(10) D'Ans, J. et al., Eds. "Landolt-Börnstein Tabellen"; Springer-Verlag, 1969; II Band, 5 Teil.
(11) (a) Harned, H. S.; Owen, B. B. "The Physical Chemistry of Electrolytic Solutions"; Reinhold: New York, 1958; eq (6-9-4), p 240. (b) *Ibid.*, p 231.
(12) Kay, R. L.; Vidulich, G. A.; Pribadi, K. S. *J. Phys. Chem.* **1969**, *73*, 445.
(13) Korson, L.; Drost-Hansen, W.; Millero, F. J. *J. Phys. Chem.* **1969**, *73*, 34.

Received for review June 23, 1980. Accepted October 20, 1980. This work was financially supported by the Natural Sciences and Engineering Research Council of Canada.

Vapor–Liquid Equilibria in the Dichloromethane–Chlorobromomethane–Dibromomethane System and Its Binaries

Alexander Apelblat,* Jaime Wisniak, and Abraham Tamir

Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel

Vapor–liquid equilibria were measured at 760 mmHg for the systems dichloromethane–dibromomethane, dichloromethane–chlorobromomethane, dibromomethane–chlorobromomethane, and dichloromethane–chlorobromomethane–dibromomethane. Boiling points of the systems were correlated by an empirical expression. None of the systems exhibited azeotropic behavior. The activity coefficients in the binary and ternary systems were correlated by the Redlich–Kister and Wilson equations.

Introduction

Halogen derivatives of methane have been studied only in mixtures with aliphatic and aromatic hydrocarbons (*1*, *2*) or with dimethyl sulfoxide (*3*). No data are available on mixtures of derivatives alone. The review by Kehiaian (*4*) also indicates that the number of systems involving halomethanes is very small. Halomethanes have found application in organic synthesis as alkylating agents, in preparation of surface-active agents, and in the manufacture of dyes and pharmaceuticals.

We report here the vapor–liquid equilibrium in the ternary dichloromethane (DCM)–chlorobromomethane (BCM)–dibromomethane (DBM) system and the corresponding binary systems at 760 mmHg. The experimental procedure has already been reported (*5*). The accuracy in determination of pressure and temperature was $\Delta P = \pm 2$ mmHg and $\Delta T = \pm 0.02$ °C, while the mole fractions in both phases were measured within ±0.001. DCM and DBM were supplied by Bromine Compounds Ltd., Beer-Sheva, and CBM was supplied by Fluka. No significant impurities were detected by gas-chromatographic analysis of these reagents. Except for DBM—which was dried and redistilled—the reagents were used without further purification. Physical properties of the halomethanes are collected in Table I, and they agree with the literature data (*6*). The analyses were carried out by gas chromatography using a Packard-Becker Model 417 apparatus equipped with a thermal conductivitiy detector and an Autolab Minigrator electronic integrator. The column (0.32 × 200 cm) was filled with O.V.17 and maintained at 90 °C; the injection port temperature was 220 °C, and that of the detector 250 °C.

Table I. Physical Properties of Pure Compounds

compd	refractive index at 20 °C	bp, °C
CH_2Cl_2 (1)	1.4230	39.50
	1.4242 (*6*)	39.75 (*6*)
CH_2ClBr (2)	1.4824	68.25
	1.4837 (*6*)	68.11 (*6*)
CH_2Br_2 (3)	1.5400	96.50
	1.5420 (*6*)	96.95 (*6*)

Table II. Vapor-Pressure Constants (*6*)

compd	α_i	β_i	δ_i
CH_2Cl_2 (1)	7.08030	1138.91	231.45
CH_2ClBr (2)	6.86624	1132.30	216.00
CH_2Br_2 (3)	7.06250	1327.80	220.58

Table III. Experimental Vapor–Liquid Equilibria Data for Dichloromethane (1)–Chlorobromomethane (2) at 760 mmHg

temp, °C	x_1	y_1	y_1 calcd[a]
66.44	0.027	0.064	0.064
63.27	0.087	0.186	0.188
62.90	0.101	0.213	0.216
61.78	0.125	0.259	0.258
60.67	0.145	0.291	0.290
59.60	0.173	0.338	0.335
55.80	0.277	0.487	0.475
52.90	0.371	0.588	0.580
51.04	0.434	0.657	0.639
49.20	0.502	0.717	0.695
47.35	0.595	0.787	0.774
45.55	0.652	0.836	0.798
43.98	0.754	0.884	0.875
43.35	0.790	0.902	0.897
41.00	0.917	0.962	0.959

[a] According to Raoult's law.

