EXTRACTION OF TARTARIC ACID WITH TRIALKYLAMINE

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Extraction equilibria in the system aqueous solution of D-tartaric acid/solution of trialkylamine in binary diluent at 25 °C have been investigated. The amine used was a mixture of trialkylamines with C_7–C_9 alkyls, the diluent was a mixture hydrocarbon (n-heptane, kerosene) and a modifier (octan-1-ol, isodecanol, methyl isobutyl ketone). The effect of solvent composition on equilibrium was investigated and the experimental results were correlated using a mathematical model that takes into account chemical reactions involved in acid/amine complex formation, and the nonspecific effects of the nonideality of the system.

Key words: Extraction equilibrium; D-Tartaric acid; Carboxylic acids; Tertiary amines; Binary diluent.

Liquid–liquid extraction of various carboxylic and hydroxycarboxylic acids from aqueous solutions by long-chain aliphatic amines has been extensively investigated. It was also proposed as a separation and refining method in their manufacture[1]. The reason for using reactive rather than physical extraction in this case is the high affinity of these acids to water and hence their difficult extractability by current organic solvents[2]. An extensive study on distribution of propanoic, lactic, pyruvic, succinic, fumaric, maleic, malic, itaconic, tartaric, citric and isocitric acids in various solvents and extractants was published by Kertes and King[3]. The influence of various diluents on the extraction of acetic, lactic, succinic, maleic, malonic and fumaric acids with a commercial tertiary amine, Alamine 336, was studied by Tamada *et al.*[4]. Formation of various acid/amine complexes in organic phase was detected, in dependence of the acid concentration in aqueous phase, the concentration of amine in organic phase and the nature of acid and diluent. These results were interpreted and confirmed by infrared spectroscopy by Tamada and King[5]. The effect of extraction temperature, as well as the phenomenon of water coextraction, were observed in another paper of these authors[6].

In manufacturing carboxylic acids, free acid is often the desired product and, therefore, re-extraction into pure water should be the final step of extraction refining. Two means have been proposed for adjusting the distribution so as to favour organic phase in extraction and aqueous phase in re-extraction[6]. These are the *temperature swing* and the *diluent swing*, respectively. The first one, based on enthalpy effects of transition of solute between phases, can be realized by raising the re-extraction temperature; the second is based on *synergistic effects* of some diluents which enhance the extracting power of amine. When applied in mixture with an *inert* diluent, *e.g.*, an aliphatic hydrocarbon, the effect of the active diluent, *modifier*, can be adjusted by changing the solvent composition. In amine extraction of citric acid the influence of various single-component diluents[7], as well as the effects of temperature and solvent composition (octan-1-ol/n-heptane, ref.[8]), were investigated. In another study[9] extraction of lactic, malic and citric acids with trialkylamine in the same diluent was compared. Recently[10] the effects of solvent composition on amine extraction of citric acid have been compared for three binary diluents containing octan-1-ol, chloroform and methyl isobutyl ketone as modifiers. Various forms of a mathematical model of extraction equilibrium have been developed comprising *chemical equilibrium*, dissociation in aqueous phase, and nonidealities in both phases[7–10].

In the present study, amine extraction equilibria have been investigated at 25 °C with D-tartaric acid as solute and with trialkylamine (TAA) dissolved in octan-1-ol/n-heptane, isodecanol/kerosene and methyl isobutyl ketone (MIBK)/n-heptane binary mixtures. The data correlation and simulation models used were similar to those developed in the previous work[9,10].

THEORETICAL

When applying the mathematical model developed in previous studies, the following simplifying assumptions were made: (i) With respect to the low values of dissociation constants of D-tartaric acid[3] ($pK_1 = 3.01$; $pK_2 = 4.38$), the dissociation in aqueous phase was neglected. (ii) Specific bonding of coextracted water molecules to the amine complexes was not taken into account; the measured water content in organic phase was used only for expressing the composition of organic phase on a water-free bases. (iii) Physical extraction of acid with the organic phase, as well as the solubility of solvent components in aqueous phase, were neglected. (iv) All nonideality effects were expressed in terms of organic phase composition.

The *chemical part* of the model takes into account expressions for total acid and amine molalities in organic phase and expressions for equilibrium constants of formation of acid/amine complexes considered

$$\overline{m}_{\mathrm{a}} = \sum_{k=1}^{K} i_k (\overline{m}_{ij})_k \qquad (1)$$

$$\overline{m}_{\mathrm{e}}^{0} = \overline{m}_{\mathrm{e}} + \sum_{k=1}^{K} j_k (\overline{m}_{ij})_k \qquad (2)$$

$$\beta_{ij} = \overline{m}_{ij}\,\overline{\gamma}_{ij}\,/m_{\mathrm{a}}^{i}\,\overline{m}_{\mathrm{e}}^{j}\,\overline{\gamma}_{\mathrm{e}}^{j} = \beta'_{ij}\,\overline{\gamma}_{ij}\,/\,\overline{\gamma}_{\mathrm{e}}^{j}\ . \tag{3}$$

Here m is the molality, the subscripts a, e refer to the acid and amine, respectively, and the bar denotes the organic phase; $\overline{m}_{\mathrm{e}}^{0}$ is total molality of TAA, $(\overline{m}_{ij})_k$ the molality of k-th complex, and K the number of complexes taken into account. The subscripts i_k , j_k and i, j are the numbers of acid and amine molecules in the k-th complex. β_{ij} , β'_{ij} are thermodynamic and conditioned equilibrium constants of formation of complex containing i molecules of free acid and j molecules of amine, *i.e.*, the (i : j) complex; γ is activity coefficient. Combining Eqs (*1*) and (*2*) with (*3*) one obtains

$$\overline{m}_{\mathrm{a}} = \sum_{k=1}^{K} i_k(\beta'_{ij}\,m_{\mathrm{a}}^{i}\,\overline{m}_{\mathrm{e}}^{j})_k \tag{4}$$

$$\overline{m}_{\mathrm{e}}^{0} = \overline{m}_{\mathrm{e}} + \sum_{k=1}^{K} j_k(\beta'_{ij}\,m_{\mathrm{a}}^{i}\,\overline{m}_{\mathrm{e}}^{j})_k\ . \tag{5}$$

