Volume Changes on Mixing Solutions of Lithium Chloride, Sodium Chloride, Lithium Sulfate, and Sodium Sulfate at Constant Ionic Strength

HENRY E. WIRTH and WILLARD L. MILLS
Department of Chemistry, Syracuse University, Syracuse, N. Y. 13210

The volume changes at 25° C. on mixing two solutions of equal ionic strength were determined for the six combinations of the four electrolytes, LiCl, NaCl, Li_2SO_4, and Na_2SO_4 at ionic strengths of 1 and 4. Single-mixing experiments were made at an ionic strength of 2.25 for the six combinations, and at ionic strengths of 0.25, 0.50, 1.5, and 3.0 for the Na_2SO_4–NaCl system in order to determine the concentration dependence of the volume changes. The volume changes on mixing the heterionic solutions (Na_2SO_4–LiCl and Li_2SO_4–NaCl) could be calculated from the volume changes observed in homoionic solutions to within 0.03 ml. per equivalent.

IN previous work (*11*) the volume changes at 25° C. on mixing two solutions of equal ionic strength were determined for all six combinations of the four electrolytes, NaCl, HCl, $NaClO_4$, and $HClO_4$ at two ionic strengths in order to determine the correction terms in Young's rule (*14*). This paper extends the work to solutions containing the divalent sulfate ion and evaluates the concentration dependence of the correction terms.

EXPERIMENTAL

Materials. Stock solutions were prepared from C. P. chemicals, and their concentrations were determined by evaporation of weighed portions to dryness and heating at 350° C. to constant weight. Solutions having ionic strengths of exactly 1.000_0, 2.250_0, and 3.997_2 were prepared by weight dilution.

Apparatus. The Geffcken (*2*) apparatus previously described (*11*) was used. It was modified to give better internal pressure control (*9*) for the determination of the small volume changes observed with Na_2SO_4–LiCl mixtures. In the Geffcken apparatus, about 100 ml. of a solution, II, is introduced into a 350-ml. bulb, *A*, which is originally filled with mercury. The volume of solution introduced is determined from the weight of mercury displaced. Another solution, III, is placed in an adjacent system which is connected to bulb *A* at the top and bottom with stopcocks. A known volume of solution III can be introduced into bulb *A* by permitting mercury from the bottom of bulb *A* to flow into calibrated bulbs, displacing solution III through the upper stopcock into bulb *A*. A capillary tube, attached to the bottom of bulb *A*, dips into a removable cup partially filled with mercury. After mixing the solution in bulb *A*, the resulting volume change is determined from the gain or loss in weight of the removable cup. The weight changes were determined to ±0.2 mg. corresponding to a volume change (ΔV) of $\pm 2 \times 10^{-5}$ ml. Repeated additions of solution III to solution II can be made until a total volume of 125 ml. is added. To complete a single series, the experiment is repeated with solutions II and III interchanged. The agreement between the two experiments at overlapping equivalent fractions (Figures 2 to 7) is an indication of the precision of the measurements. The temperature of the apparatus is maintained constant to within ±0.0005° at 25° C. The internal pressure on the solution in bulb *A* is maintained constant to ±0.5 mm. of Hg by adjustment of the external pressure on the mercury cup.

The correction term to Young's rule, $D' = \Delta v/(e_2 + e_3)$, where e_2 is the number of equivalents of electrolyte in solution II, and e_3 is the number of equivalents added with solution III. In the least favorable case (sulfate solutions at an ionic strength of 1), e_2 is about 0.07 and e_3 varies from 0.0007 to 0.10. The concentrations were known to at least 0.1%. Possible variations of 2 mm. in the internal pressure and 0.001° C. in the temperature give volume differences of 1×10^{-4} and 2×10^{-4} ml., respectively (*9*). Combination of these differences with a possible error of 2×10^{-4} in the determination of a single volume change owing to break-off errors in removing the mercury cup gives a maximum error of $5 \times 10^{-4}/0.07 = 7 \times 10^{-3}$ ml. per equivalent in a single determination of D' in 1μ solutions. In the revised apparatus (*9*), which was used for the Li_2SO_4–NaCl mixings at $\mu = 1$, the errors owing to measurement of volume changes and changes in internal pressure were reduced to 5×10^{-5} and 5×10^{-6} ml., respectively. The maximum error, owing primarily to possible temperature changes, is $2.5 \times 10^{-5}/0.07 = 4 \times 10^{-3}$ ml. per equivalent. In 4μ solutions, the estimated error is one fourth of that in 1μ solutions.

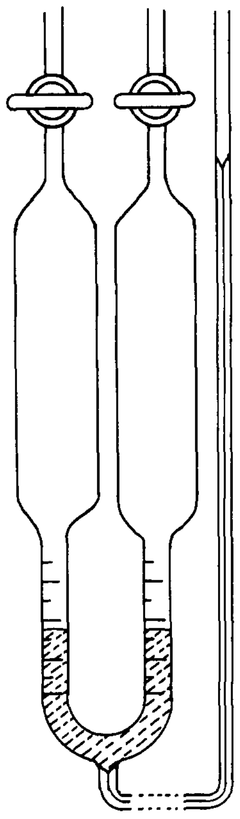
Single-mixing dilatometers (Figure 1) were used to determine the volume change on mixing two solutions to give an equivalent fraction of 0.5. The design was suggested by the Carlsberg dilatometer described by Rasper and Kauzmann (*8*).

