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Ion Exhange Equilibria in Nonaqueous and Mixed Solvents on the Cationic Exchanger Amberlite IR-120

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Na^+/K^+ equilibrium ion exchange isotherms on Amberlite IR-120 (known as a strong acid resin) in pure methanol, ethanol, 2-propanol, 1-butanol, and 1-penthanol and in mixtures of methanol + water, ethanol + water, 2-propanol + water, 1-butanol + methanol, and 1-penthanol + methanol at 313 K have been determined. Experimental equilibrium data have been satisfactorily correlated using the homogeneous mass action law model (LAM). This model assumes nonideal behavior for both the solution and the solid phase. Wilson and Debye−Hückel equations have been used to calculate activity coefficients in the solid and liquid phase, respectively. It has been observed that the dielectric constant of the solvent or the mixture exerts a strong influence not only on the useful capacity of the resin but also on the equilibrium behavior of the system.

Introduction

One of the controlling factors governing the use of ion exchange as a separation method is the equilibrium distribution of ions between the resin and the solution phase. For this reason, ion exchange equilibrium in aqueous media has been widely studied whereas few experimental or theoretical studies have been developed over ion exchange equilibrium in nonaqueous media. As showed in earlier works[1,2] the resin capacity could be however exhausted using highly polar solvents. This is not the case for less polar solvents or organic cations with high molecular weights.[3−5] Anyway, it seems clear that the ion exchange equilibrium in nonaqueous media is mainly affected by the solvent polarity, the swelling of the ion exchange beads, and the ion size.[6,7]

In this paper, Na^+-K^+ ion exchange equilibrium data were obtained at 313 K using different alcohols and mixtures (water−alcohol, alcohol−alcohol) as solvents. The total concentration in the solution was 32 mmol/kg. The fit of experimental data to the homogeneous mass action law[8,9] model allowed us to obtain the thermodynamic equilibrium constant and the binary interaction parameters. Wilson and Debye−Hückel equations were used to calculate activity coefficients in the solid and liquid phase, respectively.

Experimental Section

Chemical. All the solvents used in this investigation were PRS grade and were supplied by Panreac (99%). Sodium and potassium terbutoxide (Alfa, 99%) were used in the preparation of ionic solutions. Demineralized water was used with a conductivity value lower than 1 μS. The cationic resin Amberlite IR-120 supplied by Rohm & Haas was used as exchanger. As described by Lucas et al.,[10] the resin was pretreated and regenerated to convert it to the Na^+ form. In the experiments with anhydrous solvents, the commercial solvent was previously dried with calcium oxide and then with sodium under reflux. Prior to runs, the resin was exhaustively washed with the anhydrous solvent in order to attain the complete moisture removal and swelling of the resin.

Procedure. The experimental setup consisted of nine 0.25 L Pyrex containers, hermetically sealed and submerged in a temperature controlled thermostatic bath. The temperature was kept constant with maximum deviations of ±0.1 K. The suspensions formed by the resin and solution were vigorously agitated by means of a multipoint magnetic stirrer.

Equilibrium resin loading data were generated for the pure solvents and the water + alcohol and methanol + alcohol (<0.01 wt % mass of water) mixtures. To obtain these data, 70 g of an ionic solution of known composition was weighed and added into each flask. Different amounts of resin, in the sodium form and prewetted with the solvent, were previously added to each flask. The flasks were weighed before and after the equilibrium experiments to confirm that no losses of solvent occurred during equilibration. The accuracy of weighing was ±0.0001 g. Suspensions were maintained under vigorous stirring at fixed temperature (±0.1 K) until the equilibrium was achieved (3 days). At the end of this period, the mixtures were filtered to remove the ion exchange resin. Next the filtrate was analyzed for potassium content by atomic emission spectrophotometry in a Thermo Jarrel Ash (Smith Hiejfe II) atomic absorption spectrophotometer. Different standard solutions must be prepared to account for the matrix effect of each type of solvent or mixture on the spectrophotometer meaurements. The uncertainty and reproducibility of measurements was found to be ±0.1%.