In the *physical part* of the model, the nonspecific effects on the equilibrium are expressed by means of mass fraction of modifier in the diluent, $\overline{x}$, and total molalities of TAA and acid, $\overline{m}_{\mathrm{e}}^{0}$, $\overline{m}_{\mathrm{a}}$, in the organic phase

$$\beta'_{ij} = \beta_{ij}\,\exp\,(A_{ij}\,\overline{m}_{\mathrm{e}}^{0} + B_{ij}\,\overline{x} + C_{ij}\,\overline{m}_{\mathrm{a}})\ , \tag{6}$$

where β_{ij}, A_{ij}, B_{ij} and C_{ij} are the model parameters.

The model solution consists in solving Eqs (*3*) to (*6*). In the present work, three complexes have been considered; accordingly, the model contained 12 parameters. For correlating the data and evaluating the parameters, an optimization algorithm was used based on the Marquardt procedure BSOLVE (refs[11,12]). The weighted sum of squares of relative deviations of measured and calculated acid concentrations in both phases was used as objective function

$$S = \sum_{k=1}^{N} W_k\,[(1 - m_{\mathrm{a(cal)}}\,/m_{\mathrm{a(exp)}})^2 + (1 - \overline{m}_{\mathrm{a(cal)}}\,/\,\overline{m}_{\mathrm{a(exp)}})^2]_k\,N/\sum_{k=1}^{N} W_k\ . \tag{7}$$

Here N is the number of experimental points and W_k are the weights ascribed to individual points.

EXPERIMENTAL

The trialkylamine used (TAA) was a Russian commercial product, a mixture of tertiary straight-chain aliphatic amines with C_7–C_9 linear-chain alkyls (average molecular weight 363.3). Before use the product was extracted successively with aqueous hydrochloric acid, aqueous sodium hydroxide and water. Kerosene was a hydrocarbon fraction with boiling points ranging from 180 to 220 °C, with the average molecular weight 163 and with density 790 kg/m^3. D-Tartaric acid (Lachema Co.) and other reagents used were of analytical grade purity. Isodecanol was a commercial mixture of isomers (Riedel de Haen a.g.).

Both coexisting phases were analyzed. The acid concentration was determined by potentiometric titration with sodium methanolate solution in a (3 : 1) methanol/dimethylformamide mixture. The amine in organic phase was titrated with perchloric acid in acetic acid. The water content in organic phase was determined using the Carl Fischer method. The desired ratio of diluents was prepared by weighing and expressed as mass fraction of modifier in the mixed diluent. The acid content in aqueous phase was expressed in molalities, the contents of acid and TAA in organic phase in mol/kg of binary diluent. The phases were contacted in separating funnels, which were shaken in a thermostatted bath for one hour. All experiments were done at 25 °C.

RESULTS AND DISCUSSION

Experimental Results

The measured equilibrium acid molalities in aqueous and organic phases and the molalities of TAA in the diluent are presented in Tables I to III. They are also depicted as points in Figs 1–11. In these figures, the equilibrium acid content in organic phase is

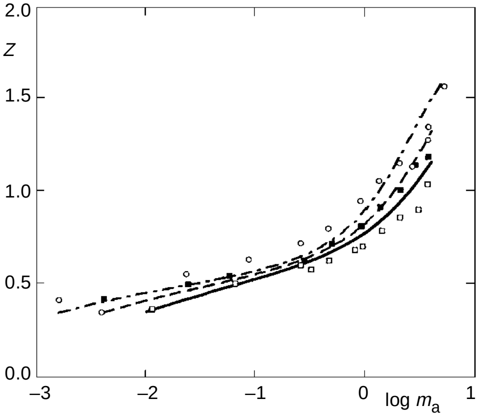

FIG. 1
System with octan-1-ol, $\overline{m}_e^0$ = 0.3 (model I). Points: experimental data; lines: calculated data. ❐, —— $\overline{x}$ = 0.4; ■, – – – – $\overline{x}$ = 0.7; ❍, – · – · – · $\overline{x}$ = 1.0

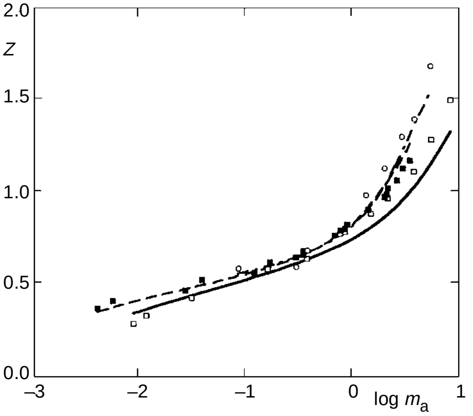

FIG. 2
System with octan-1-ol, $\overline{m}_e^0$ = 1.0 (model I). ❐, —— $\overline{x}$ = 0.4; ■, – – – – $\overline{x}$ = 0.7; ❍, – · – · – · $\overline{x}$ = 1.0