For use with NaCl–LiCl and Na_2SO_4–Li_2SO_4, each bulb of the dilatometer had a volume of *ca.* 140 ml. For use with LiCl–Li_2SO_4, NaCl–Na_2SO_4, etc., the bulbs had volumes of *ca.* 140 ml. and of *ca.* 90 ml., and were calibrated to ±0.02 ml. to a reference mark on the buret tubing attached to the bottom of each bulb. The capillary tubing attached to the bottom of the apparatus had a volume of *ca.* 6×10^{-4} ml. per mm., and the height of the mercury in the capillary was determined by a cathetometer to ±0.05 mm.

Mercury to fill the bottom of the dilatometer to about the level indicated in Figure 1 is introduced, the dilatometer is placed on its side, and all three openings are connected to a vacuum system. After the dilatometer is evacuated, it is set upright, and the vacuum released. This prevents

Figure 1. Single-mixing dilatometer (schematic)

In the actual apparatus, the capillary tube is mounted in front of the bulbs



the trapping of air bubbles which might later dissolve in the solutions. The appropriate solutions, which had been kept at 35° to 40° C. for 12 to 24 hours, are run into the two bulbs, and the apparatus is placed in a thermostat regulated to ±0.0005° at 25.0° C. After 2 hours, the stopcocks are closed, the mercury levels in the U-tube are read to ±0.02 ml., and the position of the mercury in the capillary is determined. The apparatus is then mechanically oscillated through an 180° arc for 30 minutes to mix the solutions thoroughly. With the dilatometer again in the upright position, the mercury levels in the U-tube are approximately equalized, and the volume change is determined on the capillary. The pressure over the capillary is adjusted so that the internal pressure on the solutions is the same as at the beginning of the experiment to within 1 mm. The volume change owing to changes in internal pressure is 2×10^{-5} ml. per mm.

When water was placed in both bulbs, the maximum volume change observed on mixing was 2×10^{-4} ml. The maximum error in D', obtained with sulfate solutions of ionic strength 1 ($e_2 + e_3 \cong 0.18$), is 1×10^{-3} ml. per equivalent.

The densities of the solutions of single electrolytes were determined by the sinker method (*10*).

RESULTS AND DISCUSSION

The maximum volume change on mixing a 2 to 1 electrolyte with a 1 to 1 electrolyte occurs at an equivalent fraction near 0.5. This was also observed for heats of mixing by Wu, Smith, and Young (*12*). Therefore, the quantities of interest, can be conveniently expressed in terms of equivalents.

The mean equivalent volume (Φ') of a mixture of electrolytes is defined by

$$\Phi' = \frac{V - n_1 \bar{v}_1^\circ}{e_2 + e_3} \qquad (1)$$

where V is the volume of solution containing n_1 moles of water and e_2 and e_3 equivalents of the two salts, and $\bar{v}_1^\circ$ is the molar volume of pure water. Young's rule (*14*) then becomes

$$\Phi' = \frac{e_2\phi_2' + e_3\phi_3'}{e_2 + e_3} = E_2\phi_2' + E_3\phi_3' \qquad (2)$$

where ϕ_2' (or ϕ_3') is the apparent equivalent volume of one of the electrolytes in a solution containing only water and this electrolyte at an ionic strength (μ) corresponding to ($e_2 + e_3$) equivalents per n_1 moles of water. [For a 1 to 1 electrolyte $\mu = 55.51e/n_1$ and for a 2 to 1 electrolyte $\mu = (3 \times 55.51e)/2n_1$.] The (weight) equivalent fraction E_2 is equal to $e_2/(e_2 + e_3)$ and $E_3 = e_3/(e_2 + e_3)$.

According to Young's rule there should be no volume change on mixing solutions of equal ionic strength. The volume change (Δv) actually observed gives the correction term for Young's rule through the relation:

$$D' = \Phi' - (E_2\phi_2' + E_3\phi_3') = \Delta v/(e_2 + e_3) \qquad (3)$$

At a given ionic strength,

$$D' = kE_2E_3 + k'E_2^2E_3 \qquad (4)$$

where k and k' are empirical constants. Both k and k' at $\mu_w = 4$ were obtained by least squares treatment of the data. In solutions in which $\mu = 1$, k' was taken to be ¼ of the value in the 4μ solution (see discussion of concentration dependence below), and k was taken as the average value calculated from the data between $E_2 = 0.2$ and $E_2 = 0.8$. Except for the system Li_2SO_4-NaCl, agreement between calculated and observed values of D' was as good as that obtained by direct least squares treatment of the data.

