

Table I. Solubility of Benzene, Toluene, and Chlorobenzene in Water

	Weight in vacuo, grams		Ratio of gas chro- matograph peak areas	Concn of std soln, g/g soln	Solubility (21° ± 1°C) g/100 g H ₂ O	Mean value	Av dev measure- ments	% Dev from mean lit. value	Lit. value, g/ 100 g H ₂ O	Ref.
	H ₂ O soln	Eluent								
Benzene	24.7267	11.1539	0.7936	0.004968	0.178			2.3	0.171 ± 0.002	(3)
	37.2681	11.6291	0.8774	0.005548	0.152	0.174	0.011	12	0.179	(4)
	37.3462	9.4237	1.3067	0.005548	0.183			5.2	0.174	(6)
	39.9882	10.0274	1.3197	0.005548	0.184			3.7	0.174	(2)
Toluene	30.4742	9.0561	0.2401	0.005515	0.0394			7		
	28.2919	9.1872	0.3388	0.005515	0.0607	0.0479	0.0086	32	0.0627	(4)
	19.7750	4.5221	0.3810	0.004968	0.0435			25	0.055	(7)
									0.053	(2)
Chlorobenzene	35.4719	10.1696	0.3426	0.005556	0.0546	0.0534	0.0011	11	0.050	(8)
	29.9234	11.2880	0.2492	0.005556	0.0523			4		

amount of water dissolved in the isopropyl ether. Separate experiments verified that the solute concentration was unaffected by the addition of the molecular sieve. A 1.5- μ l. sample of the ether solution was injected into a Carle gas chromatograph Model 8004 fitted with a 5 ft \times 1/8 in. o.d. stainless steel column packed with 80-100 mesh Chromosorb which supported a 15% by weight liquid phase of Carbowax 20M. A flow rate of 15 cc He/min at 25°C was used, and the effluents were detected by a dual thermistor. The sample inlet, column, and detector were maintained at 100°C. Immediately before or after each sample injection the chromatograph was calibrated using a standard solution of the compound in isopropyl ether. The areas of the peaks were measured planimetrically. The recorder parameters were adjusted so as to maintain a peak height to peak width ratio between 10:1 and 5:1 to minimize errors in the planimetry.

RESULTS AND DISCUSSION

The solubility of the test compounds—benzene, toluene, and chlorobenzene—presented in Table I are generally in good agreement with values obtained from other methods. Because the purpose of this work was only to demonstrate the feasibility of the method, certain experimental variables were not so rigidly controlled as would be desired for accurate quantitative data. For example, the water should be deaerated and care-

fully thermostated, equilibrium of the solute should be checked by successive determinations over an extended period of time, and light scattering experiments should be carried out on the solution to ensure that the solute is not suspended in the solution rather than relying on visual examination. The data suggest that results of the order of 5-10% accuracy are possible even without these precautions, and that results of accuracy comparable to more sophisticated methods are attainable.

LITERATURE CITED

- (1) "Amberlite XAD Macroreticular Absorbants," Rohm and Haas Co., Philadelphia, Pa., 1970.
- (2) Andrews, L. J., Keefer, R. M., *J. Amer. Chem. Soc.*, **71**, 3645 (1949).
- (3) Arnold, D. S., Plank, C. A., Erickson, E. E., Pike, F. P., *J. Chem. Eng. Data*, **3**, 253 (1958).
- (4) Bohon, R. L., Claussen, W. F., *J. Amer. Chem. Soc.*, **73**, 1571 (1951).
- (5) Burnham, A. K., Calder, G. V., Fritz, J. S., Junk, G. A., Svec, H. J., Willis, R., *Anal. Chem.*, **44**, 139 (1972).
- (6) Dreisbach, R. R., *Advan. Chem. Ser.*, **15**, 11 (1955).
- (7) Dreisbach, R. R., *ibid.*, p 12.
- (8) Dreisbach, R. R., *ibid.*, p 134.

RECEIVED for review September 15, 1971. Accepted December 16, 1971. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

Electrical Conductance of Binary Nitrate Mixtures

HARISH C. GAUR¹ and SURENDER K. JAIN

Department of Chemistry, University of Delhi, Delhi-7, India

The electrical conductance of molten NaNO₃-Sr(NO₃)₂, KNO₃-Sr(NO₃)₂, NaNO₃-Pb(NO₃)₂, KNO₃-Pb(NO₃)₂, AgNO₃-Pb(NO₃)₂, and TlNO₃-Pb(NO₃)₂ mixtures has been measured as a function of temperature and the divalent ion content in the mixture.