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Table 1. *A* and *B* Parameters of the Debye−Hückel Equation of Pure Solvents and Mixtures at 313 K

system (S_1/S_2)	mass % S_1:S_2	ϵ^a	A (mol/kg)$^{-1/2}$	10^9B (mol/kg)$^{-1/2}$
CH_3OH	100:0	32.35	3.66	4.44
C_2H_5OH	100:0	25.00	5.33	4.99
i-C_3H_7OH	100:0	18.62	8.33	5.82
1-C_4H_9OH	100:0	17.80	9.06	6.05
1-$C_5H_{11}OH$	100:0	15.13	11.6	6.58
$CH_3OH + H_2O$	50:50	56.32	1.71	3.60
$C_2H_5OH + H_2O$	50:50	51.35	1.94	3.73
i-$C_3H_7OH + H_2O$	50:50	45.65	2.42	4.14
1-$C_4H_9OH + CH_3OH$	50:50	25.52	5.27	5.05
1-$C_5H_{11}OH + CH_3OH$	50:50	24.07	5.74	5.18

[a] Dielectric constant from Wohlfarth.[12]

The resin phase composition was determined by mass balance according to eq 1:

$$q^* = \frac{V}{W}(C_0 - C^*) \tag{1}$$

where C_0 and C^* are the initial concentration and the equilibrium concentration of potassium in the liquid phase (mmol/kg of solution), respectively. q^* denotes the resin-phase equilibrium concentration of potassium (mmol/g of dry resin). V and W are the mass of solution and dry ion exchange resin (kg and g), respectively.

Model and Prediction

Ion exchange equilibrium is attained when an ion exchanger is placed in an electrolyte solution containing a counterion which is different from that in the ion exchanger. Suppose that the ion exchanger (r) is initially in the A form, and that the counterion in the solution (s) is B. Counterion exchange occurs, and the ion A in the ion exchanger is partially replaced by B:

$$\beta A_r^{\alpha+} + \alpha B_s^{\beta+} \Leftrightarrow \beta A_s^{\alpha+} + \alpha B_r^{\beta+} \tag{2}$$

In this reversible equilibrium, both the ion exchanger and the solution contain both competing counterion species, A and B.

The ionic fraction can be introduced as follows:

$$x_A = \frac{\alpha C_A}{N}; \quad x_B = \frac{\beta C_B}{N} \tag{3}$$

$$y_A = \frac{\alpha q_A}{q_0}; \quad y_B = \frac{\beta q_B}{q_0} \tag{4}$$

where C_i represents the concentration of the ith ionic species in solution. N is the total ionic concentration in the solution phase or the solution normality, q_i is the solute concentration in the solid phase, and q_0 is the useful capacity of the resin in the system studied.

The equilibrium constant for the exchange reaction 2 assuming real behavior for both phases could be calculated from the following equation:

$$K_{AB}(T) = \frac{(y_B\bar{\gamma}_B)^\alpha[(1 - x_B)C_T\gamma_A]^\beta}{[(1 - y_B)\bar{\gamma}_A]^\beta[x_B\gamma_BC_T]^\alpha} \tag{5}$$

where $\bar{\gamma}$ and γ are the activity coefficients of each ion in the ion exchanger and the solution, C_T is the total normality of the solution, and y_B and x_B are the ionic fraction of the ion B in the solid phase and in the solution.

Table 2. Comparing Experimental and Predicted Ion Exchange Equilibrium Data for K^+ in Pure Solvents with Amberlite IR-120^a

exp		theor
X	Y	Y
(a) Methanol (q_0 = 4.3 mmol/g of dry resin)		
0.03	0.08	0.0827
0.08	0.25	0.2516
0.10	0.42	0.2992
0.21	0.51	0.4855
0.34	0.61	0.6303
0.45	0.69	0.7220
0.51	0.74	0.7644
0.64	0.90	0.8430
0.69	0.92	0.8694
0.83	0.97	0.9344
0.87	0.98	0.9510
(b) Ethanol (q_0 = 3.8 mmol/g of dry resin)		
0.05	0.07	0.0700
0.31	0.24	0.2336
0.43	0.23	0.2937
0.50	0.33	0.3300
0.55	0.37	0.3573
0.56	0.46	0.3630
0.65	0.37	0.4181
0.66	0.43	0.4248
0.78	0.48	0.5201
0.88	0.76	0.6403
(c) 2-Propanol (q_0 = 3.20 mmol/g of dry resin)		
0.10	0.05	0.0063
0.12	0.03	0.0075
0.22	0.03	0.0152
0.26	0.04	0.0187
0.30	0.05	0.0228
0.45	0.03	0.0432
0.54	0.06	0.0616
0.63	0.08	0.0890
0.74	0.20	0.1471
0.87	0.24	0.3214
0.87	0.44	0.3214
(d) 1-Butanol (q = 3.03 mmol/g of resin Seca)		
0.02	0.01	0.0100
0.03	0.02	0.0145
0.12	0.05	0.0470
0.19	0.06	0.0661
0.33	0.09	0.0996
0.43	0.15	0.1231
0.54	0.15	0.1515
0.64	0.20	0.1824
0.89	0.50	0.3400
(e) 1-Pentanol (q_0 = 2.2 mmol/g of dry resin)		
0.10	0.07	0.0063
0.18	0.08	0.0185
0.29	0.12	0.0561
0.42	0.07	0.0980
0.54	0.14	0.1400
0.88	0.39	0.3747

