | 1613 | 1.3591 | 47.37 | −11 281.4 |
| 2.1100 | 1092.2 | 1635 | 1.3647 | 47.56 | −10 440.3 |
| 2.4578 | 1099.3 | 1648 | 1.3680 | 47.71 | −9922.0 |
| 3.0010 | 1109.9 | 1668 | 1.3729 | 47.89 | −9259.9 |

both electrolyte and glycine, water + electrolyte is considered as the solvent. As the linear trends of the $V_\phi$ and $K_\phi$ experimental data with respect to glycine molality suggest, their values at a fixed electrolyte molality are correlated with the molality of glycine using the following relations:

$$V_\phi = V_\phi^0 + \chi_v m_A \tag{4}$$

$$K_\phi = K_\phi^0 + \chi_S m_A \tag{5}$$

where $m_A$ is the molality of glycine, $V_\phi^0$ and $K_\phi^0$ are, respectively the infinite dilution apparent molar volume and infinite dilution apparent molar isentropic compressibility of glycine $\chi_v$ and $\chi_S$ and are two empirical parameters. The values of these parameters can be calculated by fitting the values of $V_\phi$ and $K_\phi$ to the molality of glycine at a fixed electrolyte molality using Eqs. (4),(5), respectively. The values of $V_\phi^0$ and $K_\phi^0$ of glycine together with the values of $\chi_v$ and $\chi_S$ at different KCl, $KNO_3$ or $NaNO_3$ concentrations are presented in Table 4. These values provide valuable information about the interactions between glycine and the solvent (water + electrolyte) as at infinite dilution the interactions between glycine molecules are negligible.

Fig. 1 depicts the effect of glycine concentration on its apparent molar volume at two KCl, NaCl, $KNO_3$ or $NaNO_3$ molalities. As similar behaviour was observed throughout the whole range of electrolyte concentration studied and for the sake of clarity, only electrolyte molalities equal to 0.4 and 0.8 are shown. The experimental data for water + glycine + NaCl, shown in Fig. 1, are obtained from a previous study [8]. As shown in this figure the value of $V_\phi$ of glycine for all four electrolytes studied increases as the concentration of either glycine or the electrolyte increases. This indicates that glycine molecules are larger in

Table 2
Measured values of density, sound velocity and refractive index and calculated values of apparent molar volume and isentropic compressibility in water + glycine + $NaNO_3$ system