TABLE I
Equilibrium data, binary diluent: octan-1-ol/n-heptane, 25 °C

$\overline{m}_e^0$	m_a	$\overline{m}_a$	$\overline{m}_e^0$	m_a	$\overline{m}_a$	$\overline{m}_e^0$	m_a	$\overline{m}_a$
	$\overline{x}$ = 0.4			$\overline{x}$ = 0.7			$\overline{x}$ = 1.0	
0.296	0.0112	0.1080	0.297	0.0041	0.1252	0.295	0.0016	0.1227
0.296	0.0114	0.1091	0.290	0.0241	0.1445	0.295	0.0039	0.1033
0.288	0.0640	0.1451	0.297	0.0562	0.1620	0.292	0.0232	0.1625
0.310	0.2538	0.1870	0.295	0.2729	0.1859	0.292	0.0849	0.1858
0.308	0.3159	0.1794	0.295	0.4893	0.2129	0.301	0.2530	0.2182
0.293	0.4626	0.1843	0.295	0.8994	0.2401	0.283	0.4526	0.2277
0.297	0.7943	0.2039	0.293	0.9131	0.2402	0.294	0.8866	0.2798
0.294	0.9290	0.2087	0.294	1.346	0.2712	0.295	1.313	0.3132
0.296	1.395	0.2347	0.295	2.063	0.2989	0.295	2.019	0.3416
0.295	2.048	0.2551	0.293	2.827	0.3367	0.284	2.648	0.3240
0.295	3.006	0.2676	0.292	3.709	0.3481	0.295	3.688	0.3789
0.291	3.658	0.3042	1.003	0.0040	0.3670	0.302	3.710	0.4090
1.025	0.0088	0.2930	1.026	0.0056	0.4179	0.280	5.176	0.4409
0.999	0.0116	0.3282	1.183	0.0268	0.5515	0.965	0.0848	0.5645
1.020	0.0304	0.4336	1.003	0.0381	0.5260	0.988	0.2956	0.5883
1.009	0.1600	0.5885	1.020	0.1193	0.5732	1.005	0.3745	0.6883
1.006	0.3704	0.6454	1.016	0.1664	0.6308	0.927	1.334	0.9152
0.998	0.7574	0.7773	1.046	0.2911	0.6789	0.927	1.987	1.051
0.993	0.8412	0.7834	0.848	0.3428	0.5622	0.921	2.902	1.205
1.002	1.472	0.8916	1.005	0.3438	0.6872	0.974	3.798	1.368
0.989	2.136	0.9626	0.831	0.6695	0.6400	0.995	5.365	1.685
0.995	3.738	1.112	0.825	0.7598	0.6561	2.071	0.0022	0.6109
0.987	5.465	1.278	1.020	0.8422	0.8216	1.962	0.0043	0.5877
1.008	8.220	1.521	0.830	0.8794	0.6874	1.990	0.0372	0.9858
2.007	0.0045	0.5210	1.021	1.401	0.9291	1.948	0.0382	1.094
2.016	0.0774	1.100	0.993	1.985	0.9734	1.986	0.1787	1.068
1.887	0.2261	1.272	0.997	2.095	0.9894	2.004	0.3730	1.439
1.990	0.4033	1.487	1.010	2.146	1.036	2.007	0.3848	1.409
2.011	0.4747	1.560	0.978	2.604	1.045	1.900	2.859	2.190
1.953	0.9419	1.667	0.996	2.954	1.129	1.925	3.872	2.085
2.065	1.079	1.738	0.983	3.454	1.159	1.985	4.240	2.356
2.025	1.248	1.766	2.099	0.0046	0.5873	–	–	–
1.944	1.963	1.843	2.107	0.0068	0.7485	–	–	–
1.963	2.160	1.732	2.025	0.0324	1.040	–	–	–
1.961	2.925	1.861	2.052	0.1016	1.204	–	–	–
1.989	3.001	2.114	2.086	0.3511	1.474	–	–	–

TABLE I
(*Continued*)

$\overline{m}_e^0$	m_a	$\overline{m}_a$	$\overline{m}_e^0$	m_a	$\overline{m}_a$	$\overline{m}_e^0$	m_a	$\overline{m}_a$
	$\overline{x}$ = 0.4			$\overline{x}$ = 0.7			$\overline{x}$ = 1.0	
2.037	3.134	2.136	2.096	0.3726	1.549	–	–	–
2.038	4.100	2.248	2.160	0.4822	1.631	–	–	–
–	–	–	2.048	1.529	1.901	–	–	–
–	–	–	2.051	2.306	1.840	–	–	–
–	–	–	2.197	2.901	2.313	–	–	–
–	–	–	2.127	3.458	2.391	–	–	–
–	–	–	1.996	5.440	2.357	–	–	–

expressed as loading of amine $Z = \overline{m}_a/\overline{m}_e^0$. In systems with octan-1-ol and MIBK the independent parameters were varied in the following ranges: the aqueous phase acid molality $m_a \in \langle 2 \,.\, 10^{-3};8.4\rangle$ mol/kg of water, the molality of amine $\overline{m}_e^0 \in \langle 0.3;2.0\rangle$ mol/kg of diluent, the mass fraction of modifier in diluent $\overline{x} \in \langle 0.4;1.0\rangle$ kg/kg of diluent. Measurements in the system containing isodecanol/kerosene as diluent were limited to the TAA molalities 0.3 and 1.0. Maximum loading of amine, $Z = 2.4$, was

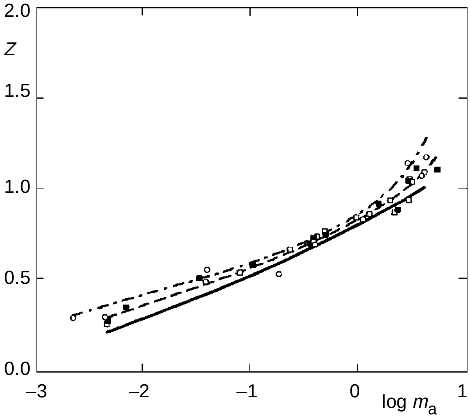

FIG. 3
System with octan-1-ol, $\overline{m}_e^0$ = 2.0 (model I). ❒, —— $\overline{x}$ = 0.4; ■, – – – – $\overline{x}$ = 0.7; ❍, – · – · – · $\overline{x}$ = 1.0

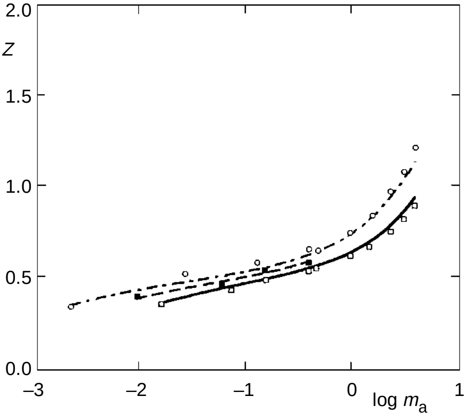

FIG. 4
System with isodecanol, $\overline{m}_e^0$ = 0.3 (model I). ❒, —— $\overline{x}$ = 0.4; ■, – – – – $\overline{x}$ = 0.7; ❍, – · – · – · $\overline{x}$ = 1.0

reached in the system with MIBK at m_a = 8.2 mol/kg of water and $\overline{m}_e^0$ = 0.3 mol/kg of diluent.

