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

S. Subba Reddy, K. Dayananda Reddy, and M. V. Prabhakara Rao*

Sri Venkateswara University Chemical Laboratories, Tirupati 517 502, Andhra Pradesh, India

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-

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Table I. Boiling Points and Densities (ρ) of the Pure Components

	bp, K		ρ, g cm^{-3}	
	present work	ref *6*	present work	ref *6*
n-heptane	371.60	371.65	0.675 25	0.675 26
n-octane	398.76	398.81	0.694 47	0.694 50
n-nonane	423.82	423.92	0.709 92	0.709 94
chlorobenzene	404.82	404.87	1.095 69	1.095 74
nitrobenzene	483.71	483.81	1.193 38	1.193 41
benzonitrile	464.15	464.25	0.996 21	0.996 28

scribed by Rao and Naidu (*1*). The excess volumes are accurate to ±0.003 cm^3 mol^{-1}. The dilatometer was standardized with the cyclohexane–benzene system at 298.15 K. The measured excess volumes are in agreement with the earlier values reported (*5*).

Purification of Materials. Chlorobenzene (BDH) was dried with either calcium chloride or phosphorus pentoxide and fractionally distilled. Nitrobenzene (BDH) was dried over anhydrous calcium chloride for 2 days and the dried sample was distilled by using a 1-m fractionating column. Benzonitrile (Riedel) was dried over freshly fused calcium chloride and distilled at atmospheric pressure. *n*-Heptane (BDH) was thoroughly shaken twice with concentrated sulfuric acid and washed with water, dilute potassium hydroxide solution, and again with water. The sample was kept over KOH pellets for 24 h and finally fractionated. *n*-Octane (BDH) was passed through silica gel and fractionally distilled. *n*-Nonane (VEB) was fractionally distilled twice. The purity of the above samples has been verified from densities and boiling points reported in the literature (*6*); the densities are accurate to 5 parts in 10^5 parts (see Table I).

Results and Discussion

The excess volume data at 313.15 K of all nine binary liquid mixtures are presented in Table II. The excess volumes, V^E, are negative over the entire range of composition in all of the binary liquid mixtures, except in the system *n*-nonane with chlorobenzene at 313.15 K. The negative excess volumes for the above mixtures fall in the following order: *n*-heptane + chlorobenzene > *n*-octane + chlorobenzene > *n*-nonane + chlorobenzene; *n*-heptane + nitrobenzene > *n*-octane + nitrobenzene > *n*-nonane + nitrobenzene; *n*-heptane + benzonitrile > *n*-octane + benzonitrile > *n*-nonane + benzonitrile.

The excess volume–composition curves are symmetric over the entire range of composition in the case of aliphatic hydrocarbons with chlorobenzene, and the curves for all other systems show a maximum value at 0.3 mole fraction of the hydrocarbon. The excess volume–composition curves of the systems are given by the equation

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

where x_A and x_B are the mole fractions of the 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. The values of these constants are included in Table III along with the standard deviation σ, which is evaluated from the equation

$$\sigma = +[(V^E(\text{exptl}) - V^E(\text{calcd}))^2/(n - p)]^{1/2} \qquad (2)$$

where *n* is the number of results and *p* is the number of parameters used in eq 1.

Table II. Excess Volumes of Aliphatic Hydrocarbons with Chlorobenzene, Nitrobenzene, and Benzonitrile at 313.15 K