| Glycine molality | Density (km/m$^3$) | Sound velocity (m/s) | Refractive index | $V_\phi \times 10^6$ (m$^3$/mol) | $K_\phi \times 10^{15}$ (m$^3$/kPa.mol) |
|---|---|---|---|---|---|
| $NaNO_3$ concentration = 0.2 m | | | | | |
| 0.0000 | 1008.1 | 1506 | 1.3342 | – | – |
| 0.5128 | 1023.4 | 1532 | 1.3406 | 44.43 | −22 198.5 |
| 0.9824 | 1036.4 | 1554 | 1.3464 | 44.86 | −20 263.1 |
| 1.5054 | 1050.1 | 1578 | 1.3524 | 45.13 | −18 939.2 |
| 2.0016 | 1062.2 | 1599 | 1.3575 | 45.43 | −17 545.3 |
| 2.4845 | 1073.3 | 1619 | 1.3624 | 45.69 | −16 465.0 |
| 2.9884 | 1084.2 | 1639 | 1.3673 | 45.94 | −15 436.5 |
| $NaNO_3$ concentration = 0.4 m | | | | | |
| 0.0000 | 1018.9 | 1515 | 1.3360 | – | – |
| 0.5027 | 1033.4 | 1540 | 1.3422 | 45.25 | −19 760.2 |
| 0.9918 | 1046.6 | 1562 | 1.3479 | 45.53 | −17 785.1 |
| 1.5193 | 1059.9 | 1586 | 1.3538 | 45.84 | −16 736.0 |
| 1.9532 | 1070.2 | 1604 | 1.3584 | 46.06 | −15 644.1 |
| 2.5028 | 1082.5 | 1627 | 1.3639 | 46.31 | −14 673.6 |
| 2.9456 | 1091.8 | 1644 | 1.3680 | 46.51 | −13 800.0 |
| $NaNO_3$ concentration = 0.6 m | | | | | |
| 0.0000 | 1029.5 | 1523 | 1.3377 | – | – |
| 0.4791 | 1042.9 | 1547 | 1.3436 | 45.93 | −18 310.4 |
| 1.0125 | 1056.8 | 1571 | 1.3497 | 46.25 | −16 196.4 |
| 1.4414 | 1067.4 | 1590 | 1.3545 | 46.40 | −15 281.3 |
| 1.9387 | 1078.9 | 1611 | 1.3596 | 46.64 | −14 226.8 |
| 2.4779 | 1090.7 | 1633 | 1.3648 | 46.83 | −13 282.5 |
| 2.9959 | 1101.3 | 1653 | 1.3697 | 47.02 | −12 404.0 |
| $NaNO_3$ concentration = 0.8 m | | | | | |
| 0.0000 | 1039.8 | 1531 | 1.3394 | – | – |
| 0.4964 | 1053.2 | 1555 | 1.3456 | 46.62 | −15 843.8 |
| 1.0102 | 1066.2 | 1579 | 1.3512 | 46.83 | −14 862.3 |
| 1.4942 | 1077.8 | 1600 | 1.3563 | 46.96 | −13 793.3 |
| 1.9881 | 1088.8 | 1620 | 1.3613 | 47.17 | −12 677.5 |
| 2.6514 | 1102.7 | 1646 | 1.3677 | 47.38 | −11 553.0 |
| 3.0404 | 1110.3 | 1661 | 1.3712 | 47.52 | −11 007.1 |
| $NaNO_3$ concentration = 1.0 m | | | | | |
| 0.0000 | 1049.9 | 1539 | 1.3411 | – | – |
| 0.4979 | 1063.0 | 1563 | 1.3470 | 47.04 | −14 519.6 |
| 1.0270 | 1076.0 | 1587 | 1.3528 | 47.27 | −13 284.8 |
| 1.4026 | 1084.7 | 1603 | 1.3569 | 47.42 | −12 433.4 |
| 2.0006 | 1097.7 | 1627 | 1.3628 | 47.65 | −11 210.3 |
| 2.4136 | 1106.2 | 1643 | 1.3668 | 47.78 | −10 542.0 |
| 2.8993 | 1115.6 | 1662 | 1.3713 | 47.94 | −9944.4 |

volume in solutions with higher electrolyte concentration. It can also be seen that for a fixed glycine and electrolyte concentration the nature of both the cation and the anion of the electrolyte affect the value of $V_\phi$ of glycine. As also shown in this figure, for two electrolytes with the same

Table 3
Measured values of density, sound velocity and refractive index and calculated values of apparent molar volume and isentropic compressibility in water + glycine + $KNO_3$ system