Table I lists values of k and k' in solutions of ionic strengths of 1 and 4, the calculated value of the maximum ($D'_{\max}$) and the corresponding value of E_2. Values for $D'_{0.5}$, the observed value of D' when $E_2 = 0.5$, are also given. Table II gives the results of single-mixing experiments at an ionic strength of 2.25. The value of D' observed is also $D'_{0.5}$ within experimental error. Figures 2 to 7 give plots of the experimental values and the values calculated from Equation 4.

The square-cross rule (*11, 13, 15*) was applied to the values of $D'_{0.5}$. At each concentration, the sum of the volume changes on mixing the heterionic electrolytes (ΣX) is slightly greater than the sum of the volume changes on mixing

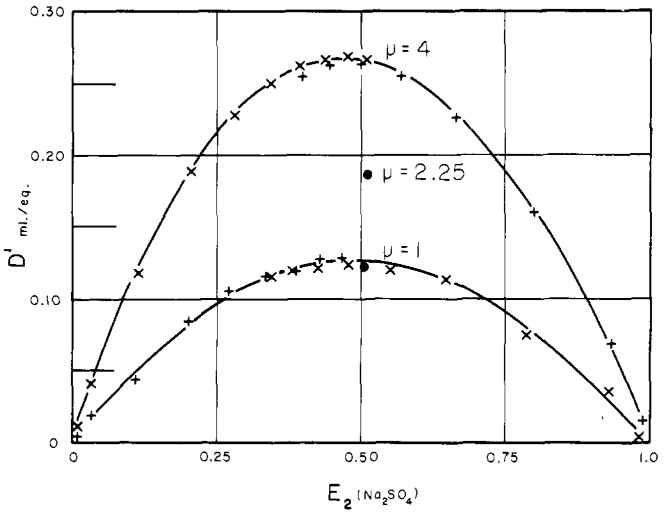


Figure 2. Volume changes on mixing solutions of Na_2SO_4 and NaCl at constant ionic strength

× Solution II added to solution III

+ Solution III added to solution II

O Single-mixing experiments

— Values calculated using Equation 4 and constants from Table I

Table I. Volume Changes on Mixing Electrolyte Solutions

Salt 2	Salt 3	k	k'	Av. Dev., Ml./Eq.	D'_{max}, Ml./Eq.	$E_{2(max)}$	$D'_{0.5}$, Ml./Eq.
			$\mu_w = 3.997$				
Na_2SO_4	NaCl	1.2039	−0.2735	±0.0015	0.268	0.47	0.267
LiCl	NaCl	−0.2360	−0.0392	±0.0006	−0.064	0.52	−0.064
Li_2SO_4	LiCl	0.9589	−0.2750	±0.0011	0.207	0.46	0.205
Li_2SO_4	Na_2SO_4	−0.1633	−0.0078	±0.0010	−0.042	0.51	−0.042
						Σ□ =	0.366
Li_2SO_4	NaCl	1.6986	−0.4354	±0.0009	0.372	0.46	0.370
Na_2SO_4	LiCl	0.0167	0.1113	±0.0007	0.020	0.64	0.018
						ΣX =	0.388
						Difference (½ R') =	0.352
			$\mu_w = 1.000$				
Na_2SO_4	NaCl	0.5357	−0.0684	±0.0028	0.126	0.48	0.125
LiCl	NaCl	−0.0911	−0.0098	±0.0014	−0.024	0.51	−0.024
Li_2SO_4	LiCl	0.3738	−0.0688	±0.0018	0.085	0.48	0.085
Li_2SO_4	Na_2SO_4	−0.1020	−0.0020	±0.0007	−0.026	0.50	−0.026
						Σ□ =	0.160
Li_2SO_4	NaCl	0.8657 (0.789)	−0.2868 (−0.109)	±0.0008 (±0.004)	0.182	0.45	0.181
Na_2SO_4	LiCl	−0.0550	0.0278	±0.0005	−0.011	0.42	−0.010
						ΣX =	0.171
						Difference (½ R') =	0.190

Table II. Single-Mixing Experiments

Salt 2	Salt 3	E_2	D'
	$\mu_w = 2.250$		
Na_2SO_4	NaCl	0.511	0.187
LiCl	NaCl	0.497	−0.042
Li_2SO_4	LiCl	0.511	0.134
Li_2SO_4	Na_2SO_4	0.497	−0.037
		Σ□ =	0.242
Li_2SO_4	LiCl	0.511	0.271
Na_2SO_4	LiCl	0.510	−0.015
		ΣX =	0.256
		Difference (½ R') =	0.286