The electrical conductance of molten alkali metal nitrates and their binary/ternary mixtures has been reported by several workers (2, 3, 11-14). There are relatively fewer such studies for the mixtures of monovalent and divalent/trivalent metal nitrates. In continuation of our previous studies of such mixtures (4-7), specific conductance data for the systems (Na,K)-NO₃-(Sr, Pb)(NO₃)₂, (Ag, Tl)NO₃-Pb(NO₃)₂ at various com-

positions and over a wide temperature range are presented in this paper.

EXPERIMENTAL

LR(BDH)-grade thallium and strontium nitrates were recrystallized from demineralized water. All other reagents were of AnalaR (BDH) grade; these were desiccated in the following

¹ To whom correspondence should be addressed.

manner: Sodium, potassium, and strontium nitrates were baked at 200–50°C for several days. Thallium and lead nitrates were kept at 100–10°C for 8–10 hr. Silver nitrate was vacuum-desiccated at room temperature for several days. All the salts were stored over magnesium perchlorate until used. Mixtures of varying compositions were separately prepared by melting the requisite amounts of the components under nitrogen atmosphere, bubbling the gas through the melt for about 30 min, rapidly cooling in a porcelain trough, and grinding to a fine powder in a glove box. About 30 grams of the salt mixture was loaded into one limb of a capillary-type conductivity cell and fused in situ under a nitrogen stream. Disc electrodes (diam \approx 6 mm) were fabricated from bright platinum. A Beckmann conductivity bridge (Model RC-18A), based upon the Wheatstone-bridge principle, provided with a phase-sensitive CRT null detector, a Wagner-ground circuit, and a sharply tuned amplifier, was employed. A decade capacitance box was externally connected in parallel with the resistance in the balancing arm of the bridge. All leads to and from the

bridge were made with coaxial cables. Capillary-type conductivity cells made from borosilicate glass were used. The cell constants were determined using 1N KCl and saturated NaCl solutions at $18.00 \pm 0.02^\circ\text{C}$ using platinized platinum electrodes of large area; for different cells, these ranged between 125 and 350 cm^{-1} . All the measurements were made at an ac frequency of 1 kHz. The bridge made possible conductance measurements with an accuracy of $\pm 0.05\%$. Melt temperatures were controlled and known with a precision better than $\pm 0.5^\circ\text{C}$.

RESULTS AND DISCUSSION

In the bridge as employed, a parallel combination of resistance (R_p) and capacitance (C_p) formed the balancing arm and the resistances of the ratio arms (R_{std}) were matched. Considering the cell impedance as series combination of a resistance (R_s) and capacitance (C_s) (β), the following conditions must be

