Young's rule. The first-order correction would involve adding $y(1-y)I^2Rc_0$ to eq 14 (*12*, *16*, *17*) and adjusting c_0 to fit the experimental results on mixtures.) The partial molar heat capacity of $NiCl_2$ in this mixed solution is then given by

$$\bar{C}_p(\mathrm{NiCl_2}) = (\partial C_p/\partial m_{\mathrm{NiCl_2}})_{T,P,m_{\mathrm{NaCl}}} = C'_{p,\phi}(\mathrm{NiCl_2},I) + m_{\mathrm{NiCl_2}}(\partial C'_{p,\phi}(\mathrm{NiCl_2},I)/\partial m_{\mathrm{NiCl_2}}) \qquad (15)$$

Using the definition for the partial molar heat capacity of a pure solution, eq 8, and $I = 3m$ in a pure $NiCl_2$ solution, we find

$$\bar{C}_p(\mathrm{NiCl_2}) = (1 - 3m/I)C'_{p,\phi}(\mathrm{NiCl_2},I) + (3m/I)\bar{C}'_p(\mathrm{NiCl_2},I)$$
$$= (1-y)C'_{p,\phi}(\mathrm{NiCl_2},I) + y\bar{C}'_p(\mathrm{NiCl_2},I) \qquad (16)$$

where y is the ionic strength fraction of $NiCl_2$ in the mixture. Thus, using eq 16 we can estimate the partial molar heat capacity of $NiCl_2$ in any mixture, and this estimate has been found to be reasonably accurate in the case of $NiCl_2$–NaCl mixtures. (This prediction would probably be reasonably accurate for mixtures with other alkali metal chlorides. It could be very inaccurate in mixtures with other anions because of the change in nickel complexes formed.) To calculate the partial molar heat capacity of $NiCl_2$ in any mixture, we use eq 16 and the present results for $C'_{p,\phi}$ and $\bar{C}'_p$ in Table III, parts A1 and D1. If integrals of the partial molar heat capacity are desired, they can be obtained by integrating eq 16 and using the integrals in Table III, parts B1 and E1.

It is interesting to note the two extreme cases of eq 16; in a pure $NiCl_2$ solution ($y = 1$) the partial molar heat capacity is, of course, just the partial molar heat capacity of pure $NiCl_2$. However, in a NaCl solution with just a trace of $NiCl_2$ ($y = 0$), the *partial* molar heat capacity of $NiCl_2$ is equal to the *apparent* molar heat capacity of pure $NiCl_2$ at the same ionic strength as the NaCl solution. Thus, if Young's rule is accurate, the partial molar heat capacity of $NiCl_2$ at low concentrations in any mixture of electrolytes is equal to the apparent molar heat capacity of pure $NiCl_2$ at the ionic strength of the mixture.

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Isopiestic Determination of the Osmotic and Activity Coefficients of Aqueous Mixtures of NaCl and $SrCl_2$ at 25 °C

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The osmotic and activity coefficients of aqueous mixtures of NaCl and $SrCl_2$ have been determined at 25 °C by the isopiestic method. These measurements extend from moderate concentrations to the crystallization limits of the mixtures; results are in excellent agreement (0.1–0.2%) with published isopiestic data in overlapping regions of concentration. Osmotic and activity coefficients for NaCl–$SrCl_2$ mixtures are reliably represented by both Pitzer's equations and Scatchard's neutral electrolyte equations.

Introduction

Mixed electrolyte solutions occur in many important geochemical, biochemical, and industrial systems. Activity coefficient data are important for understanding chemical speciation, reactions, and solubility for these solutions.

Activity measurements are available for a fair number of mixed electrolyte aqueous solutions (*1*), mainly at 25 °C. Analysis of activity data for mixed electrolyte solutions involves relating these data to activities of the constituent binary solutions, generally at the total ionic strength of the mixture. However, the ionic strengths of concentrated mixtures can become higher than that of the least-soluble constituent in its binary solution. Most experimenters restrict their mixed-electrolyte measurements to ionic strengths for which binary data exist. This is unfortunate since some important processes, such as dissolution and leaching in salt beds, may require activity data at higher concentrations. Also, data for these higher concentrations will become analyzable by standard methods when better estimation procedures become available for properties of supersaturated binary solutions.