In comparing Figs 1–3 (systems with octan-1-ol as modifier) and Figs 4 and 5 (systems with isodecanol as modifier), the similarity of the corresponding isotherms is apparent. A faint plateau at Z = 0.5 can be detected on some isotherms indicating predomination of the (1 : 2) acid/amine complex at low acid molalities. At high acid molalities, especially in combination with a high modifier content, moderate overloading ($Z > 1$) occurs, suggesting formation of the (2 : 1) complex. At medium acid molalities the (1 : 1) complex can be expected to dominate.

TABLE II
Equilibrium data, binary diluent: isodecanol/kerosene, 25 °C

$\overline{m}_e^0$	m_a	$\overline{m}_a$	$\overline{m}_e^0$	m_a	$\overline{m}_a$	$\overline{m}_e^0$	m_a	$\overline{m}_a$
$\bar{x} = 0.4$			$\bar{x} = 0.7$			$\bar{x} = 1.0$		
0.309	0.0155	0.1134	0.300	0.0092	0.1221	0.301	0.0022	0.1041
0.305	0.0696	0.1382	0.300	0.0563	0.1450	0.298	0.0255	0.1597
0.299	0.1470	0.1527	0.297	0.1428	0.1667	0.302	0.1214	0.1828
0.300	0.3693	0.1687	0.297	0.3714	0.1804	0.301	0.3693	0.2048
0.299	0.4352	0.1723	–	–	–	0.299	0.4548	0.2016
0.299	0.9248	0.1936	–	–	–	0.303	0.9064	0.2356
0.298	1.385	0.2085	–	–	–	0.308	1.474	0.2689
0.297	2.201	0.2341	–	–	–	0.299	2.173	0.3015
0.298	2.920	0.2560	–	–	–	0.299	2.894	0.3340
0.299	3.692	0.2788	–	–	–	0.302	3.677	0.3778
0.990	0.0155	0.4254	–	–	–	1.013	0.0044	0.4164
1.002	0.1006	0.5756	–	–	–	1.015	0.0707	0.5597
0.996	0.2961	0.6335	–	–	–	1.012	0.2406	0.6467
0.988	0.3233	0.6364	–	–	–	0.997	0.8167	0.7909
0.981	0.8664	0.7443	–	–	–	0.993	1.371	0.9044
0.999	1.417	0.8609	–	–	–	0.993	2.708	1.066
0.989	2.777	0.9963	–	–	–	0.990	4.228	1.224
0.997	3.854	1.100	–	–	–	1.004	6.233	1.361
0.980	4.475	1.102	–	–	–	–	–	–
0.974	7.585	1.390	–	–	–	–	–	–

The isotherms in the systems with MIBK as modifier display a quite different shape (Figs 6–11). Here a plateau at $Z = 1$ and a less pronounced one at $Z = 0.5$ can be observed and all curves show overloading at high acid molalities. With pure MIBK as diluent, loadings higher than 2 have been reached, indicating formation of the (3 : 1) complex.

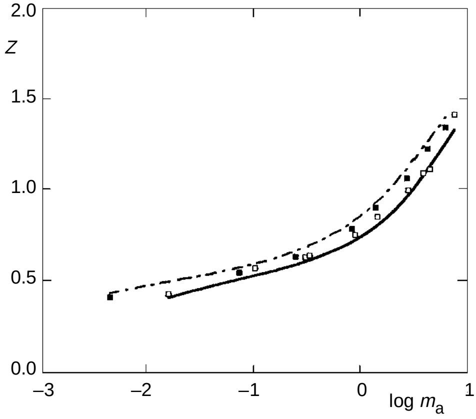

FIG. 5
System with isodecanol, $\overline{m}_\mathrm{e}^0 = 1.0$ (model I). ❐, —— $\bar{x} = 0.4$; ■, – – – – $\bar{x} = 1.0$

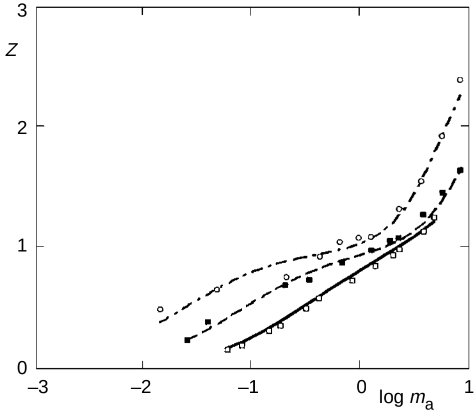

FIG. 6
System with MIBK, $\overline{m}_\mathrm{e}^0 = 0.3$ (model III). ❐, —— $\bar{x} = 0.4$; ■, – – – – $\bar{x} = 0.7$; ❍, – · – · – · $\bar{x} = 1.0$

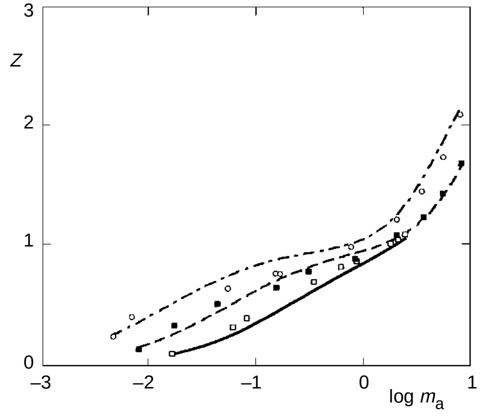

FIG. 7
System with MIBK, $\overline{m}_\mathrm{e}^0 = 1.0$ (model III). ❐, —— $\bar{x} = 0.4$; ■, – – – – $\bar{x} = 0.7$; ❍, – · – · – · $\bar{x} = 1.0$