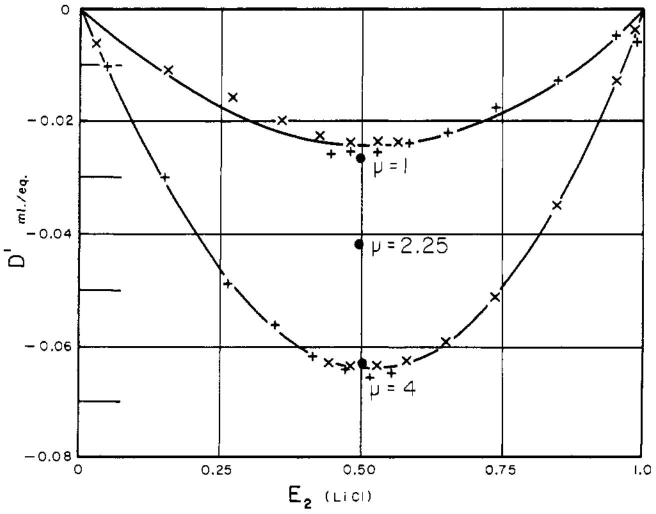


Figure 3. Volume changes on mixing solutions of LiCl and NaCl at constant ionic strength

× Solution II added to solution III

+ Solution III added to solution II

O Single-mixing experiments

— Values calculated using Equation 4 and constants from Table I

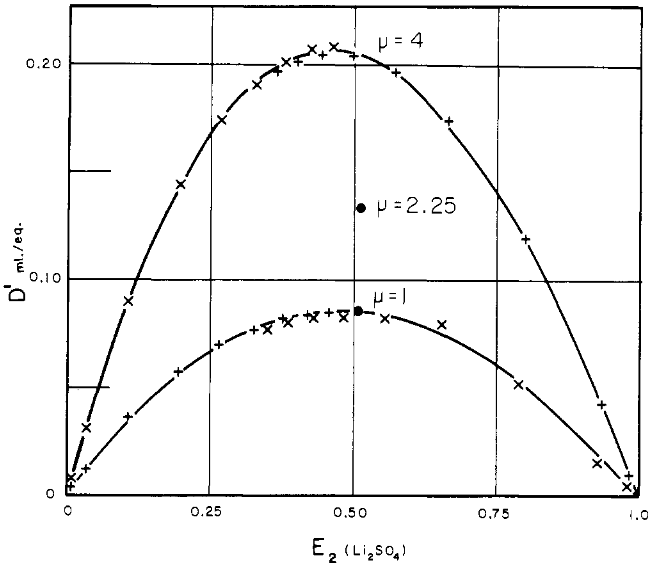


Figure 4. Volume changes on mixing solutions of Li_2SO_4 and LiCl at constant ionic strength

× Solution II added to solution III

+ Solution III added to solution II

— Values calculated using Equation 4 and constants from Table I

O Single-mixing experiments

the homoionic electrolytes (Σ□). The difference is less than the estimated experimental error, so the square-cross rule can be considered valid.

Apparent Equivalent Volumes for Single Electrolyte Solutions. The values of ϕ' for LiCl, Na_2SO_4, and Li_2SO_4 at μ = 1, 2.25, and 4.0 are compared in Figure 8 with the results in the literature. The results of Pearce and Eckstrom (7) for sulfates and of Jones and Bradshaw (5) for LiCl are not considered to be reliable.

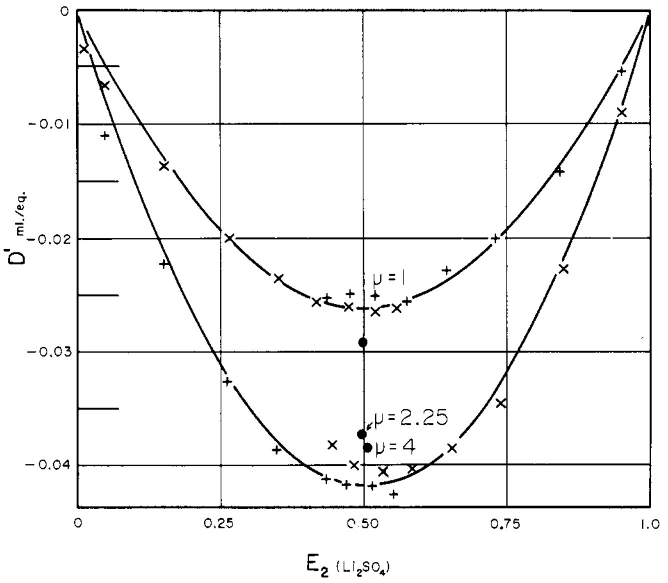


Figure 5. Volume changes on mixing solutions of Li_2SO_4 and Na_2SO_4 at constant ionic strength

