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and C_2 result from regression of just the ternary data.

Second virial coefficients B_{ij} required for estimation of vapor-phase nonidealities come from the correlation of Hayden and O'Connell (*13*).

Results of correlation for the binary systems, together with all ancillary information, are summarized in Table VI. With parameters for the binary systems fixed at the values of Table VI, the ternary-mixture data are correlated when the parameters of eq 2 have the values $C_0 = 2.460 \pm 0.032$, $C_1 = 1.396 \pm 0.035$, and $C_2 = 1.377 \pm 0.061$. The root-mean-square (rms) value of δP for the ternary data is 0.053 kPa; the maximum $|\delta P|$ is 0.181 kPa.

Discussion

No previous work comparable with ours appears in the literature for the ternary system or for the acetone/1,4-dioxane binary. The data of Chaudhry et al. (*4*) for acetone/water at 50 °C and the data of Balcázar-Ortiz et al. (*5*) for 1,4-dioxane/water at 50 °C are both nearly as well correlated by our equations for G^E as are our own data sets. The rms δP in each case is ~0.03 kPa.

The results of this study appear pictorially in Figures 1-3. Figure 1 is a contour diagram showing lines of constant G^E on a triangular mole-fraction grid. Figure 2 is an oblique view of the same surface, and Figure 3 is a similar representation of the P-x surface. There is no ternary azeotrope and only one binary azeotrope: for 1,4-dioxane/water at $x_{\text{dioxane}} = 0.5664$ and $P^{az} = 22.040$ kPa.

Glossary

A_{ij}, A_{ji}	parameters in eq 1
B_{ij}	second virial coefficient
C_0, C_1, C_2	parameters in eq 2
G^E	excess Gibbs function, liquid phase
g	$G^E/(RT)$
P	total pressure
P_i^{sat}	vapor pressure of pure i
R	universal gas constant
T	absolute temperature
V_i^L	molar volume of pure liquid i
x	mole fraction, liquid phase

Greek Letters

λ_{ij}, λ_{ji}, η	parameters in eq 1
δ	denotes the difference, calculated - experimental

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Solubility of Benzoic Acid in Aqueous Polymeric Solutions

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Solubility of benzoic acid in distilled water and aqueous solutions of poly(vinyl alcohol) (PVA) and poly(vinylpyrrolidone) (PVP) containing 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, and 6.0% polymer by weight has been determined in the temperature range of 30-55 °C. It has been observed that, at any given temperature, the solubility in polymer solution is more than that in water, increases with increasing polymer concentration, and approaches a constant value at higher concentrations.

Introduction

Solid-liquid mass-transfer investigations with both Newtonian and non-Newtonian fluids are frequently made by following the rate of dissolution of a low-solubility solute such as benzoic acid because of many inherent advantages (*1*) In all such studies, accurate solubility data are required. This communication reports the solubility of benzoic acid in distilled water and a number of aqueous solutions of poly(vinyl alcohol) (PVA) and poly(vinylpyrrolidone) (PVP) over a polymer concentration range of 0.5-6.0% polymer by weight. Besides applications in the above area, these data will also be useful to the pharmaceutical industry where benzoic acid, PVA, and PVP are used in many pharmacuetical preparations.

Experimental Section

Materials. Conductivity-grade distilled water was prepared in the laboratory. Poly(vinyl alcohol) (mol wt = 14000; natural granules; viscosity of 4% aqueous solution at 20 °C, 4-6 cP; degree of hydrolysis, 98.5-100%; residual monomer content, 0-3%; product number, 30573) was obtained from BDH Chemicals Ltd., (Poole, England) and poly(vinylpyrrolidone) (PVP) (mol wt = 25000; natural powder; residual monomer content, 12.6 ± 0.3%; product number, 39579A; batch number,