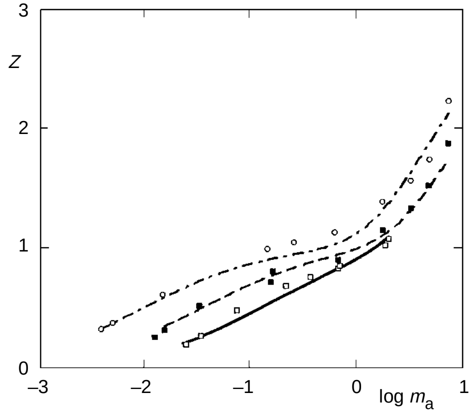

FIG. 8
System with MIBK, $\overline{m}_\mathrm{e}^0 = 2.0$ (model III). ❐, —— $\bar{x} = 0.4$; ■, – – – – $\bar{x} = 0.7$; ❍, – · – · – · $\bar{x} = 1.0$

TABLE III
Equilibrium data, binary diluent: MIBK/n-heptane, 25 °C

$\overline{m}_e^0$	m_a	$\overline{m}_a$	$\overline{m}_e^0$	m_a	$\overline{m}_a$	$\overline{m}_e^0$	m_a	$\overline{m}_a$
$\overline{x} = 0.4$			$\overline{x} = 0.7$			$\overline{x} = 1.0$		
0.278	0.0577	0.0437	0.289	0.0244	0.0677	0.301	0.0138	0.1474
0.273	0.0795	0.0532	0.286	0.0379	0.1105	0.288	0.0460	0.1885
0.278	0.1419	0.0874	0.292	0.2017	0.2030	0.293	0.2051	0.2247
0.283	0.1809	0.1013	0.288	0.3348	0.2141	0.294	0.4171	0.2743
0.287	0.3127	0.1429	0.289	0.6727	0.2549	0.297	0.6340	0.3134
0.280	0.4119	0.1637	0.279	1.266	0.2766	0.291	0.9495	0.3175
0.307	0.8335	0.2255	0.291	1.891	0.3090	0.297	1.239	0.3262
0.291	1.372	0.2495	0.294	2.256	0.3208	0.306	2.280	0.4083
0.292	2.021	0.2775	0.286	3.808	0.3677	0.299	3.646	0.4682
0.279	2.290	0.2781	0.285	5.726	0.4200	0.301	5.634	0.5850
0.273	3.828	0.3124	0.283	8.387	0.4702	0.299	8.223	0.7210
0.263	4.806	0.3327	0.955	0.0079	0.1256	1.017	0.0045	0.2415
0.929	0.0160	0.0887	0.969	0.0168	0.3247	1.024	0.0067	0.4095
0.954	0.0585	0.3075	0.969	0.0421	0.4979	1.004	0.0522	0.6482
0.964	0.0787	0.3829	0.990	0.1486	0.6499	1.035	0.1461	0.8021
0.951	0.3294	0.6721	0.991	0.2966	0.7863	1.007	0.1601	0.7785
0.939	0.5933	0.7839	0.995	0.8069	0.8991	1.031	0.7356	1.031
0.949	0.8256	0.8354	0.982	1.975	1.082	1.055	1.977	1.301
0.945	1.727	0.9713	0.985	3.519	1.237	1.027	3.377	1.514
0.965	2.033	1.026	0.973	5.347	1.415	1.031	5.338	1.812
0.950	2.365	1.054	0.959	7.928	1.638	1.027	7.717	2.174
2.046	0.0242	0.3958	2.102	0.0154	0.6654	–	–	–
2.069	0.0336	0.5501	2.097	0.0123	0.5351	–	–	–
2.063	0.0726	0.9962	2.091	0.0322	1.082	–	–	–
2.022	0.2109	1.390	2.121	0.1524	1.531	–	–	–
2.053	0.3605	1.567	2.183	0.1602	1.774	–	–	–
2.085	0.6524	1.747	2.135	0.6541	1.945	–	–	–
2.083	0.6763	1.789	2.253	1.758	2.615	–	–	–
2.135	1.865	2.205	2.183	3.295	2.938	–	–	–
2.136	2.012	2.324	2.221	4.861	3.414	–	–	–
–	–	–	2.221	7.371	4.193	–	–	–

According to Tamada *et al.*[4] and Bizek *et al.*[8] in systems containing only acid/amine complexes with one amine molecule in the complex, $j = 1$, the loading Z should not depend on $\overline{m}_{\mathrm{e}}^{0}$, except for nonspecific effects. If $(i : j)$ complexes with $j > 1$ occur, Z should increase with increasing TAA molality. However, when comparing Figs 1–5 (systems with alcoholic modifiers) one cannot detect any marked effect of $\overline{m}_{\mathrm{e}}^{0}$ on Z. This contradicts the expected formation of the (1 : 2) complex at low acid molalities in these systems. On the other hand, the systems with MIBK show a marked growth of Z with increasing TAA molality (Figs 6–11). These inconsistencies may be due to the competition of specific and nonspecific effects of amine, as will be explained below.