Table I. Specific Conductance Equations for Several Binary Nitrate Mixtures

Equivalents of divalent ion, κ'	Temp range, $^\circ\text{C}$	$k = a + bt + ct^2(\text{ohm}^{-1}\text{ cm}^{-1})$			Std dev $\text{ohm}^{-1}\text{ cm}^{-1}$	Energy of activation, E_k (kcal)
		a	$b \cdot 10^3$	$c \cdot 10^5$		
NaNO ₃ -Sr(NO ₃) ₂ System						
0.0	346-462	-0.892	0.756	-0.453	0.006	2.75-2.20
0.120	292-482	-1.0940	0.7985	-0.5625	0.0055	3.78-2.05
0.261	337-494	-1.8291	1.0371	-0.7967	0.0068	4.48-2.09
0.333	341-451	-1.8146	0.9853	-0.7887	0.0016	5.00-2.80
0.462	443-468	-1.2574	0.4685	...	0.000008	2.32
KNO ₃ -Sr(NO ₃) ₂ System ^a						
0.0	337-506	-0.826	0.528	-0.287	0.0030	3.70-2.64
0.095	316-490	-0.7177	0.4513	-0.1955	0.0025	4.24-2.89
0.181	324-486	-0.6577	0.4102	-0.1613	0.0022	4.29-3.08
0.260	290-463	-0.5432	0.3374	-0.0818	0.0028	4.75-3.38
0.400	363-463	-0.5987	0.3288	-0.0813	0.0008	4.63-3.70
0.518	386-490	-1.3809	0.5806	-0.3025	0.0018	6.66-4.31
0.571	485-495	-0.9029	0.3629	-0.0717	0.0021	4.707
NaNO ₃ -Pb(NO ₃) ₂ System						
0.095	302-397	-1.1854	0.8784	-0.6421	0.0023	3.69-2.52
0.182	291-380	-1.1688	0.8721	-0.7161	0.0019	3.59-2.55
0.261	278-370	-1.1673	0.8484	-0.6776	0.0033	4.34-2.67
0.339	287-351	-4.2729	2.7363	-3.6092	0.0073	5.41-1.8
0.400	282-334	-12.834	7.9698	-11.644	0.0008	10.78-3.7
KNO ₃ -Pb(NO ₃) ₂ System						
0.095	315-373	-0.2860	0.2306	0.1065	0.0013	3.70-3.52
0.182	290-368	-0.3897	0.2890	0.0130	0.0017	3.95-3.50
0.261	268-375	-0.4714	0.3445	-0.0912	0.0011	4.31-3.21
0.333	239-354	-0.4046	0.2958	-0.0078	0.0005	5.60-3.60
0.400	239-364	-0.4519	0.3267	-0.0700	0.0010	5.87-3.29
0.462	234-351	-1.0033	0.6846	-0.6461	0.0049	9.24-2.98
0.519	271-336	-2.9266	1.8387	-2.3654	0.0036	9.41-2.30
0.571	310-348	-5.0087	2.9584	-3.8727	0.0030	10.86-3.17
AgNO ₃ -Pb(NO ₃) ₂ System						
0.0	232-328	-0.5337	0.6588	-0.4385	0.0014	3.13-2.32
0.095	208-319	-0.3743	0.4696	-0.09477	0.0009	3.64-2.76
0.182	283-349	-2.3122	1.7342	-2.2211	0.0008	3.93-1.33
0.333	295-331	-0.1632	0.2647	...	0.0107	2.70
TlNO ₃ -Pb(NO ₃) ₂ System						
0.0	215-415	-0.3335	0.3702	-0.2002	0.0019	3.47-2.20
0.095	212-396	-0.1722	0.2521	-0.0227	0.0006	3.11-2.62
0.182	246-380	-0.2830	0.3092	-0.1059	0.0011	3.29-2.58
0.261	203-371	-0.2869	0.3081	-0.1119	0.0019	4.11-2.56
0.400	230-356	-0.3080	0.3277	-0.1696	0.0025	3.61-2.45
0.519	277-344	-0.5129	0.4364	-0.3238	0.0026	3.48-2.41
0.571	311-344	-3.0362	1.9070	-2.4750	0.0008	3.87-2.21

^a Extrapolation of data corresponding to $\kappa' = 0.182, 0.353,$ and 0.461 showed agreement within $\pm 1\%$ of the values reported by De Nooijer (13) at these compositions.

Table II. Specific Conductance Values for Pure Salts in Comparison with Literature Values, Temperature, °C

Salt	225	250	275	300	325	350	375	400	425	450	475	500	Reference
NaNO ₃	1.182	1.286	1.376	1.474	1.570	Murgulescu and Zuca (3 kHz) (12)
	1.1770	1.2846	1.3876	1.4863	1.5803	King and Duke (DC) (11)
	1.1994	1.3064	1.4077	1.5033	1.5933	1.6777	...	Present work (1 kHz)
KNO ₃	0.664	0.755	0.840	0.914	0.988	Murgulescu and Zuca (3 kHz) (12)
	0.6656	0.7462	0.8233	0.8969	0.9672	King and Duke (DC) (11)
	0.6719	0.7520	0.8286	0.9016	0.9710	1.0370	1.0990	Present work (1 kHz)
	0.6596	0.7385	0.8148	0.8886	0.9598	1.0286	1.0948	Robbins and Braunstein (14) ^a
AgNO ₃	...	0.836	0.938	1.038	1.138	1.230	Duke and Fleming (3)
	0.7118	0.8296	0.9404	1.0479	1.1554	1.2629	De Nooijer (20 kHz) (13)
	0.7266	0.8392	0.9464	1.0481	1.1443	1.2350	Present work (1 kHz)
TlNO ₃	0.3956	0.4638	0.5228	0.5888	0.6548	0.7028	De Nooijer (20 kHz) (13)
	0.3982	0.4670	0.5332	0.5970	0.6583	0.7171	0.7734	0.8271	0.8784	0.9272	Present work (1 kHz)

^a Reported to be frequency-independent over the range 1-50 kHz.

satisfied at balance (15):

$$\frac{R_s}{R_p} + \frac{C_p}{C_s} = \frac{R_{std}}{R_{std}} = 1 \quad (1)$$

and

$$R_s R_p C_s C_p (2 \pi f)^2 = 1 \quad (2)$$

where f is the frequency of the ac signal in Hz.

Combining Equations 1 and 2, one has

$$R_s = \left[\frac{R_p}{1 + (R_p C_p 2 \pi f)^2} \right] \quad (3)$$

which was used to evaluate R_s , the solution resistances.

