Subscripts

1 methane
2 hydrocarbon

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Received for review July 21, 1981. Accepted November 9, 1981. We are grateful to "Délégation Générale à la Recherche Scientifique et Technique" for financial support.

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

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The osmotic coefficients of aqueous CsCl, $SrCl_2$, and mixtures of NaCl and CsCl have been measured at 25 °C by the isopiestic method. The solubilities of CsCl and $SrCl_2 \cdot 6H_2O$ have also been measured at this temperature. These experimental data are compared with other available activity and solubility data and are in good agreement in most cases. Least-squares equations were used to represent the single-salt osmotic coefficients, and these equations were used to calculate water activities and mean molal activity coefficients. Data for the NaCl–CsCl solutions are accurately represented by the two-parameter form of Pitzer's equations.

Introduction

The osmotic coefficients of aqueous solutions of CsCl and $SrCl_2$ at 25 °C have been measured numerous times (*1–12*). The reported CsCl measurements exhibit systematic differences of up to 1%, while those for $SrCl_2$ vary up to 2%. These differences exceed by several times the expected errors for isopiestic measurements. Likewise, results for the two previous NaCl–CsCl mixed-salt isopiestic studies differ by 0.5% (*2*, *4*). While the major errors appear to be due to low-purity chemicals used in some of the earlier studies (*1*, *9*), additional measurements would help to clarify the situation.

Both ^{90}Sr and ^{137}Cs have the potential of becoming major biological hazards. Thermodynamic data for their chloride salts and mixtures with NaCl may help to understand their transport in the natural environment. Diffusion data for the individual salts in water have also been reported (*13*, *14*).

In this paper isopiestic data are reported for CsCl, $SrCl_2$, and NaCl–CsCl mixtures. Data for NaCl–$SrCl_2$ mixtures will be given elsewhere (*15*). Isopiestic data for some of these systems at higher temperatures are being measured at Oak Ridge National Laboratory (*16*).

Experimental Section

Isopiestic measurements were performed at 25.00 ± 0.005 °C by using the chambers described elsewhere (*17*). Tables I and II contain the isopiestic equilibrium molalities (total molalities for the mixed salts) and the osmotic coefficients of the NaCl and $CaCl_2$ reference solutions (*18*, *19*). These reported molalities are the average of triplicate samples for $CaCl_2$ and duplicate samples for the other electrolytes. Each isopiestic concentration is known to better than ±0.1%. Molecular

Table I. Isopiestic Molalities of CsCl, $SrCl_2$, and $CaCl_2$ Solutions at 25 °C

[CsCl], *m*	[$SrCl_2$], *m*	[$CaCl_2$], *m*	ϕ, $CaCl_2$
11.382[a]		3.7438	2.0749
11.034		3.6734	2.0457
10.829		3.6305	2.0279
10.751	3.8426	3.6136	2.0209
10.607		3.5843	2.0088
10.579	3.8012	3.5785	2.0064
10.429		3.5480	1.9937
10.398	3.7577	3.5408	1.9907
10.372		3.5376	1.9894
10.268		3.5140	1.9796
10.043		3.4645	1.9591
9.8162		3.4163	1.9391
9.6485		3.3787	1.9236
9.4810	3.5306	3.3402	1.9076
9.4445		3.3316	1.9041
9.4359	3.5231	3.3308	1.9038
9.4242	3.5195[b]	3.3280	1.9026
9.2848	3.4855	3.2971	1.8898
9.1402	3.4459	3.2614	1.8751
8.9903	3.4096	3.2280	1.8613
8.8705	3.3780	3.1999	1.8497
8.6588	3.3224	3.1504	1.8294
8.5441	3.2921	3.1225	1.8179
8.4055	3.2545	3.0887	1.8041
8.2792	3.2235	3.0604	1.7925
8.1648	3.1909	3.0310	1.7804
8.0337	3.1545	2.9969	1.7665
7.9146	3.1238	2.9689	1.7551
7.8034	3.0935	2.9405	1.7435
7.6963	3.0653	2.9154	1.7333
7.6898	3.0637	2.9125	1.7321
7.5528	3.0265	2.8783	1.7183
7.4328	2.9904	2.8464	1.7053
7.3307	2.9636	2.8204	1.6948
7.1658	2.9138	2.7772	1.6774
6.9960	2.8666	2.7330	1.6596
6.8196	2.8155	2.6848	1.6403
6.6493	2.7659	2.6380	1.6216
6.4850	2.7188	2.5939	1.6041
	2.6789	2.5589	1.5902