× Solution II added to solution III

+ Solution III added to solution II

— Values calculated using Equation 4 and constants from Table I

O Single-mixing experiments

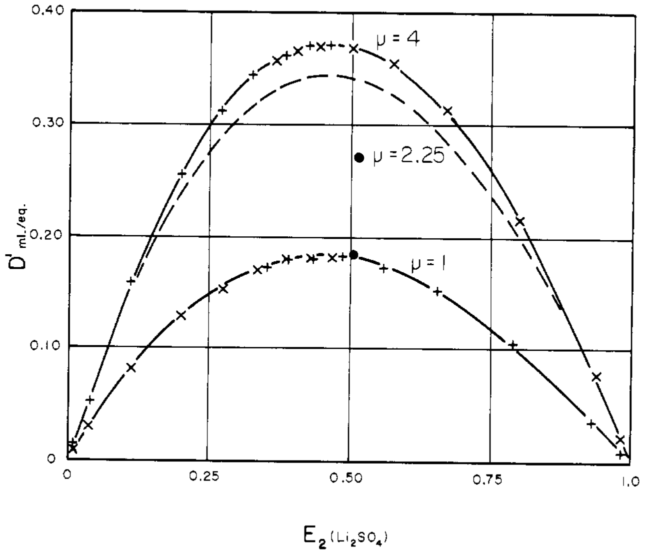


Figure 6. Volume changes on mixing solutions of Li_2SO_4 and NaCl at constant ionic strength

× Solution II added to solution III

+ Solution III added to solution II

— Values calculated using Equation 4 and constants from Table I

--- Values calculated using Equation 9 and $R' = 0.62_4$ (4μ)

O Single-mixing experiments

The constants in the equation:

$$\phi' = a + b\mu^{1/2} + c\mu \qquad (5)$$

which can be used for interpolation in the range $\mu = 1$ to 4 are given in Table III. The equation for NaCl is given in reference *(10)*. The values of ϕ' given by these equations are believed to be reliable to ±0.02 ml. per equivalent.

The values of

$$R' \ (= \phi'_{Na_2SO_4} + \phi'_{LiCl} - \phi'_{Li_2SO_4} - \phi'_{NaCl}) \qquad (6)$$

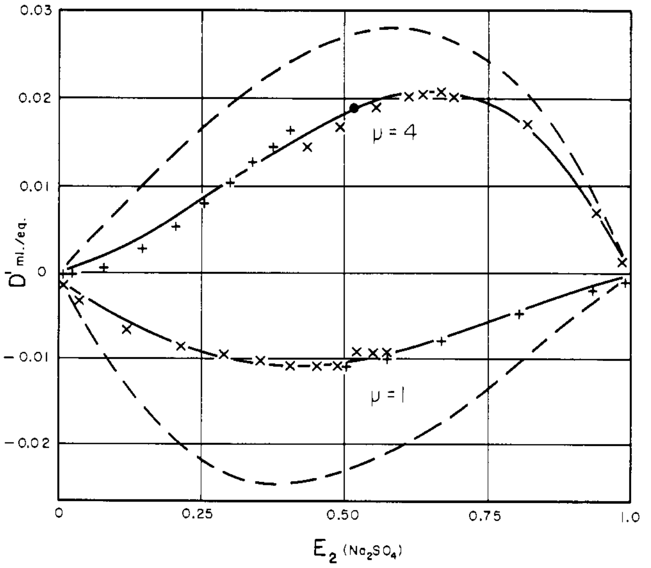


Figure 7. Volume changes on mixing solutions of Na_2SO_4 and LiCl at constant ionic strength

× Solution II added to solution III

+ Solution III added to solution II

— Values calculated using Equation 4 and constants from Table I

--- Values calculated using Equation 12 $(R' = 0.62_4, 4\mu)$ and Equation 13 $(R' = 0.41_2, 1\mu)$

O Single-mixing experiments

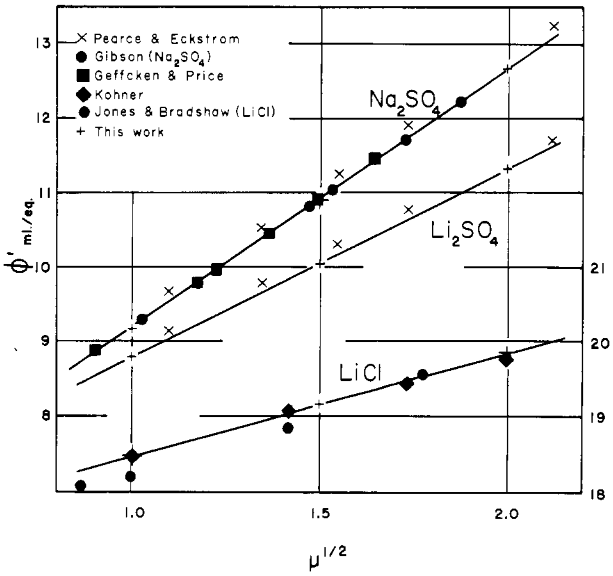


Figure 8. Apparent equivalent volumes of LiCl, Na_2SO_4, and Li_2SO_4 vs. $\mu^{1/2}$ in the concentration range μ = 1 to 4

References: Pearce and Eckstrom (7), Gibson (4), Geffcken and Price (3), Kohner (6), Jones and Bradshaw (5)

Table III. Constants for the Equation $\phi' = a + b\mu^{1/2} + c\mu$

Salt	a	b	c	Based on Data of:
LiCl	16.940	1.624	−0.0932	Wirth and Mills, Kohner *(6)*
Li_2SO_4	6.308	2.446	0.0340	Wirth and Mills
Na_2SO_4	5.719	3.504	−0.0078	Wirth and Mills, Gibson *(4)*

which represents the deviation from additivity of the apparent equivalent volumes at a given ionic strength, are 0.41_2, 0.54_9, and 0.62_4 at $\mu = 1$, 2.25, and 4, respectively. These values obtained from the difference between the $D'_{0.5}$ values for the heterionic mixtures (Tables I and II) are 0.38_0, 0.57_2, and 0.70_4, respectively.

