Pitzer's equation are useful approaches for modeling activity data of aqueous KCl–$MgSO_4$ mixtures from low to high concentrations.

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Glossary

A	symbols subscripted A refer to KCl
B	symbols subscripted B refer to $MgSO_4$
*	symbols with asterisks refer to KCl isopiestic standard
m_i	molal concentration of electrolyte i, mol·kg^{-1}
y_i	ionic strength fraction of electrolyte i
I	total ionic strength, mol·kg^{-1}
Φ	molal osmotic coefficient
ν_i	number of ions formed by the complete dissociation of one molecule of electrolyte i
b, α_1, α_2, $B^{\Phi}{}_i$, $C^{\Phi}{}_i$, $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$	parameters in Pitzer's equations for single electrolytes
${}^s\theta_{i,j}$, ${}^e\theta_{i,j}$, ${}^s\theta'_{i,j}$, ${}^e\theta'_{i,j}$, $\psi_{i,j,k}$	parameters in Pitzer's equations for mixed electrolytes
$\Phi_i{}^{\circ}$	molal osmotic coefficient of a solution containing electrolyte i only at the total ionic strength of the mixed solution
b_{01}, b_{02}, b_{03}, b_{12}, b_{13}	mixing parameters for Scatchard's neutral electrolyte treatment
$\sigma(\Phi)$	standard deviation of osmotic coefficients
$\gamma_{\pm}$	mean molal activity coefficient

Registry No. KCl, 7447-40-7; $MgSO_4$, 7487-88-9.

Literature Cited

(1) Pitzer, K. S. In "Activity Coefficients in Electrolyte Solutions"; CRC Press: Boca Raton, FL, 1979; Vol. 1, Chapter 7.
(2) Harned, H. S.; Robinson, R. A. "Multicomponent Electrolyte Solutions"; Pergamon Press: Oxford, 1968.
(3) Rard, J. A.; Miller, D. G. *J. Chem. Eng. Data* **1982**, *27*, 342.
(4) Ananthaswamy, J.; Atkinson, G. *J. Solution Chem.* **1982**, *11*, 509.
(5) Harvie, C. E.; Weare, J. H. *Geochim. Cosmochim. Acta* **1980**, *44*, 981.
(6) de Lima, M. C. P.; Pitzer, K. S. *J. Solution Chem.* **1983**, *12*, 171.
(7) de Lima, M. C. P.; Pitzer, K. S. *J. Solution Chem.* **1983**, *12*, 187.
(8) Platford, R. F. In "Activity Coefficients in Electrolyte Solutions"; CRC Press: Boca Raton, FL, 1979; Vol. 1, Chapter 3.
(9) Hamer, W. J.; Wu, Y. C. *J. Phys. Chem. Ref. Data* **1972**, *1*, 1074.
(10) Rard, J. A.; Habenschuss, A.; Spedding, F. H. *J. Chem. Eng. Data* **1976**, *21*, 374.
(11) Rard, J. A.; Miller, D. G. *J. Chem. Eng. Data* **1981**, *26*, 33.
(12) Scatchard, G. *J. Am. Chem. Soc.* **1961**, *83*, 2636.
(13) Rush, R. M. *Oak Ridge Natl. Lab.*, [*Rep.*] *ORNL* (*U.S.*) **1969**, *ORNL-4402*.
(14) Pitzer, K. S. *J. Solution Chem.* **1975**, *4*, 249.

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Osmotic Coefficients of Low-Equivalent-Weight Organic Salts. 2

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The osmotic coefficients of aqueous solutions of sodium benzoate, sodium salicylate, sodium 3-methylsalicylate, and sodium 3,5-diisopropylsalicylate by isopiestic measurements at 25 °C are reported. The osmotic coefficients decline with increasing molality of these salts except sodium benzoate. With sodium benzoate, the osmotic coefficients of the aqueous solution increase at low molality (>0.2 *m*), reach a maximum at ca. 1.2 *m*, and then descend slowly. Activity coefficients of these salts were computed from least-squares fits to the water activities.