[a] Stirring speed = 200 rpm; T = 313 K; V = 70 g.

The activity coefficients in the solid phase were calculated using the Wilson equations:

$$\bar{\gamma}_{AB} = \exp\{1 - \ln(y_A + (1 - y_A)\Lambda_{AB})\} - \left(\frac{y_A}{y_A + (1 - y_A)\Lambda_{AB}}\right) - \left(\frac{(1 - y_A)\Lambda_{AB}}{(1 - y_A) + y_A\Lambda_{BA}}\right) \tag{6}$$

$$\bar{\gamma}_{BA} = \exp\{1 - \ln((1 - y_A) + y_A\Lambda_{BA})\} - \left(\frac{1 - y_A}{(1 - y_A) + y_A\Lambda_{BA}}\right) - \left(\frac{y_A\Lambda_{BA}}{y_A + (1 - y_A)\Lambda_{AB}}\right) \tag{7}$$

where Λ_{AB} and Λ_{BA} are the Wilson coefficients.

Table 3. Comparing Experimental and Predicted Ion Exchange Equilibrium Data for K^+ in Mixed Solvents with Amberlite IR-120. Stirring Speed = 200 rpm; T= 313 K; V= 70 g.

exp		theor
X	Y	Y
(a) 50% Methanol + 50% Water (q_0 = 5 mmol/g of dry resin)		
0.05	0.10	0.0822
0.09	0.26	0.1435
0.19	0.39	0.2794
0.29	0.54	0.4714
0.40	0.59	0.5941
0.52	0.64	0.7050
0.61	0.72	0.7759
0.77	0.91	0.8816
(b) 50% Ethanol + 50% Water (q_0 = 5 mmol/g of dry resin)		
0.04	0.14	0.0710
0.05	0.09	0.0881
0.10	0.17	0.1707
0.15	0.24	0.2478
0.21	0.28	0.3338
0.38	0.46	0.5423
0.44	0.63	0.6050
0.63	0.77	0.7726
0.72	0.89	0.8382
(c) 50% 2-Propanol + 50% Water (q_0 = 5 mmol/g of dry resin)		
0.07	0.07	0.0711
0.11	0.12	0.1155
0.20	0.22	0.2232
0.34	0.43	0.3999
0.48	0.53	0.5674
0.61	0.70	0.7037
(d) 50% 1-Butanol + 50% Methanol (q_0 = 4.3 mmol/g of dry resin)		
0.03	0.19	0.1917
0.07	0.35	0.2470
0.23	0.49	0.3490
0.56	0.44	0.4717
0.65	0.50	0.5085
0.78	0.62	0.5606
0.92	0.62	0.6567
(e) 50% 1-Pentanol + 50% Metanol (q_0 = 4.3 mequiv/g of dry resin)		
0.03	0.12	0.1281
0.07	0.23	0.2377
0.18	0.41	0.4047
0.42	0.57	0.5781
0.54	0.63	0.6357
0.70	0.69	0.7044
0.80	0.72	0.7488

The activity coefficients in the liquid phase were determined from the Debye−Hückel limiting law:

$$\gamma_i = \exp\left(-\frac{A\sqrt{I}}{1 + Ba\sqrt{I}}\right) \tag{8}$$

where A and B denote the Debye−Hückel equation parameters (Table 1), I is the ionic strength in the bulk phase in molal units, and a refers to the average ionic diameter (Å) of the hydrated ions Na^+ and K^+.

In this set of equations, there are three unknown parameters, the equilibrium constant and the Wilson parameters. These can be obtained by fitting the experimental data to the model. A nonlinear regression method based on the Marquardt algorithm, as described in previous works,[11,12] has been used to obtain the required parameters.

