

Table III. Relative Adsorptivities for Binary Systems

Binary System	Experimental α	Correlation α
<i>n</i> -Hexane- <i>n</i> -decane	5.2	5.2
<i>n</i> -Hexane- <i>n</i> -dodecane	4.3	4.3
<i>n</i> -Hexane- <i>n</i> -tetradecane	10.0	10.3
<i>n</i> -Decane- <i>n</i> -dodecane	3.0	3.0
<i>n</i> -Decane- <i>n</i> -tetradecane	7.1	7.2
<i>n</i> -Dodecane- <i>n</i> -tetradecane	6.2	6.0

measured. Liquid at the external surface of the sieves evaporated at a faster rate than the internally adsorbed liquid. The change in drying rate, however, was not abrupt enough in many cases to distinguish clearly between liquid at the external surface and internally adsorbed liquid. The calculated results for the binary systems are based on the assumption that the total quantity of selectively adsorbed material is related linearly to weight fraction of adsorbate.

$$N_T = N_H + (N_L - N_H)Z_L \quad (1)$$

This assumption gives total equilibrium loadings within about 0.3 gram of the loadings indicated by the drying runs.

Various modifications and extensions of the Freundlich, Langmuir, and Brunauer-Emmett-Teller relations have shown promise in describing vapor phase adsorption on molecular sieves (5, 6). These equations however were not adequate for correlating the liquid phase data of this study. Instead, the selectivity for the lower molecular weight paraffin was described by a relative adsorptivity:

$$\alpha = \frac{Y_L X_H}{Y_H X_L} \quad (2)$$

where Y refers to adsorbate mole fractions and X to liquid phase mole fractions. Since the relative adsorptivities for each binary were essentially independent of concentration and temperature, a single value of α was obtained for each binary by minimizing the standard deviation between calculated and experimental mole fractions. The solid lines on Figures 1 and 2 were calculated from an α value of 5.2 for the heptane-decane binary.

Peterson and Redlich (5, 6) have proposed an equation for predicting the relative adsorptivities of liquid normal paraffins on molecular sieves. Their expression was an extension of an equation developed for vapor phase adsorption. Relative adsorptivity values calculated from their suggested equation differed significantly from the experimental values of this study, particularly at the higher temperature levels.

The relative adsorptivities for the six binary systems were correlated by the following empirical relation:

$$\alpha = \frac{C_H}{C_L} \gamma_H \quad (3)$$

where C_H and C_L are the number of carbon atoms in the two components, and γ_H is an empirical constant based on the higher molecular weight paraffin. The average values of γ_H for tetradecane, dodecane, and decane were 5.12, 2.50, and 3.64, respectively. Table III lists the relative adsorptivities obtained for each binary system from experimental data and from the above correlating equation.

NOMENCLATURE

- C = number of carbon atoms in the normal paraffin
 N = grams of n -paraffin adsorbed as pure component per 100 grams of molecular sieves
 T = temperature, °C.
 W = grams of n -paraffin adsorbed from binary solution per 100 grams of molecular sieves
 X = mole fraction in liquid phase at equilibrium
 Y = mole fraction in adsorbate phase at equilibrium
 Z = weight fraction in adsorbate phase at equilibrium
 α = relative adsorptivity of lower molecular weight n -paraffin with respect to higher molecular weight n -paraffin
 γ = empirical constant

Subscripts

- H = higher molecular weight n -paraffin
 L = lower molecular weight n -paraffin
 T = total n -paraffin

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Temperature Dependence of Volume Changes on Mixing Electrolyte Solutions

HENRY E. WIRTH and ANTONIO LoSURDO

Department of Chemistry, Syracuse University, Syracuse, N. Y. 13210

IN a previous paper (3) the volume changes on mixing all possible pairs of solutions of NaCl, Na₂SO₄, LiCl, and Na₂SO₄ were determined for ionic strengths of 1 and 4. The observed volume changes were used to calculate D' , the correction term in Young's rule (5), where;

$$D' = \Phi' - (E_2\phi_2' + E_3\phi_3') \quad (1)$$

Φ' is the observed mean equivalent volume of the solutes in the mixed solutions at a given ionic strength, ϕ_2' and ϕ_3' are the equivalent volumes of the individual solutes

in solutions of the same ionic strength, and E_2 and E_3 are the (weight) equivalent fractions of the two solutes.

Since D' is a measure of the interaction between like-charged ions, the determination of the effect of temperature on this type of interaction is interesting.