A comparison of the graphs of systems with alcoholic modifiers on one hand, and those with the ketone modifier on the other, shows a higher extraction power of the latter modifier. Another difference in the behaviour of these systems concerns forma-

TABLE IV
Model variants

Variant No.	Complexes
I	(1 : 1); (1 : 2); (2 : 1)
II	(1 : 1); (2 : 1)
III	(1 : 1); (2 : 1); (3 : 1)
IV	(1 : 1); (1 : 2); (3 : 1)

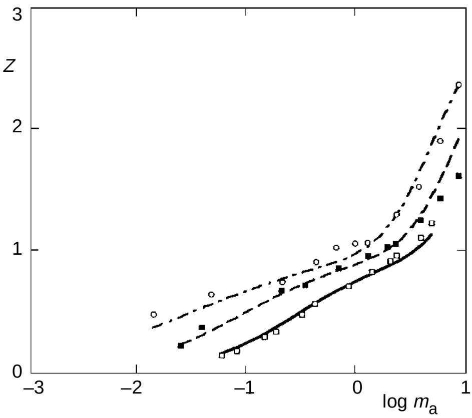

FIG. 9
System with MIBK, $\overline{m}_{\mathrm{e}}^{0}$ = 0.3 (model IV). ❐, —— $\overline{x}$ = 0.4; ■, – – – – $\overline{x}$ = 0.7; ❍, – · – · – · $\overline{x}$ = 1.0

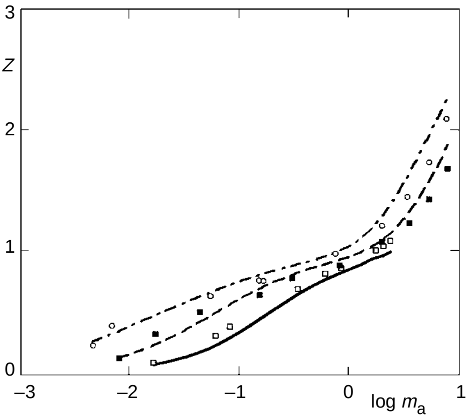

FIG. 10
System with MIBK, $\overline{m}_{\mathrm{e}}^{0}$ = 1.0 (model IV). ❐, —— $\overline{x}$ = 0.4; ■, – – – – $\overline{x}$ = 0.7; ❍, – · – · – · $\overline{x}$ = 1.0

tion of the third phase. In the systems with alcoholic modifiers no third phase formation was observed. In the system with MIBK, a third phase formed at $\overline{x} = 0.4$. The ends of the respective isotherms in Figs 6–11 mark the acid molalities at which the third phase appears.

TABLE V
Parameter values of models

$(i : j)$	β_{ij}	A_{ij}	B_{ij}	C_{ij}
System with octan-1-ol/n-heptane – model I $s_r = 5.70 . 10^{-2}$; $N = 112$				
(1 : 1)	$7.848 . 10^{0}$	$1.283 . 10^{-2}$	$1.640 . 10^{0}$	$-1.482 . 10^{-1}$
(1 : 2)	$3.813 . 10^{2}$	$-1.494 . 10^{0}$	$3.333 . 10^{0}$	$-6.836 . 10^{-1}$
(2 : 1)	$5.740 . 10^{-1}$	$-1.861 . 10^{0}$	$3.379 . 10^{0}$	$8.169 . 10^{-1}$
System with octan-1-ol/n-heptane – model II $s_r = 1.70 . 10^{-1}$; $N = 112$; $F_{II/I} = 8.91$; $F_{0.05} = 1.41$				
(1 : 1)	$1.307 . 10^{1}$	$2.991 . 10^{-1}$	$2.706 . 10^{0}$	$-2.017 . 10^{0}$
(1 : 2)	$4.156 . 10^{-2}$	$-2.598 . 10^{0}$	$3.711 . 10^{0}$	$4.025 . 10^{-1}$
System with isodecanol/kerosene – model I $s_r = 3.08 . 10^{-2}$; $N = 42$				
(1 : 1)	$2.768 . 10^{0}$	$-7.951 . 10^{-2}$	$2.185 . 10^{0}$	$2.085 . 10^{0}$
(1 : 2)	$3.603 . 10^{2}$	$-2.218 . 10^{0}$	$3.039 . 10^{0}$	$2.910 . 10^{0}$
(2 : 1)	$2.513 . 10^{-1}$	$-1.051 . 10^{0}$	$2.727 . 10^{0}$	$2.606 . 10^{0}$
System with MIBK/n-heptane – model III $s_r = 6.19 . 10^{-2}$; $N = 92$				
(1 : 1)	$6.170 . 10^{-1}$	$7.178 . 10^{-1}$	$4.234 . 10^{0}$	$-5.368 . 10^{-1}$
(2 : 1)	$1.791 . 10^{-1}$	$1.388 . 10^{-1}$	$9.673 . 10^{-3}$	$3.207 . 10^{-1}$
(3 : 1)	$1.024 . 10^{-4}$	$1.964 . 10^{0}$	$9.240 . 10^{0}$	$-1.113 . 10^{0}$
System with MIBK/n-heptane – model IV $s_r = 6.44 . 10^{-2}$; $N = 92$; $F_{IV/III} = 1.08$; $F_{0.05} = 1.48$				
(1 : 1)	$6.403 . 10^{-1}$	$4.588 . 10^{-1}$	$3.796 . 10^{0}$	$4.341 . 10^{-1}$
(1 : 2)	$9.000 . 10^{-2}$	$-1.395 . 10^{0}$	$8.122 . 10^{0}$	$6.161 . 10^{-1}$
(3 : 1)	$8.669 . 10^{-4}$	$1.444 . 10^{0}$	$7.190 . 10^{0}$	$-1.390 . 10^{-1}$

In a previous study on amine extraction of citric acid with octan-1-ol and MIBK as modifiers[10], it was found that whereas the system with octanol did not show any overloading, the system with MIBK exhibited a strong overloading. This phenomenon was explained by the proton-donating character of the alcohol and the electron-donating character of the ketone, respectively. The results of the present study indicate that the nature of both the acid and the modifier may contribute to the effect of overloading.

Data Correlation and Simulation

The above analysis of the experimental results suggests that in the case of systems with octanol and isodecanol as modifiers the mathematical model should include formation of (1 : 1) and (2 : 1) complexes in organic phase. In the systems with MIBK as modifier (1 : 1) and (3 : 1) complexes should be incorporated. As the algorithm used allows to include three parallel chemical reactions, a third complex has been considered, namely (1 : 2), in the systems with alcohols and (2 : 1) or (1 : 2) in the system with ketone. To corroborate the assumption of importance of the (1 : 2) complex in the systems with alcohols the models with complexes (1 : 1), (1 : 2), (2 : 1) and (1 : 1), (2 : 1) have been compared. The four model variants used are shown in Table IV.