Results and Discussion

Table 4. Equilibrium Parameters of the Binary System $Na^+ + K^+$ in Pure Solvents and Mixtures on the Resin Amberlite IR-120 at 313 K

system (S_1/S_2)	mass % S_1:S_2	q_0 (mmol/g of dry resin)	K_{AB}	Λ_{AB}	Λ_{BA}	avg dev (%)	ϵ^a (293 K)
H_2O^b	100:0	5.01	1.15	2.08	0.48	4.9	80.37
CH_3OH	100:0	4.30	3.20	2.96	0.02	10.79	32.35
C_2H_5OH	100:0	3.80	0.46	1.32	1.04	13.42	25.00
i-C_3H_7OH	100:0	3.20	0.08	0.86	0.40	23.78	18.62
1-C_4H_9OH	100:0	3.03	0.01	6.37	1.51	11.46	17.80
1-$C_5H_{11}OH$	100:0	2.20	0.02	0.65	9.30	20.90	15.13
CH_3OH/H_2O	50:50	5.01	2.23	0.84	1.33	11.51	56.32
C_2H_5OH/H_2O	50:50	5.01	1.98	1.29	0.80	11.70	51.35
i-C_3H_7OH/H_2O	50:50	5.01	1.28	1.18	0.69	3.20	45.65
1-C_4H_9OH/CH_3OH	50:50	4.30	1.00	17.71	8.30	27.15	25.52
1-$C_5H_{11}OH/CH_3OH$	50:50	4.30	1.36	0.67	5.73	3.54	24.07

[a] Dielectric constant from Wohlfarth.[12] [b] Values from de Lucas et al.[8]

The capacity of the resin in different pure solvents and mixtures was obtained in order to calculate the corresponding ionic fractions. As shown in Table 4, the available exchange capacity decreases as the polarity of the pure solvent decreases. In mixtures, the available capacity is determined by the most polar solvent of the mixture.

Experimental and theoretical data calculated from the model are shown in Tables 2 and 3. The equilibrium constant (K) and the binary interaction parameters of the Wilson model (Λ_{AB} and Λ_{BA}) obtained by nonlinear regression are shown in Table 4. These values were used to plot the theoretical equilibrium isotherms (Figures 1 and 2). Calculated values are in good agreement with experimental ones.

The average deviation from experiment was calculated from the difference, in absolute value (ABS), of the experimental concentration of potassium in the resin and the calculated one from the model, according to the following formula:

$$\text{Avg Dev (\%)} = \frac{\sum_{i=1}^{m} \text{ABS}\left(\frac{Y^{\text{exp}} - Y^{\text{calc}}}{Y^{\text{exp}}}\right) \times 100}{m} \tag{9}$$

The average deviation is less than 15% in most cases. The greatest deviation is obtained for the mixture of methanol and 1-butanol with the highest nonideal behavior. This fact is probably due to the fact that methanol is not preferred by the resin as a solvating agent.

In pure organic solvents, a change in selectivity can be noted as the polarity of the solvent decreases. While the exchanger is more selective to K^+ in methanol (like in pure water, $K > 1$), in the rest of the solvents the resin is more selective to Na^+.

In the aqueous−organic mixtures, the selectivity of the resin is greater for the K^+, as in aqueous media. The behavior of these mixed systems is quite ideal with values of the Wilson's coefficients close to unity. It seems clear that the presence of water in the mixture exerts a stronger influence than that of the organic solvent on the behavior the system, as probably the resin prefers the water as the solvating agent.

In the mixtures of both 1-butanol + methanol and 1-penthanol + methanol, a change of selectivity is observed