Introduction

We have reported the isopiestic results of four two-component systems composed of sodium alkylbenzenesulfonate and water, and one three-component system containing sodium *p*-cymenesulfonate/NaCl/H_2O at 25 °C (*1*). Although we found some indication in these low-equivalent-weight sulfonate systems of the presence of either small aggregates or strong interactions between the ions, there appeared to be no evidence for micelles, commonly encountered with surfactants.

In this paper we present isopiestic measurements of sodium benzoate and three alkyl-substituted sodium salicylates. The salicylates are sodium salicylate ($S_{AC} = 0$), 3-methylsalicylate ($S_{AC} = 1$), and 3,5-diisopropylsalicylate ($S_{AC} = 6$). S_{AC} is the number of alkyl carbons on the benzene ring of the salicylates. These salts are also recognized as hydrotropes; that is, their aqueous solutions can solubilize substantial quantities of hydrocarbons (*2*–*5*). Among all the groups of low-equivalent-weight organic salts (protosurfactants) we have studied, salicylates show the most pronounced increases in solubilization in comparison with the analogous benzenesulfonates or benzoates (*4*). Sodium benzoate has about the same hydrotropic ability as benzenesulfonate (*3*). The solubilizing effect of the organic hydrotropic salts depends heavily on the average degree of alkyl substitution, but the un-ionized *o*-hydroxy group appears also to have a substantial effect on the hydrotropic property. The highest alkyl-substituted salicylate in this paper, sodium 3,5-diisopropylsalicylate, has not only the strongest hydrotropic properties among the protosurfactants we have studied (*4*), but also mimics most closely surfactants in chemical and phase behavior of multicomponent systems (*6*). Free energy studies of the aqueous solutions of these organic salts may help in understanding their hydrotropic properties and the role they play in solubilization.

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Table I. Isopiestic Molalities and Osmotic Coefficients for the Two-Component Systems (Organic Salt/H_2O)

organic salt	m_{KCl}[a]	m_{NaCl}[b]	m	organic salt ϕ_{obsd}	organic salt ϕ_{calcd}[c]
sodium benzoate		0.261	0.258	0.933	0.935
		0.360	0.353	0.940	0.938
		0.551	0.539	0.943	0.944
		0.713	0.697	0.948	0.948
		0.877	0.859	0.951	0.951
		1.051	1.034	0.953	0.953
		1.437	1.432	0.957	0.955
		1.610	1.637	0.953	0.955
		1.848	1.888	0.954	0.953
		1.962	2.024	0.951	0.951
sodium salicylate		0.203	0.204	0.920	0.920
		0.265	0.267	0.916	0.913
		0.379	0.386	0.905	0.903
		0.499	0.515	0.893	0.894
		0.604	0.628	0.887	0.887
		0.666	0.701	0.879	0.882
		0.972	1.049	0.866	0.864
		1.109	1.221	0.854	0.856
		1.585	1.831	0.832	0.831
		2.233	2.768	0.804	0.805
		2.720	3.508	0.796	0.796
sodium 3-methylsalicylate	0.124		0.125	0.917	0.912
	0.313		0.330	0.860	0.867
	0.537		0.581	0.831	0.828
	0.898		1.030	0.781	0.778
	1.301		1.612	0.726	0.728
	1.380		1.730	0.718	0.719
	1.657		2.186	0.686	0.685
	1.702		2.267	0.680	0.680
	2.218		3.092	0.658	0.658
sodium 3,5-diisopropylsalicylate		0.118	0.160	0.687	0.665
		0.122	0.185	0.614	0.632
		0.203	0.480	0.391	0.397
		0.232	0.588	0.364	0.363
		0.290	0.782	0.342	0.338
		0.320	0.874	0.337	0.335
		0.379	1.065	0.328	0.333
		0.498	1.403	0.322	0.321
		0.603	1.733	0.322	0.322

[a] Reference electrolyte was KCl. [b] Reference electrolyte was NaCl. [c] From least-squares fit; parameters in Table II.