Macaskill et al. (*2*) have recently published highly accurate isopiestic data for NaCl–$SrCl_2$ mixtures to ionic strengths at 4.3–5.9. In the present publication these measurements are extended to the highest accessible concentrations for these mixtures (I = 6.7–11.2), thereby completing the study at 25 °C. These data have potential applications to the transport of ^{90}Sr in the natural environment.

Experimental Section

The isopiestic measurements were performed at 25.00 ± 0.005 °C (IPTS-68) using chambers that have previously been

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Table I. Isopiestic Molalities of $CaCl_2$ and NaCl-$SrCl_2$ Mixtures at 25 °C

m_T				
y_A = 0.82701	y_A = 0.64653	y_A = 0.47397	[$CaCl_2$], m	$\Phi(CaCl_2)$
		5.4034	3.2285	1.8615
		5.3554	3.2065	1.8525
		5.2550	3.1549	1.8312
	5.6705	5.1607	3.1072	1.8116
		5.1589	3.1063	1.8113
	5.5897	5.0880	3.0690	1.7960
5.9477	5.5196	5.0277	3.0391	1.7837
	5.5080	5.0158	3.0337	1.7815
5.8058	5.3887	4.9096	2.9798	1.7595
5.7273	5.3190	4.8475	2.9475	1.7464
5.6465	5.2452	4.7792	2.9120	1.7319
5.5264	5.1334	4.6840	2.8626	1.7119
5.4436	5.0595	4.6193	2.8281	1.6979
5.4334	5.0493	4.6078	2.8235	1.6961
5.3710	4.9950	4.5616	2.7967	1.6853
5.2959	4.9258	4.4999	2.7655	1.6727
5.1555	4.7982	4.3848	2.7046	1.6482
5.0262	4.6803	4.2792	2.6488	1.6259
4.9192	4.5813	4.1904	2.6023	1.6074
4.7952	4.4673	4.0908	2.5491	1.5863
4.6683	4.3544	3.9910	2.4939	1.5646
4.5722	4.2671	3.9118	2.4522	1.5482
4.4569	4.1603	3.8167	2.4002	1.5279
4.2902	4.0068	3.6773	2.3258	1.4990
4.1409	3.8682	3.5536	2.2578	1.4728
4.0207	3.7611	3.4582	2.2040	1.4523
3.8617	3.6160	3.3287	2.1322	1.4251
3.7138	3.4810	3.2086	2.0644	1.3996
3.5600	3.3403	3.0803	1.9934	1.3732

described (*3*). Solution samples were allowed 4–9 days to reach equilibrium. Duplicate samples of each solution were used, and the molalities at isopiestic equilibrium agreed to ±0.1% or better (most agreed to better than ±0.05%). $CaCl_2$ solutions were used as isopiestic standards. The molecular masses used were 158.53 g mol^{-1} for $SrCl_2$, 183.68 g mol^{-1} for $SrSO_4$, 58.443 g mol^{-1} for NaCl, and 110.986 g mol^{-1} for $CaCl_2$.

The highest concentrations investigated were obtained by removal of water from the samples while evacuating air from the isopiestic chambers before starting the equilibrations. Attempts to reach even higher concentrations resulted in spontaneous crystallization. Since $SrCl_2$ has a slight tendency to form supersaturated solutions (*4*), some of these higher-concentration mixtures may be supersaturated.