The particular forms of Eqs (*3*)–(*5*) for the individual model variants are:

Model I:

$$\overline{m}_a = \beta'_{11} m_a \overline{m}_e + \beta'_{12} m_a \overline{m}_e^2 + 2\,\beta'_{21} m_a^2\,\overline{m}_e \qquad (8)$$

$$\overline{m}_e^0 = \overline{m}_e + \beta'_{11} m_a \overline{m}_e + 2\,\beta'_{12} m_a \overline{m}_e^2 + \beta'_{21} m_a^2\,\overline{m}_e \qquad (9)$$

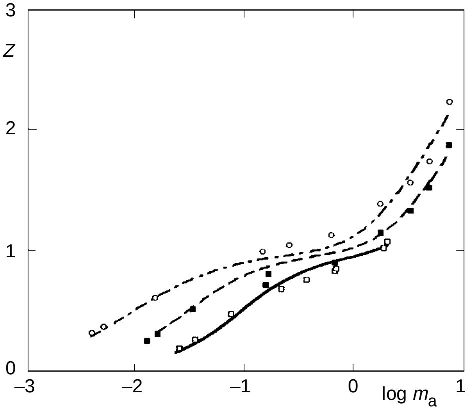

FIG. 11
System with MIBK, $\overline{m}_e^0$ = 2.0 (model IV). ❐, —— $\bar{x}$ = 0.4; ■, – – – – $\bar{x}$ = 0.7; ❍, – · – · – · $\bar{x}$ = 1.0

Model II:

$$\overline{m}_\mathrm{a} = \beta'_{11} m_\mathrm{a} \overline{m}_\mathrm{e} + 2\,\beta'_{21} m_\mathrm{a}^2\,\overline{m}_\mathrm{e} \tag{10}$$

$$\overline{m}_\mathrm{e}^0 = \overline{m}_\mathrm{e} + \beta'_{11} m_\mathrm{a} \overline{m}_\mathrm{e} + \beta'_{21} m_\mathrm{a}^2\,\overline{m}_\mathrm{e} \tag{11}$$

Model III:

$$\overline{m}_\mathrm{a} = \beta'_{11} m_\mathrm{a} \overline{m}_\mathrm{e} + 2\,\beta'_{21} m_\mathrm{a}^2\,\overline{m}_\mathrm{e} + 3\,\beta'_{31} m_\mathrm{a}^3\,\overline{m}_\mathrm{e} \tag{12}$$

$$\overline{m}_\mathrm{e}^0 = \overline{m}_\mathrm{e} + \beta'_{11} m_\mathrm{a} \overline{m}_\mathrm{e} + \beta'_{21} m_\mathrm{a}^2\,\overline{m}_\mathrm{e} + \beta'_{31} m_\mathrm{a}^3\,\overline{m}_\mathrm{e} \tag{13}$$

Model IV:

$$\overline{m}_\mathrm{a} = \beta'_{11} m_\mathrm{a} \overline{m}_\mathrm{e} + \beta'_{12} m_\mathrm{a} \overline{m}_\mathrm{e}^2 + 3\,\beta'_{31} m_\mathrm{a}^3\,\overline{m}_\mathrm{e} \tag{14}$$

$$\overline{m}_\mathrm{e}^0 = \overline{m}_\mathrm{e} + \beta'_{11} m_\mathrm{a} \overline{m}_\mathrm{e} + 2\,\beta'_{12} m_\mathrm{a} \overline{m}_\mathrm{e}^2 + \beta'_{31} m_\mathrm{a}^3\,\overline{m}_\mathrm{e} \tag{15}$$

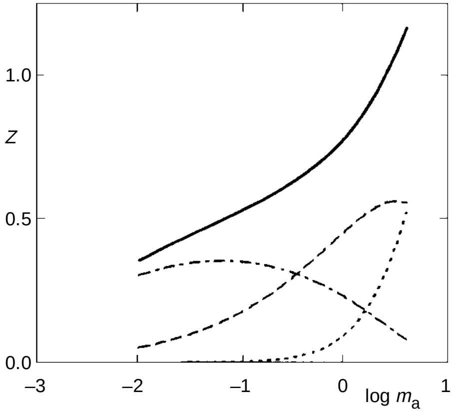

FIG. 12
System with octan-1-ol, $\overline{m}_\mathrm{e}^0 = 0.3$; $\overline{x} = 0.4$. Contributions of individual complexes to the amine loading. Simulation using model I: —— Z, – – – Z_{11}, – · – · – Z_{12}, · · · · Z_{21}

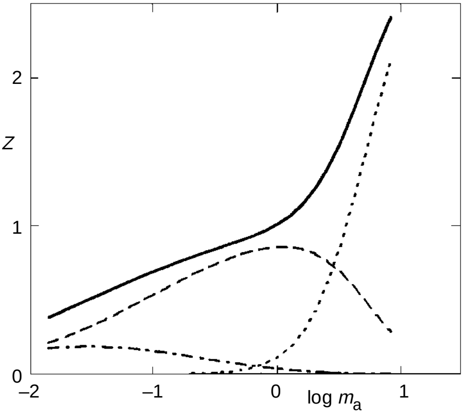

FIG. 13
System with MIBK, $\overline{m}_\mathrm{e}^0 = 2.0$; $\overline{x} = 1.0$. Simulation using model IV: —— Z, – – – Z_{11}, – · – · – Z_{12}, · · · · Z_{31}

and

$$\beta'_{11} = \overline{m}_{11}/m_a\overline{m}_e; \quad \beta'_{12} = \overline{m}_{12}/m_a\overline{m}_e^2; \quad \beta'_{21} = \overline{m}_{21}/m_a^2\,\overline{m}_e; \quad \beta'_{31} = \overline{m}_{31}/m_a^3\,\overline{m}_e \ . \qquad (16)$$