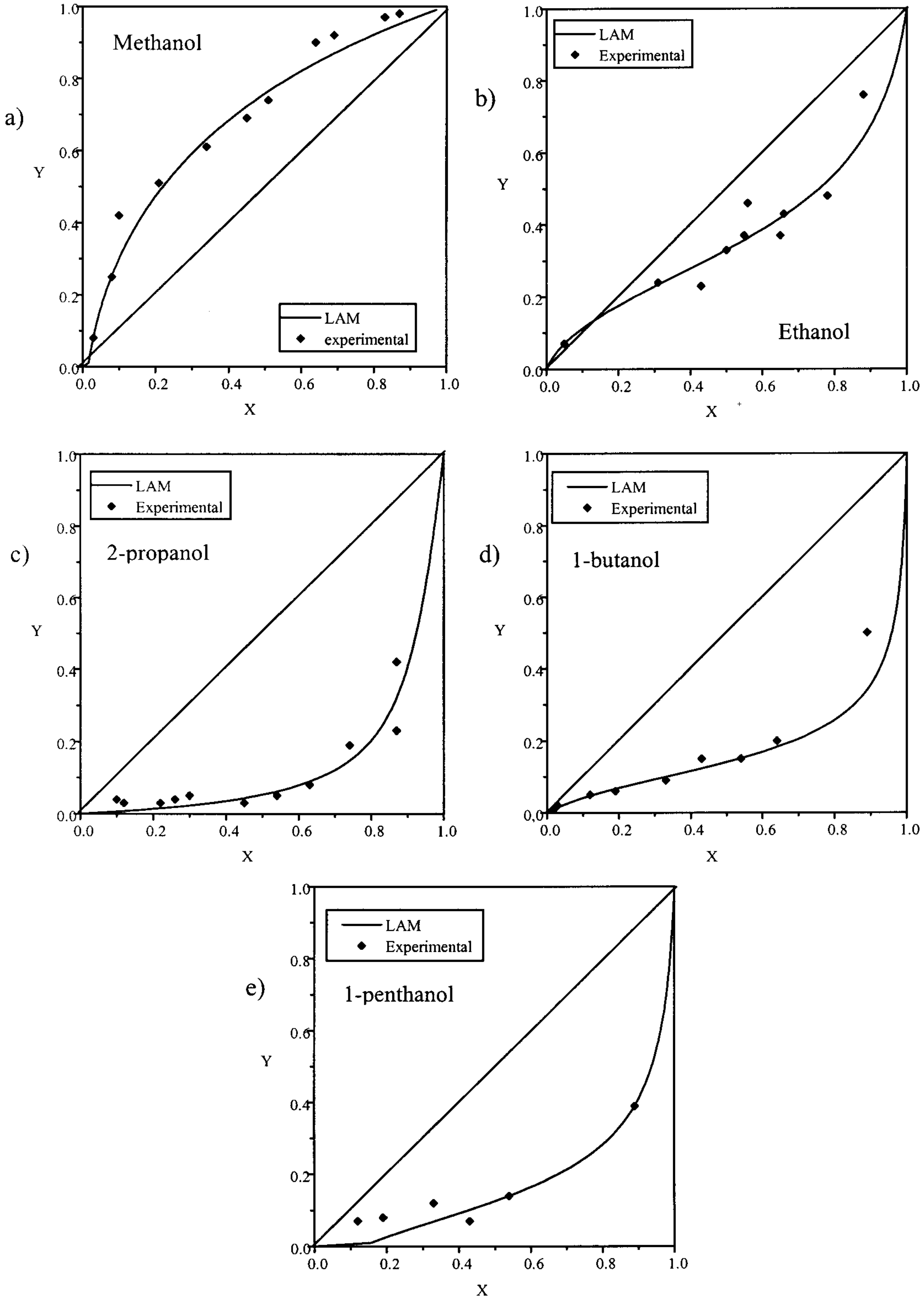

Figure 1. Equilibrium isotherms of K^+-Na^+ in pure solvents with Amberlite IR-120: (a) methanol; (b) ethanol; (c) 2-propanol; (d) 1-butanol; (e) 1-penthanol. Stirring speed = 200 rpm; T = 313 K; V = 70 g.

with increasing mole fractions of potassium ion in solution. In this case, the influence of methanol on the behavior of the system is not too much stronger if it is compared to that of water. In fact, the change of selectivity is greater in the 1-penthanol + methanol mixture and lower in the case of the 1-butanol + methanol one. It is also observed that the selectivity of the resin changes with potassium concentration. It is probable in this case that the solvation of the resin depends on the resin composition as well.

Conclusions

Na^+-K^+ ion exchange equilibrium systems on different organic and mixed solvents using the cationic exchanger Amberlite IR-120 have been measured at 313 K. Experimental equilibrium data can be satisfactorily correlated to the homogeneous mass action model (LAM) using Wilson and Debye–Hückel equations to calculate activity coefficients in the solid and liquid phase, respectively.