The $SrCl_2$ stock solution was prepared from filtered Baker-analyzed "low in magnesium" $SrCl_2 \cdot 6H_2O$. This same lot of $SrCl_2 \cdot 6H_2O$ was used for the $SrCl_2$ isopiestic (*4*) and diffusion (*5*) measurements. Direct current arc optical emission spectroscopy analysis for impurities indicated ~30 ppm Ca, ~50 ppm Ba, ~10 ppm Al, ~2 ppm Fe, and <10 ppm each Mg and Si (by weight). The Na present was below its 100 ppm quantitative detection limit. Mixed salt solutions were prepared from weighed amounts of $SrCl_2$ and NaCl stock solutions, and their mixture compositions were chosen to correspond to those used by Macaskill et al. (*2*) at lower concentrations. Vacuum corrections were made for all weights.

The $SrCl_2$ stock solution concentration was determined to be 3.1728 ± 0.0007 mol kg^{-1} by sulfate precipitation, and 3.1721 ± 0.0007 mol kg^{-1} by dehydration. Direct weighing of oven-dried Mallinckrodt analytical reagent NaCl was used for the NaCl stock solution preparation, and the calculated concentration was 4.9979 mol kg^{-1}. Dehydration analysis yielded 4.9962 ± 0.0006 mol kg^{-1}. These cited uncertainty limits are average deviations for triplicate analyses. The preparation and analysis of the $CaCl_2$ No. 1 reference solution has already been described (*6*).

Table II. Isopiestic Molalities of $CaCl_2$ and NaCl-$SrCl_2$ Mixtures at 25 °C

m_T			
y_A = 0.32813	y_A = 0.17085	[$CaCl_2$], m	$\Phi(CaCl_2)$
	5.0214	3.7382	2.0726
	4.9336	3.6835	2.0499
	4.8480	3.6295	2.0275
	4.7728	3.5818	2.0077
	4.6956	3.5295	1.9860
	4.6135	3.4776	1.9645
	4.5447	3.4314	1.9454
	4.4783	3.3883	1.9275
5.1666	4.4710	3.3829	1.9253
5.0369	4.3629	3.3113	1.8957
4.9737	4.3083	3.2741	1.8803
4.8980	4.2498	3.2342	1.8639
4.8311	4.1918	3.1937	1.8472
4.7584	4.1387	3.1558	1.8316
4.6732	4.0615	3.1054	1.8109
4.5647	3.9683	3.0399	1.7841
4.4404	3.8660	2.9705	1.7557
4.3369	3.7786	2.9098	1.7310
4.2238	3.6833	2.8436	1.7042
4.1161	3.5941	2.7793	1.6782
4.0409	3.5334	2.7339	1.6600
3.9314	3.4386	2.6698	1.6343
3.8464	3.3678	2.6187	1.6139
3.6603	3.2122	2.5079	1.5701
3.5218	3.0938	2.4216	1.5362
3.3705	2.9646	2.3292	1.5003
3.2708	2.8812	2.2680	1.4767
3.1362	2.7664	2.1835	1.4445
2.9658	2.6222	2.0794	1.4052
2.8431	2.5183	2.0010	1.3760
2.7599	2.4472	1.9495	1.3570

Let A denote NaCl and B $SrCl_2$. The total molality of a mixed salt solution is given by

$$m_T = m_A + m_B \tag{1}$$

Tables I and II list the m_T values at isopiestic equilibrium, and the ionic strength fraction of NaCl

$$y_A = m_A/(m_A + 3m_B) \tag{2}$$

in the mixed electrolyte solutions. Also given are the equilibrium molalities of the $CaCl_2$ reference solution and the osmotic coefficients of $CaCl_2$ (*7*).

Calculations and Discussion

The osmotic coefficients of the solutions were calculated from the equation for isopiestic equilibrium

$$\Phi = \nu^* m^* \Phi^* / (\sum_i \nu_i m_i) \tag{3}$$

where ν is the number of ions formed by the dissociation of one molecule of solute, and Φ is the molal osmotic coefficient. The asterisks refer to the isopiestic reference solution in equilibrium with the mixed electrolytes. The $CaCl_2$ reference solution Φ^* values were calculated with an available equation (*7*).