[a] Saturated solution in equilibrium with solid CsCl. [b] Saturated solution in equilibrium with $SrCl_2 \cdot 6H_2O$.

Table II. Isopiestic Molalities of NaCl, CsCl, and NaCl–CsCl Mixtures at 25 °C

y = 1.00000	y = 0.66687	y = 0.33341	y = 0.00000	ϕ, NaCl
5.7526	6.4167	7.0001	7.3551	1.2495
5.6503	6.2945	6.8579	7.1935	1.2414
5.5566	6.1848	6.7290	7.0520	1.2341
5.4733	6.0856	6.6169	6.9292	1.2275
5.3752	5.9726	6.4894	6.7932	1.2198
5.3042	5.8869	6.3932	6.6813	1.2143
5.2236	5.7912	6.2812	6.5652	1.2080
5.1354	5.6858	6.1662	6.4332	1.2011
5.0492	5.5844	6.0415	6.3077	1.1944
4.9696	5.4947	5.9368	6.1956	1.1882
4.8886	5.3985	5.8309	6.0760	1.1819
4.8176	5.3162	5.7364	5.9724	1.1764
4.7359	5.2205	5.6318	5.8566	1.1701
4.6699	5.1442		5.7614	1.1651
4.5832	5.0405	5.4308	5.6411	1.1584
4.5211	4.9697	5.3460	5.5510	1.1537
4.4625	4.9014	5.2701	5.4697	1.1492
4.3851	4.8101	5.1694	5.3659	1.1434
4.3598	4.7804	5.1329	5.3241	1.1415
4.3154	4.7305	5.0796	5.2656	1.1381
4.2362	4.6398	4.9707	5.1555	1.1322
4.1371	4.5235	4.8398	5.0107	1.1248
4.0509			4.9009	1.1184
4.0244			4.8668	1.1164
3.8714	4.2171	4.5020	4.6556	1.1052
3.8580	4.2022		4.6369	1.1043
3.6976	4.0182	4.2785	4.4207	1.0927
3.5785	3.8841	4.1315	4.2653	1.0842
3.4556	3.7408	3.9729	4.0979	1.0755
3.3237	3.5916	3.8095	3.9255	1.0663
3.2166	3.4712	3.6760	3.7878	1.0589
3.0811	3.3175	3.5091	3.6117	1.0498
2.9453	3.1644	3.3406	3.4377	1.0407
2.8179	3.0215	3.1835	3.2751	1.0324
2.6960	2.8851	3.0368	3.1211	1.0245
2.6098	2.7895	2.9313	3.0142	1.0191
2.4893	2.6544	2.7870	2.8626	1.0116
2.4137	2.5691	2.6965	2.7667	1.0070
2.3627	2.5148	2.6360	2.7059	1.0039
2.3477	2.5014	2.6224	2.6917	1.0030
2.3231	2.4697	2.5874	2.6549	1.0015
2.2778	2.4231	2.5352	2.6013	0.9988
2.2010	2.3345	2.4420	2.5057	0.9943
2.0867	2.2075	2.3058	2.3646	0.9877
1.9859	2.0982	2.1888	2.2445	0.9820
1.8704	1.9712	2.0528	2.1048	0.9757
1.7602	1.8508	1.9251	1.9717	0.9698
1.6941	1.7808	1.8498	1.8954	0.9663
1.4200	1.4844	1.5334	1.5719	0.9528
1.3797	1.4407	1.4888	1.5250	0.9509
1.3421	1.4012	1.4468	1.4806	0.9492
1.3317	1.3894	1.4349	1.4685	0.9487
1.2146	1.2650	1.3033	1.3339	0.9435
1.0992	1.1420	1.1739	1.2013	0.9386
0.96366	0.99726	1.0234	1.0456	0.9334
0.84237	0.86909	0.88978	0.90786	0.9291
0.75763	0.77939	0.79741	0.81286	0.9264
0.69432	0.71329	0.72846	0.74244	0.9246