Calculation of *D′* for Heterionic Mixtures. The equation [Equation 3, (*11*)] which represents the apparent equivalent volume of all possible combinations of the four salts, written in terms of equivalent fractions, becomes:

$$\begin{aligned}\Phi' = {} & E_{Li}(\phi'_{Li} + E_{SO_4}E_{Cl}k_{Li} + E^2_{SO_4}E_{Cl}k'_{Li}) \\ & + E_{SO_4}(\phi'_{SO_4} + E_{Li}E_{Na}k_{SO_4} + E^2_{Li}E_{Na}k'_{SO_4}) \\ & + E_{Na}(\phi'_{Na} + E_{SO_4}E_{Cl}k_{Na} + E^2_{SO_4}E_{Cl}k'_{Na}) \\ & + E_{Cl}(\phi'_{Cl} + E_{Li}R' + E_{Li}E_{Na}k_{Cl} + E^2_{Li}E_{Na}k'_{Cl}) \qquad (7)\end{aligned}$$

where $E_{Li} = e_{Li}/(e_{Li} + e_{Na})$, $E_{SO_4} = e_{SO_4}/(e_{SO_4} + e_{Cl})$, etc., and k_{Li} and k'_{Li} are the observed values of k and k' for the pair LiCl–Li_2SO_4 in which the lithium ion is common, etc. For purposes of calculation, the deviation from additivity (R') is assigned to LiCl.

For the system Li_2SO_4–NaCl, where $E_{Li} = E_{SO_4} = E_{Li_2SO_4}$ and $E_{Na} = E_{Cl} = E_{NaCl}$, Equation 7 becomes:

$$\begin{aligned}D' = {} & \Phi' - [E_{Li_2SO_4}(\phi'_{Li} + \phi'_{SO_4}) + E_{NaCl}(\phi'_{Na} + \phi'_{Cl})] \\ = {} & (R' + k_{Na} + k_{Cl})\, E_{Li_2SO_4}E_{NaCl} \\ & + (k_{Li} + k_{SO_4} - k_{Na} - k_{Cl} + k'_{Li} + k'_{SO_4})\, E^2_{Li_2SO_4}E_{NaCl} \\ & + (k'_{Na} + k'_{Cl} - k'_{Li} - k'_{SO_4})\, E^2_{Li_2SO_4}E^2_{NaCl} \qquad (8)\end{aligned}$$

Introduction of numerical values, using $R' = 0.62_4$, gives

$$\begin{aligned}D' = {} & 1.592\, E_{Li_2SO_4}E_{NaCl} - 0.455\, E^2_{Li_2SO_4}E_{NaCl} \\ & - 0.030\, E^2_{Li_2SO_4}E^2_{NaCl}\ (4\mu) \qquad (9)\end{aligned}$$

and, with $R' = 0.412$,

$$\begin{aligned}D' = {} & 0.857\, E_{Li_2SO_4}E_{NaCl} - 0.244\, E^2_{Li_2SO_4}E_{NaCl} \\ & - 0.007\, E^2_{Li_2SO_4}E^2_{NaCl}\ (1\mu) \qquad (10)\end{aligned}$$

Values calculated from Equation 9, neglecting the term involving $E^2_{Li_2SO_4}E^2_{NaCl}$, are compared with the experimental results at $\mu = 4$ in Figure 6. While the shape of the experimental curve is correctly predicted, the calculated values of D' are approximately 0.03 ml. per equivalent less than the experimental values near $E_2 = 0.5$. To reproduce the experimental values, R' must be 0.738 ml. per equivalent, a value which is larger than that calculated from the data in Table I. On the other hand, the experimental results at $\mu = 1$ are in excellent agreement with those predicted by Equation 10; the calculated values of D' are approximately 0.003 ml. per equivalent higher than the observed values near $E_2 = 0.5$.

