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Liquid−Liquid Equilibria in (2,3-Butanediol + 2-Butoxyethanol + Water + Potassium Chloride) at 70 °C

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The effect of potassium chloride on the liquid−liquid equilibrium in the ternary system (2-butoxyethanol + 2,3-butanediol + water) at 70 °C is reported. Two salt concentrations were studied, (0.43 and 3.03) mass %. The addition of potassium chloride increases the heterogeneity region of the ternary diagram and also the selectivity. The consistency of the results was tested with the Othmer−Tobias, Hand, Brown, and Campbell correlations. Tie-line results have been correlated by the Eisen−Joffe equation and the empirical correlation of Vainerman et al. (mixtures with salt) and UNIQUAC and NRTL (salt-free basis).

Introduction

2,3-Butanediol is used for the production of synthetic fibers, printing inks, drugs, and pharmaceuticals (Tegtmeier, 1989). 2,3-Butanediol is obtained by fermentation, reaching concentrations of 100 g·L^{-1}, but low yields, in the range of (1 to 1.1) g·L^{-1}·h^{-1}), are obtained (Afschar et al., 1991), partially due to the low levels of dissolved oxygen in the fermentation broth (Quereshi and Cheryan, 1990).

The recovery of 2,3-butanediol from the fermentation broth can be accomplished by distillation, membrane processes, and solvent extraction. Distillation is not a very suitable method because 2,3-butanediol has to be recovered as the bottom product and it can be contaminated with other low-volatility components. Membrane processes have been used successfully for the recovery of 2,3-butanediol. Reverse osmosis followed by distillation compares economically favorably with other methods (Sridhar, 1989), and vacuum membrane distillation integrated with a fed-batch reactor allows concentrations of 2,3-butanediol to reach over 430 g·L^{-1} (Quereshi et al., 1994). Physical solvent extraction has also been suggested for the recovery of 2,3-butanediol, using alcohols and esters as solvents (Othmer et al., 1945) and chlorinated and phenolic compounds (Escudero et al., 1994, 1996). Salting-out using dehydrated K_2CO_3 at (53 to 65) mass % allows recovery of (94 to 96)% of 2,3-butanediol from a fermentation broth (Afschar et al., 1993).

Homogeneous liquid−liquid extraction or consolute point extraction avoids the two-phase mixing energy input and it has shown promising results in their applications to downstream processing of bioproducts. In a consolute system the solvent is miscible with the aqueous phase at a certain temperature, but only partially miscible at another temperature. If a common solvent such as 2-butoxyethanol (butylcellosolve) is mixed with water at 25 °C, it forms a homogeneous phase, but if the mixture is heated to a certain temperature, two phases are formed. The lower critical solution temperature (LCST) is (48.8 ± 0.1) °C at (27.4 ± 0.5)% by mass 2-butoxyethanol and the upper critical solution temperature (UCST) is (130.2 ± 0.2) °C at (29.7 ± 0.5) mass % (Ellis, 1967). Any organic compound originally present in the aqueous phase will tend to concentrate in the organic phase (Hanigan and Hughes, 1989).

The addition of salt to consolute systems alters the consolute diagram, decreasing the LCST. The salting-out effect depends on the type and concentration of salt. The order of salting-out efficiency of alkali metal halides on 2-butoxyethanol + water follows a trend opposite to that of the solubility of the salts in water at the same temperature (Ellis, 1967). Hence, potassium chloride was selected for these experiments.

In this work the use of homogeneous liquid−liquid extraction for the recovery of 2,3-butanediol with 2-butoxyethanol as solvent was investigated. Results are reported at 70 °C with the pure solvent and also for the addition of potassium chloride to the extraction mixture, at two different concentrations, in order to study the salting-out effect on the extraction equilibria. The salt concentrations were 0.43 mass % and 3.03 mass %, which are within the saturation limit (<1.20 mass % in 2,3-butanediol, < 0.01 mass % in 2-butoxyethanol, 23.80 mass % in water, at room temperature).

Experimental Section

A. Chemicals. 2,3-Butanediol (Merck, synthesis grade) was used as supplied by the manufacturer. 2-Butoxyethanol (Panreac, >98%) is a very toxic liquid with TLV = 25 ppm in air. It was further purified by distillation in a packed Oldershaw-type column in a nitrogen atmosphere, and water was bidistilled in an all-glass apparatus. Commercial 2,3-butanediol was a mixture of the D,L-, and meso isomers, and a chromatographic analysis showed a purity higher than 99% for 2,3-butanediol (>14% for the DL-form and >85% for the meso form). Potassium chloride (Panreac, high-purity grade) was used without further purification.