Results and Discussion

The temperature-composition data at constant pressure ($P = 760$ mmHg) for the systems under consideration are presented in Tables III–VI. The boiling points of the binary and ternary systems were correlated by eq 1 and 2, where T^0 is

$$T = \sum_{i=1}^{2} T_i^0 x_i + x_1 x_2 \sum_{k=0}^{l} C_k (x_i - x_j)^k \qquad (1)$$

$$T = \sum_{i=1}^{3} T_i^0 x_i + \sum_{i,j=1}^{3} x_i x_j \sum_{k=0}^{l} C_k (x_i - x_j)^k + x_1 x_2 x_3 [A + B(x_1 - x_2) + C(x_1 - x_3) + D(x_2 - x_3)] \qquad (2)$$

the boiling point of the pure component expressed in °C, C_k values are the binary constants, and A, B, C, and D are the

0021-9568/81/1726-0144$01.25/0

Table IV. Experimental Vapor-Liquid Equilibria Data for Chlorobromomethane (2)-Dibromomethane (3) at 760 mmHg

temp, °C	x_2	y_2	y_2 calcd[a]
95.22	0.034	0.082	0.084
94.50	0.046	0.112	0.115
93.90	0.062	0.141	0.146
92.62	0.071	0.196	0.186
91.02	0.129	0.271	0.275
88.26	0.206	0.387	0.394
87.17	0.229	0.424	0.432
85.15	0.271	0.470	0.497
84.90	0.293	0.524	0.516
84.11	0.317	0.533	0.544
82.95	0.337	0.538	0.575
81.93	0.372	0.599	0.610
80.95	0.424	0.643	0.654
80.10	0.426	0.637	0.665
79.10	0.450	0.675	0.690
79.13	0.485	0.693	0.709
78.16	0.490	0.710	0.722
77.80	0.500	0.725	0.730
76.80	0.550	0.742	0.766
75.05	0.594	0.798	0.801
73.85	0.660	0.840	0.840
74.60	0.663	0.829	0.837
73.66	0.702	0.857	0.861
72.72	0.725	0.874	0.876
71.47	0.786	0.903	0.908
69.66	0.906	0.952	0.962

[a] According to Raoult's law.

Table V. Experimental Vapor-Liquid Equilibria Data for Dichloromethane (1)-Dibromomethane (3) at 760 mmHg

temp, °C	x_1	y_1	γ_1*[a]	γ_3*[a]
89.00	0.080	0.255	2.672	1.024
84.65	0.110	0.315	2.325	1.083
82.70	0.125	0.390	2.375	1.066
81.80	0.130	0.365	2.227	1.114
80.00	0.155	0.465	2.197	1.073
76.90	0.170	0.485	2.142	1.129
76.30	0.190	0.530	2.032	1.111
76.00	0.190	0.495	1.964	1.163
67.90	0.275	0.620	1.733	1.284
66.90	0.280	0.615	1.720	1.328
61.60	0.355	0.730	1.620	1.345
61.30	0.385	0.720	1.489	1.449
58.10	0.435	0.775	1.445	1.486
55.00	0.480	0.805	1.407	1.587
54.90	0.490	0.810	1.385	1.597
52.85	0.550	0.895	1.351	1.338
51.10	0.590	0.880	1.293	1.569
49.70	0.610	0.895	1.284	1.656
48.10	0.670	0.920	1.221	1.725
47.10	0.680	0.925	1.228	1.750
44.80	0.785	0.960	1.132	1.863
43.58	0.840	0.975	1.091	1.899
43.20	0.880	0.980	1.052	2.201
42.10	0.915	0.995	1.043	1.145

[a] Assuming heteroassociation, eq 7.