EXPERIMENTAL

The dilatometer used (Figure 1) was constructed of Vycor and had an internal volume of approximately 280 ml. In

The densities of solutions of Li_2SO_4 , LiCl , Na_2SO_4 , and NaCl and of mixtures of Li_2SO_4 and LiCl , of Na_2SO_4 and NaCl , and of Li_2SO_4 and Na_2SO_4 were determined for an ionic strength of 4 in the temperature range 5° to 45°C . From these densities the apparent equivalent volumes of single salts and the mean equivalent volumes of the mixtures were calculated at 5° intervals through the same temperature range. The correction term for Young's rule was obtained for each of the mixtures as a function of temperature. The volume changes on mixing to give solutions having a weight equivalent fraction of 0.5 were directly determined for all six combinations of the four salts at temperatures near 12° , 25° , and 38°C .

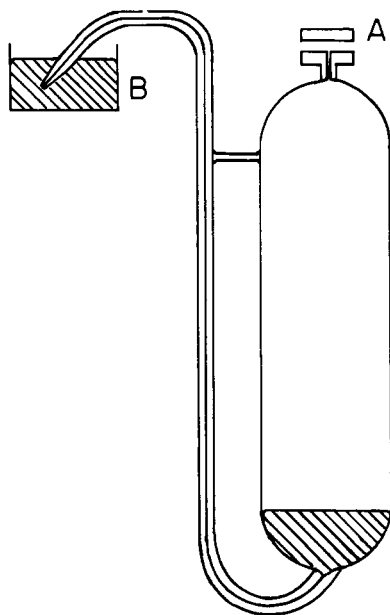


Figure 1. Vycor dilatometer

- A. Flat plate
B. Weighed Hg in cup

an experiment, about 170 grams of Hg is placed in the dilatometer, and the dilatometer is evacuated to remove trapped air bubbles. The dilatometer is then filled with water or solution which had been held at 50°C . for at least 12 hours prior to the filling. The flat plate, A, lightly greased with silicone grease, is clamped on top. The weights of the empty dilatometer, the mercury, and the solution are determined to ± 1 mg. and are corrected to vacuum. After weighing, the dilatometer is transferred to a thermostated bath at 45°C . The mercury in the dilatometer then makes contact with the weighed mercury in cup B. After temperature equilibrium is attained, the cup is lowered and the weight of the mercury redetermined. This process is repeated at 10° intervals between 5° and 45°C .

The density of the solution is calculated at each temperature from the relation:

$$d_t = \frac{Wt_{\text{soln}}}{V_t - Wt_{\text{Hg}}/d_{\text{Hg}}} \quad (2)$$

where Wt_{soln} is the weight of the solution, Wt_{Hg} is the weight of the mercury in the dilatometer at the temperature t ; d_{Hg} is the density of mercury at the same temperature, and V_t is the volume of the dilatometer as determined by calibration using water.

The end of the capillary and the cup are enclosed in a box in which the pressure is kept constant in order to prevent errors due to pressure changes.

The thermostated bath is controlled at constant temperature ($\pm 0.005^\circ\text{C}$.) at each of the temperatures used by means of a sensitive thermistor controller (Sargent

Thermonitor S-82050). It is immersed in an outer bath whose temperature is kept constant to $\pm 0.1^\circ\text{C}$. by a less sensitive controller (Sargent Thermonitor S-82065), which activates heaters or a refrigerator system as needed. The thermometers used were marked at 0.01° intervals and were calibrated against a platinum resistance thermometer.

The coefficient of thermal expansion of the dilatometer was 2.2×10^{-6} ml. per ml. degree, as compared with 2.4×10^{-6} calculated from the linear coefficient of expansion for Vycor (1).

The coefficients of thermal expansion, which depend primarily on the weight of mercury in the dilatometer, are determined with higher precision than the absolute densities by the procedure used. The determined densities were, therefore, adjusted to match the values at 25°C . given by the equations in reference (3). The absolute densities are believed to be reliable to $\pm 3 \times 10^{-5}$ grams per ml.

Direct mixing experiments, using the single-mixing dilatometers previously described (3), were performed at temperatures near 12° , 25° , and 38° on all six combinations of the four salts: NaCl , Na_2SO_4 , LiCl , and Li_2SO_4 . The capillary of the unequal volume dilatometer was replaced by one having a volume of 1.77×10^{-3} ml. per mm. to accommodate larger volume changes.

Stock solutions of the individual salts were analyzed by evaporation and drying to constant weight. Solutions exactly 4.000 molal (LiCl and NaCl) or 1.3333 molal (Li_2SO_4 and Na_2SO_4) were made by weight dilution of the stock solutions. Mixtures were prepared by weight.