Table I gives the least-square fitted equations representing the temperature dependence of specific conductance over the specified temperature range for mixtures of varying composition for the different systems. In all cases specific conductance has a positive temperature coefficient and decreases with the increase in divalent ion content in the mixture. The specific conductance data on pure salts, viz NaNO₃, KNO₃, AgNO₃, and TlNO₃ obtained in this study (Table II), are in good agreement with those reported in the literature (3, 11-14). Comparison of observed specific conductance for pure salts (Table II) with the literature values at various frequencies led us to believe that the polarization effects were negligible. Electrical conductance in pure and mixed molten nitrate systems seems to be ionic and no structural transformation (complexation etc.) due to the addition of divalent ion is apparent from the conductance-composition isotherms. The gradual decrease in conductance on the addition of divalent ion could be considered to come about because of "hindered" ion migration resulting from the increased coulombic interactions. Plots of $\ln k$ vs. $1/T$ were curved indicating that the temperature dependence of specific conductance could not be described by a conventional Arrhenius-type equation. Activation energies (Arrhenius coefficient, E_k) included in Table I, were evaluated from

$$E_k = -R \left[\frac{d \ln \kappa}{(1/T)} \right]$$

Some attempts have been made to correlate E_k with the lattice energy (U_0) of single salts (1). This has been examined in this case for single monovalent nitrates at $T/T_m = 1.1$ where T_m refers to the melting temperature (°K) for the nitrate under consideration. Lattice energies were evaluated using Kapustinskii's approximate expression (9, 10):

$$U_0 = \frac{256 \nu Z_+ Z_-}{r_+ + r_-}$$

where ν is the number of ions in one molecule. Z_+ and Z_- are the charges and r_+ , r_- the ionic radii for cation and anion, respectively. For the ionic "radius" of the nitrate ion, the generally accepted value of 2.19 Å was adopted. E_k is seen (Figure 1) to be inversely proportional to U_0 , LiNO₃ being an exception. Such a correlation appears to be reasonable, as one would expect the temperature dependence of the conductivity to be inversely proportional to the attractive force field between the ions in the melt.

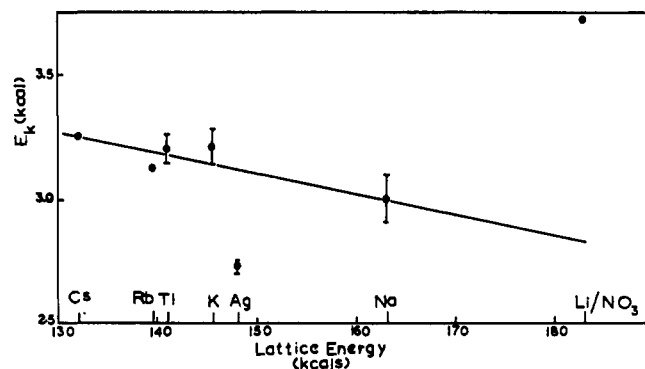


Figure 1. Variation of energy of activation for conductance with lattice energies

LITERATURE CITED

- (1) Bell, M. C., Flengas, S. N., *J. Electrochem. Soc.*, **111**, 575 (1964).
- (2) Cowen, H. C., Axon, H. J., *Trans. Faraday Soc.*, **52**, 242 (1956).
- (3) Duke, F. R., Fleming, R. A., *J. Electrochem. Soc.*, **105**, 412 (1958).
- (4) Gaur, H. C., Jain, S. K., *Ind. J. Chem.*, **9**, 860 (1971).
- (5) Gaur, H. C., Jain, S. K., *ibid.*, in press, 1972.
- (6) Gaur, H. C., Jain, S. K., *Rev. Roumaine Chim.*, **16**, 1157 (1971).
- (7) Gaur, H. C., Mehta, O. P., Jain, S. K., *Ind. J. Chem.*, **9**, 570 (1971).
- (8) Grahame, D. C., *J. Amer. Chem. Soc.*, **63**, 1207 (1941).
- (9) Kapustinskii, A. F., *Quart. Rev. (London)*, **10**, 283 (1956).
- (10) Kapustinskii, A. F., *Z. Physik. Chem.*, **22B**, 257 (1933).
- (11) King, L. A., Duke, F. R., *J. Electrochem. Soc.*, **111**, 712 (1964).
- (12) Murgulescu, I. G., Zuca, S., *Rev. Roumaine de Chim.*, **2**, 272 (1959).
- (13) Nooijer, B. De, PhD thesis, University of Amsterdam, 1965.
- (14) Robbins, G. D., Braunstein, J., *J. Electrochem. Soc.*, **116**, 1218 (1969).
- (15) Robbins, G. D., Braunstein, J., "Molten Salts—Characterizations and Analysis," Ed. G. Mamantov, Ed., 1969.