For NaCl–$SrCl_2$ mixtures the following equations apply. The osmolality of the solution is given by

$$\sum_i \nu_i m_i = 2m_A + 3m_B \tag{4}$$

The experimental data in Tables I and II are reported in terms of the total molality m_T. This is related to the osmolality by

$$\sum_i \nu_i m_i = \frac{3(1 + y_A)}{1 + 2y_A} m_T \tag{5}$$

The total ionic strength is then given by

$$I = \frac{1}{(1 + y_A)} \sum_i \nu_i m_i = m_A + 3m_B \tag{6}$$

Table III. Parameters for Pitzer Equation Treatment of Aqueous NaCl-SrCl$_2$[a]

θ^0	θ'	ψ	$\sigma(\phi)$	max deviation
			0.0029	0.0087
−0.00419			0.0023	0.0063
0.00940		−0.003 23	0.0021	0.0058
0.00435	0.006 92	−0.010 40	0.0018	0.0055

[a] Based on fits of isopiestic data to $I \leqslant 6.16$; Debye-Hückel constant $A^{\phi} = 0.3920$.

The isopiestic data of Macaskill et al. (*2*) were measured relative to a NaCl reference solution. These data were recalculated with Hamer and Wu's (*8*) NaCl Φ^* values. In the overlapping regions of concentration, our data and Macaskill et al.'s are consistent to about 0.1% for four of the five y_A values. At $y_A = 0.474$ these two studies differ by 0.2%. Since isopiestic measurements are only reproducible to 0.1–0.2% under optimum conditions, the two sets of data are in excellent agreement. Both sets of data were given equal weights in least-squares fits.

Pitzer's equations (*9*, *10*) were fitted to the combined NaCl–SrCl$_2$ isopiestic data up to I = 6.16 mol kg^{-1} (the NaCl solubility limit). A total of 97 points were thereby included. In Pitzer's approach the Debye-Hückel term, f^{ϕ}, and the B^{ϕ} parameter for each constituent electrolyte are evaluated at the total ionic strength of the mixture. These binary parameters are then multiplied by functions of the ionic molalities. The differences between the experimental Φ values and these modified binary solution contributions are fitted to an expression containing up to three mixing parameters, θ^0, θ', and ψ. The parameters θ^0 and θ' are defined by assuming Pitzer's θ is linear in I (e.g., $\theta = \theta^0 + \theta' I$). The binary constants for NaCl were taken from Pitzer (*10*); those of SrCl$_2$ are given elsewhere (*4*).

The mixing parameter values for several combinations of these parameters are given in Table III. Also given are the standard deviation of the osmotic coefficients $\sigma(\phi)$ and the maximum deviation for each fit. Pitzer's equations do a fairly good job in representing the NaCl-SrCl$_2$ Φ data even without mixing parameters. Including one to three mixing parameters reduces the standard deviation of Φ by about 20–38% from the no mixing parameter case. The simpler two-parameter fit is our preferred representation of the data because including θ' made little improvement.

These fits to Pitzer's equations were based on SrCl$_2$ binary Pitzer constants (*4*) by fitting SrCl$_2$ data to the highest experimental concentrations ($I \leq 11.53$). Restricting the binary SrCl$_2$ fit to $I \leq 7$ gave almost no improvement in the mixture fits.

Scatchard's neutral electrolyte treatment (*11*, *12*) was also used to represent the NaCl–SrCl$_2$ Φ data. Scatchard's Φ equation can be written in the general form

$$\Phi \frac{(\sum_i \nu_i m_i)}{I} = \frac{\nu_A m_A \phi_A{}^\circ}{I} + \frac{\nu_B m_B \phi_B{}^\circ}{I} + y_A y_B I (b_{01} + b_{02} I + b_{03} I^2) + y_A y_B (y_A - y_B) I^2 (b_{12} + b_{13} I) \quad (7)$$

for any mixture of two electrolytes in one solvent. Here $\phi_1{}^\circ$ is the osmotic coefficient of the pure constituent electrolyte i evaluated at the total ionic strength of the mixture. The b_{0j} values are parameters for symmetrical mixing while the b_{1j} values represent asymmetrical mixing effects. Satchard's equation can be rearranged to give

$$f(I) = \frac{\Phi(\sum_i \nu_i m_i) - \nu_A m_A \phi_A{}^\circ - \nu_B m_B \phi_B{}^\circ}{y_A y_B I^2} \quad (8)$$