RESULTS

The observed densities for the four solutions of the pure salts, and for three mixtures at three equivalent fractions, all at an ionic strength of 4 are given in Table I and are represented by the equation:

$$d_t = d_0 + \alpha t + \beta t^2 + \gamma t^3 \quad (3)$$

where the constants were determined by the method of least squares. The values of α , β , and γ given in Table II are those derived directly from the data, while the value of d_0 has been adjusted to give agreement with density at 25°C . determined previously (3). The densities obtained from these equations at 5° intervals between 5° and 45°C . were used to calculate the apparent equivalent volumes (ϕ') of the pure electrolytes or the mean apparent equivalent volumes (Φ') for the mixtures of electrolytes.

The apparent equivalent volume of a single electrolyte is given by the relation:

$$\phi'_2 = \frac{1000 + m_2 M_2}{d_2} - \frac{1000}{d_1} \quad (4)$$

pm_2

and the mean apparent equivalent volume for a mixture of electrolytes is given by

$$\Phi' = \frac{1000 + m_2 M_2 + m_3 M_3}{pm_2 + p'm_3} - \frac{1000}{d_1} \quad (5)$$

Table I. Observed Densities as a Function of Temperature

$t, ^\circ\text{C.}$	$d_{\text{obsd}},$ G./Ml.	$(d_0 - d_t) \times$ $10^3, \text{Obsd.}$	$(D_0 - d_t) \times$ $10^3, \text{Calcd.}$	$\Delta d \times 10^6$ $d_{\text{obsd}} -$ d_{calcd}	$t, ^\circ\text{C.}$	$d_{\text{obsd}},$ G./Ml.	$(d_0 - d_t) \times$ $10^3, \text{Obsd.}$	$(D_0 - d_t) \times$ $10^3, \text{Calcd.}$	$\Delta d \times 10^6$ $d_{\text{obsd}} -$ d_{calcd}
$\text{Na}_2\text{SO}_4(\mu = 4.000, m = 1.333_4)$					$\text{Li}_2\text{SO}_4\text{-LiCl}(\mu = 4.000, E_{\text{Li}_2\text{SO}_4} = 0.5000)$				
0	1.156807 ^a				0	1.103080 ^a			
5.12 ₂	1.155017	1.790	1.802	-12	5.09 ₂	1.102125	0.955	0.955	0
15.08 ₄	1.151158	5.649	5.676	-27	15.01 ₉	1.099826	3.254	3.255	-1
24.61 ₃	1.146990	9.817	9.805	12	24.59 ₈	1.097094	5.986	5.985	1
34.89 ₁	1.142112	14.695	14.683	12	34.91 ₁	1.093643	9.437	9.438	-1
45.25 ₇	1.136786	20.021	20.005	16	45.07 ₂	1.089768	13.312	13.312	0
0	1.156897 ^a				$\text{Li}_2\text{SO}_4\text{-LiCl}(\mu = 4.000, E_{\text{Li}_2\text{SO}_4} = 0.2500)$				
5.12 ₂	1.155093	1.804	1.802	2	0	1.095206 ^a			
15.06 ₄	1.151236	5.661	5.668	-7	5.10 ₇	1.094286	0.920	0.918	2
24.62 ₃	1.147082	9.815	9.810	5	15.01 ₉	1.092082	3.124	3.127	-3
34.94 ₆	1.142186	14.711	14.711	0	24.59 ₈	1.089448	5.758	5.757	1
45.05 ₂	1.137002	19.895	19.896	-1	34.93 ₅	1.086117	9.089	9.088	1
$\text{Li}_2\text{SO}_4(\mu = 4.000, m = 1.333_4)$					45.04 ₇	1.082422	12.784	12.784	0
0	1.116285 ^a				$\text{Na}_2\text{SO}_4\text{-NaCl}(\mu = 4.000, E_{\text{Na}_2\text{SO}_4} = 0.6835)$				
5.12 ₃	1.115194	1.091	1.090	1	0	1.153921 ^a			
15.04 ₄	1.112678	3.607	3.618	-11	5.12 ₃	1.152056	1.865	1.863	2
24.60 ₃	1.109735	6.550	6.550	0	15.03 ₄	1.148134	5.787	5.793	-6