| Glycine molality | Density ($kg/m^3$) | Sound velocity (m/s) | Refractive index | $V_\phi \times 10^6$ ($m^3/mol$) | $K_\phi \times 10^{15}$ ($m^3/kPa.mol$) |
|---|---|---|---|---|---|
| $KNO_3$ concentration = 0.2 m | | | | | |
| 0.0000 | 1009.3 | 1504 | 1.3342 | – | – |
| 0.5048 | 1024.3 | 1530 | 1.3407 | 44.54 | −22558.6 |
| 0.9991 | 1038.0 | 1553 | 1.3467 | 44.90 | −20306.7 |
| 1.5086 | 1051.2 | 1576 | 1.3524 | 45.23 | −18802.1 |
| 2.0144 | 1063.5 | 1598 | 1.3579 | 45.52 | −17565.1 |
| 2.4428 | 1073.3 | 1616 | 1.3622 | 45.75 | −16623.7 |
| 3.0409 | 1086.3 | 1639 | 1.3679 | 46.01 | −15293.4 |
| $KNO_3$ concentration = 0.4 m | | | | | |
| 0.0000 | 1021.2 | 1511 | 1.336 | – | – |
| 0.4836 | 1035.1 | 1535 | 1.3418 | 45.33 | −19660.6 |
| 1.0024 | 1049.0 | 1559 | 1.3482 | 45.67 | −17921.2 |
| 1.4484 | 1060.2 | 1579 | 1.3531 | 45.93 | −16828.5 |
| 1.9568 | 1072.3 | 1601 | 1.3584 | 46.16 | −15770.4 |
| 2.4815 | 1084.0 | 1622 | 1.3637 | 46.39 | −14616.1 |
| 2.8727 | 1092.2 | 1638 | 1.3673 | 46.57 | −13988.0 |
| $KNO_3$ concentration = 0.6 m | | | | | |
| 0.0000 | 1032.9 | 1517 | 1.3378 | – | – |
| 0.4996 | 1046.7 | 1542 | 1.344 | 46.17 | −18072.9 |
| 1.0411 | 1060.6 | 1566 | 1.3502 | 46.49 | −15813.4 |
| 1.5567 | 1073.1 | 1589 | 1.3559 | 46.65 | −14888.0 |
| 2.0293 | 1083.8 | 1609 | 1.3607 | 46.86 | −13975.6 |
| 2.5001 | 1093.9 | 1628 | 1.3653 | 47.03 | −13125.1 |
| 2.8545 | 1101.1 | 1641 | 1.3685 | 47.17 | −12394.5 |
| $KNO_3$ concentration = 0.8 m | | | | | |
| 0.0000 | 1044.2 | 1523 | 1.3394 | – | – |
| 0.5115 | 1057.8 | 1547 | 1.3456 | 46.89 | −14907.9 |
| 1.0321 | 1070.8 | 1571 | 1.3514 | 47.05 | −14192.1 |
| 1.5101 | 1082.0 | 1592 | 1.3565 | 47.22 | −13356.4 |
| 2.0326 | 1093.5 | 1613 | 1.3618 | 47.41 | −12258.4 |
| 2.5410 | 1104.1 | 1634 | 1.3666 | 47.54 | −11629.8 |
| 2.8611 | 1110.4 | 1646 | 1.3695 | 47.65 | −11098.0 |
| $KNO_3$ concentration = 1.0 m | | | | | |
| 0.0000 | 1055.3 | 1529 | 1.3410 | – | – |
| 0.5200 | 1068.7 | 1553 | 1.3471 | 47.39 | −13243.9 |
| 1.0475 | 1081.4 | 1577 | 1.3528 | 47.58 | −12608.0 |
| 1.5515 | 1092.8 | 1599 | 1.3582 | 47.73 | −11884.5 |
| 2.0640 | 1103.6 | 1619 | 1.3633 | 47.93 | −10810.5 |
| 2.5458 | 1113.3 | 1638 | 1.3677 | 48.04 | −10178.8 |
| 3.0169 | 1122.2 | 1656 | 1.3720 | 48.17 | −9597.2 |

anion, the value of $V_\phi$ of glycine is larger in the presence of the electrolyte with potassium cation than the electrolyte with sodium cation. Similarly, for two electrolytes with the same cation the value of $V_\phi$ of glycine is larger in the presence of the electrolyte with nitrate anion than the elec-

Table 4
Calculated values of $V_\phi^0$(m$^3$/mol), $K_\phi^0$(m$^3$/kPa.mol) and the slopes of Eqs. (4) and (5), $\chi_v$(kg.m$^3$/mol$^2$) and $\chi_S$ (kg.m$^3$/kPa.mol$^2$), obtained from the fitting of the experimental data

| Molality | 0.0 | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 |
|---|---|---|---|---|---|---|
| Electrolyte: KCl | | | | | | |
| $V_\phi^0 \times 10^6$ | 43.235 | 44.356 | 45.018 | 45.594 | 46.246 | 46.777 |
| $\chi_v \times 10^6$ | 0.70817 | 0.52263 | 0.49065 | 0.47751 | 0.40948 | 0.37596 |
| $K_\phi^0 \times 10^{15}$ | −26 954.0 | −22 963.1 | −20 054.4 | −18 282.2 | −16 207.0 | −13 964.6 |
| $\chi_S \times 10^{15}$ | 3305.03 | 2689.44 | 2220.87 | 2195.63 | 1928.98 | 1633.94 |
| Electrolyte: NaNO$_3$ | | | | | | |
| $V_\phi^0 \times 10^6$ | 43.235 | 44.209 | 45.020 | 45.776 | 46.457 | 46.880 |
| $\chi_v \times 10^6$ | 0.70817 | 0.59347 | 0.51493 | 0.42614 | 0.35119 | 0.37291 |
| $K_\phi^0 \times 10^{15}$ | −26 954.0 | −23 153.1 | −20 464.1 | −18 824.4 | −16 745.6 | −15 282.7 |
| $\chi_S \times 10^{15}$ | 3305.03 | 2679.78 | 2341.33 | 2246.87 | 1941.52 | 1929.65 |
| Electrolyte: KNO$_3$ | | | | | | |
| $V_\phi^0 \times 10^6$ | 43.235 | 44.310 | 45.140 | 46.010 | 46.729 | 47.249 |
| $\chi_v \times 10^6$ | 0.70817 | 0.58005 | 0.50820 | 0.41091 | 0.32300 | 0.31080 |
| $K_\phi^0 \times 10^{15}$ | −26 954.0 | −23 382.4 | −20 448.3 | −18 665.9 | −15 806.4 | −14 111.1 |
| $\chi_S \times 10^{15}$ | 3305.03 | 2772.91 | 2333.26 | 2263.66 | 1658.57 | 1520.93 |