The polarity of the solvent and the composition of the mixture have a strong influence on the equilibrium behav-

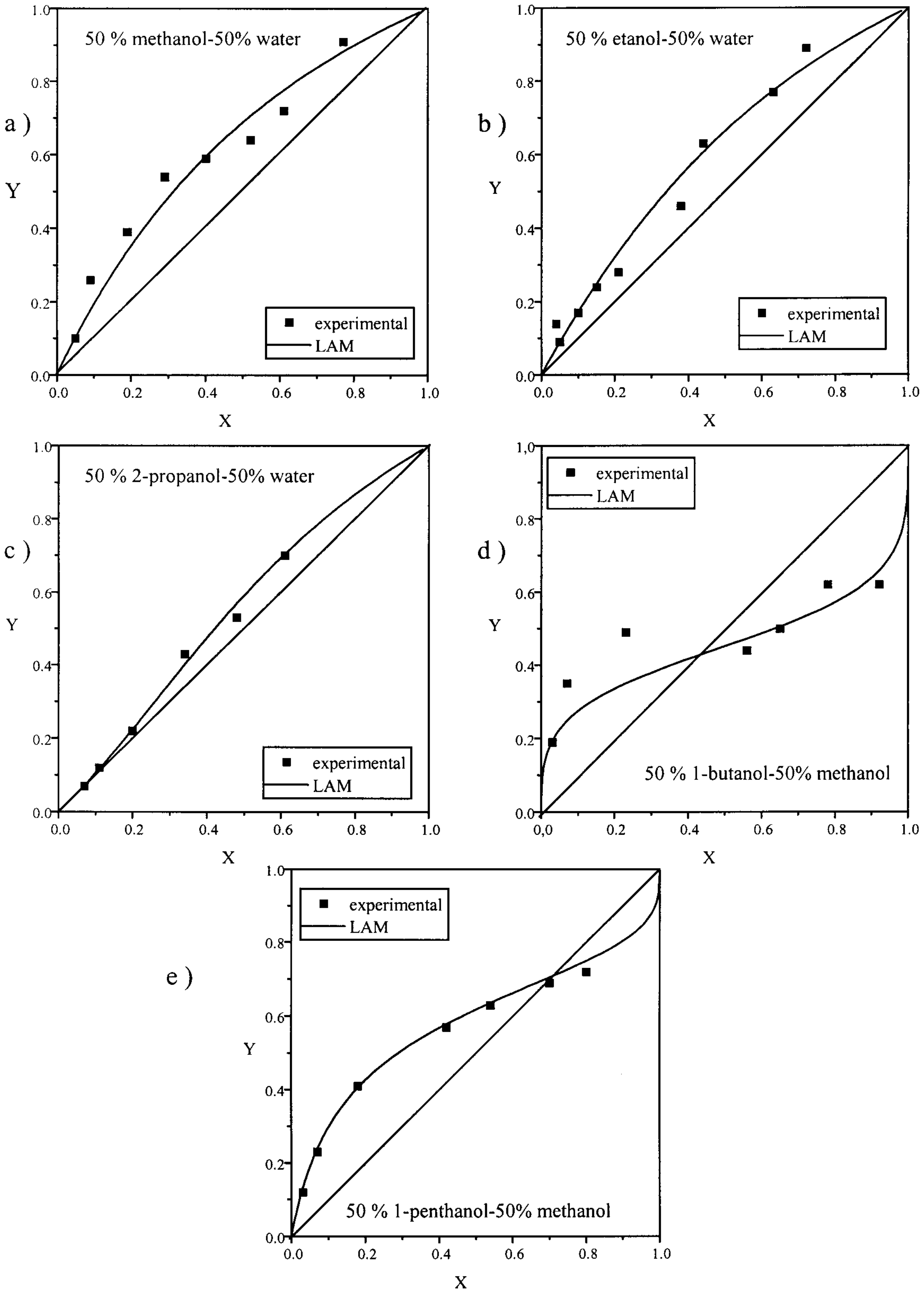

Figure 2. Equilibrium isotherms of K^+–Na^+ in mixed solvents with Amberlite IR-120: (a) 50% methanol–50% water; (b) 50% ethanol–50% water; (c) 50% 2-propanol–50% water; (d) 50% 1-butanol–50% methanol; (e) 50% 1-penthanol–50% methanol. Stirring speed = 200 rpm; T = 313 K; V = 70 g.

ior. In pure methanol, the resin prefers the potassium ion. In the rest of the solvents the selectivity of the resin changes. In aqueous mixtures, the isotherms obtained for the same ions resemble those obtained in pure water. When methanol is the more polar solvent of the mixture, the selectivity of the resin changes with the potassium concentration in solution.

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