The optimized values of model parameters for the individual systems and model variants are collected in Table V. As a measure of fit of the correlation, the relative standard deviation of measured and calculated data

$$s_r = \left(\frac{1}{2N-n} \sum_{k=1}^{N} [(1 - m_{a(cal)}/m_{a(exp)})^2 + (1 - \overline{m}_{a(cal)}/\overline{m}_{a(exp)})^2]_k \right)^{1/2} \qquad (17)$$

was used. Here n is the number of parameters evaluated. For the systems with octan-1-ol the models I and II, and for the systems with MIBK the models III and IV were also compared by means of the F-test[13]. (The value of the variance ratio for models p and q, $F_{p/q} = s_{rp}^2/s_{rq}^2$, is compared with the tabulated 5% confidence limit $F_{0.05}$.) The values of N, s_r, F and $F_{0.05}$ are included in the table.

The values of s_r in Table V show generally a good fit of the data and the models used. Model II is an exception which demonstrates the importance of including the (1 : 2) complex in the correlation. The statistics for the systems with MIBK in Table V do not indicate any improvement of fit when model IV is applied instead of model III. Figures 6–11, however, show a local improvement of correlation with model IV for $m_a < 1$.

A partial interdependence of the model parameters has been observed leading to a drop of sensitivity of the optimization procedure near the global optimum. This uncertainty increases with the growing random experimental error. Therefore a comparison of the parameter values for individual investigated systems cannot be very conclusive. Nevertheless, one can see that the values of corresponding parameters of model I for the systems with octan-1-ol and isodecanol in Table V are close to each other, in accord with the similarity of the corresponding experimental isotherms in both systems.

It is interesting to note that for the systems with alcoholic modifiers, the values of the coefficients A_{ij}, expressing the nonspecific effects of amine, are mostly *negative*. This is consistent with the assumption made above that these nonspecific effects may compensate the positive specific effect of formation of the (1 : 2) complex on loading.

A further indication of the importance of the (1 : 2) complex in the systems examined is demonstrated in Figs 12 and 13. Here the contributions Z_{ij} of the individual complexes to the overall loading, Z, are shown. The curves have been simulated using model I for the system with octan-1-ol and model IV for the system with MIBK.

CONCLUSIONS

1. A comparison of extraction equilibria in systems aqueous solution of D-tartaric acid/solution of trialkylamine in binary diluents octan-1-ol/n-heptane and isodecanol/kerosene shows practically no difference between the effects of the two diluents. A moderate overloading of amine takes place at high acid molalities indicating formation of the (2 : 1) complex. It increases with increasing content of modifier in the diluent. However, at low and medium acid contents in aqueous phase, the influence of diluent composition on extraction is low. The molality of amine has no effect on its loading. Accordingly, with these modifiers, the possibilities of utilizing the *diluent swing* effect in an extraction–re-extraction technology are limited. No third phase formation has been observed in these systems in the range of the conditions examined.

2. In contrast to the two alcoholic modifiers, MIBK exerts a pronounced effect on the extraction equilibrium of D-tartaric acid. It significantly promotes the extraction in the whole range of aqueous acid molalities and contributes, at high acid molalities, to high overloading of amine. As loadings $Z > 2$ have been found, formation of the (3 : 1) complex is to be assumed. At medium acid contents, the plateaus on the isotherms at $Z \approx 1$ suggest the predominance of the (1 : 1) complex in organic phase in this region. A less pronounced plateau at $Z \approx 0.5$ and a moderate increase in loading with TAA molality indicate formation of the (1 : 2) complex at low acid molality. At the lowest modifier content in the diluent, third phase formation was observed for all amine molalities investigated.

3. Three variants of a mathematical model have been successfully used for correlation of equilibrium data. The variant I for alcoholic modifiers and III or IV for MIBK, together with the respective sets of parameter values, can be used for prediction of the equilibria in the range covered by the experimental data.

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SYMBOLS

A_{ij}	constant in Eq. (*6*), kg of diluent/mol
B_{ij}	constant in Eq. (*6*), kg of diluent/kg of modifier
C_{ij}	constant in Eq. (*6*), kg of water/mol
$F_{p/q}$	ratio of variances of models p and q
$F_{0.05}$	value of 5% confidence limit of single sided F-test
K	number of complexes in the model
m_a	molality of acid in aqueous phase, mol/kg of water
$\overline{m}_\mathrm{a}$	total molality of acid in organic phase, mol/kg of diluent
$\overline{m}_\mathrm{e}$	molality of free amine in organic phase, mol/kg of diluent
$\overline{m}_\mathrm{e}^0$	total molality of amine in organic phase, mol/kg of diluent
$\overline{m}_{ij}$	molality of complex (i : j) in organic phase, mol/kg of diluent
MIBK	methyl isobutyl ketone

n	number of model parameters
N	number of experimental points
s_r	relative standard deviation, Eq. (*15*)
S	weighted sum of squares of relative deviations, Eq. (*7*)
TAA	trialkylamine
W_k	weight of square of *k*-th deviation
x	mass fraction of modifier in diluent, kg of modifier/kg of diluent
Z	loading of extractant, mol of acid/mol of amine
Z_{ij}	contribution of complex ($i : j$) to loading of extractant, mol of acid/mol of amine
β_{ij}	thermodynamic overall extraction equilibrium constant of complex ($i : j$), $(\mathrm{kg/mol})^{i+j-1}$
β'_{ij}	conditioned overall extraction equilibrium constant of complex ($i : j$), $(\mathrm{kg/mol})^{i+j-1}$
$\overline{\gamma}_e$	activity coefficient of free amine in organic phase
$\overline{\gamma}_{ij}$	activity coefficient of complex ($i : j$) in organic phase

Subscripts

cal	calculated values
exp	experimental values

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