Then

$$f(I) = b_{01} + b_{02} I + b_{03} I^2 + b_{12}(y_A - y_B) I + b_{13}(y_A - y_B) I^2 \quad (9)$$

and this equation can be fitted to the data, using some or all of the b_{ij} terms, by standard linear least-squares methods.

Equation 9 was fitted to the combined NaCl–SrCl$_2$ data up to I = 6.16 mol kg^{-1} using $\phi_A{}^\circ$ from Hamer and Wu (*8*) and $\phi_B{}^\circ$ from Rard and Miller's eq 3 (*4*). Results are given for various combinations of the b_{ij} in Table IV. Also given are the ratios of the standard error of each coefficient divided by the coefficient. The first asymmetrical mixing coefficient b_{12} is definitely required for a good fit to the experimental data, as are at least two of the three symmetrical mixing coefficients. However, b_{13} is not significant since including it produced no improvement in the quality of the fit, and it sometimes had a standard error larger than the coefficient. The values of individual coefficients vary considerably when different numbers of symmetrical mixing coefficients are used. However, if the same symmetrical mixing coefficients are used, their values are nearly unaffected by the inclusion of one or more asymmetrical mixing terms (even though the overall quality of the fit generally improved).

Scatchard's equation represents NaCl–SrCl$_2$ data with a standard deviation about one-half that for the Pitzer equation for the "best" combinations of mixing parameters. Scatchard's approach frequently gives a slightly better representation of experimental data because it has more adjustable constants. Pitzer's approach uses at most three mixing parameters, whereas Scatchard's approach allows up to five. Also, Pitzer's binary solution equations generally use only three adjustable parameters each, while Scatchard's $\phi_i{}^\circ$ are allowed as many parameters as are required to accurately represent the data. It is worth noting that for NaCl–Na$_2$CO$_3$ mixtures, where the binary solution equations have comparable $\sigma(\phi)$ (*13*), the two mixture approaches give equally good fits.

Table IV. Parameters for Scatchard Neutral Electrolyte Treatment of Aqueous NaCl–SrCl$_2$[a]

b_{01}	b_{02}	b_{03}	b_{12}	b_{13}	$\sigma(\phi)$	max deviation
					0.0041	0.0073
0.006 02 (0.09)					0.0027	0.0071
0.014 58 (0.09)	−0.002 03 (0.14)				0.0021	0.0050
0.005 53 (0.37)	0.004 30 (0.29)	−0.000 87 (0.19)			0.0020	0.0059
0.005 44 (0.23)	0.004 49 (0.16)	−0.000 88 (0.11)	−0.001 47 (0.08)		0.0009	0.0027
0.005 24 (0.23)	0.004 75 (0.15)	−0.000 92 (0.11)	−0.002 91 (0.20)	0.000 28 (0.40)	0.0010	0.0028
0.014 55 (0.06)	−0.001 88 (0.11)		−0.001 46 (0.10)		0.0012	0.0035
0.014 64 (0.06)	−0.001 90 (0.11)		−0.001 92 (0.42)	0.000 09 (1.72)	0.0012	0.0036
0.006 65 (0.07)			−0.001 57 (0.13)		0.0024	0.0069
0.006 64 (0.07)			−0.000 95 (1.17)	−0.000 12 (1.77)	0.0024	0.0071
	0.007 37 (0.07)	−0.001 25 (0.07)			0.0021	0.0062
	0.007 51 (0.04)	−0.001 25 (0.05)	−0.001 47 (0.08)		0.0011	0.0030
	0.007 68 (0.04)	−0.001 28 (0.05)	−0.003 08 (0.21)	0.000 32 (0.39)	0.0012	0.0033
	0.001 15 (0.12)		0.000 06 (28.3)	−0.000 30 (1.00)	0.0028	0.0077

[a] In parentheses is the standard error of the coefficient divided by the coefficient. Values are based on fits of isopiestic data to $I \leqslant 6.16$. See text for "best-fit" coefficients to $I \leqslant 11.2$.