B. Methods. The equilibrium distribution data were determined by preparing mixtures of known overall composition at 25 °C. Samples were shaken vigorously in thermostated settling cells, and then the temperature was raised to 70 °C, at which two phases were formed. The temperature was measured by a calibrated thermometer with a precision of ±0.5 K. The system was allowed to settle for 3 h to ensure complete separation of the phases and phase equilibrium. Both phases were then sampled and analyzed by gas chromatography. The potassium

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Table 1. Tie-Line Data for the System 2,3-Butanediol (1) + 2-Butoxyethanol (2) + Water (3) + Potassium Chloride (s) at 70 °C

global composition				organic phase				aqueous phase			
w_1	w_2	w_3	w_4	w_{1o}	w_{2o}	w_{3o}	w_{so}	w_{1w}	w_{2w}	w_{3w}	w_{sw}
$w_s = 0$											
0.0000	0.2963	0.7037	0.0000	0.0000	0.6020	0.3980	0.0000	0.0000	0.0980	0.9020	0.0000
0.0050	0.2947	0.7003	0.0000	0.0070	0.5750	0.4180	0.0000	0.0039	0.1050	0.8911	0.0000
0.0093	0.2973	0.6934	0.0000	0.0110	0.5430	0.4460	0.0000	0.0072	0.1150	0.8778	0.0000
0.0168	0.2962	0.6870	0.0000	0.0190	0.4925	0.4885	0.0000	0.0150	0.1360	0.8490	0.0000
0.0196	0.2971	0.6833	0.0000	0.0213	0.4670	0.5117	0.0000	0.0182	0.1500	0.8318	0.0000
0.0200	0.2980	0.6820	0.0000	0.0228	0.4550	0.5222	0.0000	0.0191	0.1530	0.8279	0.0000
0.0210	0.2992	0.6798	0.0000	0.0232	0.4400	0.5368	0.0000	0.0193	0.1580	0.8227	0.0000
0.0219	0.3002	0.6779	0.0000	0.0238	0.4310	0.5458	0.0000	0.0205	0.1670	0.8125	0.0000
$100w_s = 0.43$											
0.0000	0.2967	0.6990	0.0043	0.0000	0.6089	0.3898	0.0013	0.0000	0.0876	0.9059	0.0065
0.0105	0.2947	0.6905	0.0043	0.0130	0.5700	0.4157	0.0013	0.0090	0.0950	0.8895	0.0065
0.0123	0.2983	0.6851	0.0043	0.0145	0.5620	0.4208	0.0027	0.0110	0.0995	0.8827	0.0068
0.0166	0.3007	0.6784	0.0043	0.0182	0.5504	0.4290	0.0024	0.0145	0.1025	0.8758	0.0072
0.0197	0.2963	0.6797	0.0043	0.0220	0.5325	0.4430	0.0025	0.0180	0.1125	0.8626	0.0069
0.0266	0.3002	0.6689	0.0043	0.0294	0.4900	0.4782	0.0024	0.0255	0.1350	0.8330	0.0065
0.0309	0.3018	0.6630	0.0043	0.0328	0.4575	0.5065	0.0032	0.0293	0.1525	0.8125	0.0057
0.0326	0.2956	0.6675	0.0043	0.0345	0.4350	0.5271	0.0034	0.0310	0.1640	0.7996	0.0054
$100w_s = 3.03$											
0.0000	0.2972	0.6725	0.0303	0.0000	0.7320	0.2646	0.0034	0.0000	0.0599	0.8935	0.0466
0.0056	0.2971	0.6670	0.0303	0.0075	0.7200	0.2682	0.0043	0.0051	0.0600	0.8885	0.0464
0.0080	0.3033	0.6584	0.0303	0.0105	0.7170	0.2681	0.0044	0.0072	0.0610	0.8856	0.0462
0.0170	0.3014	0.6513	0.0303	0.0199	0.6950	0.2801	0.0050	0.0155	0.0635	0.8748	0.0462
0.0230	0.3020	0.6447	0.0303	0.0275	0.6720	0.2944	0.0061	0.0228	0.0650	0.8661	0.0461
0.0365	0.2986	0.6344	0.0303	0.0450	0.6330	0.3151	0.0069	0.0378	0.0750	0.8414	0.0458
0.0472	0.2991	0.6234	0.0303	0.0535	0.5980	0.3401	0.0084	0.0460	0.0830	0.8255	0.0455
0.0544	0.3008	0.6145	0.0303	0.0627	0.5830	0.3451	0.0092	0.0538	0.0890	0.8188	0.0454
0.0653	0.3001	0.6043	0.0303	0.0725	0.5380	0.3775	0.0120	0.0629	0.1000	0.7931	0.0440
0.0730	0.2932	0.6035	0.0303	0.0799	0.4930	0.4130	0.0141	0.0710	0.1250	0.7608	0.0432
0.0848	0.2996	0.5853	0.0303	0.0890	0.4320	0.4582	0.0208	0.0830	0.1370	0.7384	0.0416