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Table I. Solubility Data of Benzoic Acid

temp, °C	solubility, g/L													
		aq PVA soln, wt %						aq PVP soln, wt %						
	water	0.5	1.0	2.0	3.0	4.0	6.0	0.5	1.0	2.0	3.0	4.0	5.0	6.0
30.0	4.033	4.307	4.717	5.403	6.567	7.413	8.103	5.057	5.720	6.580	7.410	8.433	9.001	9.920
35.0	4.607	5.033	5.630	6.067	6.885	8.010	8.487	5.443	6.107	7.217	8.063	8.933	9.817	10.19
40.0	5.403	6.010	6.423	7.183	8.100	8.807	9.553	6.001	6.710	7.793	8.777	9.593	10.51	10.71
45.0	6.417	6.997	7.483	7.997	8.967	9.587	9.810	6.807	7.483	8.487	9.497	10.42	11.17	11.38
50.0	7.617	8.210	8.793	9.210	10.07	10.61	11.35	8.213	8.800	9.867	10.91	12.07	12.98	13.24
55.0	8.607	8.672	10.00	10.43	10.95	11.90	11.88	9.503	10.21	11.05	12.48	13.17	13.80	13.97

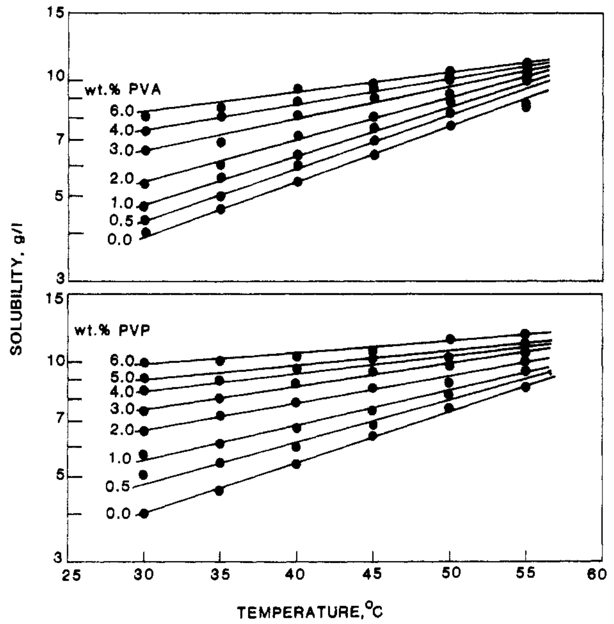

Figure 1. Effect of temperature on the solubility of benzoic acid in water and aqueous polymeric solutions.

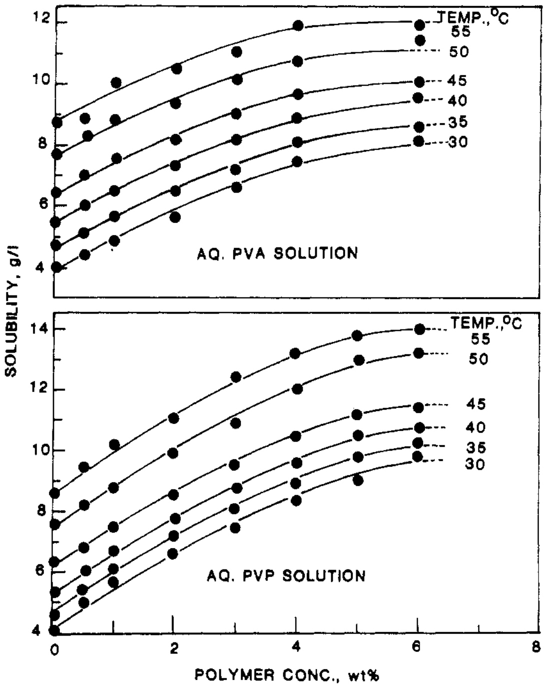

Figure 2. Effect of polymer concentration on the solubility of benzoic acid in aqueous polymeric solutions.

06096/4733) from Lab-Chem-Industry (Bombay, India). The benzoic acid (LR Grade) used was obtained from Sarabhai Merck (Baroda, India). Aqueous polymeric solutions were prepared in batches of 6 L by dissolving a known amount of polymer in an appropriate amount of distilled water. Heating up to boiling temperature was necessary for dissolving PVA. All of the polymeric solutions were allowed to stand for 36 h before use in the actual experiments.

Procedure. Solubilities were determined by equilibrating powdered benzoic acid with the solvents in 500-mL Erlenmeyer flasks shaken in a carefully controlled (±0.05 °C) thermostat. The procedure employed was exactly similar to that used earlier (*1*). Special care was taken to exclude CO_2 from all of the systems during experimentation. All measurements were made in quadruplicate, and reproducibility was within ±2%.