RECEIVED for review September 15, 1971. Accepted December 21, 1971. The authors thank the Council of Scientific and Industrial Research, India, for financial assistance for the project and for a research fellowship to one of them (SKJ).

Characterization of Iron and Rare Earth Polymers of Di(2-ethylhexyl) Phosphoric Acid

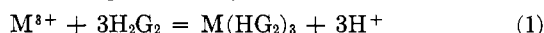
TAKEO HARADA,¹ MORTON SMUTZ,² and RENATO G. BAUTISTA³

Institute of Atomic Research and Department of Chemical Engineering, Iowa State University, Ames, Iowa 50010

The characterization of the iron, yttrium, lanthanum, praseodymium, neodymium, dysprosium, holmium and ytterbium polymers of di(2-ethylhexyl) phosphoric acid by chemical and X-ray diffraction technique are reported.

The formation of a third phase or a white precipitate in the organic phase has been observed by several investigators (2, 8, 10, 11) to limit the extraction of the lanthanides in the liquid cationic ion exchanger, di(2-ethylhexyl) phosphoric acid. The formation of chain polymers with uranium (1) and copper (9) when di(2-ethylhexyl) phosphoric acid is used as an extractant has also been reported. Harada et al. (3) have recently reported the experimental conditions under which this third phase becomes limiting during the extraction of rare earths. The formation of the polymers as a function of di(2-ethylhexyl) phosphoric acid concentration acidity and aqueous metal concentration has been studied. In this note are presented additional results obtained in characterizing the polymers of iron and rare earths with di(2-ethylhexyl) phosphoric acid.

In this liquid-liquid extraction system, the extraction of the metal in aqueous solution involves the formation of a complex with di(2-ethylhexyl) phosphoric acid which is soluble in the organic phase. The di(2-ethylhexyl) phosphoric acid is diluted with an aliphatic naphtha with a boiling range from 177–99°C and is marketed by the American Mineral Spirits Co. as AMSCO Odorless Mineral Spirits. The extraction equilibrium can be represented by the reaction



where M^{3+} is the trivalent metal ion, H_2G_2 is the di(2-ethylhexyl) phosphoric acid dimer, and $M(HG_2)_3$ is the complex soluble in the organic phase.

The addition of more metal ions into the organic phase results in an irreversible polymerization reaction which can be represented by



¹ Present address, Department of Oceanography, Faculty of Fisheries, Hokkaido University, Hakodate, Japan.

² Present address, College of Engineering, University of Florida, Gainesville, Fla. 32601.

³ To whom correspondence should be addressed.

where n is the number of moles and $(MG_3)_n$ is the metal polymers.

The degree of polymerization of the rare earth-D2EHPA was

Table I. Chemical Composition of Iron and Rare Earth-D2EHPA Polymers^a

	YG ₃		FeG ₃		LaG ₃		PrG ₃		NdG ₃	
	% Obsd	% Calcd	% Obsd	% Calcd	% Obsd	% Calcd	% Obsd	% Calcd	% Obsd	% Calcd
Metal	8.7	8.5	6.8	5.5						
C	53.6	54.7	50.2	56.5						
H	9.9	9.8	8.9	10.1						
P	8.6	8.8	8.6	9.1						
O	17.7	18.2	17.7	18.8						
Sum	98.5	100.0	92.2	100.0						
Metal	12.6	12.6	12.8	12.7	12.8	13.0				
C	49.6	52.3	50.9	52.2	51.4	52.0				
H	9.0	9.3	9.1	9.3	9.2	9.3				
P	8.3	8.4	8.4	8.4	8.4	8.4				
O	17.1	17.4	17.4	17.4	17.3	17.3				
Sum	96.6	100.0	98.6	100.0	99.1	100.0				
Metal	14.5	14.4	14.2	14.6	16.6	15.2				
C	50.0	51.2	49.5	51.1	47.3	50.7				
H	9.0	9.1	8.9	9.1	8.7	9.0				
P	8.3	8.3	8.1	8.2	7.8	8.2				
O	17.1	17.0	16.8	17.0	16.0	16.9				
Sum	98.9	100.0	97.5	100.0	96.4	100.0				

^a G = (C₈H₁₇)₂PO₄⁻. Polymer: P = P/PO₄, O = (1-P/PO₄).