Table V. Negative of the Natural Logarithm of the Activity Coefficient of NaCl in NaCl-$SrCl_2$ Mixtures

I, mol kg^{-1}	y_A 0.00	0.25	0.50	0.75	1.00
	Pitzer Equation[a]				
0.5	0.359	0.368	0.375	0.382	0.387
1.0	0.390	0.401	0.410	0.418	0.423
2.0	0.376	0.389	0.398	0.404	0.406
3.0	0.323	0.335	0.342	0.343	0.339
4.0	0.250	0.260	0.262	0.258	0.247
5.0	0.164	0.170	0.168	0.157	0.137
6.0	0.068	0.071	0.062	0.043	0.014
	Scatchard Equation[a]				
0.5	0.381	0.382	0.383	0.383	0.384
1.0	0.421	0.421	0.421	0.421	0.420
2.0	0.415	0.412	0.409	0.406	0.403
3.0	0.365	0.359	0.352	0.345	0.337
4.0	0.292	0.283	0.272	0.259	0.244
5.0	0.203	0.192	0.177	0.158	0.134
6.0	0.103	0.093	0.074	0.048	0.014

[a] Based on fits of isopiestic data up to $I \leq 6.16$. Pitzer parameters used are $\theta^0 = 0.00940$ and $\psi = -0.00323$. Scatchard parameters used are $b_{02} = 0.00751$, $b_{03} = -0.00125$, and $b_{12} = -0.00147$.

Table VI. Negative of the Natural Logarithm of the Activity Coefficient of $SrCl_2$ in NaCl-$SrCl_2$ Mixtures

I, mol kg^{-1}	y_B 0.00	0.25	0.50	0.75	1.00
	Pitzer Equation[a]				
0.5	0.702	0.714	0.725	0.733	0.740
1.0	0.748	0.772	0.793	0.810	0.823
2.0	0.698	0.743	0.782	0.814	0.840
3.0	0.575	0.639	0.694	0.741	0.779
4.0	0.414	0.496	0.567	0.627	0.676
5.0	0.228	0.327	0.413	0.486	0.547
6.0	0.024	0.140	0.241	0.328	0.400
	Scatchard Equation[a]				
0.5	0.757	0.756	0.755	0.754	0.753
1.0	0.828	0.829	0.830	0.832	0.835
2.0	0.800	0.809	0.820	0.833	0.848
3.0	0.685	0.704	0.728	0.755	0.787
4.0	0.525	0.558	0.596	0.639	0.687
5.0	0.341	0.388	0.440	0.498	0.561
6.0	0.146	0.207	0.272	0.341	0.415

[a] See footnotes to Table V.

For the above reasons Scatchard's equations generally fit experimental data slightly better than Pitzer's approach. However, another important application of mixed-electrolyte equations is to predict activities for systems lacking experimental mixture data. The $\sigma(\phi)$ values given in Tables III and IV for the cases without mixing parameters indicate that Pitzer's equations are slightly superior to Scatchard's for predicting data using only binary solution parameters. This same conclusion has been reached before for NaCl-$SrCl_2$ (*2*) and certain other mixtures (*9*). The same is probably true at higher temperatures (*14*).

