$$\ln \gamma_3 = -\ln (x_3 + A_{31}x_1) - x_1\left(\frac{A_{13}}{x_1 + A_{13}x_3} - \frac{A_{31}}{A_{31}x_1 + x_3}\right)$$

The coefficients of eq 8 and 9 are given in Table VIII. In the ternary system the Redlich–Kister equations are

$$\ln \gamma_1 = x_2x_3[(B_{12} + B_{13} - B_{23}) + C_{12}(2x_1 - x_2) + C_{13}(2x_1 - x_3) + 2C_{23}(x_3 - x_2) + D_{12}(x_1 - x_2)(3x_1 - x_2) + D_{13}(x_1 - x_3)(3x_1 - x_2) - 3D_{23}(x_3 - x_2)^2 + C_1(1 - 2x_1)] + x_2^2[B_{12} + C_{12}(3x_1 - x_2) + D_{12}(x_1 - x_2)(5x_1 - x_2)] + x_3^2[B_{13} + C_{13}(3x_1 - x_3) + D_{13}(x - x_3)(5x_1 - x_3)] \quad (10)$$

where B_{ij}, C_{ij}, and D_{ij} are the binary constants and C_1 is the ternary constant (Table VIII). The equations for the other activity coefficients can be obtained by cyclic rotation of the indexes. In this case, according to the McDermott-Ellis test, the results obtained can be considered as thermodynamically consistent.

Acknowledgment

Thanks are due to Yehudit Reizner and Moshe Golden for their contribution in the experimental and numerical work. We are also indebted to Dr. M. Dariel from the Bromine Compounds Ltd., Beer-Sheva, for suggesting the systems to be investigated and for supplying the chemicals.

Glossary

α, β, δ	constants
A, B, C, D	constants
B_{ii}, B_{ij}	second virial coefficient of pure component and the mixed virial coefficient
C_1	ternary constant
CBM	chlorobromomethane
DBM	dibromomethane
DCM	dichloromethane
K_{AB}	equilibrium constant in eq 9, in cm^{-3}
m	total number of experimental points
P_i^0	vapor pressure of pure component i
P	total pressure
R	gas contant
T	temperature, °C or K
V_i^0	molar volume of pure component i
x_i, y_i	mole fraction of component i in the liquid and vapor phases
γ_i	activity coefficient
γ_i^*	activity coefficient considering association effects

Subscripts

calcd	calculated
obsd	observed
i, j, k	components i, j, and k
1	DCM
2	CBM
3	DBM

Literature Cited

(1) Bissel, T. G.; Okafor, G. E.; Williamson, A. G. *J. Chem. Thermodyn.* **1971**, *3*, 393.

(2) Murakami S.; Benson, G. C. *J. Chem. Thermodyn.* **1969**, *1*, 559.

(3) Philippe, R. These d'Etat, Lyon, 1973.

(4) Kehiaian, V. H. "Thermodynamics of Organic Mixtures in Thermochemistry and Thermodynamics"; Physical Chemistry MPT International Review Series, Series One, V.10.121; Skinner, H. A., Ed.; Butterworths: London, 1972.

(5) Wisniak, J.; Tamir A. *J. Chem. Eng. Data* **1975**, *20*, 168.

(6) TRC Tables, "Selected Values of Properties of Chemical Compounds"; Thermodynamic Research Center Data Project, Texas A & M University: College Station, TX, 1961.

(7) Prigogine, I.; Defay R. "Chemical Thermodynamics"; Wiley: New York, 1965.

(8) Van Ness, H. C. "Classical Thermodynamics of Non-Electrolyte Solutions"; Pergamon Press: London, 1964.

(9) Tsonopoulos, C. *AIChE J.* **1974**, *20*, 263.

(10) Herrington, E. F. G. *J. Inst. Pet.* **1951**, *37*, 457.

(11) McDermott, C.; Ellis, S. R. M. *Chem. Eng. Sci.* **1965**, *20*, 293.

(12) Wisniak, J.; Tamir, A. *J. Chem. Eng. Data* **1976**, *21*, 470.

(13) Nothnagel, K. H.; Abrams, D. S.; Prausnitz, J. M. *Ind. Eng. Chem. Process Des. Dev.* **1973**, *12*, 25.

(14) Marek, J.; Standart, G. *Collect. Czech. Chem. Commun.* **1954**, *19*, 1074.

(15) Tamir, A.; Wisniak, J. *Chem. Eng. Sci.* **1975**, *30*, 335.

(16) Tamir, A.; Wisniak, J. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 274.

Received for review June 27, 1980. Accepted December 5, 1980.

Osmotic and Activity Coefficients of Sodium and Potassium Glutamate at 298.15 K

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Osmotic and activity coefficients are reported for monosodium and monopotassium glutamate. The potassium salt has the larger coefficients, as is the case for monocarboxylic acid salts. These salts differ, therefore, from the half-neutralized dicarboxylic acids where the sodium salt coefficients are larger than those of the corresponding potassium salts. This is possible because of the zwitterionic nature of the glutamate ion.

Glutamic acid is readily synthesized by the body and, upon conversion to glutamine, remains in the tissues of many organs. Monosodium glutamate is a common additive to many foods. The measurement of these osmotic and activity coefficients is part of a program to investigate the colligative properties of water-soluble components of biological systems. These salts are interesting in their own right, however, because the glutamate anion with a net negative charge of unity may actually contain two negatively charged carboxyl groups and a positively charged ammonium group. This should give the salts a distinctly different behavior in solution from the usual 1,1 electrolytes.