34.93 ₁	1.106041	10.244	10.238	6	24.59 ₈	1.143944	9.977	9.974	3
45.02 ₂	1.101952	14.333	14.330	3	34.71 ₄	1.139132	14.789	14.790	-1
0	1.116304 ^a				45.06 ₂	1.133820	20.101	20.102	-1
5.12 ₇	1.115210	1.094	1.091	3	$\text{Na}_2\text{SO}_4\text{-NaCl}(\mu = 4.000, E_{\text{Na}_2\text{SO}_4} = 0.4185)$				
24.63 ₃	1.109744	6.560	6.560	0	0	1.151339 ^a			
34.95 ₁	1.106060	10.244	10.245	-1	5.11 ₂	1.149411	1.928	1.926	2
45.12 ₂	1.101935	14.369	14.372	-3	15.02 ₄	1.145383	5.956	5.960	-4
$\text{NaCl}(\mu = 4.000, m = 4.000_0)$					24.61 ₈	1.141112	10.227	10.224	3
0	1.147477 ^a				34.98 ₂	1.136137	15.202	15.203	-1
5.10 ₂	1.145384	2.093	2.093	0	45.05 ₂	1.130951	20.388	20.388	0
15.02 ₄	1.141082	6.395	6.399	-4	$\text{Na}_2\text{SO}_4\text{-NaCl}(\mu = 4.000, E_{\text{Na}_2\text{SO}_4} = 0.1935)$				
24.59 ₃	1.136638	10.839	10.835	4	0	1.149158 ^a			
34.91 ₆	1.131567	15.910	15.914	-4	5.10 ₂	1.147161	1.997	1.996	1
45.02 ₇	1.126312	21.165	21.166	-1	15.03 ₄	1.142998	6.160	6.161	-1
5.11 ₂	1.145380	2.097	2.097	0	24.60 ₈	1.138651	10.507	10.505	2
24.60 ₃	1.136637	10.840	10.839	1	35.27 ₀	1.133465	15.693	15.693	0
45.06 ₂	1.126290	21.187	21.185	2	45.06 ₂	1.128404	20.754	20.754	0
$\text{LiCl}(\mu = 4.000, m = 3.999_8)$					$\text{Li}_2\text{SO}_4\text{-Na}_2\text{SO}_4(\mu = 4.000, E_{\text{Li}_2\text{SO}_4} = 0.7472)$				
0	1.086210 ^a				0	1.127127 ^a			
5.12 ₃	1.085310	0.900	0.901	-1	5.11 ₂	1.125846	1.281	1.279	2
15.05 ₄	1.083162	3.048	3.049	-1	15.02 ₄	1.122956	4.171	4.174	-3
24.93 ₈	1.080532	5.678	5.675	3	24.60 ₈	1.119668	7.459	7.459	0
34.87 ₆	1.077454	8.756	8.760	-4	34.95 ₆	1.115631	11.496	11.496	0
45.03 ₂	1.073880	12.330	12.326	4	45.14 ₇	1.111204	15.923	15.923	0
0	1.086190 ^a				$\text{Li}_2\text{SO}_4\text{-Na}_2\text{SO}_4(\mu = 4.000, E_{\text{Li}_2\text{SO}_4} = 0.4963)$				
5.12 ₃	1.085288	0.902	0.901	1	0	1.137080 ^a			
15.04 ₄	1.083144	3.046	3.046	0	5.11 ₇	1.135610	1.470	1.468	2
24.59 ₈	1.080613	5.577	5.577	0	15.03 ₄	1.132386	4.694	4.699	-5
34.97 ₇	1.077396	8.794	8.794	0	24.61 ₃	1.128799	8.281	8.277	4
45.01 ₂	1.073871	12.319	12.319	0	34.98 ₂	1.124460	12.620	12.623	-3
$\text{Li}_2\text{SO}_4\text{-LiCl}(\mu = 4.000, E_{\text{Li}_2\text{SO}_4} = 0.7500)$					45.62 ₉	1.119522	17.558	17.558	0
0	1.110088 ^a				$\text{Li}_2\text{SO}_4\text{-Na}_2\text{SO}_4(\mu = 4.000, E_{\text{Li}_2\text{SO}_4} = 0.2473)$				
5.13 ₂	1.109074	1.014	1.014	0	0	1.147143 ^a			
15.04 ₉	1.106676	3.412	3.415	-3	5.11 ₂	1.145511	1.632	1.630	2
24.60 ₃	1.103839	6.249	6.246	3	15.02 ₄	1.141967	5.176	5.176	0
34.96 ₂	1.100253	9.835	9.839	-4	24.58 ₃	1.138102	9.041	9.042	-1
45.01 ₂	1.096291	13.797	13.797	0	34.96 ₇	1.133451	13.692	13.691	1
					45.05 ₂	1.128535	18.608	18.608	0

^a Calculated by least squares from the data given at higher temperatures. These values are adjusted (Table II) to make the densities at 25°C. agree with those previously determined (3).