Values of the negative of the natural logarithm of the mean molal activity coefficients, $-\ln \gamma_\pm$, of NaCl and $SrCl_2$ are given in Tables V and VI at various ionic strengths and ionic strength fractions. The Pitzer and Scatchard values were calculated by using the "best-fit" parameters (θ^0 and ψ for Pitzer; b_{02}, b_{03}, and b_{12} for Scatchard approach). These parameters were judged to give the best fit of each type based on consideration of $\sigma(\phi)$, maximum deviations, coefficient errors, and economy of terms. The values of $y_i = 0$ are trace activity coefficients while $y_i = 1$ are the pure-component values. Differences in the $\gamma_\pm$ values from the two approaches were not unexpected (up to 12% in the trace $\gamma_\pm$ values), since mixed-electrolyte $\gamma_\pm$ values are generally sensitive to the method of representing experimental Φ data.

For comparison, values of $\ln \gamma_\pm$ of NaCl and $SrCl_2$ were also calculated (not reported) for several other sets of Scatchard parameters from Table IV with $\sigma(\phi) \leq 0.0012$. Values of $\ln \gamma_\pm$ of NaCl varied 0.007 or less, and for $SrCl_2$ 0.015 or less, with the largest differences occurring for trace $\ln \gamma_\pm$. However, differences in $\ln \gamma_\pm$ between the Scatchard and Pitzer methods were much larger, being as much as 0.12 for trace values of $SrCl_2$ at high concentrations. Lanier (*15*) reported NaCl activity coefficients in NaCl-$SrCl_2$ mixtures at $I = 1.0$, 3.0, and 6.0 from measurements with sodium-sensitive glass electrodes. Lanier's results are in complete agreement with the Scatchard values in Table V at $I = 1.0$ and have a maximum difference in $\ln \gamma_\pm$ of 0.025 at $I = 6.0$. This agreement with the isopiestic data is good, since it is within the variation from different fits of the same data.

Scatchard's equations were also capable of accurately representing NaCl-$SrCl_2$ experimental data up to the solution crystallization limits. The best fit recommended for this concentration range gives $b_{01} = 0.01022$, $b_{02} = 0.00128$, $b_{03} = -0.00046$, and $b_{12} = -0.00158$ with $\sigma(\phi) = 0.0014$ and a maximum deviation of 0.0042. The binary $\phi_B{}^\circ$ equation (*4*) for $SrCl_2$ applies to higher ionic strengths than occur for the mixtures so it offers no problem. However, the NaCl $\phi_A{}^\circ$ equation (*8*) is valid only to $I = 6.16$, and it probably does not give realistic results corresponding to its supersaturated concentrations (the binary approximation to Φ is 0.025 high at the highest ionic strength). These Scatchard parameters can be used to calculate Φ and water activities to the highest concentrations in Tables I and II. However, they should *not* be used above 6.16 mol kg^{-1} to give Φ for $y_A > 0.827$ or to calculate $\gamma_\pm$.

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Glossary

A	symbols subscripted A refer to NaCl
B	symbols subscripted B refer to $SrCl_2$
*	symbols with asterisks refer to $CaCl_2$ isopiestic standards
m_i	molal concentration of electrolyte i, mol kg^{-1}
m_T	total molality of mixed electrolyte
y_i	ionic strength fraction of electrolyte i in mixtures
Φ	molal osmotic coefficient
ν_i	number of ions formed by the dissociation of one molecule of electrolyte i
I	total ionic strength of mixed electrolyte solutions, mol kg^{-1}
f^ϕ	Debye-Hückel term in Pitzer's equations for single electrolytes
B^ϕ	ionic-strength-dependent parameter in Pitzer's equations for single electrolytes
θ^0, θ', ψ	mixing parameters for Pitzer's equations
$\phi_i{}^\circ$	osmotic coefficient of pure electrolyte i at the total ionic strength of the mixed electrolyte solution
b_{01}, b_{02}, b_{03}, b_{12}, b_{13}	mixing parameters for Scatchard's neutral electrolyte equations
$\sigma(\phi)$	standard deviation of fitting equations
$\gamma_\pm$	mean molal activity coefficient

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Excess Volumes of a Homologous Series of Aliphatic Alcohols with Benzonitrile

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Excess volumes of binary mixtures of 1-propanol, 1-butanol, 1-pentanol, isopropyl alcohol, isobutyl alcohol, and isopentyl alcohol with benzonitrile have been measured at 308.15 K by using a dilatometer and are reported in this paper.

