Isopiestic Study of the System Potassium Chloride–Potassium Nitrate–Water at 25° C.

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An isopiestic apparatus was devised and isopiestic vapor pressure measurements are reported for the system potassium chloride–potassium nitrate–water at 25° C. The osmotic coefficient of the mixed salt solutions and the activity coefficient of each salt in the presence of the other were evaluated. The application of Harned's rule to the system investigated is discussed and interpreted in terms of ion-ion interactions over the concentration range studied.

MUCH WORK has been done on the thermodynamics of aqueous solutions of single salts, but much less on the thermodynamics of salt mixtures, their structures, and specific interactions. As a part of a general study of the thermodynamic properties of multicomponent systems in aqueous solutions, the present investigation was undertaken to ascertain the excess free energy of mixing from the mean activity coefficients of the components. In the system chloride-nitrate, the nitrate ion is more effective than the chloride ion in changing the water structure (*3*) and large mixing effects may be expected as confirmed by heats (*13–16*) and volumes (*9*) of mixing of similar systems.

The systems $NaCl$-$NaNO_3$ (*6, 7*) and $LiCl$-$LiNO_3$ (*10*) have been investigated, but no isopiestic measurements of the system KCl-KNO_3 have been published, although some measurements of the freezing point of the reciprocal salt pair KNO_3-$LiCl$ have been reported (*12*).

In this paper isopiestic vapor pressure measurements are reported for the system potassium chloride–potassium nitrate–water at 25° C.

EXPERIMENTAL

Materials. Potassium chloride, obtained from Fluka purissium (analytical reagent grade) certified reagents, was twice recrystallized from conductivity water and dried to constant weight at 200° C., under vacuum.

Baker reagent grade potassium nitrate was purified by several crystallizations from double-distilled water and conductivity water and dried to constant weight at 250° C. under vacuum.

Apparatus. The isopiestic apparatus consisted of a glass vacuum desiccator mounted on a rocking stand and placed in a thermostated bath, the temperature of which was controlled within 0.001° C. The desiccator contained a gold-plated block, 24 cm. in diameter and 3 cm. thick, in which 18 gold-plated brass cups were placed. The cups were of a cylindrical shape and rested in 2-cm.-deep wells in the copper block. A device introduced into the desiccator via an Edwards Wilson seal allowed for removing and replacing the lids *in situ*, allaying any errors due to the evaporation of solutions. More details will be published elsewhere (*2*).

Procedure. The desiccator was placed in the thermostat and rocked for some hours at various reduced pressures, to avoid splattering of the solutions, until it was finally set for equilibration. Upon completion of the run, the lids were closed, and dry air was admitted into the desiccator, which was then removed from the bath. The cups were then weighed, all weights being corrected to vacuum. The cups were allowed to equilibrate for 4 days to 3 weeks. The longer time was required for the more dilute solutions.

Weighed aliquots of the mixed salts solutions were added to the cups for the first equilibration. For subsequent runs, water was weighed in to give a desired concentration. An excess of 100 mg. was provided to some of the dishes containing the same mixture, so that equilibrium could be approached from both directions and the attainment of equilibrium be indicated by agreement for the concentrations of replicate cups within 0.1% in the molalities. The reference salts were pure potassium chloride and potassium nitrate over the concentration range investigated. The osmotic coefficients of these electrolytes are given by Robinson and Stokes (*11*).

RESULTS

Equilibrium isopiestic concentrations are presented in Table I, together with the concentrations of the reference potassium chloride and nitrate solutions. The osmotic coefficients for the mixed salt solutions were computed with the equation:

$$\nu_R m_R \phi_R = \nu_y m_y \phi_y \quad (1)$$

where ν, the number of ions, is 2, m_y is the molality of the mixed solution, y is its osmotic coefficient, and m_R and ϕ_y are the molality and osmotic coefficient of the reference electrolyte, respectively. Taking pure potassium chloride as reference, a smooth curve could be traced through the values obtained for potassium nitrate osmotic coefficient, underlining within 1% Robinson and Stokes' values (*11*). All the calculations were referred to KCl as standard.

Mean molal activity coefficients for each salt in the mixed aqueous solutions were computed from the basic equation of McKay and Perring (*8*)

$$\ln \gamma_2 = \ln \gamma_2^\circ + \ln \frac{M}{m} + \int_0^M \left[\frac{1}{m^2} \left(\frac{\partial m}{\partial \ln y} \right)_{m\phi} + \frac{1}{m} - \frac{1}{M} \right] d(M\phi) \quad (2)$$

where γ_2 and γ_2° are the activity coefficients of electrolyte 2 (KNO_3) in the mixture with electrolyte 1 (KCl) and its own pure solution at the same ionic strength, respectively; M is the molality of the solution of pure 2 isopiestic with the mixed solution of total molality. $m = m_1 + m_2$, ϕ is the total osmotic coefficient, and y is defined by $m_2 = ym$, where m_2 is the molality of electrolyte 2.