Table VI. Ternary Vapor-Liquid Equilibrium Data for Dichloromethane (1)-Chlorobromomethane (2)-Dibromomethane (3) at 760 mmHg

temp, °C	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
46.62	0.698	0.078	0.917	0.039	1.043	1.039	1.158
49.35	0.574	0.252	0.818	0.142	1.035	1.060	1.210
50.61	0.569	0.114	0.857	0.067	1.051	1.056	1.198
50.70	0.517	0.271	0.790	0.159	1.063	1.051	1.198
52.68	0.470	0.251	0.771	0.159	1.073	1.058	1.153
52.90	0.430	0.291	0.753	0.179	1.137	1.019	1.110
54.73	0.357	0.480	0.629	0.329	1.081	1.065	1.091
54.75	0.430	0.158	0.746	0.115	1.644	1.131	1.428
55.10	0.412	0.208	0.710	0.155	1.046	1.144	1.483
55.52	0.417	0.152	0.722	0.115	1.037	1.144	1.552
56.60	0.356	0.334	0.665	0.243	1.083	1.060	1.168
57.00	0.375	0.219	0.678	0.171	1.035	1.129	1.441
57.13	0.367	0.225	0.670	0.177	1.041	1.126	1.445
57.15	0.309	0.444	0.613	0.317	1.131	1.021	1.091
57.27	0.360	0.241	0.672	0.184	1.060	1.088	1.383
59.32	0.340	0.178	0.706	0.139	1.109	1.038	1.139
61.80	0.173	0.689	0.365	0.588	1.048	1.045	1.098
62.54	0.201	0.437	0.443	0.371	1.071	1.014	1.611
63.05	0.202	0.426	0.399	0.408	0.946	1.125	1.596
64.18	0.151	0.605	0.348	0.560	1.068	1.049	1.112
64.91	0.244	0.178	0.605	0.173	1.126	1.075	1.103
65.80	0.167	0.448	0.404	0.443	1.071	1.063	1.104
66.48	0.134	0.538	0.328	0.538	1.063	1.052	1.108
67.52	0.037	0.870	0.093	0.869	1.060	1.017	1.067
67.88	0.156	0.312	0.395	0.340	1.058	1.097	1.284
69.14	0.145	0.342	0.397	0.376	1.104	1.064	1.090
69.26	0.041	0.754	0.108	0.802	1.059	1.026	1.077
69.60	0.049	0.700	0.134	0.757	1.089	1.032	1.052
69.90	0.013	0.835	0.035	0.898	1.063	1.017	1.057
70.00	0.010	0.850	0.023	0.916	0.906	1.016	1.041
72.46	0.138	0.191	0.386	0.233	1.031	1.066	1.244
74.00	0.124	0.186	0.337	0.239	0.961	1.072	1.276
74.74	0.037	0.519	0.099	0.661	0.928	1.039	1.095
74.92	0.099	0.241	0.271	0.281	0.945	0.946	1.366
76.81	0.101	0.159	0.317	0.226	1.031	1.091	1.166
77.00	0.114	0.121	0.330	0.166	0.946	1.047	1.235
79.55	0.084	0.135	0.303	0.209	1.104	1.097	1.076
80.71	0.056	0.203	0.207	0.321	1.098	1.084	1.056

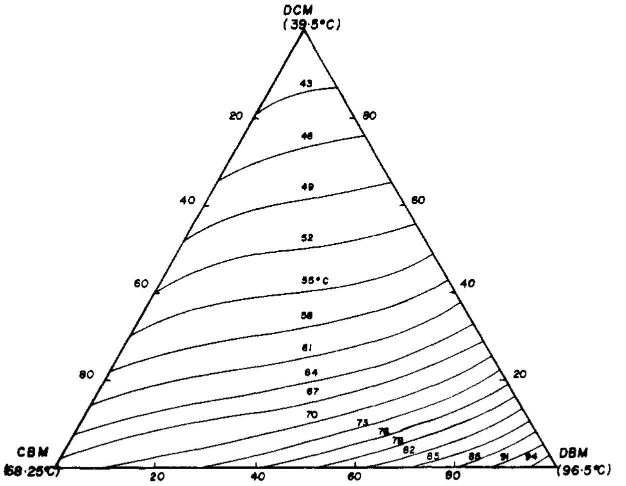

Figure 1. Isothermals at 760 mmHg for the system dichloromethane–chlorobromomethane–dibromomethane, calculated by eq 8.