trolyte with chloride anion. These effects can be explained by the fact that the amino and the carboxyl groups of glycine in aqueous solutions dissociate and become, respectively positively and negatively charged. In the presence of an electrolyte, this leads to the formation of physically bonded ion-pairs between the charged groups of glycine and the cation and the anion of the electrolyte. This increases the apparent molar volume of glycine and reduces the electrostatic interactions between glycine molecules and free simple ions as well as water molecules. It should be mentioned that the bonds forming the ion-pairs are physical and non-covalent in nature. The formation of the ion-pairs also decreases the hydrophobicity of the glycine molecules arisen from the interactions of the hydrocarbon backbone of glycine with water molecules. This results in a more favourable interaction between glycine and water molecules, which in turn increases the hydration number of glycine. This effect is also reflected in the values of $V_\phi^0$, presented in Table 4, which for all four electrolytes studied increase with an increase in the electrolyte concentration. The formation of ion-pairs between charged amino acids and ions have been shown and discussed in several previous investigations. A complete review of these investigations is published by Collins [9]. The results of these studies in general agree on the formation of ion-pairs and the fact that the presence of an electrolyte in an aqueous solution of an amino acid results in the condensation of the cation and the anion of the electrolyte on the charged groups of the amino acid and thereby their neutralization. It has also been shown that this phenomenon is the reason for the influence of the electrolytes on the solubility of amino acids [9,10] in aqueous solutions. The effect of the nature of the cation and the anion of the electrolyte on the value of $V_\phi$ can also be attributed to the formation of the ion-pairs. As sodium ion has a smaller ionic volume than potassium ion [11], for a fixed glycine and electrolyte concentration the ion-pairs formed with sodium ion have smaller apparent molar volume than the ion-pairs formed with potassium ion. The same argument holds for the apparent molar volume of the ion-pairs formed with glycine and chloride or nitrate ion. This trend can be observed by comparing the values of $V_\phi^0$ of glycine for the four electrolytes studied at different electrolyte molalities, shown in Fig. 2. As can be seen from this figure, $V_\phi^0$ increases as the concentration of the electrolyte increases. It can also be seen that for a fixed electrolyte concentration $V_\phi^0$ of glycine depends on the size of the constituent ions of the electrolyte present in the solution. For example, the value of $V_\phi^0$ of glycine is larger in the presence of KCl then NaCl. It is important to mention that the presence of an electrolyte can change the protonation behaviour of glycine, which in turn may result in the formation singly charged forms of glycine in the solution. Experimental data for the effect of the concentration of NaCl and $KNO_3$ on the first and second dissociation constants of glycine [12,13] show that in the absence of a strong proton donor or acceptor the presence of an electrolyte does not result in the formation of singly charged glycine molecules. According to these experimental data, the conditions under which our experiments have been performed ensure that the formation of different charged forms of glycine do not interfere with our results. The high quality of the water used in the experiments and its neutral pH value also minimized the possibility of the formation of singly charged glycine molecules.