For the system Na_2SO_4–LiCl, where $E_{Na} = E_{SO_4} = E_{Na_2SO_4}$ and $E_{Li} = E_{Cl} = E_{LiCl}$, Equation 7 becomes:

$$\begin{aligned}D' = {} & \Phi' - [E_{Na_2SO_4}(\phi'_{Na} + \phi'_{SO_4}) + E_{LiCl}(\phi'_{Li} + \phi'_{Cl} + R)] \\ = {} & (-R' + k_{Li} + k_{Cl} + k'_{Cl})\, E_{Na_2SO_4}E_{LiCl} \\ & + (k_{SO_4} + k_{Na} - k'_{Li} - k_{Cl} + k'_{Na} - k'_{Cl})\, E^2_{Na_2SO_4}E_{LiCl} \\ & + (k'_{Li} + k'_{SO_4} - k'_{Na} - k'_{Cl})\, E^2_{Na_2SO_4}E^2_{LiCl} \qquad (11)\end{aligned}$$

Introduction of numerical values, using $R' = 0.624$, gives

$$\begin{aligned}D' = {} & 0.060\, E_{Na_2SO_4}E_{LiCl} + 0.083\, E^2_{Na_2SO_4}E_{LiCl} \\ & + 0.030\, E^2_{Na_2SO_4}E^2_{LiCl} \qquad (4\mu) \qquad (12)\end{aligned}$$

and, with $R' = 0.412$

$$\begin{aligned}D' = {} & -0.139\, E_{Na_2SO_4}E_{LiCl} + 0.092\, E^2_{Na_2SO_4}E_{LiCl} \\ & + 0.007\, E^2_{Na_2So_4}E^2_{LiCl} \qquad (1\mu) \qquad (13)\end{aligned}$$

Equations 12 and 13 correctly predict the shape and sign of the volume changes (Figure 7), but at the maximum in 4μ solution, the predicted values are 0.01 ml. per equivalent too high, and in 1μ solution, the predicted values are 0.014 ml. too low. In 4μ solution, R' would have to be 0.659 to give a reasonable fit with the data, while the value of R' (0.738) which gave a good fit for the Li_2SO_4–NaCl case results in calculated D's' that are 0.02 ml. less than observed. In 1μ solution, R' would have to be 0.358 to fit the experimental data, whereas Equation 10, with $R' = 0.412$, fits the data for Li_2SO_4–NaCl.

Equation 7, which contains constants obtained from solutions of single electrolytes (R') and, from the homoionic mixtures, was successful in predicting the behavior of the heterionic mixtures of $HClO_4$ and NaCl and of HCl and $NaClO_4$ (*11*). The fact that Equation 7 does not correctly predict the behavior for Li_2SO_4–NaCl and for Na_2SO_4–LiCl, and in particular that a single value of R' does not apply to both systems suggests the presence of ion-ion interactions in the sulfate-chloride systems, which are not present in the perchlorate-chloride systems.

The work of Young and coworkers, cited by Baes (*1*), on the Raman spectra of sodium sulfate solutions strongly indicates that sodium sulfate is completely dissociated. The fact that the slope of the curve of apparent equivalent volume *vs.* the square root of ionic strength (Figure 8) is close to that predicted for a 2 to 1 electrolyte supports this view. The smaller slope for lithium sulfate can however be interpreted as due to ion association to give $LiSO_4^-$.

The observed behavior of mixtures of Na_2SO_4 and LiCl is explained by the assumption that the normal ion interactions give a positive value of D', which increases with increasing ionic strength, and that the association constant for $LiSO_4^-$ decreases with increasing ionic strength in the same way as the association constant for HSO_4^- (*1*). In mixtures of Na_2SO_4 and LiCl the ionic strength will be reduced owing to the formation of $LiSO_4^-$. The apparent equivalent volumes of all the components will be less at the lower ionic strength, and the volume change observed will be the difference between the normal increase and the decrease owing to change in ionic strength. The effect of change in ionic strenght will be relatively greater at low concentrations where the association constant is greater. Thus the fact that D' is negative at low ionic strength and becomes positive at higher ionic strengths can be interpreted as owing to the formation of $LiSO_4^-$.

If $LiSO_4^-$ is present, the original Li_2SO_4 solutions have an ionic strength less than that calculated from their molalities, and the mixtures obtained by adding NaCl, LiCl, or Na_2SO_4 will have ionic strengths intermediate between that of the Li_2SO_4 and that of the other component. The change in ionic strength will increase the apparent equivalent volume of the Li_2SO_4 but will decrease the apparent equivalent volume of the other component. There will also be a volume change owing to decrease in concentration of $LiSO_4^-$. The net effect may be a small increase or decrease in volume which is obscured by the normal ion interaction.

Concentration Dependence of *k* and *k′*. In previous work (*11*), the authors assumed that the variation of k and k' with ionic strength could be represented by the equations:

$$k = \alpha\mu + \beta\mu^2, \text{ and } k' = \gamma\mu^2 \qquad (14)$$

A series of single-mixing experiments with the system Na_2SO_4–NaCl at $\mu = 0.25$, 0.50, 1.5, and 3.0 (Figure 9) gave values of $D'_{0.5}$ which could be used to test the equations. The results are better represented by the equations:

$$k = r\mu^{1/2} + s\mu^2, \text{ and } k' = t\mu \qquad (15)$$

These equations gave good agreement for the homoionic pairs. With Li_2SO_4–NaCl the $D'_{0.5}$ values were well represent-