masses used were 168.358 g/mol for CsCl, 58.443 g/mol for NaCl, 158.53 g/mol for $SrCl_2$, 183.68 g/mol for $SrSO_4$, and 18.0152 g/mol for H_2O. Vacuum corrections were made for all masses.

Isopiestic equilibrium times ranged from 4 days to 2 weeks, with the longer times required at lower concentrations. Saturated solution concentrations were determined by equilibrating duplicate samples of stock solution with another cup containing saturated solution and crystals.

The solubility of $SrCl_2 \cdot 6H_2O$ was determined to be 3.5195 ± 0.0022 mol/kg (average of 5-, 8-, and 10-day equilibrations). Linke (*20*) and Stokes (*10*) both report 3.520 for this value. Measurements into the supersaturated concentration region were difficult to perform since crystallization occurred in about half of the attempts. $SrCl_2$ samples were examined for crystals after each high-concentration run, and only those runs without crystallization are reported.

A solubility of 11.382 ± 0.008 mol/kg was measured for CsCl by using 10- and 12-day equilibrations. This result agrees well with the Earl of Berkeley's value of 11.39 ± 0.01 after interpolation to 25 °C (*21*). Linke's average (*22*) of 11.30 is somewhat lower, while Makarov et al. (*3*) obtained 11.41.

The $SrCl_2$ stock solution was prepared from filtered Baker-analyzed "low in magnesium" $SrCl_2 \cdot 6H_2O$. Filtered Apache optical-grade 99.999% CsCl was used for the two CsCl stock solutions. Separately prepared and analyzed CsCl stock solutions were used for the results in Tables I and II.

CsCl stock solution concentrations were determined by dehydration and by chloride analyses; the $SrCl_2$ stock was analyzed by dehydration and by sulfate precipitation (*14*). The isopiestic reference solutions were $CaCl_2$ stock No. 1 and NaCl stock No. 2; they are described elsewhere (*23*). The concentration analyses for each stock solution agreed within ±0.03–0.04%.

CsCl and $SrCl_2$ were analyzed for impurities by using direct current arc optical emission spectroscopy. The CsCl contained by weight ~2 ppm Li, <10 ppm each Rb and Sr, <6 ppm Si, <4 ppm Ca, and <1 ppm each Mg and Na. There was ~30 ppm Ca, ~50 ppm Ba, ~10 ppm Al, ~2 ppm Fe, and <10 ppm each Mg and Si in the $SrCl_2$. Na was below its 100 ppm quantitative detection limit.

Calculations and Discussion

The osmotic coefficients of the solutions were calculated from

$$\phi = \nu^* m^* \phi^* / (\nu m) \qquad (1)$$

where m is the molality of the solution, ϕ its molal osmotic coefficient, and ν the number of ions formed by the complete dissociation of one molecule of solute. The corresponding quantities for the isopiestic reference solutions ($CaCl_2$ or NaCl), in isopiestic equilibrium with the solution being studied, are indicated with asterisks. The ϕ^* values were calculated by using available equations (*18*, *19*). For the NaCl–CsCl mixed-salt solutions, νm is equal to twice the total molality. Other isopiestic data for these systems (*1*–*12*) were recalculated to conform to the same reference solution values.