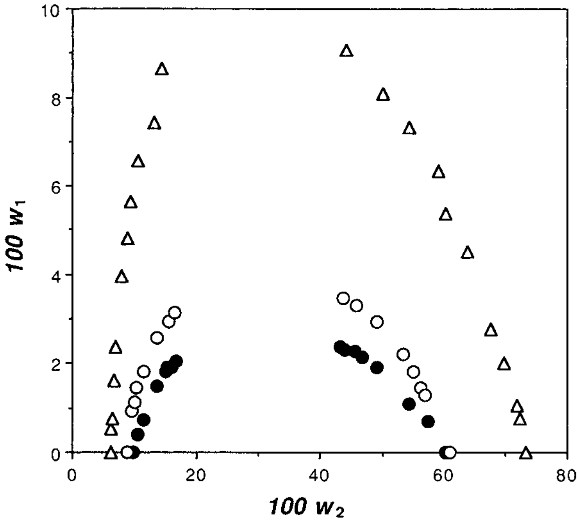

Figure 1. End of the tie lines for the systems 2,3-butanediol (1) + 2-butoxyethanol (2) + water (3), without KCl and with KCl: (●) no KCl; (○) 0.43 mass % of KCl; (△) 3.03 mass % of KCl.

chloride composition, in both phases, was determined by the Volhard method (Williams, 1979).

The chromatographic analysis of the aqueous phase samples was carried out with a Perkin-Elmer Sigma 4B gas chromatograph equipped with a thermal conductivity detector. The column was a Carbowax 20M (10 mass %) on Chromosorb WHP 50/100 column (2 m × $^1/_8$ in.), the oven temperature was 110 °C, and helium was used as the carrier gas with a flow of 27 $\text{cm}^3\cdot\text{min}^{-1}$. The chromatographic analysis of the organic phase samples was carried out with a Perkin-Elmer 990 gas chromatograph equipped with a flame ionization detector. The column was of Porapak QS 80/100 (2 m × $^1/_8$ in.), the oven temperature was 220 °C, and nitrogen was used as the carrier gas with a flow of 33 $\text{cm}^3\cdot\text{min}^{-1}$. For the quantitative results we have applied the internal standard method, ethylene glycol being the standard compound used for this purpose. Each sample was measured three times, and the average value was considered. The precision in the estimation of the compositions in mass fraction was $\pm 1 \times 10^{-4}$.

Compositions determined by measuring densities and volumes of each phase and carrying out the corresponding mass balance gave a closure of ±0.001 mass fraction.

Results and Discussion

Tie-line results for the system 2,3-butanediol (1) + 2-butoxyethanol (2) + water (3) and with addition of KCl (s) (0.43 and 3.03) mass % at 70 °C are listed in Table 1. Figure 1 shows the end of the tie lines represented on a salt-free basis. It shows that the heterogeneous region becomes larger as the salt concentration increases. The salting-out effect tends to withdraw the polar organic molecules, such as 2-butoxyethanol, which behaves as a typically basic polar nonelectrolyte, from the aqueous phase into the organic phase. Equilibrium distribution diagrams of 2,3-butanediol for the three systems studied are shown in Figure 2, which represents the mole fraction of 2,3-butanediol in the organic phase (x_{1o}) against the mole fraction of 2,3-butanediol in the aqueous phase (x_{1w}). It was found that the dissolved KCl has a negligible effect on the distribution coefficient for small concentrations of 2,3-butanediol. This fact can be explained by the salting-out of the solute into the aqueous phase where the salt increases the ionic strength of the organic layer. Selectivity increases as the concentration of salt increases, as shown in Figure 3, which has $w_{1o}/(w_{1o} + w_{3o})$ on the ordinate and $w_{1w}/(w_{1w} + w_{3w})$ on the abscissa, where w_{io} and w_{iw} are the mass fraction of component i in the organic and aqueous phases respectively.