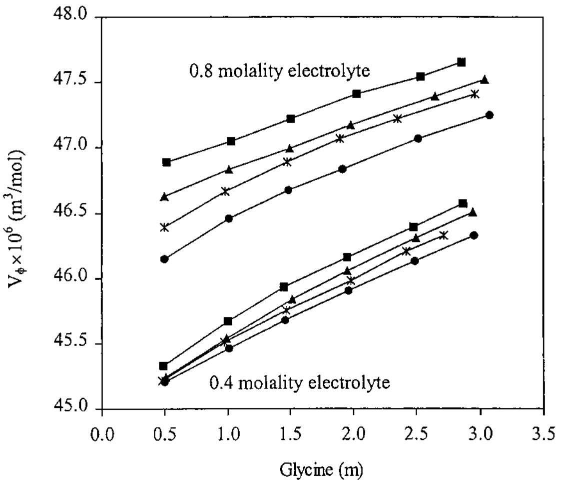

Fig. 1. Effect of glycine concentration on the value of $V_\phi$ of glycine in aqueous solutions of 0.4 and 0.8 molality ●: NaCl, *: KCl, ▲: $NaNO_3$, ■: $KNO_3$.

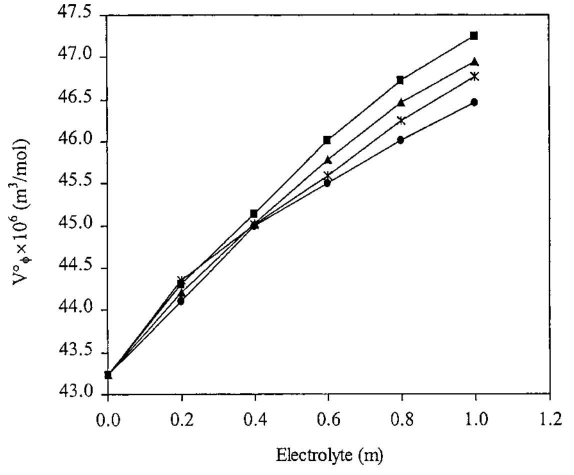

Fig. 2. Effect of electrolyte concentration on the value of $V_\phi^0$ of glycine. ●: NaCl, *: KCl, ▲: $NaNO_3$, ■: $KNO_3$.

Fig. 3 depicts the effect of glycine concentration on its isentropic compressibility in the presence of KCl, NaCl, $KNO_3$ or $NaNO_3$. As similar behaviour was observed throughout the whole range of electrolyte concentration studied and for the sake of clarity, only electrolyte molalities equal to 1.0 are shown. The experimental data for water + glycine + NaCl, shown in Fig. 3, are obtained from a previous study [8]. From Fig. 3 it can be seen that the value of $K_\phi$ of glycine is negative throughout the entire range of electrolyte and glycine concentration studied and it increases as the concentration of glycine increases. The experimental data presented in Tables 1–3 and those reported previously [8] suggest that for a fixed glycine concentration, the value of is $K_\phi$ larger at higher electrolyte concentrations. As shown in Fig. 3 for two electrolytes with the same cation the value of $K_\phi$ of glycine is smaller in the presence of the electrolyte with nitrate anion than the electrolyte with chloride anion. For two electrolytes with the same anion the value of $K_\phi$ of glycine is smaller in the presence of the electrolyte with sodium cation than the electrolyte with potassium cation. However, for a fixed glycine and electrolyte concentration, the difference between the value of $K_\phi$ of glycine in the presence of NaCl and KCl is much smaller than the difference between the value of $K_\phi$ of glycine in the presence of $NaNO_3$ and $KNO_3$. Also, experimental data show that at lower electrolyte concentrations $K_\phi$ of glycine is less affected by the nature of the cation or the anion of the electrolyte. From the negative values of $K_\phi$ and $K_\phi^0$, presented in Tables 1–4, it can be deduced that the water molecules around the glycine molecules are less compressible than the water molecules in the bulk solution. It should be mentioned that $K_\phi$ reflects the interactions between the solute and solvent, which in turn can be related to the hydration of the molecules. Hydration phenomenon plays an important role in the interactions in water + amino acid + electrolyte systems. This is owing to the doubly charged behaviour of glycine in aqueous solutions, which influences the structure of the water molecules in the vicinity of the glycine molecules. This phenomenon is called elecrostrication, which means the water molecules around a glycine molecule are under the influence of electrostatic field produced by the charged groups of the glycine. At higher electrolyte concentrations, as a result of the mass action law, the charges on more glycine molecules are neutralized and the electrostatic interactions between glycine and water molecules are suppressed therefore the water molecules become more compressible. The difference between the effect of electrolytes with different ions can also be related to the formation of ion-pairs between glycine molecules and simple ions. Since the ion-pairs formed with different ions have different physicochemical characteristics, the value of $K_\phi$ of glycine is different in the presence of different ions.