ternary constants (Table VII). l is an arbitrary number of terms in the series expansion of $x_i - x_j$ which was equal to 3 in the present work.

Additional information indicating the degree of goodness of the correlations is also reported in Table VII. Using eq 2, we calculated isothermals in the ternary system, and they are presented in Figure 1. The shape of the curves indicated that the system did not exhibit azeotropic behavior.

It was found that the T–x–y data for the dichloromethane–chlorobromethane and chlorobromomethane–dibromomethane systems could be correlated by assuming ideal behavior of the systems. Using Raoult's law

$$P_i = y_i P = P_i^0 x_i \qquad i = 1, 2 \tag{3}$$

it was possible to evaluate $y_i(T)$ from known $T - x_i$ values by taking into consideration that the vapor pressure of the pure component, P_i^0, was given by the Antoine equation (eq 4). The

$$\log P_i^0 = (\alpha_i - \beta_i/\delta_i + t) \tag{4}$$

constants α_i, b_i, and δ_i reported in ref 6 are presented in Table II. Calculated values of y_i are presented in Table III and IV. It is found that the calculated results are in satisfactory agreement with experimental values only if constants of the

Table VII. Correlation of Boiling Points, Eq 1 and 2

system	C_0	C_1	C_2	C_3	rmsd[a]	Y[b]
DCM-CBM	−18.260	6.7020	−2.9539	3.9149	0.140	0.223
DCM-DBM	−56.364	26.503	9.0121	−14.358	0.587	0.791
CBM-DBM	−17.789	0.24250	0.8813	10.032	0.353	0.364

system	A	B	C	D	rmsd	Y
DCM-CBM-DBM	−19.259	−47.531	124.04	14.404	0.504	0.690

[a] rmsd = $(\Sigma(T_{\mathrm{obsd},i} - T_{\mathrm{calcd},i})^2/m)^{1/2}$. [b] $Y = \sum_{i=1}^{m} |(T_{\mathrm{obsd}} - T_{\mathrm{calcd}})/T_{\mathrm{obsd}}100/m)_i|$.

Table VIII. Correlation of Activity Coefficients, Eq 8–10

				rmsd[a]		
system	B_{ij} or A_{13}	C_{ij} or A_{31}	D_{ij}	γ_i	γ_j	y_1
DCM-CBM	0.21199	−0.13865	0.11689			
DCM-DBM	0.83519	−0.52389	−0.97690	0.71	0.33	
CBM-DBM	0.17261	0.02679	−0.09046			
DCM-DBM (eq 9)	3.0445	0.3305				0.05

	Y[c]			overall rmsd[b]	
DCM-CBM-DBM	DCM	CBM	DBM	γ	y
$C_1 = 0$	38.16	7.74	16.61	0.3082	0.0946
$C_1 = -3.554$	12.96	15.66	17.49	0.2222	0.0511

[a] rmsd = $(\sum_{i=1}^{m} (\gamma_{\mathrm{obsd},i} - \gamma_{\mathrm{calcd},1})^2/m)^{1/2}$. [b] rmsd = $(\sum_{i=1}^{m} \sum_{j=1}^{n} (\gamma_{ij,\mathrm{obsd}} - \gamma_{ij,\mathrm{calcd}})^2/mn)^{1/2}$, similarly for y. [c] $Y = \sum_{i=1}^{m} |[(y_{\mathrm{obsd}} - \gamma_{\mathrm{calcd}}100/m)_i|$.