Experimental Section

The source of sodium benzoate and salicylates used in this paper can be found in ref 3 and 4.

Osmotic coefficients

$$\phi = -(55.51/\sum_i m_i) \ln a_S \qquad (1)$$

were measured by the isopiestic method, in which solutions are equilibrated to the same vapor pressure with a solution of a reference salt of known dependence of solvent activity (a_s, pure solvent being the standard state) on molality. The reference salts (subscript r) were NaCl or KCl, and the osmotic coefficients of NaCl and KCl were taken from ref 7. The number 55.51 is for an aqueous solution and refers to the moles of water/kg solvent, and $\sum_i m_i$ is the total number of moles of solute ions/kg of solvent. Solute or solution of known molality, m, is initially weighed into cups and the concentration determined after equilibration by weighing. Osmotic coefficients were computed from the equation

$$\phi = \frac{\nu_r m_r \phi_r}{\sum m_i} \qquad (2)$$

ν being the number of moles of ions per mole of electrolyte (here 2). The apparatus used allows simultaneous equilibration of 12 samples in platinum cups; two of these were usually duplicate reference and five other duplicates were unknown. A series was started with concentrated solutions, and after each equilibration, solvent was added to the cups, in different amounts to the duplicates, so that equilibrium was approached from different molalities. The apparatus and procedure is described in more detail in ref 8.

Results

The results of isopiestic measurements at 25 °C of aqueous sodium benzoate and substituted sodium salicylates are given in Table I. The osmotic coefficients were fitted to an equation having a Debye–Hückel term ($S = -1.1708$ for 25 °C in aqueous solutions) and a power series in ionic strength, I (for these 1,1 electrolytes, the same as m)

$$\phi = 1 + \alpha^{DH}/2 + \tfrac{1}{2}[a^{(1)}I + a^{(2)}I^2 + a^{(3)}I^3 + a^{(4)}I^4] \qquad (3)$$

$$\alpha^{DH} = (2S/a^3 I)[1 + aI^{1/2} - 1/(1 + aI^{1/2}) - 2 \ln (1 + aI^{1/2})] \qquad (4)$$

a being the Debye–Hückel distance-of-closest-approach parameter. The lower limit of molality for which ϕ can be measured with fair accuracy by this technique is too high to determine a precise value of the Debye–Hückel a parameter. Instead of varying a in the least-squares analysis, we ran, as before (*1*) fits for each solute for a series of values between 1.0 and 3.0 at intervals of 0.5. From the deviations between observed and computed values, we selected rather arbitrarily a's of 1.0 for sodium benzoate, 2.0 for sodium salicylate and sodium 3-methylsalicylate, and 2.5 for sodium 3,5-diisopropylsalicylate, and fixed these in the fits. The parameters are given in Table II. The deviations for the least-squares fit except sodium 3,5-diisopropylsalicylate were comparable to inorganic salts. The absolute value of the $a^{()}$ power series terms necessary to fit the data, except in the case of sodium salicylate, were greater than most strong inorganic electrolytes (*9*). From these coefficients, values of activity coefficients were computed by the equation: (*10*)

$$\ln \gamma_\pm = \frac{SI^{1/2}}{1 + aI^{1/2}} + \tfrac{1}{2}(2a^{(1)}I + \tfrac{3}{2}a^{(2)}I^2 + \tfrac{4}{3}a^{(3)}I^3 + \tfrac{5}{4}a^{(4)}I^4) \qquad (5)$$

Values of ϕ and $\gamma_\pm$ at rounded molalities from these fits are given in Table III.