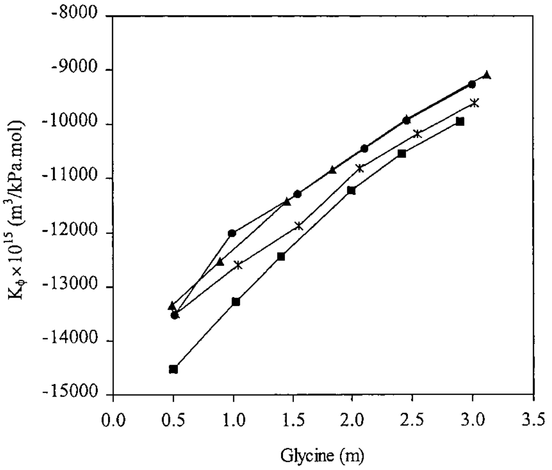

Fig. 3. Effect of glycine concentration on the value of $K_\phi$ of glycine in aqueous solutions at 1.0 molality ●: NaCl, *: KCl, ▲: $NaNO_3$ or ■: $KNO_3$.

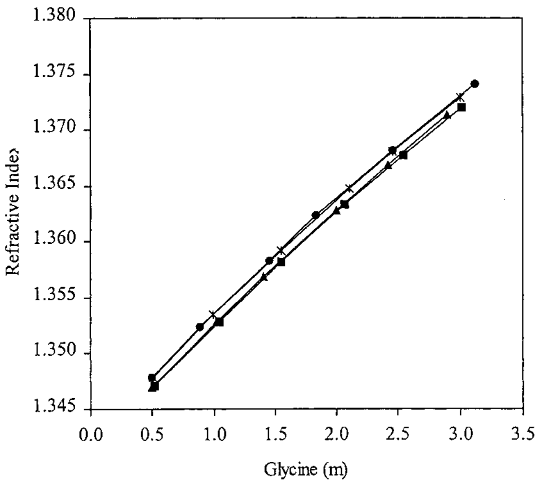

Fig. 4. Effect of glycine concentration on the refractive index of its aqueous solutions in the presence of 1.0 molality ●: NaCl, *: KCl, ▲: $NaNO_3$ or ■: $KNO_3$.

Fig. 4 depicts the effect of glycine concentration on the refractive index of four water + glycine + electrolyte systems studied here or in a previous study [8] at 1.0 molality electrolyte concentration. The electrolytes studied are KCl, NaCl, $KNO_3$ and $NaNO_3$. As shown in this figure, for a fixed glycine and electrolyte concentration, the nature of the cation of the electrolyte does not influence the refractive index of the solution while the nature of the anion of the electrolyte affects the refractive index of the solution. The same phenomenon can be observed for the effect of the nature of the cation and the anion of the electrolytes studied on the refractive index of their aqueous solutions without the presence of an amino acid.

## 4. Conclusions

Experimental data at 298.15 K of density, velocity of sound and refractive index of glycine in aqueous solutions KCl, $KNO_3$ and $NaNO_3$ have been reported. The values of apparent molar volume and isentropic compressibility of glycine were calculated from the measured data. The obtained results in this work and those previously measured for water + glycine + NaCl were comparatively studied. The results indicated that the interactions between glycine and an electrolyte influence its properties in aqueous solutions. The results also showed that the nature of both the cation and the anion of the electrolyte play an important role in the interactions between an electrolyte and glycine. For all four electrolytes studied, it was found that these interactions result in a positive transfer volume of glycine from one electrolyte solution to another with higher electrolyte concentration. This may be an indication of the increase in the volume of glycine with an increase in the electrolyte concentration. It was also found that the value of $K_{\phi}$ of glycine is negative throughout the entire range of glycine and electrolyte concentration studied. The negative value of $K_{\phi}$ of glycine implied that the water molecules around the glycine molecules were less compressible than the water molecules in the bulk solution. These effects were attributed to the doubly charged behaviour of glycine and the formation of ion-pairs with weak non-covalent bonds between the charged groups of glycine and the ions present in the solution. The reason for the different effect of different ions on the properties of glycine in aqueous electrolyte solutions was related to the different physicochemical characteristics of the ion-pairs formed with different ions. This effect was also related to the size difference of different ions.

## Acknowledgements

This work was partly financed by the CICYT, Spain, project QUI 97–1078.

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