Results and Discussion

The solubility values of benzoic acid in distilled water and aqueous solutions of PVA and PVP are listed in Table I. Present experimental values for water are in close agreement with those reported by others (*1-6*).

Solubility-temperature plots for benzoic acid-aqueous PVA and benzoic acid-aqueous PVP solutions are given on semilogarithmic coordinates in Figure 1. At a particular temperature, the solubility in polymeric solutions is observed to be always higher than that in water and increases with increasing polymer concentration.

Figure 2 gives a plot of solubility against polymer concentration with temperature as the parameter. This figure shows that the solubility of benzoic acid in both aqueous PVA and aqueous PVP solutions increases with increasing polymer concentration and approaches a constant value at higher concentrations (>6.0 wt %). A similar effect of polymer concentration on solubility has been reported by Kumar et al. (*1*) and Hansford and Litt (*7*) for benzoic acid-aqueous cmc systems. Their explanation for this, however, does not seem to hold because an acid-base-type reaction may not take place in the case of PVA or PVP-benzoic acid systems.

Enhancement in the solubility in polymer solutions over that in water is probably due to the solvation of more solute molecules caused by the increased solute-water-polymer interactions. Such interactions cause increased free-energy or entropy changes and hence an increase in the solubility. At higher polymer concentrations, the presence of large numbers of polymer chains and their own interactions are likely to hinder and limit the earlier mentioned interactions with solute molecules. These in turn may reduce and limit the free-energy or entropy changes and may lead to a constant value of the saturation solubility. These speculations, however, are only of qualitative importance, and a better explanation would require rather more rigorous experimental and theoretical treatment of the problem.

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Activity and Osmotic Coefficients in Dilute Aqueous Solutions of Uni-Univalent Electrolytes at 25 °C

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Activity and osmotic coefficients in dilute aqueous solutions of some uni-univalent electrolytes are calculated from the simplified forms of the Stokes and Robinson equation. The required hydration parameters in these equations are taken from Guggenheim and Stokes. Electrolytes studied in this article include HCl, HBr, HI, $HClO_4$, $LiClO_4$, $NaClO_4$, LiCl, LiBr, LiI, NaCl, NaBr, NaI, KCl, KBr, KI, RbCl, RbBr, and RbI over the concentration range 0.0001–0.1 *m*.

In nonassociative dilute electrolyte solutions, the Stokes and Robinson two-parameter equation reduces to a simpler form (*1*). Activity coefficients in dilute hydrochloric acid solutions and sodium solutions calculated from the simplified equation are in agreement with the existing data (*1*). By use of the Gibbs–Duhem relation, a corresponding equation for calculating osmotic coefficients is also derived. The activity and osmotic coefficients in dilute solutions of bi-univalent electrolytes have been calculated from these equations and compiled in a previous paper (*2*). The hydration parameters, å and *h*, required in the calculations are obtained experimentally from the measurements of solutions at higher concentrations. They are used to evaluate thermodynamic properties of solutions in dilute regions where experimental difficulties are encountered. Detailed thermodynamic data in dilute solutions of uni-univalent electrolytes have not been reported, in general, except some limited information by Hamer and Wu (*3*). The present article is an attempt to remove this deficiency.

The simplified forms of the Stokes and Robinson equation for activity and osmotic coefficients of 1–1 electrolytes (*2*) are

$$\ln \gamma_\pm = \frac{K_1 m^{1/2}}{1 + K_2 m^{1/2}} + 0.036(h - 1)m \qquad (1)$$

$$\phi = 1 + \frac{K_1}{K_2{}^3 m}[(1 + K_2 m^{1/2}) - 2 \ln (1 + K_2 m^{1/2}) - (1 + K_2 m^{1/2})^{-1}] + 0.018(h - 1)m \qquad (2)$$

in which $\gamma_\pm$ is the mean molal activity coefficient, ϕ is the molal osmotic coefficient, $K_1 = -1.17604$, $K_2 = 0.328618$å, *h* is the hydration number, å is the ion-size parameter in Å units, and *m* is the molality of the solution.