Table II. Parameters for the Two-Component System[a]

parameters	organic salts: sodium benzoate	sodium salicylate	sodium 3-methylsalicylate	sodium 3,5-diisopropylsalicylate
a	(1.0)	(2.0)	(2.0)	(2.5)
$a^{(1)}$	0.38917 ± 0.016927	−0.15528 ± 0.0097477	−0.46328 ± 0.029775	−4.353 ± 0.15447
$a^{(2)}$	−0.33229 ± 0.045202	0.029297 ± 0.017007	0.24287 ± 0.05410	5.7435 ± 0.47063
$a^{(3)}$	0.13914 ± 0.036827	−0.004758 ± 0.0086077	−0.093914 ± 0.030109	−3.3148 ± 0.45178
$a^{(4)}$	−0.023831 ± 0.009320	0.0006595 ± 0.0013114	0.014487 ± 0.005102	0.69737 ± 0.13539
deviations[b]	0.0017	0.0022	0.0043	0.131

[a] Debye–Hückel a fixed at listed values. [b] $(\sum(\text{observed } \phi - \text{computed } \phi)^2/(\text{no. observations} - \text{no. of varied parameters}))^{1/2}$.

Table III. Osmotic and Activity Coefficients of Organic Salts[a]

	ϕ^b				$\gamma_{\pm}{}^b$			
molality	(1)	(2)	(3)	(4)	(1)	(2)	(3)	(4)
0.1	0.937	0.934	0.920	0.759	0.783	0.785	0.762	0.548
0.2	0.934	0.920	0.893	0.613	0.746	0.736	0.696	0.382
0.3	0.936	0.910	0.873	0.508	0.729	0.704	0.650	0.288
0.4	0.939	0.902	0.855	0.436	0.717	0.680	0.615	0.230
0.5	0.943	0.895	0.840	0.389	0.710	0.660	0.585	0.192
0.6	0.946	0.889	0.826	0.360	0.705	0.643	0.560	0.166
0.7	0.948	0.883	0.814	0.344	0.701	0.628	0.538	0.149
0.8	0.950	0.877	0.802	0.337	0.698	0.614	0.518	0.135
0.9	0.952	0.871	0.791	0.334	0.695	0.602	0.500	0.125
1.0	0.953	0.866	0.781	0.333	0.692	0.591	0.484	0.116
1.5	0.955	0.844	0.737	0.318	0.681	0.545	0.421	0.0870
2.0	0.952	0.825	0.698	0.405	0.670	0.510	0.373	0.0784
2.5	0.931	0.811	0.667		0.648	0.482	0.337	

[a] At round concentration from least-squares fit. [b] (1) Sodium benzoate; (2) sodium salicylate; (3) sodium 3-methylsalicylate; (4) sodium 3,5-diiospropylsalicylate.

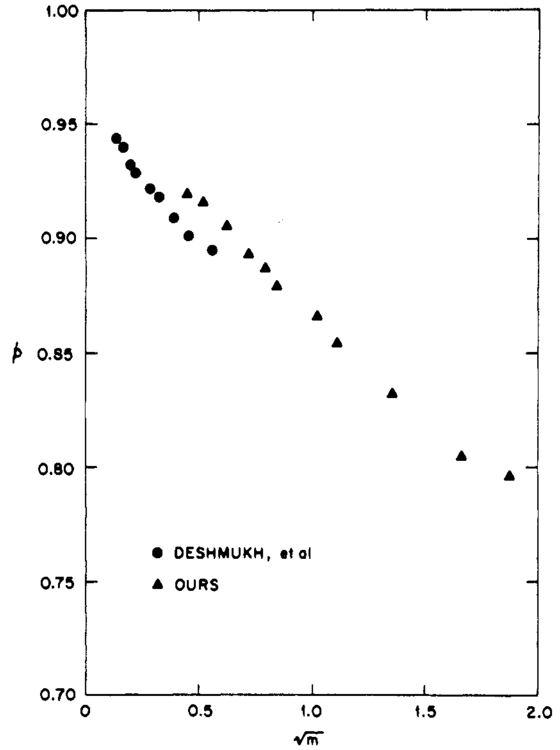

Figure 1. Comparison of osmotic coefficients of sodium salicylate between literature (ref 11) values and our results.