Several emf studies have also been reported for aqueous CsCl and $SrCl_2$ at 25 °C (*24*–*28*). These studies utilized metal amalgam electrodes. Amalgam electrodes are difficult to use, and most of the derived activity coefficients are several percent in error when compared to other methods of activity measurements. However, the most recent CsCl measurements (*27*) appear to be quite accurate. Mussini et al. (*27*) fitted their results to Guggenheim's equation. Inserting Guggenheim's equation into the Gibbs–Duhem equation and integrating yields the osmotic coefficient

$$\phi = 1 - \frac{1.1762}{m}\left[\frac{m + 2m^{1/2}}{1 + m^{1/2}} - 2\ln\left(1 + m^{1/2}\right)\right] - 0.00932545m \qquad (2)$$

The computed ϕ results are listed in Table III.

Freezing point depression data for CsCl solutions (*29*) were converted to osmotic coefficients at 25 °C (Table III) by using standard methods (*30*) and available enthalpy (*31*) and heat capacity (*32*) data. Momicchioli et al.'s freezing point depression results (*29*) above 0.76 mol/kg were not used since complete thermal data are not available at the higher concentrations. Early freezing point depression data for $SrCl_2$ are referenced by Goldberg et al. (*33*), but they are of low accuracy and were not utilized.

Table III. Freezing Point Depression and Emf Data for CsCl Solutions

m	$\phi_f{}^a$	ϕ^b	m	$\phi_f{}^a$	ϕ^b
Momicchioli et al. (*29*), Freezing Point Depression					
0.013 34	0.9678	0.9672	0.202 58	0.8907	0.8963
0.021 86	0.9571	0.9567	0.271 15	0.8814	0.8893
0.032 58	0.9383	0.9381	0.354 24	0.8724	0.8828
0.051 29	0.9347	0.9351	0.449 27	0.8635	0.8768
0.069 34	0.9256	0.9266	0.597 82	0.8529	0.8705
0.094 64	0.9157	0.9176	0.762 13	0.8444	0.8667
0.142 64	0.9044	0.9079			
Mussini et al. (*27*), Emf Measurements					
0.05		0.9350	0.4		0.8795
0.1		0.9174	0.5		0.8736
0.2		0.8984	0.6		0.8691
0.3		0.8873	0.7		0.8653

[a] The osmotic coefficient at the freezing temperature. [b] The osmotic coefficient at 25 °C.

Table IV. Coefficients and Powers for the Osmotic Coefficient Polynominal at 25 °C

	$CsCl^a$		$SrCl_2{}^b$	
i	r_i	A_i	r_i	A_i
1	1.00	0.669 456 4	0.75	−1.418 489
2	1.25	−0.325 588 5	1.00	18.281 02
3	1.50	−0.556 458 5	1.25	−45.045 00
4	1.75	0.742 922 3	1.50	58.868 39
5	2.00	−0.326 312 2	1.75	−44.795 51
6	2.25	0.049 482 6	2.00	18.842 56
7			2.25	−3.370 30
σ		0.001 2		0.001 6

[a] Maximum concentration, 11.382 mol/kg. [b] Maximum concentration, 3.8426 mol/kg.

The available osmotic coefficients of pure CsCl and $SrCl_2$ solutions were fitted by least-squares equations of the form

$$\phi = 1 - (A/3)m^{1/2} + \sum_i A_i m^{r_i} \tag{3}$$

where A is the Debye–Hückel limiting slope (1.1762 for CsCl; 4.0744 for $SrCl_2$). Quarter power series worked best for both electrolytes. The least-squares coefficients and the standard deviations, σ, for the best fits are listed in Table IV.

The corresponding expression for the mean molal activity coefficient $\gamma_\pm$ of the solute is

$$\ln \gamma_\pm = -Am^{1/2} + \sum_i A_i \left(\frac{r_i + 1}{r_i} \right) m^{r_i} \tag{4}$$

Values of ϕ, a_1 (water activity), and $\gamma_\pm$ at selected molalities are listed in Table V.