Table II. Constants for the Equation $d_t = d_0 + \alpha t + \beta t^2 + \gamma t^3$

Ionic strength = 4.000, 5° to 45° C.

Salt or Salt Mixture	d_0	$-\alpha \times 10^4$	$-\beta \times 10^6$	$\gamma \times 10^9$	Std. Dev., G./M. $\times 10^{6a}$
Na ₂ SO ₄	1.157177	3.3879	2.587 ₂	6.76 ₃	13
Li ₂ SO ₄	1.116471	1.9806	2.892 ₉	4.94 ₆	5
NaCl	1.148000	4.0185	1.644 ₀	2.85 ₈	3
LiCl	1.086447	1.6148	2.844 ₆	7.81 ₇	2
Li ₂ SO ₄ (2)-LiCl(3)					
$E_2 = 0.7500$	1.110248	1.8166	3.131 ₂	7.93 ₉	3
$E_2 = 0.5000$	1.103278	1.7212	3.088 ₃	7.85 ₁	1
$E_2 = 0.2500$	1.095407	1.6437	3.051 ₄	8.88 ₆	2
Na ₂ SO ₄ (2)-NaCl(3)					
$E_2 = 0.6835$	1.154156	3.5198	2.284 ₃	4.33 ₉	4
$E_2 = 0.4185$	1.151633	3.6615	2.091 ₄	3.85 ₉	3
$E_2 = 0.1935$	1.149582	3.8119	1.973 ₈	4.71 ₄	1
Li ₂ SO ₄ (2)-Na ₂ SO ₄ (3)					
$E_2 = 0.7472$	1.126969	2.3549	2.929 ₀	7.37 ₂	2
$E_2 = 0.4963$	1.137226	2.7333	2.693 ₁	5.48 ₁	4
$E_2 = 0.2473$	1.147298	3.0515	2.736 ₀	7.57 ₉	1

^aThis standard deviation refers to the agreement between observed and calculated values of $(d_t - d_0)$, not to values of d_t .

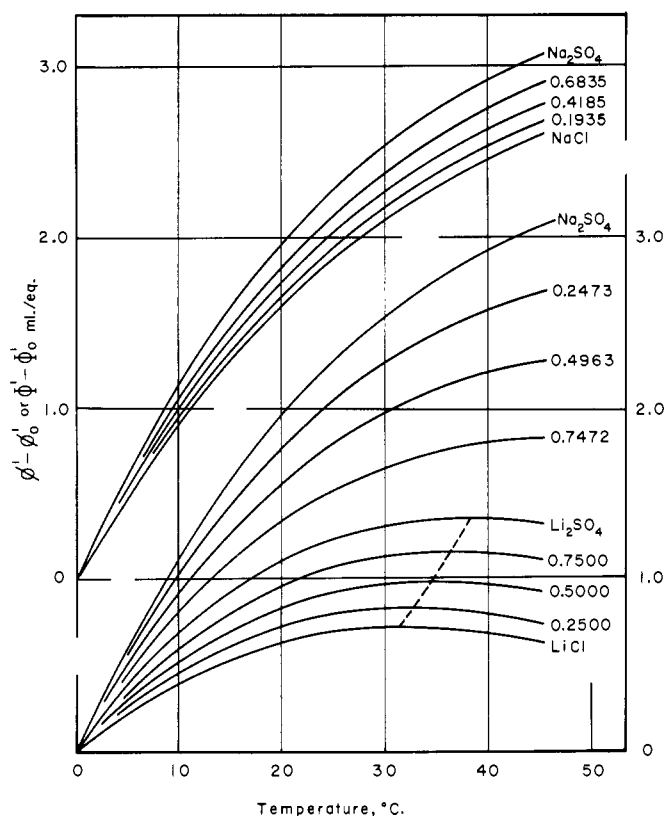


Figure 2. Change in apparent equivalent volume (ionic strength = 4) with temperature for Na₂SO₄, Li₂SO₄, and LiCl, and for mixtures with the indicated equivalent fractions. The broken line connects points at which $\phi' - \phi_0$ or $\Phi' - \Phi_0$ is a maximum