Discussion

Several research groups (*11*–*13*) have studied the osmotic and activity coefficients of aqueous sodium benzoate and sodium salicylate at 25 °C. Unfortunately only one of them (*11*) reported the experimental data of osmotic coefficients of sodium salicylate, at rounded concentrations, from 0.02 to 0.3 *m*; none reported them at experimental concentrations. For consistent comparison with our results, we fitted them to eq 3 with Debye–Hückel *a* parameter of 2.0, the value adopted in experiments of our results.

Figure 1 compares our ϕ values with the calculated ϕ from ref 11 vs. the square root of molality. In the concentration range of 0.1 to ca. 0.3 *m*, the two sets of data differ from each other in ϕ by an almost constant difference of 0.02 (our data are about 2% higher than theirs at corresponding molalities); in agreement, ref 13 states that their data were also about 2–3% different from those in ref 11. The three sets of data were produced by different techniques (the experiment was done by thermoelectric osmometer in ref 11, by vapor pressure osmometric measurement in ref 13, and by isopiestic measurement in our work), and the difference may be related to this.

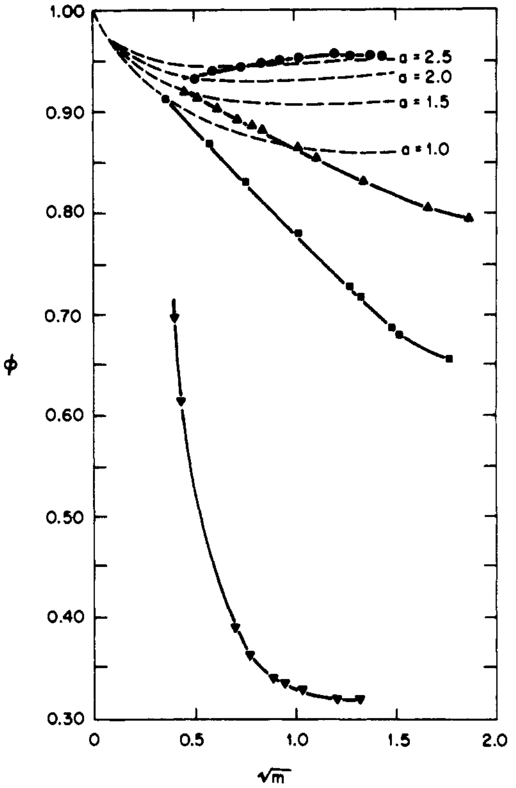

Figure 2. Osmotic coefficients of aqueous solution of organic salts: dashed curves, Debye–Hückel with indicated values of distance-of-closest-approach parameter; solid curves, calculated from least-squares fit; points, experimental points (●, sodium benzoate; △, sodium salicylate; ♦, sodium 3-methylsalicylate, and ▽, sodium 3,5-diisopropylsalicylate).

Figure 2 shows the trend of ϕ with increase of molality varies with the substitutions on the benzene ring. The osmotic coefficients of salicylates decline with the increasing molality, more steeply at higher S_{AC}. The extra *o*-hydroxy group also affects the ϕ values (compare benzoate and salicylate). The ϕ values of the alkyl-substituted salicylates at low molalities fall below those computed from the Debye–Hückel for reasonable values of the *a* parameter, a behavior also seen with sodium alkylbenzenesulfonate/H_2O systems (*1*). However, the ϕ values of sodium benzoate at low concentrations increase with increasing molality and reach a maximum at ca. 1.2 *m*, then decrease steadily. This is in agreement with the findings of ref 12 that the activity coefficients of sodium benzoate go through a maximum plateau near 1 *m* and descend above it. In this respect, there is a qualitative resemblance to the behavior of benzoates substituted with one and more than one methyl group (*p*-methylbenzoate (*13*), 2,4-dimethylbenzoate, and 2,4,6-trimethylbenzoate (*14*)) and to those sodium salts of fatty acids with more than four alkyl carbons (*15*). These systems also have maximums in ϕ as a function of molality. However, the peak here is indistinct and the ϕ values not greatly different from those of sodium benzenesulfonate (*16*). Robinson et al. (*15*) reported maximum in the osmotic and activity coefficients of sodium salts of fatty acids starting from valerate (C_5 salt) to caprate (C_{10} salt) and concluded that polymerization of anions in a certain molality of different salt had occurred. Desnoyers et al. (*12*) also suggested the existence of the maximum in the activity coefficient curve of sodium benzoate above 1 *m* and interpreted it as micelle formation. The osmotic and activity