The consistency of the equilibrium data was tested by the Brown, Campbell, Hand, and Othmer–Tobias equations on a salt-free basis (Ladha and Degaleesan, 1978).

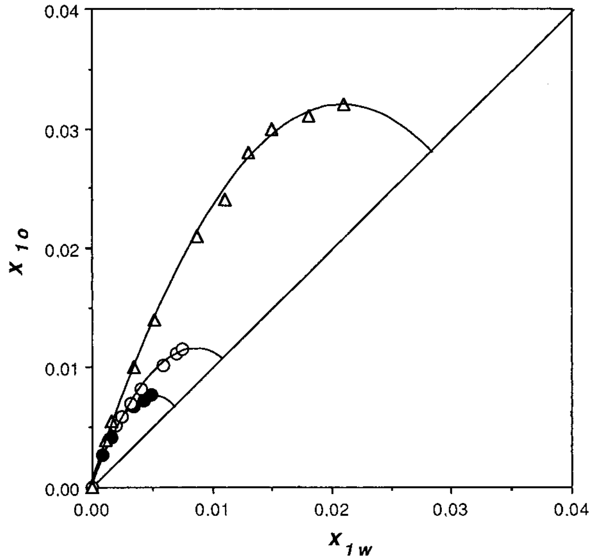

Figure 2. Equilibrium distribution diagrams for the systems 2,3-butanediol (1) + 2-butoxyethanol (2) + water (3), without KCl and with KCl: (●) no KCl; (○) 0.43 mass % of KCl; (△) 3.03 mass % of KCl.

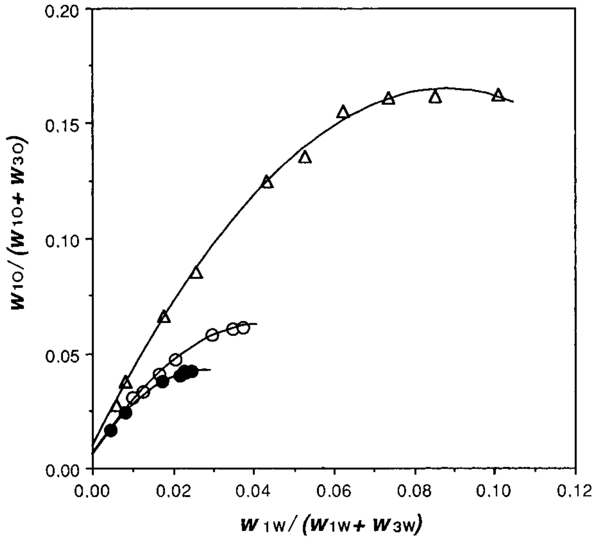

Figure 3. Selectivity diagram for the systems 2,3-butanediol (1) + 2-butoxyethanol (2) + water, without KCl and with KCl: (●) no KCl; (○) 0.43 mass % of KCl; (△) 3.03 mass % of KCl.

Table 2. Eisen−Joffe Correlation Constants and Regressions

amt of KCl/ mass %	A	B	C	D	r
0	0.103 051		0.858 309		0.998 624
0.43	0.103 051	0.091 557	0.858 309	0.092 331	0.996 884
3.03	0.103 051	0.012 982	0.858 309	0.030 519	0.997 925

Good correlations were found by all these methods.

Tie-line data have also been correlated by the Eisen−Joffe equation (Eisen and Joffe, 1966)

$$\log \frac{w_{1o}}{w_{2o}} = (A + B100w_S) + (C + D100w_S) \log \frac{w_{1w}}{w_{3w}} \qquad (1)$$

where w_{io} and w_{iw} are as described earlier, w_s is the mass fraction of KCl in the initial mixture and A, B, C, and D are constants. Parameters in eq 1 were obtained using a two-step calculation. In the first step constants A and C were determined from the equilibrium data with no addition of salt, i.e. $w_s = 0$. In the second step B and D were calculated from the equilibrium data at two salt concentrations, along with the previously calculated values of A and C. Table 2 shows these constants along with the regressions.