The osmotic coefficients of CsCl and $SrCl_2$ were also fitted by Pitzer's equation (*34*) with $A^\phi = 0.3920$, and the resulting parameters are given in Table VI. When the entire concentration range was fitted for CsCl, the equation cycled significantly around the experimental data and $\sigma = 0.0033$. By restricting the equation to concentrations of 7.355 mol/kg and lower, a much better fit was obtained ($\sigma = 0.0017$). Parameters for both fits are given in Table VI. The better-fit parameters were used in the mixed-salt calculations.

In the least-squares fits of eq 3 and Pitzer's equation (*34*) to CsCl data, unit weights were given to our data, the isopiestic data of Jones (*6*) and Bahia et al. (*8*), Kirgintsev and Luk'yanov's set with NaCl standard (*5*), and the freezing point depression (*29*) and emf data (*27*). Figure 1 shows the good agreement between these data and eq 3.

Several low-accuracy isopiestic data sets for CsCl (*1*, *2*, *4*, *5*, *7*) were given zero weight in the least-squares fits. Robinson's data are low (*1*, *2*), Frolov et al.'s results are also low and badly scattered (*7*), while Kirginstev and Luk'yanov's 1963 data are high (*4*). Kirgintsev and Luk'yanov's 1966 data with KCl standard (*5*) were in better agreement with eq 3 but were scattered. Makarov et al.'s (*3*) high-concentration results seem accurate. However, their experimental data could not be referred to the isopiestic reference values used here because only smoothed results were reported.

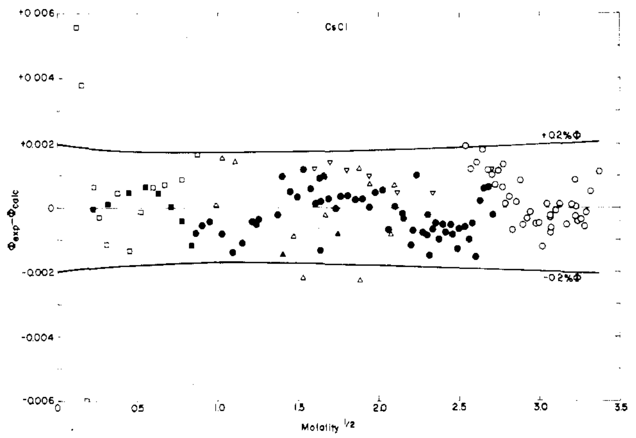

Figure 1. Differences between experimental and calculated osmotic coefficients of CsCl at 25 °C: (▽) Kirgintsev and Luk'yanov (*5*); (▲) Jones (*6*); (△) Bahia et al. (*8*); (□) Momicchioli et al. (*29*); (■) Mussini et al. (*27*); (●) this research NaCl standard; (○) this research $CaCl_2$ standard.

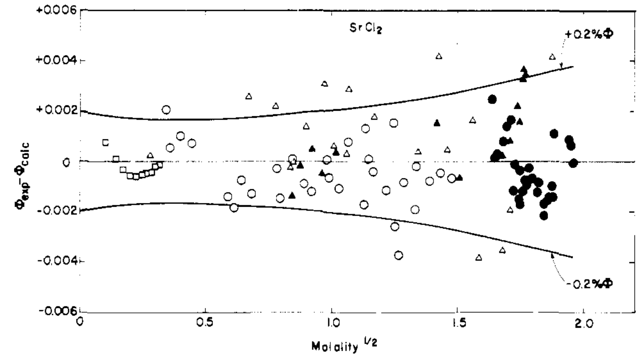

Figure 2. Differences between experimental and calculated osmotic coefficients of $SrCl_2$ at 25 °C: (△) Stokes (*10*); (○) Downes (*11*); (▲) Macaskill et al. (*12*); (●) this research; (□) estimated dilute solution data based on $CaCl_2$.