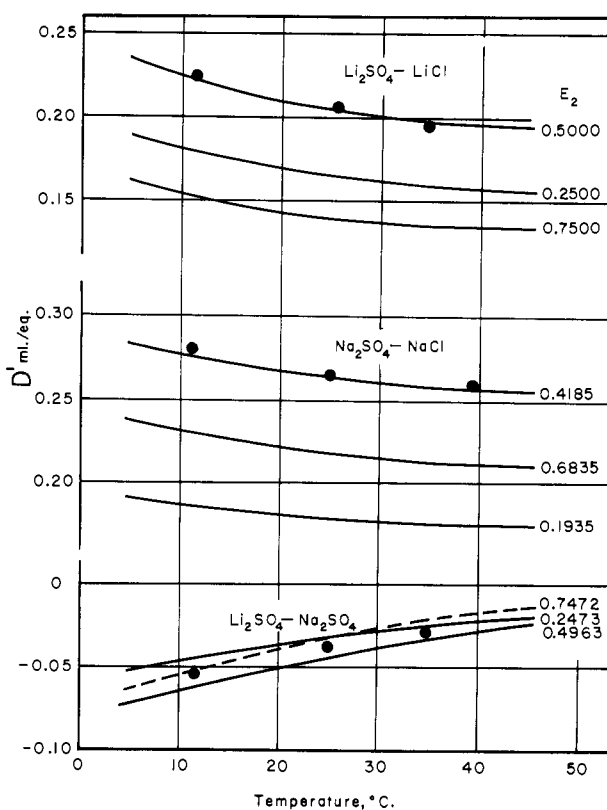


Figure 3. Variation of D' with temperature for various salt mixtures (ionic strength = 4)
● Values obtained by direct mixing

where the terms used are defined in the section on nomenclature.

These equivalent volumes were represented by the equation

$$\phi'_i - \phi'_0 \text{ or } \Phi'_i - \Phi'_0 = at + bt^2 + ct^3 \quad (6)$$

The coefficients of the equation are given in Table III, and plots of $\phi'_i - \phi'_0$ are given in Figure 2. Values of $\phi'_i - \phi'_0$ are believed reliable to ± 0.003 ml. per equivalent.

The apparent equivalent expansibilities of the solutes ($d\phi'/dt$) are given by

$$d\phi'/dt = a + 2bt + 3ct^2 \quad (7)$$

D' was calculated at each temperature using Equation 1. The results are given in Figure 3, where they are compared with the direct mixing experiments (Table IV). The results of direct mixing experiments for the salt pairs Li₂SO₄-NaCl, Na₂SO₄-LiCl, and LiCl-NaCl are given in Table IV and Figure 4.

Table III. Constants for the Equation: $\phi'_i = \phi'_0 + at + bt^2 + ct^3$

Ionic strength = 4.000, 5° to 45° C.

Salt	ϕ'_0	a	$-b \times 10^3$	$c \times 10^5$
Na ₂ SO ₄	10.408	0.13149	1.8621	1.0148
Li ₂ SO ₄	10.092	0.08665	1.7350	1.0464
NaCl	18.661	0.10632	1.4116	0.7421
LiCl	19.114	0.05232	1.1251	0.6229

CONSTANTS FOR THE EQUATION: $\Phi'_i = \Phi'_0 + at + bt^2 + ct^3$

Salt	Φ'_0	a	$-b \times 10^3$	$c \times 10^5$
Li ₂ SO ₄ (2)-LiCl(3)				
$E_2 = 0.7500$	12.523	0.07515	1.5023	0.8606
$E_2 = 0.5000$	14.853	0.06631	1.3065	0.7758
$E_2 = 0.2500$	17.058	0.05858	1.2228	0.6700
Na ₂ SO ₄ (2)-NaCl(3)				
$E_2 = 0.6835$	13.261	0.12267	1.7278	0.9576
$E_2 = 0.4185$	15.495	0.11581	1.6010	0.8747
$E_2 = 0.1935$	17.260	0.10998	1.4689	0.7650
Li ₂ SO ₄ (2)-Na ₂ SO ₄ (3)				
$E_2 = 0.7472$	10.103	0.09897	1.7324	0.9751
$E_2 = 0.4963$	10.171	0.11104	1.8140	1.0404
$E_2 = 0.2473$	10.276	0.12066	1.7908	0.9609