Antoine equation of DCM and DBM are used in calculations in the DCM–CBM and CBM–DBM systems. A poor correlation is achieved with the constants of chlorobromomethane and prevents construction of the complete phase diagram of T–y,x, without previous knowledge of T–x values. In principle, for the ideal systems the vapor–liquid equilibrium can be calculated by the method described by Prigogine and Defay (*7*) using only the temperature dependence of the vapor pressures (the heat of vaporization of pure components is evaluated by differentiation of eq 4). The binary DCM–DBM and the ternary DCM–CBM–DBM systems show moderate deviations from ideality. The liquid activity coefficients were calculated from eq 5 (*8*), where

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^0} + \frac{(B_{ii} - V_i^0)(P - P_i^0)}{RT} + \frac{P}{2RT} \sum_{j=1}^{m} \sum_{k=1}^{m} y_j y_k (2\delta_{ji} - \delta_{jk}) \qquad (5)$$

the excess virial coefficients are defined by eq 6. The virial

$$\delta_{ji} = 2B_{ji} - B_{jj} - B_{ii} \qquad (6)$$

coefficients Bi_i and the mixed virial coefficients B_{ij} were evaluated from the correlation proposed by Tsonopoulos (*9*). The binary data were tested for thermodynamic consistency by the Herrington test (*10*), and the ternary data by the McDermott–Ellis method (*11*). The detailed procedure has already been reported (*12*).

The activity coefficients for the DCM–DBM system calculated with eq 5 were found to be thermodynamically inconsistent by the area test. However, it can be supposed that experimental errors are not a main source of the inconsistency because, in spite of rechecking the analytical procedure and duplication of experiments, a normal scattering of y,x points was observed. It should also be noted that application of eq 5 to the system DCM–DBM requires using the Antoine equation for DCM far beyond its boiling point, with the corresponding uncertainty. No vapor-pressure data are available to improve the calculations. In addition, the DCM–DBM system presents a maximum difference in boiling points (i.e., in vapor pressures) of pure components. The possibility of association reactions in the vapor phase was also investigated since dipole–dipole interactions can be expected.

We found that the simplest heteroassociation of the type A + B = AB gave an adequate description of the system. Since the equilibrium constant of the reaction, K_{AB}, is unknown, it was estimated by the method proposed by Nothnagel, Abrams, and Prausnitz (*13*):

$$\ln K_{AB}(RT/P) = -1000/T + 7.4113 \qquad (7)$$

Using $K_{AB}(T)$ values from eq 7, we calculated the liquid activity coefficients from previously derived expressions for the extended Marek–Standart model of associated solutions (14–16), and they are denoted as γ_1^* and γ_3^* in Table V. From eq 7 it follows that the temperature dependence of K_{AB} is relatively weak in the temperature range between the boiling points of DCM and DBM. The formation of H-bonded AB or even AB_2 complexes has been postulated by Phillippe (*9*) in the dimethyl sulfoxide–halomethane systems; however, it seems that in the present case the dipole–dipole interaction between components is probably the dominant interaction (μ_{DCM} = 1.60D and μ_{DBM} = 1.43D).

Association effects did not produce any significant change in the calculated activity coefficients in the ternary system (using the McDermott–Ellis consistency test). At present we can explain binary inconsistency only by assuming the heteroassociation.

The activity coefficients in the DCM–DBM system as calculated by eq 5 can be correlated by the Redlich–Kister equations

$$\ln \gamma_1 = (B_{13} + 3C_{13} + 5D_{13})x_3^2 - 4(C_{13} + 4D_{13})x_3^3 + 12D_{13}x^4 \qquad (8)$$

$$\ln \gamma_3 = (B_{13} - 3C_{13} + 5D_{13})x_1^2 + 4(C_{13} - 4D_{13})x_1^3 + 12D_{13}x_1^4$$

or by the Wilson equations

$$\ln \gamma_1 = -\ln (x_1 + A_{13}x_3) + x_3\left(\frac{A_{13}}{x_1 + A_{13}x_3} - \frac{A_{31}}{A_{31}x_1 + x_3}\right) \qquad (9)$$

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

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) Kehlaian, 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

Oscar D. Bonner

Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208

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

0021-9568/81/1726-0147$01.25/0