The total molality, m, could be expressed as a power series in y and the integral

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[1] Deceased

Table I. Results for Isopiestic Solutions of Mixed KCl–KNO$_3$

y^a	Molalities of Total Salt in Solution for Isopiestic Equilibrations							
	1st	2nd	3rd	4th	5th	6th	7th	8th
0.0	2.0429	1.8039	1.6195	1.0024	0.80083	0.63336	0.40557	0.10183
0.1090	2.1078	1.8463	1.6720	1.0121	0.81757	0.63961	0.40940	
0.2857	2.2150	1.9415	1.7538	1.0448	0.83593	0.64925	0.41517	
0.3420								0.10323
0.4266	2.3341	2.0326	1.8337	1.0726	0.85453	0.66506	0.41864	
0.5713	2.4702	2.1420	1.9339	1.1003	0.87531	0.67499	0.42653	
0.58572								0.10341
0.71041	2.6249	2.2511	2.0043		0.88958	0.68476		
0.71848								0.10425
0.8573	2.8374	2.4544	2.1309	1.1765	0.92135	0.69827	0.43879	
0.86146								0.10537
1.0	3.0998	2.6005	2.2726	1.2165	0.95100	0.72790	0.44597	0.10569

[a] Mole fraction of nitrate in salt mixture, $m_2/(m_1 + m_2)$.

$$\mathrm{I} = \int_0^{M\phi} \left[\frac{1}{m^2} \left(\frac{dm}{d\ln y} \right)_{m\phi} + \frac{1}{m} - \frac{1}{M} \right] d(m\phi) \qquad (3)$$

evaluated numerically at constant y.

The calculated values of $\ln\gamma_1$ and $\ln\gamma_2$ were used to obtain values for the Harned coefficients (*5*) α_{12} and α_{21} from the equation

$$\alpha_{ij} = -\frac{1}{m_j} \log (\gamma_i/\gamma_i^\circ) \qquad (4)$$

However, in the case of KNO$_3$ there was evidence that the interaction coefficient, α_{21}, was dependent on y, implying a quadratic dependence of the activity coefficient on the molality according to the expression

$$\log \gamma_i = \log \gamma_i^\circ - \alpha_{ij} m_j - \beta_{ij} m_j^2 \qquad (5)$$

The Harned's rule coefficients are given in Table II.

The numerical integration method of calculating the activity coefficients gave more consistent results for the Harned coefficients. This may be due to the relatively large number of dishes in the desiccator (18 altogether), which allows for a smooth curve of m as a function of y.

From Friedman's theory (*4*) the free energy of mixing ΔG^E may be written as

$$\Delta G^E = m^2(1 - y)\, yRT\, [g_0 + g_1(1 - 2y)] \qquad (6)$$

with

$$g_0 = -2.303\, (\alpha_{12} + \alpha_{21}) + m\beta_{21} \qquad (7)$$

$$g_1 = 2.305\, m\beta_{21}/3 \qquad (8)$$

since currently, the experimental work is only accurate enough to determine the first two Harned coefficients, α_{ij} and β_{ij}.

According to Friedman (*4*) g_0 is the major term for 1 to 1 common ion mixtures and the major interactions contributing to g_0 are those of like charged ion pairs. Hence the value of g_0 at $m = 0$ should represent a measure of anion-anion pair interactions only. Moreover, anion cation anion interaction will give a g_0 proportional to m, and contribute to g_1.

Table II. Harned Rule Coefficients for KCl–KNO$_3$–H$_2$O

m	α_{12}	α_{12}^a	α_{21}	β_{21}
0.2	0.143		−0.165	0.530
0.5	0.097	0.100	−0.102	0.162
1.0	0.088	0.090	−0.056	0.029
1.5	0.085		−0.060	0.020
2.0	0.081	0.080	−0.068	0.027
2.5	0.079	0.078	−0.059	0.033

[a] Estimated by Robinson and Stokes' method (*11*) where much scattering was observed.

Overlooking the value obtained for $m < 1$, and extrapolating to $m = 0$, it may be shown that the chloride-nitrate pair interactions are rather weak, whereas the decrease in g_0 with increasing m could be due to either chloride-potassium-nitrate or nitrate-chloride interactions. On the other hand, for $m < 1$, g_0 seems to decrease with decreasing m, pointing to higher interactions taking place at lower concentrations.

As far as the authors are aware, the β_{ij} coefficients obtained for the KNO$_3$ are much larger than any of the values reported up to date and point to the importance of triplet interactions in mixed solutions of electrolyte. We feel that these findings should be highly relevant to thermodynamics of solutions. However, further investigations (*1*) are necessary before anything can be said conclusively and we have therefore turned to the detailed study of mixtures of tetraalkylammonium ions with alkali halides.

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