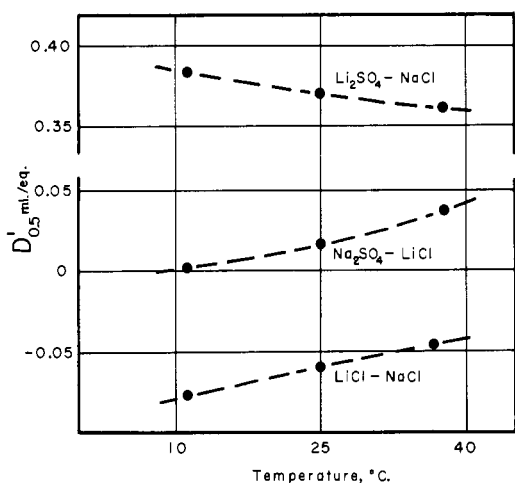


Figure 4. Values of D' ($E_2 = 0.5$) obtained by single-mixing experiments

The cross-square rule (2, 4, 6) was applied to the results obtained by direct mixing (Table V). The observed values in Table IV were first corrected to an equivalent fraction of 0.5 by use of Equation 4 and the constants of Table I in reference (3).

These values were then corrected graphically to temperatures of 12°, 25°, and 38° C. In all cases, the sum of $D'_{0.5}$ for the homoionic solutions is less than the sum of $D'_{0.5}$ for the heteroionic solutions.

In five of the six cases, the absolute value of $D'_{0.5}$ decreases with increasing temperature as expected. The value of $D'_{0.5}$ for the Na₂SO₄-LiCl mixture increases in value with increasing temperature. This can be explained if one assumes (3) that there is ion association to form LiSO₄⁻. The resultant decrease in ionic strength decreases the apparent equivalent volumes of the ions, and partially compensates for the increase in volume owing to normal ion interaction. Decrease in the association constant with increasing temperature would decrease this effect, and at the higher temperatures, $D'_{0.5}$ is approaching the values expected owing to ion interaction alone.

Table IV. Single-Mixing Experiments

Salt 2	Salt 3	$t, ^\circ\text{C.}$	E_2	$D', \text{Ml./Eq.}$		
Li ₂ SO ₄	LiCl	11.3	0.517	0.225 ₁		
		11.5	0.517	0.225 ₁		
		24.9	0.517	0.204 ₁		
		25.2	0.517	0.205 ₁		
		25.0 ^a	0.517 ^a	0.203 ₉ ^a		
		34.7	0.517	0.196 ₄		
Na ₂ SO ₄	NaCl	35.1	0.516	0.196 ₅		
		11.2	0.517	0.281 ₀		
		11.5	0.517	0.278 ₅		
		24.9	0.517	0.263 ₃		
		24.9	0.516	0.263 ₁		
		25.0 ^a	0.517 ^a	0.265 ₃ ^a		
Li ₂ SO ₄	Na ₂ SO ₄	37.8	0.516	0.260 ₁		
		37.8	0.517	0.259 ₅		
		11.4	0.508	-0.053 ₉		
		11.4	0.498	-0.054 ₂		
		25.0	0.498	-0.040 ₀		
		25.0	0.504	-0.038 ₃		
		25.0 ^a	0.504 ^a	-0.041 ₈ ^a		
		34.7	0.498	-0.028 ₁		
		34.7	0.498	-0.026 ₆		
		LiCl	NaCl	12.3	0.497	-0.078 ₆
				12.3	0.497	-0.078 ₃
				24.9	0.498	-0.059 ₇
24.9	0.499			-0.060 ₄		
25.0 ^a	0.499 ^a			-0.063 ₉ ^a		
37.8	0.498			-0.044 ₇		
Li ₂ SO ₄	NaCl	37.8	0.496	-0.044 ₇		
		12.3	0.516	0.383 ₇		
		12.3	0.517	0.382 ₉		
		24.9	0.520	0.370 ₅		
		24.9	0.517	0.369 ₉		
		25.0 ^a	0.517 ^a	0.367 ₉ ^a		
Na ₂ SO ₄	LiCl	37.8	0.518	0.362 ₈		
		37.8	0.517	0.360 ₄		
		12.2	0.516	0.002 ₂		
		12.2	0.517	0.002 ₂		
		25.0	0.516	0.017 ₀		
		25.0	0.516	0.017 ₀		
Na ₂ SO ₄	LiCl	25.0 ^a	0.516 ^a	0.018 ₅ ^a		
		37.8	0.515	0.036 ₅		
		37.8	0.514	0.036 ₇		
		37.8	0.514	0.036 ₇		

^a Calculated, Equation 4 and constants in Table I (3).