For $SrCl_2$, equal weights were given to the present results and three other sets of isopiestic data (*10*–*12*) in the least-squares fits. These four sets of data agree within ±0.25% and extend slightly into the supersaturated region. Stokes' single supersaturated concentration point was inconsistent with ours and was not included in the calculations. Robinson's isopiestic data (*9*) are as much as 2% low and were given zero weight in the least-squares fits.

Accurate low-concentration activity data are required for the integration of osmotic coefficient data to obtain activity coefficients. These low-concentration data are available for CsCl but not for $SrCl_2$. Dilute-solution osmotic coefficients for $SrCl_2$ were estimated by the following procedure.

An extension of the Åkerlöf–Thomas (*35*) approach was used as for $MgCl_2$ (*23*), employing accurate activity data for $CaCl_2$ (*19*). The difference between the experimental $SrCl_2$ osmotic coefficients and smoothed $CaCl_2$ osmotic coefficients is accurately represented by

$$\Delta\phi = -0.0544m + 0.0177m^{3/2} \tag{5}$$

using isopiestic data from 0.1 to 1.0 mol/kg. Equation 5 was then used to generate 10 points for $SrCl_2$ from 0.01 to 0.10 mol/kg at equal intervals, and these estimated values were also

Table V. Osmotic Coefficients, Water Activities, and Activity Coefficients at Round Molalities at 25 °C

m	ϕ	a_1	$\gamma_\pm$
	CsCl		
0.01	0.9661	0.999 652	0.8988
0.02	0.9546	0.999 312	0.8646
0.03	0.9466	0.998 977	0.8406
0.05	0.9351	0.998 317	0.8063
0.07	0.9267	0.997 665	0.7813
0.10	0.9173	0.996 700	0.7527
0.2	0.8979	0.993 550	0.6925
0.3	0.8866	0.990 462	0.6555
0.4	0.8790	0.987 41	0.6289
0.5	0.8736	0.984 39	0.6085
0.6	0.8695	0.981 38	0.5920
0.7	0.8665	0.978 38	0.5783
0.8	0.8642	0.975 40	0.5667
0.9	0.8626	0.972 42	0.5568
1.0	0.8614	0.969 44	0.5481
1.2	0.8603	0.963 49	0.5337
1.4	0.8603	0.957 53	0.5224
1.6	0.8613	0.951 56	0.5132
1.8	0.8629	0.945 57	0.5058
2.0	0.8652	0.939 56	0.4997
2.5	0.8727	0.924 40	0.4890
3.0	0.8821	0.909 05	0.4827
3.5	0.8928	0.893 5	0.4794
4.0	0.9041	0.877 8	0.4783
4.5	0.9157	0.862 0	0.4788
5.0	0 9274	0.846 1	0.4805
5.5	0.9390	0.830 2	0.4829
6.0	0.9501	0.814 3	0.4860
6.5	0.9608	0.798 5	0.4895
7.0	0.9708	0.782 8	0.4931
7.5	0.9801	0.767 3	0.4969
8.0	0.9886	0.752 0	0.5007
8.5	0.9963	0.737 0	0.5043
9.0	1.0031	0.722 3	0.5077
9.5	1.0089	0.708 0	0.5109
10.0	1.0139	0.694 0	0.5137
10.5	1.0178	0.680 4	0.5161
11.0	1.0209	0.667 2	0.5182
11.382[a]	1.0226	0.657 5	0.5194
	$SrCl_2$		
0.1	0.8478	0.995 429	0.5096
0.2	0.8494	0.990 860	0.4591
0.3	0.8612	0.986 13	0.4379
0.4	0.8770	0.981 22	0.4284
0.5	0.8951	0.976 10	0.4252
0.6	0.9147	0.970 77	0.4261
0.7	0.9356	0.965 22	0.4301
0.8	0.9576	0.959 44	0.4365
0.9	0.9806	0.953 42	0.4450
1.0	1.0045	0.947 16	0.4554
1.2	1.0552	0.933 85	0.4816
1.4	1.1093	0.919 49	0.5148
1.6	1.1666	0.904 04	0.5553
1.8	1.2269	0.887 5	0.6035
2.0	1.2898	0.869 9	0.6604
2.2	1.3548	0.851 2	0.7267
2.4	1.4216	0.831 6	0.8035
2.6	1.4895	0.811 1	0.8919
2.8	1.5581	0.790 0	0.9929
3.0	1.6266	0.768 2	1.108
3.2	1.6946	0.746 0	1.237
3.4	1.7612	0.723 5	1.382
3.5195[a]	1.8001	0.710 1	1.476
3.6	1.8259	0.701 0	1.543
3.8	1.8878	0.678 6	1.719
3.8426	1.9006	0.673 9	1.759