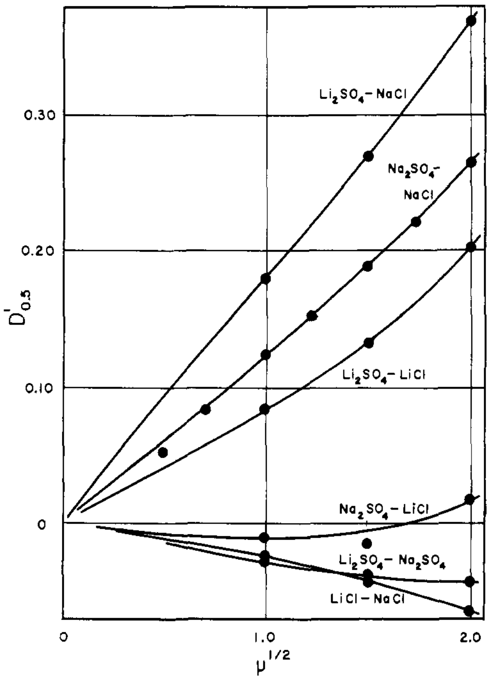


Figure 9. Variation of $D'_{0.5}$ with ionic strength

Solid lines are values from the equation $D'_{0.5} = 0.25\,k + 0.125\,k'$, where k and k' are given by Equation 15

Table IV. Constants for Equation 15

Electrolyte Pair	*r*	*s*	*t*
Na_2SO_4-NaCl	0.5262	0.0095	−0.0684
LiCl-NaCl	−0.0873	−0.0038	−0.0098
Li_2SO_4-LiCl	0.3587	0.0151	−0.0688
Li_2SO_4-Na_2SO_4	−0.1049	0.0029	−0.0020
Li_2SO_4-NaCl	0.7804	0.0086	−0.1088
Na_2SO_4-LiCl	−0.0761	0.0211	0.0278

ed, but the agreement was not good for k and k' in a solution of unit ionic strength (Table I). With Na_2SO_4-LiCl, the predicted value of $D'_{0.5}$ in a solution of ionic strength 2.25 was low by 0.01 ml. per equivalent (Figure 5).

The calculated values of r, s, and t are given in Table IV.

Partial Equivalent Volumes. Equation 7 represents the mean equivalent volume of the dissolved electrolytes in all possible combinations of the four electrolytes LiCl, Li_2SO_4, NaCl, and Na_2SO_4. Combination with Equation 1 gives an expression for the volume of any such solution in terms of the number of equivalents of each salt present, the ionic strength, and the constants in Tables II and IV. Differentiation of this expression with respect to the number of equivalents of a component will give an estimate of the partial equivalent volume of that component for any equivalent fraction, and at any concentration up to $\mu = 4$.

NOMENCLATURE

a, b, c = constants in the equation $\phi' = a + b\mu^{1/2} + c\mu$, representing the apparent equivalent volume of a single electrolyte as a function of ionic strength

D' = volume change in ml. per equivalent observed on mixing two solutions at constant ionic strength

$D'_{0.5}$ = volume change in ml. per equivalent observed on mixing two solutions at constant ionic strength to give an equivalent fraction of 0.5

e_2 = equivalents of salt 2 per n_1 moles water

e_3 = equivalents of salt 3 per n_1 moles water

E_2 = $e_2/(e_2 + e_3)$ weight equivalent fraction of salt 2

E_3 = $e_3/(e_2 + e_3)$ weight equivalent fraction of salt 3, $E_2 = 1 - E_3$

E_A = weight equivalent fraction of ion A in a homoionic mixture in which A is the common ion

k, k' = constants in the equation $D' = kE_2E_3 + k'E_2^2E_3$, representing the volume change on mixing of two solutions at constant ionic strength to give an equivalent fraction of E_2 for salt 2

n_1 = moles of water

μ = ionic strength of a solution, in moles per 1000 grams of water

ϕ'_2 = apparent equivalent volume in ml. per equivalent of salt 2 in a solution containing only salt 2 and water

ϕ'_3 = apparent equivalent volume in ml. per equivalent of salt 3 in solution containing only salt 3 and water

Φ' = mean equivalent volume in ml. per equivalent of the solutes present in a solution

R' = $(\phi'_{Na_2SO_4} + \phi'_{Li_2SO_4} - \phi'_{Li_2SO_4} - \phi'_{NaCl})_\mu$ represents the deviation from additivity of the apparent equivalent volumes in ml. per equivalent of the four salts having 2 common anions and 2 common cations at a constant ionic strength

r, s, t = constants in the equations $k = r\mu^{1/2} + s\mu^2$ and $k' = t\mu$ representing the variation in k and k' with ionic strength

V = total volume in ml. of a solution containing e_2 equivalents of salt 2 and e_3 equivalents of salt 3 in n_1 moles of water

$\bar{v}_1^\circ$ = volume in ml. occupied by 1 mole of pure water

Δv = observed change in volume in ml. on adding a solution containing e_2 equivalents of salt 2 to a solution containing e_3 equivalents of salt 3 at constant ionic strength

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