Furthermore, assuming that quaternary LLE data with salt can be converted to ternary LLE data without salt, the experimental tie-line data on a salt-free basis were correlated by NRTL (Renon and Prausnitz, 1968) and UNIQUAC (Abrams and Prausnitz, 1975) equations. The binary parameters in these correlations were estimated by a nonlinear regression method using the weighted orthogonal distance regression algorithm, developed by the National Institute of Standard and Technology (NIST), from the equilibrium data. The objective function used for LLE models, S, is given by eq 2:

$$S = \sum_{i=1}^{N_1}\sum_{j=1}^{N_2}\left[1.0 - \frac{K_{D_{ij}\text{calc}}}{K_{D_{ij}\text{expt}}}\right]^2 \qquad (2)$$

where K_D is the distribution coefficient, N_1 is the number of data, and N_2 is the number of components.

The nonrandomness parameter in the NRTL equation was kept constant, $\alpha_{ij} = 0.2$, in all cases. The size parameter, r, and surface parameter, q, used in the UNIQUAC model are the following: for water $r = 0.9200$, $q = 1.4000$; for 2,3-butanediol $r = 3.7561$, $q = 3.3200$; for 2-butoxyethanol $r = 5.0470$, $q = 4.3720$.

The goodness of fit was measured by the root-mean-squared deviation or residual function F (mol %):

$$F = 100[\sum_k\sum_i\sum_j(x_{ijk} - \hat{x}_{ijk})^2/6M]^{0.5} \qquad (3)$$

where x and $\hat{x}$ are the experimental mole fraction of the liquid phase and the mole fraction of the predicted tie-line lying close to the considered experimental tie line, respectively, k is the number of tie lines from 1 to M, i is the number of components, and j is the number of coexisting phases. Table 3 shows the interaction parameter values and their root-mean-squared deviation. There is good agreement between the correlated and experimental data, as shown in Figures 4−6. Triangular diagrams are not depicted because of the very low concentration of the components expressed in mole fractions. Deviations are higher for the system without salt because of its smaller concentration in 2,3-butanediol.

The correlation developed by Vainerman et al. (1990), eq 4, for the distribution coefficient of a liquid−liquid quaternary system (solute + solvent + water + salt) was also tested,

$$\ln K_D = a + b \ln \Phi \qquad (4)$$

where K_D and Φ are the solute and the solvent distribution coefficients, respectively, expressed as the ratio of concentration, in mole fraction, between the organic and the aqueous phases and a and b are constants related to activity coefficients and salting-out constants of solute and solvent by salt. This approach results from the assumption of a linear behavior between the solvent and solute distribution coefficients and the difference in salt concentration in the coexisting phases, as expressed by

$$\ln K_D = c + d\,(x_{sw} - x_{so}) \qquad (5)$$

$$\ln \Phi = e + f(x_{sw} - x_{so}) \qquad (6)$$

where K_D and Φ are as described earlier, x_{sw} and x_{so} are

Table 3. UNIQUAC and NRTL Interaction Parameter Values and Root−Mean−Squared Deviation for 2,3−Butanediol (1) + 2−butoxyethanol (2) + Water or KCl Solution (3) Systems at 70 °C

UNIQUAC Model

amt of KCl/mass %	U_{12}/K	U_{21}/K	U_{13}/K	U_{31}/K	U_{23}/K	U_{32}/K	RMSD/mol %
0	11.536	6.068	−36.704	−23.001	89.980	104.34	0.1038
0.43	16.161	−8.217	−27.038	−154.146	253.298	34.318	0.0038
3.03	−146.914	104.227	−187.006	−15.837	141.926	100.658	0.0001

NRTL Model

amt of KCl/mass %	g_{12}/K	g_{21}/K	g_{13}/K	g_{31}/K	g_{23}/K	g_{32}/K	RMSD/mol %
0	−493.979	1000.546	−1006.251	−100.012	499.528	1476.752	0.1204
0.43	−59.110	224.009	320.868	−1072.469	499.139	1487.222	0.0484
3.03	−606.079	885.590	−1056.740	−99.522	526.966	1447.272	0.0254