[a] Saturated solution.

Table VI. Parameters for Pitzer's Equation at 25 °C

	CsCl[a]	CsCl[b]		$SrCl_2$[c]
$\beta^{(0)}$	0.034 78	0.039 17	$(4/3)\beta^{(0)}$	0.377 92
$\beta^{(1)}$	0.039 74	−0.002 984	$(4/3)\beta^{(1)}$	2.167 5
C^{Φ}	−0.000 496	−0.001 183	$(2^{5/2}/3)C^{\Phi}$	−0.001 68
σ	0.001 7	0.003 3		0.002 4

[a] Maximum concentration, 7.3551 mol/kg. These parameters were used for mixed-salt calculations. [b] Maximum concentration, 11.382 mol/kg. [c] Maximum concentration, 3.8426 mol/kg.

included in the least-squares calculations. Figure 2 illustrates the difference between the experimental osmotic coefficents and eq 3 for the $SrCl_2$ best fit. The smoothed osmotic coefficients in Table V agree to within 0.2% with those recommended by Macaskill et al. (*12*) up to 3.0 mol/kg, but larger differences occur at higher concentratgions. Goldberg and Nuttall's recommended values (*36*) are also in reasonable agreement.

Pitzer and co-workers have developed equations for analyzing mixed-salt activity data in terms of the binary-solution equations and a two-parameter mixing term (*34*, *37*). Since these equations have been successfully applied to other alkali chloride mixtures (*8*, *37*, *38*), they were chosen to represent the NaCl-CsCl mixtures.

The 110 NaCl-CsCl points in Table II, and Kirgintsev and Luk'yanov's 45 points (*4*), were fitted to Pitzer's equations using equal weights. Least-squares fitting gave $\theta = -0.03886$ and $\psi = -0.00135$ with $\sigma = 0.0015$. Both parameters were statistically significant, and we consider this fit the "best" representation of the data. If ψ is fixed at zero, $\theta = -0.0456$ and $\sigma = 0.0021$. This second fit is less accurate for high concentrations of the NaCl-rich mixtures (maximum deviation 0.0066 vs. 0.0038) and low concentrations of CsCl-rich mixtures. With $\psi = \theta = 0$ the errors increased by 1 order of magnitude ($\sigma = 0.040$).

Mixed-salt data in Table II cover a wide variation in total concentration but are for only two mixed-salt ratios. Kirgintsev and Luk'yanov (*4*) studied a smaller concentration range, but with nine mixture compositions. These two studies agree well in the overlap region. Robinson's data (*2*) are systematically low by 1.0–3.0σ and were given zero weights in the least-squares fits. These deviations were expected since the "pure" CsCl solution osmotic coefficients from that study (*2*) are also low.