x_A[a]	V^E, cm^3 mol^{-1}	ΔV^E, cm^3 mol^{-1}	x_A[a]	V^E, cm^3 mol^{-1}	ΔV^E, cm^3 mol^{-1}
		n-Heptane + Chlorobenzene			
0.1326	−0.189	+0.003	0.5080	−0.293	+0.008
0.2187	−0.237	−0.003	0.6514	−0.217	−0.007
0.3188	−0.247	−0.005	0.7488	−0.175	−0.004
0.4954	−0.240	−0.006	0.8102	−0.148	+0.001
		n-Octane + Chlorobenzene			
0.1167	−0.064	+0.004	0.5223	−0.135	+0.009
0.2268	−0.089	−0.007	0.6610	−0.110	+0.000
0.3800	−0.120	−0.004	0.7430	−0.090	−0.002
0.4116	−0.130	+0.004	0.9247	−0.065	−0.004
		n-Nonane + Chlorobenzene			
0.1207	−0.038	+0.001	0.4598	0.060	+0.000
0.2414	0.050	−0.003	0.5955	0.061	−0.000
0.3153	0.055	−0.001	0.7726	0.063	+0.007
0.3937	0.059	+0.000	0.8276	0.045	−0.005
		n-Heptane + Nitrobenzene			
0.1276	−0.427	−0.000	0.5676	−0.606	−0.003
0.2008	−0.555	−0.005	0.6526	−0.553	+0.004
0.3023	−0.702	+0.002	0.7432	−0.460	+0.008
0.4250	−0.679	−0.004	0.8244	−0.344	+0.003
		n-Octane + Nitrobenzene			
0.1230	−0.300	−0.003	0.5245	−0.483	+0.000
0.2265	−0.450	+0.009	0.6752	−0.375	−0.004
0.3791	−0.518	+0.001	0.7870	−0.269	−0.002
0.4198	−0.517	+0.000	0.8398	−0.215	+0.003
		n-Nonane + Nitrobenzene			
0.1252	−0.225	+0.002	0.5006	−0.313	+0.002
0.1912	−0.286	−0.005	0.6522	−0.222	−0.008
0.3661	−0.346	+0.001	0.7224	−0.182	−0.003
0.4827	−0.326	+0.009	0.8274	−0.119	+0.004
		n-Heptane + Benzonitrile			
0.1344	−0.369	+0.005	0.5060	−0.541	+0.007
0.2031	−0.469	−0.006	0.6619	−0.401	+0.009
0.3763	−0.575	−0.004	0.7282	−0.314	−0.007
0.4530	−0.555	−0.008	0.8293	−0.190	−0.003
		n-Octane + Benzonitrile			
0.1374	−0.168	−0.000	0.5301	−0.292	+0.003
0.2366	−0.249	−0.004	0.6272	−0.227	−0.004
0.3907	−0.317	+0.006	0.7211	−0.171	−0.005
0.4142	−0.320	+0.008	0.8158	−0.109	+0.005
		n-Nonane + Benzonitrile			
0.1091	−0.174	+0.001	0.5038	−0.150	+0.000
0.2000	−0.224	−0.001	0.6383	−0.103	+0.000
0.3607	−0.202	−0.006	0.7072	−0.093	+0.007
0.4765	−0.162	+0.001	0.8050	−0.063	−0.004

[a] Mole fraction of hydrocarbon.

Table III. Values of the Arbitrary Constants in Eq 1 and Standard Deviation, σ, at 313.15 K for All Nine Binary Liquid Mixtures[a]

system	a_0	a_1	a_2	σ
n-heptane + chlorobenzene	−0.9837	+0.3894	−0.6502	0.006
n-octane + chlorobenzene	−0.5078	+0.0656	−0.0256	0.005
n-nonane + chlorobenzene	+0.2399	+0.0230	+0.2184	0.003
n-heptane + nitrobenzene	−2.6336	+0.9456	−0.8051	0.004
n-octane + nitrobenzene	−1.9752	+0.8318	−0.3614	0.004
n-nonane + nitrobenzene	−1.2436	+0.8463	−0.2877	0.005
n-heptane + benzonitrile	−2.1496	+1.2668	−0.0983	0.006
n-octane + benzonitrile	−1.1974	+0.5755	+0.3641	0.005
n-nonane + benzonitrile	−0.6041	+0.8211	−0.8676	0.003

[a] All numbers in units of cm^3 mol^{-1}.

$$\Delta V^E = V^E(\text{obsd}) - V^E(\text{calcd (eq 1)})$$

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Received for review July 8, 1981. Accepted November 18, 1981. S.S.R. is thankful to the University Grants Comission for giving financial assistance under the faculty improvement program.

Two-Liquid-Phase Boundaries and Critical Phenomena at 275–400 °C for High-Temperature Aqueous Potassium Phosphate and Sodium Phosphate Solutions. Potential Applications for Steam Generators

William L. Marshall
Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

Two-liquid-phase boundaries at temperatures between 275 and 400 °C were determined for potassium phosphate and sodium phosphate aqueous solutions for compositions from 0 to 60 wt % dissolved salt. The stoichiometric mole ratios, K/PO$_4$ or Na/PO$_4$, were varied from 1.00 to 2.12 and from 1.00 to 2.16 for the potassium and sodium systems, respectively. Liquid–vapor critical temperatures were also determined for most of the dilute liquid phases that formed. The minimum temperatures (below which a single solution existed) of two-liquid-phase formation were 360 °C for the potassium system and 279 °C for the sodium system at mole ratios of 2.00 and 2.16, respectively. For the sodium system at mole ratios greater than 2.16, solids crystallized at lower temperatures as expected from earlier studies. In contrast, potassium solutions that were explored at mole ratios from 2.12 to 3.16 and at temperatures below 360 °C did not produce solid phases or liquid–liquid immiscibilities. Aside from the generally unusual observations of two immiscible liquids in an aqueous inorganic salt system, the results could possibly be applied to the use of phosphate additives in steam power generators.