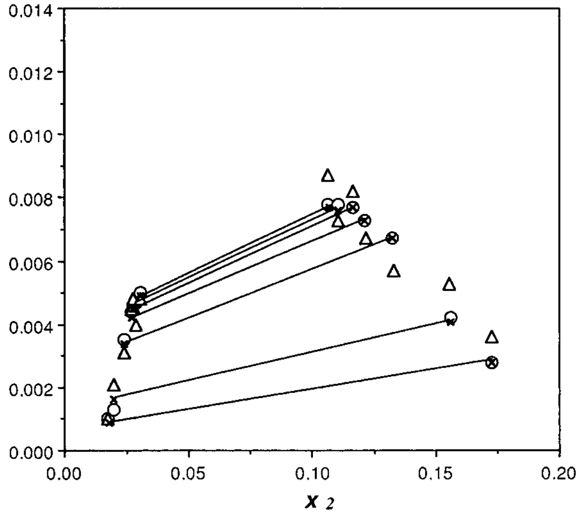

Figure 4. Liquid−liquid equilibrium data for the system 2,3-butanediol (1) + 2-butoxyethanol (2) + water (3) at 70 °C in mole fraction: (×) experimental data; (○) calculated with the UNIQUAC equation; (△) calculated with the NRTL equation.

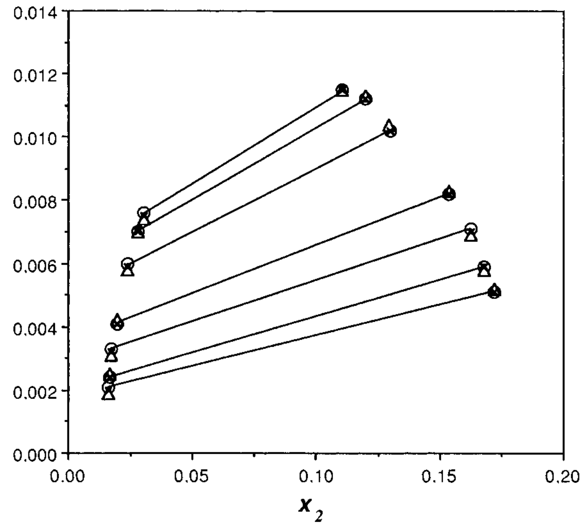

Figure 5. Liquid−liquid equilibrium data for the system 2,3-butanediol (1) + 2-butoxyethanol (2) + water (3) + KCl (0.43 mass %) at 70 °C in mole fraction: (×) experimental data; (○) calculated with the UNIQUAC equation; (△) calculated with the NRTL equation.

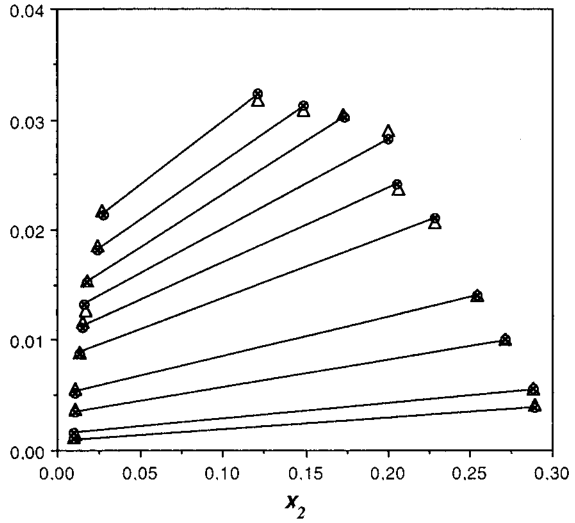

Figure 6. Liquid−liquid equilibrium data for the system 2,3-butanediol (1) + 2-butoxyethanol (2) + water (3) + KCl (3.03 mass %) at 70 °C in mole fraction: (×) experimental data; (○) calculated with the UNIQUAC equation; (△) calculated with the NRTL equation.

Table 4. Vainerman et al. Correlation Constants and Regressions

amt of KCl/mass %	eq 4	eq 5	eq 6
0.43	$a = -0.1804$ $b = 0.4471$ $r = 0.9788$	$c = 0.2844$ $d = 605.57$ $r = 0.9762$	$e = 1.0644$ $f = 1316.2$ $r = 0.9695$
3.03	$a = -0.2523$ $b = 0.4199$ $r = 0.9742$	$c = 0.2417$ $d = 141.56$ $r = 0.8689$	$e = -0.0907$ $f = 351.89$ $r = 0.9306$

the salt concentration, in mole fraction in aqueous and organic phases, respectively, and *c*, *d*, *e*, and *f* are constants. These constants along with the regressions are listed in Table 4. Large deviations between experimental and correlated data by eq 5 are observed, especially for the system with 3 mass % KCl. This fact would be consistent with the assumption made by the authors of these correlations, which are valid only at low concentrations of solute in the system, which is not the case in our investigation since the overall two-phase region was studied.

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