The values of å and *h* for 18 different kinds of 1–1 electrolytes are taken from Guggenheim and Stokes (*4*). These values (å and *h*) are as follows: HCl (4.47 Å, 8.0), HBr (5.18 Å, 8.6),

Table I. Activity and Osmotic Coefficients in Dilute Solutions of Uni-Univalent Electrolytes at 25 °C

	HCl		HBr		HI	
m	$\gamma_\pm$	ϕ	$\gamma_\pm$	ϕ	$\gamma_\pm$	ϕ
0.0001	0.9885	0.9963	0.9885	0.9962	0.9886	0.9961
0.0005	0.9750	0.9917	0.9751	0.9918	0.9752	0.9918
0.001	0.9653	0.9886	0.9656	0.9887	0.9658	0.9888
0.002	0.9523	0.9843	0.9528	0.9846	0.9533	0.9848
0.003	0.9383	0.9812	0.9436	0.9816	0.9442	0.9820
0.004	0.9351	0.9788	0.9361	0.9793	0.9369	0.9797
0.005	0.9286	0.9768	0.9297	0.9773	0.9308	0.9779
0.006	0.9229	0.9749	0.9242	0.9756	0.9254	0.9763
0.007	0.9177	0.9733	0.9192	0.9741	0.9207	0.9747
0.008	0.9131	0.9719	0.9148	0.9728	0.9164	0.9736
0.009	0.9088	0.9706	0.9107	0.9716	0.9124	0.9725
0.01	0.9048	0.9693	0.9069	0.9705	0.9088	0.9715
0.02	0.8758	0.9609	0.8793	0.9628	0.8828	0.9646
0.03	0.8566	0.9556	0.8615	0.9583	0.8663	0.9609
0.04	0.8422	0.9520	0.8483	0.9553	0.8544	0.9586
0.05	0.8308	0.9494	0.8380	0.9532	0.8452	0.9572
0.06	0.8214	0.9474	0.8295	0.9518	0.8379	0.9564
0.07	0.8135	0.9460	0.8225	0.9508	0.8320	0.9560
0.08	0.8067	0.9448	0.8166	0.9502	0.8270	0.9559
0.09	0.9007	0.9440	0.8115	0.9498	0.8229	0.9561
0.1	0.7955	0.9434	0.8070	0.9496	0.8194	0.9565

Table II. Activity and Osmotic Coefficients in Dilute Solutions of Uni-Univalent Electrolytes at 25 °C

	$HClO_4$		$LiClO_4$		$NaClO_4$	
m	$\gamma_\pm$	ϕ	$\gamma_\pm$	ϕ	$\gamma_\pm$	ϕ
0.0001	0.9885	0.9961	0.9885	0.9962	0.9885	0.9960
0.0005	0.9751	0.9918	0.9752	0.9918	0.9748	0.9916
0.001	0.9655	0.9887	0.9657	0.9888	0.9650	0.9884
0.002	0.9527	0.9845	0.9531	0.9847	0.9516	0.9840
0.003	0.9434	0.9815	0.9440	0.9819	0.9418	0.9807
0.004	0.9358	0.9792	0.9366	0.9790	0.9338	0.9781
0.005	0.9294	0.9772	0.9304	0.9777	0.9270	0.9759
0.006	0.9238	0.9754	0.9250	0.9760	0.9209	0.9739
0.007	0.9188	0.9739	0.9201	0.9746	0.9155	0.9722
0.008	0.9142	0.9725	0.9157	0.9733	0.9105	0.9706
0.009	0.9101	0.9713	0.9117	0.9721	0.9060	0.9691
0.01	0.9062	0.9701	0.9080	0.9711	0.9017	0.9677
0.02	0.8782	0.9621	0.8814	0.9638	0.8700	0.9577
0.03	0.8598	0.9573	0.8642	0.9597	0.8484	0.9510
0.04	0.8462	0.9541	0.8516	0.9570	0.8317	0.9459
0.05	0.8354	0.9517	0.8418	0.9552	0.8181	0.9419
0.06	0.8265	0.9500	0.8339	0.9541	0.8065	0.9386
0.07	0.8191	0.9488	0.8274	0.9533	0.7965	0.9358
0.08	0.8127	0.9479	0.8219	0.9529	0.7877	0.9334
0.09	0.8072	0.9473	0.8171	0.9527	0.7798	0.9313
0.1	0.8024	0.9468	0.8131	0.9527	0.7726	0.9294

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