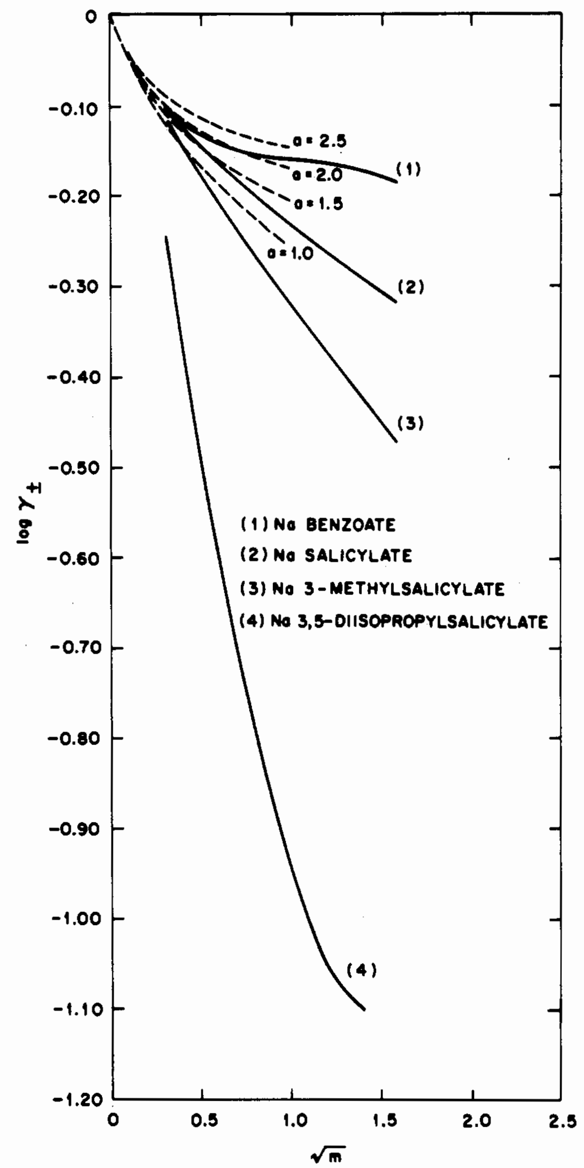

Figure 3. Activity coefficients of aqueous solutions of organic salts: dashed curves, Debye-Hückel with indicated values of *a*.

coefficient curves of benzoate resemble those of benzenesulfonate and the maxima of these curves are insignificant compared to those of sodium salts of fatty acids. Although there is the possibility of aggregate formation, it is questionable that these aggregates are as large as micelles.

It is very interesting to note that the ϕ values of the substituted salicylates fall faster than the analogous alkylbenzenesulfonates at corresponding alkyl carbon numbers and at corresponding molalities. The curves of ϕ vs. $m^{1/2}$ of sodium salicylate approximates that of sodium *p*-toluenesulfonate (*1*), and 3-methylsalicylate approximates that of *p*-ethylbenzenesulfonate or 2,4,6-trimethylbenzenesulfonate (*16*). The decline of 3,5-diisopropylsalicylate is much steeper than sodium 2,5-diisopropylbenzenesulfonate (*1*). The pattern may correlate with the relative hydrotropic nature of these organic salts. On the other hand, sodium benzoate has a hydrotropic property approximately that of benzenesulfonate, while the ϕ values of the former are about 3% higher than those of the latter at corresponding molalities. The exact reason for this is not clear, but the differences in any case are not large.