Table V. Application of the Cross-Square Rule

Salt Pair	$D_{0.5}$		
	12° C.	25° C.	38° C.
Li ₂ SO ₄ -LiCl	0.225	0.206	0.196
Na ₂ SO ₄ -NaCl	0.280	0.265	0.261
Li ₂ SO ₄ -Na ₂ SO ₄	-0.054	-0.039	-0.023
LiCl-NaCl	-0.079	-0.060	-0.044
$\Sigma \square =$	0.372	0.372	0.390
Li ₂ SO ₄ -NaCl	0.386	0.373	0.363
Na ₂ SO ₄ -LiCl	0.002	0.017	0.038
$\Sigma X =$	0.388	0.390	0.401

NOMENCLATURE

- a, b, c = constants in the equation $\phi'_i - \phi'_0$ or $\Phi'_i - \Phi'_0 = at + bt^2 + ct^3$ representing the equivalent volume or mean equivalent volume as a function of the temperature at constant ionic strength
- α, β, γ = constants in the equation $d_t - d_0 = \alpha t + \beta t^2 + \gamma t^3$ representing the density of a solution as a function of temperature
- d_0 = density (g./ml.) of a solution at 0° C.
- d_1 = density (g./ml.) of water at a given temperature
- d_2 = density (g./ml.) of a solution containing a single electrolyte
- d_3 = density (g./ml.) of a solution containing two electrolytes
- d_t = density (g./ml.) of a solution at temperature t
- 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 to give an equivalent fraction of 0.5

- E_2 = weight equivalent fraction of salt 2
- E_3 = weight equivalent fraction of salt 3
- m = molality (moles solute per 1000 grams of water)
- M = molecular weight of a solute
- μ = ionic strength of a solution in moles per 1000 grams of water
- p, p' = numerical factor to convert molality to equivalents per 1000 grams of water. $p = 1$ for NaCl and LiCl, $p = 2$ for Na₂SO₄ and Li₂SO₄
- ϕ'_2 = apparent equivalent volume (ml. per equiv.) of salt 2 in a solution containing only salt 2 and water
- ϕ'_3 = apparent equivalent volume (ml. per equiv.) of salt 3 in a solution containing only salt 3 and water
- Φ' = mean apparent equivalent volume (ml. per equivalent) of the solutes present in a solution
- t = temperature in degrees centigrade

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Melting Point of 98.9 to 99.6% Pure Boron

ROBERT F. KIMPEL and ROBERT G. MOSS¹
Aerojet-General Corp., Azusa, Calif. 91702

The melting points of four grades of boron varying in their respective purities from 98.9 to 99.6% were determined to be in the range of 3733° to 3766° F. (2056° to 2074° C.), respectively. The values were obtained by using four methods of experimental approach, and comparison of the values for each approach is presented. An endothermic action on heating boron was noted at about 3625° F., and supercooling of liquid boron as much as 200° F. below its melting point was encountered.

PUBLISHED values for the melting point of boron differ appreciably, ranging from 3550° to 4170° F. (1950° to 2300° C.) (1, 2, 4, 6-8). During the course of related work with boron, for which a more accurate value of its melting point was needed, melting points were determined in the present investigation for four grades of boron ranging in purity from 98.9 to 99.6% of boron. The results are reported to provide additional and more statistical information concerning the melting point of this material.

GRADES OF BORON INVESTIGATED

Sources and Analyses. Four grades of boron powder from four vendor sources were employed in this investigation. The sources are identified and reported purity of respective grades are given in Table I. All powders except that of Callery Chemical Co. were within the sieve-size range of from 100- to 20-mesh and were free flowing. The Callery powder was of extremely small size (1 micron), fluffy, and difficult to work with until prepressed pellets were formed

in a boron nitride die to achieve adequate weight loading of crucibles. All analyses for impurities other than for carbon were made spectrographically. Carbon was determined by the Pregyl method (9).

Effect of Remelt on Specimen Purity. In the course of preliminary work to determine a satisfactory material for the containment of boron, boron nitride was most successful. Although this crucible material seemed from outward appearances to be completely compatible with a boron melt, its compatibility was quantitatively investigated to determine whether specimen melts were significantly affected in composition. Crucibles were machined from BN stock supplied by the Carborundum Co. with reported impurities of 0.10% alkaline earth oxides, 0.2% alumina-silica, and 0.01% carbon. Prior to use, the crucibles were subjected to 2800° F. for 30 minutes at 10⁻³ torr pressure followed by 15 minutes' exposure to 3150° F. in argon at atmospheric pressure. This procedure removed the boric oxide binder used in preparing the crucible stock and precluded its subsequent reappearance at high temperature as a white vapor hindrance to optical temperature measurement.

The results of melting a single specimen of Callery boron three times are shown in Table II, in which the composition

¹ Present address: Jet Propulsion Laboratories, California Institute of Technology, Pasadena, Calif. 91103