Hamer and Wu's equation for NaCl osmotic coefficients (*18*) was used to calculate reference solution osmotic coefficients for the mixed-salt solutions since it applies accurately to the NaCl solubility limit. On the other hand, Pitzer's binary equation (*34*) was used to represent NaCl and CsCl for the mixed-salt fits because Pitzer's binary constants are required to represent ternary-solution data. Unfortunately, Pitzer's NaCl equation has a minor end effect problem near its 6.0 mol/kg limit of application. Pitzer's NaCl ϕ values (*34*) agree quite well with Hamer and Wu (*18*) and Robinson and Stokes (*39*) up to 5.6 mol/kg but are higher by 0.003 at 6.0 mol/kg and 0.004 at saturation (6.16 mol/kg).

This use of one NaCl ϕ equation to calculate the experimental ϕ values, and a different one to represent the NaCl-CsCl ϕ data, has almost no effect on the internal consistency because the highest mixed-salt concentrations are isopiestic with 5.75 mol/kg NaCl, and calculated differences are small at this NaCl concentration. However, Pitzer's high ϕ values can affect the ψ and θ calculations since NaCl ϕ parameters are required to describe the mixed-salt ϕ at the maximum total molality of 7.00 (which is above the NaCl solubility limit).

In Pitzer's approach the differences between the single-salt osmotic coefficients and mixed-salt values, weighted by a function of the molality, are fitted to two mixing terms. The largest deviation of 2.6σ occurs at the highest concentration of NaCl-rich solution. The next largest deviation is 2.2σ, and several high concentration points have deviations larger than 2.1σ. These deviations seem to be due to the slight deficiency of Pitzer's binary NaCl equation near and above saturation.

rather than in the mixing terms (the calculations involve using NaCl ϕ parameters above the concentration region on which they are based). Apart from this minor problem, Pitzer's mixed-salt approach (*37*) does an excellent job in representing the NaCl–CsCl data and does a fairly good job even above the NaCl solubility limit.

Several recent studies (*8*, *38*) have found that a single mixing parameter is adequate for certain alkali chloride mixtures. The need for two mixing parameters for NaCl–CsCl may be partially due to compensation for the inadequacy of the binary NaCl equation above 5.6 mol/kg.

Acknowledgment

We thank F. H. Spedding for the loan of the isopiestic chambers, T. H. Lilley and A. Pethybridge for supplying the data of ref *6*, and Chris Peiper and K. S. Pitzer for copies of their computer programs. Chris Peiper also helped with some of the calculations.

Glossary

ϕ	molal osmotic coefficient
ν	number of ions formed by the dissociation of one molecule of solute
m	molal concentration, mol/kg, of the solute
$\gamma_\pm$	mean molal activity coefficient
a_1	water activity
A	Debye–Hückel constant
A_i	least-squares coefficients of eq 3 and 4
r_i	powers of eq 3 and 4
$\beta^{(0)}$, $\beta^{(1)}$,C^ϕ	parameters of Pitzer's equations for single electrolytes
θ, ψ	mixing parameters for Pitzer's equations
σ	standard deviation for fitting equations
y	ionic strength fraction of NaCl in mixed-salt solutions

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Received for review September 1, 1981. Accepted November 16, 1981. This work was performed under the auspices of the US Department of Energy by Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48. Support was provided by Geosciences, Office of Basic Energy Sciences, US DOE.

Excess Volumes of Homologous Series of Aliphatic Hydrocarbons with Chlorobenzene, Nitrobenzene, and Benzonitrile

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Excess volumes of nonelectrolyte solutions of *n*-heptane, *n*-octane, and *n*-nonane with chlorobenzene, nitrobenzene, and benzonitrile were measured at 313.15 K by using a dilatometer and are reported in this paper.

Introduction

The purpose of this paper is to report measurements of the excess volume of nonelectrolyte solutions of aliphatic hydrocarbons (*n*-heptane, *n*-octane, and *n*-nonane) with chlorobenzene, nitrobenzene, and benzonitrile. These measurements were made as a part of a continuing project on the thermodynamic and physical properties of nonelectrolyte solutions (1–4).

Experimental Section

The excess volumes have been determined at 313.15 K by using a single composition per loading type dilatometer de-

0021-9568/82/1727-0173$01.25/0