Introduction

High-temperature aqueous sodium phosphate solutions of very low concentrations (0–100 ppm) have been applied to reducing scale formation in power plant steam generators as critically reviewed by Garnsey (*1*). However, in recent times a particular corrosion of steam generator tubes in nuclear pressurized water systems (the corrosion commonly defined as "thinning") was attributed in part to sodium phosphate additives. Consequently, their use in nuclear pressurized water power plants was greatly reduced, which appeared to diminish the problem of thinning. In some steam generators corrosion subsequently occurred to form oxides in the holes of support plates through which steam generator tubes passed. Continued corrosion has "dented" steam generator tubes and has even necessitated costly replacement of some of the steam generators.

After the discovery by Broadbent et al. (*2*) that aqueous solutions of disodium hydrogen phosphate form two immiscible liquids at temperatures near 300 °C, Garnsey (*1*) proposed that the resulting concentrated and strongly corrosive solution, possibly produced by boiling concentration, may have corroded the steam generator tubes to cause thinning. Recently, the analogous dipotassium hydrogen phosphate–water system has been studied at this laboratory at temperatures from 100 to 400 °C (*3*), motivated by the earlier work of Broadbent et al. (*2*), by the proposals of Garnsey (*1*), and by knowledge that at temperatures below 100 °C potassium salts are more soluble than the analogous sodium salts (*4*, *5*). This recent work showed that aqueous K_2HPO_4 solutions at high temperatures still were much more soluble than those of Na_2HPO_4. A two-liquid-phase region was also discovered but with a minimum temperature of 360 °C, which was approximately 85 °C higher than that estimated for corresponding Na_2HPO_4 solutions (*2*). Substitution of potassium phosphate for sodium phosphate as an additive would therefore prevent the formation of a second liquid phase in the region of steam generator operation (275–325 °C) that otherwise could have caused thinning as proposed by Garnsey (*1*). This substitution might again make phosphates useful in eliminating particular problems of corrosion (including denting) as suggested earlier (*3*).

The present study on liquid–liquid immiscibilities expands upon those presented previously by Broadbent et al. (*2*), very recently by Wetton (*6*), and by Marshall et al. (*3*) to quantitatively describe comparative temperature–composition immiscibility boundaries for aqueous sodium phosphate and potassium phosphate solutions of mole ratios, Na/PO$_4$ and K/PO$_4$, varying from 1.0 to just above 2.0. The two systems are explored at higher mole ratios and show the expected formation of solid phases for the sodium system (*6*–*10*) but none for the potassium system over the range of exploration.

Experimental Procedures

Reagents. Dipotassium hydrogen phosphate (K_2HPO_4) and tripotassium phosphate hydrate ($K_3PO_4 \cdot nH_2O$) used were J. T. Baker Chemical Co. analyzed reagent grade, and potassium dihydrogen phosphate (KH_2PO_4) was Fisher Scientific Co. certified ACS grade. Disodium hydrogen phosphate (Na_2HPO_4) and trisodium phosphate hydrate (analyzed to be $Na_{3.16}(OH)_{0.16}PO_4 \cdot 12H_2O$) were obtained from Fisher Scientific Co., and sodium dihydrogen phosphate hydrate ($NaH_2PO_4 \cdot H_2O$) was obtained from J. T. Baker Co.; these salts were the same grades of purity as those for the potassium phosphates.

Liquid–Liquid Immiscibility. Several series of solutions, each of a given constant mole ratio, K/PO$_4$ or NaPO$_4$, but with differing weight percents for each solution, were prepared gravimetrically from the above solids and distilled water. Some compositions with high weight percent solid were not entirely soluble at 25 °C, as expected from the literature (*4*, *5*). These particular compositions were heated at 50–75 °C in order to

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