Method

Reagent-grade L(+)-glutamic acid as received from Fisher Scientific Co. was exactly neutralized with 1 equiv of sodium or potassium hydroxide solution. The salts were evaporated to dryness under vacuum at room temperature over H_2SO_4. The dried salts were then recrystallized 3 times from methanol–acetone–water mixtures and again dried under vacuum over P_2O_5. The molecular weights of the salts were determined by passing solutions of weighed quantities of each salt through a

Table I. Experimental Results: Molalities of Isopiestic Solutions at $T = 298.15$ K

NaCl	NaGlu	KGlu	NaCl	NaGlu	KGlu
0.2982	0.3011	0.2988	2.295	2.266	2.177
0.615	0.625	0.613	2.579	2.538	2.431
0.930	0.946	0.921	3.243	3.165	3.004
1.135	1.148	1.114	3.778	3.658	
1.466	1.473	1.425	4.194	4.051	
1.788	1.785	1.721			

Table II. Osmotic and Activity Coefficients at 298.15 K

molality,	NaGlu		KGlu	
m	ϕ	γ	ϕ	γ'
0.1	0.928	0.773	0.931	0.776
0.2	0.919	0.725	0.924	0.732
0.3	0.913	0.695	0.921	0.708
0.4	0.909	0.676	0.920	0.691
0.5	0.907	0.661	0.922	0.680
0.6	0.908	0.651	0.926	0.674
0.7	0.909	0.642	0.931	0.670
0.8	0.910	0.636	0.936	0.667
0.9	0.915	0.632	0.940	0.665
1.0	0.921	0.630	0.948	0.666
1.2	0.934	0.629	0.964	0.671
1.4	0.945	0.632	0.930	0.680
1.6	0.961	0.636	0.997	0.691
1.8	0.976	0.645	1.015	0.702
2.0	0.992	0.654	1.035	0.718
2.5	1.032	0.682	1.085	0.767
3.0	1.073	0.718	1.146	0.827
3.5	1.120	0.763		
4.0	1.167	0.813		

cation exchange column in the hydrogen form. The results were in agreement with those expected for pure anhydrous salts. The isopiestic equilibrations of solutions of the two salts with sodium chloride solutions were performed in the manner described in detail in a previous paper (*1*).

Results and Discussion

The experimental results of the isopiestic equilibrations are presented in Table I. The osmotic and activity coefficients at rounded concentrations are given in Table II. Osmotic coefficients were calculated from the relationship

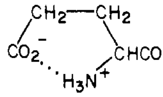
$$\phi = (m_{ref}/m)\phi_{ref}$$

Activity coefficients were calculated from the equation (*2*)

$$\ln \gamma = \ln \gamma_{ref} + \ln (m_{ref}/m) + 2\int_0^{m_{ref}} [(m_{ref}/m) - 1] \, d \ln (m_{ref}\gamma_{ref}]^{1/2}$$

The values of the osmotic and activity coefficients of sodium chloride, the reference salt, are those of Robinson and Stokes (*3*).

A comparison of the coefficients of these salts reveals that the potassium salt has the larger coefficients at any concentration. This is similar to the behavior observed for the salts of monocarboxylic acids. It is different, however, from the behavior of the half-neutralized aliphatic dicarboxylic acids (*4*) where the sodium salts have the larger coefficients. These observations suggest that, whereas there is some type of interaction between the carboxylic acid proton and the carboxylate group of the normal diprotic acid, this does not occur in the glutamate anion. A zwitterionic structure $^{-}O_2CCH_2CH_2CHNH_3^{+}CO_2^{-}$, such as is known to exist in monocarboxylic amino acids, would seem to be reasonable, but the resultant anion would possess *two* negative and one positive charge centers. A cyclical, hydrogen-bonded structure of the type



would leave *one* free carboxylate anion and would seem to be more probable.

Literature Cited

(1) Bonner, O. D. *J. Chem. Thermodyn.* **1979**, *11*, 559.
(2) Robinson, R. A.; Sinclair, D. A. *J. Am. Chem. Soc.* **1934**, *56*, 1830.
(3) Robinson, R. A.; Stokes, R. H. "Electrolyte Solutions", 2nd ed.; Academic Press: New York, 1959; pp 483, 492.
(4) Reference 3, pp 484, 485.

Received for review May 2, 1980. Accepted November 23, 1980.

Osmotic and Activity Coefficients of Methyl-Substituted Ammonium Nitrates at 298.15 K

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Osmotic and activity coefficient data are reported for three methyl-substituted ammonium nitrates. A comparison of these data with those for the other two members of the family which have already been reported enables one to note the effect of successive methyl substitution on ion–solvent and ion–ion interactions.

Osmotic and activity coefficient data have been reported for ammonium nitrate (*1*) and tetramethylammonium nitrate (*2*) but not for any of the intermediate methyl-substituted ammonium salts. For the two salts for which data have been reported, the osmotic coefficients of the ammonium salt are larger in dilute solutions while the tetramethylammonium salt has much the larger coefficients in the more concentrated solutions. This observation suggests that data for the remainder of the family might be desirable.

Method

The free bases methylamine and trimethylamine in aqueous solution were obtained from Aldrich Chemical Co. The aqueous solution of dimethylamine was from Eastman Kodak Co. The free bases, as received, were almost neutralized with aqueous nitric acid. The water and excess base from each of the solutions were removed by drying in a vacuum desiccator over

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