Figure 3 shows the activity coefficient curves of these organic salts computed from parameters of the least-squares fit of osmotic coefficients (*10*) at rounded concentrations.

Despite the steeper decline in ϕ and $\gamma_\pm$ of substituted salicylates, the osmotic coefficients in Figure 2 do not exhibit in the concentration range of these measurements a sharp discontinuity, seen at critical micelle concentrations of surfactants (*17*–*20*). However, the decline in ϕ with molality, especially in the diisopropylsalicylate/H_2O system, in which the ϕ values drastically fall below the predicted for reasonable Debye–Hückel parameters, may suggest the possibility of formation of small aggregates or the existence of moderate to strong interaction between the organic anions. It is doubtful that large aggregates, i.e., micelles are formed. Our preliminary small-angle neutron scattering measurements of aqueous solutions of diisopropylsalicylate supports this conclusion.

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Registry No. Sodium benzoate, 532-32-1; sodium salicylate, 54-21-7; sodium 3-methylsalicylate, 32768-20-0; sodium 3,5-diisopropylsalicylate, 79427-97-7.

Literature Cited

(1) Ho, P. C.; Kahlow, M. A.; Bender, T. M.; Johnson, J. S., Jr. *J. Phys. Chem.* **1984**, *88*, 4152–4158.
(2) Ho, P. C.; Ho, C.-h.; Kraus, K. A. *J. Chem. Eng. Data* **1979**, *24*, 115–118.
(3) Ho, P. C.; Ogden, S. B. *J. Chem. Eng. Data* **1979**, *24*, 234–237.
(4) Ho, P. C.; Kraus, K. A. *Soc. Pet. Eng. J.* **1982**, *22*, 363–370.
(5) Ho, P. C. *J. Chem. Eng. Data*, **1985**, *30*, 88–90.
(6) Ho, P. C. *J. Phys. Chem.* **1982**, *86*, 4634–4642.
(7) Robinson, R. A.; Stokes, R. H. "Electrolyte Solutions", 2nd ed.; Butterworths: London, 1965.
(8) Rush, R. M.; Johnson, J. S. Jr. *J. Chem. Eng. Data* **1966**, *11*, 590–592.
(9) Rush, R. M. Report ORNL-4402; Oak Ridge National Laboratory: Oak Ridge, TN, 1969.
(10) Lietzke, M. H.; Stoughton, R. W. *J. Phys. Chem.* **1961**, *65*, 508–509.
(11) Deshmukh, A.; Fleming, R. *J. Pharm. Pharmacol.* **1969**, *21*, (*Suppl.*), 91s–97s.
(12) Desnoyers, J. E.; Pa'ge, R.; Perron, G.; Fortier, J.-L.; Leduc, P.-A.; Platford, R. F. *Can. J. Chem.* **1973**, *51*, 2129–2137.
(13) Wesselmann, G.; Rohdewald, P. *J. Chem. Res., Miniprint* **1976**, 2701–2719.
(14) Ho, P. C., unpublished results.
(15) Smith, E. R. B.; Robinson, R. A. *Trans. Faraday Soc.* **1942**, *38*, 70–78.
(16) Bonner, O. D.; Rogers, O. C. *J. Phys. Chem.* **1960**, *64*, 1499–1501.
(17) McBain, J. W.; Boulduan, O. E. A. *J. Phys. Chem.* **1943**, *47*, 94–103.
(18) Desnoyers, J. E.; Caron, G.; Delisi, R.; Robers, D.; Roux, A.; Peron, G. *J. Phys. Chem.* **1983**, *87*, 1397–1406.
(19) Burchfield, T. E.; Woolley, E. M. *J. Phys. Chem.* **1984**, *88*, 2149–2155.
(20) Woolley, E. M.; Burchfield, T. E. *J. Phys. Chem.* **1984**, *88*, 2155–2163.

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