Introduction

In continuation of earlier work on excess volumes of binary mixtures of alcohols in a common solvent (*1–4*), V^E values of binary mixtures of 1-propanol, 1-butanol, 1-pentanol, isopropyl alcohol, isobutyl alcohol, and isopentyl alcohol with benzonitrile at 308.15 K are reported here. A literature survey showed that no one has reported V^E data for the mixtures of the six alcohols with benzonitrile at 308.15 K.

Experimental Section

Mixing Cell. The cell used for measuring excess volumes was similar to that used by Brown and Smith (*5*) except for the detachable capillary arrangement. The cell was basically a U-tube with mercury at the bottom to separate the two components. One arm of the U-tube was closed with a ground-glass stopper, and the other arm was fitted with a capillary (1-mm i.d.) having a Teflon cap with a small orifice at the top, which was detachable. Composition was determined directly by weighing. The cell was immersed in a thermostatic bath maintained at 308.15 ± 0.01 K. The change in liquid level after mixing in the capillary with reference to a fixed mark was read by a traveling microscope which had an accuracy of ±0.01 mm. Excess volumes were accurate to ±0.003 $cm^3\ mol^{-1}$. Four cells with different capacities were used to cover the mole fraction range from 0.1 to 0.9.

Purification of Materials

Benzonitrile (Riedel) was dried over freshly fused calcium chloride for 2 days and distilled at atmospheric pressure. 1-Propanol (E. Merck) was refluxed over lime for 5 h and then distilled through a 1-m fractionating column.

1-Butanol (BDH) was refluxed over freshly ignited calcium oxide for 4 h. The alcohol was decanted from the lime, refluxed with magnesium turnings, and then fractionally distilled. The middle fraction which boiled at 390.75 K was collected.

Table I. Boiling Points and Densities of Pure Components

component	bp, K present work	bp, K lit. (*6*)	density, g cm^{-3} present work	density, g cm^{-3} lit. (*6*)
1-propanol	370.15	370.15	0.795 60	0.795 67
1-butanol	390.15	390.22	0.802 05	0.802 06
1-pentanol	411.00	411.10	0.807 54	0.807 64
isopropyl alcohol	354.85	355.35	0.776 85	0.776 90
isobutyl alcohol	380.94	381.04	0.794 31	0.794 37
isopentyl alcohol	404.35	405.05	0.801 67	0.801 79
benzonitrile	463.93	464.04	0.996 19	0.996 28

1-Pentanol (E. Merck) was dried over Drierite and fractionally distilled.

Isopropyl alcohol (BDH) was dried first with calcium chloride and then with barium oxide and fractionally distilled.

Isobutyl alcohol (BDH) was purified by repeated fractional distillation through a 1-in.-90-plate column.

Isopentyl alcohol (BDH) was dried with calcium chloride and then purified by careful fractional distillation.

The purity of the above samples has been verified from densities at 303.15 K and boiling points reported in the literature (*6*) and presented in Table I. The densities are accurate to 5 parts in 10^5 parts.

Results and Discussion

The excess volume data at 308.15 K of the six binary mixtures are presented in Table II and represented in Figures 1 and 2. The values of V^E are negative over the entire range of composition in all of the mixtures. The negative excess volumes of the six binary mixtures fall in order. The normal alcohols fall in the order 1-propanol > 1-butanol > 1-pentanol, and the isoalcohols also fall in the same order, i.e., isopropyl alcohol > isobutyl alcohol > isopentyl alcohol.

The excess volume–composition curves of the systems are given by

$$V^E/(x_A x_B) = a_0 + a_1(x_A - x_B) + a_2(x_A - x_B)^2 \qquad (1)$$

where x_A and x_B are the mole fractions of components A and B, respectively, and a_0, a_1, and a_2 are arbitrary constants which have been evaluated by the principle of least squares.

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